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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Fine particulate matter source apportionment using a hybrid chemical transport and receptor model approach" *by* Y. Hu et al.

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Reply to Referee #1

General Response:

In response to Referee #1's comments, first we would like to clarify two points that seem to concern the referee the most as they were expressed a few times.

The first point is regarding the critique why we didn't choose a contemporary chemical transport model (CTM) with a recent emissions inventory. First, we are developing a hybrid method that aims to "correct" CMAQ DDM-based PM2.5 source apportion-

ment results by using regularly available measurements (e.g., routine observations from monitoring networks). The hybrid method as expressed in our Eq. (14) can be applied to "correct" source apportionment results obtained from CMAQ with DDM, CMAQ using other source apportionment approaches (including brute force methods) or other CTM-based methods as well. We are not developing a method that has to be attached to a specific CTM framework. We will revise our manuscript accordingly to explicitly express this point. Therefore the CTM-based results to be "corrected" can be from applications of a new CTM model with a recent emissions inventory or a "seasoned" but still widely used CTM with an extensively evaluated emissions inventory as in our case study. We used CMAQ because it is widely used, and the choice of version was made because it was the version available that had DDM at the time. Since that time, a more recent version of CMAQ (i.e. v4.7.1) now has DDM, though CMAQ v5.0.1 has not yet been released with DDM. The universal applicability is a very desirable feature because there are many CTM-based source apportionment datasets which have been produced using several different models for previous years, and this approach can be used. In particular, there exist a number of multi-year, spatially-distributed source apportionment datasets for health studies developed from different CTM applications. These applications were conducted with different models (contemporary at the time) and different NEI inventories (appropriate for the application year) for different years (http://www.epa.gov/heasd/research/cdc.html). An approach to help correct CTM-based source apportionment results is important due to not only the uncertainties in the underlying emissions inventory and the host model representation of physical and chemical processes, but also the various theoretical limitations of each method itself determining source impacts in the complex atmospheric system (Koo et al. 2009, Burr and Zhang 2011). Additionally, NEI inventories are available for every fourth year in the US, but not for years in between. For in between years, the projected inventories certainly have higher uncertainties, though results from utilizing CTM-based source apportionment results for any year needs to be done with careful examination. As is described in the response below, we did, however, repeat part of

the study using CMAQ v4.7.1, and as noted, the sensitivity results (we chose biomass burning because that was the category that was most adjusted and it involves both primary and secondary aerosol formation) are highly correlated between versions 4.5 and 4.7.1, much more so than between the observations and the model results and even between the PM2.5 simulated by the two models.

Our choice of year (2004) was chosen because we are using this method to support multiple health studies. There are significant limitations on the availability of health data. In this case, 2004 was chosen as a year that overlapped with the availability of the health data in multiple locations around the US.

In summary, a contemporary CTM model is not a necessary condition for our hybrid method development or use. A recent emissions inventory is only necessary for recent application years and it is more important to apply an appropriate NEI inventory for a specific year.

The second point is regarding some unfounded remarks the referee made about our hybrid results. Note that in our case study we have applied our hybrid method to 807 cases individually, each for a unique location and time (i.e., 164 CSN monitors in the U.S. with one-in-three and one-in-six day sampling for January 2004). The hybrid method has achieved varying results over the 164 CSN sites for a one-month winter period. However, the referee suggests that: 1) our approach does not seem to make meaningful adjustments where sectors do not emit primary PM2.5 and 2) our method only changes sectors that have primary PM2.5 emissions. However, the method does change secondary species concentrations (e.g., those resulting from ammonia from livestock emissions). Further, a minimal change in the initial estimate after the hybrid method is applied does not mean the hybrid results are not reasonable. It means that the initial CMAQ-DDM results for that case were not in need of as much adjustment (or "correction"). This is not surprising for sulfate, one of the major contributors to secondary PM2.5 formation, as most of the sulfate comes from the oxidation of SO2, which is viewed as being accurately inventoried as most of the emissions are measured

directly by continuous emissions monitors, which is also true for a large fraction of the NOx emissions. The other major NOx emission source, mobile sources, is viewed as being more accurately inventoried than the sources that were adjusted most in this application (e.g., dust, biomass burning). Thus, it is not surprising that those other sources were adjusted much more.

Receptor models (RM) construct and solve the species balance equations can lead to unrealistic source apportionment results. The hybrid method, however, reduces the likelihood of obtaining unrealistic changes by constructing the species balance equations using CTM-based initial source impact estimates and various constraints (i.e., observed species concentrations, measurement uncertainty, CTM modeling uncertainty, assessment of the uncertainties in the inventories). We should point out that with this kind of formulation there are still risks of obtaining incorrect adjustments. This is particularly true for the sectors that only contribute to one or two secondary PM2.5 species, such as livestock and biogenics, however, the results are still constrained by the observations, and account for knowledge of likely sources impacting those observations.

Responses to specific comments

Comment: This manuscript illustrates an approach to estimate source sector contribution to PM2.5 by combining well known source and receptor based methods. The source based method is the application of the CMAQ photochemical transport model using DDM sensitivity coefficients to estimate the impacts for a wide range of source sectors. The receptor based approach is a traditional Chemical Mass Balance (CMB) receptor model that uses source fingerprints of trace metal compounds to differentiate chemically speciated measurements into various source groups. The source based approach estimates of sector contributions (CMAQ DDM) are adjusted based on source sector contributions estimated with CMB using 24-hr average CSN speciated measurement data. Ultimately, source sectors with very poorly estimated primary PM2.5 emissions (such as the dust sector) in the 2002 National Emission Inventory (NEI) are reduced through ambient based constraints.

Response: Referee #1's understanding of our hybrid method is not quite correct as stated: "The source based approach estimates of sector contributions (CMAQ DDM) are adjusted based on source sector contributions estimated with CMB using 24-hr average CSN speciated measurement data". Our adjustments of the original source based approach estimates of sector contributions are not based on source sector contributions estimated by independently applying CMB. In particular, we start with the source impacts estimated from the CTM, and adjust those results using observed concentrations of PM2.5 species, as is shown in Eq. (14): We begin with the original CTM estimates of sector contributions, SAinit(i,j), and solve the species balance equations with constraints to obtain scaling factors Rj that would adjust the original SAinit(i,j) for a better fit to the species balance equations that were constructed using 24-hr average CSN speciated measurements. The fingerprints are not solely for primary PM2.5 species and include the impacts of meteorological processing on the emissions. The physical meaning of the obtained scaling factors Rj is a set of "corrections" on the original CTM-based estimates of source impacts, which includes sector specific contributions to both primary and secondary PM2.5. The "corrections" are used to minimize potential errors in CTM source impacts estimates at a specific location and time.

Referee #1's observation, "Ultimately, source sectors with very poorly estimated primary PM2.5 emissions (such as the dust sector) in the 2002 National Emission Inventory (NEI) are reduced through ambient based constraints", is quite true, but is an understatement of the capability of the method. Our results have shown that sectors such as prescribed burns whose emissions are subject to high day-to-day variability while typical inventories use very smooth, averaged emission rates (Figure S1a and Table 4), are much better captured. Our results have also shown that the adjustments can also be significant for sectors such as solvents that emit little primary PM2.5 emissions and mainly contribute to secondary PM2.5 (Figure S1d). Note that dust is the only sector that contributes solely to primary PM2.5 in our case study. Similar significant changes are also seen for many other sectors such as domestic woodstove and other biomass burning sectors, natural gas combustion, fuel oil combustion and

on-road gasoline (Figure S1). All these sectors have both primary PM2.5 and PM2.5 precursor emissions.

Comment: The authors start from an interesting premise that seeks to utilize strengths of both systems to better estimate source contribution to PM2.5. Photochemical model approaches are powerful in that collinearity is never an issue and they can attribute secondarily formed pollutants, but the estimates are only as good as the underlying emissions inventory and host model representation of physical and chemical processes in the atmosphere. Receptor models using routinely measured speciated PM2.5 (e.g. CSN, IMPROVE) are severely limited by collinearity issues (many sources have similar emissions profiles) and rarely attribute the bulk of the measured mass to specific sources as most is generally secondarily formed.

Response: Thank you.

Comment: With regard to the general approach, I have several concerns. It is not clear that the limitation inherent with CMB in apportioning secondary PM2.5 mass does not translate to a similar limitation in this "hybrid" approach. Since the receptor modeling (CMB) used to adjust the CMAQ DDM source estimates only can resolve sources that emit primarily emitted PM2.5 this approach only really changes CMAQ DDM source sectors that have primary PM2.5 emissions. Based on presented Tables showing contribution as a concentration, sectors such as confined animal operations ("livestock") that emit ammonia and biogenics that emit nitrogen oxide and VOC do not substantively change after the "refined hybrid approach" is applied.

Response: As we have stated at the opening of our reply, there is a substantial difference between the traditional CMB method and our hybrid method. As shown in Eq. (14), we begin with the original CTM estimates of sector contributions, SAinit(i,j), and solve the species balance equations (with constraints) to obtain scaling factors Rj that would adjust the original SAinit(i,j) for a better fit to the species balance equations. The initial CTM estimates of sector contributions, SAinit(i,j), adjusted by the hybrid method,

already include sector specific contributions to either primary PM2.5 only (dust), or secondary PM2.5 only (livestock and biogenics) or both primary and secondary PM2.5 (all other sectors). Consequently, the hybrid method naturally resolves sectors that only contribute to the secondary PM2.5 such as livestock and biogenics. Tables 4 and 5 show the hybrid results of source impact estimates resolved for these sectors that only contribute to secondary PM2.5.

Our results do show changes in hybrid results compared to the initial CTM estimates for biogenics and livestock impacts, and their adjustments were sometimes significant (Figure S1d), though on average they were not as large as others. This shows that the method does act locally, as well as regionally, to make adjustments, and modify sources of secondary PM2.5. The hybrid method conserves original CTM source impact estimates when those estimates agree with observed concentrations. Our results also show little changes on some source sectors that have primary PM2.5 emissions (e.g. railroads, aircraft, sea salt, etc.) when the observations do not provide evidence that the impacts from those sources are not very inconsistent with the observations.

Comment: This approach does well for sources that are grossly overestimated due to emissions inventory errors such as the fugitive dust sector. However, that could be achieved by simply applying model performance bias ratios against the model predicted species to obtain similar results without a back-end receptor model.

Response: We disagree with "that could be achieved by simply applying model performance bias ratios against the model predicted species to obtain similar results". Note that dust sector shares multiple PM2.5 components (elements) with many other sectors that have primary PM2.5 emissions. Our hybrid results show that differing scaling factors were obtained for different sectors, which were also changing from day to day (Figure S1). We don't think "simply applying model performance bias ratios against the model predicted species" can give similar results. Further, the method provides changes that are consistent with all of the observed species and are adjusted after including estimates of uncertainties in the observations and emissions inventory.

Comment: This approach may have promise as a diagnostic tool to identify parts of the emission inventory with overestimated primarily emitted PM2.5. A major limitation is this approach does not seem to make meaningful adjustments where sectors do not emit primary PM2.5 and since contributions go down after hybrid method application it also may not work well where emissions are underestimated. I encourage the authors to test how robust this tool is with extra diagnostics such as excluding a known source from the photochemical model or making a systematic adjustment to a well characterized category such as EGUs and see how well the hybrid system "corrects" the perturbation.

Response: Much of this comment is addressed previously. We further note that it works to increase source impacts when the observations support such, e.g., for biomass burning on multiple days (Fig. S1 and Table 4). Biomass burning impacts are very weather dependent and variable, so while some days those estimated impacts decrease, other days they increase markedly. Further, as Koo et al. (2009) has concluded, DDM gave good predictions for the impact of removing 100% of SOA precursor emissions (as evaluated with brute-force method (BFM)). We don't agree with that minimal adjustments are not meaningful adjustments.

Comment: The current description, formulation, and presentation of results gives the appearance that the hybrid approach somehow "improves" sector estimates that are entirely secondary in nature. Perhaps that is why such a short episode in a winter month was chosen for the evaluation period; to minimize the limitations in the approach that would be even more evident in the warmer seasons when secondary PM2.5 is greater. Why was January 2004 selected? Does it coincide with elevated PM2.5 in the areas selected? Is this method too inefficient to apply for longer periods of time? The authors need to apply this approach to a variety of seasons to include the range of physical and chemical processes important for PM2.5 formation.

Response: Again, as discussed above, our results show that the method works for source that contributes to both primary and secondary PM2.5. Our choice of period

had nothing to do with looking to minimize any limitations or with considering secondary species. Indeed, secondary ammonium nitrate, which is one of the most difficult secondary PM2.5 species to model accurately, is more abundant in the winter. We chose a winter episode for our case study for a number of reasons: (1) the time period of study provided us a complete range of source sectors for a better evaluation of CTM source impact results. A summer episode will miss many important source sectors such as prescribed burns and open fires, etc. We have a split of total emissions into 33 sectors. This has never been done in the past for any CTM or RM source apportionment effort, (2) PM2.5 pollution happens more frequently during the winter season, as there were many elevated PM2.5 measurements during the selected month-long period. (3) Secondary nitrate PM2.5 is much more abundant during winter and becomes a major portion of PM2.5, especially in the west coast. Although oxidation rates are lower during winter, sulfate and SOA are still formed through secondary processes during the winter, and the modeling domain covers areas that are relatively warm during the episode. Note that our modeling domain covers the entire continental US. As noted above, the choice of 2004 was driven by our desire to use this approach in health studies.

As for the choice of just one month, this article is a method development article, similar to other method development studies. For example Kowk et al. (2013) evaluated the ISAM method for January 2005, Wang et al. (2009) evaluated the TSSA method for January and July 2002, and Wagstrom et al. (2009) evaluated the OPSA and PSAT methods for just one week, 12-19 July 2001. For a method development paper, we think a one-month long episode during a time of year that modelers find challenging is by no means a short episode as compared with current relevant literature. In future analyses, this method will be applied for an extended period.

Comment: The manuscript needs to clearly explain why the authors choose an emissions sensitivity approach to estimate sector impacts rather than photochemical model source apportionment techniques like PSAT in CAMx (ENVIRON, 2013) or TSSA in

CMAQ (Wang et al., 2009). Source apportionment for PM2.5 has been available in CAMx since version 4.5 of CMAQ was released (which was used for this study) and TSSA was implemented in a version of CMAQ contemporary with version 4.5. Receptor models like CMB, PMF, and UNMIX provide information about a specific measurement and do not provide information about how that measurement would be different if emissions were zeroed out from large sectors because chemistry would fundamentally change especially in nonlinear systems like PM2.5 nitrate. It seems to make sense to match a photochemical model source apportionment approach with receptor model source apportionment as opposed to matching a source sensitivity approach (e.g. DDM, brute force emissions changes) with source apportionment. Please provide some discussion in the manuscript that supports why a source sensitivity approach better matches the type of information obtained from a receptor model source attribution approach.

Response: Our goal of developing the hybrid method is mainly for improving the CTM-based source impact estimates developed by any of a number of methods. Any of the source impact estimation methods, including DDM, have limitations as discussed in the literature (see below). As the referee has acknowledged, for the original CTM results, "the estimates are only as good as the underlying emissions inventory and host model representation of physical and chemical processes in the atmosphere", there always is an opportunity for "corrections" on source impacts results obtained from source-based methods. This is because although host model representation of physical and chemical processes in the atmosphere can be improved gradually (usually slowly in practice), the underlying emissions inventory can rarely be "good" enough especially at a specific location for a specific time. This makes the "correction" effort we are developing with the hybrid method development important. So, our answer to the referee's question of why we chose an emissions sensitivity approach for "correcting" its source impact estimates is: the emissions sensitivity approach we chose for our case study is one of the source-based methods. The referee has acknowledged in the very beginning that the emissions sensitivity approach we chose in our case study is one of the well

known source-based methods: “This manuscript illustrates an approach to estimate source sector contribution to PM2.5 by combining well known source and receptor based methods. The source based method is the application of the CMAQ photochemical transport model using DDM sensitivity coefficients to estimate the impacts for a wide range of source sectors.”

As noted in the beginning, we don’t have a preference for which source-based method’s results should be “corrected”. In fact, our hybrid method as described in Eq. (14) has been formulated in such a way that the initial CTM estimates of sector contributions, SAinit(i,j), can be generated using many source-based methods, such as the “source apportionment techniques” the referee recommended. There were comparisons of emissions sensitivity approaches versus “source apportionment techniques” for source impact estimation (Burr and Zhang 2011, Koo et al. 2009). Their conclusions were none of the methods were perfect, due not only to the uncertainties in the underlying emissions inventory and the host model representation of physical and chemical processes in the atmosphere, but also to the theory limitation of each method itself determining source impacts from such a complex system. For example, Koo et al. (2009) has pointed out, “Neither PSAT nor first-order (DDM) sensitivities provide an ideal method to relate PM components to sources”. The study of Koo et al. (2009) has shown that PSAT did not performed well (Figure 5 in the literature) in determining the source impact from on-road mobile emissions, while on-road mobile emissions is one of the most important contributors to PM2.5 at most locations and times. Burr and Zhang (2011) has also shown that “the use of CAMx/PSAT source apportionment data for exposure analysis will over- or under- estimate exposure to certain species due to the exclusion of indirect effects and oxidant-limiting effects that occur in the atmosphere”. We will include the above information in our revised manuscript.

Lastly, since the DDM approach we used its results is one of the “well known source-based methods” for source impact estimates, we don’t see any problem in comparing the further “improved” results to receptor model methods as we did in our results sec-

tion. We should reemphasize that we don’t match the initial CTM estimates of sector contributions, SAinit(i,j), to CMB source apportionment results. In stead, we somehow “match” the total of the initial CTM estimates of sector contributions to species concentrations measured in order to solve a set of scaling factors Rj, as described in Eq. (14). In fact, our hybrid method is a receptor-model framework approach, but uses CTM-based results as inputs.

Comment: The author’s choice of first order sensitivities using DDM is not supported. First order DDM sensitivities best approximate a small perturbation in a linear system, which is the reason higher order sensitivities were later included in the method (HDDM). PM2.5 nitrate is not a known linear system and would seem to need higher order terms and possibly interaction terms. The reference provided to support the use of first order DDM sensitivity coefficients to represent PM2.5 impacts is to (Hakami et al., 2004), which is a comparison of small perturbations in ozone precursors to DDM estimated ozone. An evaluation of the ozone DDM system is not a substitute for the PM system.

Response: We agree that "First order DDM sensitivities best approximate a small perturbation in a linear system", and that including higher order sensitivities will make more accurate initial source impacts estimates as inputs in our hybrid method.

We will add citation of Koo et al. (2009) here. As Koo et al. (2009) have shown that first order DDM gave reasonably good predictions for impacts of SOA precursors, primary aerosols and on-road mobile source emissions. Their results in Figures 4, 6 and 7 also show that first-order DDM compared reasonably well with BFM for 100% reductions at apportioning sulfate, nitrate and ammonium to sources emitting SO2, NOx and NH3 in winter times, with nitrate estimation slightly worse. They have found that first-order DDM is good in determining the impact of sources that have indirect effects, such as motor vehicles emissions that have substantial emissions of multiple pollutants. Note that our first-order DDM sensitivities were calculated for all emitted compounds from the sources, and this process utilized the DDM’s proven advantage of capturing indirect

effects from multiple pollutants. In addition, we have split the total emissions into 33 sectors, which made most of the sectors have a small portion of emissions compared to the total. This further diminishes the disadvantage of first-order DDM not capturing well the impacts from large changes of emissions. In fact, "First order DDM sensitivities best approximate a small perturbation in a linear system", and by using 33 sources, we are minimizing the impact of any one source. Let us reemphasize that our hybrid method is designed to improve on an imperfect CTM-based source impact estimation method (no method is perfect on source apportionment), though we only showed the improvement with a DDM-sensitivity-based source impact estimation method here.

Comment: Finally, I am very concerned by the author's choice of an outdated photochemical transport model to illustrate their approach. CMAQ version 4.5 (most notably for this work) has outdated PM chemistry, particularly related to organic aerosol. CMAQ version 4.5 was released in September of 2005. CMAQ 5.0 was released in February of 2012 and version 5.0.1 in September of 2012 with versions 4.6 and 4.7 released in the years between 2005 and 2012.

Response: We agree that the initial CTM based source impacts estimates that were adjusted using our developed hybrid method have been obtained by using a relatively "outdated" model, which is CMAQ v4.5. We discuss our choice of method in the beginning. As DDM is being added to CMAQ v5.0.2, we hope to use that version in the future.

While CMAQ v4.6, v4.7, v4.7.1, v5.0 and v5.0.1 have been improved on theory as compared to v4.5 in many aspects, the improvements in the ability to simulate PM2.5 and its components haven't been substantial (Simon et al. 2012, Appel et. al. 2013), as in the model performance evaluation of CMAQv5.0.1 in its application to the southeastern US (http://semap.ce.gatech.edu/node/1835).

Additionally, of these newer CMAQ versions, DDM-3D is only available in v4.7.1. The implementation of DDM-3D and higher order DDM-3D for PM2.5 to CMAQ 5.0.2 is

still ongoing. We don't find that DDM source impacts estimates produced by using CMAQ v4.7.1 and those using CMAQ v4.5 will substantially impact our results. In responding to the referee, we reran the model using v4.7.1 and assessed the impact on the prescribed burn sensitivities (which were chosen as they were one of the sources most adjusted and also contribute to SOA). The correlation (R2) in the sensitivities is 0.92, which is more correlated than the simulated PM2.5 between the two versions (0.86), and is much more correlated than between the simulated and observed PM2.5 as using any contemporary CTM (Figure 8 of Simon et al. 2012 shows that most of the correlations were between approximately 0.2-0.5).

Comment: The use of emissions based on the 2002 NEI is also puzzling. Updated national emission inventories have been released for 2005 and 2011 and have improved on many sectors, including the "dust" category.

Response: The case study episode was in 2004, and we used 2004 CEM data for emissions of large point sources in the US. The reason we didn't use NEI2005 (as base for projection to 2004) was because "EPA developed the 2005 NEI v2 based on a reduced level of effort. Part of this reduced effort involved using some NEI 2002 v3 data in the NEI 2005 v2 as surrogates for emissions data representing 2005" (http://www.epa.gov/ttnchie1/net/2005inventory.html). It would be impropriate and difficult to do emissions projection based upon an inventory of mixture emissions from different years. EPA has issued warning for the use of NEI2005 on their website: "Prior to using the 2005 NEI for analyses, users should consider whether the use of 2002 data as a surrogate for the selected sources documented above materially affects their analysis." We also note that the dust sector emissions in the 2005NEI were kept the same as the 2002NEI dust emissions (see the release note on the page http://www.epa.gov/ttnchie1/net/2005inventory.html). We note, the initial version of NEI2011 was only released on September 30, 2013 (http://www.epa.gov/ttn/chief/net/2011inventory.html) after we submitted our manuscript.

Comment: The authors need to work within a modeling system framework that is relevant and contemporary. That means using a photochemical model version that is a recent representation of the state of the science, a recent emission inventory, and applying the photochemical model for at least an entire calendar year (preferably a recent year or a meaningful period of time that coincides with elevated PM2.5 or a special field campaign).

Response: Addressed above.

Comment: While not a requirement, it would be preferable to use 12 km sized grid cells rather than 36 km and employ a vertical representation from the surface to at least 100 mb, which is how most ozone and PM2.5 photochemical model applications for regional and urban scales are currently applied.

Response: We do have a vertical representation in the model "from the surface to at least 100mb", as stated on page 7: "The modeling domain (Fig. 1) covers the continental United States as well as portions of Canada and Mexico with 36-km x 36-km horizontal grids and 13 vertical layers of variable thickness extending from the surface to 70 hPa."

Comment: More specific comments follow. Abstract. I disagree that this approach accounts for emissions uncertainties. The authors provide an estimate of uncertainty for each emissions sector but the method itself does not estimate these.

Response: As shown in Eq. (14), the method "accounts for emissions uncertainties". The second term of the Eq. (14) accounts for uncertainties in the CTM-derived individual source impacts due to emissions error. As such, the scaling factors were obtained by solving the Eq. (14) which used the emissions uncertainties.

Comment: I would agree that all photochemical model applications must be evaluated with observations as noted in the abstract (regardless of intended use) but the abstract seems to suggest this hybrid method must be done for every source attribution

approach as the "evaluation".

Response: The only related statement in our abstract is: "The rankings of source impacts changed from the initial estimates, revealing that CTM-only results should be evaluated with observations". We stand by the statement that model results should be evaluated with observations. The only other related sentence in the manuscript is at Line 15 on page 26674: "This shows that it is necessary to evaluate SM source apportionment results using measurements." This still does not "suggest this hybrid method must be done for every source attribution approach as the 'evaluation'." And we still view that one should evaluate model results using observations.

Comment: Introduction. Please provide some references to support the sentence at lines 11-15 of 26659.

Response: Lines 11-15 of 26659: "However, that is far from measuring multiple sources' impacts at the same time and is typically limited to special studies. Instead, source apportionment results are typically evaluated by comparing simulated concentrations of individual component and total mass of PM2.5 with observations".

There are two sentences here. The first sentence reflects our comment on studies that use tracer gases to directly measure source impacts from certain sources following its previous sentence: "Tracer gases such as cyclic perfluoroalkanes and SF6 can be utilized to help quantify source impacts (Martin et al., 2011)". We will cite Watson et al. 2008 and Viana et al. 2008 to support the second sentence: "Instead, source apportionment results are typically evaluated by comparing simulated concentrations of individual component and total mass of PM2.5 with observations".

Comment: Since this paper is about source apportionment it is important that the authors specifically acknowledge the existence of photochemical model source apportionment ((ENVIRON, 2013; Fann et al., 2013; Kwok et al., 2013; Wagstrom et al., 2008; Wang et al., 2009)) and provide some explanation why this approach would not be better suited to be matched with a receptor based source apportionment model.

Response: We have already cited Wagstrom et al. (2008) for the PSAT method development and Burr and Zhang (2011) for their applcation of PSAT as a third party user to acknowledge PSAT as one of the impotrant CTM source apportionment appoaches. Of the five papers noted above, three of them (ENVIRON, 2013; Fann et al., 2013; Wagstrom et al. 2008) are PSAT method related. ENVIRON (2013) is a user guide for CAMx and we are not sure why it, too, should be cited as it is not apparent what additional crucial information it supplies. The other two papers, discussing ISAM (Kwok et al., 2013) and TSSA (Wang et al., 2009) methods are "tagged species" methods and are very similar to PSAT (see Kwok et al., 2013 and Wang et al., 2009 for the authors' description on their methods' relation to PSAT). Note, we already cite a large number of source apportionment methods based on CTMs:

"Source-oriented modeling (SM) approaches, such as chemical transport models (CTMs), follow the emission, transport, transformation and loss of chemical species in the atmosphere to simulate ambient concentrations and source impacts. CTMs can compensate for limitations in RM methods (Burr and Zhang, 2011a; b; Doraiswamy et al., 2007; Held et al., 2005; Henze et al., 2009; Kleeman et al., 2007; Lowenthal et al., 2010; Marmur et al., 2006; Russell, 2008; Schichtel et al., 2006; Wagstrom et al., 2008; Ying et al., 2008) because they describe processes affecting source-receptor relationships from a first principles basis".

We will cite Kwok et al. (2013) and Wang et al. (2009) for the variations of PSAT and their application in CMAQ. Again, the method can be linked to a variety of approaches. Our hybrid method aimed to "correct" initial source impacts estimates using a CTM-based method, but not for developing a new CTM-based method.

Comment: Methods. The authors need a much more contemporary model and model application. An advantage of using one of the more recent CMAQ releases is that they include most crustal species which would require fewer assumptions about speciation in the post processing steps.

Response: This point has been addressed above. We should point out that CMAQ v5.0 and v5.0.1 added many metal species as their model species, and the complete list of the explicitly modeled metals are: Al, Ca, Fe, Mg, Mn, K, Na, Si, and Ti. This is still far from simulating all the 35 measured element species that were used in the case study of our hybrid method, and, as discussed previously, DDM in CMAQ 5.01 is not yet available.

Comment: Support for ignoring higher order sensitivities for nonlinear systems like PM2.5 nitrate formation is needed. Do the first order sensitivities add up to the bulk estimate?

Response: Koo et al. (2009) have shown that first order DDM gave reasonably good predictions for impacts of SOA precursors, primary aerosols and on-road mobile source emissions. Their results in Figures 4, 6 and 7 also show that first-order DDM compared reasonably well with BFM for 100% reductions at apportioning sulfate, nitrate and ammonium to sources emitting SO2, NOx and NH3 in winter times, with the nitrate estimation being slightly worse. They have also proved that first-order DDM performs well in determining the impact of sources that have indirect effects, for example, such as the motor vehicles emissions that have substantial emissions of multiple pollutants. Note that our first-order DDM sensitivities were calculated for all emitted compounds from the sources, and this process utilized the DDM's proved advantage of capturing indirect effects. Also, we have split the total emissions into 33 sectors, which made most of the sectors have a small portion of emissions compared to the total emissions. This further diminishes the disadvantage of first-order DDM not capturing well the impacts from large changes of emissions. In fact, "First order DDM sensitivities best approximate a small perturbation in a liner system". Let us reemphasize that our hybrid method is designed to improve on an imperfect CTM-based source impact estimation method (no method is perfect on source apportionment), though we only showed the improvement with a DDM-sensitivity-based source impact estimation method here. Napelenok et al. (2006), Hakami et al. (2003, 2004) and Cohan et al. (2005) have also done numerous

CMAQ-DDM-based studies and have come to largely the same conclusions.

It's true that, the first order DDM sensitivities usually don't exactly add up to the predicted total PM2.5 concentrations due to ignoring the higher order sensitivities. However, among the 932 cases we have tested with our hybrid method, only 125 cases (13.4%) had a larger than 30% difference. We have done the analysis both with and without these 125 cases (from 164 CSN sites for one-month measurements) from our hybrid method application, and the changes are limited. In addition, both Burr and Zhang (2011) and Koo et al. (2009) have found that the sum of BFM estimated source contributions will not equal to the simulated concentrations in the base case either.

Comment: How are the authors able to show full mass closure in the Tables showing percent contribution when lateral boundary inflow is ignored? It would likely be small for a winter month but bigger than many of the small categories chosen for this analysis.

Response: We did find the initial CTM estimates of impacts negligible from lateral boundary conditions at the CSN sites for the winter period studied. CSN sites are all located in urban/suburban areas with two thirds of them located in the east coast areas. We excluded impacts of lateral boundary conditions when reporting the total source impacts for simplification. However, as our hybrid method is formulated (Eq. 14) the SAinit(i,j) is defined as "initial estimate of impact of source j (or initial or boundary conditions)", and the method can be used to adjust impacts from boundary conditions as well if needed. In this case, the impact is small. For example, the calculated boundary conditions' contribution to PM2.5 at the select CSN site in Los Angeles (site 060658001) is less than 0.01 μg m-3 on daily basis in January 2014. Further, we do include the impact of the boundary conditions in the method in the initial calculation of the species concentration. The Tables were developed only for the source impacts.

Comment: On page 26665 at the bottom of the page, the authors state they are ignoring higher order DDM terms based on (Hakami et al., 2004). This paper only evaluated first and higher order terms for ozone and provides no such evaluation for PM2.5! Other

papers by the same authors suggest higher order terms are needed to approximate a 50% change in NOX on modeled ozone (Hakami et al., 2003). Here, the authors are assuming far beyond 50% reductions as sensitivities are being used to approximate model response when 100% of the emissions for a particular sector are not included in the simulation.

Response: First we should state that when higher order sensitivities are available for CMAQ (for a complete coverage of PM2.5 processes), our method can be applied with them. We have addressed the rest of this question above, though to reiterate:

We will add citation of Koo et al. (2009) here. As Koo et al. (2009) have shown that first order DDM gave reasonably good predictions for impacts of SOA precursors, primary aerosols and on-road mobile source emissions. Their results in Figures 4, 6 and 7 also show that first-order DDM compared reasonably well with BFM for 100% reductions at apportioning sulfate, nitrate and ammonium to sources emitting SO2, NOx and NH3 in winter times, with nitrate estimation slightly worse. They have also proved that first-order DDM are good in determining the impact of sources that have indirect effects, such as motor vehicles emissions that have substantial emissions of multiple pollutants. Note that our first-order DDM sensitivities were calculated for all emitted compounds from the sources, and this process utilized the DDM's proven advantage of capturing indirect effects from multiple pollutants. In addition, we have split the total emissions into 33 sectors, which made most of the sectors have a small portion of emissions compared to the total. This further diminishes the disadvantage of first-order DDM not capturing well the impacts from large changes of emissions. Note that while Hakami et al. (2003)'s 50% NOx reduction was domain-wide for all NOx sources, here most of the 33 source sectors is a small fraction of the total emissions. In fact, "First order DDM sensitivities best approximate a small perturbation in a liner system". Let us reemphasize that our hybrid method is designed to improve on an imperfect CTM-based source impact estimation method (no method is perfect on source apportionment), though we only showed the improvement with a DDM-sensitivity-based source

impact estimation method here.

Comment: Results. The comparisons with other receptor model studies should only be included for Atlanta since they are both on similar (the same actually which is good) time scales. The others should not be included unless the authors apply their approach for at least an entire year otherwise it makes little sense to compare January 2004 with studies that looked at contributions over multiple years.

Response: We disagree with the statement, "it makes little sense to compare January 2004 with studies that looked at contributions over multiple years". This is because we didn't compare the results in a sense of absolute-values. Instead we compared the results in their major features such as what sources being resolved and the relative contributions between certain sources such as gasoline vs. diesel vehicles etc. Those features were captured by those selected RM method studies with longer simulation periods. Indeed, when we have discussed this method with others, they view that the more we can compare our results with other study results, the better. We agree. If our results were totally out of line with other study results, this would be indicative of a problem.

Comment: Table 3. It is peculiar that this approach doesn't result in substantially better model performance. PM2.5 nitrate performance seems to be worse using the refined approach.

Response: When multiple species (41 species in this study) are evaluated to assess model performance, it has been suggested to use a weighted X2 (Watson et al. 1984) for an overal evaluation. Our results do show substantial better overall model performance for the hybrid method, which has the index for remaining error X2(c,refnd) reduced from X2(c,init) by over 98% on average (Figure 3). The average modeled concentration of PM2.5 nitrate was lower after application of the hybrid method. This doesn't mean the overall PM2.5 nitrate performance became worse. In fact, results do show a slightly better PM2.5 nitrate performance with the hybrid method (Figure 2).

Comment: Are the authors sure this method should be mandatory for people using source based attribution methods?

Response: We never suggested that "this method should be mandatory for people using source based attribution methods".

Comment: Table 4. The "refined" total absolute contribution (as a concentration) always seems to be lower or the same as the original estimate. Does this approach work best in situations where the model is clearly overestimating primarily emitted PM2.5 and not as well when the model is missing a sector or grossly underestimating the primarily emitted emissions for a sector? That seems like a very important aspect of this that needs explanation and discussion.

Response: As we have pointed out earlier, our results did show underestimated sectors, such as prescribed burning (due to high day-to-day variability) which are increased on some days, decreased on others (Figure S1a and Table 4)..

Comment: Table 5 is redundant with later Tables.

Response: Table 5 is needed because it lists the largest five contributing sources from the 33 source categories, while later tables report results for the regrouped 13 source categories (Table 6) and for the primary and secondary further-separated source categories (Table 7a and 7b).

Comment: Figure 1 is very difficult to read. Please just include the areas and monitors used in this analysis.

Response: We will revise Figure 1 and its legend for a clearer presentation. However, we should clarify that we used all the CSN monitors in our case study for application of the hybrid method. We also used measurements from IMPROVE and SEARCH monitors for evaluating speciated PM2.5 components. Specific information is listed in Table S7 for the select six CNS sites.

Comment: Table S8 provides emissions totals for each category. PM10 should not be

on this table as it is not relevant to this paper.

Response: We will remove PM10 emission totals from the Table S8.

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Equations:

$$\chi^2 = \sum_{i=1}^{N} \frac{\left(c_i^{obs} - c_i^{base} - \sum_{j=1}^{J^{CTM}} (R_j - 1) SA_{i,j}^{base} \right)^2}{{\sigma_{c_i^{obs}}}^2} \quad \textbf{(13)}$$

$$\chi^2 = \sum_{i=1}^{N} \left[\frac{\left(c_i^{obs} - c_i^{init} - \sum_{j=1}^{J^{CTM}} (R_j - 1) SA_{i,j}^{init} \right)^2}{{\sigma_{c_i^{obs}}}^2 + {\sigma_{SR_i^{CTM}}}^2} \right] + \Gamma \sum_{j=1}^{J^{CTM}} \frac{(\ln R_j)^2}{\sigma_{\ln R_j}^2} \quad \textbf{(14)}$$

Fig. 1.