Comparison of Source Apportionment and Sensitivity Analysis in a Particulate Matter Air Quality Model

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Two efficient methods to study relationships between particulate matter (PM) concentrations and emission sources are compared in the three-dimensional comprehensive air quality model with extensions (CAMx). Particulate source apportionment technology (PSAT) is a tagged species method that apportions concentrations of PM components to their respective primary precursors, e.g., sulfate is apportioned to SO_x, nitrate to NO_x, etc. The decoupled direct method (DDM) calculates first-order sensitivities of PM concentrations to model inputs. Both tools were applied to two month long (February and July) PM modeling episodes and evaluated against changes in PM concentrations due to various emission reductions. The results show that source contributions calculated by PSAT start to deviate from the actual model responses as indirect effects from limiting reactants or nonprimary precursor emissions become important. The DDM first-order sensitivity is useful for determining source contributions only if the model response to input changes is reasonably linear. For secondary inorganic PM, the response is linear for emission reductions of 20% in all cases considered and reasonably linear for reductions of 100% in the case of on-road mobile sources. The model response for secondary organic aerosols and primary PM remains nearly linear to 100% reductions in anthropogenic emissions.

Introduction

Particulate matter (PM) is an important atmospheric pollutant that can be directly emitted into the atmosphere (primary PM) or produced via chemical reactions of precursors (secondary PM). Understanding relationships between emissions from various sources and ambient PM concentrations is often vital in establishing effective control strategies.

Two different approaches to quantifying source−receptor relationships for PM are investigated here. Source apportionment assumes that clear mass continuity relationships exist between emissions and concentrations (e.g., between SO_2 and sulfate) and uses them to determine contributions from different sources to pollutant concentrations at receptor locations. However, sensitivity analysis measures how pollutant concentrations at receptors respond to perturbations at sources. In many cases, these quantities cannot be directly measured; thus, air quality models have been widely used. The most straightforward sensitivity method (brute force method or BFM) is to run a model simulation, repeat it with perturbed emissions, and compare the two simulation results. The BFM is not always practical because computational cost increases linearly with the number of perturbations to examine, and the smaller concentration changes between the simulations may be strongly influenced by numerical errors.

The particulate source apportionment technology (PSAT) was developed as an efficient alternative to the BFM for PM source apportionment (*1*). PSAT uses tagged species (also called reactive tracers) to apportion PM components to different source types and locations. Computational efficiency results from using computed changes in bulk species concentrations to determine the changes for tagged species within individual atmospheric processes (advection, chemistry, etc.). PSAT has been implemented in the comprehensive air quality model with extensions (CAMx). Similar source apportionment tools include tagged species source apportionment (TSSA) developed by Tonnesen and Wang (*2*) and implemented in the community multiscale air quality (CMAQ) model. Unlike PSAT, TSSA adopts an "online" approach and explicitly solves tagged species using the same algorithms as the host model for physical atmospheric processes like advection and diffusion. Wagstrom et al. (*1*) implemented an online approach and "offline" PSAT approach in PMCAMx and showed that the computationally more efficient offline method agreed well with the online method for source apportionment of PM sulfate. Kleeman et al. (*3*) took a more rigorous approach and their source-oriented external mixture (SOEM) model simulates each tagged species separately through every modeled atmospheric process (physical and chemical). The SOEM is potentially the most accurate tagged species method but is computationally very demanding. With these and other methods, it is important to recognize that there is no unique apportionment of ambient concentrations to sources when nonlinear chemistry is present. Different methods will inherently give different results, and there is no "true" apportionment to which all methods can be compared.

The decoupled direct method (DDM) is an efficient and accurate alternative to the BFM for sensitivity analysis (*4, 5*). The DDM directly solves sensitivity equations derived from the governing equations of the atmospheric processes modeled in the host model. Yang et al. (*6*) introduced a variant of the DDM called DDM-3D that uses different and less rigorous numerical algorithms to solve time evolution of the chemistry sensitivity equations than those used to solve concentrations. This improves numerical efficiency at the expense of potential inconsistencies between sensitivities and concentrations (*7*). The DDM was originally implemented for gas-phase species in CAMx (*8*) and later extended to PM species (*9*). The DDM-3D implementation in CMAQ has also been extended to PM (*10*). While a higher-order DDM has been implemented for gas-phase species (*11−13*), the DDM for PM species is currently limited to first-order sensitivity.

There have been a few attempts to compare source apportionment and sensitivity analysis for ozone. Dunker et al. (*14*) compared source impacts on ozone estimated using ozone source apportionment technology (OSAT) and first-order DDM sensitivities. Cohan et al. (*12*) approximated the zero-out contribution (change in the pollutant concentration

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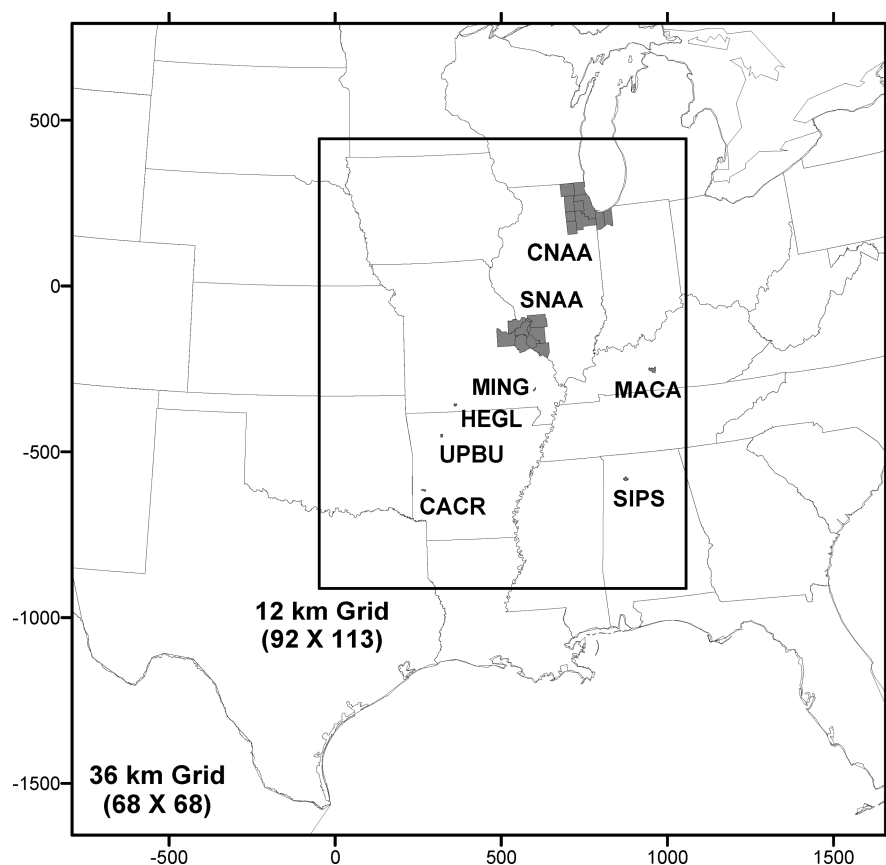‡ General Motors Research and Development Center.

FIGURE 1. Modeling domain with locations of the eight receptors selected: Chicago PM$_{2.5}$ nonattainment area (CNAA), St. Louis PM$_{2.5}$ nonattainment area (SNAA), Mingo Wilderness area (MING), Hercules–Glades Wilderness area (HEGL), Upper Buffalo Wilderness area (UPBU), Caney Creek Wilderness area (CACR), Mammoth Cave National Park (MACA), and Sipsey Wilderness area (SIPS).

that would occur if a source is removed) using first- and second-order DDM sensitivities of ozone to NO$_x$ and VOC emissions. In this paper, the model responses of atmospheric PM components to various emission reductions calculated by PSAT and first-order DDM sensitivities are compared with those by the BFM, and the differences between their results are discussed.

Methods

The PSAT and DDM are implemented in CAMx, and they can be compared using the same modeling framework. Details of the PSAT and DDM implementation in CAMx are given in the references mentioned above. Two month long (February and July) episodes from the St. Louis 36/12 km 2002 PM$_{2.5}$ state implementation plan modeling database were selected for evaluating the PSAT and DDM with 10 spin-up days before each month. The Pennsylvania State University/National Center for Atmospheric Research (PSU/NCAR) mesoscale model (MM5) and sparse matrix operator kernel emissions (SMOKE) were used to prepare meteorological field and emission inputs, respectively. On-road mobile source emissions were processed by MOBILE6, and biogenic emissions were generated by model of emissions of gases and aerosols from nature (MEGAN). Figure 1 shows the modeling domain that consists of a master grid with 36 km resolution and a 12 km nested grid. Sixteen vertical layers extend up to about 15 km. We selected eight receptor locations that cover urban (two receptors) and rural (six receptors) conditions for the analysis. In general, there was no notable distinction between the model results at the urban and rural sites, with the only exception being PM$_{2.5}$ ammonium which showed slightly more nonlinear responses to emission changes at the rural sites.

Brute force emission reductions of 100% (zero-out) and 20% were simulated for the following anthropogenic emissions: SO$_2$ and NO$_x$ from point sources; NO$_x$, VOC, and NH$_3$ from area sources (including mobile sources); and all emission species from on-road mobile sources (see Table S1 of the Supporting Information for average daily emissions from each source category). The BFM contributions were calculated by subtracting the PM concentrations of the emission reduction case from those of the base case. PSAT source contributions and first-order DDM sensitivities are computed in concentration units and may be directly compared with the BFM response to 100% emissions reduction. Both quantities were linearly scaled for comparison with the 20% reduction BFM results. However, nonlinear model response affects the PSAT and DDM results but in different ways. As illustrated in Figure 2, in a strongly nonlinear system, the first-order DDM sensitivity is useful only for relatively small input changes, while good agreement between the PSAT and BFM is expected only near 100% emission reduction.

The BFM inherently accounts for nonlinear model response but may suffer limitations as a source apportionment method when the model response includes an indirect effect resulting from influence by chemicals other than the direct precursor. For example, consider an oxidant-limiting case of sulfate formation where oxidation of SO$_2$ is limited by availability of H$_2$O$_2$ or O$_3$. Removing an SO$_2$ source in an oxidant-limited case makes more oxidant available to convert SO$_2$ from other sources, resulting in a smaller zero-out contribution for the source than in an oxidant abundant case. Furthermore, the sum of the zero-out contributions calculated separately for each source will likely not add up to the total sulfate concentration in the base case. Indirect
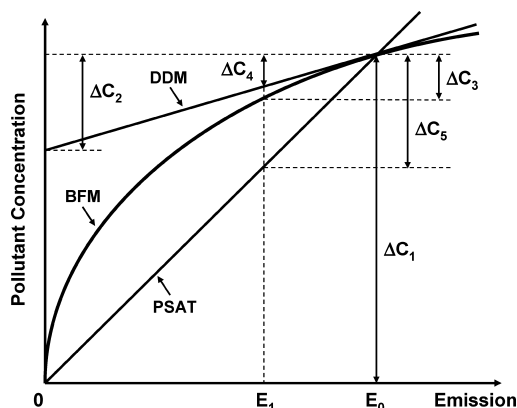
FIGURE 2. Nonlinear responses of pollutant concentration to emission reductions. ΔC_1 and ΔC_2 represent the changes in the pollutant concentration due to 100% reduction in the emission (from E_0 to 0) estimated using zero-out BFM and first-order DDM sensitivity, respectively. If no indirect effects exist, PSAT gives the same answer (ΔC_1) as the BFM. ΔC_3, ΔC_4, and ΔC_5 represent the model responses due to a smaller emission change (from E_0 to E_1) estimated by the BFM, DDM and PSAT, respectively.

effects also can influence PSAT contributions for multipollutant sources where emissions of nondirect precursors have significant impact on the PM component of interest.

Results

Sulfate. Monthly averaged contributions of point source SO_2 emissions to $PM_{2.5}$ sulfate concentrations are compared in Figure 3 for the zero-out, PSAT, and DDM runs. (See Figure S7 of the Supporting Information for monthly average concentrations from the base case simulation.) Close to large SO_2 sources, PSAT shows higher source contributions than those estimated by the BFM. This is a consequence of sulfate formation being limited by availability of oxidants (see the description of oxidant-limiting case in Methods). By design, PSAT does not take such indirect effects into account. This effect is less noticeable in July when the oxidant concentrations are higher. The DDM mostly underestimates the sulfate changes calculated by the zero-out method. This difference results from the nonlinear response of sulfate concentrations to large changes in SO_2 emissions. As noted earlier, the current DDM implementation for PM in CAMx is limited to first-order sensitivities, which cannot capture such nonlinearities. First-order DDM sensitivities compare well with the 20% BFM emission changes as discussed below.

Scatter plots comparing the PSAT (or DDM) and BFM results are shown in Figure 4 for the eight receptor sites selected (hereafter, we will focus on the analyses at the receptor locations). With 100% reduction in the point source SO_2 emissions, PSAT shows excellent agreement with the BFM in July, while exhibiting slight overestimation in February when oxidant-limiting effects are more important. With smaller (20%) reduction in point source SO_2 emissions, the oxidant-limiting effect has greater impact because a greater fraction of the freed oxidant can oxidize SO_2 from nonpoint sources (this happens because point sources dominate the SO_2 emissions; see Table S1 of the Supporting Information). This results in more difference between the PSAT and BFM for the 20% reduction rather than the 100% SO_2 reduction. (See Table S2 of the Supporting Information for quantitative statistics.) However, the DDM and BFM agree better with the 20% reduction than the 100% reduction as the model response becomes more linear with smaller input changes.

Scatter plots for sulfate changes due to reduced emissions of all species from mobile sources illustrate another indirect

effect that is not accounted for by PSAT (Figure 5). Under winter conditions (low temperature), more nitric acid can dissolve into water. Therefore, reducing mobile source NO_x emissions decreases the acidity of the aqueous phase, which in turn increases sulfate concentrations as more SO_2 dissolves and then is oxidized in the aqueous phase. In summer, reducing NO_x emissions means less oxidant available to oxidize SO_2, which decreases sulfate formation beyond reductions attributable to SO_2 emissions reductions alone. However, because PSAT is designed to apportion PM to its primary precursor (in this case, sulfate is apportioned to SO_x emissions, and the indirect effect of reduced NO_x emissions is ignored), the changes in sulfate estimated by PSAT are much smaller than those estimated using the zero-out BFM in summer, with an opposite direction in winter. The zero-out BFM is a sensitivity method, and it is debatable whether the zero-out result can be considered a source apportionment in this case. The DDM agrees much better with the zero-out result in this case because the DDM can calculate sensitivity to multiple inputs and account for indirect effects.

Ammonium. Figure 6 presents a clear example of the limitations of the PSAT and DDM. With 100% reduction of NH_3 emissions from area sources, the changes in $PM_{2.5}$ ammonium concentrations by PSAT are in excellent agreement with those from the BFM, while the DDM performance is impaired by nonlinearity in the gas–aerosol thermodynamic equilibrium for NH_3 and ammonium. The same nonlinearity also weakens agreement between the PSAT and BFM in the case of a 20% emission reduction. Small emission changes can also emphasize any existing indirect effects (e.g., ammonium formation limited by sulfate or nitric acid). As seen in the above cases, the first-order DDM sensitivity performs well in describing a model response to the smaller emission change. Comparison of the PSAT and BFM for the changes in ammonium concentrations due to reduced mobile source emissions also shows the influence of indirect effects (Figure S1 of the Supporting Information).

Nitrate. Scatter plots shown in Figure 7 compare $PM_{2.5}$ nitrate changes due to reductions in area NO_x emissions. PSAT slightly overestimates nitrate changes by the zero-out BFM because availability of ammonia can limit nitrate partitioning into particle phase (similar to the effect of oxidant-limiting sulfate formation, discussed above). The differences between the PSAT and BFM become larger for smaller emission reduction due to the nonlinear system. The DDM again performs better with a smaller change in NO_x emissions. Similar behaviors were observed with reductions in point source NO_x emissions (Figure S2 of the Supporting Information), although in this case the differences between the PSAT and BFM for a 100% reduction in emissions are nearly as large as for a 20% reduction (Table S2 of the Supporting Information). Because NO_x is the dominant component of on-road mobile source emissions (Table S1 of the Supporting Information), there is much less indirect effect due to other emission species from the sources. This explains the relatively good agreement between the PSAT and BFM in the case with all species from mobile emissions reduced (Figure S3 of the Supporting Information).

Secondary Organic Aerosol (SOA). The PSAT and DDM perform well in predicting the BFM responses of SOA concentrations to reductions in anthropogenic VOC emissions from area sources (Figure S4 of the Supporting Information). DDM shows good performance even with 100% emission reduction demonstrating that the SOA module in CAMx responded nearly linearly to this emission change. PSAT also shows reasonable agreement with the BFM for 100% and 20% reductions probably because enough oxidant is available to convert VOC precursors to SOA, and there are minimal indirect effects (although a hint of the oxidant-limiting effect can be seen in February). However, reducing
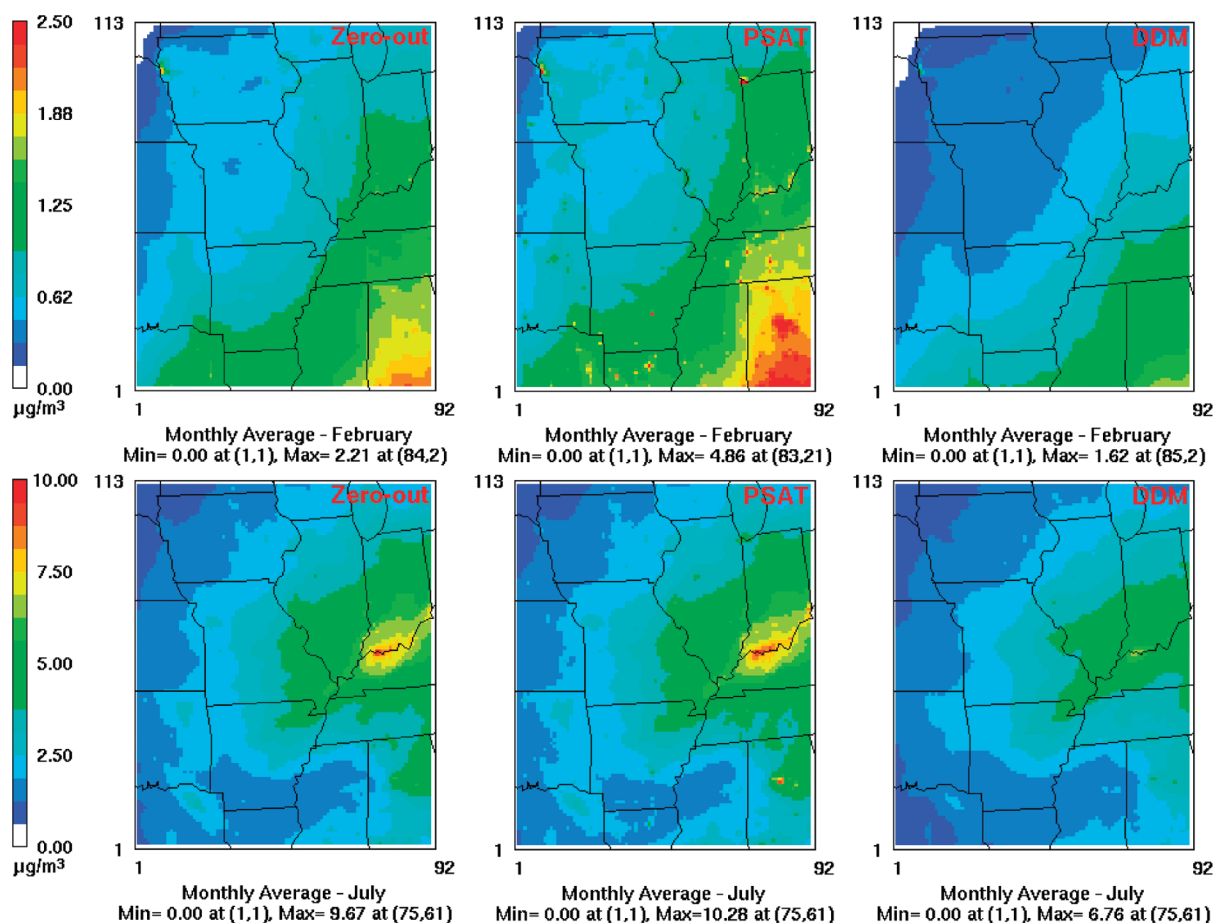
FIGURE 3. Monthly averaged contributions of domain-wide point source emissions of SO_2 to surface concentrations of $PM_{2.5}$ sulfate calculated by the zero-out, PSAT, and DDM simulations for February (top) and July (bottom).

NO_x as part of mobile source emission reductions can significantly alter ambient oxidant levels, which changes SOA formation from not only anthropogenic but also biogenic VOC precursors. Source apportionment by PSAT excludes this kind of indirect effect, and thus significantly underestimates the model response by BFM in summer, when mobile source NO_x emissions strongly influence oxidants (Figure S5 of the Supporting Information).

Primary PM. Because the source−receptor relationship for primary PM is essentially linear and not affected by any indirect effects, it is expected that the PSAT and DDM should accurately predict the model response of primary PM species to their emissions. Excellent agreement was found between the PSAT (or DDM) and BFM for changes in primary $PM_{2.5}$ concentrations from mobile sources (Figure S6 of the Supporting Information).

Discussion

The PSAT and DDM were applied in the same regional modeling framework to estimate the model responses to various BFM emission reductions by 100% and 20%. The results demonstrate that source sensitivity and source apportionment are equivalent for pollutants that are linearly related to emissions but otherwise differ because of nonlinearity and/or indirect effects.

On the basis of the simulations conducted in this study, the first-order DDM sensitivities can adequately predict the model responses of inorganic secondary aerosols to 20% emission changes (and in some cases larger changes). For SOA and primary aerosols, the DDM agreed reasonably well with the BFM up to 100% emission reductions. The DDM also gave reasonably good predictions for the impact of

removing 100% of on-road mobile source emissions (all VOC, NO_x, and particulate emissions) because the DDM accounts for indirect effects. However, as the size of model input changes increases, higher-order sensitivities become more important in general, and first-order sensitivity alone is not adequate to describe the model response for all magnitudes of emission reductions for all sources (e.g., Figure 6).

Source apportionment by PSAT could successfully approximate the zero-out contributions for primary aerosols. Results for ammonium demonstrate that PSAT source apportionment and zero-out are nearly equivalent in a case (reduction in area source NH_3 emissions) where the emissions−concentration relationship is highly nonlinear, but there is no indirect effect. Results for sulfate demonstrate that indirect effects (i.e., oxidant-limited sulfate formation) can limit the ability of zero-out to provide source apportionment, and therefore, that PSAT and zero-out may disagree when there are indirect effects.

Neither PSAT nor first-order sensitivities provide an ideal method to relate PM components to sources. PSAT is best at apportioning sulfate, nitrate, and ammonium to sources emitting SO_2, NO_x, and NH_3, respectively. PSAT is also better at estimating the impact on PM concentrations of removing all emissions from a source rather than removing a fraction of the emissions. First-order sensitivities are more accurate than PSAT in determining the impact of emissions that have indirect effects on secondary PM. This is especially true for sources such as motor vehicles that have substantial emissions of multiple pollutants (e.g., VOC and NO_x) because complicated indirect effects are more likely for such sources. In contrast to PSAT, first-order sensitivities are better at estimating the effects of eliminating a fraction of emissions
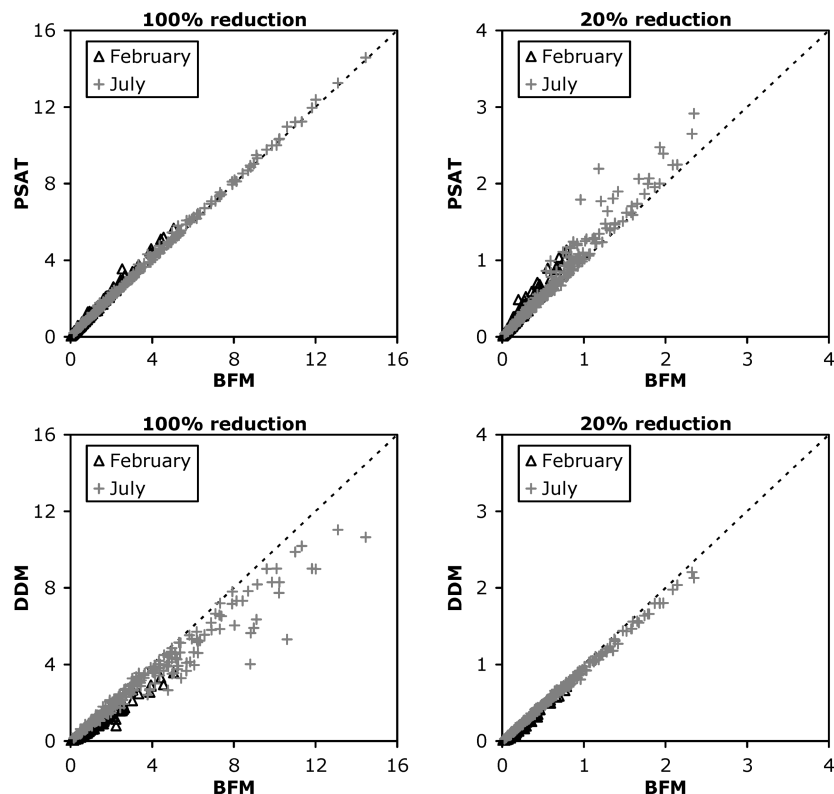
FIGURE 4. Comparison of the PM$_{2.5}$ sulfate changes (μg/m^3) due to reductions in point source SO$_2$ emissions calculated by the PSAT or DDM and BFM. Each point represents the change in the 24 h average sulfate concentration due to the emission reduction at one receptor on 1 day. (Positive number means a decrease in ambient sulfate with a decrease in emissions.)
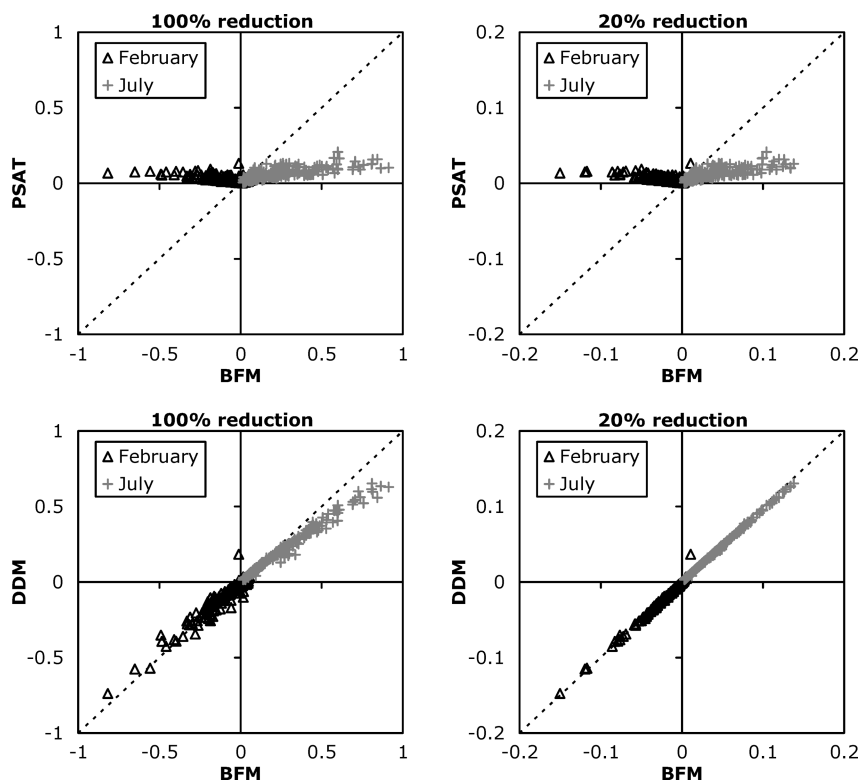

FIGURE 5. Comparison of the PM$_{2.5}$ sulfate changes (μg/m^3) due to reductions in on-road mobile source emissions calculated by PSAT or DDM and BFM. Each point represents the change in the 24 h average sulfate concentration due to the emission reduction at one receptor on 1 day. (Positive number means a decrease in ambient sulfate with a decrease in emissions, and negative number means an increase in ambient sulfate with a decrease in emissions.)

from a source than eliminating all emissions from the source. PSAT and first-order sensitivities are accurate for apportioning primary PM to emission sources. To some extent, PSAT and first-order sensitivities are complementary methods. Depending on which PM components, sources, and magnitude of emission reductions are being examined, we find
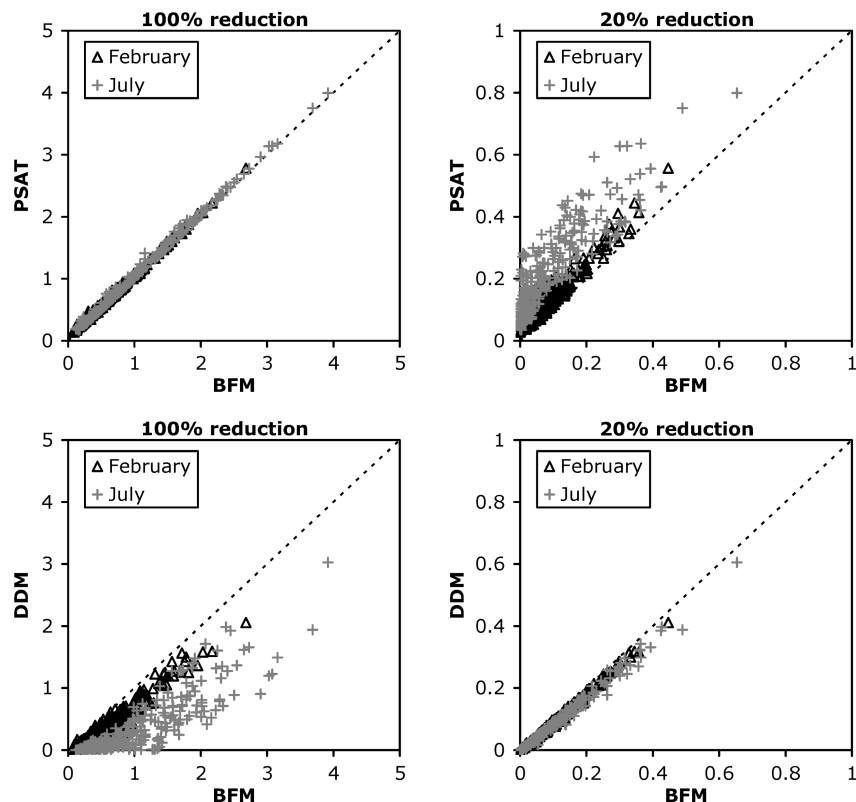
FIGURE 6. Comparison of the PM$_{2.5}$ ammonium changes (μg/m^3) due to reductions in area source anthropogenic NH$_3$ emissions calculated by PSAT or DDM and BFM. Each point represents the change in the 24 h average ammonium concentration due to the emission reduction at one receptor on 1 day.

FIGURE 7. Comparison of the PM$_{2.5}$ nitrate changes (μg/m^3) due to reductions in area source anthropogenic NO$_x$ emissions calculated by PSAT or DDM and BFM. Each point represents the change in the 24 h average nitrate concentration due to the emission reduction at one receptor on 1 day.
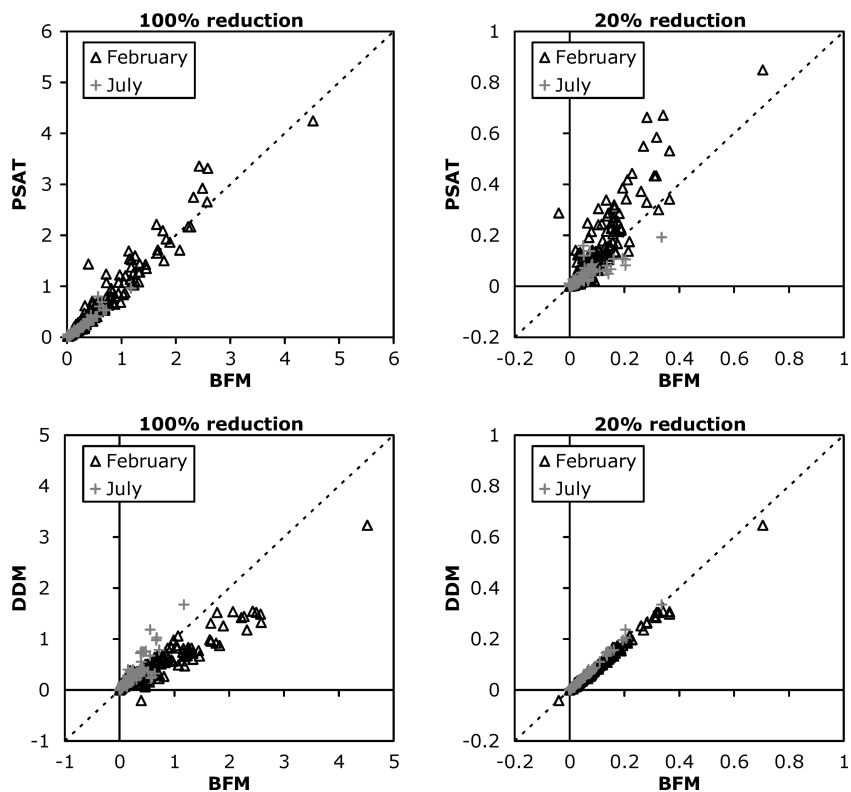
the considerations given above can be used as a guide in deciding which method to apply: PSAT or first-order sensitivities.

Although we have used the BFM as a standard against which to compare the two other methods, it too has limitations. It is the most computationally expensive when

determining the contributions of multiple sources. Also, the BFM is normally applied by removing each source individually from the base case, e.g., base case minus source i to determine the contribution of source i. Whenever model response is nonlinear, e.g., due to chemistry, the sum of these source contributions will not equal the simulated concentrations in the base case.

Acknowledgments

Supporting Information Available

Summary table showing emissions from each source sector, table of coefficient of determination and normalized mean error for PSAT versus BFM and DDM versus BFM, scatter plots for ammonium changes at the receptors due to reductions in on-road mobile source emissions, scatter plots for nitrate changes at the receptors due to reductions in point source NO_x emissions; scatter plots for nitrate changes at the receptors due to reductions in on-road mobile source emissions, scatter plots for SOA changes at the receptors due to reductions in area source VOC emissions, scatter plots for SOA changes at the receptors due to reductions in on-road mobile source emissions, scatter plots for primary PM changes at the receptors due to reductions in on-road mobile source emissions, and spatial plots for the base case monthly average PM concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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