

PARTICULATE MATTER SOURCE APPORTIONMENT TECHNOLOGY (PSAT) IN THE CAMX PHOTOCHEMICAL GRID MODEL

Greg Yarwood, Ralph E. Morris and Gary M. Wilson^{*}

1. INTRODUCTION

Airborne particulate matter (PM) is important because it causes health problems and environmental degradation and so many countries implement programs to control PM pollution (e.g., EPA, 1996). In recent years the emphasis on controlling PM pollution has shifted toward problems associated with fine PM (PM_{2.5} with particle diameter less than 2.5 µm) because it is more strongly associated with serious health effects than coarse PM. Knowing what sources contribute to fine PM_{2.5} is essential for developing effective control strategies. Many components of PM_{2.5} are secondary pollutants and so photochemical models are important tools for PM air quality planning. The Comprehensive Air quality Model with extensions (CAMx; ENVIRON, 2004) is one of the photochemical grid models being used to understand PM pollution and visibility impairment in the US and Europe. The Particulate Matter Source Apportioning Technology (PSAT) has been developed for CAMx to provide geographic region and source category specific PM source apportionment. PM source apportionment information from PSAT is useful for:

- (1) Understanding model performance and thereby improving model inputs/formulation
- (2) Performing culpability assessments to identify sources that contribute significantly to PM pollution
- (3) Designing the most effective and cost-effective PM control strategies.

^{*} ENVIRON International Corporation, 101 Rowland Way, Suite 220, Novato, CA 94945-5010.
e-mail: gyarwood@environcorp.com

Source apportionment for primary PM is relatively simple to obtain from any air pollution model because source-receptor relationships are essentially linear for primary pollutants. Gaussian steady-state models and Lagrangian puff models have been used extensively to model primary PM pollution from specific sources, which is source apportionment. The Gaussian and Lagrangian approaches work for primary PM because the models can assume that emissions from separate sources do not interact. This assumption breaks down for secondary PM pollutants (e.g., sulfate, nitrate, ammonium, secondary organic aerosol) and so puff models may dramatically simplify the chemistry (to eliminate interactions between sources) so that they can be applied to secondary PM. Eulerian photochemical grid models are better suited to modeling secondary pollutants because they account for chemical interactions between sources. Grid models do not naturally provide source apportionment because the impact of all sources has been combined in the total pollutant concentration. PSAT has been developed to retain the advantage of using a grid model to describe the chemistry of secondary PM formation and also provide source apportionment.

This paper starts by reviewing several approaches to PM source attribution in grid models that were considered when PSAT was designed. Next, the PSAT algorithms are explained. Finally, example PSAT results are presented and compared to results from some other methods.

2. APPROACHES TO PM SOURCE ATTRIBUTION IN GRID MODELS

The need for PM source apportionment (PSAT) in CAMx was discussed in the introduction. Several potential approaches were considered at the PSAT design stage and these are discussed below. The approaches considered fall into two general categories, which we have called sensitivity analysis and reactive tracers. The reactive tracer approaches also could be called tagged species approaches. This section concludes with a discussion of an important fundamental difference between sensitivity analysis and source apportionment that explains why these two concepts should not be confused for secondary pollutants.

2.1. Sensitivity Analysis Methods

Sensitivity analysis methods measure the model output response to an input change, e.g., the change in sulfate concentration due to a change in SO_x emissions. In general, sensitivity methods will not provide source apportionment if the relationship between model input and output is non-linear. For example, if sulfate formation is non-linearly related to SO_x emissions, the sum of sulfate (SO₄) sensitivities over all SO_x sources will not equal the model total sulfate concentration. This concept is discussed further in section 2.3.

Brute Force or Direct Method. The brute force method estimates first-order sensitivity coefficients (e.g., dSO_4/dSO_x) by making a small input change (dSO_x) and measuring the change in model output (dSO_4). This method is simple and can be applied to any model, but is inefficient because a complete model run is required for each sensitivity

coefficient to be determined. Accuracy also may be an issue for the brute force method because ideally the input change (dSO_x) should be vanishingly small but for small input changes the output change may be contaminated by numerical precision or model “noise.” Higher-order sensitivity coefficients also can be estimated by the brute force method.

Zero-out modeling. The zero-out method differs from the brute force method in that a specific emissions input is set to zero and the change in output measured. Zero-out modeling can be used with any model but is inefficient because a complete model run is required for each source. Accuracy also may be an issue if the zero-out method is applied to a small emissions source. This method has been used extensively for source attribution because it seems intuitively obvious that removing a source should reveal the source’s impact. However, because zero-out modeling is a sensitivity method it does not provide source apportionment for non-linear systems because the sum of zero-out impacts over all sources will not equal the total concentration, as discussed further in section 2.3.

Decoupled direct method (DDM). The DDM provides the same type of sensitivity information as the brute force method but using a computational method that is directly implemented in the host model (Dunker, 1981). The DDM has potential advantages of greater efficiency and accuracy relative to the brute force method (Dunker et al., 2002a) and the DDM implementation in CAMx (Dunker et al., 2002a,b) is currently being extended to PM species. Drawbacks of DDM are that the implementation is technically challenging, that using DDM for many sensitivities simultaneously requires large computer memory, and because DDM is a sensitivity method it does not provide source apportionment for non-linear systems (section 2.3.)

Other sensitivity methods. There are other sensitivity methods that provide similar information to DDM such as adjoint methods (e.g., Menut et al., 2000; Elbern and Schmidt, 1999) and automatic differentiation in FORTRAN (ADIFOR; e.g., Sandhu, 1997). They have similar advantages and disadvantages as DDM but may be less computationally efficient (Dunker et al., 2002a).

2.2. Reactive Tracer Methods

Reactive tracers (or tagged species) are extra species added to a grid model to track pollutants from specific sources. For example, a standard grid model calculates concentrations for a species X that has many sources and so the concentration of X is the total concentration due to all sources. A reactive tracer (x_i) is assigned to for each source (i) with the intention that the sum of the reactive tracers will equal total concentration ($X = \sum x_i$). The challenge is to develop numerical algorithms for solving the reactive tracer concentrations that ensure that this equality is maintained. Depending upon the formulation of the tracer algorithms, it may be possible to model tracers for a single source of interest and omit tracers for all other sources, or it may be necessary to include tracers for all sources (as is the case for PSAT). Reactive tracers can potentially provide true source apportionment ($X = \sum x_i$), however the numerical value of the source apportionment will depend upon assumptions within the reactive tracer formulation. In particular, for any process that is non-linear in species concentrations (e.g., chemistry)

there is no unique way to assign the total concentration change to the reactive tracers. This issue is discussed further in section 2.3.

Source Oriented External Mixture (SOEM). Kleeman and Cass (1999) developed an approach called SOEM that tracks primary PM from different source categories/regions using that tagged species that are considered to represent seed particles. Reactive tracers are added to track secondary PM and related gases from different source categories/regions and source apportioned secondary PM condenses onto the seed particles. Chemical change for secondary PM and related gases is accounted for by expanding the chemical mechanism to treat different source regions/categories as separate precursor and product species. This requires thousands of chemical reactions and hundreds to thousands of chemical species, depending upon the number of source regions/categories. The main advantage of the SOME method is that it is potentially accurate, and the main disadvantage is computational demand.

PSAT and TSSA. The PM Source Apportionment Technology (PSAT) uses reactive tracers to apportion primary PM, secondary PM and gaseous precursors to secondary PM among different source categories and source regions. The PSAT methodology is described in section 4. PSAT was developed from the related ozone source apportionment method (OSAT) already implemented in CAMx (Dunker et al., 2002b). Tonnesen and Wang (2004) are independently developing a method very similar to PSAT called Tagged Species Source Apportionment (TSSA) in a different photochemical grid model. Advantages of PSAT and TSSA are expected to be high efficiency and flexibility to study different source categories/regions. The accuracy of the PSAT (and TSSA) source apportionment results must be evaluated, as for any other method.

2.3. Source Apportionment and Source Sensitivity

Consider a chemical species X that has two sources A and B (so $X = x_A + x_B$) and which undergoes a second order self-reaction with rate constant k. The rate of chemical change is:

$$dX/dt = -kX^2$$

$$dX/dt = -k(x_A + x_B)^2$$

$$dX/dt = -kx_A^2 - kx_B^2 - 2kx_Ax_B$$

The homogeneous rate terms kx_A^2 and kx_B^2 clearly describe chemical change for pollutants from sources A and B (x_A and x_B), but the inhomogeneous rate term $2kx_Ax_B$ is not uniquely associated with either source A or B. A reactive tracer (or tagged species) source apportionment method must deal with this inhomogeneous rate term either by developing rules to apportion the inhomogeneous term to sources A and B or modifying the chemistry to eliminate the inhomogeneous term. For a sensitivity method, the homogeneous quadratic rate terms generate second-order homogeneous sensitivity coefficients (s_{AA} and s_{BB}) and the inhomogeneous rate term generates a second-order inhomogeneous sensitivity coefficient (s_{AB}). Consequently, the total concentration of X

is incompletely described by the first-order sensitivity coefficients (s_A and s_B) that resemble source apportionments.

The example presented above is a simple case of a non-linear chemical system that illustrates why source apportionment and source sensitivity are not the same thing for nonlinear systems. The implications are:

- (1) There is no unique source apportionment for chemical species that depend upon nonlinear reactions, such as secondary PM species and ozone. Nonetheless, reasonable source apportionment schemes can be developed and are useful tools for achieving the objectives listed in the introduction.
- (2) Sensitivity coefficients are not source apportionments for chemical species that depend upon nonlinear reactions, such as secondary PM species and ozone. Sensitivity coefficients are most applicable for predicting the model response to an input change (e.g., control strategy) and are very useful for this purpose (within the range of linear model response), but sensitivity coefficients should be used with care for source apportionment or culpability assessment. Likewise, source apportionments should be used with care for predicting model response to input changes.

3. PSAT METHODOLOGY

PSAT is designed to source apportion the following PM species modeled in CAMx:

- Sulfate
- Particulate nitrate
- Ammonium
- Particulate mercury
- Secondary organic aerosol (SOA)
- Six categories of primary PM

The PSAT “reactive tracers” that are added for each source category/region (i) are described below. In general, a single tracer can track primary PM species whereas secondary PM species require several tracers to track the relationship between gaseous precursors and the resulting PM. Nitrate and secondary organic PM are the most complex aerosol species to apportion because the emitted gases (NO, VOCs) are several steps removed from the resulting PM (nitrate, SOA). The reactive tracers used by PSAT are listed below for each class of PM.

Sulfur

SO_{2i} Primary SO₂ emissions

PS_{4i} Particulate sulfate ion from primary emissions plus secondarily formed sulfate

Nitrogen

RGN_i Reactive gaseous nitrogen including primary NO_x (NO + NO₂) emissions plus nitrate radical (NO₃), nitrous acid (HONO) and dinitrogen pentoxide (N₂O₅).

TPN_i Gaseous peroxy acetyl nitrate (PAN) plus peroxy nitric acid (PNA)

NTR_i Organic nitrates (RNO₃)

HN3_i Gaseous nitric acid (HNO₃)

PN3_i Particulate nitrate ion from primary emissions plus secondarily formed nitrate

Ammonia/Ammonium

NH3_i Gaseous ammonia (NH₃)

PN4_i Particulate ammonium (NH₄)

Secondary Organic

ALK_i Alkane/Paraffin secondary organic aerosol precursors

ARO_i Aromatic (toluene and xylene) secondary organic aerosol precursors

CRE_i Cresol Secondary secondary organic aerosol precursors

TRP_i Biogenic olefin (terpene) secondary organic aerosol precursors

CG1_i Condensable gases from toluene and xylene reactions (low volatility)

CG2_i Condensable gases from toluene and xylene reactions (high volatility)

CG3_i Condensable gases from alkane reactions

CG4_i Condensable gases from terpene reactions

CG5_i Condensable gases from cresol reactions

PS1_i Secondary organic aerosol associated with CG1

PS2_i Secondary organic aerosol associated with CG2

PS3_i Secondary organic aerosol associated with CG3

PS4_i Secondary organic aerosol associated with CG4

PS5_i Secondary organic aerosol associated with CG5

Mercury

HG0_i Elemental Mercury vapor

HG2_i Reactive gaseous Mercury vapor

HGP_i Particulate Mercury

Primary Particulate

PEC_i Primary Elemental Carbon

POA_i Primary Organic Aerosol

PFC_i Fine Crustal PM

PFN_i Other Fine Particulate

PCC_i Coarse Crustal PM

PCS_i Other Coarse Particulate

PSAT includes a total of 32 tracers for each source group (i) if source apportionment is applied to all types of PM. Since source apportionment may not always be needed for all species, the PSAT implementation is flexible and allows source apportionment of selected chemical classes in each CAMx simulation. For example, source apportionment for sulfate/nitrate/ammonium requires just 9 tracers per source group.

The PSAT approach to source apportionment is described below. Consider two model species A and B that are apportioned by reactive tracers a_i and b_i, respectively. Reactive tracers must be included for all sources of A and B including emissions, initial conditions and boundary conditions so that complete source apportionment is obtained, i.e., $A = \sum a_i$ and $B = \sum b_i$.

The general approach to modeling change over a model time step Δt is illustrated for a chemical reaction:



The general equation for species destruction is:

$$a_i(t+\Delta t) = a_i(t) + \Delta A \times [a_i / \Sigma a_i]$$

Here the relative apportionment of A is preserved as the total amount changes. This equation applies to chemical removal of A and also physical removal by processes such as deposition.

The general equation for species production (e.g., chemical production) is:

$$b_i(t+\Delta t) = b_i(t) + \Delta B \times [a_i / \Sigma a_i]$$

Here the product B inherits the apportionment of the precursor A.

In some cases, source category specific weighting factors (w_i) must be added to the equation for species destruction:

$$a_i(t+\Delta t) = a_i(t) + \Delta A \times [w_i a_i / \Sigma w_i a_i]$$

An example is chemical decay of the aromatic VOC tracers (ARO), which must be weighted by the average OH rate constant of each ARO_i. ARO tracers for different source groups have different average VOC reactivities because the relative amounts of toluenes and xylenes differ between source categories.

In some cases, source category specific weighting factors (w_i) must be added to the equation for species production:

$$b_i(t+\Delta t) = b_i(t) + \Delta B \times [w_i a_i / \Sigma w_i a_i]$$

An example is chemical production of condensable gases (CG1 or CG2) from aromatic VOC tracers, which must be weighted by aerosol yield weighting factors. The aerosol yield weighting factors depend upon the relative amounts of toluenes and xylenes in each source group.

Several aerosol reactions are treated as equilibria:



If A and B reach equilibrium at each time step, it follows that their source apportionments also reach equilibrium:

$$\begin{aligned} a_i(t+\Delta t) &= [a_i(t) + b_i(t)] \times [A / (A+B)] \\ b_i(t+\Delta t) &= [a_i(t) + b_i(t)] \times [B / (A+B)] \end{aligned}$$

Examples are the equilibrium between gas phase nitric acid and aerosol nitrate, gas phase ammonium and aerosol ammonium, and condensable organic gases (CG) and secondary organic aerosols (SOA).

4. TESTING PSAT

The initial PSAT testing was for primary PM species (e.g., fine crustal material) because these species are the most straightforward to implement and test (because there is

no chemistry). The results for primary PM species are not shown here but the tests were successful in that sum of PSAT tracers over all source groups remained identical to the total model concentration ($A = \sum a_i$) for all grid cells and hours. The primary PM tests confirmed the implementation of PSAT for all CAMx algorithms except chemistry.

The next stage of PSAT testing included the chemistry algorithms and results are shown here for two different types of testing for sulfate and nitrate. Sulfate was tested by comparing PSAT to zero out results in full 3-D CAMx simulations. As discussed above, zero out results are not expected to agree perfectly with PSAT because zero out does not give true source apportionment in non-linear systems. However, non-linearity in sulfate formation chemistry is expected to be less important than for other secondary PM species making sulfate the best candidate for zero out testing.

The most complex PSAT chemistry algorithm is for nitrate. Zero out tests were not used for nitrate because the relationship between NO emissions and nitric acid may be highly non-linear. Therefore, conduct 1-D (box model) tests were used to evaluate PSAT results for nitrate by comparing against the method used by Kleeman and Cass (2001) to track nitrate apportionment in the Source-Oriented External Mixture (SOME) method, discussed above.

4.1. PSAT Sulfate Testing

The PSAT performance for sulfate was tested using a CAMx database developed by the Midwest RPO (MPRO) for PM and visibility modeling of the Eastern US. The modeling was from June 18 to July 21, 2001 and used a 36-km modeling grid with meteorology developed using the mesoscale model version 5 (MM5). The modeling domain was sub-divided to geographic areas according to regional planning organizations (RPOs) responsible for developing regional visibility and PM control strategies in the U.S. The sub division of the modeling domain to RPOs is shown in Figure 1 and the RPOs are labeled by their respective acronyms (MRPO, MANE-VU, VISTAS, CERAP and WRAP). The state of Illinois (IL) was split out from the Midwest RPO (MPRO) to test the ability of PSAT to apportion the contribution from a single state. Four hypothetical point sources were added near the middle of the MRPO, MANE-VU, VISTAS and CENRAP areas (shown by the + symbols in Figure 1) to test the ability of PSAT to track contributions from single sources. The hypothetical point sources were chosen to be generally representative of a large coal-fired utility source but do not represent actual sources at these locations. In total, sulfate was apportioned to 11 source groups including a remainder area for Canada, Mexico and over water.

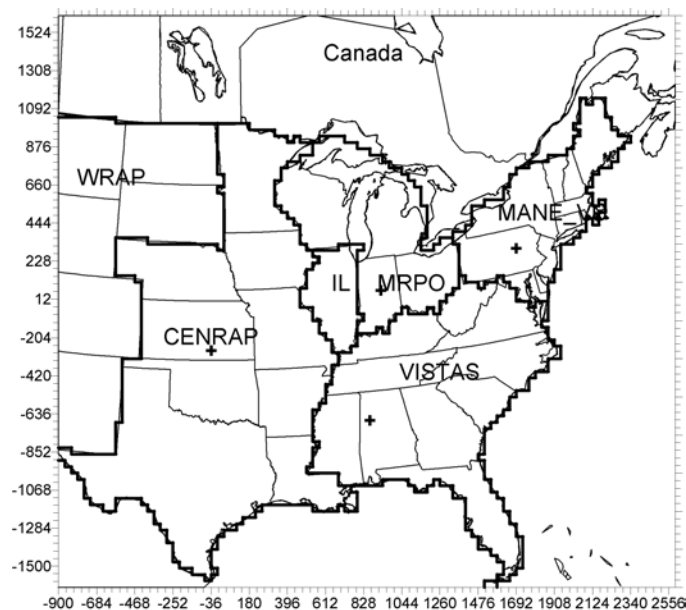


Figure 1. The CAMx modeling domain for PSAT testing showing subdivision to geographic areas and locations of four hypothetical point sources (+ symbols).

The sulfate impacts from the hypothetical MRPO point source are compared in Figure 2 at a single hour (hour 15) on 28 June 2001. The spatial distribution of sulfate impacts is very similar in the PSAT and zero out results as shown by the edge of impacts plume ($0.1 \mu\text{g}/\text{m}^3$ level). There are differences in the areas of larger impacts (e.g. the 1 and $2 \mu\text{g}/\text{m}^3$ levels) and these are due to the effects of non-linear chemistry in the zero out test. As discussed above, sensitivity methods such as zero out do not provide accurate source apportionments for non-linear processes. Sulfate formation can be limited by the availability of oxidants, especially hydrogen peroxide, which will tend to depress the maximum impact levels in zero out runs as well as shift impacts further downwind (to where oxidant availability is no longer limiting). The oxidant limiting effect on zero out sulfate impacts is most easily seen from the $2 \mu\text{g}/\text{m}^3$ level extending further downwind over Lake Michigan in the zero out result than the PSAT result.

(a) PSAT

(b) Zero Out

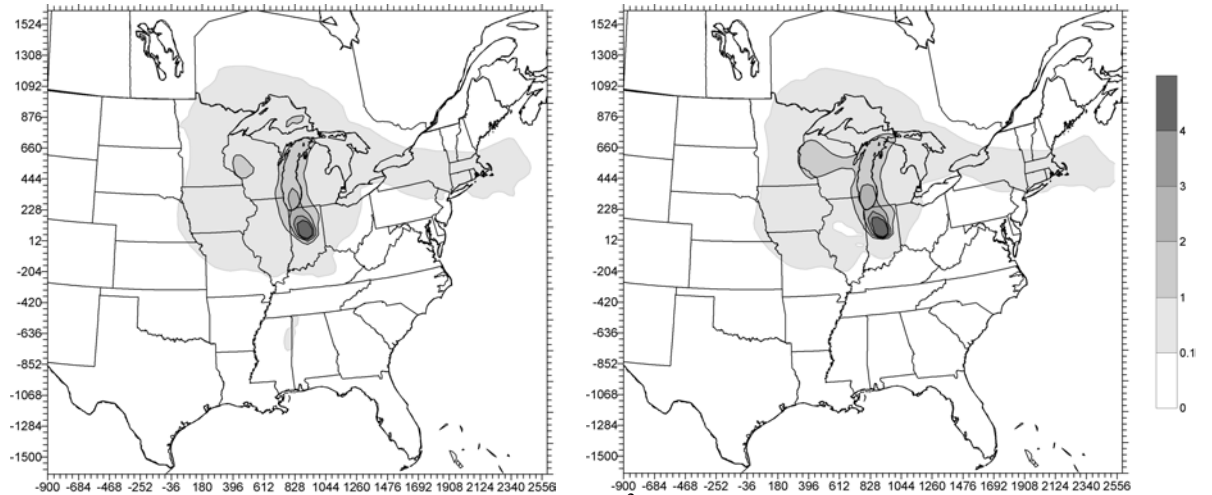


Figure 2. Comparison of sulfate impacts ($\mu\text{g}/\text{m}^3$) from the hypothetical MRPO point source on 28 June 2001 at hour 15: (a) PSAT result; (b) Zero out result.

The episode average sulfate impacts from the hypothetical MRPO point source are compared in Figure 3 for the entire 28 June to July 21, 2001 modeling period. The spatial distribution of sulfate impacts is very similar in the PSAT and zero out results. The maximum impact occurs very close to the source and is higher in the PSAT result ($2.2 \mu\text{g}/\text{m}^3$) than the zero out result ($1.8 \mu\text{g}/\text{m}^3$) due to the effect of oxidant limitation on sulfate impacts determined by the zero out method.

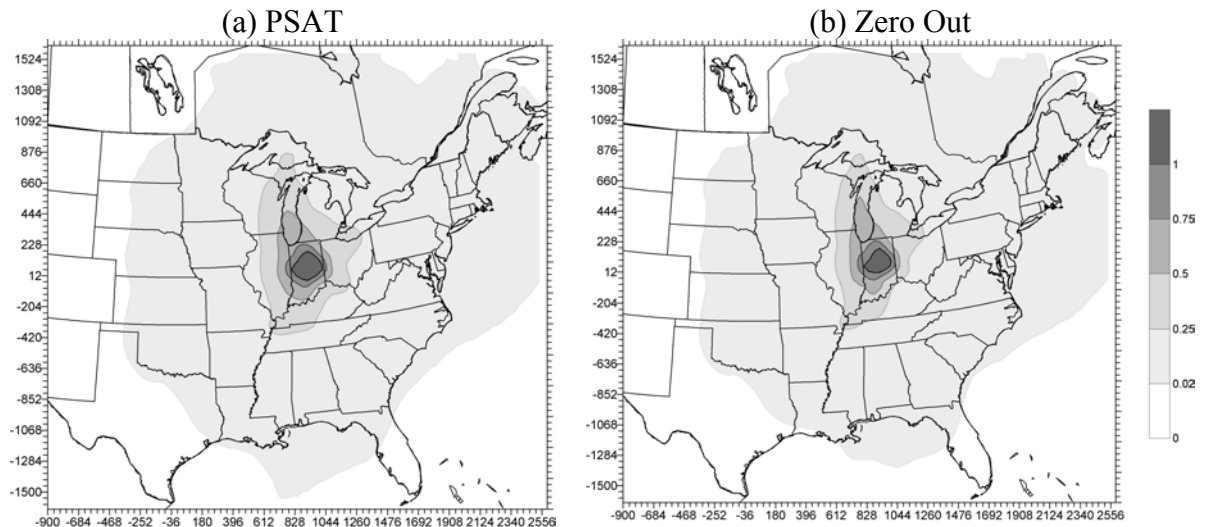


Figure 3. Comparison of episode average (June 18 to July 21, 2001) sulfate impacts ($\mu\text{g}/\text{m}^3$) from the hypothetical MRPO point source: (a) PSAT result; (b) Zero out result.

The PSAT sulfate tests provided a comparison of the efficiency of the PSAT method compared to zero out modeling. Zero out modeling requires a new model run for each source contribution determined, so the incremental time for each “apportionment” is the same as for the model base case. In contrast, the marginal cost for each PSAT source apportionment was about 2% of the time required for the base case.

4.2. PSAT Nitrate Testing

The PSAT nitrate algorithms were tested using CAMx for a 1-D (box model) problem in order to focus upon the ability of the PSAT chemical algorithms to track nitrate apportionment. The box model problem was for summer conditions and PSAT was used to apportion nitrated between 20 ppb of initial NO_x and 100 ppb of NO_x emission injected continuously through the 24 hour run. The PSAT results were compared to the SOME algorithm of Kleeman and Cass (2001) where the reactive nitrogen (NO_y) reactions in the chemical mechanism are duplicated to provide two different types of NO_y (think of them as “red” NO_y and “blue” NO_y). There was no ammonia in the box model so that nitric acid remained in the gas phase rather than forming PM nitrate.

The PSAT apportionment of NO_y to initial conditions (ICs) and emissions during the 24 hour box model simulation is shown in Figure 4. The total NO_y apportioned to ICs remains constant at 20 ppb throughout the simulation but the apportionment changes over time from NO_x (RGN-IC) at the start to PAN (TPN-IC), organic nitrates (NTR-IC) and nitric acid (HN3-IC). The NO_y apportioned to emissions increased linearly throughout the simulation and the apportionment also evolved as the NO_x emissions (RGN-E) reacted. At the start of the simulation RGN (NO_x) is dominated by ICs whereas late in the day (hour 18) RGN is dominated by emissions. The source apportionments shown in Figure 4 are reasonable and show necessary attributes (such as conserving the total 20 ppb of ICs).

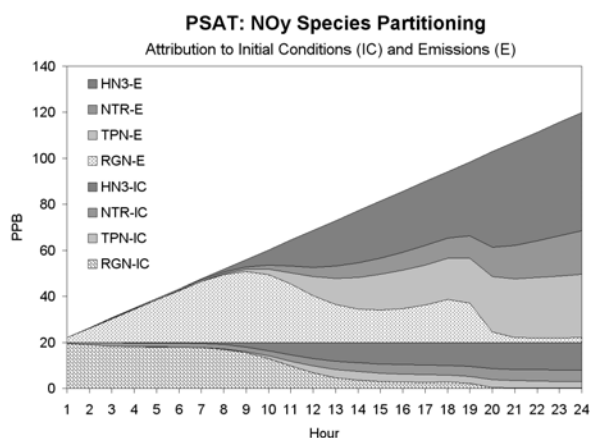


Figure 4. PSAT apportionment of reactive nitrogen species to initial conditions and emissions during a 24 hour box model simulation.

The SOEM apportionment of NO_y to ICs and emissions during the 24-hour box model simulation is shown in Figure 5. The time evolution of the source apportionments for the ICs and emissions is very similar for SOME (Figure 5) and PSAT (Figure 4). It is not clear that either method is more “correct,” or indeed that a correct source apportionment result exists for this test, but the consistency between the PSAT and SOME results is encouraging.

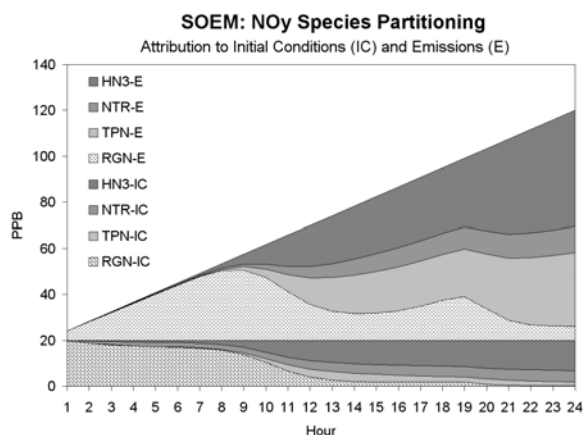


Figure 5. Source-Oriented External Mixture (SOME) apportionment of reactive nitrogen species to initial conditions and emissions during a 24-hour box model simulation.

5. SUMMARY

Several approaches to PM source apportionment were considered and a reactive tracer (or tagged species) method has been developed for the PM Source Apportionment Technology (PSAT) implemented in CAMx. Initial tests show that PSAT results are reasonable and that PSAT is much more efficient than sensitivity methods such as zero out modeling. Theoretical considerations suggest that PSAT may be a better approach to source apportionment than sensitivity methods because it is better able to deal with non-linear chemistry. Further testing is needed in real world applications. The PSAT algorithms will become publicly available in a future CAMx release.

6. ACKNOWLEDGMENT

The Midwest Regional Planning Organization (MRPO) and the Lake Michigan Air Directors Consortium (LADCO) sponsored the PSAT development. The authors acknowledge assistance from and helpful discussions with Mike Koerber and Kirk Baker of LADCO.

7. REFERENCES

- Dunker A.M., 1981. *Atmos. Environ.* 1981, 15, 1155-1161.
- Dunker A.M., G. Yarwood, J.P. Ortmann, G.M. Wilson, 2002a, The decoupled direct method for sensitivity analysis in a three-dimensional air quality model – implementation, accuracy and efficiency, *Environ. Sci. Technol.*, **36**:2965-2976.
- Dunker A.M., G. Yarwood, J.P. Ortmann, G.M. Wilson, 2002b, Comparison of source apportionment and source sensitivity of ozone in a three-dimensional air quality model, *Environ. Sci. Technol.*, **36**:2953-2964.
- Elbern, H.; Schmidt, H. *J. Geophys. Res.* 1999, 104, 18583-18598.1999
- ENVIRON, 2003, User's guide to the Comprehensive Air Quality model with extensions (CAMx) version 4.00 (January, 2003); <http://www.camx.com>
- EPA, 1996, Air quality criteria for particulate matter, Environmental Protection Agency report EPA/600/P-95/001aF-cF.3v. Research Triangle Park, NC
- EPA, 2003, Air quality criteria for particulate matter, Environmental Protection Agency draft report EPA/600/P-99/002aB. Research Triangle Park, NC
- Kleeman M.J., G.R. Cass, 2001, A 3D Eulerian source-oriented model for an externally mixed aerosol, *Environmental Science and Technology*, **35**: 4834-4848.
- Menut L., R.Vautard, M.Beekmann, C.Honoré, 2000, Sensitivity of Photochemical Pollution using the Adjoint of a Simplified Chemistry-Transport Model, *Journal of Geophysical Research – Atmospheres*, **105**, D12: 15,379-15,402,
- Sandhu A. 1997
- Tonnesen G., B. Wang, 2004,
- CMAQ Tagged Species Source Apportionment, July 22, 2004;
http://www.wrapair.org/forums/aoh/meetings/040722/UCR_tssa_tracer_v2.ppt