

Description of the ISAM Chemistry Method

After determining how chemistry affects concentrations of bulk species at time= dt , we use the below algorithm (Table 1.) to update the source or tag concentrations of the tracked species. In the algorithm, $P_T(s)$ sums the amount of the s^{th} species from its production reactions; $c_T(s)$ equals the bulk concentration of the s^{th} chemistry species; $L_T(s)$ sums the amount of s^{th} species from its destruction reactions; $Loss_Fact(s)$ equals the loss frequency of the s^{th} species based on $L_T(s)$ times dt ; $c(s,j)$ equals the concentration of s^{th} species from the j^{th} tagged source out of N source tags; $P(s,j)$ sums the amount of the s^{th} species from the j^{th} tagged source in its production reactions. $OUT(s)$ equals the amount of the species produced that is not accounted

Table

<p>– If $P_T(s) > 1e-30$ ppm</p> <p>a. Determine how production affects tag concentrations.</p> <p>i. If $L_T(s) > 1e-30$ ppm</p> <ul style="list-style-type: none"> • If $Loss_Fact(s) > 14.0$, initial concentrations replaced by production <ul style="list-style-type: none"> ○ $\Delta c(j, s)_{t=dt} = -c(j, s)_{t=0} + \frac{c_i(s)_{t=dt} P(s, j)}{P_T(s)}$ ○ $OUT(s) = \frac{c_i(s)_{t=dt} (P_T(s) - \sum_{i=1}^N P(s, j))}{P_T(s)}$ ○ Note that $OUT(s)$ tracks production outside tags • Else using solution to inhomogeneous 1st order ODE with constant coefficients <ul style="list-style-type: none"> ○ $\Delta c(j, s)_{t=dt} = -c(j, s)_{t=0} \exp(Loss_Fact(s)) + \frac{P(s, j)(1 - \exp(-Loss_Fact(s)))}{Loss_Fact(s)}$ ○ $OUT(s) = \frac{(P_T(s) - \sum_{i=1}^N (P(s, j))(1 - \exp(-Loss_Fact(s))))}{Loss_Fact(s)}$ • May require normalizing tag concentrations against bulk concentration because nothing forces $(\sum_{j=1}^N \Delta c(s, j)_{t=dt} + OUT(s))$ to equal $\Delta c_T(s)$ or $(c_T(s)_{t=dt} - c_T(s)_{t=0})$ <p>ii. Else, scale change by relative production to the total</p> <ul style="list-style-type: none"> • $\Delta c(s, j)_{t=dt} = \frac{\Delta c_T(s) P(s, j)}{P_T(s)}$ • $OUT(s) = \frac{\Delta c_T(s) (P_T(s) - \sum_{i=1}^N P(s, j))}{P_T(s)}$ <p>b. Determine how to distribute $OUT(s)$ to tag concentrations.</p> <ul style="list-style-type: none"> ▪ If $\sum_{i=1}^N P(s, i) > 1.0e-30$, apportion out among tags based on relative production between tags <ul style="list-style-type: none"> • $\Delta c(s, j)_{t=dt} = \Delta c(s, j)_{t=dt} + \frac{OUT(s) P(s, j)}{P_T(s)}$ ▪ Else just add to other tag <ul style="list-style-type: none"> • $\Delta c(s, j_{other})_{t=dt} = \Delta c(s, j_{other})_{t=dt} + OUT(s)$ <p>– Else, (assume bulk species decreases)</p> <ul style="list-style-type: none"> • tag change proportional change in total concentration $\Delta c_T(s)$. <ul style="list-style-type: none"> a. $\Delta c(s, j)_{t=dt} = \frac{c(s, j) \Delta c_T(s)}{c_T(s)}$

by the tagged sources, i.e., $P_T(s) - \sum_{j=1}^N P(s, j)$. It should not be confused with the other tag. See section on the *Weakness of the Method* for why the difference can be greater the zero.

To use the algorithm, we first determine $P_T(s)$ and $P(s, j)$. Each depends on the NR reactions that have a positive stoichiometric coefficient, a , for the species.

$$P_T(s) = \sum_{i=1}^{NR} a(i, s) R(i) dt$$

$$P(s, j) = \sum_{i=1}^{NR} a(i, s) f(i, j) R(i) dt \quad (\text{EQ \#1})$$

The dimensionless variable, $f(i, j)$, equals the fraction for how much the source's concentrations contributes to the rate, $R(i)$, of reaction i after dt . Note that reaction rates depend on the product of reaction rate constant and concentrations of the bulk reactants at $t=dt$. We determine f by using $p(s, j)$, reactant concentrations from j^{th} source divided by the bulk reactants concentrations or

$$p(s, j) = \frac{c(s, j)}{c_T(s)}.$$

We could derive a formula for f based on all the ways that a source's reactants interact with reactants not from the source. The derivation becomes difficult as the number of reactants and sources increase. Perhaps, a simpler method uses the fraction that none of the reactants came from the source, $q(i, j)$, because $(1-q(i, j))$ is proportional to $f(i, j)$ by a normalization constant. The constant equals the reciprocal of $(1-q(i, j))$ summed over the N sources plus one, $N+1$.

$$f(i, j) = \frac{(1 - q(i, j))}{\sum_{J=1}^{N+1} (1 - q(i, J))} \quad (\text{EQ \#2})$$

Normalizing prevents the sum of $f(i, j)$ from exceeding one for reactions with multiple reactants. It includes the $(N+1)^{\text{th}}$ term because CMAQ-ISAM does not track all chemical reactants. The term can be considered as from the $(N+1)^{\text{th}}$ source so j goes from 1 to $N+1$.

We need to express $q(i, j)$ in terms of the $p(k, j)$ for the reactants where k equals 1 to the JR reactants of the reaction. For each reactant, $(1-p(k, j))$ equals the fraction of a k^{th} reactant not from the source and equals q for unimolecular reactions. If the reaction has more than one reactant, q equals the product of $(1-p)$ over the reactants.

$$q(i, j) = \prod_{k=1}^{JR(i)} (1 - p(k, j))$$

Substituting $q(i, j)$ into equation 2 produces the below formula for f .

$$f(i, j) = \frac{(1 - \prod_{k=1}^{JR(i)} (1 - p(k, j)))}{\sum_{s=1}^{N+1} (1 - \prod_{k=1}^{JR(i)} (1 - p(k, j)))}$$

We must determine what to do with $f(i, N+1)$ when reactants include untracked species because $c(s, j)$ will underestimate production from the source such as when tracked organic compounds and untracked hydroxyl radicals react and produce formaldehyde. The solution adds a second term to $f(i, j \neq N+1)$. The term equals $f(i, N+1)$ weighted by how a source contributes relative to all N tagged sources.

$$f(i, j \neq N+1) = \frac{(1 - \prod_{k=1}^{JR(i)} (1 - p(k, j)))}{\sum_{s=1}^{N+1} (1 - \prod_{k=1}^{JR(i)} (1 - p(k, j)))} + \frac{(1 - \prod_{k=1}^{JR(i)} (1 - p(k, j)))}{\sum_{s=1}^N (1 - \prod_{k=1}^{JR(i)} (1 - p(k, j)))} * \frac{(1 - \prod_{k=1}^{JR(i)} (1 - p(k, N+1)))}{\sum_{s=1}^{N+1} (1 - \prod_{k=1}^{JR(i)} (1 - p(k, j)))}$$

Or

$$f(i, j \neq N+1) = \frac{(1 - \prod_{k=1}^{JR(i)} (1 - p(k, j)))}{\sum_{s=1}^{N+1} (1 - \prod_{k=1}^{JR(i)} (1 - p(k, j)))} \left(1 + \frac{(1 - \prod_{k=1}^{JR(i)} (1 - p(k, N+1)))}{\sum_{s=1}^N (1 - \prod_{k=1}^{JR(i)} (1 - p(k, j)))} \right)$$

Note that the p matrix is updated after each sub-timestep that solves for $c_T(s)$.

We can simplify f based on the number of reactants. For unimolecular reactions with a reactant u , f is simple,

$$f(i, j) = p(u, j),$$

because $\sum_{j=1}^N f(i, j)$ equals one if the reactant is tracked. For bimolecular reactions with reactants u and v , f is more complex because it includes products between each source's concentrations. The expression for f reduces to the below if either reactant is tracked.

$$f(i, j) = \frac{(p(u, j) + p(v, j) - p(u, j)p(v, j))}{\sum_{s=1}^{N+1} (p(u, s) + p(v, s) - p(u, s)p(v, s))} \left(1 + \frac{(p(u, N+1) + p(v, N+1) - p(u, N+1)p(v, N+1))}{\sum_{s=1}^N (p(u, s) + p(v, s) - p(u, s)p(v, s))} \right)$$

If both reactants are tracked species, f simplifies because $p(u, N+1)$ and $p(v, N+1)$ equal zero so $f(i, N+1)$ equals zero.

$$f(i, j) = \frac{(p(u, j) + p(v, j) - p(u, j)p(v, j))}{\sum_{s=1}^N (p(u, s) + p(v, s) - p(u, s)p(v, s))} \quad (\text{EQ \#3})$$

We can prove that f equals one when summed over N values of the j index. Analogous formulas can be derived for termolecular reactions.

The next step determines how much the reactions destroy $c_T(s)$ and the implied loss frequency multiplied by dt . The former is easily determined from the mechanism's reactions,

$$L_T(s) = \sum_{i=1}^{NS} |a(i,s)| R(i) dt,$$

where NS equals the number of reactions with negative stoichiometric coefficients, a , for the chemistry species. We use $c_T(s)$ to determine $Loss_Fact(s)$.

$$Loss_Fact(s) = \frac{L_T(s)}{c_T(s)}$$

Once the above quantities are determined, the algorithm described in Table 1 is used.

Weaknesses of the Source Apportionment Method.

When a chemistry species has significant production, results depend on what other species are tracked. They need to compose the main production pathways from emissions to the target species. Otherwise, results will underestimate production linked to a source. Tracking all chemistry species is a complete way to accomplish the goal but the step is computationally expensive. More subtle ways exist. They require understanding or identifying the pathways in each chemical mechanism. For sulfate production in chemistry mechanisms available in the CMAQ model, the goal is relatively easy because additional tracked species in chemistry are sulfur dioxide and in one mechanism dimethyl sulfate. For ozone apportionment, the goal becomes complex because it identifies dominant species controlling O_x , NO_y , HO_2 and organic peroxy radicals. Additional tracked species will include species controlling or counting interactions between these groups of chemistry species. Besides viewing how a mechanism's reactions determine the interplay between the chemistry species, tools exist to identify what species should be tracked to estimate apportionment for a target species. They include Integrated Reaction Rate Analysis and the Directed Decouple Method.

Another weakness is that results can change if a species has chemical production from reactions with more than one reactant. The problem occurs between applications that have the same input data but differ in sources selected for apportionment calculations. Between the applications, numbers and values of p change because unselected sources are lumped into a single source representing their emissions and their chemical impacts. While each application initially have the same values of $\sum_{i=1}^N p(i, j)$, they do not have equal cross products between fractions of reactants for each source such as the $p(u,s)p(v,s)$ terms in f for bimolecular reactions. The formula for f depends on these products so the applications will differ in fractions of reactions apportioned to each source. Relative differences in source apportionment inversely depend on the fraction of reactants from each on source.

We give an example of the latter weakness using equations (1) and (3). Consider the scenario with three sources: X, Y and Z. Each have portions of reactants A and B that produce C (X_A, X_B, Y_A, Y_B, Z_A and Z_B).



Further assume a scenario where $Y_A = Y_B = Z_A = Z_B = 0.5Q$ and $X_A = X_B = 1-Q$ where Q sums the fractions of reactants from sources Y and Z. One application tags all sources for their individual contributions to C. Equations (1) and (2) simplifies each sources' fraction of C production to f for the source by setting $R_{AB}dt$ to one.

$$f_1(i = C, j = X) = \frac{(1-Q^2)}{(1+2Q-(1+0.5)Q^2)}$$

$$f_1(i = C, j = Y) = f_1(i = C, j = Z) = \frac{(Q-0.25Q^2)}{(1+2Q-(1+0.5)Q^2)}$$

The second application selects only source X in apportionment calculations, so sources Y and Z are lumped into one source, (Y+Z). This application determines the contributions from source X and the lumped source. The values of f become the below.

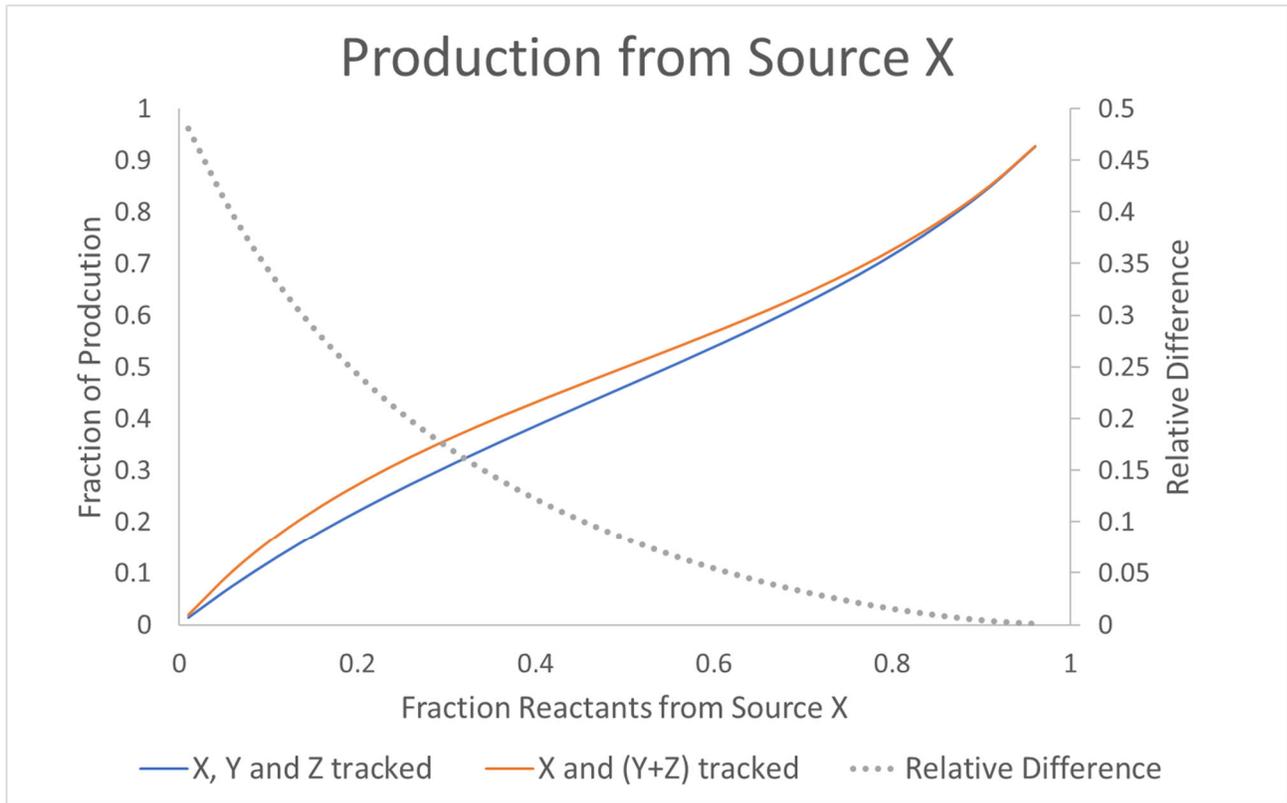
$$f_2(i = C, j = X) = \frac{(1-Q^2)}{(1+2Q-2Q^2)}$$

$$f_2(i = C, j = (Y + Z)) = \frac{(2Q-Q^2)}{(1+2Q-2Q^2)}$$

The f for source X differs between the two applications. The below formulas give the absolute and relative difference in f for X from application 1 to 2. Figure 1 shows how both applications' f and their relative difference varies as $(1-Q)$ increases.

$$f_2 - f_1 = (1-Q^2) \left(\frac{1}{(1+2Q-2Q^2)} - \frac{1}{(1+2Q-(1+0.5)Q^2)} \right)$$

$$\frac{f_2 - f_1}{f_1} = \left(\frac{(1+2Q-(1+0.5)Q^2)}{(1+2Q-2Q^2)} - 1 \right)$$



We can generalize the scenario by replacing the two sources, Y and Z, with (N-1) sources where N equals the total number of sources. Only the expression for f_1 changes,

$$f_1(i = C, j = X) = \frac{(1 - Q^2)}{(1 + 2Q - (1 + \left(\frac{1}{(N-1)}\right))Q^2)}$$

and the difference metrics become the below expressions.

$$f_2 - f_1 = (1 - Q^2) \left(\frac{1}{(1 + 2Q - 2Q^2)} - \frac{1}{(1 + 2Q - (1 + \left(\frac{1}{(N-1)}\right))Q^2)} \right)$$

$$\frac{f_2 - f_1}{f_1} = \left(\frac{(1 + 2Q - (1 + \left(\frac{1}{(N-1)}\right)Q^2))}{(1 + 2Q - 2Q^2)} - 1 \right)$$

Figure 2 shows how N-1 or number of lumped sources affects the relative difference between applications for different fraction of reactants from X, 1-Q.

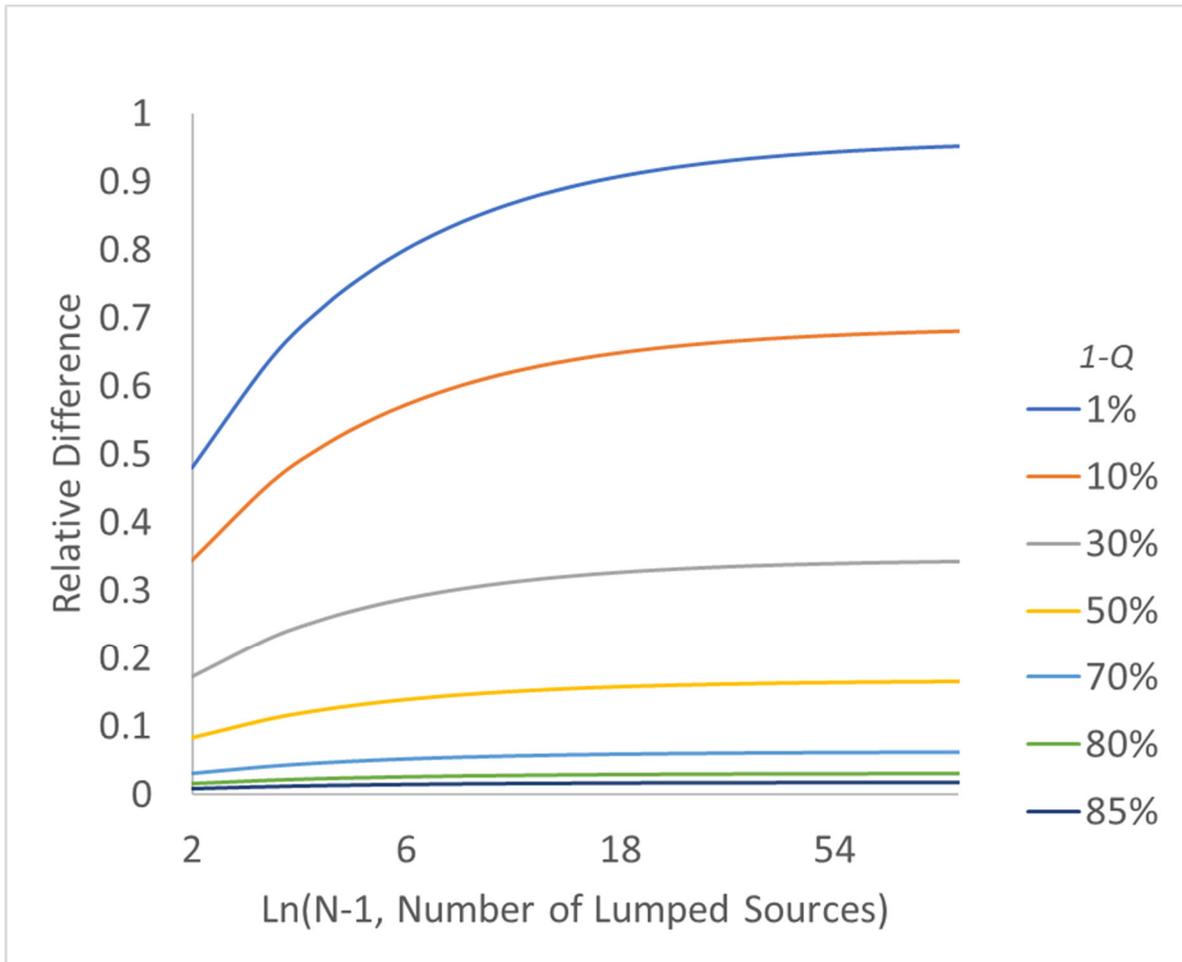


Figure 2.