DEVELOPMENT AND APPLICATION
OF A PROCESS ANALYSIS METHOD
FOR PHOTOCHEMICAL OXIDANT MODELS

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production, but photolysis of HONO which had been produced by reaction of \( \cdot \)OH with NO simply releases an existing \( \cdot \)OH radical.

\[
\begin{align*}
\{22\} & \quad \text{OH} + \text{NO} = \text{HONO} \\
\{23\} & \quad \text{HONO} = \text{OH} + \text{NO} \\
\{24\} & \quad \text{OH} + \text{HONO} = \text{NO} + \text{NO}_2 \\
\{25\} & \quad \text{HONO} + \text{HONO} = \text{NO} + \text{NO}_2 + 2.00 \ast \text{HONO}
\end{align*}
\]

**H2O2 Cycle**

\[
\begin{align*}
\{32\} & \quad \text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 \\
\{33\} & \quad \text{H}_2\text{O}_2 + \text{HO}_2 + \text{H}_2\text{O} = \text{H}_2\text{O}_2 \\
\{34\} & \quad \text{H}_2\text{O}_2 = 2.00 \ast \text{OH} \\
\{35\} & \quad \text{OH} + \text{H}_2\text{O}_2 = \text{HO}_2
\end{align*}
\]

Reaction of \( \cdot \)OH and \( \text{HO}_2 \) are summed in the \( \text{O}_3/\text{HO}_x \) Cycle:

\[
\begin{align*}
\text{O}_3 + \cdot \text{OH} &= \text{HO}_2 \\
\text{O}_3 + \text{HO}_2 &= \text{OH}
\end{align*}
\]

**History Matrices.**

The photochemical degradation of VOCs may involve several intermediate reactions and intermediate products. For example, when \( \cdot \)OH attacks an olefin, it will produce organic peroxy radicals and then aldehydes. These aldehydes may also react with \( \cdot \)OH or photolyze to produce more organic intermediates. We would like to know the total number of \( \text{NO}_2 \) and \( \cdot \)OH produced by the reaction chain for each VOC. This task is complicated because condensed mechanisms frequently use common intermediates to represent the reactions of several VOCs. Our processing program contains an algorithm that tracks the mass of all products of each VOC and re-attributes \( \text{O}_x \) and \( \cdot \)OH production by intermediate species to initial concentration, emissions, or the original VOC species. In the IRR command file, the command \texttt{REPLACE} is used to identify species which are organic intermediates. The algorithm uses three matrices: a history matrix, \( X \), that stores the sources of the current mass of replaced species, a production matrix (\texttt{PROD}) that stores the sources of each replaced species during the current time interval, and a reaction matrix \( \text{XR} \) that attributes the mass reacted during the interval to the original sources.

I will use a simple example with a mixture of \( \text{CH}_4 \), \( \text{H}_2\text{C}=\text{O} \) and CO to illustrate the method. Each of the these species react to produce \( \text{RO}_2 \) or \( \text{HO}_2 \) radicals which lead to \( \text{O}_x \) production. In addition, \( \text{CH}_4 \) reacts to produce \( \text{H}_2\text{C}=\text{O} \), and \( \text{H}_2\text{C}=\text{O} \) reacts to produce CO. There are three sources of \( \text{H}_2\text{C}=\text{O} \): the initial concentration, fresh emissions, and chemical
production by CH₄. There are four sources of CO: initial concentration, emissions, direct chemical production by H₂C=O, and indirect chemical production by CH₄. In this example, original organic species are CH₆ and H₂C=O. Intermediated, or replaced species, are CO and H₂C=O. The matrices contain one row for each replaced species, and the column headings indicate the sources of the replaced species. The second through fifth columns account for total sources of the species as initial mass, emissions, entrainment from aloft, and total chemical production. Remaining column headings account for total chemical production by individual VOCs. In this example, at the beginning of this time interval there is a total of 100.9 ppb CO with 100 ppb attributed to the initial mass and 0.9 ppb attributed to chemical production by H₂C=O.

<table>
<thead>
<tr>
<th>Species</th>
<th>Init</th>
<th>Emis</th>
<th>Entrain</th>
<th>TotChem</th>
<th>FORM</th>
<th>CH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.9</td>
<td>0.9</td>
<td>0.0</td>
</tr>
<tr>
<td>FORM</td>
<td>99.1</td>
<td>0.1</td>
<td>0.0</td>
<td>0.6</td>
<td>0.0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The production matrix (PROD) stores the source of during a given time interval. In this simple example, the total concentration of CO at the beginning of the interval is 101.0 ppb, total production is 42.9 ppb, and total loss is 0.9 ppb.

| PROD matrix (ppb) |                   |                  |                  |                  |                  |                  |                  |
|-------------------|--------------------|------------------|------------------|------------------|------------------|------------------|
| Species           | Xinit | PT | LT | Emis | TotChem | FORM | CH4 |
| CO                | 101.0 | 42.9 | 0.9 | 0.0  | 42.9    | 42.9  | 0.0  |
| FORM              | 99.8  | 32.2 | 42.9 | 5.4  | 26.8    | 0.0   | 26.8 |

At each time interval in the post-processing program, we solve a simple system of differential equations using production and loss rates during the interval to determine how much CO and HCHO of from each source was produced and reacted during the interval, and how much was left over at the end of the interval. We can express the change in concentration from source \( j \) as

\[
dC_j = P_j - LC_j.
\]

which, for constant production \( P_j \) and loss frequency \( L_j \) over a time interval of \( \Delta t \) has a solution

\[
C_j^{t_{n+1}} = \frac{P_j}{L_j} \left( 1 - e^{-L_j \Delta t} \right) + C_j^{t_n} e^{-L_j \Delta t}
\]

If there are multiple sources, (i.e., \( P_j^1, P_j^2, \ldots, P_j^n \)) and multiple loss processes, (i.e., \( l_j^1, l_j^2, \ldots, l_j^m \)) then

\[
L_j = l_j^1 + l_j^2 + \ldots + l_j^m
\]

and

\[
C_j^{t_{n+1}} = \left( P_j^1 + P_j^2 + \ldots + P_j^n \right) \left( \frac{1 - e^{-L_j \Delta t}}{L_j} \right) + C_j^{t_n} e^{-L_j \Delta t}
\]
This enables us to calculate the total mass of HCHO attributed to each VOC at any time during the simulation. If we perform this calculation for each chemical intermediate, we can determine the NO₂ and OH production attributed to each emitted VOC. The source code which performs this calculation in the Cycles program is in the subroutine \texttt{INTSPE.FOR}. The old history matrix, \( X \), is stored in the \texttt{ MATRIX \_Histor} subroutine. The new history array is calculated using the production and loss terms given above. Using H₂C=O as an example, at the beginning of the interval there are 99.1 ppb H₂C=O left from the initial concentration at time zero, and 0.6 ppb left from reactions of CH₄ during the previous step. During the interval, sources of H₂C=O are 5.4 ppb from emissions and 26.8 ppb from reactions of CH₄. Total loss of H₂C=O is 42.9 ppb. Using equation 2, we calculate a new history matrix \( X \) at the end of the interval:

\[
\text{New \( X \) conc matrix (ppb)}
\]

\[
\text{Replaced}
\]

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{Species} & \text{Init} & \text{Emis} & \text{Entrain} & \text{TotChem} & \text{FORM} & \text{CH4} \\
\hline
\text{CO} & 99.3 & 0.0 & 0.0 & 0.9 & 43.6 & 0.0 \\
\text{FORM} & 62.9 & 4.4 & 0.0 & 21.9 & 0.0 & 22.0 \\
\hline
\end{array}
\]

and we calculate the reaction matrix \( XR \) using:

\[
XR = X_{old} + PROD - X_{old}
\]

\[
\text{XR reacted matrix before elimination (ppb)}
\]

\[
\text{Init} & \quad \text{Emis} & \quad \text{Entrain} & \quad \text{TotChem} & \quad \text{FORM} & \quad \text{CH4} \\
\hline
\text{CO} & 0.7 & 0.0 & 0.0 & 0.16 & 0.16 & 0.00 \\
\text{FORM} & 36.3 & 1.1 & 0.0 & 5.50 & 0.00 & 5.50 \\
\hline
\end{array}
\]

Thus, we see that of the H₂C=O reacted during the interval, 36.3 ppb was initial mass and 5.5 ppb was H₂C=O produced from CH₄. We also know that some CO was produced indirectly from CH₄, and some of this CO must have reacted during the interval. The XR matrix shows that 5.5 ppb, or 12.8% of the H₂C=O that reacted was produced from CH₄, and 0.16 ppb of the CO which reacted had been produced from H₂C=O, so the algorithm will re-attribute 12.8% of this 0.16 ppb to CH₄.

\[
\text{XR reacted matrix after elimination (ppb)}
\]

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{Species} & \text{Init} & \text{Emis} & \text{Entrain} & \text{TotChem} & \text{FORM} & \text{CH4} \\
\hline
\text{CO} & 0.7 & 0.0 & 0.0 & 0.16 & 0.14 & 0.02 \\
\text{FORM} & 36.3 & 1.1 & 0.0 & 5.50 & 0.00 & 5.50 \\
\hline
\end{array}
\]

The re- attribution of the XR reacted matrix is carried out in the subroutine \texttt{ELIMXR.FOR}. The corrected XR matrix is then used by the program to re-attribute production and loss of Oₓ, OH, and nitrogen compounds to the original VOCs. Using this approach, no Oₓ production will be attributed to species which are produced only as intermediates in the reaction of other VOCs. In the CB4 mechanism these intermediate species are C₂O₃, CRO, MGLY, OPEN, CRES, ROR, and TO2. Other species CO, H₂C=O, ALD2 and others have some initial and emitted mass and are also produced as intermediates. Only the fraction of Oₓ produced by the initial and emitted mass will be attributed to these species.