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 ˙OH with NO simply releases an existing ˙OH radical.

```
{ 22} OH+NO=HONO
{ 23} HONO=OH+NO
{ 24} OH+HONO=NO2
{ 25} HONO+HONO=NO+NO2
{ 21} NO+NO2+H2O=2.00*HONO
```

H2O2 Cycle

```
{ 32} HO2+HO2=H2O2
{ 33} HO2+HO2+H2O=H2O2
{ 34} H2O2=2.00*OH
{ 35} OH+H2O2=HO2
```

Reaction of ˙OH and HO_2^- are summed in the O_3/HOx Cycle:

```
O3+OH=HO2
O3+HO2=OH
```

History Matrices.

The photochemical degradation of VOCs may involve several intermediate reactions and intermediate products. For example, when ˙OH attacks an olefin, it will produce organic peroxy radicals and then aldehydes. These aldehydes may also react with ˙OH or photolyze to produce more organic intermediates. We would like to know the total number of NO_2 and ˙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 O_x and ˙OH production by intermediate species to initial concentration, emissions, or the original VOC species. In the IRR command file, the command 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 (PROD) that stores the sources of each replaced species during the current time interval, and a reaction matrix XR that attributes the mass reacted during the interval to the original sources.

I will use a simple example with a mixture of CH_4, $H_2C=O$ and CO to illustrate the method. Each of the these species react to produce RO_2^- or HO_2^- radicals which lead to O_x production. In addition, CH_4 reacts to produce $H_2C=O$, and $H_2C=O$ reacts to produce CO. There are three sources of $H_2C=O$: the initial concentration, fresh emissions, and chemical

production by CH_4. There are four sources of CO: initial concentration, emissions, direct chemical production by $H_2C{=}O$, and indirect chemical production by CH_4. In this example, original organic species are CH_4 and $H_2C{=}O$. Intermediated, or replaced species, are CO and $H_2C{=}O$. 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, emisssions, 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$H_2C{=}O$.

```
X conc matrix  (ppb)
Replaced
Species   Init   Emis  Entrain TotChem  FORM   CH4
CO        100.0  0.0    0.0       0.9    0.9    0.0
FORM       99.1  0.1    0.0       0.6    0.0    0.6
```

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

$$dC_j = P_j - LC_j. \tag{1}$$

which, for constant production P_j and loss frequency L_j over a time interval of Δt has a solution

$$C_j^{t_{n+1}} = \frac{P_j}{L_j}\left(1 - e^{-L_j \Delta t}\right) + C_j^{t_n} e^{-L_j \Delta t} \tag{2}$$

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 NO_2 and ·OH production attributed to each emitted VOC. The source code which performs thiss calculation in the IRR program is in the subroutine `INTSPE.FOR`. The old history matrix, `X`, is stored in the the matrix `XR`, and the new history array is calculated using the production and loss terms given above. Using $H_2C{=}O$ as an example, at the beginning of the interval there are 99.1 ppb $H_2C{=}O$ left from the initial concentration at time zero, and 0.6 ppb left from reactions of CH_4 during the previous step. During the interval, sources of $H_2C{=}O$ are 5.4 ppb from emissions and 26.8 ppb from reactions of CH_4. Total loss of $H_2C{=}O$ is 42.9 ppb. Using equation 2, we calculate a new histroy maxtrix `X` at the end of the interval:

```
New X conc matrix   (ppb)
Replaced
Species   Init   Emis  Entrain TotChem  FORM   CH4
CO        99.3   0.0    0.0      0.9    43.6   0.0
FORM      62.9   4.4    0.0     21.9     0.0  22.0
```

and we calculate the reaction matrix `XR` using:

$$XR = X_{old} + PROD - X_{old}$$

```
XR reacted matrix before elimination (ppb)
Species   Init   Emis  Entrain TotChem  FORM   CH4
CO         0.7   0.0    0.0      0.16    0.16   0.00
FORM      36.3   1.1    0.0      5.50    0.00   5.50
```

Thus, we see that of the $H_2C{=}O$ reacted during the interval, 36.3 ppb was initial mass and 5.5 ppb was $H_2C{=}O$ produced from CH_4. We also know that some CO was produced indirectly from CH_4, and some of this CO must have reacted during the interval. The `XR` matrix shows that 5.5 ppb, or 12.8% of the $H_2C{=}O$ that reacted was produced from CH_4, and 0.16 ppb of the CO which reacted had been produced from $H_2C{=}O$, so the algorithm will re-attribute 12.8% of this 0.16 ppb to CH_4.

```
XR reacted matrix after elimination (ppb)
Species   Init   Emis  Entrain TotChem  FORM   CH4
CO         0.7   0.0    0.0      0.16    0.14   0.02
FORM      36.3   1.1    0.0      5.50    0.00   5.50
```

The re-atrribution of the `XR` reacted matrix is carried out in the subroutine `ELIMXR.FOR`. The corrected `XR` matrix is then used by the program to re-atribbute production and loss of O_x, ·OH, and nitrogen compounds to the original VOCs. Using this approach, no O_x 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, $H_2C{=}O$, ALD2 and others have some initial and emitted mass and are also produced as intermediates. Only the fraction of O_x produced by the initial and emitted mass will be attributed to these species.

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