

## Abstract

Photochemical oxidant models are used to determine the level of control of anthropogenic hydrocarbon and nitrogen oxide emissions needed to meet the national ambient air quality standard for ozone. Current models have sophisticated representations of the physical processes controlling the sources, sinks, transport and transformations of tropospheric trace gasses. The output from these models is often simply the time dependent concentration of the trace gasses. This makes it difficult to understand exactly why the model predicts what it does. It is desirable to perform a mass balance analysis of the model output to determine the relative importance of the physical processes and chemistry which control the gas concentrations simulated by the model. A mass balance analysis would provide:

- a tool for understanding how a model or how a specific chemical mechanism works;
- insights into the source of urban oxidant problems and the appropriateness of various control strategies;
- the ability to treat urban areas as large chemical reactors which process anthropogenic trace gas emissions before they are released to the free troposphere.

In Chapter 2, I describe modifications to a photochemical oxidant model OZIPR, a research version of EPA's Ozone Isopleth Plotting Program (OZIP). OZIPR produces output that includes time integrated reaction rates for each reaction, and time integrated dilution, deposition and emissions for each trace gas. I then describe a FORTRAN program, IRREVAL, which can be used to analyze the integrated reaction rates and provide a series of tables showing mass balance information for ozone, nitrogen oxides, OH radicals, and other species of importance. In Chapter 7, I use OZIPR and the Empirical Kinetic Modeling Approach to evaluate the sensitivity of VOC control requirement predictions to CO concentrations. Doubling the initial and aloft CO concentrations increased the VOC control requirement from 23 to 43%. I used these model simulations as an example to illustrate the use of the IRREVAL analysis program.

## Acknowledgements

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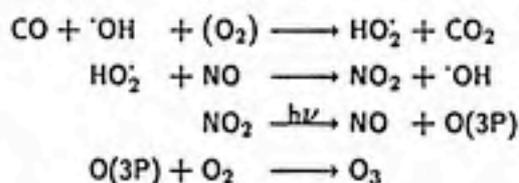
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# Introduction

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## Background

Ozone ( $O_3$ ) is a trace species normally present in the troposphere at concentrations below 60 parts per billion volume (ppbv).  $O_3$  can be transported to the troposphere from the stratosphere or produced directly in the troposphere by photo-chemical reactions of nitrogen oxides ( $NO_x = NO + NO_2$ ), hydrocarbons (HC) and carbon monoxide (CO). These compounds are precursors to the formation of  $O_3$ . The simplest reaction sequence leading to  $O_3$  production is:



Net Reaction:



HC and  $NO_x$  also react to produce  $O_3$  in a similar but more complicated mechanism. HC and  $NO_x$  precursors are emitted both by natural sources and by human activities. Globally, biogenic and anthropogenic sources of  $NO_x$  and HC are highly uncertain but are roughly of the same magnitude [Logan *et al.*, 1981]. Anthropogenic emissions, however, are concentrated in urban areas. Under conditions which enhance  $O_3$  formation,  $O_3$  concentrations in or near urban areas often range from 120 to over 300 ppbv.  $O_3$  formation is enhanced by clear skies and stagnant air masses which reduce dispersion of precursors.

Ozone is also a strong oxidant which can react with and damage sensitive surfaces. The U.S Environmental Protection Agency (EPA) has designated  $O_3$  as one of seven criteria pollutants and has set National Ambient Air Quality Standards

for  $O_3$  as a maximum one hour average concentration of 120 ppbv. Any state which exceeds the 120 ppbv standard more than 4 times in 3 years must develop a State Implementation Plan (SIP) demonstrating how the state will attain the standard. A SIP includes emissions inventories of volatile organic compounds (VOC) and  $NO_x$ , control measures designed to reduce the emissions, and a modeling study demonstrating that the controls are sufficient to attain the standard. Compounds such as CO, methane and ethane react relatively slowly, so EPA has defined VOC to be those hydrocarbons which react faster than ethane.

Both VOC and  $NO_x$  are needed for  $O_3$  production to occur. In theory, one could reduce  $O_3$  by reducing VOC emissions alone,  $NO_x$  emissions alone, or both VOC and  $NO_x$  emissions simultaneously. If the air mass were  $NO_x$  rich and VOC poor, it would be easier to meet the standard by controlling just VOC emissions. If the air mass were  $NO_x$  poor and VOC rich, it might be easier, and more economical, to control only  $NO_x$  emissions. In some case, it might be necessary to control both VOC and  $NO_x$ . In the past, EPA has encouraged only VOC controls but has allowed  $NO_x$  controls if modeling studies demonstrated them to be effective. There currently exists some controversy over which type of control is more effective and more economical [Chameides *et al.*, 1988].

## History of the OZIPM Model

The EPA has sponsored basic research in photochemical mechanisms and the development of photochemical oxidant models. Until recently, EPA has recommended two modeling approaches for use in the SIP  $O_3$  attainment demonstration. One approach requires the use of sophisticated three-dimensional airshed models. The second method, the Empirical Kinetic Modeling Approach (EKMA), is described in detail by Hogo and Gery [1988]. EKMA requires multiple simulations of  $O_3$  production with a range of initial VOC and  $NO_x$  concentrations. The computer program which performs the simulations is called the Ozone Isopleth Plotting with Optional Mechanism - Version 4 (OZIPM4). OZIPM4 was based on an earlier program called the Ozone Isopleth Plotting Package (OZIPP). Although current revisions to the Clean Air Act may require the use of the more sophisticated airshed models, EPA has continued to sponsor work on the Ozone Isopleth Method. The most recent is a research oriented version of OZIPP called OZIPR.

Like the earlier versions, OZIPR is a simple trajectory model. The user specifies the initial VOC and  $NO_x$  concentrations, typically at 8 AM at the city center. OZIPR then models a column of air moving from the city center to the location of the observed  $O_3$  maximum. Emissions along the trajectory are added to the column,

and the height of the column is allowed to rise following a specified mixing height profile. The species within the column may be diluted by the mixing height rise, or species may be entrained from air aloft. For example, if the initial  $O_3$  in the column is zero and the aloft air contains 40 ppb  $O_3$ , then  $O_3$  will be entrained into the box until the  $O_3$  concentration in the column reaches 40 ppb. If it exceeds 40 ppb, then  $O_3$  in the column will be diluted until the mixing height rise ends. For guidance on using OZIPR see *Gery and Crouse* [1990]. For a complete description of the model, its assumptions and limitations, see *Hogo and Gery* [1988].

OZIPR models the reacting species in the column of air by solving a stiff system of ordinary differential equations using a Gear-type method. There is one equation for the concentration of each species  $i$ :

$$\frac{dC_i}{dt} = \left. \frac{\partial C_i}{\partial t} \right|_{\text{reac}} + \left. \frac{\partial C_i}{\partial t} \right|_{\text{emis}} + \left. \frac{\partial C_i}{\partial t} \right|_{\text{dilution}} + \left. \frac{\partial C_i}{\partial t} \right|_{\text{entrain}} + \left. \frac{\partial C_i}{\partial t} \right|_{\text{deposition}}$$

The term  $\partial C_i / \partial t|_{\text{reac}}$  is the sum of chemical production and chemical loss of species  $i$  at the current time. It is determined by calculating the rates of each reaction in the chemical mechanism. OZIPR, like most photochemical models, does not normally calculate the mass of species  $i$  which reacted during the time interval; it need only calculate the rate of change to correctly predict the concentration at the end of the time interval. The normal output of OZIPR, and most models, is the concentration profile of each species as a function of time. In fact, the user need not even see the concentration profiles. Using the EKMA approach, OZIPR reports the  $O_3$  maximum for each simulation and the predicted control VOC requirement. The concentration profiles can be requested. In addition, the rate of each reaction can be requested at certain intervals. This information is, however, difficult to extract and difficult to interpret.

## GOAL OF THIS WORK

*Jeffries* [1984] developed a method of analysis which integrates the reaction rates over time. Using his Photochemical Kinetics Simulation System (PKSS) he produces a file containing the integrated reaction rate for each reaction in the mechanism. This is the total mass, in parts per million volume (ppm), of a species with a coefficient of one, that was produced or consumed in that reaction. For example, an integrated reaction rate (IRR) of 3.0 ppm for the reaction:



would indicate that 3 ppm of NO were consumed, 3 ppm of  $O_3$  were consumed, and 3 ppm of  $NO_2$  were produced. By summing over all the reactions, one can calculate

the total mass of any species produced and consumed during the simulation. Using this method, Jeffries explained the final  $O_3$  concentration predicted by the model in terms of the ppm of new  $\cdot OH$  radicals produced, the chain length of  $\cdot OH$  propagation reactions, and the ppm of  $NO_2$  and  $O_3$  produced per ppm of new  $\cdot OH$ , (with new  $\cdot OH$  defined as photolytic sources of  $\cdot OH$  radicals).

Integrated reaction rates can also be used to perform a mass balance analysis on any species in the reacting system and to gain insights that are not possible by simply looking at the concentration profiles and  $O_3$  maximum. For example, an integrated reaction rate analysis could be used to determine how much  $O_3$  is produced by each VOC in the VOC mixture. The process of extracting the information from the integrated rates is, however, very tedious. A computer program is needed to perform the analysis. Furthermore, the computer program must be general enough that it can read any reaction mechanism and its integrated rate file.

This report describes a FORTRAN computer program, IRREVAL, which performs an integrated rate analysis for any reaction mechanism and any photochemical model which produces output files in the correct format. Chapter Two begins by describing modifications made to OZIPR to produce the integrated rate file. Chapter Three describes the format of the OZIPR output files which are read as input files by IRREVAL. Chapter Four describes a simple example mass balance analysis which illustrates the algorithms used in IRREVAL. Chapter Five contains a more detailed listing and description of the IRREVAL output files, and Chapter Six contains a listing of IRREVAL commands and explains their use. Finally, Chapter Seven describes an example analysis using IRREVAL on a number of OZIPR simulations designed to study the sensitivity of urban  $O_3$  formation to CO concentrations.

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## Modifications to OZIPR

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I made several modifications to OZIPR to produce the integrated reaction rate file. In this section I will briefly review the operation of the numerical solver in OZIPR. I will then discuss modifications made to OZIPR and the equations used to integrate the rates. Finally, I will present integrated reaction rate output and discuss the accuracy of the integration scheme used.

OZIPR uses a Gear-type numerical integration scheme to solve the system of differential equations and to predict the species concentration profiles. The method used is described by *Hogo and Gery* [1988] and in more detail by *Spellman and Hindmarsh* [1975]. The integration begins with a time step of  $10^{-10}$  minutes and uses the total rate of change of each species to predict the concentration at the end of the time step. A variable-order, Taylor-series-type polynomial is used to more accurately predict the concentration in subsequent steps. This allows larger time steps to be used. The Jacobian matrix containing the partial derivatives of the rate of change of concentration of each species with respect to each other species is used to correct the concentrations, update the Taylor series polynomial, and estimate the error at each step. The FORTRAN subroutines which perform the numerical integration are described below.

Figure 1 summarizes subroutine calls made by the numerical solver in OZIPR. In the OZIPR computer code OZIPMAIN is the main code which reads input files and controls the model run. SIM is the first routine called by OZIPMAIN after the input files are read. SIM sets up and controls the individual simulations and provides much of the time step dependent output. SIM calls DRIVES which is the driver routine for the integration scheme. At each time step, DRIVES calls the subroutines which implement the Gear integration scheme. These routines will also call DIFFUN which calculates the rate of change of each species due to chemical reactions, emissions, entrainment, dilution, and deposition. Several attempts may be made with successively smaller



I also made several modifications to the numerical solver described above to integrate the reaction rates. When the `IRR` command is used, `OZIPMAIN` will call `IRRINIT` before calling `SIM` to save the initial species concentration in the array `initconc`. `OZIPMAIN` then begins the simulation by calling `SIM`. After successfully completing a time step (as described above), `DRIVES` makes one additional call to `DIFFUN` passing it the current time and species concentrations. These are used to calculate the instantaneous rates of reactions, emissions, and deposition. The rates are integrated by averaging the rate from the current time with the rates from the previous time step and multiplied by the length of the time step. This calculates the incremental change in mass:

$$\Delta R_i^t \approx \left( k_i^t \prod_{1 \leq j \leq 3} C_j^t + k_i^{t-1} \prod_{1 \leq j \leq 3} C_j^{t-1} \right) \frac{\Delta t}{2}$$

where  $\Delta R_i^t$  is the integrated reaction rate for the time step in units of ppm,  $k_i$  is the rate constant for reaction  $i$ , and  $C_j$  are the reactants in reaction  $i$ .

The integrated rates of diluted emissions, total emissions, net entrainment, and deposition are also calculated for each species. The increment of production or loss of species  $i$  due to process  $k$  during each time interval  $t - 1$  to  $t$  is calculated as:

$$\Delta C_{k,i}^t \approx \left( \left. \frac{dC_i}{dt} \right|_k^t - \left. \frac{dC_i}{dt} \right|_k^{t-1} \right) \frac{\Delta t}{2}$$

To summarize, the instantaneous rates at each time step is averaged with the rate from the previous time step and then multiplied by the length of the time step. This calculates the incremental change in mass, in units of ppm, during the time step.

At the end of the simulation `OZIPMAIN` calls `IRRMASBAL`. `IRRMASBAL` sums the chemical loss and production of each species, and then calculates the predicted final concentration using a mass balance on all the sink/source terms for each species. Finally, `IRRMASBAL` writes the integrated reaction rate for each reaction and the integrated rates of change due to the various sink and source terms for each species to the `*.IRR` file.

Table 1 lists an example `OZIPR` input file which illustrates the use of the `IRR` command. When the `OZIPR` command:

```
IRR = CMP;
```

Table 1. Example OZIPR input file using IRR command

```

1 | Example OZIPR input file with IRR Command
2 | @f:\ozipr\mec\mecn.cb4
3 | @f:\ozipr\mec\zern.cb4
4 | PLACE > CITY = Atlanta, GA;
5 |     LAT = 33.65,     LON = 84.417,     TZone = 4,
6 |     YEAR = 1984,     MONTH = 6,     DAY = 4; <
7 | BOUNDary >
8 | REAC =
9 | PAR,      0.5640,      0.4980,      0.4980,
10 | ETH,      0.0370,      0.0340,      0.0340,
11 | OLE,      0.0350,      0.0200,      0.0200,
12 | TOL,      0.0890,      0.0420,      0.0420,
13 | XYL,      0.1170,      0.0260,      0.0260,
14 | FORM,     0.0210,      0.0700,      0.0700,
15 | ALD2,     0.0520,      0.0370,      0.0370,
16 | HR,       0.0850,      0.2730,      0.2730;
17 | IFraction_NO2 = 0.25;
18 | TRANsport =
19 |   O3Surface = 0,
20 |   O3ALeft  = 0.039,
21 |   HCSurface = 0.038,
22 |   HCALeft  = 0.02,
23 |   NOXSurface = 0,
24 |   NOXALeft = 0,
25 |   COSU     = 1.2,
26 |   COAL     = 0.5;< (BOUN)
27 | MET > DILU =
28 |     MHINITIAL = 250, (DF = 510)
29 |     MHFINAL  = 1515;< (DF = 630)
30 | TITLE > Base Case 0.6:0.1, Std VOC <
31 | @f:\inc_reac\base.ems
32 | MODIFY > AC = 0.00001; <
33 | TIME > 800, 2100 <
34 | IRR = TIME, CMP;
35 | CALC >
36 |   NMOC = 0.6;
37 |   NOX  = 0.1;
38 |   PRINT [BRIEF] =
39 |     TINI=60,
40 |     TSTE=60;
41 |   FILE[1]=ALL;< (CALC)
42 | END.

```

is used, OZIPMAIN will call the subroutine MECCMP which creates a \*.CMP file that contains an abbreviated form of the mechanism listing the reactants and products for each reaction. Example \*.IRR and \*.CMP files are shown in Table 2 and Table 3. They are described in detail in Chapter 3.

Integrated rate output can also be requested at specified time intervals during the simulation using the OZIPR command:

```
IRR = TIME;
```

The time intervals for IRR output are specified using the TIMEI and ISTEP options under the PRINT command (default values are 60 minutes). This is the same command used to specify the time interval at which to print species concentrations to the screen and to the OZIPR \*.OUT file. When OZIPR reaches one of these output time intervals, DRIVES returns to SIM to write the output. If the IRR = TIME; option is used, IRRMASBAL will be called each time DRIVES returns to SIM. This will cause the integrated rates for the time interval to be printed to the \*.IRR file for each output interval. IRRMASBAL will also call REINITIRR to re-initialize the integrated rate arrays for the next time interval.

## Accuracy of Integrated Reaction Rates

We need a test to verify that the method used above to integrate the rates is performing adequately. If the method is sound, one would expect a mass balance on the integrated rates to predict nearly the same final concentration as does the Gear method. The subroutine IRRMASBAL performs the mass balance and writes the Gear predicted concentrations and the mass balance calculated concentrations to the IRR file. Table 2 is the IRR file created by the OZIPR input file shown in Table 1. The last two columns of the second page of Table 2 shows the comparison of the OZIPR predicted final concentrations to the final concentrations calculated using a mass balance on the integrated rates. The two values for the final concentrations are nearly equal for species with significant concentrations at the end of the simulation. For example, OZIPR predicts a final O<sub>3</sub> concentration of 0.1444 ppm, and a mass balance on the integrated rates also predicts a final O<sub>3</sub> concentration of 0.1444 ppm.

The final concentrations differ for species which approach zero concentration at the end of the simulation. This occurs because of round-off errors when summing relatively large sink and source terms that nearly cancel out. For example, several ppb of OH may react during the simulation, but the final concentration is nearly

zero. The discrepancy occurs at final concentrations lower than  $10^{-8}$  ppm. This is essentially zero and may be neglected.

Table 2. Example IRR file created from the OZIPR input file shown in Table 1.

```

IRR
"Base Case 0.6:0.1, Std VOC"
I"09/29/90 17:14:27"
I"Rxn No      Int Rate"
( 1)  4.15165404937557E+00      ( 43)  1.69006642799491E-02
( 2)  5.51936044644063E+00      ( 44)  1.16072976340762E-05
( 3)  4.00236333137808E+00      ( 45)  7.10814647201706E-04
( 4)  3.06801707259495E-04      ( 46)  1.69653135162211E-02
( 5)  4.96062624624798E-05      ( 47)  5.26967701755859E-02
( 6)  4.69868006113115E-05      ( 48)  5.04751929078723E-02
( 7)  1.89740009972245E-02      ( 49)  4.78777564193362E-05
( 8)  1.30293045499928E+00      ( 50)  7.33516621482771E-04
( 9)  7.09891146994088E-02      ( 51)  4.21381514210787E-03
( 10) 6.13601937618200E-02      ( 52)  1.72138315136152E-02
( 11) 9.62892905979182E-03      ( 53)  9.16003875757504E-03
( 12) 1.79981487997829E-03      ( 54)  4.09556861921389E-03
( 13) 5.32501027765866E-03      ( 55)  1.01058142969628E-05
( 14) 4.32742745733808E-03      ( 56)  1.89491298546057E-05
( 15) 1.43333300384620E-02      ( 57)  4.06054398030878E-03
( 16) 1.79497338300671E-06      ( 58)  4.32897314842512E-04
( 17) 5.19155600098287E-03      ( 59)  7.12430830799501E-07
( 18) 3.83159375772563E-05      ( 60)  5.24117650963277E-06
( 19) 5.11733006035235E-03      ( 61)  3.12256223434871E-03
( 20) 5.14944861606306E-05      ( 62)  2.03403584042478E-04
( 21) 6.47762242533742E-08      ( 63)  1.84414720728490E-03
( 22) 6.26221481954433E-03      ( 64)  6.16203718485416E-04
( 23) 5.85598452339812E-03      ( 65)  1.42272027576837E-03
( 24) 1.09179186726886E-04      ( 66)  1.66052432376600E-03
( 25) 1.36818038400354E-10      ( 67)  7.18848599254689E-04
( 26) 2.42100444288025E-02      ( 68)  1.38305079682046E-03
( 27) 5.13348723413648E-04      ( 69)  5.12246117503721E-04
( 28) 1.07326064330375E-01      ( 70)  3.59252993611738E-04
( 29) 8.69611250035314E-02      ( 71)  2.85556312473819E-05
( 30) 8.69270601187410E-02      ( 72)  3.35405320131073E-03
( 31) 2.50874350310208E-05      ( 73)  5.80309844377548E-04
( 32) 2.09113025370469E-03      ( 74)  1.63464467140638E-03
( 33) 1.70133949693297E-03      ( 75)  0.00000000000000E+00
( 34) 1.75096423736573E-04      ( 76)  0.00000000000000E+00
( 35) 3.22647730929988E-04      ( 77)  0.00000000000000E+00
( 36) 3.72808690770314E-02      ( 78)  0.00000000000000E+00
( 37) 1.49206616471732E-02      ( 79)  5.65245621722099E-02
( 38) 6.18464466803960E-03      ( 80)  4.20964992618864E-04
( 39) 1.06643652779432E-02      ( 81)  2.59288563342004E-03
( 40) 2.40768978595708E-06      ( 82)  1.81303732083587E+01
( 41) 5.49877140165445E-06      ;
( 42) 5.74738432788049E-06

```

Table 2a. Example IRR File, cont

I"specie"	Initial	Reacted	Produced	Net Entrain	Emis	Tot Emis	Final C"	Calc C"
"NO2 "	2.50E-02	4.34E+00	4.35E+00	-4.25E-02	1.52E-03	3.0E-03	1.587E-03	1.581E-03
"NO "	7.50E-02	4.20E+00	4.15E+00	-5.50E-02	2.89E-02	5.7E-02	3.271E-08	1.061E-05
"O "	0.00E+00	5.51E+00	5.51E+00	-4.79E-09	0.00E+00	0.0E+00	1.567E-19	-8.287E-08
"O3 "	0.00E+00	5.40E+00	5.51E+00	2.81E-02	0.00E+00	0.0E+00	1.444E-01	1.444E-01
"NO3 "	0.00E+00	2.45E-02	2.46E-02	-1.03E-07	0.00E+00	0.0E+00	6.332E-05	6.340E-05
"O1D "	0.00E+00	7.09E-02	7.09E-02	-1.56E-10	0.00E+00	0.0E+00	0.000E+00	-8.279E-09
"H2O "	2.00E+04	1.13E-02	0.00E+00	0.00E+00	0.00E+00	0.0E+00	2.000E+04	1.999E+04
"OH "	0.00E+00	1.38E-01	1.38E-01	-2.02E-07	0.00E+00	0.0E+00	4.917E-09	-9.536E-08
"HO2 "	0.00E+00	2.07E-01	2.07E-01	-2.29E-06	0.00E+00	0.0E+00	4.735E-06	4.896E-06
"H2O5 "	0.00E+00	5.15E-03	5.19E-03	-6.09E-07	0.00E+00	0.0E+00	3.526E-05	3.530E-05
"HNO3 "	0.00E+00	5.13E-04	2.50E-02	-4.97E-03	0.00E+00	0.0E+00	1.953E-02	1.953E-02
"HONO "	0.00E+00	5.96E-03	6.26E-03	-2.96E-04	0.00E+00	0.0E+00	8.163E-07	9.168E-07
"PNA "	0.00E+00	8.69E-02	8.69E-02	-7.41E-06	0.00E+00	0.0E+00	1.633E-06	1.566E-06
"H2O2 "	0.00E+00	4.97E-04	3.79E-03	-3.35E-06	0.00E+00	0.0E+00	3.291E-03	3.291E-03
"CO "	1.20E+00	3.72E-02	3.56E-02	-5.88E-01	0.00E+00	0.0E+00	6.101E-01	6.101E-01
"FORM "	1.52E-02	3.17E-02	3.24E-02	-1.34E-02	2.18E-03	4.9E-03	4.633E-03	4.633E-03
"ALD2 "	1.63E-02	1.76E-02	1.69E-02	-1.59E-02	2.70E-03	6.0E-03	2.339E-03	2.339E-03
"C2O3 "	0.00E+00	7.04E-02	7.04E-02	-2.29E-07	0.00E+00	0.0E+00	5.774E-06	5.784E-06
"XO2 "	0.00E+00	5.73E-02	5.73E-02	-1.16E-06	0.00E+00	0.0E+00	1.642E-05	1.645E-05
"PAN "	0.00E+00	5.04E-02	5.26E-02	-5.11E-04	0.00E+00	0.0E+00	1.710E-03	1.710E-03
"PAR "	3.57E-01	1.72E-02	-2.19E-02	-3.21E-01	5.86E-02	1.3E-01	5.563E-02	5.564E-02
"XO2K "	0.00E+00	2.59E-03	2.60E-03	-5.93E-07	0.00E+00	0.0E+00	1.116E-05	1.116E-05
"ROR "	0.00E+00	1.32E-02	1.32E-02	-7.79E-11	0.00E+00	0.0E+00	8.209E-13	-7.118E-10
"OLE "	1.08E-02	4.51E-03	0.00E+00	-8.17E-03	1.81E-03	4.0E-03	1.535E-05	1.549E-05
"ETH "	1.17E-02	3.33E-03	0.00E+00	-9.99E-03	1.92E-03	4.3E-03	3.467E-04	3.469E-04
"TOL "	7.85E-03	1.84E-03	0.00E+00	-6.92E-03	1.32E-03	2.9E-03	4.097E-04	4.098E-04
"CRES "	0.00E+00	2.37E-03	2.75E-03	-3.78E-04	0.00E+00	0.0E+00	9.856E-09	2.796E-09
"TO2 "	0.00E+00	2.03E-03	2.03E-03	-1.45E-08	0.00E+00	0.0E+00	4.637E-11	-6.464E-11
"OPEN "	0.00E+00	9.00E-04	1.05E-03	-1.48E-04	0.00E+00	0.0E+00	4.538E-06	4.550E-06
"CRO "	0.00E+00	1.38E-03	1.38E-03	-6.75E-09	0.00E+00	0.0E+00	6.389E-10	7.863E-10
"MGLY "	0.00E+00	2.21E-03	2.68E-03	-4.59E-04	0.00E+00	0.0E+00	1.467E-05	1.468E-05
"XYL "	8.89E-03	3.35E-03	0.00E+00	-7.03E-03	1.52E-03	3.4E-03	2.734E-05	2.745E-05
"ISOP "	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.0E+00	0.000E+00	0.000E+00
"NR "	6.13E-02	1.81E+01	1.81E+01	-5.22E-02	8.83E-03	1.9E-02	1.793E-02	1.793E-02
;								

**Table 3.** Example CMP file created from the OZIPR input file shown in Table 1. The CMP file has been further modified to include CH<sub>4</sub> and ORNIT.

```

MECH *
( 1) NO2=NO+O
( 2) O=O3
( 3) O3+NO=NO2
( 4) O+NO2=NO
( 5) O+NO2=NO3
( 6) O+NO=NO2
( 7) O3+NO2=NO3
( 8) O3=O
( 9) O3=O1D
(10) O1D=O
(11) H2O+O1D=2.0*OH
(12) O3+OH=NO2
(13) O3+NO2=OH
(14) NO3=0.89*NO2+0.89*O+0.11*NO
(15) NO3+NO=2.0*NO2
(16) NO3+NO2=NO+NO2
(17) NO3+NO2=H2O5
(18) H2O5+H2O=2.0*HNO3
(19) H2O5=NO3+NO2
...
...
...
( 51) METH+OH=XO2+FORM+HO2
( 52) PAR+OH=0.87*XO2+0.13*XO2N+0.11*HO2+0.11*ALD2+0.76*ROR+-0.11*PAR+0.13*CO2
( 53) ROR=1.1*ALD2+0.96*XO2+0.94*HO2+-2.10*PAR+0.04*XO2N+0.020*ROR
( 54) ROR=HO2+CO2
( 55) ROR+NO2=ORNIT
( 56) O+OLE=0.63*ALD2+0.38*HO2+0.28*XO2+0.3*CO+0.2*FORM+0.02*XO2N+0.22*PAR+0.2*OH
( 57) OH+OLE=FORM+ALD2+XO2+HO2+-1.*PAR
( 58) O3+OLE=0.5*ALD2+0.74*FORM+0.33*CO+0.44*HO2+0.22*XO2+0.1*OH+-1.00*PAR+0.93*CO2
( 59) NO3+OLE=0.91*XO2+0.09*XO2N+FORM+ALD2+-1.*PAR+NO2
( 60) O+ETH=FORM+0.7*XO2+CO+1.7*HO2+0.3*OH
( 61) OH+ETH=XO2+1.56*FORM+HO2+0.22*ALD2
( 62) O3+ETH=FORM+0.42*CO+0.12*HO2+0.58*CO2
( 63) OH+TOL=0.08*XO2+0.36*CRES+0.44*HO2+0.56*TO2+0.08*ARO
( 64) TO2+NO=0.9*HO2+0.9*HO2+0.9*OPEN+0.1*ORNIT
( 65) TO2=CRES+HO2
( 66) OH+CRES=0.4*CRO+0.6*XO2+0.6*HO2+0.3*OPEN
( 67) NO3+CRES=CRO+HNO3
( 68) CRO+HO2=ORNIT
( 69) OPEN=C2O3+HO2+CO+0.59*ARO
( 70) OPEN+OH=XO2+2.*CO+2.*HO2+C2O3+FORM+0.29*ARO
( 71) OPEN+O3=0.03*ALD2+0.62*C2O3+0.7*FORM+0.03*XO2+0.69*CO+0.08*OH+0.76*HO2+0.2*MGLY+0.2*ARO
( 72) OH+XYL=0.7*HO2+0.5*XO2+0.2*CRES+0.8*MGLY+1.1*PAR+0.3*TO2+0.5*CO2
( 73) OH+MGLY=XO2+C2O3
( 74) MGLY=C2O3+HO2+CO
( 75) O+ISOP=0.6*HO2+0.8*ALD2+0.55*OLE+0.5*XO2+0.5*CO+0.45*ETH+0.90*PAR
( 76) OH+ISOP=XO2+FORM+0.67*HO2+0.13*XO2N+ETH+0.4*MGLY+0.2*C2O3+0.2*ALD2
( 77) O3+ISOP=FORM+0.4*ALD2+0.55*ETH+0.2*MGLY+0.1*PAR+0.06*CO+0.44*HO2+0.1*OH+1.34*CO2
( 78) NO3+ISOP=XO2N+ORNIT
( 79) XO2+NO=NO2
( 80) XO2+XO2=
( 81) XO2N+NO=ORNIT
( 82) NR=NR |

```

---

# IRREVAL Input Files

---

Three files are required as input for the IRREVAL program: (1) an \*.CMD input file which identifies the \*.CMP and \*.IRR input files and allows the user to give commands for processing them; (2) an \*.CMP input file containing an abbreviated form of the mechanism used for the simulation; and (3) an \*.IRR input file containing the integrated reaction rate for each reaction, and the sink and source terms for each species. The \*.CMP and \*.IRR files must be created by using the IRR command when running OZIPR or the /I command line option when running PKSS. Each input file is described in detail below.

## CMD Input File

The \*.CMD file can be created using any text editor.

It has an unstructured format subject to the following rules:

- Comments are allowed between curly brackets and on lines with the ! symbol in column one.
- Blank spaces and blank lines are ignored, although blank spaces can be used to separate numbers or words.
- The first significant line must begin with the @ symbol in column one and then the directory pathway and name of the CMP file. The second significant line also begins with the @ symbol and lists the directory and name of the IRR file. Only the file name need be given for files in the same directory as the CMD file. A semicolon is not required after the file name.
- Commands must end with a semicolon. Commands may be given in any order with these exceptions: the CYCLES command should precede the REPLACE command; the BALANCE or EVALUATE command should be last; and the

CMD file must end with the END command and a punctuation mark. Commands are described in Chapter Six.

An example CMD file is shown in Table 4.

## CMP Input File

The \*.CMP file is created at runtime by OZIPR and PKSS. The \* is replaced by the file name of the OZIPR input file or the PKSS initial condition (\*.IC) file name. The CMP file lists the reactants, products, and product coefficients for each reaction in the mechanism, but it excludes rate constants and documentation in the mechanism file. An example CMP file was shown in Table 3.

In most cases, the user will further modify the CMP file before using it with IRREVAL. In many photochemical models, the mechanism has been simplified by ignoring unreactive products or treating some species implicitly. The user can restore the missing species by using a text editor to add them to the reactions in the CMP file. For example, CB4 treats CH<sub>4</sub> implicitly by writing a reaction with 'OH and modifying the rate constant to account for the CH<sub>4</sub> concentration. For IRR to calculate the CH<sub>4</sub> contribution to O<sub>3</sub> production, CH<sub>4</sub> must be added to the 'OH reaction. In the CMP file in Table 3, CH<sub>4</sub> has been added as a reactant to Reaction 51. The user can also add other species to the analysis, for example CO<sub>2</sub> or organic nitrates can be added as products in the appropriate reactions. Currently, the generic name ORNIT is coded into the Subroutine OUTNO2.FOR and should be used for all organic nitrogen sinks to get a correct balance in the NO<sub>y</sub> table in the \*.NOX output file.

When adding species to the CMP file, no blank spaces are allowed between the equal sign and the first product. Comments can be included between curly brackets or on lines with the ! symbol in the first column. When adding reactants to the CMP file, *e.g.* CH<sub>4</sub>, the IRR file must include source terms for the reactants. (If a species is reacting it must have a source.) If CH<sub>4</sub> is not included in the OZIPR mechanism, OZIPR automatically adds an initial concentration of 1.79 ppm CH<sub>4</sub> to the sink/source section of the IRR file.

## IRR Input File

An example \*.IRR file was shown in Table 2. The \*.IRR input file begins with the IRR command and is followed by one or more lines of documentation enclosed in double quotes. The first line of documentation is printed at the beginning of

Table 4. Example CMD input file

```

1 | Example CMD file using EVALUATE command.
2
3 @f:\irr\base.cmp
4 @base.irr
5
6 NOY = NO3, N2O5*2, HNO3, HONO, PNA, PAN, ORNIT;
7 NEW (New Radical Reactions) =
8 11, (H2O+OH=2.0*OH)
9 23, (HONO=OH+NO)
10 30, (PNA=HO2+NO2)
11 34, (H2O2=2.*OH)
12 38, (FORM=2.*HO2+CO)
13 45, (ALD2=XO2+2.*HO2+CO+FORM)
14 54, (ROR=HO2)
15 65, (TO2=CRES+HO2)
16 69, (OPEN=C2O3+HO2+CO)
17 74, (MGLY=C2O3+HO2+CO)
18     40,42,56,58,60,62,71,75,77, (O and O3 rxns)
19
20
21 CYCLES = "PNA Cycle", "PAN Cycle", "HONO Cycle", "H2O2 Cycle",
22           "O3/NO2 Chemistry" = [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 14, 15, 16, 17, 18, 19],
23           "O3/HOx Cycle" = [12, 13];
24
25 ORGANIC = CO, METH, PAR, 2*ETH, 2*OLE, 7*TOL, 8*XYL, FORM, 2*ALD2,
26           C2O3, MGLY, OPEN, CRES, CRO, ROR, TO2, 2*PAN;
27
28 REPLACE = XO2, CO, FORM, C2O3, ALD2, CRO, ROR, MGLY, OPEN,
29           CRES, TO2, PAN, ETH, PAR;
30
31 EVAL;
32 END.

```

all output files. For OZIPR, there is one line of documentation which will be the title from the OZIPR \*.INP file. For \*.IRR files from PKSS, the first line of documentation is saved, others are ignored. The IRR file then contains a list of integrated reaction rates with each value separated by at least one blank space. Comments in curly brackets can be included to identify reaction numbers or other documentation. The number of integrated reaction rates must be equal to the number of reactions listed in the CMP file. This occurs naturally if the correct CMP file is used, but no additional checking is performed to verify that the named CMP file corresponds to the mechanism which was used to generate the IRR file. The last integrated reaction rate is followed by a semicolon. The IRR file then has a section listing sink and source terms for each species. In OZIPR IRR files, each line begins with the species name enclosed in double quotes and then nine numbers separated by blank spaces. In order these are:

- 1) Initial concentration,

- 2) Chemical loss,
- 3) Chemical production,
- 4) Net entrainment,
- 5) Emissions (ppm) corrected for dilution,
- 6) Total emissions (ppm) into a box with the initial mixing height,
- 7) Deposition,
- 8) Final concentration calculated by OZIPR, and
- 9) Final concentration as determined from a mass balance on the the integrated rates.

The sink/source section ends with a semicolon. The chemical loss and production terms are used to check the mass balance on each species and are not used by IRREVAL. Deposition is read by IRREVAL but is not yet included in the output files.

OZIPR will create time dependent IRR files if the `IRR = TIME;` command is used in the OZIPR \*.INP file. Time dependent IRR files have the following structure:

```
IRR = n
"Title from OZIPR input file."
Time = x
!"Rxn No" "Int Rate"
( 1) y1
( 2) y2
... ..
```

where  $n$  is the number of time intervals,  $x$  is the time in minutes at the end of the  $i^{\text{th}}$  time interval, and the  $y_i$  values are the integrated reaction rates. The IRR file will have an integrated reaction rate and a sink/source section for each of  $n$  time intervals. Each time interval begins with the `Time = x` line and ends with a semicolon. The last interval has the `|` symbol after the semicolon.

Time dependent output provides a more realistic analysis of the contributions of initial  $\text{NO}_2$ , chemically produced  $\text{NO}_2$ , and individual organics to the final  $\text{O}_3$  concentration.

---

# Algorithms

---

## Some Simple Examples

IRREVAL started as a simple program designed to show the reactions which produced or consumed any given species. It has gradually evolved into a more comprehensive program. It utilizes several complicated algorithms which can provide a detailed mass balance analysis of key species in photochemical oxidant mechanisms. I will begin with a very simple implementation of IRREVAL, illustrate its use, and then explain why more detailed information is desired. This will show the motivation for the addition of new features to the simple case. It will also illustrate their value and serve as an introduction to the algorithms used to implement each feature.

I will use the example IRR file shown in Table 2, and the example compressed mechanism file shown in Table 3. These files were generated from the example OZIPR input file shown in Table 1. For this example, OZIPR predicted a final O<sub>3</sub> concentration of 144.47 ppb. The goal is to understand why OZIPR predicted this value, or, in other words, to explain how and why this amount of O<sub>3</sub> was produced.

The mechanism in Table 4 shows that O<sub>3</sub> is chemically produced exclusively by:



The IRR file shows that this reaction produced 5.519 ppm of O<sub>3</sub>. To understand the O<sub>3</sub> production, we must determine what produced the O(3P) (triplet state monatomic oxygen). The mechanism shows that O(3P) is produced in four different reactions, and that O(3P) is formed largely from NO<sub>2</sub> which is produced in more than 15 different reactions. It quickly becomes very tedious to identify and sum the reactions which

produce these species. In the simplest case, IRREVAL can be used to show the processes which produce or consume any species in the mechanism. I used the simple command (CMD) file:

```
@f:\irr\base.cmp
@baseave.irr
End.
```

which identifies the compressed mechanism and IRR files to be analyzed. If no other commands are listed, the program prompts the user first for a search type and then for a species name with the menu:

```
Enter number for search type:
(1) Show Production of a Species
(2) Show Consumption of a Species
(3) Show Reaction Products
(4) Do all 3 searches
(5) Quit

Enter Search Type (Choices are 1 to 4, 5 to exit):
```

I used search type (1) to request the production of  $O_3$ , O(3P), and  $NO_2$ . The resulting mass balance file (BAL) is shown in Table 5. The structure of the BAL file is explained in detail in Chapter 4: IRREVAL Output Files.

Table 5 shows all sources of  $O_3$ , O(3P), and  $NO_2$ . In line 9, it reports the final  $O_3$  concentration of 0.1445 ppm determined from a mass balance of sink and source terms. Line 5 shows the gross chemical  $O_3$  production of 5.51936 ppm. Line 7 shows that net  $O_3$  entrainment from air aloft contributed an additional 0.02818 ppm, or 0.508% of the gross  $O_3$  sources.

We can attempt to trace  $O_3$  production back to its original sources by examining how O(3P) was produced. Line 14 of Table 5 shows that 75.2% of O(3P) is produced from photolysis of  $NO_2$ , and in line 15, 23.6% is produced from photolysis of  $O_3$ . Tracing the  $O_3$  source back one step farther, we see in line 26 that 91.82% of the  $NO_2$  was produced by



In other words,  $O_3$  is produced from O(3P), most of the O(3P) is produced from  $NO_2$ , and most of the  $NO_2$  is produced from  $O_3$ . It is difficult to determine which came

Table 5. Example of a simple BAL output file showing sources of O<sub>3</sub>, O(3P), and NO<sub>2</sub>.

```

1 ***** O3
2 O3 is produced in reactions:
3 Percent Rxn No.          IRR Mass
4 100.00 Rxn 2 O          -> 5.519E+00 * ( 1.000*O3 )
5 Total O3 Produced:      5.51936  99.492%
6 Init O3 Conc:          .00000  .000%
7 O3 Net Entrainment:    .02818  .508%
8 TOTAL O3:              5.54754
9 Final O3 Conc:         .14450  2.605%
10 O3 Reacted:           5.40305  97.395%
11 ***** O
12 O is produced in reactions:
13 Percent Rxn No.          IRR Mass
14 75.21 Rxn 1 NO2        -> 4.152E+00 * ( 1.000*NO + 1.000*O )
15 23.60 Rxn 8 O3         -> 1.303E+00 * ( 1.000*O )
16 1.11 Rxn 10 O1D        -> 6.136E-02 * ( 1.000*O )
17 .07 Rxn 14 NO3         -> 4.327E-03 * ( .890*NO2 + .890*O + .110*NO )
18 Total O Produced:      5.51980  100.000%
19 Init O Conc:          .00000  .000%
20 TOTAL O:              5.51980
21 O Net Dilution:      .00000  .000%
22 Final O Conc:         .00000  .000%
23 O Reacted:           5.51980  100.000%
24 ***** NO2
25 NO2 is produced in reactions:
26 Percent Rxn No.          IRR Mass
27 91.82 Rxn 3 O3+NO       -> 4.002E+00 * ( 1.000*NO2 )
28 .00 Rxn 6 O+NO         -> 4.699E-05 * ( 1.000*NO2 )
29 .09 Rxn 14 NO3         -> 4.327E-03 * ( .890*NO2 + .890*O + .110*NO )
30 .66 Rxn 15 NO3+NO      -> 1.433E-02 * ( 2.000*NO2 )
31 .12 Rxn 19 N2O5        -> 5.117E-03 * ( 1.000*NO3 + 1.000*NO2 )
32 .00 Rxn 20 NO          -> 1.030E-04 * ( 1.000*NO2 )
33 .00 Rxn 24 OH+HONO     -> 1.092E-04 * ( 1.000*NO2 )
34 .00 Rxn 25 HONO        -> 2.736E-10 * ( .500*NO + .500*NO2 )
35 2.46 Rxn 28 HO2+NO     -> 1.073E-01 * ( 1.000*OH + 1.000*NO2 )
36 1.99 Rxn 30 PNA        -> 8.693E-02 * ( 1.000*HO2 + 1.000*NO2 )
37 .00 Rxn 31 OH+PNA      -> 2.509E-05 * ( 1.000*NO2 )
38 .39 Rxn 46 C2O3+NO     -> 1.697E-02 * ( 1.000*NO2 + 1.000*XO2 + 1.000*FORM + 1.000*HO2 + 1.000*CO2 )
39 1.16 Rxn 48 PAM        -> 5.048E-02 * ( 1.000*C2O3 + 1.000*NO2 )
40 .00 Rxn 59 NO3+OLE     -> 7.124E-07 * ( .910*XO2 + .090*XO2M + 1.000*FORM + 1.000*ALD2 +-1.000*PA )
41 .01 Rxn 64 TO2+NO     -> 6.162E-04 * ( .900*NO2 + .900*NO2 + .900*OPEH + .100*ORNIT )
42 1.30 Rxn 79 XO2+NO     -> 5.652E-02 * ( 1.000*NO2 )
43 Total NO2 Produced:    4.35906  99.395%
44 Init NO2 Conc:        .02500  .570%
45 NO2 Diluted Emissions .00152  .035%
46 (Total Emissions were .00304 ppm)
47 TOTAL NO2:            4.38558
48 NO2 Net Dilution:     -.04256  .970%
49 Final NO2 Conc:       .00158  .036%
50 NO2 Reacted:          4.34144  98.993%

```

first, the  $O_3$  or the  $NO_2$ . This phenomenon arises from the rapid interconversion of  $NO$ ,  $NO_2$ , and  $O_3$  in the reactions:

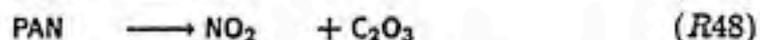


Although  $NO_2$  photolyzes and produces  $O_3$  on a time scale of minutes, the  $NO_2$  is rapidly reproduced by reaction with  $O_3$ . As a result, the observed concentrations may change very slowly over a period of hours. This illustrates the process of a pseudo-steady-state. The species are rapidly reacting, but the concentration does not change significantly over short time periods. Because we are attempting to explain a small increase in the net  $O_3$  concentration, it would be more useful to know the net  $O_3$  production from the  $NO_2/O_3$  cycle shown above.

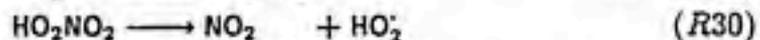
## Removing Cycling Processes

IRREVAL includes a CYCLES command which allows the user to identify a group of reactions which are part of a cycling process. The program then sums the mass of each species produced or consumed in those reactions. The net production (or loss) of each species is then stored in the product coefficients in a single net reaction. The integrated reaction rate of the single net reaction is assigned a value of one because it is more convenient to store the mass reacted in the product coefficients than in the integrated reaction rate array. Details on the use of the CYCLES command is explained in Chapter 6: IRREVAL Commands. This Section explains how the CYCLES command works.

In any photochemical oxidant mechanism, there will be several processes which cycle or interconvert species. In addition to the  $NO_2/O_3$  cycle described above, peroxyacetylnitrate (PAN) and pernitric acid (PNA) also cycle  $NO_2$  in the reactions:



and



In Table 5, lines 28 to 30, 35 and 38 show that another 4% of the total chemical  $NO_2$  production was actually recycled  $NO_2$  from the  $NO_3$ ,  $HO_2NO_2$  and PAN cycles. Only

Table 6. Command file with all major cycles in CB4 removed.

```

zf:\frr\base.cmp
@baseave.frr
CYCLES = "PKA Cycle", "PAH Cycle", "HONO Cycle", "H2O2 Cycle",
         "O3/NO2 Chemistry" = [1, 2, 3, 4, 5, 6, 7, 8, 9,
                             10, 11, 14, 15, 16, 17, 18, 19],
         "O3/HOx Cycle" = [12, 13];
END.

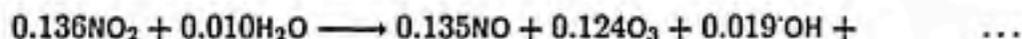
```

about 4.2% was produced from new sources (lines 34, 37 and 41) in the reactions:

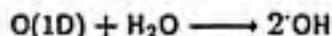


Table 6 shows a command file which uses the CYCLES command to remove all major cycling processes in the Carbon Bond Four (CB4) mechanism. The resulting net production of O<sub>3</sub>, O(3P), and NO<sub>2</sub> are shown in Table 7.

Line 6 of Table 7 shows that there was a net photochemical production of only 0.12411 ppm O<sub>3</sub> compared to 5.51936 ppm of gross O<sub>3</sub> production in line 5 of Table 5. In line 8, net entrainment of O<sub>3</sub> is now seen to be 18.339% of the net O<sub>3</sub> sources. The major species in the net O<sub>3</sub>/NO<sub>2</sub> Chemistry cycle (now stored in a single reaction with coefficient units of ppm) in lines 4 and 5 are:



The yield of O<sub>3</sub> per NO<sub>2</sub> consumed in this net reaction is less than one because the cycle includes (1) the effect of odd oxygen losses in nitrate chemistry and (2) the loss of odd oxygen in the reaction:



Monatomic oxygen production and losses have approximately cancelled out (lines 13 to 22). Lines 28 and 33 of Table 7 show that 59.14% and 31.11% of the net NO<sub>2</sub> production resulted from the reactions of NO with HO<sub>2</sub> and NO with XO<sub>2</sub>. Another 9.63% came from reactions of other organic intermediates with NO in lines 29 and 32. In lines 35 and 36, initial NO<sub>2</sub> and emissions of NO<sub>2</sub> produced another 0.02651 ppm of NO<sub>2</sub>.

I will use "gross chemical production" and "gross chemical loss" to refer to chemical production and chemical loss of a species before cycling reactions are

Table 7. BAL file with all major cycles in CB4 removed.

```

1 ***** O3
2 O3 is produced in reactions:
3 Percent Rxn No.          IRR Mass
4 100.00 Rxn 1 O3/NO2 Chemistr-> 1.000E+00 * ( -.136*NO2 + .135*NO + .000*O + .124*O3 + .000*NO3
5                                     + .000*O1D + -.010*H2O + .019*OH + .000*N2O5 + .000*HN03)
6 Total O3 Produced:      .12411  81.661%
7 Init O3 Conc:           .00000  .000%
8 O3 Net Entrainment:    .02787  18.339%
9 TOTAL O3:               .15198
10 Final O3 Conc:         .14442  95.023%
11 O3 Reacted:            .00756  4.977%
12 ***** O
13 O is produced in reactions:
14 Percent Rxn No.          IRR Mass
15 100.00 Rxn 1 O3/NO2 Chemistr-> 1.000E+00 * ( -.136*NO2 + .135*NO + .000*O + .124*O3 + .000*NO3
16                                     + .000*O1D + -.010*H2O + .019*OH + .000*N2O5 + .000*HN03)
17 Total O Produced:      .00003  100.000%
18 Init O Conc:           .00000  .000%
19 TOTAL O:               .00003
20 O Net Dilution:       .00000  .015%
21 Final O Conc:          .00000  -.935%
22 O Reacted:             .00003  100.205%
23 ***** NO2
24 NO2 is produced in reactions:
25 Percent Rxn No.          IRR Mass
26 .06 Rxn 20 NO           -> 1.020E-04 * ( 1.000*NO2 )
27 .06 Rxn 21 HONO Cycle  -> 1.000E+00 * ( .000*NO + .000*NO2 + .000*H2O + .000*HONO + -.001*OH)
28 59.14 Rxn 28 NO2+NO     -> 1.071E-01 * ( 1.000*OH + 1.000*NO2 )
29 9.33 Rxn 46 C2O3+NO     -> 1.689E-02 * ( 1.000*NO2 + 1.000*NO2 + 1.000*FORM + 1.000*NO2 )
30 .00 Rxn 59 NO3+OLE      -> 5.390E-07 * ( .910*NO2 + .090*NO2W + 1.000*FORM + 1.000*ALD2
31                                     + -1.000*PAR + 1.000*NO2 )
32 .30 Rxn 64 TO2+NO       -> 6.127E-04 * ( .900*NO2 + .900*NO2 + .900*OPEN )
33 31.11 Rxn 79 XO2+NO     -> 5.634E-02 * ( 1.000*NO2 )
34 Total NO2 Produced:    .18112  87.232%
35 Init NO2 Conc:         .02500  12.041%
36 NO2 Diluted Emissions .00151  .727%
37 (Total Emissions were .00301 ppm)
38 TOTAL NO2:             .20763
39 NO2 Net Dilution:     -.04224  20.346%
40 Final NO2 Conc:        .00185  .891%
41 NO2 Reacted:           .16353  78.763%

```

removed. "Total chemical production" and "total chemical loss" will refer to the production or loss after all cycling processes are removed.

I will define the total sources of  $\text{NO}_2$  during the simulation as the sum of the chemical  $\text{NO}_2$  production (after the removal of cycling processes) plus the  $\text{NO}_2$  contributed by physical processes such as emissions, initial concentration, or net entrainment. For any species  $j$ :

$$\text{Total Sources} = \text{Total Chemical Production} + \text{Initial} + \text{Emissions} + \text{Net Entrainment}$$

The total sources of  $\text{NO}_2$  must be balanced by sink processes. Sinks are chemical reaction losses, net dilution to the air aloft, deposition and final concentration:

$$\text{Total Sinks} = \text{Total Chemical Loss} + \text{Net Dilution} + \text{Deposition} + \text{Final Concentration}$$

Chemical loss of  $\text{NO}_2$  can result in production of either  $\text{O}_3$  or other nitrogen products such as  $\text{HNO}_3$  or organic nitrates. I will define the  $\text{O}_3$  yield per  $\text{NO}_2$  produced as the number of  $\text{O}_3$  molecules produced from  $\text{NO}_2$  divided by the total sources of  $\text{NO}_2$  in the simulation.

## Replacing Intermediates

Using Table 7 it is now possible to attribute the chemical production of  $\text{O}_3$  back to the processes which produced the  $\text{NO}_2$ . Thirty-one percent of  $\text{NO}_2$  was produced by  $\text{XO}_2$ . ( $\text{XO}_2$  is an operator used in CB4 to represent the conversion of  $\text{NO}$  to  $\text{NO}_2$  by all  $\text{RO}_2$ .)  $\text{XO}_2$  is produced by the decomposition of organic compounds. It would be informative to know which organics produced the  $\text{XO}_2$ . This would enable us to attribute the  $\text{O}_3$  production back to the organics which produced the  $\text{XO}_2$ . The REPLACE command can be used to perform these calculations. To explain the replace function, I will first perform a mass balance on  $\text{XO}_2$ . Using the command file in Table 6, I requested search type (4) for  $\text{XO}_2$ . The new BAL file is shown in Table 8.  $\text{XO}_2$  is produced by 19 different reactions of organics. It is consumed (lines 43 and 44) in only two reactions:



and 0.029% is unreacted (line 39) and is present as final concentration. The last section in Table 8 shows that for each ppm of  $\text{XO}_2$  that reacts, 0.986 ppm of  $\text{NO}$  are consumed and 0.986 ppm of  $\text{NO}_2$  are produced (lines 49 to 51).

Table 8. BAL file for XO2 with all major cycles in CB4 removed.

```

1 ***** XO2
2 XO2 is produced in reactions:
3 Percent  Rxn No.          IRR Mass
4   1.24  Rxn 45  ALD2      -> 7.087E-04 * ( 1.000*XO2 + 2.000*HO2 + 1.000*CO + 1.000*FORM )
5   29.56 Rxn 46  C2O3+NO   -> 1.689E-02 * ( 1.000*HO2 + 1.000*XO2 + 1.000*FORM + 1.000*HO2
6                                     + 1.000*CO2 )
7    .15  Rxn 49  C2O3      -> 8.391E-05 * ( 1.000*XO2 + 1.000*FORM + 1.000*HO2 + 1.000*CO2 )
8    .98  Rxn 50  C2O3      -> 7.108E-04 * ( .790*FORM + .790*XO2 + -.210*HO2 + .790*OH )
9    7.34 Rxn 51  METH+OH    -> 4.195E-03 * ( 1.000*XO2 + 1.000*FORM + 1.000*HO2 )
10   26.12 Rxn 52  +OH      -> 1.716E-02 * ( .870*XO2 + .130*XO2N + .110*HO2
11                                     + .110*ALD2 + .760*ROR +-1.110*PAR )
12   15.34 Rxn 53          -> 9.131E-03 * ( 1.100*ALD2 + .960*XO2 + .940*HO2
13                                     +-2.100*PAR + .040*XO2N + -.980*ROR )
14    .01  Rxn 56  O+OLE     -> 1.882E-05 * ( .630*ALD2 + .380*HO2 + .280*XO2
15                                     + .300*CO + .200*FORM + .020*XO2N
16                                     + .220*PAR + .200*OH )
17    7.07 Rxn 57  OH+OLE    -> 4.040E-03 * ( 1.000*FORM + 1.000*ALD2 + 1.000*XO2
18                                     + 1.000*HO2 +-1.000*PAR )
19    .16  Rxn 58  O3+OLE    -> 4.282E-04 * ( .500*ALD2 + .740*FORM + .330*CO + .440*HO2
20                                     + .220*XO2 + .100*OH +-1.000*PAR + .930*CO2 )
21    .00  Rxn 59  HO3+OLE   -> 5.390E-07 * ( .910*XO2 + .090*XO2N + 1.000*FORM
22                                     + 1.000*ALD2 +-1.000*PAR + 1.000*HO2 )
23    .01  Rxn 60  O+ETH     -> 5.210E-06 * ( 1.000*FORM + .700*XO2 + 1.000*CO
24                                     + 1.700*HO2 + .300*OH )
25    5.45 Rxn 61  OH+ETH    -> 3.113E-03 * ( 1.000*XO2 + 1.560*FORM + 1.000*HO2 + .220*ALD2 )
26    .26  Rxn 63  OH+TOL    -> 1.839E-03 * ( .080*XO2 + .360*CRES + .440*HO2 + .560*TO2 )
27    1.74 Rxn 66  OH+CRES   -> 1.658E-03 * ( .400*CO + .600*XO2 + .600*HO2 + .300*OPEN )
28    .63  Rxn 70  OPEN+OH   -> 3.587E-04 * ( 1.000*XO2 + 2.000*CO + 2.000*HO2
29                                     + 1.000*C2O3 + 1.000*FORM )
30    .00  Rxn 71  OPEN+O3   -> 2.790E-05 * ( .030*ALD2 + .620*C2O3 + .700*FORM + .030*XO2
31                                     + .690*CO + .080*OH + .760*HO2 + .200*MGLY )
32    2.92 Rxn 72  OH+XYL    -> 3.338E-03 * ( .700*HO2 + .500*XO2 + .200*CRES
33                                     + .800*MGLY + 1.100*PAR + .300*TO2 )
34    1.01 Rxn 73  OH+MGLY   -> 5.790E-04 * ( 1.000*XO2 + 1.000*C2O3 )
35 Total XO2 Produced:      .05715  100.000%
36 Init XO2 Conc:          .00000   .000%
37 TOTAL XO2:              .05715
38 XO2 Net Dilution:      .00000   .002%
39 Final XO2 Conc:         .00002   .029%
40 XO2 Reacted:            .05713  99.969%
41 XO2 is Consumed in the Following Reactions:
42 Percent  Rxn No.          IRR Mass
43   98.62  Rxn 79  XO2+NO   -> 5.634E-02 * ( 1.000*HO2 )
44    1.38  Rxn 80  XO2      -> 7.873E-04 * ( )
45 Total XO2 Reacted:      5.712736E-02
46 The products of XO2 are:
47 Product      Mass  Yield per  Percent of
48 Species      Produced  XO2  Total Prod
49  HO2          .05634   .98622   1.293
50  XO2         -.05713  -1.00000  -99.969
51  NO          -.05634   -.98622  -1.328

```

### How REPLACE Works

The REPLACE command algorithm is divided into two FORTRAN subroutines. DECOMPOSE.FOR identifies all reactions in which  $XO_2$  is consumed and creates a single net reaction, or array, which has negative coefficients for species that are consumed with  $XO_2$  and positive coefficients for species that are produced from  $XO_2$ . Each coefficient is divided by the total mass of  $XO_2$  reacted. This converts the array to production (or loss) of each product per  $XO_2$  reacted. The array is then multiplied by the fraction of the total  $XO_2$  source which is consumed in chemical reactions (in this case 99.97%). This gives a replacement array which has production (or loss) of each product per  $XO_2$  produced. In this example, each  $XO_2$  that is produced results in the consumption of 0.9859 NO and production of 0.9859  $NO_2$ . Thus, we know that for any source which produces 1 ppm of  $XO_2$ , that  $XO_2$  will react to produce 0.9859 ppm of  $NO_2$ .

The second subroutine, REPLACE.FOR, then passes through the mechanism and identifies reactions where  $XO_2$  is produced. The product coefficient of  $XO_2$  in a reaction is multiplied by the replacement array, and the values are added to the products of the reaction.  $XO_2$  is then eliminated from the products in that reaction.

Finally, the reactions with  $XO_2$  as a reactant must be removed or corrected. If  $XO_2$  is only produced chemically, then reactions with  $XO_2$  as a reactant are deleted (because the mass of reactants consumed in these reactions has been distributed among the reactions which produced the  $XO_2$ ). If some fraction of  $XO_2$  is contributed by other sources, such as initial concentration, then the reactions with  $XO_2$  as a reactant are reduced only by the fraction of total  $XO_2$  sources due to chemical production. For example, if 10% of HCHO were present initially and 90% was chemically produced, reactions of HCHO would be multiplied by 0.1. The remaining mass in the HCHO reactions would be distributed among the reactions which produce HCHO.

I added the command "REPLACE =  $XO_2$ :" to the command file shown in Table 6 and requested production of  $NO_2$ . The resulting BAL file is shown in Table 9. The effect of replacing  $XO_2$  can now be seen by comparing  $NO_2$  production in Table 8 and Table 9. The 31% of  $NO_2$  which had been produced by  $XO_2$  is now distributed among the 19 reactions which produce  $XO_2$ . For example in reaction 51,  $CH_4$  produced  $(4.195E-3)(0.986)$  ppm of  $NO_2$ , or 2.28% of chemical  $NO_2$  production (line 13). In addition,  $CH_4$  produces HCHO and  $HO_2$  which also react to produce  $NO_2$ . The REPLACE command can be used on most species which are produced as intermediates in the reaction mechanism. If HCHO is replaced, the HCHO replacement array will be

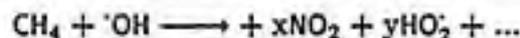
substituted for HCHO in reactions which produce HCHO. The reactions with HCHO as a reactant will be reduced by the fraction of total HCHO sources due to chemical production.

It is inconvenient to enter species names interactively, so a BALANCE command was added to allow the user to list the species names in the command file. The program will then show production, consumption, and the net products of each species listed in the BALANCE command. It will not prompt the user for species names.

## Using EVALUATE for a Full Mass Balance

Usually, the user will request a balance on many of the species in the mechanism. This creates a very large BAL file and contains much information that may be of little interest. It would be difficult to scan the BAL file for key information. An EVALUATE command will extract the important information from the BAL file and organize it into tables in the O<sub>3</sub>, NO<sub>x</sub>, HO<sub>x</sub>, and HC output files. Examples of these files are presented and explained in Chapter Five: IRREVAL Output Files. This section continues with an explanation of the algorithms used to produce the files.

To produce the O<sub>3</sub>, NO<sub>x</sub>, HO<sub>x</sub> and HC files, several new commands and special rules must be introduced. When the EVALUATE command is used, the species HO<sub>2</sub> and NO<sub>2</sub> should *not* be replaced. This is because IRREVAL calculates the number of molecules of O<sub>3</sub> produced per HO<sub>2</sub> produced (Yield NO<sub>2</sub> per HO<sub>2</sub>) and the number of molecules of O<sub>3</sub> produced per NO<sub>2</sub> produced (Yield O<sub>3</sub> per NO<sub>2</sub>). IRREVAL stores the production of HO<sub>2</sub> and NO<sub>2</sub> from each organic, and these yields are used to calculate the O<sub>3</sub> production. For example, the CH<sub>4</sub> reaction must be in the form:



To repeat, NO<sub>2</sub> and HO<sub>2</sub> should *not* be REPLACED when the EVALUATE command is used.

IRREVAL distinguishes between organic and inorganic reactions. The user must identify which species are organic using the ORGANIC command. The NO<sub>x</sub> table contains a nitrogen balance, so the user must also identify nitrogen containing compound using the NOY command. The HOX file shows 'OH radical initiation, propagation, and termination. The user must identify the 'OH initiation reactions using the NEW command. An example CMD file using these commands was shown in Table 5.

Table 9. BAL file showing NO<sub>2</sub> sources with XO<sub>2</sub> replaced and all major cycles in CB4 removed.

```

1 ***** NO2
2 NO2 is produced in reactions:
3 Percent  Rxn No.          IRR Mass
4   .06  Rxn 20  NO          -> 1.020E-04 * ( 1.000*NO2 )
5   .06  Rxn 21  HONO Cycle  -> 1.000E+00 * ( .000*NO + .000*NO2 + .000*HONO + -.001*OH )
6  59.14 Rxn 28  HO2+NO      -> 1.071E-01 * ( 1.000*OH + 1.000*NO2 )
7   .39  Rxn 45  ALD2        -> 7.087E-04 * ( 2.000*NO2 + 1.000*CO + 1.000*FORM
8                                     + -.986*NO + .986*NO2 )
9  18.52 Rxn 46  C2O3+NO     -> 1.689E-02 * ( 1.986*NO2 + 1.000*FORM + 1.000*HO2 + -.986*NO )
10   .05  Rxn 49  C2O3        -> 8.391E-05 * ( 1.000*FORM + 1.000*HO2 + -.986*NO + .986*NO2 )
11   .31  Rxn 50  C2O3        -> 7.108E-04 * ( .790*FORM + -.210*HO2 + .790*OH
12                                     + -.779*NO + .779*NO2 )
13   2.28 Rxn 51  METH+OH     -> 4.195E-03 * ( 1.000*FORM + 1.000*HO2 + -.986*NO + .986*NO2 )
14   8.13 Rxn 52  +OH         -> 1.716E-02 * ( .130*XO2M + .110*HO2 + .110*ALD2 + .760*ROR
15                                     +-1.110*PAR + -.858*NO + .858*NO2 )
16   4.77 Rxn 53              -> 9.131E-03 * ( 1.100*ALD2 + .940*HO2 +-2.100*PAR + .040*XO2M
17                                     + -.980*ROR + -.946*NO + .946*NO2 )
18   .00  Rxn 56  O+OLE       -> 1.882E-05 * ( .630*ALD2 + .380*HO2 + .300*CO + .200*FORM
19                                     + .020*XO2M + .220*PAR + .200*OH + -.276*NO + .276*NO2 )
20   2.20 Rxn 57  OH+OLE      -> 4.040E-03 * ( 1.000*FORM + 1.000*ALD2 + 1.000*HO2
21                                     +-1.000*PAR + -.986*NO + .986*NO2 )
22   .05  Rxn 58  O3+OLE      -> 4.282E-04 * ( .500*ALD2 + .740*FORM + .330*CO + .440*HO2
23                                     + .100*OH +-1.000*PAR + .930*CO2 + -.217*NO + .217*NO2 )
24   .00  Rxn 59  NO3+OLE     -> 5.390E-07 * ( .090*XO2M + 1.000*FORM + 1.000*ALD2
25                                     +-1.000*PAR + 1.897*NO2 + -.897*NO )
26   .00  Rxn 60  O+ETH       -> 5.210E-06 * ( 1.000*FORM + 1.000*CO + 1.700*HO2
27                                     + .300*OH + -.690*NO + .690*NO2 )
28   1.69 Rxn 61  OH+ETH      -> 3.113E-03 * ( 1.560*FORM + 1.000*HO2 + .220*ALD2
29                                     + -.986*NO + .986*NO2 )
30   .08  Rxn 63  OH+TOL      -> 1.839E-03 * ( .360*CRES + .440*HO2 + .560*TO2
31                                     + -.079*NO + .079*NO2 )
32   .30  Rxn 64  TO2+NO      -> 6.127E-04 * ( .900*NO2 + .900*HO2 + .900*OPEN + .100*CRNIT )
33   .54  Rxn 66  OH+CRES     -> 1.658E-03 * ( .400*CRO + .600*HO2 + .300*OPEN
34                                     + -.592*NO + .592*NO2 )
35   .20  Rxn 70  OPEN+OH     -> 3.587E-04 * ( 2.000*CO + 2.000*HO2 + 1.000*C2O3
36                                     + 1.000*FORM + -.986*NO + .986*NO2 )
37   .00  Rxn 71  OPEN+O3     -> 2.790E-05 * ( .030*ALD2 + .620*C2O3 + .700*FORM + .690*CO
38                                     + .080*OH + .760*HO2 + .200*MGly + .200*ARO + -.030*NO + .030*NO2 )
39   .91  Rxn 72  OH+XYL      -> 3.338E-03 * ( .700*HO2 + .200*CRES + .800*MGly + 1.100*PAR
40                                     + .300*TO2 + .500*CO2 + -.493*NO + .493*NO2 )
41   .32  Rxn 73  OH+MGly     -> 5.790E-04 * ( 1.000*C2O3 + -.986*NO + .986*NO2 )
42
43 Total NO2 Produced:      .18112  87.232%
44 Init NO2 Conc:           .02500  12.041%
45 NO2 Diluted Emissions    .00151  .727%
46 (Total Emissions were    .00301 ppm)
47 TOTAL NO2:               .20763
48 NO2 Net Dilution:       -.04224  20.346%
49 Final NO2 Conc:         .00185  .891%
50 NO2 Reacted:             .16353  78.763%

```

IRREVAL will process the CYCLES and REPLACE commands and produce a modified mechanism array with considerably fewer reactions than the original reaction. The number of reactants in each reaction however, will increase. For example, reactions of  $C_2O_3$  (an organic intermediate) will have been eliminated, but each reaction which produced  $C_2O_3$  will contain all of the species that  $C_2O_3$  ultimately produced in its degradation reactions. The WRITE command can be used at any time to see the current form of the mechanism array. The program will then store the amount of  $HO_2$  and  $NO_2$  produced and the amount of  $\cdot OH$  consumed by each organic species, reactions in which  $NO_y$  is produced or consumed, and reactions in which  $\cdot OH$  is produced and consumed. The rate of  $O_3$  production from the  $i^{th}$  hydrocarbon could then be calculated as:

$$\left. \frac{\partial O_3}{\partial t} \right|_{HC_i} = \frac{dHC_i}{dt} \left( \frac{\partial HO_2}{\partial HC_i} \frac{\partial NO_2}{\partial HO_2} + \frac{\partial NO_2}{\partial HC_i} \right) \frac{\partial O_3}{\partial NO_2} \quad (A)$$

The production of  $O_3$  from initial  $NO_2$  could be calculated as:

$$\left. \frac{\partial O_3}{\partial t} \right|_{NO_{2initial}} = \frac{dNO_{2initial}}{dt} \frac{\partial O_3}{\partial NO_2} \quad (B)$$

If the integrated reaction rates are given simply as the total integrated rate for the entire simulation period, it is not possible to integrate the derivatives in equations (A) and (B), but the derivatives can be approximated as:

$$\int \frac{dHC_i}{dt} dt = \Delta HC_i$$

$$\frac{\partial HO_2}{\partial HC_i} \approx \frac{\Delta HO_2}{\Delta HC_i}$$

$$\frac{\partial NO_2}{\partial HC_i} \approx \frac{\Delta NO_{2i}}{\Delta HC_i}$$

$$\frac{dNO_2}{dHO_2} \approx \frac{\Delta NO_2}{\Delta HO_2} = \text{Yield of } NO_2 \text{ per } HO_2 \text{ produced (ppm/ppm)}$$

$$\frac{dO_3}{dNO_2} \approx \frac{\Delta O_3}{\Delta NO_2} = \text{Yield of } O_3 \text{ per } NO_2 \text{ produced (ppm/ppm)}$$

and then the integrals over time of equations (A) and (B) can be approximated as:

$$[O_3]_i = \Delta HC_i \left( \frac{\Delta HO_{2i}}{\Delta HC_i} \frac{\Delta NO_2}{\Delta HO_2} + \frac{\Delta NO_{2i}}{\Delta HC_i} \right) \frac{\Delta O_3}{\Delta NO_2}$$

$$[O_3]_{initialNO_2} = \Delta NO_{2initial} \frac{\Delta O_3}{\Delta NO_2}$$

where  $\Delta O_3$  is the incremental production of  $O_3$  in ppm.

The yield of  $NO_2$  per  $HO_2$  produced is calculated by summing  $NO_2$  production in reactions of  $HO_2$ , and then dividing by the total  $HO_2$  sources in the simulation (after eliminating all cycling of  $NO_2$  and  $HO_2$ ).

$$\frac{\Delta NO_2}{\Delta HO_2} = \frac{\text{Sum of } NO_2 \text{ production in } HO_2 \text{ reactions}}{\text{Total } HO_2 \text{ production}}$$

Its value is listed at the end of the \*.HC output file. The yield of  $O_3$  per  $NO_2$  produced is calculated by dividing  $O_3$  production in the  $O_3/NO_2$  chemistry cycle by total  $NO_2$  sources.

$$\frac{\Delta O_3}{\Delta NO_2} = \frac{\text{Sum of } O_3 \text{ production in } NO_2 \text{ reactions}}{\text{Total } NO_2 \text{ production}}$$

Its value is listed in the \*.NOX output file.

The \*.O3 file will show the mass of each organic reacted, the  $O_3$  yield per organic reacted, and the total  $O_3$  attributed to each organic. Appendix A shows the chain reaction of ethene and illustrates the calculation of  $\delta O_3/\delta ETH$ . These output files are described in detail in chapter 5.

## Time Dependent Analysis

The method described in the previous section provides an approximation of how the predicted  $O_3$  is produced. Its major weakness is that the calculated yields of  $O_3$  per  $NO_2$  and  $NO_2$  per  $HO_2$  in equations (A) and (B) are calculated as averages for the entire simulation period. In this example, chemical production of  $O_3$  was 124 ppb. The total sources of  $NO_2$  were 181 ppb chemical production plus 26 ppb of initial  $NO_2$  and  $NO_2$  emissions, for a total of 207 ppb  $NO_2$ . So, averaged over the simulation period, for each ppb of  $NO_2$  produced, 0.6 ppb of  $O_3$  are produced. The initial  $NO_2$  concentration is 25 ppb, so using this method  $(0.6)(25) = 15$  ppb of  $O_3$  is attributed to the initial  $NO_2$ . Likewise, for each ppb of  $NO_2$  produced by an organic species, 0.6 ppb of  $O_3$  is attributed to that organic.

The efficiency of conversion of  $NO_2$  to  $O_3$ , however, varies as a function of time. In the early morning,  $NO$  is high and little net production of  $O_3$  occurs, so much of the initial  $NO_2$  may be lost to dilution. Chemical  $NO_2$  production is largest later in

the day when  $\text{NO}_2$  is converted more efficiently to  $\text{O}_3$ . The yields of these conversion processes must be known as a function of time to correctly attribute  $\text{O}_3$  production to the various sources. The `IRR = TIME` command saves the integrated reactions rates periodically, e.g. at 60 minute intervals, throughout the simulation. This allows a complete mass balance analysis to be performed for each interval, and the yields of conversion processes can be calculated for each interval.

This approach gives a more accurate description of the contribution of initial  $\text{NO}_2$  and chemically produced  $\text{NO}_2$  to the  $\text{O}_3$  production. It treats more accurately all of the time-dependent yields and conversion processes. For example, the yield of conversion of  $\text{HO}_2$  to  $\text{NO}_2$  depends on the abundance of  $\text{NO}$ . A compound which produced  $\text{HO}_2$  late in the day when  $\text{NO}$  is depleted would not have the same impact on  $\text{O}_3$  production as a compound which produced  $\text{HO}_2$  earlier in the day.

This approach also presents new difficulties. In the time-averaged case, the simulation consisted of one interval.  $\text{O}_3$  produced from species present at the beginning of the simulation could be attributed to the initial concentration of those species.

In the time-dependent case, the simulation is divided into several intervals. At the beginning of any interval after the first, there will be some concentration of each species, e.g.  $\text{NO}_2$ . This  $\text{NO}_2$  can be partially attributed to  $\text{NO}_2$  present at the beginning of the simulation and partially attributed to the various new sources of  $\text{NO}_2$  during each interval after the beginning of the simulation. I have tried to distinguish the initial  $\text{NO}_2$  present at the beginning of the first interval from that present at the beginning of subsequent intervals by calling the latter "old  $\text{NO}_2$ " or the "current concentration at the beginning of the interval".

OZIPR reports the concentration of  $\text{NO}_2$  at the beginning of any interval (the "old  $\text{NO}_2$ "), but IRREVAL must determine what fraction of the old  $\text{NO}_2$  is left over from initial  $\text{NO}_2$  and what fraction has been produced chemically since the beginning of the simulation. (Remember that  $\text{NO}_2$  is rapidly photolyzed, so that the identical  $\text{NO}_2$  molecule which was initially present will no longer exist, but, because of the pseudo-steady-state equilibrium, an  $\text{NO}_2$  formed from the initial  $\text{NO}_2$  may be present.)

I included an algorithm (described below) to trace the  $\text{NO}_2$  produced from each source and from each species in the mechanism. I assumed that the rate of  $\text{NO}_2$  production is constant during an interval and that the rate loss processes are constant and act proportionally to the concentration of  $\text{NO}_2$  present from each

source at any given time. I will use the following simple example to describe the algorithm and the calculations it performs:

Suppose a simulation consists of one interval lasting one hour. At the beginning of the interval there is an initial NO<sub>2</sub> concentration of 100 ppb. Another 50 ppb of NO<sub>2</sub> is emitted linearly during the interval, and NO<sub>2</sub> loss occurs linearly during the interval with a total loss of 30 ppb. Let

$X_{1,t}$  = the concentration of NO<sub>2</sub> due to initial NO<sub>2</sub> at time  $t$

$X_{2,t}$  = the concentration of NO<sub>2</sub> due to NO<sub>2</sub> emissions at time  $t$

$X_{T,t} = X_{1,t} + X_{2,t}$  = total NO<sub>2</sub> concentration at time  $t$

$P_{2,t}$  = rate of new NO<sub>2</sub> from emissions = 50 ppb/hr

$P_{T,t}$  = total production rate of NO<sub>2</sub> from all new sources

$L_t$  = loss rate of NO<sub>2</sub> = 30/hr

At time  $t = 0$ ,  $X_{2,0} = 0$  and  $X_{T,0} = X_{1,0} = 100$  ppb.  $X_T$  can be expressed as a function of time:

$$X_{T,t} = X_{T,t-1} + (P_{T,t} - L_t)t$$

and the rate of change of  $X_1$  and  $X_2$  are linear first-order differential equations:

$$\frac{dX_1}{dt} = -L\left(\frac{X_1}{X_T}\right)$$

$$\frac{dX_2}{dt} = P_2 - L\left(\frac{X_2}{X_T}\right)$$

which can also be expressed as:

$$\frac{dX_1}{X_1} = -\frac{Ldt}{X_{T,0} + (P_T - L)t} \quad (C)$$

$$\frac{dX_2}{dt} + \frac{X_2 L}{X_{T,0} + (P_T - L)t} = P_2 \quad (D)$$

The analytical solutions to (C) and (D) are:

$$X_1 = X_{1,0} \left( \frac{X_{T,0} + (P_T - L)t}{X_{T,0}} \right)^{\left(\frac{-1}{1-P_T}\right)} \quad (E)$$

$$X_2 = \frac{P_2}{P_T} [X_{T,0} + (P_T - L)t] + X_{2,0} X_{T,0}^{L/(L-P_T)} - X_{T,0}^{P_T/(P_T-L)} [X_{T,0} + (P_T - L)t]^{L/(L-P_T)} \quad (F)$$

For the example given above, 76 ppb of the initial  $\text{NO}_2$  would be left and 44 ppb of emitted  $\text{NO}_2$  would have accumulated by the end of the hour.

For each additional source of new  $\text{NO}_2$ , for example, chemical production by organic species  $j$ , equation (F) is solved with the appropriate values for  $X_{j,0}$  and  $P_j$ .

Source and sink terms are not linear in a typical simulation, but a simulation can be split into intervals with nearly linear sink and source terms. In OZIPR the command `IRR = TIME;` is used to request time dependent integrated reaction rate output. The time interval for output is set using the command `PRINT> TSTEP=X;`. The default time interval is one hour.

To summarize this discussion, in a time-dependent IRREVAL analysis,  $\text{NO}_2$  present at the end of interval  $t$  is made up of some mass that was present initially and some mass that was produced since the beginning of the simulation. At the beginning of interval  $t + 1$ , IRREVAL requires a method to determine how much of the current  $\text{NO}_2$  concentration is attributed to initial  $\text{NO}_2$  and how much is attributed to new production in all previous intervals.

I added two subroutines to implement the algorithms described above. Subroutine SAVEPROD.FOR saves the amount of  $\text{NO}_2$  each organic during each interval. SAVEPROD is called after cycles have been eliminated and before species have been replaced. SAVEPROD.FOR builds an array  $P(i,j)$  which is the mass in ppm of species  $i$  produced by source  $j$ . The subroutine INTSPE.FOR then uses  $P(i,j)$  to solve equations (E) and (F) above for  $\text{NO}_2$ . It updates an array  $X(i,j)$ , where  $X(i,j)$  is the mass in ppm of species  $i$  attributed to source  $j$ , and

$$XT(i) = \sum_{j=1}^n X(i,j)$$

is the current concentration of species  $i$ .

The same problem occurs for intermediates species which are eliminated using the REPLACE command, *e.g.* FORM and C2O3 in CB4. When the REPLACE command is used, IRREVAL attempts to attribute  $\text{O}_3$  produced from intermediates to the primary organic which originally produced the intermediate. In a time-averaged analysis, the chemically produced fraction of these species is eliminated. The fraction present initially or emitted is considered a primary organic and is not eliminated. In a time-dependent analysis, each replaced species will have a non-zero

concentration at the beginning of each interval after the first. The "old" concentration at the beginning of each of these intervals must be correctly attributed to the sources which produced the species in the earlier intervals. The same method described above for  $\text{NO}_2$  is used to determine, in each interval, the fraction of the "old" intermediate concentration to be attributed to each primary organic species.

The calculation is further complicated, however, for replaced organic intermediates because a replaced species may be produced by another replaced species. I used the method described above for  $\text{NO}_2$  to calculate  $X(i,j)$  for each replaced species, where  $i$  is an index for the replaced species and  $j$  is an index showing which organic species produced replaced species  $i$ . I then added another subroutine, `ELIMREP.FOR`, to sort the array  $X(i,j)$ . It attributes all production of species  $i$  to primary organics. Briefly, when a source species  $j$  is itself a replaced species, the array  $X(j,k)$  is used to determine which species produced the  $j$ , so that the mass of  $i$  produced by  $j$  is attributed to the organic species which produced  $j$ .

The primary goal of these calculations is to attribute the  $\text{O}_3$  production from intermediates to primary organics. The subroutine `TIMOUT.FOR` checks if  $\text{O}_3$  is conserved in the substitution process. If  $\text{O}_3$  is lost, a message is printed to the `TI3` output file and the  $\text{O}_3$  production by each organic is increased to make up for the lost mass.

---

# IRREVAL Output Files

---

IRREVAL can be used in three different modes which determine the number of output files. In the simplest case, the user wishes to view detailed information about the sources, sinks and reactions of one or several species. The CMP and IRR input files must be specified; the CYCLES and REPLACE commands may be used to eliminate cycling processes and intermediates; and the IGNORE and NEW commands may be used to determine the number and types of species shown in the output. Species names can be entered interactively or the BALANCE command can be used to list the species for which an analysis is desired. Output is listed in the \*.BAL file.

The EVALUATE command performs a complete mass balance analysis of organic and nitrogen containing species. It creates the additional output files \*.O3, \*.NOX, \*.HOX, and \*.HC, where the \* is replaced by the name of the command file. Figure 5 showed a typical CMD file used for CB4 which illustrates the EVALUATE command. This CMD file was used to generate the output files listed below.

If a time dependent IRR file is used, the complete analysis is performed for each interval in the \*.IRR file. The O<sub>3</sub>, NO<sub>y</sub>, HO<sub>x</sub> and HC Tables are written to the output files for each interval, so these files may be as large as 100K. The \*.BAL file may be larger than one Mbyte, and it is possible to avoid creating it with the SUPPRESS command. Four additional files are then created which summarize key time dependent information. These are \*.TIM, \*.TI2, \*.TI3 and \*.TI4. Each output file is described below.

## BAL Output File

An example BAL file is shown in Table 10. When IRREVAL reads the mechanism, it

will combine coefficients of species which occur twice in the reaction. (This simplifies the analysis.) The BAL file will first list reactions which have been modified by combining coefficients. For example, the reaction



generates the message shown in line 5 of Figure 10.

The BAL file then displays information for the reactions which were summed using the CYCLES command. Line 9 lists the reactions which were found to contain HONO and which are summed to calculate the net cycle reaction. Lines 11 and 12 show the net reaction produced by the summation. In net cycle reactions, the reaction's integrated reaction mass is set to 1.0 while the mass of species reacted and produced is actually stored in the net reaction coefficients. This simplifies the summing of masses for species which occur in reactions which have different integrated masses.

A warning message will occur for species which are found to have no source, as in lines 14 to 15. In this case, odd oxygen was summed with the CYCLE command so that atomic oxygen sinks and sources cancelled out. As discussed in Section 2, there are small errors in the mass balance for each species so that line 16 shows a small amount of O reacted while none is produced. The difference is small in this case so no error has occurred, but this warning message can indicate problems when the error is large or if a species expected to be present has zero sources.

Lines 19 to 23 show the message displayed when a species is replaced. The replacement array is shown in lines 21 and 22. It is the sum of all species produced by or reacted with the replaced species. In this simple example, one NO is consumed by XO<sub>2</sub> to produce one NO<sub>2</sub>. The yields are less than the "Percent Reacted" because some XO<sub>2</sub> reacts with itself to form no products.

For each species listed in the BALANCE or EVALUATE commands, the detailed mass balance information is in a block with three sections. Table 3 shows an example output for CO. The first section, lines 26 to 41 lists all reactions which produce CO and the percent produced via each reaction. The amount produced by a given reaction is the product of the integrated reaction rate (first number after the arrow) and the CO product coefficient. Lines 35 to 40 then show all sinks and sources of CO. The second section, lines 43 to 46, lists all reactions which consume

Table 10. Example BAL Output File

```

1
2
3
4
5 Adjusted Rxn 16 NO3          -> 1.00*NO .00*NO2
6
7 Cycle = HONO Cycle
8 Rxns found = 6
9 Summed Reactions: 21 21 22 23 24 25
10 Net Reaction is:
11 .00038530*NO .00000011*NO2O .00049225*OH
12 -> .00010695*NO2 .00027835*HONO
13
14 Warning: Species "O" had 0 Total Mass in IRMB.
15 Prod = .00 Init conc = .00 Emiss = .00
16 Sum Reacted = 5.257712E-05
17
18 Replaced specie is: X02
19 Prod Specie Yield per X02 produced
20 NO2 .9767
21 NO -.9767
22 Percent Reacted = 99.926 %
23
24
25 ***** CO
26 CO is produced in reactions:
27 Percent via irr prod
28 43.27 Rxn 37 FORM+OH -> .172E-01 * ( 1.000*NO2 + 1.000*CO )
29 16.93 Rxn 38 FORM -> .672E-02 * ( 2.000*NO2 + 1.000*CO )
30 29.10 Rxn 39 FORM -> .115E-01 * ( 1.000*CO )
31 .01 Rxn 40 FORM+O -> .257E-05 * ( 1.000*OH + 1.000*NO2 + 1.000*CO )
32 .23 Rxn 62 O3+ETH -> .217E-03 * ( 1.000*FORM + .420*CO + .120*NO2 )
33 1.41 Rxn 69 OPEN -> .558E-03 * ( 1.000*CO2O3 + 1.000*NO2 + 1.000*CO )
34 4.55 Rxn 74 MGLY -> .180E-02 * ( 1.000*CO2O3 + 1.000*NO2 + 1.000*CO )
35 Total CO produced is .03965 3.199%
36 Init CO conc was 1.20000 96.801%
37 TOTAL CO = 1.23965
38 CO Net Dilution was -.55157 44.494%
39 Final CO Conc = .64863 52.324%
40 CO Reacted = .03945 3.183%
41 (net entrainment only added to total if positive)
42
43 CO is consumed in rxns below to produce:
44 Percent via
45 100.000 Rxn 36 OH+CO -> .03945 * ( 1.000*NO2 )
46 Total CO reacted was 3.945234E-02
47
48 The products of CO are:
49 prod specie production Yield per CO % of Tot Prod
50 NO2 .0394523 1.00000 30.280
51 OH -.0394523 -1.00000 -27.806
52 CO -.0394523 -1.00000 -3.183

```

CO and the percent of the total reacted lost via each reaction. The third section, lines 48 to 52, contains a row for each species that is produced by or reacts with CO. The first column is the name of species *i*, the second column is the amount of species *i* produced (or reacted if negative), the third column is the yield of species *i* per CO reacted. The fourth column is the percent of total species *i* sources that is produced (or lost) by reactions involving CO. In this example, 30% of the total HO<sub>2</sub> is produced by CO, while 28% of the OH is consumed by CO.

If the WRITE command is used, the mechanism and integrated reaction rate arrays will appear in the BAL file. Warnings may also occur in the mass balance blocks if IRREVAL finds that species *i* is producing species *j* in one reaction and species *j* is producing species *i* in another reaction.

## O3 Output File

The \*.O3 file will contain "Table 1: Ozone Production". See Table 11 for an example O<sub>3</sub> file. A row for each hydrocarbon shows the amount of the hydrocarbon (HC) reacted (ppm), the number of NO<sub>2</sub> molecules produced per HC reacted, the total NO<sub>2</sub> production (ppm) due to each HC, the O<sub>3</sub> production (ppm) due to each HC, the fraction of total O<sub>3</sub> sources due to each HC, and number of O<sub>3</sub> molecules produced per HC reacted. Similar information is shown for each inorganic reaction which produces NO<sub>2</sub> (lines 17 to 19). Lines 21 to 28 summarize the processes which produce or consume O<sub>3</sub>. There are two error checks in Figure 11. Line 26 compares the total O<sub>3</sub> sources calculated by IRREVAL to the total sources given in the IRR file. The total should be very close to 100%. Lines 28 and 29 compare the final O<sub>3</sub> concentration calculated by IRR with that calculated by mass balance within the IRR file.

Line 9 of Table 11 shows that the average yield of O<sub>3</sub> (ppm) per ETH (ppmV) reacted is 1.735. Appendix A shows the chain reaction of ethene and illustrates the calculation of  $\Delta O_3/\Delta ETH$ .

## NOX Output File

The \*.NOX file contains a table labeled "Table 2: NO<sub>x</sub> Balance" (see Table 12 for an example NOX file). The NOX file has rows showing individual chemical sources and sinks for NO in ppm, for NO<sub>2</sub> in both ppm and percent, and for NO<sub>z</sub> in ppm, (NO<sub>z</sub> = NO<sub>y</sub> - NO<sub>x</sub>). Conservation of nitrogen requires that, within any row, the total of NO<sub>y</sub> sources must equal the total of NO<sub>y</sub> sinks, where NO<sub>y</sub> = NO + NO<sub>2</sub> + NO<sub>z</sub>. Lines 16

Table 11. Example O<sub>3</sub> output file

```

1 Table 1: O3 Production
2 -----
3 Source          Reacted(ppmV)  YNO2/ppm  NO2 Prod  O3 Prod  XTot O3  YO3/ppm
4 -----
5 Organic Sources
6 CO              .03621         .908      .03289   .01996   13.11    .551
7 METH           .00421         2.408    .01015   .00616   4.04     1.461
8 PAR            .02360         2.947    .05876   .03566   23.42    1.788
9 ETH            .00333         2.858    .00952   .00578   3.79     1.735
10 OLE            .00451         3.593    .01082   .00657   4.31     2.180
11 TOL            .00184         2.424    .00447   .00271   1.78     1.471
12 XYL            .00335         4.664    .01564   .00949   6.23     2.830
13 FORM           .01112         .808     .00898   .00545   3.58     .490
14 ALD2           .00932         2.846    .02652   .01609   10.57    1.727
15 -----
16 Organic Subtotal .09750         1.823    .17775   .10787   70.84    1.106
17 Inorganic Reactions
18 Rxn 20 NO      .00010         .00006   .04
19 Rxn 21 HONO Cycle .00011         .00007   .04
20 -----
21 Inorganic Subtotal .00021         .00013   .08
22 Total Org+Inorg Prod .17796         .10800   70.92
23 O3 from old NO2 .02500         .01517   9.96
24 NO2 Emissions .00152         .00092   .61
25 Net O3 Entrainment .02818         18.51
26 TOTAL O3 Sources .15228         100.00
27 O3 Reacted .00779         5.12
28 Final O3 Conc .14449
29 Correct conc from IRR .14450
30 -----

```

to 20 show the contribution of initial concentrations, emissions, dilution, and final concentration to the NO<sub>y</sub> balance. Within each set of paired source/sink columns (for NO, NO<sub>2</sub>, NO<sub>2</sub>) mass conservation requires that the total sources must equal the total sinks. In addition, for NO<sub>2</sub>, the summed NO<sub>2</sub> sources and sinks calculated by IRR are compared to the correct total NO<sub>2</sub> sources. Thus, in Table 12, line 22 of the "%" column should be 100%. This is a check for errors in the routine which identifies and sums NO<sub>2</sub> production.

Lines 24 to 28 summarize important information from Table 12 which can be used to compare different reacting systems or different photochemical mechanism. O<sub>3</sub> is produced (perhaps exclusively) by photolysis of NO<sub>2</sub>. Line 24 shows the fraction of total sources of NO<sub>2</sub> consumed in the O<sub>3</sub>/NO<sub>2</sub> chemistry cycle. The value will depend on which reactions are included in the O<sub>3</sub>/NO<sub>2</sub> cycle. I normally include the O<sub>3</sub> and NO<sub>2</sub> photolysis reactions, inorganic NO<sub>3</sub> reactions and the O(1D) + H<sub>2</sub>O reaction (see the command file in Figure 5 for a complete list of reaction numbers). This choice of reactions removes all cycling effects of photolysis reactions on NO<sub>2</sub>

Table 12. Example NO<sub>x</sub> output file

1 Table 2: NO <sub>x</sub> Balance									
2 =====									
3 Reaction	NO		NO <sub>2</sub>				NO <sub>2</sub> = NO <sub>y</sub> - NO <sub>x</sub>		
4	Sources	Sinks	Sources	%	Sinks	%	Sources	Sinks	
5	-----								
6 Total Organic Rxns	.00000	.07411	.07043	34.44	.00000	.00	.00441	.00074	
7	-----								
8 Rxn 28 NO+HO <sub>2</sub> ->NO <sub>2</sub> +OH		.10733	.10733	52.48					
9 Rxn 1 O <sub>3</sub> /NO <sub>2</sub> Chemistry	.13570	.00000	.00000	.00	.13613	66.57	.00044	.00000	
10 Rxn 20 NO	.00000	.00010	.00010	.05	.00000	.00	.00000	.00000	
11 Rxn 21 HO <sub>2</sub> Cycle	.00000	.00041	.00011	.05	.00000	.00	.00030	.00000	
12 Rxn 26 OH+NO <sub>2</sub>	.00000	.00000	.00000	.00	.02421	11.84	.02421	.00000	
13 Rxn 29 PVA Cycle	.00000	.00000	.00000	.00	.00001	.00	.00001	.00000	
14 Rxn 81 NO <sub>2</sub> +NO	.00000	.00259	.00000	.00	.00000	.00	.00259	.00000	
15 Rxn 27 OH+HO <sub>2</sub>	.00000	.00000	.00000	.00	.00000	.00	.00051	.00051	
16 Total Chemical Rxns	.13570	.18453	.17797	87.03	.16035	78.41	.03247	.00125	
17 Initial Concentration	.07500		.02500	12.23			.00000		
18 Emissions	.02892		.00152	.74			.00000		
19 Net Dilution		.05507			.04256	20.81		.00580	
20 Final Concentration		.00001			.00158	.77		.02542	
21	-----								
22 Totals	.23961	.23961	.20449	100.00	.20449	100.00	.03247	.03247	
23	=====								
24 Fraction of NO <sub>2</sub> Consumed in Photolysis Rxns			= .665706						
25 Fraction of NO <sub>2</sub> Consumed in Non-Photolysis Rxns			= .118436						
26 Fraction of NO <sub>2</sub> Unreacted			= .215858						
27 Yield O <sub>3</sub> per NO <sub>2</sub> Photolysed			= .911652						
28 Yield O <sub>3</sub> per NO <sub>2</sub> Produced			= .606893						

and O<sub>3</sub>. Line 27 shows the average yield of O<sub>3</sub> per NO<sub>2</sub> consumed in the O<sub>3</sub>/NO<sub>2</sub> chemistry cycle. It is a measure of the extent to which NO<sub>3</sub> chemistry and 'OH production remove odd oxygen from the system. When NO<sub>2</sub> concentrations are high, there may be a net loss of odd oxygen in these reactions, and the yield of O<sub>3</sub> per NO<sub>2</sub> photolysed would be zero.

Line 25 shows the fraction of NO<sub>2</sub> sources consumed in reactions other than the O<sub>3</sub>/NO<sub>2</sub> chemistry cycle. This is a measure of how effectively reactions with 'OH and organic intermediates remove NO<sub>2</sub> from the system.

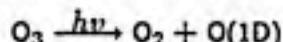
Line 26 is the fraction of NO<sub>2</sub> sources that are unreacted, either as final NO<sub>2</sub> or NO<sub>2</sub> dilution. Finally, line 28 shows the yield of O<sub>3</sub> per molecule of NO<sub>2</sub> produced. It should be equal to the product of lines 24 and 27.

Line 24 showed that 66% of the total NO<sub>2</sub> source, or 136 ppb, was consumed in the O<sub>3</sub>/NO<sub>2</sub> chemistry cycle. It would be physically incorrect to conclude that only 136 ppb of NO<sub>2</sub> photolyzed. In fact, NO<sub>2</sub> rapidly photolyzes to produce O<sub>3</sub> and NO

throughout the day. And much of the  $O_3$  and  $NO$  rapidly react to reproduce  $NO_2$ . As discussed in Section 4, the total  $NO_2$  used here is the sum of  $NO_2$  sources after all cycling processes are removed. The 136 ppb of  $NO_2$  consumed in the  $O_3/NO_2$  chemistry is the mass of  $NO_2$  which reacted to form  $O_3$  and was not subsequently converted back to  $NO_2$ .

## HOX Output File

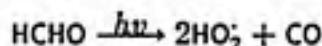
VOCs react primarily with  $\cdot OH$  radicals in a chain-type reaction sequence. Chain-reactions consist of a radical initiation step, a propagation step, and a radical termination step. A radical is a species with an unpaired electron, also called a "free" electron. Free electrons are created in pairs by photolysis reaction of photo-acceptor species. For example, photolysis of  $O_3$ :



creates  $O(1D)$  which can then abstract a hydrogen atom from water:



creating two "new"  $\cdot OH$  radicals. New  $\cdot OH$  radicals can also be generated by the photolysis of organic photo-acceptors such as aldehydes:



and the subsequent reaction of  $NO$  with  $HO_2$ :



An  $\cdot OH$  radical can react with a VOC in the propagation step. For example,  $\cdot OH$  abstracts an H atom from an  $CH_4$ :

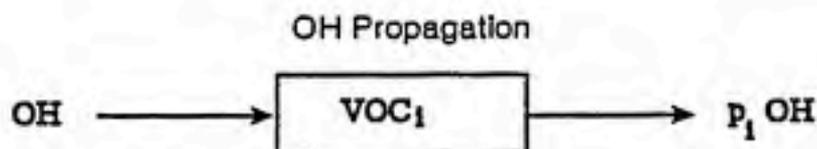


Molecular oxygen adds to the radical to form a methylperoxy radical.



The methylperoxy radical converts an  $NO$  to  $NO_2$ , forming a methoxy radical, and  $O_2$  abstracts an H atom from the methoxy radical to form  $HO_2$ .





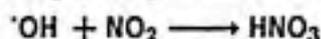
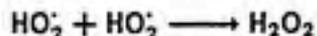
**Figure 2.** Propagation of  $\cdot\text{OH}$  radicals by reaction with a single VOC. and the  $\text{HO}_2$  can then react with  $\text{NO}$  regenerating the  $\cdot\text{OH}$  radical.



The net reaction for this propagation chain is:



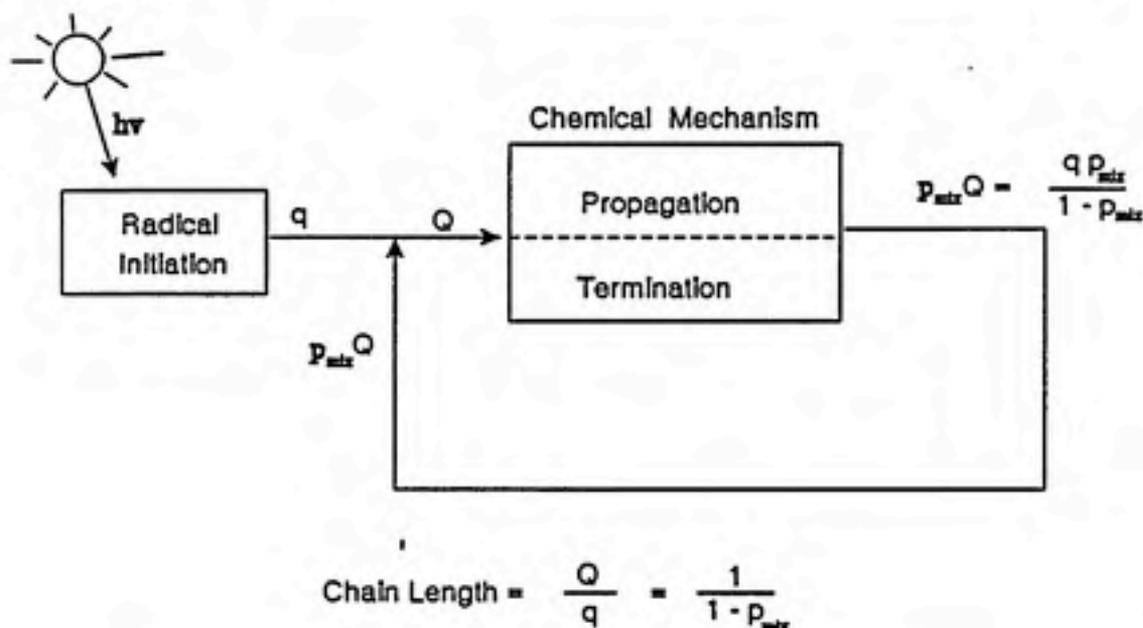
The chain-termination reactions are those in which radicals are lost by the recombination of free electrons, *e.g.*:



If a mixture is to produce a significant amount of  $\text{O}_3$ , there must be a source of "new"  $\cdot\text{OH}$  radicals which start and maintain the chain process. In the early morning, photolysis of  $\text{HCHO}$  or  $\text{HONO}$  are often significant sources of new  $\cdot\text{OH}$ , while later in the day, photolysis of  $\text{O}_3$  may produce much of the new  $\cdot\text{OH}$ .

To produce  $\text{O}_3$ , the VOC mixture must also regenerate significant quantities of  $\cdot\text{OH}$  in the propagation step. In other words, the rate of chain propagation reactions must be large compared to the rate of chain termination reactions. Because of chain termination reactions, less than one  $\cdot\text{OH}$  is regenerated from each  $\cdot\text{OH}$  which reacts with an organic. A propagation factor for an individual  $\text{VOC}_i$  can be defined as the number of  $\cdot\text{OH}$  radicals produced in the final step of the chain. In Figure 2,  $p_i$  is the number of  $\cdot\text{OH}$  radicals regenerated per  $\cdot\text{OH}$  that reacts with  $\text{VOC}_i$ . The value of  $p_i$  must be less than or equal to one. (It would be equal to one if there were no chain termination reactions.)

The propagation factor of the mixture is the sum of the propagation factors of the individual VOCs weighted by the fraction of  $\cdot\text{OH}$  which reacts with each VOC. Chain termination reactions have a propagation factor of zero. Figure 3 illustrates



**Figure 3.** Relation of the propagation factor of the mixture to the ·OH chain length.

the ·OH chain-reaction. Photolysis reactions generate  $q$  new ·OH radicals. The second box in Figure 3 represents the propagation and consumption of ·OH radicals in chain-propagation and chain-termination reactions. For each ·OH consumed,  $p_{mix}$  ·OH radicals are regenerated in propagation reactions, where  $p_{mix}$  is the propagation factor of the mixture. If  $p_{mix}$  is low, termination reactions are fast relative to propagation reactions. The total amount of ·OH reacted,  $Q$ , is:

$$Q = q + qP_{mix} + qP_{mix}^2 + \dots + qP_{mix}^{\infty}$$

$$Q = \frac{q}{1 - P_{mix}}$$

The ·OH chain length is defined as the total ·OH reacted per new ·OH produced and can be calculated as:

$$\text{·OH Chain Length} = \frac{Q}{q}$$

$$\text{·OH Chain Length} = \frac{1}{1 - P_{mix}}$$

The propagation reactions described above also produces new organic photo-acceptors. These can photolyses to produce additional new ·OH radicals. As a result,

the number of new  $\cdot\text{OH}$  radicals produced will depend on

- The actinic flux,
- The presence of photo-acceptor species in the mixture, and
- The production of new photo-acceptors in the chemical mechanism

One method of characterizing  $\text{O}_3$  production is in terms of the sources of new  $\cdot\text{OH}$  radicals and the propagation factor or chain length of the mixture. This is useful both as an explanation of how the  $\text{O}_3$  is formed, and as a tool for comparing  $\text{O}_3$  production predicted using different photochemical mechanisms. The HOX file contains information on the  $\cdot\text{OH}$  cycle described above.

The \*.HOX output file contains the three tables labeled: "Table 4: New OH Sources"; "Table 5: OH Propagation"; and "Table 6: HOx Mass Balance" (see the example file in Table 13). If the NEW command has been used to identify reactions producing new  $\text{HO}_x$  radicals, the table labeled "Table 4" will list the contribution of individual organic species and individual inorganic reactions to new  $\cdot\text{OH}$ . The  $\cdot\text{OH}$  radicals produced from new  $\text{HO}_2$  radicals are also considered to be new. If organic photo-acceptors are produced as intermediates by a primary hydrocarbon, new  $\cdot\text{OH}$  will be attributed to the primary hydrocarbons which produced the organic photo-acceptor.

The table labeled "Table 5" lists the contribution of individual organic species to  $\cdot\text{OH}$  propagation. The first pair of columns shows the ppb of  $\cdot\text{OH}$  reacted with each organic. The third column shows the ppb of  $\text{HO}_2$  produced by each organic. The fourth and fifth columns show the  $\cdot\text{OH}$  produced by reactions of each organic. This is calculated as the product of the  $\text{HO}_2$  production and the yield of  $\cdot\text{OH}$  per  $\text{HO}_2$ . The last column in "Table 5" is the propagation factor for each organic. It is the number of  $\cdot\text{OH}$  molecules regenerated by the organic per molecule of  $\cdot\text{OH}$  consumed by reactions of the organic. The last line in "Table 12" shows the average  $\cdot\text{OH}$  chain length. A low chain length might indicate a large loss of  $\cdot\text{OH}$  radicals with  $\text{NO}_2$  or inefficient conversion of  $\text{HO}_2$  to  $\cdot\text{OH}$  under low NO conditions.

The table labeled "Table 6" shows a mass balance on  $\cdot\text{OH}$  and  $\text{HO}_2$  sinks and sources.

## HC Output File

An \*.HC output file is produced if either the PATHWAYS or SHOW commands are used. The PATHWAYS command produces a table labeled "Table 7: Pathway

Table 13. Example HOx output file

Table 4: New OH Sources

Source	New OH (ppb)	New HO2 (ppb)	Tot New OH (ppb)	% of Total
METH	.00	1.05	.98	2.38
PAR	.00	6.45	6.06	14.67
ETH	.00	1.40	1.31	3.18
OLE	.00	1.30	1.22	2.95
TOL	.00	1.28	1.20	2.92
XYL	.00	4.86	4.56	11.05
FORM	.00	4.33	4.06	9.84
ALD2	.00	2.81	2.64	6.39
Rxn 1 O3/NO2 Chemistry	19.26	.00	19.26	46.63
<b>Total New Radicals</b>	<b>19.26</b>	<b>23.48</b>	<b>41.30</b>	<b>100.00</b>

Table 5: OH Propagation (based on OH Yield per HO2 = .9384)

Species	OH Loss (ppb)	XLoss	HO2 Prod (ppb)	Tot OH Prop (ppb)	XProp	Propagation Factor
CO	36.21	27.82	36.21	33.98	38.25	.938
METH	5.56	4.27	5.56	5.21	5.87	.938
PAR	26.76	20.56	19.32	18.13	20.41	.678
ETH	5.15	3.96	5.11	4.79	5.40	.931
OLE	5.27	4.05	5.11	4.79	5.39	.910
TOL	3.05	2.35	2.40	2.25	2.53	.737
XYL	6.02	4.62	5.23	4.91	5.53	.816
FORM	5.56	4.27	5.56	5.21	5.87	.938
ALD2	11.32	8.69	10.18	9.56	10.76	.845
<b>Organic Total</b>	<b>104.88</b>	<b>80.59</b>	<b>94.67</b>	<b>88.84</b>	<b>100.00</b>	<b>.847</b>
Average OH Chain Length = 3.15						

Table 6: HOx Mass Balance

	Loss HO2 (ppb)	XLoss	Prod HO2 (ppb)	XProd	Loss OH (ppb)	XLoss	Prod OH (ppb)	XProd
<b>Inorganic Rxns</b>								
Rxn HO2+NO->OH+HO2	107.33	90.84	.00	.00	.00	.00	107.33	82.47
O3/NO2 Chemistry	.00	.00	.00	.00	.00	.00	19.26	14.80
O3/HOx Cycle	3.53	2.98	.00	.00	.00	.00	3.53	2.71
HOHO Cycle	.00	.00	.00	.00	.52	.40	.00	.00
OH+HO2	.00	.00	.00	.00	24.21	18.60	.00	.00
PNA Cycle	.03	.03	.00	.00	.03	.02	.00	.00
HO2 Cycle	7.26	6.15	.00	.00	.00	.00	.03	.02
OH+HO3	.00	.00	.00	.00	.51	.39	.00	.00
<b>Inorganic Subtotal</b>	<b>118.15</b>	<b>99.99</b>	<b>.00</b>	<b>.00</b>	<b>25.26</b>	<b>19.41</b>	<b>130.14</b>	<b>100.00</b>
<b>Organic Subtotal</b>	<b>.00</b>	<b>.00</b>	<b>118.15</b>	<b>100.00</b>	<b>104.88</b>	<b>80.59</b>	<b>.00</b>	<b>.00</b>
<b>Final Concentration</b>	<b>.00</b>	<b>.00</b>			<b>.00</b>	<b>.00</b>		
<b>Total HOx Sinks</b>	<b>118.15</b>	<b>100.00</b>	<b>118.15</b>	<b>100.00</b>	<b>130.14</b>	<b>100.00</b>	<b>130.14</b>	<b>100.00</b>

Table 14. Example HC output file

Table 7: Pathway Specific Yields

Percent Reacted		YOH	YO3	YHO2	YNO2	YFORM	Net YOH	Net YO3
.42%	.0000 Rxn 56 O+OLE	-.26	.00	.95	.78	.17	.63	1.00
89.97%	.0040 Rxn 57 OH+OLE	-1.91	.00	2.25	1.76	.52	.20	2.31
9.59%	.0004 Rxn 58 O3+OLE	-.44	-1.00	1.21	.60	.35	.69	.03
.02%	.0000 Rxn 59 NO3+OLE	-.91	.00	1.25	2.67	.52	.26	2.31
100.00%	.00447 ppm OLE	-1.77	-1.10	2.15	1.64	.50	.25	2.08

Table 8: Gross Organic Production of Key Species

Source	Reacted(ppm)	FORM Prod	Y FORM	%	HO2 Prod	YHO2	%	NO2 Prod	YNO2	%
Organic Reactions										
CO	.036206	.00000	.000	.00	.03621	1.000	30.64	.00000	.000	.00
METH	.004214	.00153	.363	13.00	.00660	1.567	5.59	.00415	.985	5.89
PAR	.023394	.00262	.112	22.26	.02577	1.102	21.81	.03483	1.489	49.46
ETH	.003331	.00195	.585	16.59	.00651	1.953	5.51	.00361	1.084	5.13
OLE	.004474	.00150	.335	12.75	.00640	1.431	5.42	.00491	1.097	6.97
TOL	.001844	.00021	.116	1.82	.00368	1.996	3.11	.00113	.612	1.60
XYL	.003354	.00095	.284	8.10	.01010	3.011	8.55	.00708	2.111	10.05
FORM	.011119	.00000	.000	.00	.00989	.889	8.37	.00000	.000	.00
ALD2	.009319	.00299	.321	25.47	.01299	1.394	11.00	.01472	1.579	20.90
Organic Total	.097255	.01175	.121		.11815	1.215		.07043	.724	
Organic FORM production		.01175		40.251%						
Init FORM conc was		.01526		52.270%						
FORM Emissions were		.00218		7.480%						
TOTAL FORM =		.02919								
FORM Net Dilution		-.01344		46.043%						
Final FORM Conc =		.00463		15.872%						
FORM Reacted		.01112		38.086%						
Yield OH per HO2 =		.93842								
Yield NO2 per HO2 =		.90828								
Yield O3 per NO2 =		.60689								

Specific Yields". An example \*.HC file is shown in Table 14. For each organic listed in the PATHWAY command, it shows the mass and fraction of that organic reacted in each of the reactions which consume it. It also shows the yields of key species produced per VOC reacted in units of ppm/ppm. The first two columns show yield for the 'OH and O<sub>3</sub> consumed directly in reactions with the organic. The third and fourth columns show HO<sub>2</sub> and NO<sub>2</sub> yields. The fifth column shows the yield of the species requested in the SHOW command. The last two columns show the net yield of 'OH and O<sub>3</sub>, where the yields of 'OH per HO<sub>2</sub>, NO<sub>2</sub> per HO<sub>2</sub>, and O<sub>3</sub> per NO<sub>2</sub> are used to calculate the net yield:

$$\text{Net Yield } ^\circ\text{OH} = \left( \frac{\partial ^\circ\text{OH}}{\partial \text{VOC}_j} \right)_{\text{direct}} + \frac{\partial \text{HO}_2}{\partial \text{VOC}_j} \frac{\partial ^\circ\text{OH}}{\partial \text{HO}_2}$$

$$\text{Net Yield } \text{O}_3 = \left( \frac{\partial \text{O}_3}{\partial \text{VOC}_j} \right)_{\text{direct}} + \left( \frac{\partial \text{NO}_2}{\partial \text{VOC}_j} + \frac{\partial \text{HO}_2}{\partial \text{VOC}_j} \frac{\partial \text{NO}_2}{\partial \text{HO}_2} \right) \frac{\partial \text{O}_3}{\partial \text{NO}_2}$$

The sum of the VOC reacted and average yields are shown in the last row for each species.

If the SHOW command is used, IRREVAL produces a table labeled "Table 8: Organic Production of Key Species." The first two columns list the organic species and the mass of each reacted in ppm. If the species requested in the SHOW command is HCHO, the next three columns will show the total ppm of HCHO produced by each organic, the yield of HCHO from each VOC<sub>j</sub> per VOC<sub>j</sub> reacted, and the percentage of total HCHO production contributed by each organic. The table shows the same information for HO<sub>2</sub> and NO<sub>2</sub> production by each organic.

## TIM Output File

IRREVAL currently produces three time dependent output files when a time dependent \*.IRR input file is read.

The first time dependent output file is \*.TIM. It contains a table labeled "Table 1a: Time Dependent O<sub>3</sub> Mass Balance" (see Table 15). It shows the O<sub>3</sub> production, in ppm, from: initial NO<sub>2</sub>, emissions of NO<sub>2</sub>, net O<sub>3</sub> entrainment, and chemical production of NO<sub>2</sub>. It also shows chemical loss of O<sub>3</sub> during each time interval. The sink and source terms across a row sum to give the final O<sub>3</sub> concentration, at the end of the interval, in the last column.

The \*.TIM file contains a second table labeled "Table 2a: Time Dependent O<sub>3</sub> Chemical Production" (see Table 15a). It summarizes important chemical reaction information for each time interval. The first column of "Table 2a" in Table 15a shows the end time of the time interval. The second column, "dVOC<sub>r</sub>", shows the mass (ppm) of organics reacted during each interval. The third column "dHO<sub>2</sub>/dVOC<sub>r</sub>" shows the average production of HO<sub>2</sub> per VOC reacted (ppm/ppm) during the interval. The fourth "dNO<sub>2</sub>/dHO<sub>2</sub>" shows the average yield of NO<sub>2</sub> per HO<sub>2</sub> produced (ppm/ppm) during the interval. The fifth column "dNO<sub>2</sub>/dVOC<sub>r</sub>" shows the average production of NO<sub>2</sub> per VOC reacted (ppm/ppm). The sixth column "dNO<sub>2t</sub>/dVOC<sub>r</sub>" is the average production of NO<sub>2</sub> per VOC (ppm/ppm) during the interval calculated as:

Table 15a. Example TIM output file

"Command File is base.cmd"  
 "Output File created at 15:43 on 10/05/90"  
 "Base Case 0.6:0.1, Std VOC"

"Table 1a: Time Dependent O3 Mass Balance"

"Time"	"Init O3"	"Init NO2"	"Emis NO2"	"Entrain"	"Chem Prod"	"Chem Loss"	"Final"
1	.00000	.00192	.00000	.00026	.00000	.00000	.00219
60	.00219	.00000	.00000	.01565	.00000	.01010	.00774
122	.00774	.00000	.00000	.01290	.00000	.00157	.01908
182	.01908	.00135	.00013	.00500	.00537	.00013	.03081
241	.03081	.00117	.00015	.00059	.01064	.00015	.04321
300	.04321	.00056	.00011	-.00136	.01466	.00018	.05699
361	.05699	.00018	.00005	-.00224	.01974	.00028	.07446
420	.07446	.00002	.00001	-.00263	.02341	.00051	.09478
482	.09478	.00000	.00000	.00000	.02487	.00121	.11846
541	.11846	.00000	.00001	.00000	.01522	.00164	.13208
603	.13208	.00000	.00000	.00000	.00941	.00160	.13992
661	.13992	.00000	.00000	.00000	.00479	.00107	.14366
720	.14366	.00000	.00000	.00000	.00169	.00061	.14475
780	.14475	.00000	.00000	.00000	.00000	.00025	.14450
"TOT"	.00000	.00520	.00048	.02818	.12981	.01929	.14450

"Table 2: Time Dependent O3 Chem Prod"

"Time"	"dVCr"	"dNO2"	"dNO2"	"dNO2"	"dNO2t"	"dO3"	"dO3"	"dO3o"	"dO3n"	"dO3p"	
"Time"	"dVCr"	"dNO2"	"dVCr"	"dVCr"	"dVCr"	"dNO2"	"dVCr"	"dt"	"dVCr"	"dt"	"dt"
1	.00005	.7135	.9893	.4345	1.1404	.0768	.0876	.000005	.0000	.000000	.000005
60	.00518	.8023	.9994	.5640	1.3659	.0000	.0000	.000000	.0117	.000000	.000000
122	.00754	.9398	.9992	.6639	1.6030	.0000	.0000	.000000	1.8097	.000000	.000000
182	.00735	1.0961	.9990	.7432	1.8382	.1711	.3145	.002312	2.4274	.003054	.005366
241	.00788	1.2401	.9987	.8113	2.0499	.3129	.6414	.005056	2.2598	.005574	.010630
300	.00850	1.3677	.9982	.8605	2.2258	.4147	.9229	.007842	1.9262	.006787	.014629
361	.00983	1.4549	.9963	.8656	2.3151	.5338	1.2357	.012148	1.4370	.007540	.019688
420	.01123	1.4750	.9871	.8085	2.2644	.6526	1.4777	.016587	.9252	.006777	.023364
482	.01267	1.4611	.9150	.7463	2.0832	.7622	1.5878	.020118	.4902	.004734	.024852
541	.00877	1.4826	.7468	.7940	1.9011	.7711	1.4659	.012852	.3457	.002337	.015190
603	.00569	1.5260	.6332	.8990	1.8652	.7500	1.3990	.007957	.3330	.001421	.009378
661	.00277	1.5755	.5910	1.0492	1.9804	.6733	1.3333	.003698	.5700	.001064	.004763
720	.00102	1.6245	.4992	1.2367	2.0477	.4528	.9272	.000945	1.5884	.000733	.001678
780	.00023	1.5052	.2155	.9514	1.2758	-.0003	-.0004	.000000	7.5694	.000000	-.000001
Ave	.08871	1.3319	.9062	.7961	2.0013	.5043	1.0092	.089521	1.1983	.040021	.129542

dO3o -- organic produced O3  
 dO3n -- older chem NO2 produced O3  
 dO3p -- total chemical produced O3

Table 15b. Example TIM output file

"Table 2(b): Time Dependent OH Summary"

"Time"	"ppb"	"organ"	"inorg"	"Ch.L."	"dHO2"	"%org"	"%inorg"
1	.02	99.7	.3	2.33	.9942	69.1	30.8
60	1.50	98.6	1.4	2.84	.9997	76.2	23.8
122	2.41	93.1	6.9	2.92	.9995	75.0	25.0
182	3.13	82.1	17.9	2.76	.9994	71.9	28.1
241	4.17	70.9	29.1	2.68	.9992	71.5	28.5
300	5.20	62.2	37.8	2.66	.9986	72.4	27.6
361	6.23	55.9	44.1	2.70	.9969	74.7	25.3
420	7.00	51.9	48.1	2.86	.9878	79.7	20.3
482	6.88	47.8	52.2	2.95	.9330	86.3	13.7
541	5.07	41.0	59.0	2.70	.8141	91.2	8.8
603	3.05	40.4	59.6	2.65	.7543	93.0	7.0
661	1.34	49.6	50.4	3.06	.7718	93.3	6.7
720	.36	67.0	33.0	3.96	.7994	93.1	6.9
780	.05	84.8	15.2	5.11	.8237	93.0	7.1
Ave	46.48	58.5	41.5	2.81	.9367	80.4	19.6

Note: PPM new OH is normalized to 60 min intervals.

$$\frac{dNO_t}{dVOC_r} = \frac{dHO_2}{dVOC_r} \frac{dNO_2}{dHO_2} + \frac{dNO_2}{dVOC_r}$$

The eighth column, " $dO_3/dVOC_r$ ", is the  $O_3$  production per VOC reacted during the interval calculated as:

$$\frac{dO_3}{dVOC_r} = \frac{dNO_{2t}}{dVOC_r} \frac{dO_3}{dNO_2}$$

where  $dO_3/dNO_2$  is the yield of  $O_3$  per  $NO_2$  produced (ppm/ppm) shown in the seventh column. The ninth column is the direct  $O_3$  production from organics during the interval calculated as:

$$\frac{dO_{3o}}{dt} = \frac{dO_3}{dVOC_r} \frac{dVOC_r}{dt}$$

As described in Section 3, the  $NO_2$  present at the beginning of any interval can be attributed in part to initial and emitted  $NO_2$  and to chemical production of  $NO_2$  in earlier intervals. The eleventh column shows the  $O_3$  produced from this beginning or "older"  $NO_2$  during the interval. Using the method described in Section 3, this  $O_3$  production is attributed to the various sources which originally produced the  $NO_2$ . The last column in "Table 2a" shows the total  $O_3$  production during the interval.

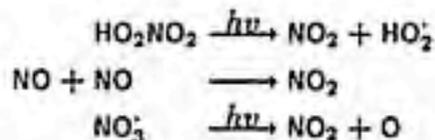
The \*.TIM file contains a third table labeled "Table 2b: Time Dependent 'OH Summary" (see Table 15b). The first column shows the end time of the time interval. The second through fourth columns show the number of new 'OH radicals (ppb) formed during each interval, and the percentage produced by organic and inorganic reactions. More detailed information for each time step is contained in the \*.HOX file. The fifth column "OH Ch.L." shows the 'OH chain length during each interval. The product of "new 'OH" and "Chain Length" is the total 'OH produced in the interval. The sixth column shows the average yield of 'OH per HO<sub>2</sub> produced (ppm/ppm) during the interval which affects the 'OH chain length. The last two columns in "Table 2b" show the percentage of 'OH which reacts with organic and inorganic compounds during each interval.

The values shown in the tables labeled "Table 2a" and "Table 2b" are included to give insight into the time dependence of factors effecting O<sub>3</sub> production. The changes in these values for different simulations may also give insight into the factors effecting changes in O<sub>3</sub> production for different simulations or different mechanisms.

The second time dependent output file is \*.TI2 (see Table 16). It contains a table labeled "Table 3" which shows the mass of NO<sub>2</sub> attributed to each source process at the beginning of each interval. The mass of NO<sub>2</sub> attributed to each source at the beginning of each interval is calculated using the algorithm described in Section 4. It is used to correctly attribute O<sub>3</sub> production to the sources which originally produced the NO<sub>2</sub>.

An example TI4 output file is shown in Table 17. The TI4 file shows the cumulative O<sub>3</sub> production by each VOC and from initial NO<sub>2</sub>, emitted NO<sub>2</sub>, entrained O<sub>3</sub>, and inorganic sources of NO<sub>2</sub>. It also shows the cumulative chemical loss of O<sub>3</sub> and the cumulative O<sub>3</sub> total.

The inorganic production of NO<sub>2</sub> could be from the reactions:



or other inorganic reactions. A time averaged analysis of O<sub>3</sub> production shows that inorganic reactions generally produce less than 0.1% of total NO<sub>2</sub>. In a time dependent analysis, however, the total appears to be about 2%. This is due primarily to the production of NO<sub>2</sub> from entrained O<sub>3</sub> in the first few intervals. This NO<sub>2</sub> production is classified as inorganic. The fraction of this NO<sub>2</sub> which photolyses later

Table 16. TI2 Output File Showing Composition of NO<sub>2</sub> as a function of time.

\*Command File is base.cmd\*

\*Output File created at 15:43 on 10/05/90\*

\*Base Case 0.6:0.1, Std VOC\*

Table 3: Contributions to Current NO<sub>2</sub> Concentrations

Time	Current Conc	Initial ppm	Initial %	Emissions ppm	Emissions %	Entrainment ppm	Entrainment %	Production ppm	Production %	Total %
0	.0250	.0250	100.00	.0000	.00	.0000	.00	.0000	.00	100.00
1	.0230	.0229	99.65	.0000	.09	.0000	.00	.0001	.26	99.97
60	.0284	.0140	49.37	.0007	2.49	.0000	.00	.0136	48.14	99.98
122	.0264	.0079	30.01	.0006	2.32	.0000	.00	.0178	67.67	99.98
182	.0220	.0037	16.98	.0004	1.85	.0000	.00	.0178	81.16	99.97
241	.0179	.0013	7.48	.0002	1.08	.0000	.00	.0164	91.44	99.96
300	.0146	.0003	2.30	.0001	.57	.0000	.00	.0141	97.13	99.96
361	.0104	.0000	.36	.0000	.16	.0000	.00	.0104	99.48	99.94
420	.0062	.0000	.02	.0000	.02	.0000	.00	.0062	99.96	99.90
482	.0030	.0000	.00	.0000	.01	.0000	.00	.0030	99.99	99.81
541	.0019	.0000	.00	.0000	.04	.0000	.00	.0019	99.96	99.68
603	.0016	.0000	.00	.0000	.02	.0000	.00	.0016	100.04	99.67
661	.0016	.0000	.00	.0000	.03	.0000	.00	.0016	99.90	99.55
720	.0017	.0000	.00	.0000	.01	.0000	.00	.0017	99.99	99.64
780	.0016	.0000	.00	.0000	.01	.0000	.00	.0016	99.99	99.60

in the day to produce O<sub>3</sub> is attributed to an inorganic source. Total net O<sub>3</sub> entrainment is also totaled separately. The contribution of O<sub>3</sub> entrainment to the final O<sub>3</sub> concentration could be calculated as a fraction of the total net O<sub>3</sub> entrainment and the NO<sub>2</sub> produced from O<sub>3</sub> entrainment.

An inaccuracy in the time dependent analysis of the accumulation and subsequent reactions of inorganic NO<sub>2</sub> reservoirs such as NO<sub>3</sub> and HO<sub>2</sub>NO<sub>2</sub> may also contribute to the inorganic source of NO<sub>2</sub>. For example, NO<sub>3</sub> may accumulate early in the simulation while NO<sub>2</sub> levels are high. The NO<sub>3</sub> photolyses later in the simulation. In a time dependent analysis, no information is saved about the NO<sub>2</sub> sources which contributed to production of NO<sub>3</sub> earlier in the day. When NO<sub>3</sub> reacts to produce NO<sub>2</sub> later in the day, the O<sub>3</sub> produced from this NO<sub>2</sub> is incorrectly attributed to inorganic reactions. The NO<sub>2</sub> production from NO<sub>3</sub> should actually be attributed to the other sources of the NO<sub>2</sub> which originally produced the NO<sub>3</sub>. The error this causes is small because the O<sub>3</sub> attributed to inorganic sources is generally less than 2%, however, the computer code could be modified in the future to perform more sophisticated calculations.

Table 17. TI4 Output File Showing Cumulative O<sub>3</sub> Production  
and average O<sub>3</sub> yields per VOC.

"Command File is base.cmd"

"Output File created at 15:43 on 10/05/90"

"Base Case 0.6:0.1, Std VOC"

"Table 1b: Cum Organic Specie Contributions to O<sub>3</sub> (ppbv)"

"Time"	"CO	"METH	"PAR	"ETH	"OLE	"TOL	"XYL	"FORM	"ALD2
1	3.193E-04	3.844E-05	1.048E-03	2.314E-04	5.102E-04	8.396E-05	4.500E-04	1.091E-03	9.206E-04
60	3.193E-04	3.844E-05	1.048E-03	2.314E-04	5.102E-04	8.396E-05	4.500E-04	1.091E-03	9.206E-04
122	3.193E-04	3.844E-05	1.048E-03	2.314E-04	5.102E-04	8.396E-05	4.500E-04	1.091E-03	9.206E-04
182	4.178E-01	8.849E-02	1.158E+00	2.729E-01	5.635E-01	1.171E-01	7.717E-01	3.518E-01	6.962E-01
241	1.520E+00	3.615E-01	3.911E+00	9.257E-01	1.814E+00	3.969E-01	2.516E+00	8.348E-01	1.975E+00
300	3.462E+00	9.014E-01	8.325E+00	1.941E+00	3.511E+00	8.340E-01	4.828E+00	1.238E+00	3.443E+00
361	6.757E+00	1.900E+00	1.521E+01	3.412E+00	5.465E+00	1.469E+00	7.330E+00	1.545E+00	4.927E+00
420	1.169E+01	3.503E+00	2.459E+01	5.178E+00	7.119E+00	2.223E+00	9.231E+00	1.740E+00	6.039E+00
482	1.791E+01	5.688E+00	3.579E+01	6.870E+00	8.163E+00	2.926E+00	1.026E+01	1.843E+00	6.660E+00
541	2.169E+01	7.154E+00	4.346E+01	7.727E+00	8.580E+00	3.264E+00	1.060E+01	1.875E+00	6.905E+00
603	2.368E+01	7.986E+00	4.878E+01	8.150E+00	8.868E+00	3.427E+00	1.085E+01	1.888E+00	7.001E+00
661	2.458E+01	8.374E+00	5.157E+01	8.344E+00	9.060E+00	3.504E+00	1.102E+01	1.894E+00	7.043E+00
720	2.486E+01	8.496E+00	5.257E+01	8.410E+00	9.144E+00	3.531E+00	1.110E+01	1.896E+00	7.058E+00
780	2.486E+01	8.496E+00	5.257E+01	8.410E+00	9.144E+00	3.531E+00	1.110E+01	1.896E+00	7.058E+00

"Time"	"Inorganic"	"Init NO2"	"Emis NO2"	"Init O3"	"Dilu O3"	"Reac O3"	"Tot O3"
1	1.558E-04	1.920E+00	1.610E-03	0.000E+00	2.641E-01	-4.610E-04	2.190E+00
60	1.558E-04	1.920E+00	1.610E-03	0.000E+00	1.592E+01	-1.010E+01	7.742E+00
122	1.558E-04	1.920E+00	1.610E-03	0.000E+00	2.882E+01	-1.167E+01	1.908E+01
182	9.380E-01	3.274E+00	1.355E-01	0.000E+00	3.382E+01	-1.180E+01	3.081E+01
241	1.761E+00	4.441E+00	2.872E-01	0.000E+00	3.441E+01	-1.195E+01	4.321E+01
300	2.186E+00	4.996E+00	3.944E-01	0.000E+00	3.305E+01	-1.213E+01	5.698E+01
361	2.385E+00	5.174E+00	4.492E-01	0.000E+00	3.081E+01	-1.240E+01	7.443E+01
420	2.477E+00	5.199E+00	4.626E-01	0.000E+00	2.818E+01	-1.292E+01	9.471E+01
482	2.509E+00	5.200E+00	4.664E-01	0.000E+00	2.818E+01	-1.413E+01	1.183E+02
541	2.544E+00	5.200E+00	4.721E-01	0.000E+00	2.818E+01	-1.576E+01	1.319E+02
603	2.580E+00	5.200E+00	4.741E-01	0.000E+00	2.818E+01	-1.736E+01	1.397E+02
661	2.609E+00	5.200E+00	4.754E-01	0.000E+00	2.818E+01	-1.843E+01	1.434E+02
720	2.626E+00	5.200E+00	4.756E-01	0.000E+00	2.818E+01	-1.904E+01	1.445E+02
780	2.626E+00	5.200E+00	4.756E-01	0.000E+00	2.818E+01	-1.929E+01	1.443E+02

"Specie"	"Total React" "(ppbv)"	"O <sub>3</sub> Yield" "(ppbv/ppbv)"	"O <sub>3</sub> Prod" "(ppbv)"
CO	36.000	.690	24.857
METH	4.214	2.016	8.496
PAR	23.602	2.228	52.572
ETH	3.331	2.524	8.410
OLE	4.513	2.026	9.144
TOL	1.844	1.915	3.531
XYL	3.354	3.308	11.095
FORM	6.700	.283	1.896
ALD2	5.151	1.370	7.058

The last section in the TI4 file shows the total mass (ppm) of each VOC reacted, the total O<sub>3</sub> production attributed to each VOC, and the production of O<sub>3</sub> per VOC (ppm/ppm) averaged over the simulation.

---

# IRR Commands

---

**BALANCE** = name<sub>1</sub>, name<sub>2</sub>, ... name<sub>n</sub>;

**USE:** The user lists the species names for which a mass balance is desired. If **ORGANIC** is defined, the name **ORGANIC** can be used instead of listing individual hydrocarbon names. Commas are optional.

**DISCUSSION:** The **BALANCE** command performs a simple mass balance on the listed species with the output written to the \*.BAL file. To obtain a complete mass balance, the **ORGANIC** command must be used to identify hydrocarbons, and then the **EVALUATE** command must be used.

**CYCLES** = "cyclename<sub>1</sub>" [= R1, R2, ... R<sub>n</sub>], "cyclename<sub>2</sub>" [= R1, R2, ... R<sub>n</sub>];

**USE:** Each cycle name is enclosed in double quotes. The user can specify which reactions to sum by placing an equal sign and brackets with reaction numbers after the cycle name closing quote. If reaction numbers are not specified, **IRREVAL** assumes that the first word in the cycle name is a species name, and all reactions in which that species occurs are summed to produce a net reaction. Commas or blank spaces may be used as separators.

**DISCUSSION:** The **CYCLES** command allows the user to sum the reactants and products for a set of reactions to determine net chemical loss and production for each species. This is useful when reactions rapidly interconvert two species. For example, consider the reactions





Reactions (1) and (2) rapidly convert  $\text{NO}_2$  to  $\text{O}_3$  while (3) rapidly converts  $\text{O}_3$  to  $\text{NO}_2$ . This cyclic process, and other inorganic processes such as the  $\text{NO}_3$  and  $\text{CH}_3\text{C}(=\text{O})\text{O}_2\text{NO}_2$  cycles, dominate both  $\text{NO}_2$  production and  $\text{NO}_2$  consumption within the system, but the net effect of these cyclic processes on the  $\text{NO}_2$  concentration is small. Typically, organic oxidation reactions provide the bulk of the net increase in  $\text{NO}_2$  and hence are responsible for net increases in  $\text{O}_3$ . Because of the cycling processes, organic  $\text{NO}_2$  production is a small fraction of gross  $\text{NO}_2$  production and its significance is difficult to analyze unless net  $\text{NO}_2$  production is calculated. By using the CYCLES option for each set of reactions which rapidly cycles  $\text{NO}_2$ , the sources of net increases in  $\text{NO}_2$  and  $\text{O}_3$  are easily determined. Figure 5 shows an Example CMD file. All of the major processes in CB4 which cycle any species have been summed to form net reactions making it easier to determine which processes contribute to net changes in species concentrations.

## END.

USE: The END command is always the last command in the CMD file. It should be followed by a semi colon or period. Lines after END are ignored.

## EVALUATE;

USE: This should be the last command before the END command. The ORGANIC command must first be used to identify hydrocarbons.

DISCUSSION: IRREVAL performs a complete mass balance analysis of  $\text{O}_3$ ,  $\text{NO}_y$  and  $\text{HO}_x$  production with output to the \*.O3, \*.NOy, \*.HOx, and \*.HC output files. Time dependent output files are created if a time dependent IRR file is used.

IGNORE = species<sub>1</sub>, species<sub>2</sub>, ... species<sub>n</sub>;

DISCUSSION: If the mechanism in the \*.CMP file contains species which are unimportant to the user, for example  $\text{H}_2\text{O}$ , M,  $\text{O}_2$  or  $\text{N}_2$ , they can be deleted from the mechanism with the IGNORE command. This is useful for complicated mechanisms which are near the IRREVAL internal array memory limits.

## IRR [= n]

USE: The IRR command must precede the IRR file or be the first significant line of the IRR file. If a time dependent IRR file is used,  $n$  must be the number of intervals. This line is inserted automatically by OZIPR when it creates the IRR file. The structure of the IRR file is described in detail in Chapter 3.

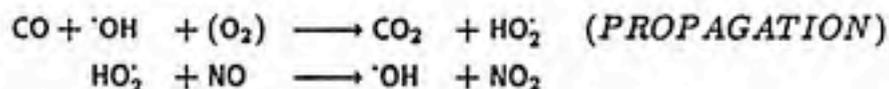
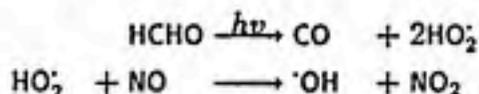
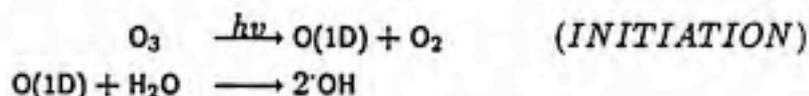
## MECH = ...;

USE: This command must immediately precede or be at the beginning of the \*.CMP file. A detailed description of the CMP file is give in Chapter 3. The CMP file ends with a semicolon.

NEW = R<sub>1</sub>, R<sub>2</sub>, ... R<sub>n</sub>;

USE: Reaction numbers are listed for reactions which are chain initiators, normally photolysis reactions which produce new 'OH radicals. If intermediate organic radicals are produced in the photolysis reaction, they should be the last species replaced in the REPLACE command. This allows new 'OH produced from the organic radicals to be attributed to the photolysis reaction.

DISCUSSION: Tropospheric gas phase chemistry is driven primarily by 'OH radical attack on organic molecules. The organics can react to regenerate 'OH radicals creating a chain reaction. The intensity of the reacting system and the amount of O<sub>3</sub> produced will depend both on the number of new 'OH radicals formed and the average chain length, or the number of times an 'OH radical reacts before being lost in a chain terminating reaction. Typical reactions in each step of the chain are listed below:





The NEW command must be used to identify which reactions are sources of new 'OH radical (initiation reactions). IRREVAL will then perform a detailed mass balance on 'OH and HO<sub>2</sub> with the output in the \*.HOX file. IRREVAL assumes that 'OH formed in any reactions other than those listed after the NEW command are formed in chain propagation reactions. It then calculates the average chain length. The number of new 'OH radicals generated and the average chain length can be valuable in comparing and understanding differences in O<sub>3</sub> predictions from different simulations or with different mechanisms. If a time dependent IRR input file is used, The number of new 'OH radical and chain length are listed as a function of time in the \*.TIM output file.

NOY = species<sub>1</sub>[\*x<sub>1</sub>] species<sub>2</sub>[\*x<sub>2</sub>] ... species<sub>n</sub>[\*x<sub>n</sub>];

USE: Identifies species which contain nitrogen. An optional \* symbol and coefficient may follow the species name to define the number of nitrogen atoms in each species. The default value is one. The name ORNIT should be added to the \*.CMP file for reactions in which nitrogen sinks were ignored in the mechanism and ORNIT should be included in the list of NOY species.

DISCUSSION: IRREVAL will attempt to perform a complete mass balance on nitrogen containing compounds. However, the NOY command must be used to identify nitrogen containing compounds. NO and NO<sub>2</sub> are treated separately and need not be listed with NOY. Output is in the \*.NOX file. Organic nitrates are typically ignored by compressed mechanisms. Currently, the name ORNIT is coded into subroutine OUTNO2, so ORNIT must be added to reactions which ignored organic nitrates in the \*.CMP file in order to obtain a correct NOY balance.

ORGANIC = species<sub>1</sub>[\*x<sub>1</sub>] species<sub>2</sub>[\*x<sub>2</sub>] ... species<sub>n</sub>[\*x<sub>n</sub>];

DISCUSSION: The ORGANIC command allows the user to define a list of organic molecules. It must be used if the EVALUATE command is used to request a complete mass balance analysis. If ORGANIC is defined, it can be used in the BALANCE command instead of listing individual hydrocarbons. An optional \* symbol and coefficient may follow the species name to define the number of carbon atoms in each species.

**PATHWAY** = species<sub>1</sub>, species<sub>2</sub>, ... species<sub>n</sub>;

**DISCUSSION:** IRREVAL normally shows the yields of key species for each organic. However, some organics may react via several different reactions. The **PATHWAY** command allows the user to request reaction specific yields and the fraction reacted via each pathway for organics that react via multiple pathways.

**PKSS;**

**USE:** PKSS and OZIPR input IRR files have a slightly different structure because OZIPR includes terms for emissions, deposition and entrainment. If a PKSS input IRR file is used, the PKSS command must be given before the IRR file is specified. The default case is an OZIPR IRR file.

**REPLACE** = species<sub>1</sub>, species<sub>2</sub>, ... species<sub>n</sub>;

**USE:** The **REPLACE** command replaces intermediate reaction products with their final products. Up to 30 species can be replaced. If the **NEW** command is used, organic radicals produced in photolysis reactions should be the last species replaced. This allows new 'OH produced by the organic radical to be attributed to the photolysis reaction which produced the organic radical.

**DISCUSSION:** Hydrocarbon oxidation reactions produce intermediates which may undergo further reactions before ultimately producing HO<sub>2</sub>, NO<sub>2</sub> and unreactive final products. It is often desirable to know the amount of NO<sub>2</sub> produced from the initial reactants rather than from the intermediates. The **REPLACE** command eliminates intermediates by replacing them with their final products.

The **REPLACE** command only operates on the fraction of species *i* which is produced chemically. If *i* is present initially but is not produced, the **REPLACE** command has no effect. If *i* is both present initially and produced chemically, *i* will be replaced wherever it is produced, and the integrated reaction rate for reactions in which *i* is consumed will be reduced by the fraction of *i* which is chemically produced. If the only source of *i* is chemical production, reactions consuming *i* are eliminated. Mass is conserved because species reacting with *i* are carried over as negative products in the reactions which produced *i*.

The algorithm used to implement the **REPLACE** command is described in more detail in Chapter 4.

**SUPPRESS;**

**DISCUSSION:** Normally, IRREVAL creates an \*.BAL file which has detailed information about array manipulations and mass balance calculations. The \*.BAL file can be larger than one Mbyte for time dependent IRR input files. The SUPPRESS option prevents IRREVAL from writing to the \*.BAL file.

**SHOW = species;**

**DISCUSSION:** The SHOW command will generate detailed information on the production of one species (in addition to the detailed information created for O<sub>3</sub>, NO<sub>y</sub>, and HO<sub>x</sub>). The SHOW speciesname is typically HCHO, CO, or H<sub>2</sub>O<sub>2</sub>. Output is in the \*.HC and \*.TI3 output files.

**WRITE;**

**DISCUSSION:** The WRITE command causes the current form of mechanism array and integrated reaction rates to be printed to the \*.BAL file. The output has a special character and a number before each reaction: an "o" or an "i" signifies either an organic or an inorganic reaction. Organic reactions are those containing any species listed in the ORGANIC command. The number indicates the number of carbons among the organic reactants. This is important because IRREVAL uses it to avoid double counting NO<sub>2</sub> production in reactions where two organics react. The WRITE command can be used at any time and may be used several times to see how the mechanism and integrated reaction rate arrays change after the use of other commands.

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# Example IRREVAL Analysis

---

## Introduction

This chapter illustrates a typical analysis which can be performed using IRREVAL. I used OZIPR and the Empirical Kinetic Modeling Approach (EKMA) to test the sensitivity of predicted  $O_3$  maximums and predicted VOC control requirements to the initial and aloft CO concentrations. I used a base case simulation which was similar to a simulation used by Chamedies (1988) in his study of biogenic hydrocarbons. In this chapter I will:

- 1) Describe the EKMA method and the OZIPR input files used,
- 2) Show the impact of doubling CO concentrations on the predicted  $O_3$  maximum and VOC control requirement,
- 3) Use IRREVAL to compare  $O_3$  production in the base case simulation to the doubled CO ( $2\times$ CO) trajectory simulation, and
- 4) Use IRREVAL to compare the base case control scenario simulation to the  $2\times$ CO control scenario simulation.

## EKMA Method

OZIPR includes an EKMA option which can be used to predict VOC control requirements. The user must specify the observed one-hour average maximum  $O_3$  concentration (the design value) and the measured initial VOC to  $NO_x$  ratio for a typical  $O_3$  episode. OZIPR then performs a series of simulations, adjusting the initial VOC and  $NO_x$  concentrations at the specified ratio until it matches the design value. After matching the design value, OZIPR performs several more simulations lowering the VOC concentration until it matches the  $O_3$  standard of 120 ppbV. This method is empirical because it arbitrarily changes the measured initial concentra-

tions to match the design value. Normally, the change made in the measured initial concentrations must be within the uncertainty range of the measured values.

The initial concentrations used are the average concentrations measured in the city center from 6 to 9 AM. These represent both the initial concentration and early morning emissions of VOC and NO<sub>x</sub>. The emissions through the rest of the day are input as a multiple of the 6 to 9 AM concentrations. Thus, the VOC and NO<sub>x</sub> emissions levels can be changed simply by changing the 6 to 9 AM concentrations.

I used the OZIPR input file shown in Table 1 as a base case scenario. I used an initial VOC to NO<sub>x</sub> ratio of 6:1 and an O<sub>3</sub> design value of 147 ppb. In the base case I used a CO surface concentration of 1.2 ppm and a CO aloft concentration of 0.5 ppm. The surface concentration of 1.2 ppm was recommended for Atlanta by the EPA. This value was chosen based on CO measurements in Atlanta on high O<sub>3</sub> days. The mean concentration of the measurements was 1.2 ppm with a one standard deviation uncertainty of  $\pm 0.85$  ppm (Baugues, 1988). The CO aloft concentration of 0.5 ppm is the default value.

I used OZIPR to perform a single trajectory simulation using initial concentrations of 600 ppbC VOC and 100 ppb NO<sub>x</sub>. OZIPR predicted a maximum one-hour average O<sub>3</sub> concentration of 144.7 ppb. I used the same simulation conditions with the EKMA option to predict the control requirement. OZIPR used initial VOC and NO<sub>x</sub> concentrations of 627 ppbC and 104 ppbv to match the O<sub>3</sub> design value of 147 ppbv. It then reduced the VOC concentration by 23.2% to meet the O<sub>3</sub> standard of 120 ppb. These results are summarized in the first three columns of Table 18.

Table 18. Summary of OZIPR Simulations.

Simulation	Base Case			Doubled CO		
	NO <sub>x</sub> (ppbv)	VOC (ppbC)	O <sub>3</sub> (ppbv)	NO <sub>x</sub> (ppbv)	VOC (ppbC)	O <sub>3</sub> (ppbv)
Trajectory	100	600	144.7	100	600	159.1
Design Day	104	627	147.0	80	477	147.0
Control Demo	104	481	120.0	80	274	120.0
Control Requirement			23.2%			42.5%

I then modified the OZIPR input file by doubling the surface and aloft CO

concentrations to 2.4 ppm and 1.0 ppm, respectively. I repeated the single trajectory simulation and the EKMA simulations for the doubled CO (2xCO) case. The results are summarized in the last three columns of Table 18. In the single trajectory simulation, doubling CO increased the O<sub>3</sub> maximum from 144.7 to 159.1 ppm. To match the design day O<sub>3</sub> value, OZIPR had to use initial VOC and NO<sub>x</sub> concentrations about 25% lower in the 2xCO case than in the base case. As a result, the EKMA control calculation uses *lower* initial VOC and NO<sub>x</sub> concentrations for the 2xCO control case than for base control case. The predicted VOC requirement increased from 23.2% for the base case to 42.5% for the 2xCO case.

### Single Trajectory o<sub>3</sub> Production

We would like to understand why a relatively small increase in the O<sub>3</sub> maximum led to relatively large increase in the VOC control requirement. I will begin by comparing the concentration profiles for the base case and 2xCO case single trajectory simulations. Figure 4 compares the O<sub>3</sub>, NO<sub>2</sub> and NO profiles for the two simulations. The top plot in Figure 4 shows that O<sub>3</sub> increased more rapidly and reached a higher value in the 2xCO case. It is difficult to see the change in the NO and NO<sub>2</sub> profiles. The second plot shows the percent change in the 2xCO concentration profiles relative to the base case. This is calculated as:

$$\text{Percent Change} = 100 \frac{(C_{2xCO} - C_{base})}{C_{base}}$$

This is a more effective way to show the change in concentration when the change is small. Figure 5 shows the percent change in radical and VOC concentration profiles.

Some qualitative observations can be made from the comparison profiles in Figure 4 and Figure 5. The 2xCO profiles of NO<sub>2</sub> increased and NO decreased slightly in the first 200 minutes of the simulation. This suggests increased conversion of NO to NO<sub>2</sub> by organic radicals. The 'OH concentration was slightly lower for the first 200 minutes in the 2xCO case due to the increased CO radical sink, but the 'OH concentration was larger in the 2xCO case from 200 to 400 minutes. VOCs react more rapidly in the 2xCO case even though there is greater competition with CO. 'OH is a important NO<sub>x</sub> sink and by 400 minutes, the NO<sub>x</sub> concentration has decreased significantly. This causes a rapid increase in HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> concentrations and a decrease in 'OH. After 450 minutes, the 2xCO system is NO<sub>x</sub> depleted and becomes less reactive. The final VOC concentrations are higher in the 2xCO case.

Comparing the profiles gives a qualitative feeling for the changes caused by increasing CO. We can get a more quantitative understanding by using the integrated rates.

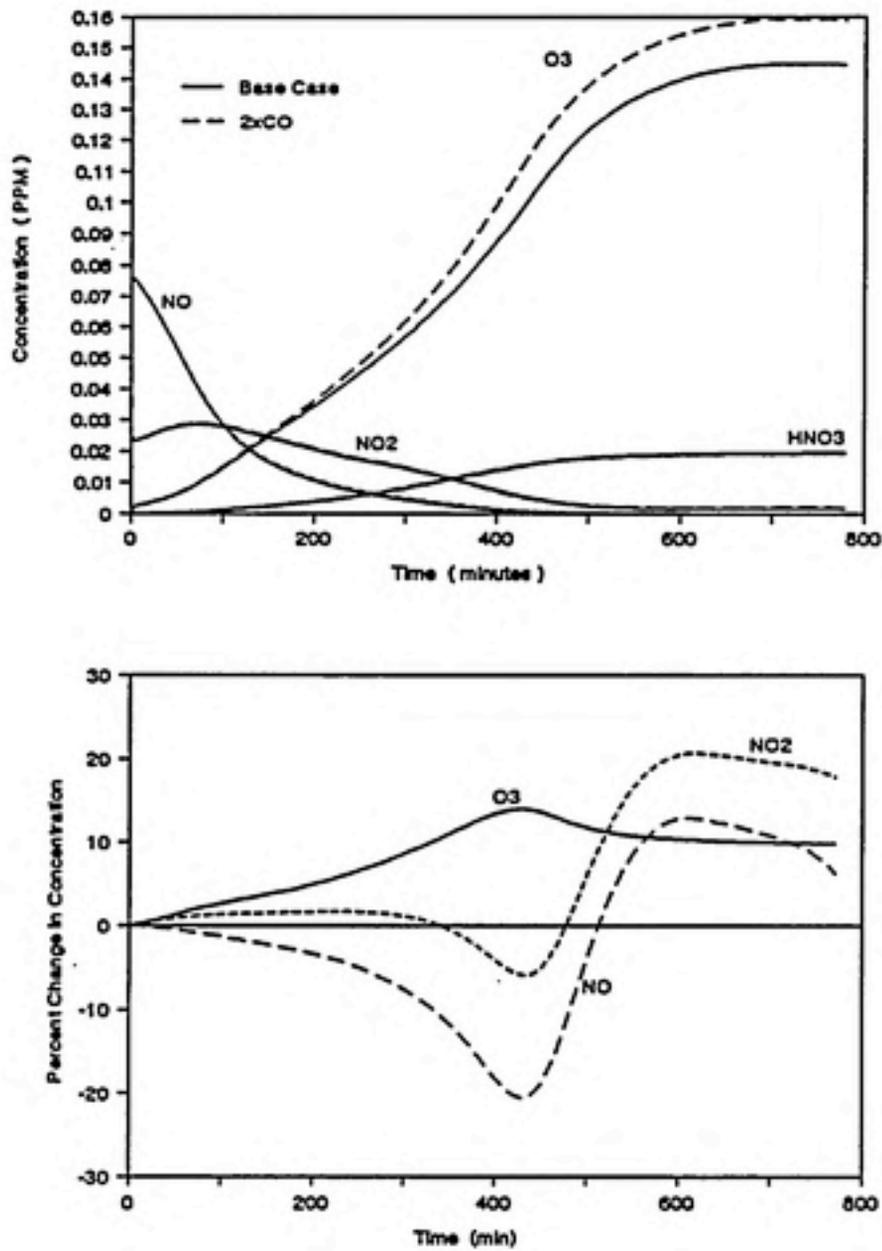


Figure 4. Comparison of O<sub>3</sub> and NO<sub>x</sub> profiles for base case and 2xCO simulations.

Table 19a shows production and loss of O<sub>3</sub> in units of ppm for each interval of the base case simulation. Table 20a shows the same information for the 2xCO simulation. Comparing the last row of each table, we see that chemical production of O<sub>3</sub> increased from 129.8 ppb to 147.3 ppb. Net entrainment of O<sub>3</sub> decreased from 28.2 ppb to 25.6 ppb, and chemical loss of O<sub>3</sub> increased from 19.3 to 20.3 ppb.

We would like to know in more detail which VOCs caused the chemical production of O<sub>3</sub>. Figure 6 and Figure 7 were prepared from the TI4 output file. Figure 6 is a pie-chart showing the percentage of O<sub>3</sub> production attributed to each source. Production of O<sub>3</sub> by CO increased from 15.2% of the total in the base case to 26.2% of the total in the 2xCO case. Figure 7 is a bar graph comparing the mass of each VOC reacted, the O<sub>3</sub> yield per VOC reacted, and the total O<sub>3</sub> production from each VOC for the two cases. It shows that, except for PAR, the mass of each VOC reacted is virtually unchanged when CO is increased. This suggests that increased 'OH propagation from the extra CO compensates for increased competition with CO for 'OH radicals. In addition, the O<sub>3</sub> yields per VOC are nearly the same so O<sub>3</sub> production from each VOC is approximately the same in the two simulations. Slightly less CH<sub>4</sub> and PAR reacted which indicates that there was increased competition for 'OH late in the day when 'OH concentrations were lower. Most of the change in O<sub>3</sub> production, 22 ppb, is attributed to the increase from 36 to 67 ppb of CO reacted.

We know that more O<sub>3</sub> was produced because more CO reacted. Now we would like to understand *why* more CO reacted. Table 21 shows the time dependent 'OH tables from the TIM output file for the two simulations. Comparing the second column, we see that nearly identical amounts of new 'OH radicals were produced in both simulations for the first four intervals. The fifth column, however, shows that the 'OH chain length was about 15% greater during the first four intervals in the 2xCO case. Looking at the last two columns, we see that a larger percentage of 'OH reacted with organics (where CO is included with organics) in the 2xCO case. The greater 'OH chain length occurs in the 2xCO case because more 'OH reacts with CO, which has a high propagation factor, and less 'OH reacts in chain termination reactions with NO<sub>x</sub>. Figure 8 show the production of new 'OH, the 'OH chain length and the percentage of 'OH consumed with organics and CO.

After the fourth interval, the O<sub>3</sub> concentration is higher in the 2xCO case and O<sub>3</sub> photolysis begins to contribute more new 'OH as well. The increase in O<sub>3</sub> production from the longer chain length is accelerated by the production of more new 'OH radicals from the increased O<sub>3</sub>. Taking the product of the total new 'OH and the average chain length in the last rows of each table, we see that a total of 158 ppb of 'OH were produced in the 2xCO case compared to only 130 ppb in the base case.

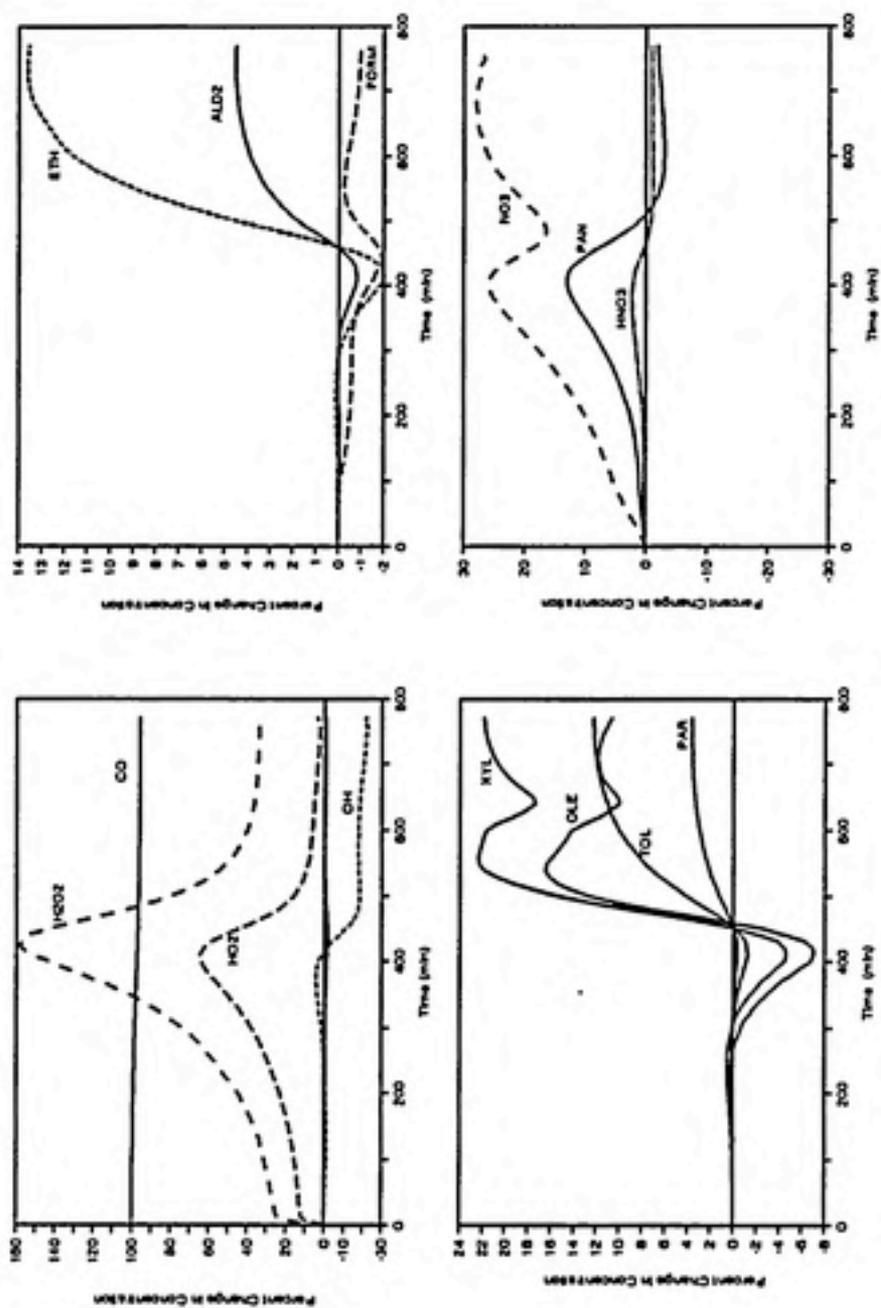


Figure 5. Comparison of radical and HC profiles for base case and 2xCO simulations.

Table 19a. Time dependent O<sub>3</sub> Mass Balance for Base Case.

"Time"	"Init O3"	"Init NO2"	"Emis NO2"	"Entrain"	"Chem Prod"	"Chem Loss"	"Final"
1	.00000	.00192	.00000	.00026	.00000	.00000	.00219
60	.00219	.00000	.00000	.01565	.00000	.01010	.00774
122	.00774	.00000	.00000	.01290	.00000	.00157	.01908
182	.01908	.00135	.00013	.00500	.00537	.00013	.03081
241	.03081	.00117	.00015	.00059	.01064	.00015	.04321
300	.04321	.00056	.00011	-.00136	.01466	.00018	.05699
361	.05699	.00018	.00005	-.00224	.01974	.00028	.07446
420	.07446	.00002	.00001	-.00263	.02341	.00051	.09478
482	.09478	.00000	.00000	.00000	.02487	.00121	.11846
541	.11846	.00000	.00001	.00000	.01522	.00164	.13208
603	.13208	.00000	.00000	.00000	.00941	.00160	.13992
661	.13992	.00000	.00000	.00000	.00479	.00107	.14366
720	.14366	.00000	.00000	.00000	.00169	.00061	.14475
780	.14475	.00000	.00000	.00000	.00000	.00025	.14450
"TOT"	.00000	.00520	.00048	.02818	.12981	.01929	.14450

Table 19b. Time dependent yields for the Base Case.

"Time"	"dO3"	"dNO2"	"dNO2"	"dNO2t"	"dO3"	"dO3"	"dO3o"	"dO3n"	"dO3p"		
"dVCr"	"dVCr"	"dVCr"	"dVCr"	"dVCr"	"dVCr"	"dt"	"dVCr"	"dt"	"dt"		
1	.00005	.7135	.9893	.4345	1.1404	.0768	.0876	.000005	.0000	.000000	.000005
60	.00518	.8027	.9994	.5642	1.3664	.0000	.0000	.000000	.0117	.000000	.000000
122	.00753	.9411	.9992	.6648	1.6052	.0000	.0000	.000000	1.8121	.000000	.000000
182	.00733	1.0989	.9990	.7451	1.8430	.1711	.3153	.002312	2.4338	.003054	.005366
241	.00785	1.2452	.9987	.8147	2.0583	.3129	.6441	.005056	2.2691	.005574	.010630
300	.00845	1.3752	.9982	.8653	2.2380	.4147	.9280	.007842	1.9368	.006787	.014629
361	.00977	1.4645	.9963	.8713	2.3304	.5338	1.2439	.012148	1.4465	.007540	.019688
420	.01114	1.4857	.9871	.8143	2.2808	.6526	1.4884	.016587	.9319	.006777	.023364
482	.01258	1.4721	.9150	.7519	2.0988	.7622	1.5997	.020118	.4939	.004734	.024852
541	.00870	1.4936	.7468	.7999	1.9153	.7711	1.4768	.012852	.3483	.002337	.015190
603	.00565	1.5371	.6332	.9055	1.8788	.7500	1.4092	.007957	.3355	.001421	.009378
661	.00275	1.5868	.5910	1.0567	1.9945	.6733	1.3429	.003698	.5741	.001064	.004763
720	.00101	1.6359	.4992	1.2454	2.0621	.4528	.9337	.000945	1.5996	.000733	.001678
780	.00023	1.5156	.2155	.9580	1.2846	-.0003	-.0004	.000000	7.6218	.000000	-.000001
Ave	.08822	1.3393	.9062	.8005	2.0123	.5043	1.0147	.089521	1.2049	.040021	.129542

dO3o -- organic produced O3  
dO3n -- older chem NO2 produced O3  
dO3p -- total chemical produced O3

Table 20a. Time dependent O<sub>3</sub> Mass Balance for 2xCO Case.

"Time"	"Init O3"	"Init NO2"	"Emis NO2"	"Entrain"	"Chem Prod"	"Chem Loss"	"Final"
1	.00000	.00192	.00000	.00026	.00001	.00000	.00219
61	.00219	.00000	.00000	.01573	.00000	.01000	.00792
121	.00792	.00000	.00000	.01245	.00000	.00101	.01936
181	.01936	.00151	.00015	.00485	.00622	.00014	.03196
241	.03196	.00123	.00016	.00021	.01233	.00016	.04572
302	.04572	.00055	.00011	-.00192	.01814	.00021	.06241
362	.06241	.00014	.00005	-.00278	.02397	.00034	.08346
420	.08346	.00001	.00001	-.00321	.02842	.00073	.10798
483	.10798	.00000	.00000	.00000	.02715	.00169	.13347
540	.13347	.00000	.00001	.00000	.01480	.00189	.14642
602	.14642	.00000	.00000	.00000	.00967	.00181	.15431
661	.15431	.00000	.00000	.00000	.00503	.00123	.15813
721	.15813	.00000	.00000	.00000	.00169	.00070	.15912
780	.15912	.00000	.00000	.00000	-.00009	.00037	.15876
"TOT"	.00000	.00536	.00050	.02560	.14734	.02027	.15876

Table 20b. Time dependent yields for the 2xCO case.

"Time"	"dVcr"	"dHO2"	"dHO2"	"dHO2"	"dHO2t"	"dO3"	"dO3"	"dO3o"	"dO3n"	"dO3p"
"Time"	"dVcr"	"dHO2"	"dVcr"	"dHO2"	"dVcr"	"dHO2"	"dVcr"	"dt"	"dVcr"	"dt"
1	.00006	.7342	.9893	.4027	1.1290	.0768	.0867	.000005	.0000	.000000
61	.00574	.8211	.9994	.5115	1.3321	.0000	.0000	.000000	.0112	.000000
121	.00826	.9453	.9992	.5805	1.5250	.0000	.0000	.000000	1.6962	.000000
181	.00873	1.0775	.9989	.6189	1.6952	.1881	.3189	.002786	2.0869	.003429
241	.00990	1.1879	.9986	.6376	1.8237	.3382	.6168	.006109	1.8534	.006209
302	.01189	1.2734	.9977	.6333	1.9038	.4586	.8731	.010383	1.4177	.007732
362	.01421	1.3152	.9945	.5909	1.8989	.5798	1.1009	.015639	1.0062	.008287
420	.01700	1.3094	.9731	.5169	1.7910	.6984	1.2508	.021268	.6012	.007139
483	.01797	1.3039	.8660	.4864	1.6156	.7774	1.2559	.022569	.3265	.004562
540	.01118	1.3251	.7139	.5355	1.4816	.7537	1.1166	.012485	.2714	.002287
602	.00759	1.3504	.6343	.6013	1.4579	.7277	1.0609	.008048	.2878	.001589
661	.00382	1.3828	.5990	.7032	1.5315	.6464	.9899	.003777	.4998	.001233
721	.00137	1.4174	.5047	.8452	1.5606	.4108	.6411	.000879	1.4199	.000800
780	.00028	1.3190	.2100	.6443	.9213	-.0395	-.0364	-.000010	7.3134	-.000081
Ave	.11800	1.2365	.8966	.5720	1.6792	.5246	.8808	.103937	.9239	.043184

dO3o -- organic produced O3  
dO3n -- older chem NO2 produced O3  
dO3p -- total chemical produced O3

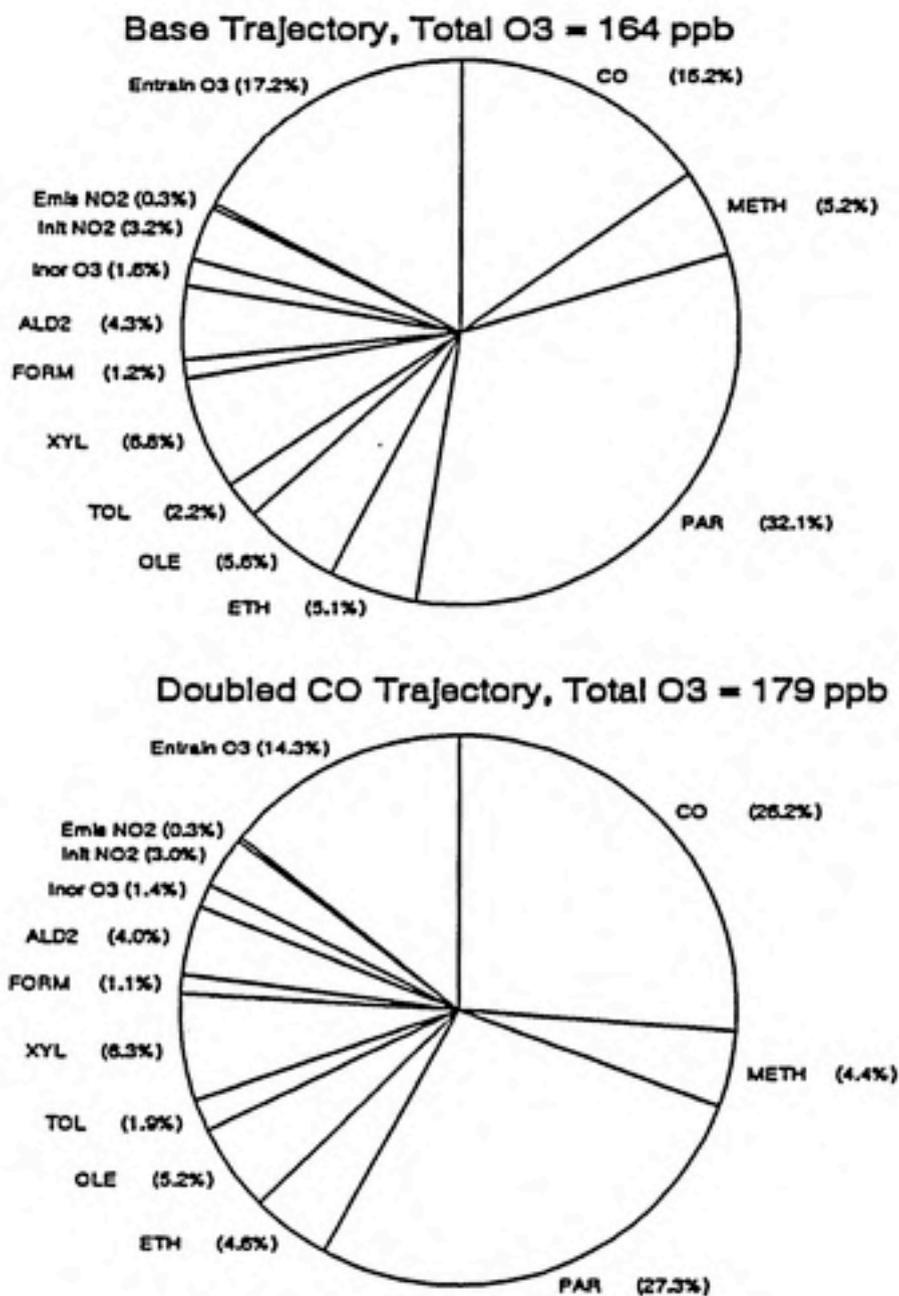


Figure 6. Pie chart of O<sub>3</sub> sources for base case and 2xCO simulations.

The increase in O<sub>3</sub> production in the 2xCO simulation can be explained by:

- the increase in the fraction of 'OH consumed by CO and the decrease in 'OH consumed in reactions with NO<sub>2</sub>;
- the subsequent increase in 'OH chain length, total 'OH production and mass of HC and CO consumed;
- a small increase in the yield of O<sub>3</sub> per NO<sub>2</sub> resulting from the decrease in the reaction of 'OH with NO<sub>2</sub>, and
- the production of more new 'OH as the O<sub>3</sub> concentration increases.

Finally, it should be noted that Figure 5 showed a small decrease in the 'OH concentration in the first 200 minutes of the 2xCO case but there is actually an increase in the mass of 'OH reacted.

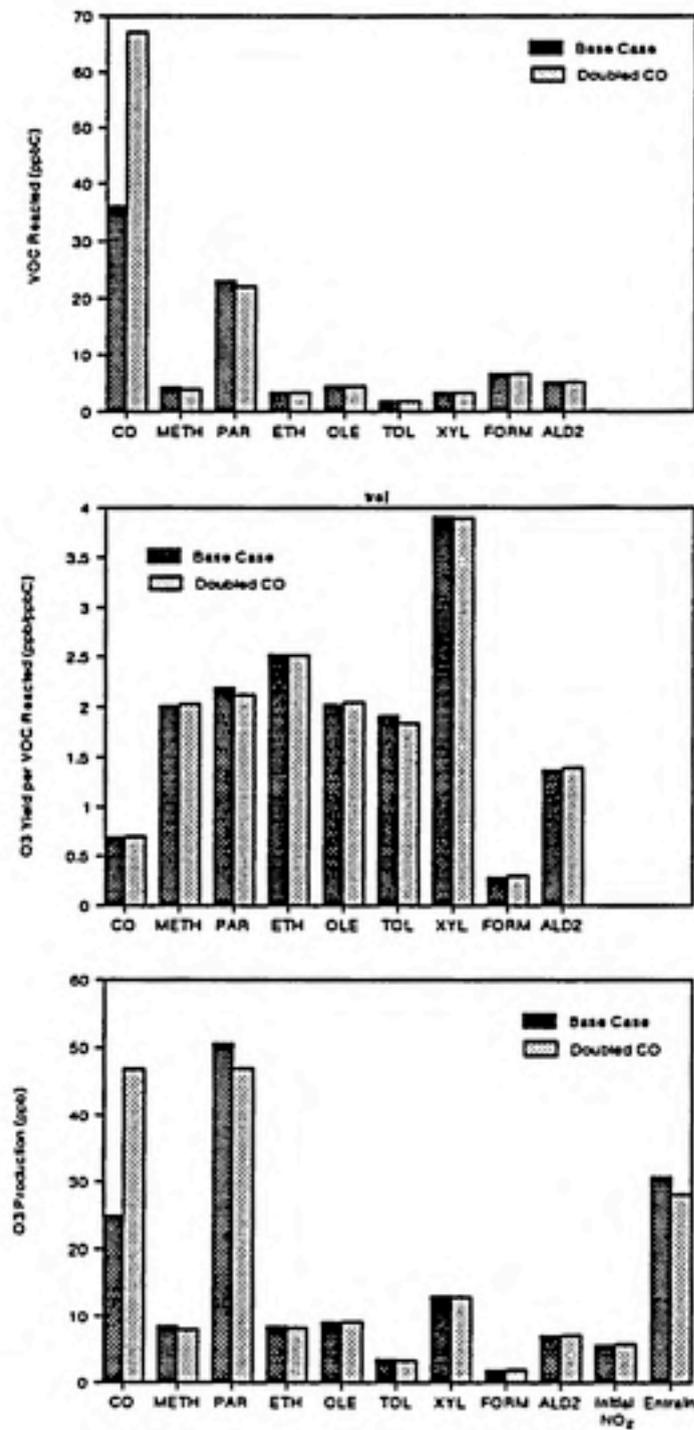


Figure 7. Bar graph comparing VOC reacted, O<sub>3</sub> yields and O<sub>3</sub> production for each source for the base case and 2xCO simulations.

Table 21. Time Dependent OH summary for base case and 2xCO case.

## "Base Case 0.6:0.1, Std VOC"

"Time"	"ppb"	"% organ"	"% inorg"	"OH" "Ch.L."	"Total" "OH"	"dOH" "dHO2"	"OH Termination" "%org" "%inorg"
1	.01	99.7	.3	2.59	.04	.9942	69.1 30.8
60	1.34	98.5	1.5	3.17	4.25	.9997	76.2 23.8
122	2.33	92.9	7.1	3.02	7.03	.9995	75.0 25.0
182	3.12	82.0	18.0	2.77	8.63	.9994	71.9 28.1
241	4.09	70.4	29.6	2.73	11.17	.9992	71.5 28.5
300	4.95	60.3	39.7	2.79	13.81	.9986	72.4 27.6
361	5.68	51.6	48.4	2.97	16.84	.9969	74.7 25.3
420	6.05	44.3	55.7	3.31	20.03	.9878	79.7 20.3
482	5.74	37.5	62.5	3.53	20.26	.9330	86.3 13.7
541	4.33	30.9	69.1	3.16	13.67	.8141	91.2 8.8
603	2.62	30.8	69.2	3.08	8.07	.7543	93.0 7.0
661	1.12	39.6	60.4	3.65	4.09	.7718	93.3 6.7
720	.28	57.8	42.2	4.97	1.41	.7994	93.1 6.9
780	.05	82.9	17.1	5.61	.26	.8237	93.0 7.1
Ave	41.78	53.8	46.2	3.12	130.48	.9367	80.4 19.6

Note: PPM new OH is normalized to 60 min intervals. \*Double CO Surf and Alof, 0.6:0.1, Std VOC"

## "Doubled CO Case"

"Time"	"ppb"	"% organ"	"% inorg"	"OH" "Ch.L."	"Total" "OH"	"dOH" "dHO2"	"OH Termination" "%org" "%inorg"
1	.01	99.7	.3	2.87	.04	.9941	72.2 27.8
61	1.33	98.4	1.6	3.57	4.74	.9997	78.9 21.1
121	2.32	92.8	7.2	3.43	7.98	.9995	78.0 22.0
181	3.14	81.6	18.4	3.19	9.99	.9994	75.7 24.3
241	4.08	69.3	30.7	3.19	13.03	.9990	75.7 24.3
302	5.12	58.4	41.6	3.33	17.04	.9983	77.0 23.0
362	6.00	49.0	51.0	3.61	21.69	.9953	79.8 20.2
420	6.46	41.0	59.0	4.07	26.30	.9779	84.8 15.2
483	6.05	32.5	67.5	3.97	24.06	.8993	90.1 9.9
540	4.58	26.8	73.2	3.42	15.64	.7959	93.3 6.7
602	2.78	27.9	72.1	3.41	9.48	.7647	94.4 5.6
661	1.20	36.4	63.6	4.09	4.89	.7878	94.6 5.4
721	.29	54.6	45.4	5.58	1.64	.8169	94.4 5.6
780	.05	82.0	18.0	5.93	.28	.8393	94.3 5.7
Ave	43.43	50.8	49.2	3.63	157.76	.9316	84.1 15.9

Note: PPM new OH is normalized to 60 min intervals.

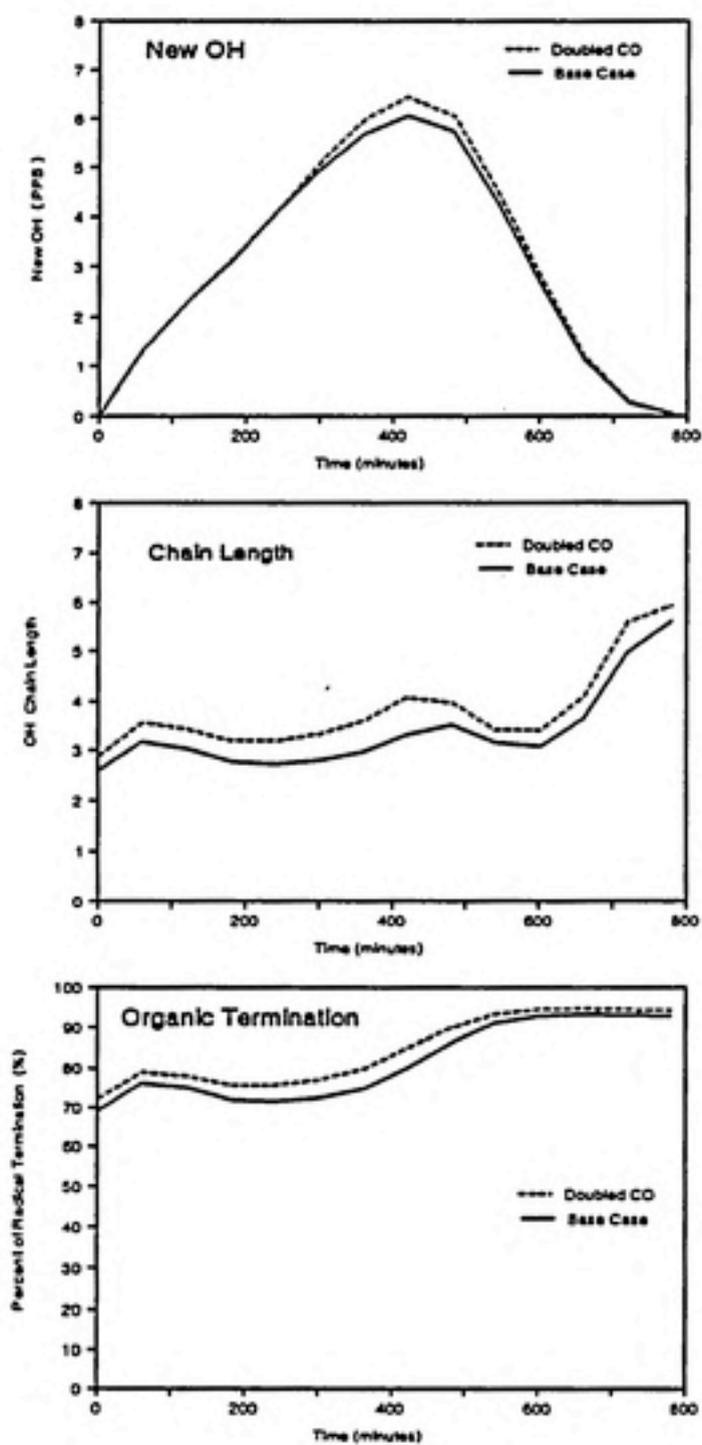


Figure 8. New O<sub>3</sub> production, the <sup>•</sup>OH chain length and percent <sup>•</sup>OH consumed by organics for the base case.

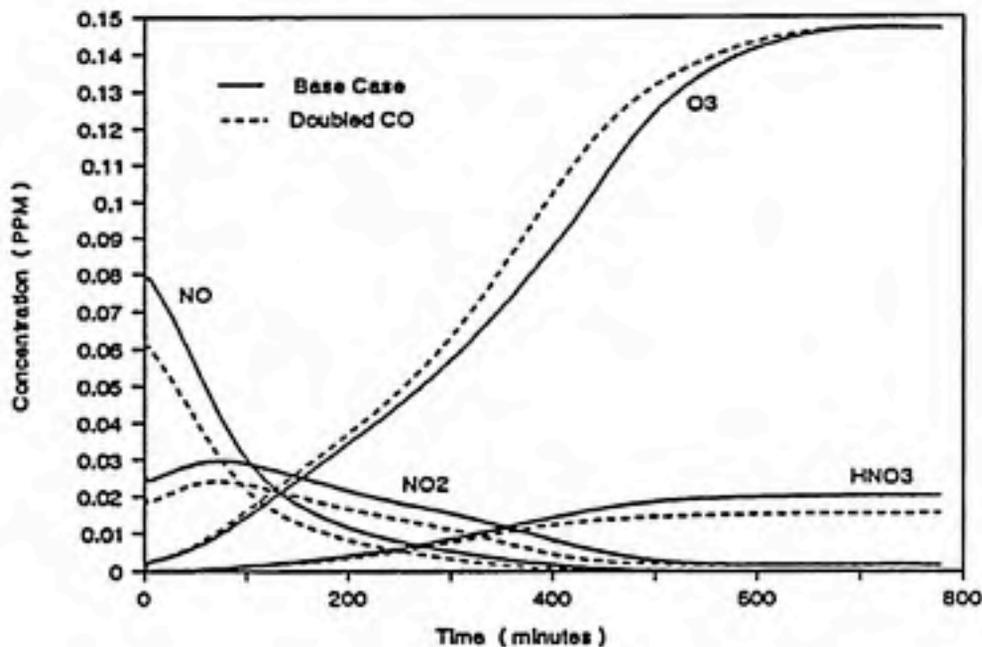


Figure 9. Design value simulation  $O_3$  and  $NO_x$  profiles.

## Design Value Simulations

As described above, the empirical aspect of EKMA is the iterative search for initial VOC and  $NO_x$  concentrations, at the specified ratio, that produce the observed  $O_3$  maximum. In this example, more  $O_3$  production occurs when CO is increased, so EKMA must use lower initial VOC and  $NO_x$  concentrations in the high CO simulation. While CO is not a VOC, it is chemically similar to VOCs. Increasing CO has the same effect as increasing the VOC to  $NO_x$  ratio. This is evident from the design value simulations in Table 18. The 2xCO simulation begins with an initial  $NO_x$  concentration of only 80 ppb compared to 104 ppb in the base case. As a result,  $NO_x$  controls will be relatively more attractive in the 2xCO simulation.

Figure 9 shows plots of the  $O_3$ ,  $NO_x$ , NO and  $HNO_3$  profiles for the base case and 2xCO design value simulations. The  $O_3$  concentration increases more rapidly in the 2xCO case, but it also becomes  $NO_x$  depleted earlier in the day. As a result, both simulations match the  $O_3$  design value of 147 ppb.

## Control Case Simulations

Table 18 showed that the control requirement increased from 23.2% for the base case to 42.5% in the 2xCO case. To understand why such a large increase occurred, I will first compare the original base case trajectory simulation to the controlled base case simulation and then compare the original 2xCO simulation to the controlled 2xCO simulation.

Figure 10 presents pie charts for the original base case simulation and the controlled base case simulation. In the original base case simulation, total O<sub>3</sub> production was 164 ppb. 19 ppb of O<sub>3</sub> reacted to give the final concentration of 144.7 ppb. In the controlled simulation, total O<sub>3</sub> production was 138 ppb. Reactions of O<sub>3</sub> consumed 18 ppb to give the final concentration of 120 ppb. In these pie charts, "inorganic O<sub>3</sub>" includes net entrainment of O<sub>3</sub> and O<sub>3</sub> produced from initial NO<sub>2</sub> and emissions of NO<sub>2</sub>.

The contribution of inorganic sources increased from 36.5 ppb in the original base case to 44.0 ppb in the controlled base case. This is due to increased net entrainment of O<sub>3</sub> in the controlled base case. The O<sub>3</sub> concentration rises more slowly in the controlled case, so more O<sub>3</sub> is entrained. The O<sub>3</sub> in the air aloft creates a buffering effect on the O<sub>3</sub> modeled concentration. If the O<sub>3</sub> concentration increases slowly, aloft air contributes more O<sub>3</sub> by entrainment. If the O<sub>3</sub> concentration increases rapidly, less O<sub>3</sub> is entrained and more O<sub>3</sub> is lost by dilution.

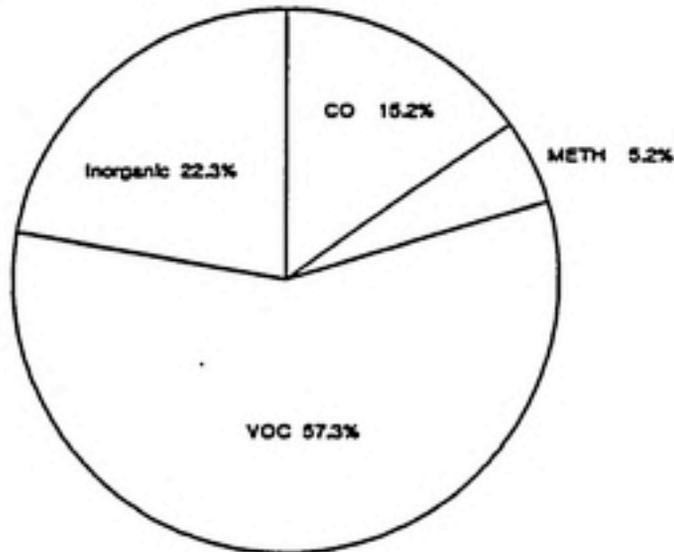
In the control simulation for the base case scenario, initial VOC and emissions of VOC were reduced by 23.3%. The contribution of O<sub>3</sub> from VOCs fell from 93.7 to 66.8 ppb, or 29%. The initial CO and CH<sub>4</sub> concentrations were unchanged, yet O<sub>3</sub> production from CO and CH<sub>4</sub> fell by about 20%. Figure 11 compares the amount of each VOC reacted for the two simulations, the average of O<sub>3</sub> per each VOC reacted, and the contribution of O<sub>3</sub> from each VOC. The middle bar graph in Figure 11 shows that the O<sub>3</sub> yields for each VOC, CO and CH<sub>4</sub> decreased slightly. The top bar graph shows that the change in O<sub>3</sub> production from each source is largely due to the decrease in the mass of the species reacted.

We would expect less VOC to react because the VOC levels have been reduced by 23%. We would like to understand why less CO and less CH<sub>4</sub> reacted, and why the O<sub>3</sub> yields were lower in the control simulation.

Table 22 shows the time dependent OH tables from the TIM output files for the original base case and controlled base case simulations. Looking at the second

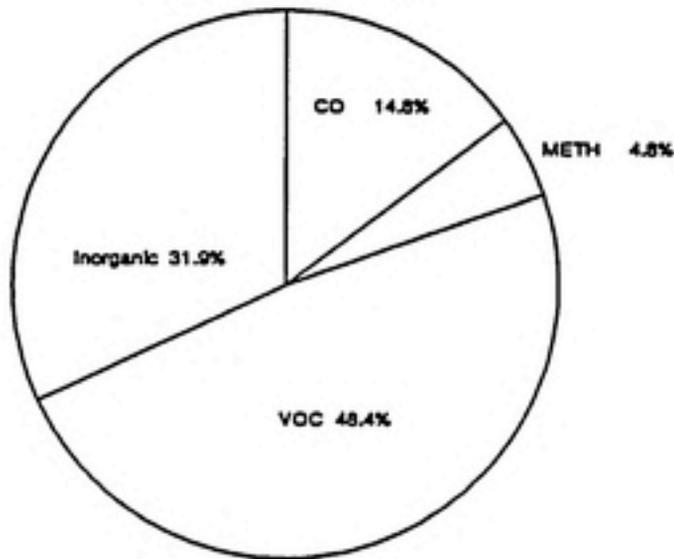
**Original Base Simulation O<sub>3</sub> Production**

Total O<sub>3</sub> Production = 164 ppb



**Controlled Base Simulation O<sub>3</sub> Production**

Total O<sub>3</sub> Production = 138 ppb



**Figure 10.** Pie chart comparing O<sub>3</sub> production in base case original and control simulations.

and third columns of both tables, we see that there is a significant reduction in organic production of new 'OH radicals throughout the simulation in the controlled case. This is due in part to the reduction in the initial aldehyde concentrations in the controlled case. Comparing the fifth column shows that the 'OH chain length was also lower in the controlled case for the first 480 minutes of the two simulation. The last two columns show that the 'OH chain length is lower in the control case because a larger fraction of 'OH radicals are consumed in chain-terminating inorganic reactions. The combination of fewer new 'OH radicals from the reduction in aldehyde photolysis (due to the lower initial VOC concentration) and the lower 'OH chain length creates a more slowly reacting mixture. The O<sub>3</sub> concentration rises more slowly, and thus fewer new 'OH radicals are produced by O<sub>3</sub> photolysis. As a result, a total of only 104 ppb of 'OH is produced in the control case compared to 130 ppb in the original base case simulation. The last row of the two tables shows that only 75.3% or 78.3 ppb of the 'OH reacted with CO and organics in the control case compared to 80.4% or 105 ppb in the base case.

This also explains the decrease in the O<sub>3</sub> yield per VOC reacted in the control case. A larger fraction of NO<sub>2</sub> is consumed in the chain terminating reaction with 'OH in the control case, so the yield of O<sub>3</sub> per NO<sub>2</sub> is also reduced.

## Doubled CO Simulations

Figure 12 shows pie charts for the 2xCO simulation and the control 2xCO simulations. In the control scenario, CO contributes 31.5% or 43.3 ppb of the total O<sub>3</sub> production. This can be compared to the base case control scenario in Figure 6, where CO contributed only 14.8% or 20.4 ppb of total O<sub>3</sub> production. In the 2xCO case, there is greater O<sub>3</sub> production from uncontrollable sources, so the VOC emissions must be more severely controlled to meet the standard. In the base case simulation, VOCs could produce 66.8 ppb of O<sub>3</sub> and still meet the standard. In the 2xCO simulation, VOCs can produce only 44.0 ppb of O<sub>3</sub>.

In the 2xCO simulation, O<sub>3</sub> production from VOCs must be reduced from 90 ppb to 44 ppb. The precise level of VOC control required will depend on the amount of VOC which reacts and the yield of O<sub>3</sub> per VOC. The VOC reacted will depend on the amount of new 'OH produced and the 'OH chain length. Figure 13 compares the mass in ppb of each VOC reacted, the O<sub>3</sub> yields, and total O<sub>3</sub> production for the 2xCO simulations. The O<sub>3</sub> yields are nearly the same for both cases, but the mass of VOCs reacted has decreased by more than 50%. This is due in part to the 49% VOC reduction and to the reduction in production of 'OH radicals. Table 23 shows that production of new 'OH radicals has fallen from 43.4 ppb to only 26.7 ppb. CO has

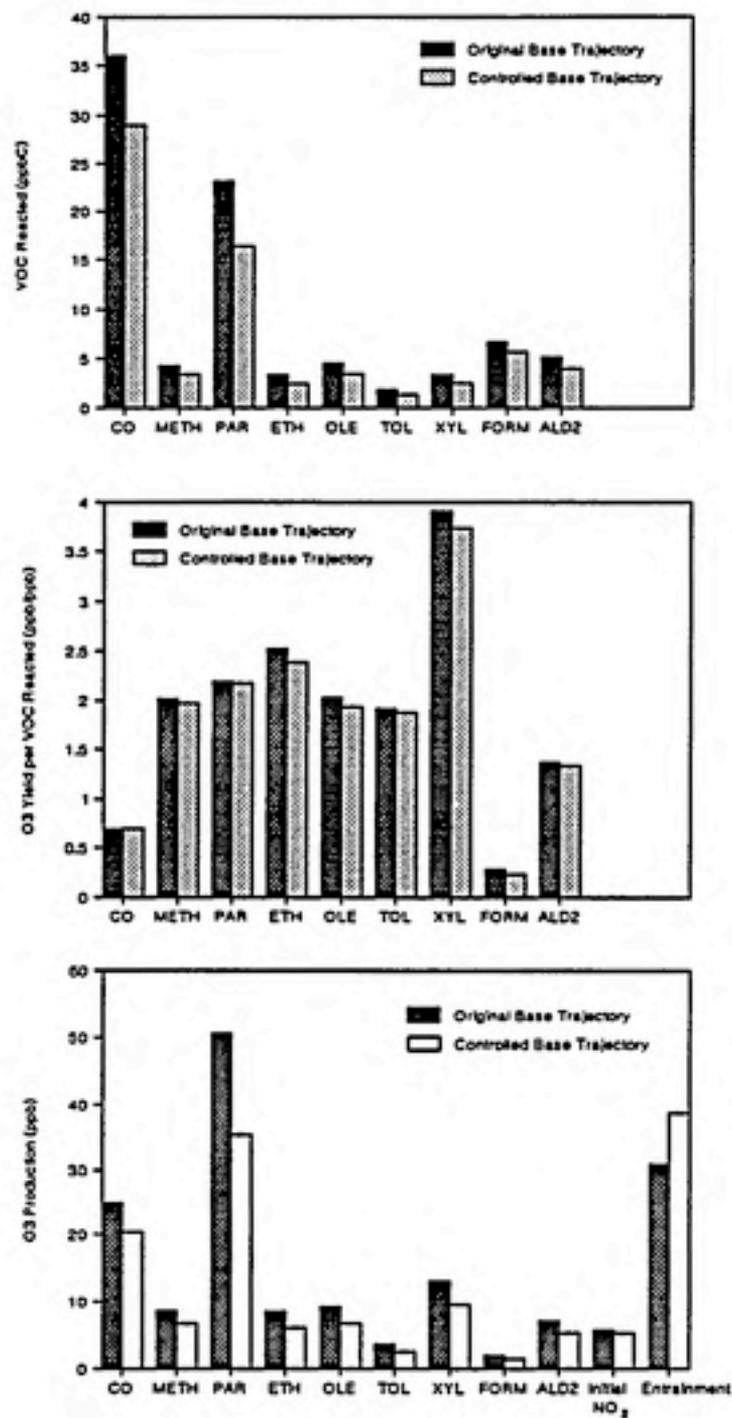


Figure 11. Bar graph comparing VOC reacted and O<sub>3</sub> yields in base case original and control simulations.

Table 22. 'OH summary for the original base case and controlled base case simulations..

"Base Case 0.6:0.1, Controlled VOC"

"Time"	"dnOH" "ppb"	"% nOH" "organ"	"% nOH" "inorg"	"OH" "Ch.L."	"Total" "OH"	"dOH" "dHO2"	"OH Termination" "%og"	"Xinorg"
1	.01	99.6	.4	2.35	.03	.9939	64.4	35.6
60	1.06	98.2	1.8	2.90	3.08	.9997	72.5	27.5
121	1.77	92.1	7.9	2.85	5.06	.9996	72.1	27.9
181	2.45	80.5	19.5	2.64	6.47	.9995	69.1	30.9
240	3.11	68.7	31.3	2.60	8.09	.9994	68.4	31.6
302	3.84	59.2	40.8	2.63	10.11	.9992	68.7	31.2
361	4.37	51.6	48.4	2.73	11.95	.9987	70.0	30.0
420	4.66	45.7	54.3	2.94	13.69	.9974	72.7	27.3
486	4.40	41.6	58.4	3.28	14.41	.9931	76.8	23.2
545	3.66	39.9	60.1	3.68	13.49	.9791	81.6	18.4
601	2.38	41.3	58.7	4.06	9.66	.9533	85.2	14.8
660	1.12	47.8	52.2	4.60	5.13	.9319	87.3	12.7
721	.28	62.8	37.2	5.60	1.56	.9152	87.7	12.3
780	.04	81.7	18.3	4.78	.21	.8790	87.7	12.3
Ave	33.30	55.7	44.3	3.11	103.64	.9858	75.3	24.7

Note: PPM new OH is normalized to 60 min intervals.

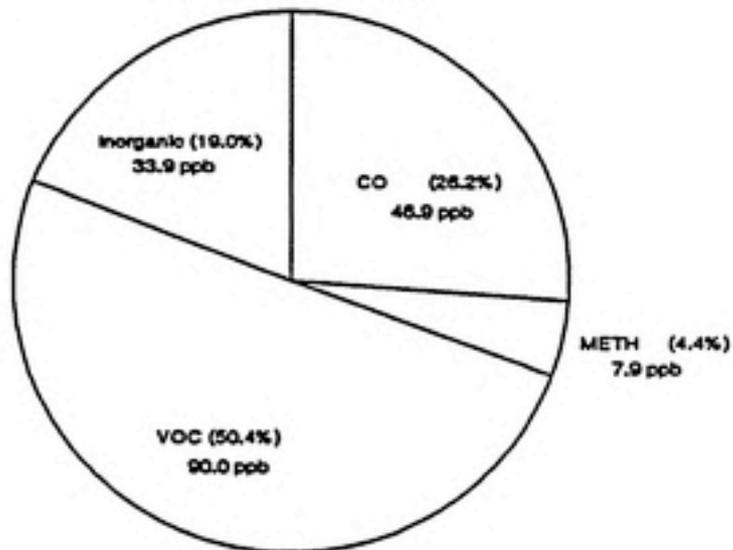
"Doubled CO Control Case"

"Time"	"dnOH" "ppb"	"% nOH" "organ"	"% nOH" "inorg"	"OH" "Ch.L."	"Total" "OH"	"dOH" "dHO2"	"OH Termination" "%og"	"Xinorg"
1	.01	99.5	.5	2.64	.02	.9937	67.3	32.7
61	.67	97.0	3.0	3.34	2.24	.9997	75.1	24.9
120	1.15	87.2	12.8	3.36	3.88	.9996	75.3	24.7
182	1.66	71.4	28.6	3.25	5.39	.9994	74.0	26.0
241	2.30	58.4	41.6	3.34	7.68	.9993	74.6	25.4
301	2.97	49.5	50.5	3.50	10.40	.9990	75.8	24.2
361	3.59	42.4	57.6	3.76	13.50	.9981	77.6	22.4
420	3.92	36.8	63.2	4.21	16.51	.9950	80.6	19.4
483	3.89	32.5	67.5	4.80	18.70	.9826	84.8	15.2
542	3.26	29.5	70.5	5.09	16.58	.9477	88.6	11.4
604	2.03	29.6	70.4	5.09	10.33	.9071	91.0	9.0
661	.87	36.0	64.0	5.64	4.92	.8961	92.0	8.0
720	.21	51.1	48.9	6.90	1.43	.8954	92.1	7.9
780	.03	74.3	25.7	6.28	.18	.8743	92.1	8.0
Ave	26.65	44.7	55.3	4.24	112.91	.9718	82.3	17.7

Note: PPM new OH is normalized to 60 min intervals.

### Doubled CO Trajectory Simulation O<sub>3</sub> Production

Total O<sub>3</sub> Production = 179 ppb



### Doubled CO Control Simulation O<sub>3</sub> Production

Total O<sub>3</sub> Production = 138 ppb

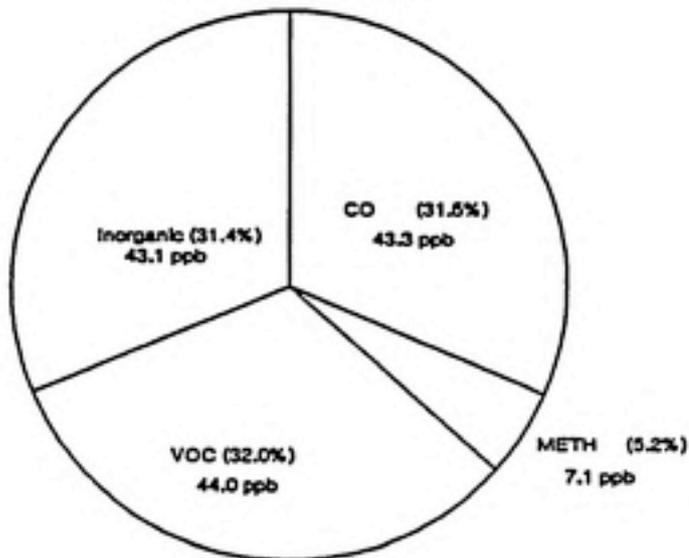


Figure 12. Pie chart comparing O<sub>3</sub> production in 2xCO simulation and control 2xCO simulation.

a high propagation factor, so the high CO concentration causes a large OH chain length. The chain length was 3.63 in the 2xCO case but increased to 4.24 in the controlled CO case. The total OH production in the 2xCO case is 158 ppb compared to 113 ppb in the 2xCO control case.

Even though new OH radical production from the photolysis of aldehydes was significantly reduced in the controlled CO case, the efficient propagation of OH radicals by CO still produced a large number of radicals.

## VOC Control Requirement Prediction

In the discussion above, we gained some insight into how the O<sub>3</sub> production occurred in each simulation. Doubling the CO concentration increased OH propagation and increased the mass of CO reacted. In the 2xCO design simulation, CO produced more O<sub>3</sub> so lower initial VOC and NO<sub>x</sub> concentrations were used to reproduce the design value. This information should improve our understanding of why the predicted VOC control requirement nearly doubled in the 2xCO case and help us to judge if these results seem physically plausible.

Figure 14 shows the production of O<sub>3</sub> attributed to VOC sources and non-VOC sources for each of the design value and control case simulations. Non-VOC sources include O<sub>3</sub> production by CO and CH<sub>4</sub>. The base case VOC control requirement was 23.2%. Figure 14 shows that for the base case simulations, the production of O<sub>3</sub> by VOCs was reduced from 96.7 ppb in the design case to 66.8 ppb in the control case, or by 31%. Using the TI4 output files, I summed the mass of VOC reacted (after converting to units of ppbC) and found that the mass of VOC reacted fell from 88.3 ppbC in the design case to 63.8 ppbC in the control case, a reduction of 27%. The average yield of O<sub>3</sub> per ppbC fell from 1.10 to 1.05. The 23.2% reduction in VOC emissions reduced new O<sub>3</sub> production and OH propagation causing a 27% reduction in VOC reacted. The yield of O<sub>3</sub> per ppbC fell because of the increase in the reaction of OH with NO<sub>2</sub>.

The 2xCO control prediction was 42.5%. For the 2xCO simulations, production of O<sub>3</sub> by VOCs was reduced from 78 ppb in the 2xCO simulation to 44 ppb in the controlled 2xCO simulation, or by 44%. The mass of VOC reacted fell from 69.9 ppbC in the design case to 39.0 ppbC in the control case, a 43% reduction.

To summarize, Figure 14 shows that when CO concentrations are doubled, VOCs contribute a smaller fraction of the total O<sub>3</sub> production, and a greater level of VOC control is required to meet the standard. Non-VOC sources contribute a greater

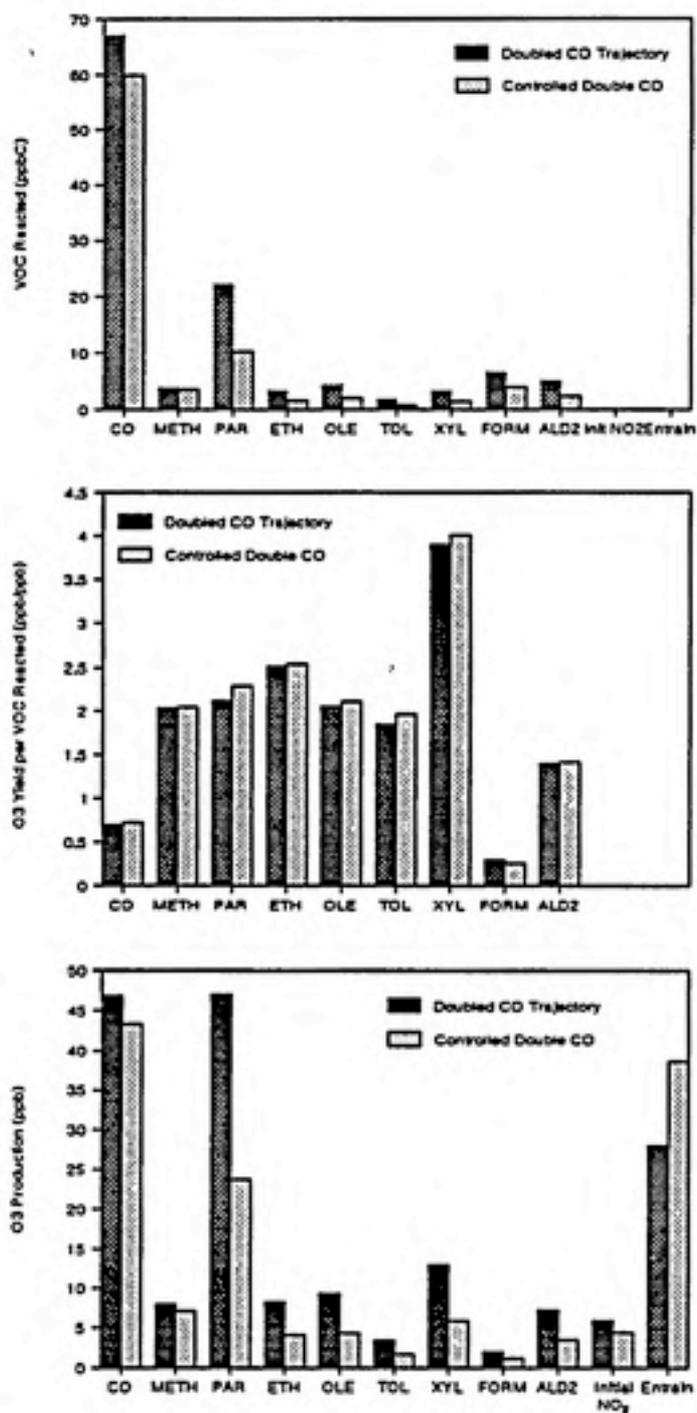


Figure 13. Bar graph comparing VOC reacted and O<sub>3</sub> yields in 2xCO case and 2xCO control simulations.

**Table 23.** Time dependent 'OH summary for 2xCO and controlled 2xCO simulations.

"Double CO Surf and Aloft, 0.6:0.1, Std VOC"

"Time"	"dnOH" "ppb"	"% nOH" "organ"	"% nOH" "inorg"	"OH" "Ch.L."	"Total" "OH"	"dOH" "dHO2"	"OH Termination" "Xog"	"Xinorg"
1	.01	99.7	.3	2.87	.04	.9941	72.2	27.8
61	1.33	98.4	1.6	3.57	4.74	.9997	78.9	21.1
121	2.32	92.8	7.2	3.43	7.98	.9995	78.0	22.0
181	3.14	81.6	18.4	3.19	9.99	.9994	75.7	24.3
241	4.08	69.3	30.7	3.19	13.03	.9990	75.7	24.3
302	5.12	58.4	41.6	3.33	17.04	.9983	77.0	23.0
362	6.00	49.0	51.0	3.61	21.69	.9953	79.8	20.2
420	6.46	41.0	59.0	4.07	26.30	.9779	84.8	15.2
483	6.05	32.5	67.5	3.97	24.06	.8993	90.1	9.9
540	4.58	26.8	73.2	3.42	15.64	.7959	93.3	6.7
602	2.78	27.9	72.1	3.41	9.48	.7647	94.4	5.6
661	1.20	36.4	63.6	4.09	4.89	.7878	94.6	5.4
721	.29	54.6	45.4	5.58	1.64	.8169	94.4	5.6
780	.05	82.0	18.0	5.93	.28	.8393	94.3	5.7

Ave 43.43 50.8 49.2 3.63 157.76 .9316 84.1 15.9

Note: PPM new OH is normalized to 60 min intervals.

"Double CO Surf and Aloft, 0.6:0.1, Std VOC"

"Time"	"dnOH" "ppb"	"% nOH" "organ"	"% nOH" "inorg"	"OH" "Ch.L."	"Total" "OH"	"dOH" "dHO2"	"OH Termination" "Xog"	"Xinorg"
1	.01	99.5	.5	2.64	.02	.9937	67.3	32.7
61	.67	97.0	3.0	3.34	2.24	.9997	75.1	24.9
120	1.15	87.2	12.8	3.36	3.88	.9996	75.3	24.7
182	1.66	71.4	28.6	3.25	5.39	.9994	74.0	26.0
241	2.30	58.4	41.6	3.34	7.68	.9993	74.6	25.4
301	2.97	49.5	50.5	3.50	10.40	.9990	75.8	24.2
361	3.59	42.4	57.6	3.76	13.50	.9981	77.6	22.4
420	3.92	36.8	63.2	4.21	16.51	.9950	80.6	19.4
483	3.89	32.5	67.5	4.80	18.70	.9826	84.8	15.2
542	3.26	29.5	70.5	5.09	16.58	.9477	88.6	11.4
604	2.03	29.6	70.4	5.09	10.33	.9071	91.0	9.0
661	.87	36.0	64.0	5.64	4.92	.8961	92.0	8.0
720	.21	51.1	48.9	6.90	1.43	.8954	92.1	7.9
780	.03	74.3	25.7	6.28	.18	.8743	92.1	8.0

Ave 26.65 44.7 55.3 4.24 112.91 .9718 82.3 17.7

Note: PPM new OH is normalized to 60 min intervals.

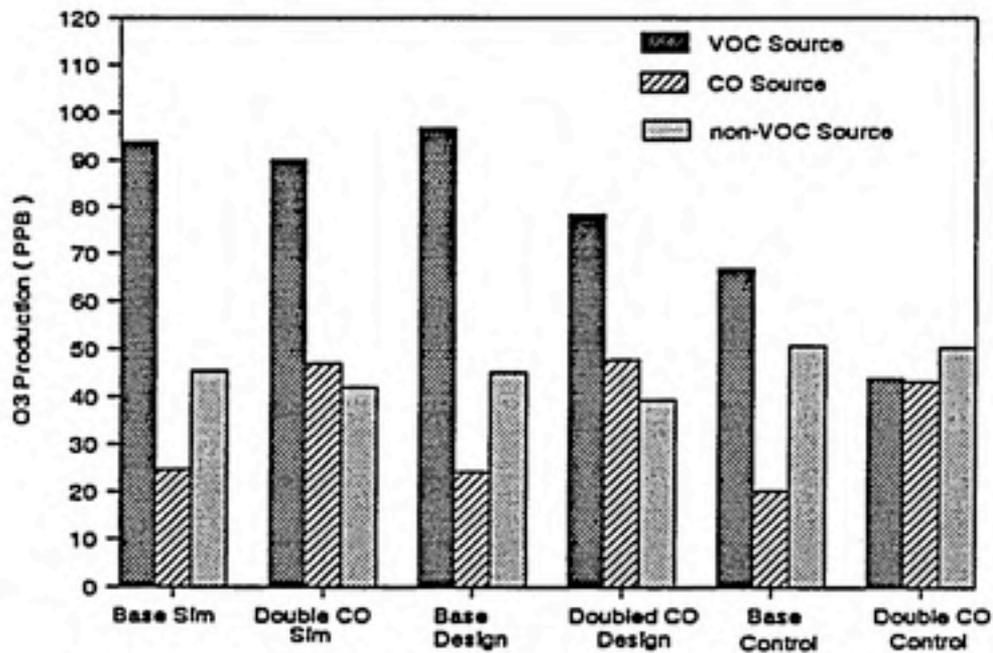


Figure 14. Bar graph comparing O<sub>3</sub> production from VOC and non-VOC sources for design value and control simulations.

fraction of the O<sub>3</sub> production in the control scenario. This suggests that CO and NO<sub>x</sub> control strategies should be considered in addition to the VOC control strategy.

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## Concluding Remarks

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Traditionally, air pollution models produce output in the form of concentration profiles. In some models, instantaneous rates of reaction can be included in the output, but these are difficult to analyze.

The integrated rate analysis method can significantly improve our understanding of model predictions. It saves information on the rates of reactions which is lost in simple concentration profiles. Integrated rates are useful because they show what happens over some time interval rather than an instantaneous point in time.

The IRREVAL program automates the analysis of the integrated rates. It enables the user to eliminate the confusing effect of groups of reactions which rapidly interconvert species. It can use a mass balance on intermediate species to show the final products of a species after all of the intermediates in its degradation chain have reacted.

IRREVAL evolved from a program which performed a simple mass analysis on a given species. As a result, it was not planned nor designed for efficiency. It has the advantage that the origin of values in each output file can be understood by going back to more primitive output files. For example, the values given in an 'OH summary table in the TIM file can be traced back to the complete HO<sub>x</sub> balance performed each interval in the HO<sub>x</sub> output file. The source of values given in the HO<sub>x</sub> balance can be found in the BAL output file. This is very useful for debugging errors when the program is modified.

IRREVAL has several potential applications which were not developed in the example in Chapter 7. It could be used, for example, to perform a complete carbon mass balance. It has the advantage that unreactive species, such as CO<sub>2</sub>, which were

ignored in the model can be reintroduced into the compressed mechanism file and included in the IRREVAL analysis.

It would also be useful for comparing different chemical mechanisms. The ability to attribute  $O_3$  production to specific organics and to show the new  $\cdot OH$  production and  $\cdot OH$  chain length over time would be especially useful for comparing mechanisms.

### Future Modifications to IRREVAL

Several improvements should be made in the program. Currently, the program shows simply the total production of  $O_3$  from each source. Some sources produce  $O_3$  at different times in the simulation, and  $O_3$  losses occur during the simulation. It would be useful to know the fraction of the final concentration of  $O_3$  attributed to each source as well as the total amount of  $O_3$  produced by each source. This can be done using the algorithm that is currently used for  $NO_2$ .

Some  $O_3$  is lost in the algorithm which eliminates the replaced species for the time dependent analysis. This is usually less than 3% of the total  $O_3$  production. Currently, the lost mass is recovered by redistributing it among the primary VOCs. This error should be reduced.

The content and structure of the output files will also continue to be changed or improved. It might be desirable to produce plots instead of tables for some of the output.

The method of analysis developed in this work could eventually be applied to the Urban Airshed model and to regional scale models.

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**Appendix A**

As described in Chapter 4, the  $O_3$  production from each VOC is calculated by summing the final  $NO_2$  and  $HO_2$  production from each VOC at the end of its reaction chain. For example, for ethene (ETH) the equation

$$\frac{\Delta O_3}{\Delta ETH} = \left( \frac{\Delta HO_2}{\Delta ETH} \frac{\Delta NO_2}{\Delta HO_2} + \frac{\Delta NO_2}{\Delta ETH} \right) \frac{\Delta O_3}{\Delta NO_2}$$

is used to calculate the  $O_3$  yield per ETH, where

$$\frac{\Delta NO_2}{\Delta HO_2} = \frac{\text{Production of } NO_2 \text{ from } HO_2}{\text{Total Production of } HO_2}$$

$$\frac{\Delta O_3}{\Delta NO_2} = \frac{\text{Production of } O_3 \text{ from } NO_2}{\text{Total Production of } NO_2}$$

$\Delta NO_2/\Delta HO_2$  is listed at the end of the \*.HC output file and  $\Delta O_3/\Delta NO_2$  is listed at the end of the \*.NOX output file.

Figure 15 shows the ETH chain reaction and the pathways which produce  $HO_2$  and  $NO_2$ . The first level in the tree shows the production of each intermediate per ppm of ETH reacted. Lower levels show the mass (ppm) of final products produced per ppm of intermediate produced in the previous step. For example, reactions of ETH produce 0.0272 ppm of CO per ppm of ETH reacted. When CO reacts, it produces one  $HO_2$ , but only 3% of the total CO reacts in this simulation, so each ppm of CO produced by ETH causes 0.03 ppm additional production of  $HO_2$ .

The production of  $NO_2$  or  $HO_2$  in each path of the chain reaction is calculated by taking the product of the coefficients at each level in the tree. The production of  $NO_2$  and  $HO_2$  per ETH are then found by summing  $HO_2$  and  $NO_2$  production in each path. For example, in Figure 15,  $NO_2$  production per ETH is calculated as

$$\begin{aligned} \frac{\Delta NO_2}{\Delta ETH} &= (0.9385)(0.9850) + 0.2062 \left\{ 0.4706 \left[ 0.7364 + (0.8811)(0.9850) \right] \right. \\ &\quad \left. + [(0.0198)(0.9850)] \right\} \\ &= 1.084 \text{ ppm/ppm} \end{aligned}$$

and  $HO_2$  per ETH production is

$$\Delta HO_2/\Delta ETH = 1.953 \text{ ppm/ppm}$$

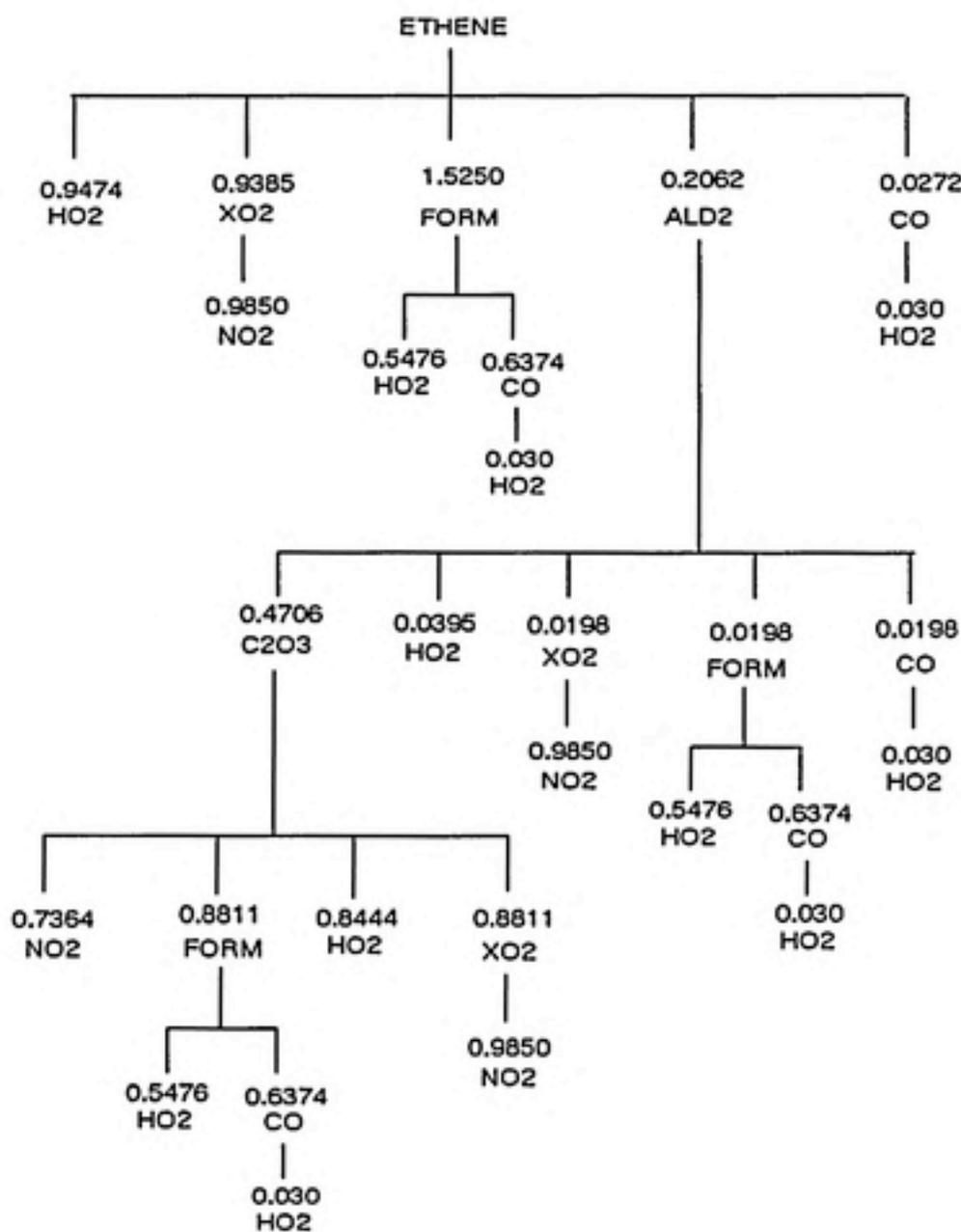


Figure 15. Example Calculation of  $\Delta O_3/\Delta ETH$ . Numbers show the products in ppm per ppm of reactant produced (see text).

From the \*.HC and \*.NOX output files in Table 12 (line 28) and Table 14 (second line from end)

$$\Delta\text{NO}_2/\Delta\text{HO}_2 = 0.9083 \text{ ppm/ppm}$$

$$\Delta\text{O}_3/\Delta\text{NO}_2 = 0.6069 \text{ ppm/ppm}$$

so the O<sub>3</sub> yield per ETH reacted is

$$\begin{aligned}\Delta\text{O}_3/\Delta\text{ETH} &= \{(1.9530)(0.9083) + 1.084\}(0.6069) \\ &= 1.735\end{aligned}$$

This is the value shown in line 9 of the \*.O3 output file in Table 11.

The calculation is more complicated for a time dependent analysis. The O<sub>3</sub> production from ETH is calculated during each interval, but some intermediates produced in ETH reactions in one interval may not react until later intervals. For example, ETH may react in the first interval to produce ALD2. This ALD2 may react in the second and third intervals to produce FORM, and this FORM may react in the second through sixth intervals. One can plot  $\Delta\text{O}_3/\Delta\text{ETH}$  as a function of time, but it might be difficult to interpret this plot because the O<sub>3</sub> production does not occur in the same interval as the ETH reaction. The O<sub>3</sub> production from ETH can be summed over the entire simulation, however, and an average O<sub>3</sub> yield can be calculated. The average values for a time dependent analysis are listed at the end of the \*.TI4 output file. They provide a better approximation of the O<sub>3</sub> yield per VOC because the time dependent analysis considers the time dependence of the various chemical reactions. For the example output files in Chapter 5, the time-averaged analysis gave a  $\Delta\text{O}_3/\Delta\text{ETH} = 1.735$ , while the time dependent analysis gave  $\Delta\text{O}_3/\Delta\text{ETH} = 2.542$ . The large difference between the two values occurs because the time-averaged analysis overestimates the contribution of initial NO<sub>2</sub> to O<sub>3</sub> production and underestimates the contribution of chemically produced NO<sub>2</sub>.