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Chapter 16

PROCESS ANALYSIS

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ABSTRACT

The implementation of process analysis techniques in the Models-3 Community Multiscale Air Quality (CMAQ) modeling system is described in this chapter. These techniques can be used in Eulerian photochemical models such as the CMAQ Chemical Transport Model (CCTM) to obtain information that provides insights into how model predictions are obtained. This type of information is particularly useful when modeling nonlinear systems such as atmospheric photochemistry. The two techniques available in the CMAQ system – integrated process rate (IPR) analysis and integrated reaction rate analysis (IRR) -- are each described. The manner in which IPR analysis can be used to determine the relative contributions of individual physical and chemical processes is presented. Descriptions of how to employ IRR analysis to elucidate important chemical pathways and to identify key chemical characteristics are included. Finally, the procedures used to apply each technique in the CMAQ system are also described.

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16.0 PROCESS ANALYSIS

A major function of air pollution models is to predict the spatial and temporal distributions of ambient air pollutants and other species. For complex Eulerian grid models, output concentration fields of these species are determined by solving systems of partial differential equations. These equations define the time-rate of change in species concentrations due to a series of physical and chemical processes (e.g., emissions, chemical reaction, horizontal advection, etc.). Since most grid models are configured to output only the concentration fields that reflect the cumulative effect of all processes, information about the impact of individual processes is usually not available. Grid models can be configured to provide quantitative information on the effects of the chemical reactions and other atmospheric processes that are being simulated, however (Pleim, 1990; Jeffries and Tonnesen, 1994; Jang et al., 1995a,b). This type of information has been used to develop various process analyses that provide descriptions of how a model obtained its predictions. This chapter provides background information on these methods and describes how process analysis is implemented in the Models-3 Community Multiscale Air Quality (CMAQ) modeling system.

Although process analysis does not have to be included in a grid model application, it can provide supplemental information that can be quite useful in assessing a model's performance. Quantifying the contributions of individual processes to model predictions provides a fundamental explanation of the reasons for a model's predictions and shows the relative importance of each process. This information can be useful in identifying potential sources of error in the model formulation or its inputs. It can also be useful in interpreting model outputs, particularly with respect to understanding differences in model predictions that occur from a change to the model itself or to its input. Further, information provided from the chemical process analysis can be used to determine important characteristics of different chemical mechanisms. This is particularly useful for investigating mechanistic differences under different chemical regimes (e.g., VOC versus NO_x limiting conditions).

The inclusion of process analysis in a model application is generally carried out in two steps. First, the model itself is “instrumented” (i.e., additional code or modules are added to the model) to produce supplemental outputs about the contributions of individual processes and different chemical reaction pathways to the model predictions. These data are then used with the concentration fields in postprocessing operations to provide quantitative explanations of the factors affecting a model's predictions. Although several specific postprocessing techniques have been developed to reveal particular model features (e.g., Jeffries and Tonnesen, 1994; Jang et al., 1995a,b), process analysis data can be extracted and analyzed in many different ways. The implementation of process analysis in the CMAQ system has been structured to facilitate data extraction for subsequent model analysis. Although the main focus of this chapter is on data extraction techniques, some example process analyses are also presented to illustrate particular applications.

For purposes of discussion, it is convenient to separate process analysis into two parts: integrated process rate (IPR) analysis and integrated reaction rate (IRR) analysis. The first deals with the effects of all the physical processes and the *net* effect of chemistry on model predictions. IRR analysis deals with the details of the chemical transformations that are described in the model's chemical mechanism. In general, IPR analyses are generally much easier to apply and understand than IRR analyses since the latter typically requires a fairly thorough understanding of atmospheric chemistry. Thus, the discussion below describes each analysis method separately, starting with IPR analyses. Users not familiar with atmospheric chemistry details may wish to omit the sections on IRR analysis. It should be added that either analysis method can be applied independently of the other.

The CMAQ implementation of process analysis includes a flexible user interface that allows the user to request only those particular outputs that are needed for model analysis. The information generated for both IPR analysis and IRR analysis is controlled by the Process Analysis Control Program (PACP). The PACP processes user-specified commands to instrument the CMAQ Chemical Transport Model (hereafter referred to as the CCTM) to generate the specific outputs that are selected by the user. As a consequence, the PACP must be invoked before configuring a CCTM and running a simulation. The details of how the PACP works and the syntax for the commands are covered in the Models-3 User Manual (EPA, 1998), and they will not be repeated in their entirety here. Nevertheless, some of the command syntax and some simple examples are presented in the discussions that follow to illustrate how the PACP is used to set up a particular process analysis.

16.1 Integrated Process Rate Analysis

The governing equation for Eulerian models is the species continuity equation. Application of the continuity equation to a group of chemically reactive species results in a system of partial differential equations (PDEs) that gives the time-rate of change in species concentration as a function of the rates of change due to various chemical and physical processes that determine the ambient species concentrations. As noted in the introduction, the concentration fields that are the numerical solutions to these PDEs reveal only the net effects of all processes. This section is concerned with how the contributions of individual processes are determined and used in process analyses. The first two subsections deal with the calculation and use of IPRs in general. The last two subsections describe the CMAQ implementation of IPR analysis and the use of the PACP to set up an IPR analysis.

16.1.1 Computation of Integrated Process Rates

All Eulerian models utilize the technique of operator splitting. As a result, it is relatively easy to obtain quantitative information about the contribution of individual processes to total concentrations. In operator splitting, solutions to the system of PDEs are obtained by separating the continuity equation for each species into several simpler PDEs or ordinary differential equations (ODEs) that give the impact of only one or two processes. These simpler PDEs or ODEs are then solved separately to arrive at the final concentration. To illustrate, consider the simple case of two-dimensional horizontal advection of a single species in the absence of any other processes, for which the governing equation can be expressed as follows:

$$\frac{\partial c}{\partial t} + \frac{\partial (uc)}{\partial x} + \frac{\partial (vc)}{\partial y} = 0 \ , \qquad (16\text{-}1)$$

where c is the species concentration, and u and v are the x- and y-components of the wind velocity vector, respectively. With operator splitting, this 2-dimensional equation is split into two 1-dimensional operators, one for each direction:

$$\frac{\partial c}{\partial t} + \frac{\partial (uc)}{\partial x} = 0 \qquad (16\text{-}2a)$$

and

$$\frac{\partial c}{\partial t} + \frac{\partial (vc)}{\partial y} = 0 \ . \qquad (16\text{-}2b)$$

These two equations are then solved sequentially, with the solution to the first being used as the initial condition for the second. The solution to the second equation then represents the final solution and gives the net effect of 2-dimensional advection.

The final solution for the example presented above can also be represented as follows:

$$c(t + \Delta t) = c(t) + (\Delta c)_x + (\Delta c)_y \ , \qquad (16\text{-}3)$$

where $c(t+\Delta t)$ is the final solution, $c(t)$ is the initial condition for the 2-dimensional problem, and $(\Delta c)_x$ and $(\Delta c)_y$ are the changes in concentration produced by each of the 1-dimensional operators. $(\Delta c)_x$ and $(\Delta c)_y$ give the impact of each operator in moving from the initial to the final concentration and are equivalent to the results obtained by integrating the process rates individually. Hence the term integrated process rates is used to describe them. Note that they can be computed with little additional work since they are simply equal to the difference between the final and initial concentrations for each operator.

From the above example, it should be evident that a general mathematical representation of IPRs for individual processes can be expressed as follows:

$$(\Delta c)_n = \int_t^{t+\Delta t} L_n \, \mathrm{d}t \ , \qquad (16\text{-}4)$$

where $(\Delta c)_n$ is the change in a species' concentration due to operator n, L_n is the differential operator associated with a process, and Δt is the model synchronization time step (which is equivalent to Δt_{sync} in Chapter 6). Refer to Chapter 6 for a discussion of the various time steps used in CMAQ. The integration in equation (16-4) is performed by the model regardless of whether it has been instrumented for process analysis. Thus, it is only necessary to save the $(\Delta c)_n$ to obtain process analysis capabilities. In a few cases, however, models may be structured such that one operator deals with two or three processes simultaneously. In those cases, the

$(\Delta c)_n$ obtained after the integration would represent the compound effect of all of those processes and it would not be possible to discern the impacts of the individual processes. Normally, the only way that information could be obtained would be to integrate the process rates separately. In some instances, however, it may still be possible to isolate the impacts of the individual processes without performing additional integrations. For example, the CCTM treats vertical diffusion, emissions, and dry deposition simultaneously in one operator, but the amount of material deposited by dry deposition is tabulated and the amount of material that is emitted is known. As a consequence, mass balance techniques can be used to compute the contribution of each process subsequent to the simultaneous integration of the process rates without separately integrating each process rate. Thus, the IPRs that are available for process analysis are to some degree determined by the underlying structure of the photochemical model that is being used and by the effort that is invested in separating individual components when processes are coupled in a single operator.

Analogous to equation (16-3), the concentration at the end of a time step can be expressed as follows:

$$c(t+\Delta t) = c(t) + \sum_{n=1}^{N} (\Delta c)_n \ , \tag{16-5}$$

where the model is assumed to have N operators. It should be noted that most IPRs can be either positive or negative since most processes can cause concentrations to either increase or decrease. Further, it should also be evident that the IPRs in the above expression are additive. Thus, for example, the IPRs for horizontal advection and vertical advection could be summed to give one IPR that represents the net impact of the two advection processes. The differential operators (L_n) themselves are most often nonlinear, however. Because of these nonlinearities, the magnitude of the IPRs for most processes would change if the order of the model's operators was altered or even if only one of the operators was changed. Thus, the additive property for IPRs holds only for a particular application of the model.

16.1.2 Example IPR Analyses

The tabulation and subsequent output of IPRs provide the user with quantitative information on the effects of individual processes, and these can be examined and depicted in a number of ways. Figures 16-1 and 16-2 contain two types of displays that were developed to depict process contribution data graphically (Jeffries, 1996). Figure 16-1 is a time series plot showing both predicted concentrations and integrated process rates. This type of plot shows the hourly variations at a cell (or group of cells if the data are aggregated) of a predicted species concentration and the change in concentration caused by each process (i.e., the IPRs). Plots of this type illustrate the variations in process contributions during the simulation period. Figure 16-2 shows process contributions and total concentrations for different model formulations, in this case, different grid resolutions. Here the data have been aggregated over several cells and hours, but could be developed for a single cell or time period just as well. This figure highlights how cumulative process contributions are altered by the different model formulations. For a more thorough discussion of how this type of data can be used to assist in the evaluation of a model's performance, the reader is referred to Jang et al. (1995a and 1995b) and to Pleim (1990).

16.1.3 Implementation of IPR Analysis in the CMAQ System

The previous section illustrated that instrumenting a model for process analysis involves providing the capability to capture IPRs. Since an IPR can be calculated for every combination of process and species, the amount of output data that can be generated is substantial. As a consequence, the PACP has been designed to allow substantial flexibility in selecting the particular IPRs for output. This is accomplished primarily by allowing the user to choose only those particular species/process combinations that are of interest. Additional control and flexibility are provided by including the ability to produce lumped IPRs, by allowing special species families to be defined, and by providing controls to limit the size of the modeling domain for which outputs are generated. These will be illustrated in the examples presented below.

The physical processes that are simulated in the CCTM and hence are available for IPR analysis are shown in Table 16-1. As will be illustrated below, these processes are referenced in the PACP by the codes shown in the first column. The procedure for selecting specific IPRs for output is species oriented. Hence, a user selects a species and then indicates which processes will be included in the IPR output. The species are referenced by their model names. In addition, the user may also define a family of species that is a linear combination of the model species (e.g., defining NOx as the sum of NO and NO_2) and extract IPRs for the family. This can be useful in saving disk space occupied by the output IPR files when information about individual members of a family is not needed.

It should be apparent from Table 16-1 that IPRs for some species will always be zero (e.g., those species not emitted always have zero IPRs for that process). Thus, the size of the output file can be minimized by not extracting those IPRs. The PACP also contains an option that allows the user to limit the amount of output data by extracting IPR outputs for only part of the modeling domain. Currently, the user is restricted to selecting a single, contiguous block of cells within the domain for the IPR outputs. The block is defined relative to the modeling domain by selecting a starting and ending column, row and level. A possible future enhancement would be to provide a graphical interface to allow the user to select any particular cell or group of cells within the domain.

The CCTM model has been instrumented to write the IPRs to an output file at the same time as the output concentration files are written. Thus, the IPR outputs represent the cumulative impact of the process integrations over the entire output time interval. Process contributions over shorter time intervals can be obtained by increasing the frequency of writing outputs of both the concentration fields and the IPRs. Finally, the IPR output files are standard Models-3 IO/API gridded files, and can be viewed with the Models-3 visualization tools described in Models-3 User Manual (EPA, 1998).

16.1.4 Use of the PACP to set up an IPR Analysis

This section illustrates how the PACP can be used to generate the IPR data for an analysis. Details on formatting inputs and using the PACP are contained in the Models-3 User Manual (EPA, 1998). This section borrows from that discussion to illustrate how the PACP is used. The user selects and controls the form of the IPR output data by means of a PACP command file. A few predefined command files are available to set up an analysis, or users can generate their own files to customize their analyses. A command file consists of a series of commands and definitions that contain instructions for generating IPR outputs. The commands are input in a free form format to facilitate encoding, and they contain special keywords that have specific meaning to the PACP. The commands related to IPR analysis have been divided into two groups: Global commands and IPR output commands. A description of the commands within each group will be presented first, followed by an example illustrating how these commands are used. In the description that follows, the syntax for each command is given first, with bold type used for PACP keywords and normal type used for user supplied input. Alternative inputs are separated by vertical bars and completely optional inputs are enclosed in curly braces.

Global Commands:

OUTPUT_DOMAIN = {**LOCOL[**n_1**] + HICOL[**n_2**] + LOROW[**n_3**] + HIROW[**n_4**]**
+ LOLEV[n_5**] + HILEV[**n_6**]**}**;**

The OUTPUT_DOMAIN command provides the capability to limit the IPR output data to only one portion of the modeling domain. The n_i in brackets are numbers that define the bounds of the output domain relative to the number of columns, rows, and vertical levels in the modeling domain. Thus, for example, the value for n_1 must be greater than or equal to one and less than or equal to the number of columns in the domain. If this command is included, at least one domain specifier must be present, and the end of the domain is used for any that are missing. If the command is omitted entirely, output is generated for the entire domain.

DEFINE FAMILY familyname **=** {c_1*****}species_1 {**+** {c_2*****}species_2 **+** ...}**;**

The DEFINE FAMILY command is used to define a group of species as members of a family. The user specified “familyname” must be unique, and can be referenced in subsequent commands. The c_i are numerical coefficients that default to one if not specified; “species_i” are the names of individual model species.

ENDPA;

The ENDPA command signifies the end of the command input in the PACP command file.

IPR Output Command:

IPR_OUTPUT species|familyname|**ALL** {= pcode$_1$ + pcode$_2$ + ...}**;**

The IPR_OUTPUT command defines specific IPR outputs to be generated during a CMAQ simulation. A species name, family name, or the keyword ALL must follow the IRR_OUTPUT keyword. The keyword ALL refers to all model species. IPRs are generated for the selected species or family, and they are controlled by the specified values of pcode$_i$, where pcode$_i$ corresponds to one of the process codes listed in Table 16-1. If no process codes are specified, IPRs will be generated for every process. The output variables that are generated are named either species_pcode$_i$ or familyname_pcode$_i$

A listing of an example PACP command file is contained in Exhibit 16-1. To facilitate the discussion that follows, the commands have been numbered, although this is not required by the PACP. (Note that all information enclosed by curly braces in a command file is treated as comments.) Each numbered line represents a command, and the input for each command is terminated by a semicolon. This particular set of commands causes the CCTM to generate several individual IPRs for a special user-defined sub-domain. Each of the commands is described below.

Command 1 is used to restrict the process analysis output to a subset of the modeling domain. As noted above, output would be generated for the entire computational domain if the OUTPUT_DOMAIN were omitted. Since keywords for columns and rows are not present, the PACP default is to include all rows and columns in the modeling domain. The keywords "LOLEV" and "HILEV" restrict the output for the vertical level to layers 1 through 2. Thus, the net effect of this command is to limit the IPR output to all cells within the first two vertical levels of the modeling domain.

Commands 2 and 3 are used to define families of species. The species names to the right of the equal sign are model species. The effect of the numerical coefficients in the definition of the VOC families is to convert the units of the IPRs for individual organics from ppm to ppmC. As will be seen, these "defined" family names are referenced in subsequent commands.

Commands 4 through 8 actually cause IPR outputs to be generated. As described above, IPRs are generated for the species and the processes that are referenced by means of the codes listed in Table 16-1. Since no process codes are specified in commands 4 and 5, IPRs will be generated for each of the twelve processes in Table 16-1 for the families NOX and VOC (i.e., a total of 24 IPRs). Command 6 causes three IPRs to be generated for species O3, one each for total transport, chemistry, and clouds. Command 7 causes an IPR for vertical diffusion to be generated for every model species. The last command signifies the end of the command inputs.

The CCTM will generate the IPR output data in a form comparable to the output concentration files. Hence, the data are written to standard Models-3 IO/API gridded data files. The units of the IPR data are normally the same as those for the species concentration data (i.e., ppm for gas-phase species and either $\mu g/m^3$ or number/m^3 for aerosols). As described in the example of creating the family VOC with units of ppmC, however, different output units can be created using special family definitions.

The example just described was formulated primarily to illustrate how IPR commands are structured to collect IPR information during a model simulation. In general, the particular data that are collected for process analysis would be determined by the needs of the study, and thus it is difficult to define a "default" process analysis. Nevertheless, a minimal process analysis for studying ozone formation might involve collecting the process contributions for NOx, VOC, and for ozone. The example in Exhibit 16-1 could be used as the starting point for such an analysis. Commands 4 and 5 capture all the IPRs for NOx and VOC. Command 6 could be modified to capture all IPRs for ozone as well. Since it would not normally be necessary to capture vertical diffusion IPRs for all species, command 7 could be dropped. Of course, the user would still be required to define the domain for outputs (command 1) and to define the VOC family for the mechanism that is being used (command 3). Thus, commands 1 through 5 with command 6 modified to collect all IPRs for ozone would provide some very basic process analysis information on the formatio of ozone during a simulation.

16.2 Integrated Reaction Rate Analysis

The second major component of process analysis is IRR analysis. It is applied to investigate gas-phase chemical transformations that are simulated in the model. Its primary use to date has been to help explain how ambient ozone is formed in the chemical mechanisms that are used in photochemical models (e.g., Jeffries and Tonnesen, 1994; Tonnesen and Jeffries, 1994). Thus, the CMAQ implementation of IRR analysis currently addresses only gas-phase reactions. Nevertheless, the concepts should be adaptable to the modules simulating aerosol formation and aqueous chemistry as well, and this is an area for future enhancement in the CCTM. The remainder of this section describes how the IRRs are calculated and generated in the CMAQ system.

16.2.1 Computation of Integrated Reaction Rates

As described in Chapter 8, the simulation of atmospheric chemistry is a key component of a photochemical air quality model. The operator splitting techniques that are used in Eulerian photochemical models typically result in a set of nonlinear, coupled, ordinary differential equations (ODEs) that describe chemical interactions in the gas-phase. Solutions to these ODEs are obtained using numerical solvers to compute species concentrations as a function of time. Again, these computed concentrations show only the net effect of chemical transformations. As has been done for physical processes, a technique has been developed to provide quantitative information on individual chemical transformations (Jeffries and Tonnesen, 1994). Since the technique involves integrating the rates of the individual chemical reaction, the method is termed integrated reaction rate analysis.

As was noted in section 8.3.1, the mathematical expression for the rate of a chemical reaction takes one of the forms of equation set 8-3. The reaction rate is used to compute the change in species concentration that is caused by the reaction. Mathematically, this can be expressed as follows:

$$M_l(t+\Delta t) = M_l(t) + \int_t^{t+\Delta t} r_l \, \mathrm{d}t \ , \tag{16-6}$$

where M_l refers to the integrated reaction rate (IRR) for reaction l, Δt is the model synchronization time step used by the chemical solver, and r_l is the rate of reaction l corresponding to one of the forms of equation set 8-3. The value of M_l represents the total throughput of the reaction, and can be used with the appropriate stoichiometry to determine the amount of an individual species that is produced or consumed by the reaction. For example, assume the IRR for the reaction $A + B \rightarrow 2C$ is 20 ppb for a given time period. Then, the amount of A and B consumed in that time period by this reaction is 20 ppb, and correspondingly, the amount of C produced is 40 ppb. Further, the net change in a species concentration due to all chemical reactions is equivalent to the sum of all its production terms less the sum of all its loss terms. As a consequence, the contribution of each reaction to the change in concentration of any species is directly available from the IRRs. With this information, it is possible to identify the important chemical pathways that affect species concentrations and thereby unravel the complex chemical interactions that are being simulated.

As described in Chapter 8-4, the chemistry solvers used in air quality models typically employ marching methods that compute species concentrations at the end of a time step given the concentrations at the beginning of the step. Since the solvers adjust the time steps to maintain stability and accuracy, the reaction rates should not vary too greatly over a given time step. As a consequence, it is possible to use a fairly simple numerical integration technique to compute the IRRs. The technique used in the CCTM is the same the one used by Jeffries and Tonnesen (1994) -- the trapezoid rule. With this method, the IRRs are computed as follows:

$$M_l(t+\Delta t) = M_l(t) + \frac{1}{2}[\, r_l(t) + r_l(t+\Delta t)] \ . \tag{16-7}$$

Thus, the IRRs are simply computed from the values of the reaction rates at the beginning and the end of each chemistry integration time step. As the chemistry solver marches through time, the variable M_l accumulates the IRRs over the simulation period. Although an IRR could be accumulated for the entire simulation, more information can be gained on how the mechanistic processes vary with time if the accumulated IRRs are periodically output and the value of M_l is reset to zero. In the CCTM, the IRR output is synchronized with the outputs for the concentration fields and the integrated process rates. Thus, just like the IPRs, the IRRs that are output represent the integral of the reaction rates over the output time interval.

16.2.2 Example IRR Analyses

Most IRR analysis performed to date has been devoted to studying mechanistic processes that affect tropospheric ozone formation. One method that has been used involves analyzing two important, interacting cycles: the OH radical cycle and the NO_x oxidation cycle. This section contains a brief discussion of these cycles and other important chemical parameters to illustrate how integrated reaction rate analysis can be used to understand different chemical pathways. For more comprehensive discussions, the reader is referred to Jeffries (1995), Jeffries and Tonnesen (1994), and Tonnesen and Jeffries (1994).

Ozone is formed in the atmosphere via the photochemical cycle

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{R1}$$

$$O(^3P) + O_2 \rightarrow O_3 \tag{R2}$$

$$NO + O_3 \rightarrow NO_2 . \tag{R3}$$

If these were the only reactions taking place in the atmosphere, an equilibrium condition would be established that would determine the ozone concentration. These levels are almost always lower than what is observed in the atmosphere because of other interactions (Seinfeld, 1998). The presence of free radicals can alter the ozone production rate through the following reactions that are competitive with R3:

$$HO_2 + NO \rightarrow NO_2 + OH \tag{R4}$$

$$RO_2 + NO \rightarrow NO_2 + RO . \tag{R5}$$

In these reactions, NO_2 is produced in reactions that do not consume ozone, thereby introducing a process by which ozone can accumulate. Furthermore, these reactions are radical propagation reactions since a hydroxyl radical (OH) is produced from the hydroperoxy radical (HO_2) and an alkoxy radical (RO) is produced from an alkylperoxy radical (RO_2). These product radicals are then available to participate in other reactions, some of which lead to the regeneration of the peroxy radicals. Thus, the production of ozone can be viewed as an autocatalytic process since O_3 can be produced without the loss of its precursor NO_2. In the atmosphere, however, ozone production is limited by termination reactions that remove either radicals or NO_2 from the system.

The ozone formation process has been represented by means of a schematic diagram, shown in Figure 16-3a, that consists of two interacting cycles (Jeffries, 1995). The top portion of the figure is the OH reaction cycle which consists of the three principal categories of reactions involving radicals: initiation, propagation, and termination. Radical initiation reactions are almost always photolytic reactions that generate “new” radicals. Examples include the photolysis of formaldehyde, hydrogen peroxide and ozone . Radical propagation reactions include reactions such as R4 and R5 in which NO is converted to NO_2 but no radicals are lost. Many reactions in which organic compounds are oxidized also propagate radicals. The termination reactions remove radicals through the formation of stable products. The bottom portion of Figure 16-3a represents the NO_x oxidation cycle. As with the radical cycle, processes in this cycle are classified as either initiation, propagation, or termination. The initiation process for NO_x corresponds to emissions of NO_x, and the termination process corresponds to reactions in which NO_x is converted to stable products. The NO_x cycle is connected to the radical cycle by means of the propagation steps that convert NO to NO_2.

One form of an IRR analysis that can be conducted involves using the IRRs to develop quantitative information about the various initiation, propagation, and termination processes. Figure 16-3b shows a cycle diagram similar to Figure 16-3a in which the IRRs have been used to compute the numerical values that are shown. These values include net throughput for several parameters that serve to further characterize the state of the reacting system. For example, the fraction of OH that is regenerated by the chemical reactions (0.776 in Figure 16-3b) can be determined from the amount of OH that reacts (142.7 ppb) and the amount that is re-created (110.8 ppb). This is directly related to the OH chain length parameter (4.46) which corresponds to the average number of times each new OH is cycled until it is removed from the system. An analogous chain length parameter (5.13) can be calculated for the NO_x oxidation cycle in the form of the NO chain length. The longer these chain lengths, the greater the potential for O_3 formation per unit of NO_x emissions. Other parameters such as the “NO oxidations per VOC consumed” $[(NO \rightarrow NO_2)/VOC = 1.71]$ and “O_3 produced per O^3P generated by NO_2 photolysis” $([O_3]_p/[O^3P] = 0.951)$ further quantify the relative efficiency of ozone production, the former being particularly useful in providing a measure of the reactivity of the organic compounds.

These types of analyses are particularly useful for comparing model results that are obtained using different chemical mechanisms or that are obtained at different locations with the same chemical mechanism. Other types of IRR analyses can provide other information as well. For example, IRRs have been used to allocate the total production of O_3 to the individual VOCs, to examine individual characteristics of various chemical mechanisms such as yields of radicals from different organics, and to quantify other entities such as the production and loss of odd-oxygen (O_x), which can serve as surrogate for tracking the formation of ozone (Jeffries and Tonnesen, 1994; Tonnesen and Jeffries, 1994). It can be expected that many other types of IRR analyses will be developed, especially as newer and possibly more complex chemical mechanisms are developed and used in models.

16.2.3 Implementation of IRR Analysis the CMAQ system

As described in Chapter 8, the CMAQ system is designed to treat chemical mechanisms in a generalized manner. Since a specific chemical mechanism is not embedded in the CCTM, a comparable generalized method is needed to link IRR analysis with the chemical mechanism.

The technique that has been incorporated in the CMAQ system is one that provides the user with the capability to formulate and then generate particular chemical parameters of interest. Presumably, these parameters would be chosen to reveal special properties of the mechanism and/or to be used in generating photochemical cycle diagrams such as Figure 16-3b. To illustrate, a special PACP command file has been prepared for the RADM2 mechanism. For reference, a listing of the RADM2 mechanism is contained in Exhibit 16-2, and the reader is referred to the Models-3 User Manual for a detailed explanation of the mechanism format. For purposes of the discussion that follows, it is sufficient to note that reaction labels are enclosed in "<" and ">" and precede each reaction, and that the reactants and products in each reaction are model species. Both the reaction labels and the species names will be referenced in PACP commands.

Table 16-2 lists the chemical parameters that are produced in this example IRR analysis for the RADM2 mechanism. Most of these parameters could also be generated for other chemical mechanisms, although the specific calculations that would have to be performed would necessarily differ because of differences in the mechanisms. The parameters in Table 16-2 are computed as simple, linear combinations of the IRRs that are calculated for each chemical reaction. The domain controls that are specified for the integrated process rate outputs apply to IRR outputs as well. Thus, both the IPR and IRR data will be generated for the same domain and written to output files at the same time intervals. Similarly, the IRR output files are standard Models-3 IO/API gridded files, and can be used with the standard Models-3 visualization tools. In addition, a special visualization tool that can generate "default" cycle diagrams similar to Figure 16-3b is available and is described in Models-3 User Manual (EPA, 1998). Note, however, that the IPR and IRR outputs are written to separate files.

One of the advantages of generating IRR data in the form of chemical parameters is that the output file storage requirements can often be minimized. Note that there are fewer IRR parameters in Table 16-2 than there are species in most mechanisms. The major disadvantage to this approach is that new or different parameters cannot be computed without rerunning a model simulation. As a consequence, the CMAQ implementation of IRR analysis also contains the option to capture the complete set of IRRs rather than chemical parameters when a model is run. With this option, one IRR is generated for each chemical reaction, and these IRRs can then be manipulated in postprocessing routines to form any particular chemical parameter of interest. Thus, it would be anticipated that the chemical parameters such as those in Table 16-2 would be generated in fairly routine model applications, whereas IRRs for each reaction would be generated for exploratory analyses. The form of the outputs is controlled by the PACP commands that are described next.

16.2.4 Use of the PACP to set up an IRR Analysis

As with IPR analysis, the IRR outputs that are generated by the CCTM are controlled by commands and special operators that are processed by the PACP. The global commands that were described in the IPR section also apply to the IRR output. Thus, family names created with the DEFINE FAMILY may also be used with several of the IRR commands and operators.

Before describing how the commands are used to construct an IRR analysis, a brief description of each IRR command and operator is first presented. These are divided into three groups: IRR global definitions, IRR operators and IRR output commands. Again, the same syntax conventions are used, i.e., PACP keywords and symbols are in bold type, user supplied values are in normal type, alternative inputs are separated by vertical bars, and completely optional inputs are enclosed in braces.

IRR Global Definitions:

IRR_TYPE = FULL|PARTIAL|NONE;

> The IRR_TYPE command defines the type of IRR analysis. With the type set to FULL, IRRs for each reaction will be calculated and written to the IRR output file, and all other IRR commands will be ignored. IRR_TYPE set to PARTIAL indicates that the IRR commands following this command are to be processed to produced user defined IRR outputs. Type set to NONE causes all other IRR commands to be ignored and no IRR output to be generated. If the command is omitted, type PARTIAL is assumed.

DEFINE CYCLE cyclename = species_1**;**

> The DEFINE CYCLE command is used to compute the net of all chemical production and loss of a species involved in more than one cyclical reaction set. Thus, this quantity is computed by summing the IRRs for all reactions in which a species is consumed, and then subtracting that sum from the sum of the IRRs for all reactions in which the species is produced. The “cyclename” is a user defined name that must be unique, and can be referenced in subsequent IRR_OUTPUT commands.

DEFINE RXNSUM sumname = {±}{c_1*****}<rxlabl_1> { ± {c_2*****} <rxlabl_2> ± ...}**;**

> The RXSUM command is used to compute a linear combination of IRRs for individual reactions that can then be referenced in a subsequent IRR_OUTPUT command; “sumname” is user defined and must be unique. The linear combination of IRRs is defined according to the expressions following the equal signs that specify the reaction IRRs to sum. The “rxlabl_i” is the reaction label that is used by the generalized mechanism to identify each reaction and is enclosed in “<” and “>”. The “c_i” are optional numerical coefficients that default to one if not specified.

IRR Output Operators:

PROD[species$_1$**]** {**FROM[**species$_2$**]** {**AND|OR [**species$_3$**]** }}

The production operator (PROD) is used to compute the total production of a species by summing the IRRs of all reactions in which species$_1$ appears as a product. The optional qualifiers FROM, AND, and OR restrict the sum to include only those reactions in which species$_2$ and/or species$_3$ are reactants; “species$_1$" can be any gas-phase mechanism species or a family of gas-phase species that was defined using the DEFINE FAMILY command as described in the IPR section; “species$_2$" or species$_3$" may also be the keyword HV to restrict the selection to photolytic reactions.

NETP[species$_1$**]** {**FROM[**species$_2$**]** {**AND**|**OR [**species$_3$**]** }}

The net production operator (NETP) is very similar to the production operator PROD since it is used to compute the production of a species. Whereas the PROD operator includes every reaction in which species occurs as a product, the NETP operator includes only those reactions in which the net production of species$_1$ is greater than zero. Thus, if species$_1$ appears as both a reactant and a product with equal stoichiometry in a reaction, the PROD operator will include it but the NETP operator will not. This operator is useful for getting the net production of a family, for example, by eliminating those reactions in which the net effect of the reaction on the family concentration is zero. The qualifiers FROM, AND and OR restrict the inclusion of reactions to those in which species$_2$ and/or species$_3$ are reactants.

LOSS[species$_1$**]** {**AND**|**OR [**species$_2$**]** }

The loss operator (LOSS) is used to compute the total loss of a species by summing the IRRs of all reactions in which species$_1$ appears as a reactant. The optional qualifier AND restricts the sum to include only those reactions in which both species$_1$ and species$_2$ are reactants. Similarly, the OR qualifier includes all reactions in which either “species$_1$" or “species$_2$" appears as a reactant. The “species$_1$" or “species$_2$" can be any gas-phase species in the mechanism, a family name that includes only gas-phase mechanism species, or the keyword HV to restrict the selection of reactions to those that are photolytic.

NETL[species$_1$**]** {**AND**|**OR [**species$_2$**]** }}

The net loss operator (NETL) is very similar to the loss operator since it is used to compute the loss of a species. However, it includes only those reactions in which there is a net loss of "species_1" and/or "species_2" . Thus, if species_1 appears as both a reactant and a product with equal stoichiometry in the reaction, the NETL operator will not include it in summing the loss of that species, whereas the LOSS operator will include the IRR for that reaction. This operator is useful for getting the net loss of a family of species.

NET[species_1**]**

The net operator (NET) is very similar to the CYCLE definition since it gives the net of the production and the loss of a species for all reactions in which "species_1" appears either as reactant or a product; "species_1" may be any gas-phase, mechanism species or any family consisting wholly of gas-phase mechanism species.

IRR Output Commands:

IRR_OUTPUT irrname = {c_1*****}op_1|cyclname{qual_1}|sumname{qual_1}|<rxlabl_1>
{ ± {c_2*****}op_2|cyclname{qual_2}|sumname{qual_2}|<rxlabl_2> + ...}**;**

The IRR_OUTPUT command defines a specific IRR output to be generated during a CCTM simulation. It is constructed by specifying a linear combination of IRR operators, IRR global definitions, or IRRs for specified reactions. Each individual term in the combination must include either one of the five IRR operators just described (i.e., op_i), a cycle name, a reaction sum name, or a reaction label enclosed in "greater than" and "less than" signs. The optional qualifiers (qual_i) for cyclename or reaction sum name can be either POSONLY or NEGONLY. With these qualifiers, the defined quantity is included as a term only when it is positive or negative, respectively. If the name is not qualified, the quantity is included regardless of sign. The numerical coefficients for each term (c_i) are assumed to be one unless they are explicitly included. The irrname that is supplied by the user will be assigned as the variable name in the IO/API IRR output file.

DESCRIPTION = 'description'**;**

The description command is provided to allow the user to specify a long description of the output variable that will be included on the

IO/API IRR output name. If a description is not specified for an IRR_OUTPUT variable, the irrname (or short name) will be used in the output file. If the description command is used, it should be located immediately following the IRR_OUTPUT command to which it applies.

Before describing how these commands are actually used, some additional comments are warranted. First, the specification of any particular IRR output might be accomplished in several different ways. For example, the net production of a species could be obtained using a CYCLE definition, a RXNSUM definition, a NET operator, or simply specifying the appropriate sum of IRRs directly in the IRR_OUTPUT command (i.e., via reaction labels). Although the user is free to choose any particular approach, some computational efficiencies may be achieved by using the CYCLE and RXNSUM definitions. The CCTM has been constructed to compute these quantities just once, and then use them whenever they are referenced in an output command. Conversely, operator quantities are recomputed every time they are referenced. Thus, it is more efficient to use the RXNSUM and CYCLE commands when they can be referenced several different times in IRR_OUTPUT commands. Second, the NETP and NETL operators are probably most useful for computing the production and loss of species families. When these operators are used, a reaction is not included in the sum if there is no net loss or production of a family member in the reaction. Thus, all reactions are eliminated from the computations when a member of a family is formed from another member of the same family and there is no net impact on the family concentration. Finally, the sign conventions employed in the CMAQ process analysis need to be defined. IRRs for individual chemical reactions are always positive. Since IRRs can be subtracted when computing CYCLE, RXNSUM, and NET quantities, the result can be either positive or negative. The production and loss operators always produce positive values, however, since individual IRRs are always summed in their computation.

To illustrate how these PACP commands are used to generate IRR output data, two examples are presented. The first illustrates how to capture IRRs for each reaction. The second demonstrates how PACP commands are used to compute the special chemical parameters in Table 16-2 for the RADM2 chemical mechanism.

Exhibit 16-3 contains the PACP commands for the first example that corresponds to a full IRR analysis since IRRs will be calculated for each and every reaction. This option is invoked by the first command that specifies that the IRR analysis type is FULL . Since no OUTPUT_DOMAIN command is present, the IRR outputs will be generated for every cell in the modeling domain.

Exhibit 16-4 shows the PACP commands for the example IRR analysis that has been set up for the RADM2 chemical mechanism. In a PACP command file, all lines that start with an exclamation point (!) in the first column are comments. To facilitate the discussion below, comment lines have been used to block the IRR commands into special groups. The first four groups contain global commands or definitions. All blocks after the first four contain the IRR commands that generate the particular parameters listed in Table 16-2.

The commands in the first group simply define the type of IRR analysis and the domain for which the IRR outputs are to be generated. The second group includes family definitions. These commands are of the same form as described for IPRs. The remaining two groups of commands define chemical cycles and reaction sums that are subsequently referenced in IRR_OUTPUT commands. As noted above, the cycle commands give the net production or loss of a species by all chemical reactions. Several of the reaction sums that are defined here are also cycles in that they generate the net effect of a few reactions on the production or loss of a few particular species. Most of the others are used to define special quantities. For example, the defined RXNSUM newMO2 in Exhibit 16-4 corresponds to the production of new MO2, where new refers to an initiation reaction for the radical MO2. As is apparent from the IRR_OUTPUT commands in the subsequent blocks, the cycle and reaction-sum names are referenced fairly frequently.

All of the remaining blocks of commands in Exhibit 16-4 contain the commands for IRR outputs. Again, one IRR output is generated for each IRR_OUTPUT command, and the outputs that are produced correspond to the chemical parameters listed in Table 16-2. As indicated above, each output is generated by the defined linear combination of predefined cycles, reaction sums, special IRR operators, and/or specified reaction IRRs referenced by reaction label. It should be evident that these commands are mechanism specific and require analysis of the mechanism itself to formulate. Thus, this particular PACP command file would not be applicable to any mechanism other than the RADM2. It should also be apparent that other important chemical parameters could be formulated and generated in an analogous manner. In fact, this command file can be used as the starting point for adding to or modifying some of the selected chemical parameters.

As with IPR outputs, the CCTM will generate the IRR output data in a form comparable to the output concentration files. That is, the data are contained in standard Models-3 IO/API gridded data files. The IRR outputs are linear combinations of individual reaction throughput, and thus have the same units as the gas-phase species concentrations (i.e., ppms). However, it should be remembered that these are throughputs calculated by integrating reaction rates over the output time interval, and not simply abundances at a particular time.

16.3 Conclusion

Process Analysis is a diagnostic method for evaluating the inner workings of a model. Although specific types of techniques have been performed and used in the past, new ways of examining and analyzing process data are likely to be developed and used in the future. As a consequence, the emphasis in the CMAQ implementation of process analysis has been placed on providing easy methods of extracting key process data from the CCTM simulations. The CMAQ implementation also provides tools to allow users to customize their analyses. These tools are designed to be easy to use and not require coding changes to the model.

As noted previously, a process analysis is set up by using the PACP before constructing and running a CCTM simulation. Both IPR and IRR data can be gathered during a simulation, but each are written to separate output files. To collect both sets of output during a single simulation requires that the PACP command file contain both the IPR commands and the IRR commands. Although the IPR and IRR examples have been presented separately, both sets of outputs can be produced with a single file containing both sets of commands. Recall, however, that the OUTPUT_DOMAIN applies to both the IPR outputs and the IRR outputs. Thus, IPR and IRR data cannot be generated for different parts of the domain in the same simulation.

The PACP program performs a substantial amount of error checking. The program will check for the proper syntax of the input commands and perform some logic checking. For example, it checks to make sure that all species referenced in IRR commands are gas-phase mechanism species and that the members of defined families are either all gas-phase species or all aerosol species. As is apparent from Exhibit 16-4, however, the inputs for a comprehensive IRR analysis can be fairly extensive. As a consequence, the PACP produces an output report that summarizes what IRR and IPR outputs are being requested. One of its major functions is to report on the effects of the special IRR operators that are used in the PACP command file. A user may wish to review this report before proceeding to run the CCTM to insure that the desired outputs will be generated. The reader is referred to the Models-3 User Manual (EPA, 1998) for an example output report.

Finally, the default configuration for the CCTM is to omit process analysis outputs entirely. Thus, no process analysis will be generated in this configuration. Any process analysis must be set up in the Science Manager of the Models-3 framework. The reader is referred to the Models-3 User Manual (EPA, 1998) for details on how this is done.

16.4 References

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This chapter is taken from *Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System*, edited by D. W. Byun and J. K. S. Ching, 1999.

Table 16-1.
CCTM Processes and PACP Codes

PACP Code	Process Description
XADV	Advection in the E-W direction
YADV	Advection in the N-S direction
ZADV	Vertical advection
ADJC	Mass adjustment for advection
HDIF	Horizontal diffusion
VDIF	Vertical diffusion
EMIS	Emissions
DDEP	Dry deposition
CHEM	Chemistry
AERO	Aerosols
CLDS	Cloud processes and aqueous chemistry
PING	Plume-in-grid

Note: The following process codes can also be used in the PACP.

XYADV	Sum of XADV and YADV
XYZADV	Sum of XADV, YADV, and ZADV
TOTADV	Sum of XADV, YADV, ZADV, and ADJC
TOTDIF	Sum of HDIF and VDIF
TOTTRAN	Sum of XADV, YADV, ZADV, ADJC, HDIF and VDIF

Table 16-2.
Chemical Parameters Used in Default IRR Analysis

{1} Production of Odd Oxygen (Ox)
{2} Loss of Odd Oxygen (Ox)
{3} Production of NOz from NOx
{4} Production of NOx from NOz
{5} Production of new OH from O1D
{6} Production of new OH other than from O1D
{7} Production of new HO2
{8} Total production of HO2
{9} Production of new RO2
{10} Total Production of RO2
{11} Loss of CO and CH4 by reaction with OH
{12} Production of OH from HO2
{13} Production of NO2 from HO2
{14} Production of NO2 from RO2
{15} Production of PAN and TPAN
{16} Net Production of organic nitrates
{17} Loss of VOCs by reaction with OH
{18} Loss of OH by reaction with organics
{19} Net Production or Loss of HNO3
{20} Loss of HCHO by reaction with OH
{21} Loss of isoprene by reaction with OH
{22} Production of new HO2 from HCHO
{23} Production of HO2 from PAN
{24} Production of HO2 from RO2 and NO
{25} Production of HO2 from RO2 reacting with RO2
{26} Production of RO2 from OH
{27} Production of HNO3 from NO2 reacting with OH
{28} Production of new OH from H2O2
{29} Production of new OH from organic peroxides
{30} Production of OH from HONO
{31} Termination of OH
{31} Termination of HO2
{31} Termination of HO2 by reaction with RO2
{34} Termination of RO2
{35} Termination of RO2 by reaction with HO2
{36} Termination of RO2 by reaction with RO2
{37} Loss of OH by reaction with daughter VOCs

Exhibit 16-1.
Example PACP Command File for IPR Analysis

```
{1} OUTPUT_DOMAIN = LOLEV[1] + HILEV[2];

{2} DEFINE FAMILY NOX   = NO + NO2;

{3} DEFINE FAMILY VOC   =  2.0*ETH + 2.9*HC3 + 4.8*HC5 + 7.9*HC8
                           + 2.0*OL2  + 3.8*OLT +
                           4.8*OLI + 5.0*ISO + 7.1*TOL + 8.9*XYL
                           + 1.0*HCHO + 2.4*ALD;

{4} IPR_OUTPUT NOX;

{5} IPR_OUTPUT VOC;

{6} IPR_OUTPUT O3 = TOTTRAN + CHEM + CLDS;

{7} IPR_OUTPUT ALL = VDIF;

{8} ENDPA;
```

Exhibit 16-2. Listing of the RADM2 Chemical Mechanism

```
REACTIONS [cm]

< P1> NO2          =      O3P    +    NO               # 1.0  /<NO2_RADM88>;
< P2> O3           =      O1D                          # 1.0  /<O3O1D_RADM88>;
< P3> O3           =      O3P                          # 1.0  /<O3O3P_RADM88>;
< P4> HONO         =      HO     +    NO               # 1.0  /<HONO_RADM88>;
< P5> HNO3         =      HO     +    NO2              # 1.0  /<HNO3_RADM88>;
< P6> HNO4         =      HO2    +    NO2              # 1.0  /<HNO4_RADM88>;
< P7> NO3          =      NO                           # 1.0  /<NO3NO_RADM88>;
< P8> NO3          =      NO2    +    O3P              # 1.0  /<NO3NO2_RADM88>;
< P9> H2O2         = 2.0* HO                           # 1.0  /<H2O2_RADM88>;
<P10> HCHO         =      CO                           # 1.0  /<HCHOmol_RADM88>;
<P11> HCHO         =      HO2    +    HO2    +    CO   # 1.0  /<HCHOrad_RADM88>;
<P12> ALD          =      MO2    +    HO2    +    CO   # 1.0  /<ALD_RADM88>;
<P13> OP1          =      HCHO   +    HO2    +    HO   # 1.0  /<MHP_RADM88>;
<P14> OP2          =      ALD    +    HO2    +    HO   # 1.0  /<HOP_RADM88>;
<P15> PAA          =      MO2    +    HO               # 1.0  /<PAA_RADM88>;
<P16> KET          =      ACO3   +    ETHP             # 1.0  /<KETONE_RADM88>;
<P17> GLY          = 0.13*HCHO + 1.870*CO              # 1.0  /<GLYform_RADM88>;
<P18> GLY          = 0.45*HCHO + 1.550*CO + 0.800*HO2  # 1.0  /<GLYmol_RADM88>;
<P19> MGLY         =      ACO3   +     HO2   +    CO   # 1.0  /<MGLY_RADM88>;
<P20> DCB          = 0.98*HO2 +  0.020*ACO3   +   TCO3 # 1.0  /<UDC_RADM88>;
<P21> ONIT         = 0.20*ALD +  0.800*KET + HO2 + NO2 # 1.0  /<ORGNIT_RADM88>;
<  1> O3P + O2 + M =      O3                           # 6.0E-34^-2.3;
<  2> O3P + NO2    =      NO                           # 6.5E-12   @ -120.0;
<  3> O1D + N2     =      O3P                          # 1.8E-11   @ -110.0;
<  4> O1D + O2     =      O3P                          # 3.2E-11   @ -70.0;
<  5> O1D + H2O    = 2.0* HO                           # 2.20E-10;
<  6> O3  +   NO   =      NO2                          # 2.00E-12  @1400.0;
<  7> O3  +   HO   =      HO2                          # 1.60E-12  @ 940.0;
<  8> O3  +   HO2  =      HO                           # 1.10E-14  @ 500.0;
<  9> HO2 +   NO   =      NO2    +     HO              # 3.70E-12  @ -240.0;
< 10> HO2 +   NO2  =     HNO4                     # 1.8E-31^-3.2 &4.7E-12^-1.4;
< 11> HNO4         =      HO2    +     NO2        # 2.1E-27 @ -10900.0 *E< 10>;
< 12> HO2 + HO2    =      H2O2          %3 # 2.20E-13@-620.0  & 1.90E-33@-980.0;
< 13> HO2 + HO2 + H2O =   H2O2          %3 # 3.08E-34@-2820.0 & 2.66E-54@-3180.0;
< 14> H2O2 + HO       =   HO2                           # 3.300E-12  @ 200.0;
< 15> NO  +  HO    =      HONO            # 7.0E-31^-2.6 &1.5E-11^-0.5;
< 16> NO  +  NO  + O2 = 2.0*NO2                         # 3.300E-39 @ -530.0;
< 17> O3  +  NO2   =      NO3                           # 1.4000E-13 @ 2500.0;
< 18> NO3 +  NO    =   2.0*NO2                          # 1.7000E-11 @ -150.0;
< 19> NO3 +  NO2   =       NO     +     NO2             # 2.5000E-14  @ 1230.0;
< 20> NO3 +  HO2   =       HNO3                         # 2.5000E-12;
< 21> NO3 +  NO2   =       N2O5                 # 2.2E-30^-4.3 &1.5E-12^-0.5;
< 22> N2O5         =       NO2    +     NO3     # 1.10E-27 @ -11200.0 *E<21>;
< 23> N2O5 + H2O   =    2.0*HNO3                # 2.00E-21;
< 24> HO  +  NO2   =       HNO3                 # 2.6E-30^-3.2 &2.4E-11^-1.3;
< 25> HO  +  HNO3  =       NO3      %2 #7.2E-15@-785&4.1E-16@-1440&1.9E-33@-725;
< 26> HO  +  HNO4  =       NO2                          # 1.3000E-12 @ -380.0;
< 27> HO  +  HO2   =                                    # 4.6000E-11  @ -230.0;
< 28> HO  +  SO2   = SULF  +  HO2 + SULAER      # 3.0E-31^-3.3 &1.5E-12^0.0;
< 29> CO  +  HO    =       HO2                %1 #1.5000E-13;
< 30> HO           =       MO2    (X 300 SQUARED)       # 28.3^2   @ 1280.0;
< 31> ETH +  HO    =       ETHP   (X 300 SQUARED)       # 1.233E-12^2 @ 444.0;
< 32> HC3 +  HO    =  0.83*HC3P + 0.17*HO2 +  0.009*HCHO  + 0.075*ALD
                  + 0.025*KET                          # 1.59E-11  @ 540.0;
< 33> HC5 +  HO    =     HC5P  +  0.250*XO2             # 1.73E-11  @ 380.0;
< 34> HC8 +  HO    =     HC8P  +  0.750*XO2 + HC8AER    # 3.64E-11  @ 380.0;
< 35> OL2 +  HO    =     OL2P                           # 2.15E-12  @ -411.0;
< 36> OLT +  HO    =     OLTP                           # 5.32E-12  @ -504.0;
< 37> OLI +  HO    =     OLIP  + OLIAER                 # 1.07E-11  @ -549.0;
< 38> TOL +  HO    = 0.75*TOLP + 0.250*CSL + 0.250*HO2
                     + TOLAER                           # 2.10E-12  @ -322.0;
< 39> XYL +  HO    = 0.83*XYLP + 0.170*CSL + 0.170*HO2
                     + XYLAER                           # 1.89E-11  @ -116.0;
< 40> CSL +  HO    = 0.10*HO2  + 0.900*XO2 + 0.900*TCO3
                     + CSLAER                           # 4.00E-11;
<40a> CSL +  HO    =     CSL                            # 0.9*K<40>;
< 41> HCHO + HO    =     HO2     +    CO                # 9.0000E-12;
< 42> ALD +  HO    =     ACO3                           # 6.8700E-12 @ -256.0;
< 43> KET +  HO    =     KETP                           # 1.2000E-11 @ 745.0;
< 44> GLY +  HO    =     HO2  +  2.000*CO               # 1.1500E-11;
< 45> MGLY + HO    =     ACO3    +    CO                # 1.7000E-11;
< 46> DCB +  HO    =     TCO3                           # 2.8E-11;
```

Exhibit 16-2. Listing of the RADM2 Chemical Mechanism

```
< 47> OP1 +  HO    = 0.5*MO2 + 0.500*HCHO +0.500*HO     # 1.0000E-11;
< 48> OP2 +  HO    = 0.5*HC3P + 0.500*ALD + 0.500*HO    # 1.0000E-11;
< 49> PAA +  HO    =     ACO3                           # 1.0000E-11;
< 50> PAN +  HO    =     HCHO + NO3 + XO2 (x 300 sq)    # 6.1650E-13^2  @ 444.0;
< 51> ONIT + HO    =     HC3P    +    NO2               # 1.5500E-11  @ 540.0;
< 52> ISO +  HO    =     OLTP                           # 2.5500E-11  @ -409.0;
< 53> ACO3 + NO2   =     PAN                            # 2.8000E-12  @ -181.0;
< 54> PAN          =     ACO3    +    NO2               # 1.9500E+16  @ 13543.0;
< 55> TCO3 + NO2   =     TPAN                           # 4.7000E-12;
< 56> TPAN         =     TCO3    +    NO2               # 1.9500E+16  @ 13543.0;
< 57> MO2 +  NO    =     HCHO    +    HO2   +    NO2    # 4.2000E-12  @ -180.0;
< 58> HC3P + NO    = 0.75*ALD  +  0.25*KET + 0.09*HCHO  + 0.036*ONIT
                  + 0.964*NO2 +  0.964*HO2              # 4.2000E-12  @ -180.0;
< 60> HC5P + NO    = 0.38*ALD + 0.69*KET + 0.08*ONIT
                  +  0.92*NO2 + 0.92*HO2                # 4.2000E-12  @ -180.0;
< 62> HC8P + NO    = 0.35*ALD + 1.06*KET + 0.04*HCHO
                   + 0.24*ONIT + 0.76*NO2 +   0.76*HO2  # 4.2000E-12  @ -180.0;
< 64> OL2P + NO    = 1.6*HCHO + HO2 + NO2 + 0.20*ALD    # 4.2000E-12  @ -180.0;
< 65> OLTP + NO    =     ALD  + HCHO + HO2 + NO2        # 4.2000E-12  @ -180.0;
< 66> OLIP + NO    =     HO2 + 1.45*ALD +  0.28*HCHO
                  +  0.1*KET   +      NO2               # 4.2000E-12  @ -180.0;
< 67> ACO3 + NO    =     MO2    +     NO2               # 4.2000E-12  @ -180.0;
< 68> TCO3 + NO    =     NO2 + 0.920*HO2 +  0.890*GLY  + 0.110*MGLY
                  + 0.050*ACO3 +  0.950*CO  +  2.000*XO2
                                                        # 4.2000E-12  @ -180.0;
< 69> TOLP + NO    =     NO2 +  HO2 +  0.17*MGLY
                  +   0.16*GLY +   0.70*DCB             # 4.2000E-12  @ -180.0;
< 70> XYLP + NO    =  NO2 + HO2 + .45*MGLY + .806*DCB   # 4.2000E-12  @ -180.0;
< 71> ETHP + NO    =  ALD  +   HO2 +    NO2             # 4.2000E-12  @ -180.0;
< 72> KETP + NO    =  MGLY +      NO2  +      HO2       # 4.2000E-12  @ -180.0;
< 73> OLN  + NO    =  HCHO   +    ALD +    2.0*NO2      # 4.2000E-12  @ -180.0;
< 74> HCHO + NO3   =  HO2    +     HNO3   +     CO      # 6.000E-13   @ 2058.0;
< 75> ALD +  NO3   =  ACO3   +     HNO3                 # 1.400E-12   @ 1900.0;
< 76> GLY +  NO3   =  HNO3    +    HO2 +  2.000*CO      # 6.000E-13   @ 2058.0;
< 77> MGLY + NO3   =  HNO3    +    ACO3    +    CO      # 1.400E-12   @ 1900.0;
< 78> DCB +  NO3   =  HNO3    +    TCO3                 # 1.400E-12   @ 1900.0;
< 79> CSL +  NO3   =  HNO3   +   XNO2  + 0.500*CSL
                   + 0.500*CSLAER                       # 2.200E-11;
< 80> OL2 +  NO3   =  OLN                               # 2.000E-12   @ 2923.0;
< 81> OLT +  NO3  =  OLN                                # 1.000E-11   @ 1895.0;
< 82> OLI +  NO3  =  OLN + OLIAER                       # 3.230E-11   @ 975.0;
< 83> ISO +  NO3  =  OLN                                # 5.810E-13;
< 84> OL2 +  O3   =  HCHO + 0.400*ORA1 + 0.420*CO
                  + 0.120*HO2                           # 1.200E-14   @ 2633.0;
< 85> OLT +  O3   = 0.53*HCHO + 0.500*ALD +  0.33*CO  + 0.20*ORA1
                  + 0.20*ORA2 + 0.23*HO2 +  0.22*MO2 +  0.10*HO
                                                        # 1.3200E-14  @ 2105.0;
< 86> OLI +  O3   = 0.18*HCHO + 0.72*ALD +  0.10*KET  + 0.23*CO  + 0.06*ORA1
                  + 0.29*ORA2 + 0.26*HO2 +  0.14*HO + 0.31*MO2
                  + OLIAER                              # 7.2900E-15  @ 1136.0;
< 87> ISO +  O3   = 0.53*HCHO + 0.500*ALD +  0.33*CO  +  0.20*ORA1
                  + 0.20*ORA2 + 0.23*HO2 +  0.22*MO2 +  0.10*HO
                                                       # 1.230E-14  @ 2013.0;
< 88> HO2 +  MO2  =    OP1                             # 7.700E-14  @ -1300.0;
< 89> HO2 +  ETHP =    OP2                             # 7.700E-14  @ -1300.0;
< 90> HO2 +  HC3P =    OP2                             # 7.700E-14  @ -1300.0;
< 91> HO2 +  HC5P =    OP2                             # 7.700E-14  @ -1300.0;
< 92> HO2 +  HC8P =    OP2                             # 7.700E-14  @ -1300.0;
< 93> HO2 +  OL2P =    OP2                             # 7.700E-14  @ -1300.0;
< 94> HO2 +  OLTP =    OP2                             # 7.700E-14  @ -1300.0;
< 95> HO2 +  OLIP =    OP2                             # 7.700E-14  @ -1300.0;
< 96> HO2 +  KETP =    OP2                             # 7.700E-14  @ -1300.0;
< 97> HO2 +  ACO3 =    PAA                             # 7.700E-14  @ -1300.0;
< 98> HO2 +  TOLP =    OP2                             # 7.700E-14  @ -1300.0;
< 99> HO2 +  XYLP =    OP2                             # 7.700E-14  @ -1300.0;
<100> HO2 +  TCO3 =    OP2                             # 7.700E-14  @ -1300.0;
<101> HO2 +  OLN  =    ONIT                            # 7.700E-14  @ -1300.0;
<102> MO2 +  MO2  = 1.5*HCHO   +    HO2                # 1.90E-13   @ -220.0;
<103> MO2 +  ETHP = 0.75*HCHO   +    HO2 +  0.75*ALD   # 1.40E-13   @ -220.0;
<104> MO2 +  HC3P = 0.84*HCHO + 0.770*ALD +  0.260*KET
                  + 1.000*HO2                          # 4.20E-14 @ -220.0;
<105> MO2 +  HC5P = 0.77*HCHO + 0.41*ALD +  0.75*KET
                  + 1.000*HO2                          # 3.40E-14  @ -220.0;
<106> MO2 +  HC8P = 0.80*HCHO + 0.46*ALD +  1.39*KET
```

Exhibit 16-2. Listing of the RADM2 Chemical Mechanism

```
                  + 1.000*HO2                          # 2.90E-14  @ -220.0;
<107> MO2 +  OL2P = 1.55*HCHO + 0.350*ALD +  HO2       # 1.40E-13   @ -220.0;
<108> MO2 +  OLTP = 1.25*HCHO + 0.750*ALD +  HO2       # 1.40E-13   @ -220.0;
<109> MO2 +  OLIP = 0.89*HCHO + 0.725*ALD +  HO2
                  + 0.55*KET                           # 1.70E-14  @ -220.0;
<110> MO2 +  KETP = 0.75*HCHO + 0.750*MGLY + HO2       # 1.70E-14  @ -220.0;
<111> MO2 +  ACO3 =  HCHO + 0.5*HO2 +  0.5*MO2
                  + 0.50*ORA2                          # 9.60E-13  @ -220.0;
<112> MO2 +  TOLP =  HCHO + 0.17*MGLY + 0.16*GLY
                  +  0.70*DCB  +  2.0*HO2              # 1.70E-14  @ -220.0;
<113> MO2 +  XYLP =  HCHO + 0.45*MGLY + 0.806*DCB
                  + 2.000*HO2                          # 1.70E-14  @ -220.0;
<114> MO2 +  TCO3 = .50*HCHO + 0.445*GLY +  0.055*MGLY
                  + 0.50*ORA2 + 0.025*ACO3 + 0.460*HO2
                  +  0.475*CO  +  XO2                  # 9.60E-13  @ -220.0;
<138> MO2 +  OLN  =  1.75*HCHO + 0.50*HO2 + ALD + NO2  # 1.70E-14  @ -220.0;
<115> ETHP + ACO3 =  ALD + 0.5*HO2 +  0.5*MO2
                  + 0.5* ORA2                          # 3.40E-13  @ -220.0;
<116> HC3P + ACO3 =  .77*ALD + 0.26* KET +  0.5*HO2
                  + 0.50*MO2 +  0.5*ORA2               # 1.00E-13  @ -220.0;
<117> HC5P + ACO3 = 0.41*ALD + 0.75*KET +  0.5*HO2
                  + 0.50*MO2 +  0.5*ORA2               # 8.40E-14  @ -220.0;
<118> HC8P + ACO3 = 0.46*ALD + 1.39*KET +  0.5*HO2
                  + 0.50*MO2 +  0.5*ORA2               # 7.20E-14  @ -220.0;
<119> OL2P + ACO3 = 0.80*HCHO + 0.6*ALD +  0.5*HO2
                  + 0.5*MO2 +  0.5*ORA2                # 3.40E-13  @ -220.0;
<120> OLTP + ACO3 =   ALD + 0.5*HCHO + 0.5*HO2
                  + 0.5*MO2 +  0.5*ORA2                # 3.40E-13  @ -220.0;
<121> OLIP + ACO3 = 0.725*ALD + 0.55*KET +  0.14*HCHO
                  + 0.5*HO2 +  0.50*MO2  + 0.5*ORA2    # 4.20E-14   @ -220.0;
<122> KETP + ACO3 =   MGLY + 0.5*HO2 +  0.5*MO2
                  + 0.5*ORA2                           # 4.20E-14   @ -220.0;
<123> ACO3 + ACO3 =  2.0*MO2                           # 1.19E-12  @ -220.0;
<124> ACO3 + TOLP =   MO2 + 0.170*MGLY + 0.16*GLY
                  +  0.70*DCB  +    HO2                # 4.20E-14   @ -220.0;
<125> ACO3 + XYLP =  MO2 + 0.45*MGLY + 0.806*DCB
                  +   HO2                              # 4.20E-14   @ -220.0;
<126> ACO3 + TCO3 =  MO2 + 0.92*HO2 +  0.89*GLY
                  +  0.11*MGLY + 0.05*ACO3 + 0.95*CO
                  + 2.0*XO2                            # 1.19E-12  @ -220.0;
<139> ACO3 + OLN  =  HCHO +  ALD +  0.5*ORA2
                  +  NO2 +  0.5* MO2                   # 4.20E-14   @ -220.0;
<140> OLN +  OLN  = 2.0*HCHO + 2.0*ALD +  2.0*NO2      # 3.60E-16  @ -220.0;

<127> XO2 +  HO2  =    OP2                             # 7.70E-14  @ -1300.0;
<128> XO2 +  MO2  =    HCHO   +     HO2                # 1.70E-14  @ -220.0;
<129> XO2 +  ACO3 =    MO2                             # 4.20E-14   @ -220.0;
<130> XO2 +  XO2  =                                    # 3.60E-16  @ -220.0;
<131> XO2 +  NO   =    NO2                             # 4.2000E-12  @ -180.0;
<132> XNO2 + NO2  =    ONIT                            # 4.2000E-12  @ -180.0;
<133> XNO2 + HO2  =    OP2                             # 7.70E-14  @ -1300.0;
<134> XNO2 + MO2  =    HCHO   +     HO2                # 1.70E-14  @ -220.0;
<135> XNO2 + ACO3 =    MO2                             # 4.20E-14   @ -220.0;
<136> XNO2 + XNO2 =                                    # 3.60E-16  @ -220.0;
<AE1> TERP + HO    = TERPAER + HO                      # 1.0*K<37>;
<AE1> TERP + NO3   = TERPAER + NO3                     # 1.0*K<82>;
<AE1> TERP + O3    = TERPAER + O3                      # 1.0*K<86>;

endmech
```

Exhibit 16-3. Example PACP Command File for a Full IRR Analysis

```
IRR_TYPE = FULL;
ENDPA;
```

Exhibit 16-4. Example PACP Commands for a Partial IRR Analysis

```
!***********************************************************************
!  Example PACP Command File illustrating Partial IRR Analysis
!***********************************************************************


!=======================================================================
! IRR type and domain commands
!=======================================================================

IRRTYPE = PARTIAL;

OUTPUT_DOMAIN = LOLEV[1] + HILEV[2];


!=======================================================================
! Family Definitions
!=======================================================================
DEFINE FAMILY OX    = O3 + NO2 + 2*NO3 + O3P +O1D + PAN + HNO4 + 3*N2O5 +
                      TPAN + OLN + HNO3 + ONIT;
DEFINE FAMILY NOZ   = PAN + TPAN + HONO + HNO4 + NO3 + N2O5 + ONIT +
                      OLN + HNO3;
DEFINE FAMILY NOX   = NO + NO2;
DEFINE FAMILY VOCA  = OL2 + OLI + OLT + ISO;
DEFINE FAMILY RO2   = MO2 + ETHP + HC3P + HC5P + HC8P + OL2P +
                      OLTP + OLIP + TOLP + XYLP + ACO3 + KETP +
                      TCO3 + XO2 + XNO2;
DEFINE FAMILY VOC   = {CH4 +} CO + ETH + HC3 + HC5 + HC8 + OL2 + OLT +
                      OLI + ISO + TOL + CSL + XYL + HCHO + ALD + KET +
                      GLY + MGLY + DCB;
DEFINE FAMILY dauHC = CSL + KET + GLY + MGLY + DCB + OP1 + OP2 +
                      PAA + PAN + ONIT;



!=======================================================================
! Cycle Definitions
!=======================================================================
DEFINE CYCLE PANcyc  = PAN;
DEFINE CYCLE TPANcyc = TPAN;
DEFINE CYCLE HONOcyc = HONO;
DEFINE CYCLE HNO4cyc = HNO4;


!=======================================================================
! Reaction Sum Definitions
!=======================================================================
DEFINE RXNSUM NO3cyc       = < 17> - < P7> - < P8> - < 18> - < 19>;
DEFINE RXNSUM N2O5cyc      = < 21> - < 22>;
DEFINE RXNSUM H2O2_OHcyc   = < P9> - < 12> - < 13>;
DEFINE RXNSUM HNO3_OHcyc   = < P5> - < 24>;
DEFINE RXNSUM OP1_OHcyc    = <P13> - < 88>;
DEFINE RXNSUM OP2_OHcyc    = <P14> - < 89> - < 90> - < 91> - < 92> -
                             < 93> - < 94> - < 95> - < 96> - < 97> -
                             < 98> - < 99> - <100>{ - <101>};
DEFINE RXNSUM PAA_OHcyc    = <P15> - < 97>;
DEFINE RXNSUM HNO4_HO2cyc  = < P6> + < 11> - < 10>;
DEFINE RXNSUM OP2_HO2cyc   = <P14> - < 89> - < 90> - < 91> - < 92> -
                             < 93> - < 94> - < 95> - < 96> - < 97> -
                             < 98> - < 99> - <100> {- <101>} - <127> -
                             <133>;
DEFINE RXNSUM HOXcyc       = <  7> - <  8>;
DEFINE RXNSUM newMO2       = <P12> + 0.22*< 85> + 0.31*< 86> + 0.22*< 87>;
DEFINE RXNSUM newACO3      = <P16> + <P19> + 0.02*<P20> + < 77>;
DEFINE RXNSUM newETHP      = <P16>;
DEFINE RXNSUM newTCO3      = <P20> + < 78>;
DEFINE RXNSUM PAN_ACO3cyc  = < 54> - < 53>;
DEFINE RXNSUM TPAN_TCO3cyc = < 56> - < 55>;
!DEFINE RXNSUM propRO2_NO   = <67> + 4.05*<68> + 1.5*<126>;

!=======================================================================
! IRR_OUTPUT 1: OX Production
!=======================================================================
```

Exhibit 16-4. Example PACP Commands for a Partial IRR Analysis

```
IRR_OUTPUT OXprod = NETP[OX];

DESCRIPTION = 'OX Production';

!=======================================================================
! IRR_OUTPUT 2: OX Loss
!=======================================================================
IRR_OUTPUT OXloss =  NETL[OX];

DESCRIPTION = 'OX Loss';


!=======================================================================
! IRR_OUTPUT 3: Production of NOZ from NOX
!=======================================================================
IRR_OUTPUT NOZfromNOX =  PANcyc[POSONLY] +
                        TPANcyc[POSONLY] +
                        HONOcyc[POSONLY] +
                        HNO4cyc[POSONLY] +
                         NO3cyc[POSONLY] +
                        N2O5cyc[POSONLY] +
                              < 24> + 0.036*< 58> + 0.08*< 60> +
                        0.024*< 62> +       <132>;
DESCRIPTION = 'NOZ produced from NOX';


!=======================================================================
! IRR_OUTPUT 4: Production of NOX from NOZ
!=======================================================================
IRR_OUTPUT NOXfromNOZ =  PANcyc[NEGONLY] +
                        TPANcyc[NEGONLY] +
                        HONOcyc[NEGONLY] +
                        HNO4cyc[NEGONLY] +
                         NO3cyc[NEGONLY] +
                        N2O5cyc[NEGONLY] +
                             < P5> +       <P21> +       < 51> +
                             < 73> +       <138> +       <139> +
                         2.0*<140>;

DESCRIPTION = 'NOX produced from NOZ';



!=======================================================================
! IRR_OUTPUT 5: Production of new OH from O1D
!=======================================================================
IRR_OUTPUT OHfromO1D = PROD [HO] FROM [O1D];

DESCRIPTION = 'OH produced from O1D';


!=======================================================================
! IRR_OUTPUT 6: Production of new OH other than from O1D
!=======================================================================
IRR_OUTPUT newOH =   0.1*< 85> +  0.14*< 86> +   0.1*< 87> +
                     2*H2O2_OHcyc[POSONLY]  +
                     HNO3_OHcyc[POSONLY]  +
                        HONOcyc[NEGONLY]  +
                      OP1_OHcyc[POSONLY]  +
                      OP2_OHcyc[POSONLY]  +
                      PAA_OHcyc[POSONLY];

DESCRIPTION = 'new OH';


!=======================================================================
! IRR_OUTPUT 7: Production of new HO2
!=======================================================================
IRR_OUTPUT newHO2 =      2.0*<P11> +       <P12> +   0.8*<P18> +
                             <P19> +  0.98*<P20> +       <P21> +
                             < 74> +       < 76> +  0.12*< 84> +
                        0.23*< 85> +  0.26*< 86> +  0.23*< 87> +
```

Exhibit 16-4. Example PACP Commands for a Partial IRR Analysis

```
                        OP1_OHcyc[POSONLY] +
                        OP2_HO2cyc[POSONLY] +
                        HNO4_HO2cyc[POSONLY];
DESCRIPTION = 'new HO2';


!=======================================================================
! IRR_OUTPUT 8: Total Production of HO2
!=======================================================================
IRR_OUTPUT totalHO2 =    2.0*<P11> +       <P12> +   0.8*<P18> +
                             <P19> +  0.98*<P20> +       <P21> +
                             < 74> +       < 76> +  0.12*< 84> +
   {HO2new}             0.23*< 85> +  0.26*< 86> +  0.23*< 87> +
                          OP1_OHcyc[POSONLY] +
                         OP2_HO2cyc[POSONLY] +
                        HNO4_HO2cyc[POSONLY] +

  {HO2propbyOH}        PROD[HO2] FROM  [HO] AND [VOC] +

  {HO2viaRO2_NO}       PROD[HO2] FROM  [NO] AND [RO2] +

  {HO2byRO2_RO2}       PROD[HO2] FROM [RO2] AND [RO2] +

  {otherOH}            HOXcyc[POSONLY];

DESCRIPTION = 'total HO2';



!=======================================================================
! IRR_OUTPUT 9: Production of new RO2
!=======================================================================
IRR_OUTPUT newRO2 =   newMO2  +
                      newACO3 +
                      newETHP +
                      newTCO3 +
                      PAN_ACO3cyc[POSONLY] +
                      TPAN_TCO3cyc[POSONLY];

DESCRIPTION = 'new RO2';



!=======================================================================
! IRR_OUTPUT 10: Total Production of RO2
!=======================================================================
IRR_OUTPUT TotalRO2 = newMO2  +
                      newACO3 +
{newRO2}              newETHP +
                      newTCO3 +
                      PAN_ACO3cyc[POSONLY] +
                      TPAN_TCO3cyc[POSONLY] +

{propRO2_OH}          PROD[RO2] FROM [HO] AND [VOC] +
                             < 30> +   0.5*< 47> +   0.5*<48> +
                             < 50> +       < 51> +

{propRO2_NO}          PROD[RO2] FROM [NO];

DESCRIPTION = 'Total RO2';

!=======================================================================
! IRR_OUTPUT 11: Loss of CO & CH4 by reaction with OH
!=======================================================================
IRR_OUTPUT Loss_CO_CH4 =     < 30> +
                         LOSS [CO];

DESCRIPTION = 'Loss of CO & CH4';


!=======================================================================
! IRR_OUTPUT 12: Production of OH from HO2
```

Exhibit 16-4. Example PACP Commands for a Partial IRR Analysis

```
!=======================================================================
IRR_OUTPUT HO2toOH =  HOXcyc[NEGONLY] +
                      <9> +
                      2.0*H2O2_OHcyc[POSONLY];

DESCRIPTION = 'HO2 to OH';


!=======================================================================
! IRR_OUTPUT 13: Production of NO2 from HO2
!=======================================================================
IRR_OUTPUT NO2fromHO2 = <  9>;

DESCRIPTION = 'NO2 FROM HO2';

!=======================================================================
! IRR_OUTPUT 14: Production of NO2 from RO2
!=======================================================================
IRR_OUTPUT NO2fromRO2 =        < 57> + 0.964*< 58> + 0.92*< 60> +
                          0.76*< 62> +       < 64> +      < 65> +
                               < 66> +       < 67> +      < 68> +
                               < 69> +       < 70> +      < 71> +
                               < 72> +       < 73> +      <131>;

DESCRIPTION = 'NO2 FROM HO2';


!=======================================================================
! IRR_OUTPUT 15: Production of PAN and TPAN
!=======================================================================
IRR_OUTPUT prodPAN_TPAN = PANcyc + TPANcyc;

DESCRIPTION = 'Production of PAN and TPAN';


!=======================================================================
! IRR_OUTPUT 16: Net Production of organic nitrates
!=======================================================================
IRR_OUTPUT netONIT = NET[ONIT];

DESCRIPTION = 'Net production of ONIT';

!=======================================================================
! IRR_OUTPUT 17: Loss of VOCs by reaction with OH
!=======================================================================
IRR_OUTPUT lossOH_HC = LOSS[VOC] AND [HO]    +
                       < 30> + < 47> + < 48> +
                       < 49> + < 50> + < 51>;

DESCRIPTION = 'Loss of HC plus OH';

!=======================================================================
! IRR_OUTPUT 18: Loss of OH by reaction with inorganics
!=======================================================================
IRR_OUTPUT lossOH_INORG = <  7> + < 14> + < 15> +
                          < 24> + < 25> + < 26> +
                          < 27>;

DESCRIPTION = 'Loss of OH with iorganics';


!=======================================================================
! IRR_OUTPUT 19: Net production or loss of HNO3
!=======================================================================
IRR_OUTPUT netHNO3 = NET[HNO3];

DESCRIPTION = 'Net change in HNO3';
```

Exhibit 16-4. Example PACP Commands for a Partial IRR Analysis

```
!=======================================================================
! IRR_OUTPUT 20: Loss of HCHO by reaction with OH
!=======================================================================
IRR_OUTPUT lossHCHO_OH = LOSS[HCHO] AND [HO];

DESCRIPTION = 'Reaction OH HCHO with OH';


!=======================================================================
! IRR_OUTPUT 21: Loss of isoprene by reaction with OH
!=======================================================================
IRR_OUTPUT lossISO_OH = LOSS[ISO] AND [HO];

DESCRIPTION = 'Reaction of ISO with OH';


!=======================================================================
! IRR_OUTPUT 22:  Production of new HO2 from HCHO
!=======================================================================
IRR_OUTPUT newHO2fromHCHO = PROD[HO2] FROM [HCHO] AND [hv];

DESCRIPTION = 'New HO2 from HCHO';


!=======================================================================
! IRR_OUTPUT 23: Production of HO2 from PAN
!=======================================================================
IRR_OUTPUT HO2fromPAN = PAN_ACO3cyc[POSONLY];

DESCRIPTION = 'HO2 from PAN';


!=======================================================================
! IRR_OUTPUT 24: Production of HO2 from RO2 and NO
!=======================================================================
IRR_OUTPUT HO2fromRO2_NO = PROD[HO2] FROM [NO] AND [RO2];

DESCRIPTION = 'HO2 from RO2 and NO';


!=======================================================================
! IRR_OUTPUT 25: Production of HO2 from RO2 and RO2
!=======================================================================
IRR_OUTPUT HO2fromRO2_RO2 = PROD[HO2] FROM [RO2] AND [RO2];

DESCRIPTION = 'HO2 from RO2 and RO2';


!=======================================================================
! IRR_OUTPUT 26: Production of RO2 from OH
!=======================================================================
IRR_OUTPUT RO2fromOH = PROD[RO2] FROM [HO];

DESCRIPTION = 'RO2 from OH';




!=======================================================================
! IRR_OUTPUT 27: Production of HNO3 from OH + NO2
!=======================================================================
IRR_OUTPUT HNO3fromOH_NO2 = < 24>;

DESCRIPTION = 'HNO3 from OH + NO2';

!=======================================================================
! IRR_OUTPUT 28: Production of new OH from H2O2
!=======================================================================
IRR_OUTPUT newOH_H2O2 = 2*H2O2_OHcyc[POSONLY];

DESCRIPTION = 'new OH from H2O2';
```

Exhibit 16-4. Example PACP Commands for a Partial IRR Analysis

```
!=======================================================================
! IRR_OUTPUT 29: Production of new OH from organic peroxides
!=======================================================================
IRR_OUTPUT newOH_OP1 =  OP1_OHcyc[POSONLY] +
                        OP2_OHcyc[POSONLY] +
                        PAA_OHcyc[POSONLY];

DESCRIPTION = 'new OH from OP1 OP2 PAA';


!=======================================================================
! IRR_OUTPUT 30: Production of OH from HONO
!=======================================================================
IRR_OUTPUT newOHfromHONO = HONOcyc[NEGONLY];

DESCRIPTION = 'new OH from HONO';


!=======================================================================
! IRR_OUTPUT 31: OH Termination
!=======================================================================
IRR_OUTPUT OHterm = < 25> + <26> + <27> + < 50> +
                     HNO3_OHcyc[NEGONLY] +
                        HONOcyc[POSONLY];

DESCRIPTION = 'OH Termination';

!=======================================================================
! IRR_OUTPUT 32: HO2 Termination
!=======================================================================
IRR_OUTPUT HO2term =    < 20> + < 27> + <101> +
                     2 *  H2O2_OHcyc[NEGONLY] +
                         HNO4_HO2cyc[NEGONLY];

DESCRIPTION = 'HO2 Termination';







!=======================================================================
! IRR_OUTPUT 33: Termination of HO2 by reaction with RO2
!=======================================================================
IRR_OUTPUT termHO2_RO2 =   OP1_OHcyc[NEGONLY] +
                          OP2_HO2cyc[NEGONLY] +
                           PAA_OHcyc[NEGONLY];

DESCRIPTION = 'HO2 term with RO2';

!=======================================================================
! IRR_OUTPUT 34: RO2 Termination
!=======================================================================
IRR_OUTPUT termRO2 = .036*<58> + .08*<60> + .24*<62> + .03*<68> +
                      PAN_ACO3cyc[NEGONLY] +
                          TPANcyc[POSONLY];

DESCRIPTION = 'RO2 Termination';


!=======================================================================
! IRR_OUTPUT 35: Termination of RO2 by reaction with with HO2
!=======================================================================
IRR_OUTPUT termRO2_HO2 =  OP1_OHcyc[NEGONLY] +
                          OP2_OHcyc[NEGONLY] +
                          PAA_OHcyc[NEGONLY];

DESCRIPTION = 'RO2 Termination with HO2';
```

Exhibit 16-4. Example PACP Commands for a Partial IRR Analysis

```
!=======================================================================
! IRR_OUTPUT 36: Termination of RO2 by reaction with RO2
!=======================================================================
IRR_OUTPUT termRO2_RO2 =    <102> + <103> + <104> + <105> + <106> +
                            <107> + <108> + <109> + <110> + <111> +
                    1.515 * <114> + <115> + <116> + <117> +
                            <118> + <119> + <120> + <121> + <122> +
                    1.030 * <126> + 0.500 * <138> +
                    0.500 * <139>;

DESCRIPTION = 'RO2 Termination with RO2';


!=======================================================================
! IRR_OUTPUTs 37: Loss of OH by reaction with daughter VOCs
!=======================================================================
IRR_OUTPUT dauHC_OH = LOSS [HO] AND [dauHC];

DESCRIPTION = 'OH + daughter HC';


ENDPA;
```

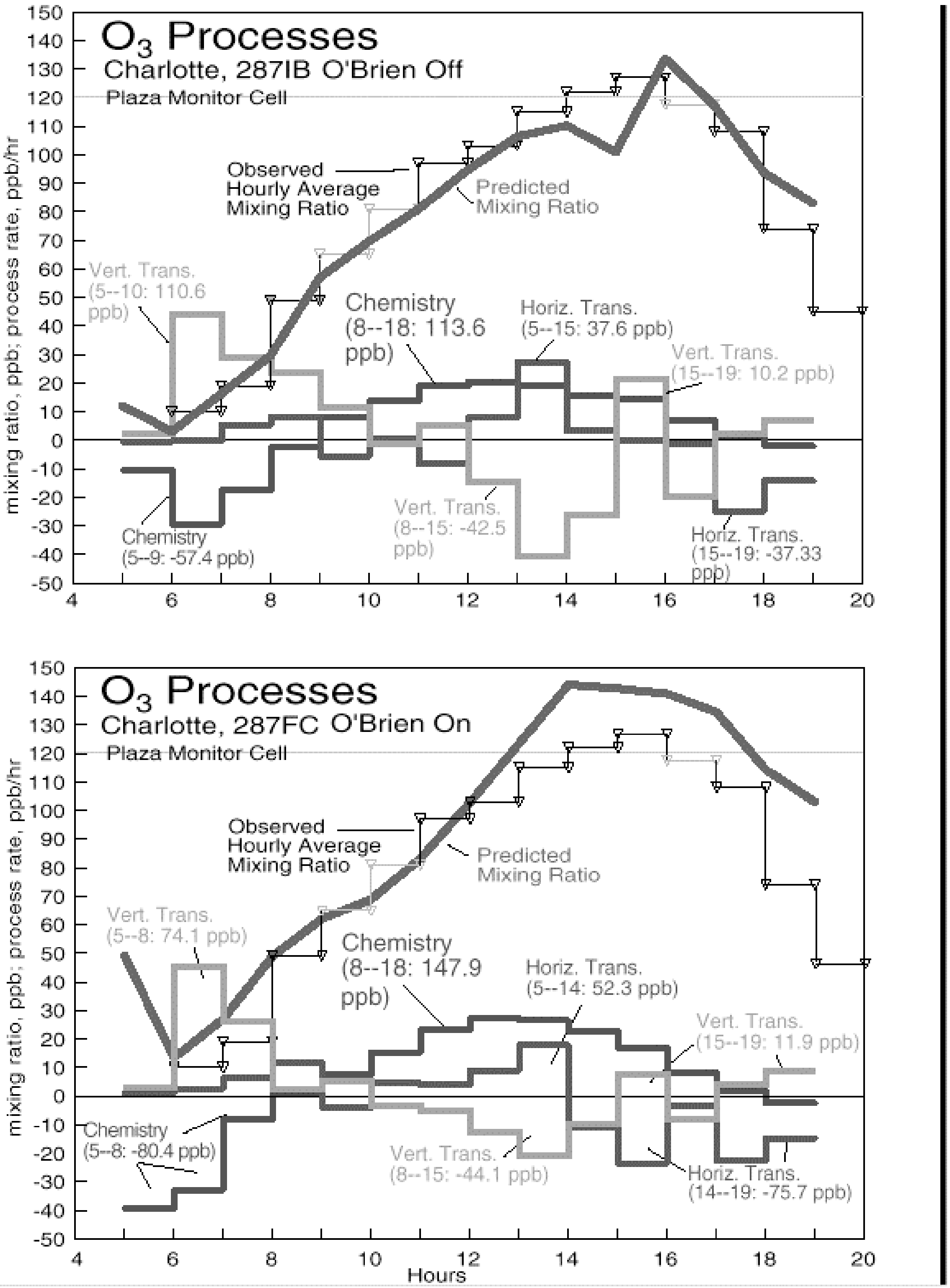

Figure 16-1. Example process analyses showing contributions of individual processes to model predicted concentrations (Source: Jeffries, 1996).

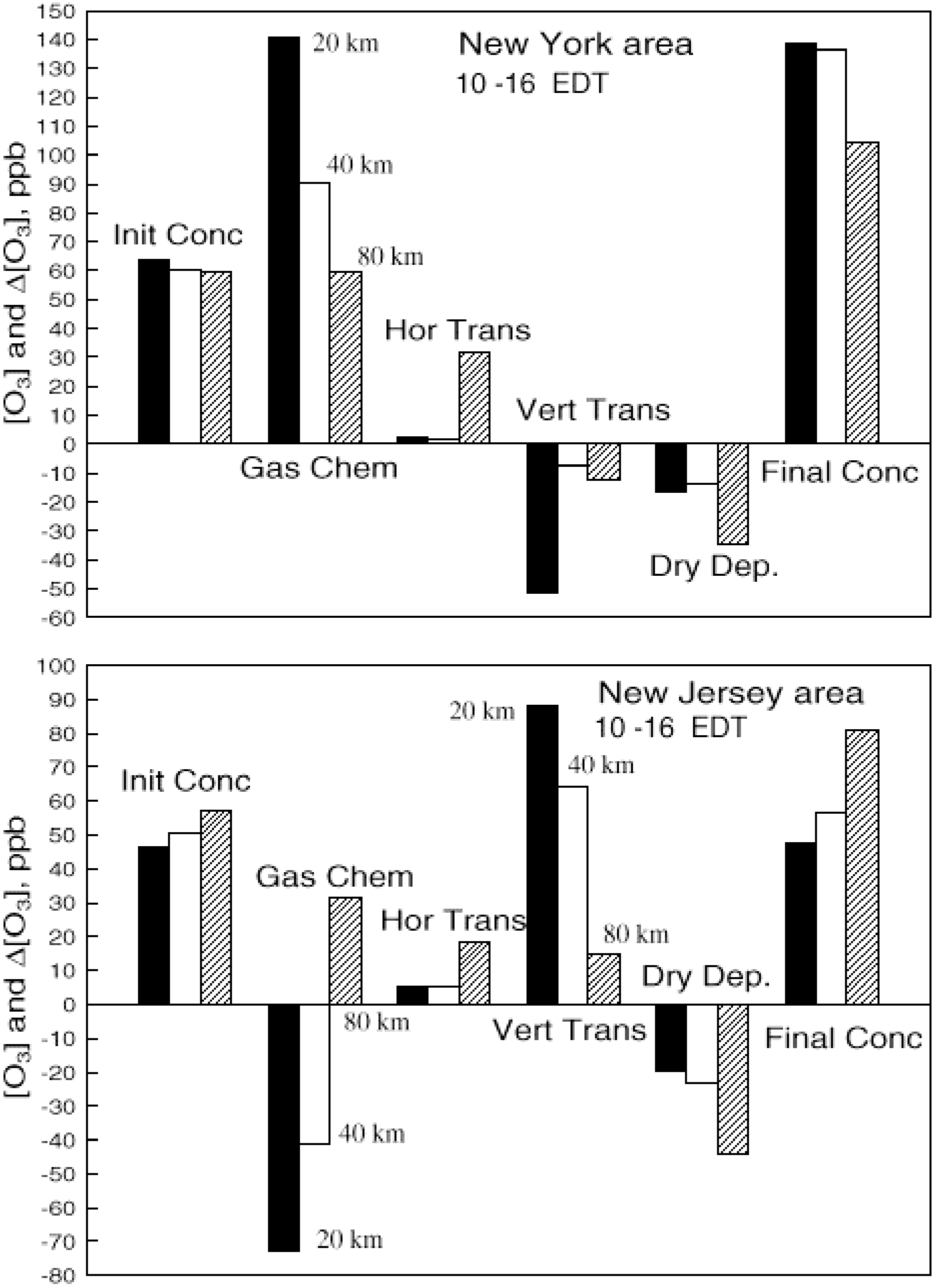

Figure 16-2. Example Process Analyses showing model predicted concentrations and process contributions for different model configurations (Source: Jeffries, 1996).

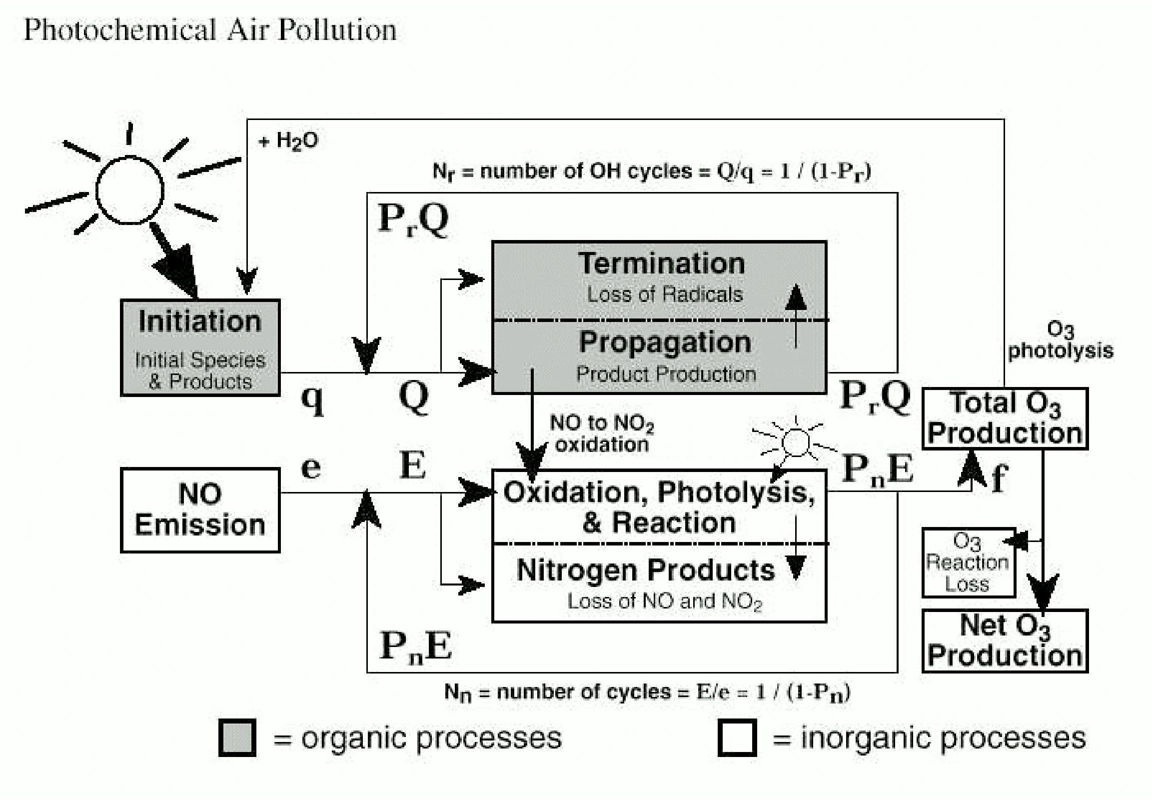

Figure 16-3a. Schematic of OH reaction with NO oxidation cycles (Source: Jeffries, 1996).

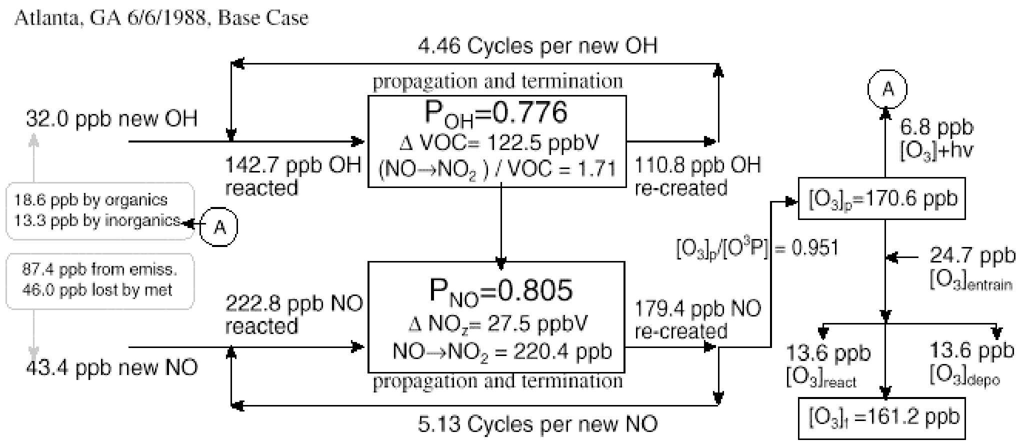

Figure 16-3b. Example photochemical cycle throughputs derived from integrated reaction rates (Source: Jeffries, 1995).