

# AIR QUALITY MODELS

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**Gail Tonnesen<sup>1</sup>, Jay Olaguer<sup>2</sup>, Michelle Bergin<sup>3</sup>, Ted Russell<sup>3</sup>,  
Adel Hanna<sup>4</sup>, Paul Makar<sup>5</sup>, Dick Derwent<sup>6</sup>, and Zion Wang<sup>7</sup>**

<sup>1</sup> University of California at Riverside

<sup>2</sup> Dow Chemical Co.

<sup>3</sup> University of Colorado and Georgia Institute of Technology, Atlanta

<sup>4</sup> MCNC

<sup>5</sup> Environment Canada

<sup>6</sup> Meteorological Office, Bracknell, UK

<sup>7</sup> University of North Carolina at Chapel Hill

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## **INTRODUCTION: AIR QUALITY MODEL ASSESSMENT**

Many variabilities are inherent in different urban airsheds, such as the natural background chemical composition, incident radiation from the sun, and the chemical profile and emission rates of local sources. As is well known, tropospheric ozone is not emitted, but is formed in the atmosphere through a complex, non-linear process involving oxides of nitrogen (NO<sub>x</sub>), different types of volatile organic compounds (VOCs), and sunlight. For this reason, it is difficult to predict how the reduction of differing source emissions may effect the formation of ozone in a given location. Because of the financial commitment required to implement almost any pollution control strategy, the potential impact of any control strategy on the atmosphere must be as fully assessed as possible before one is selected.

Air quality models (AQMs) are computerized representations of the atmospheric processes responsible for air pollution, including ozone formation. The models simulate the atmosphere in varying degree of detail by mathematically representing emissions; initial and boundary concentrations of chemical species; the chemical reactions of the emitted species and of their products; and the local meteorology such as sunlight, wind, and temperature. In this way, an understanding of the atmosphere's chemistry and meteorology is combined with estimates of source emissions to predict possible control strategy effects. AQMs are also an important tool in gaining understanding about the behavior of various compounds in the atmosphere, such as the reactivity of VOCs. Models can also be designed to optimize the costs of control strategy implementation. These models are essential to evaluating control strategies aimed at reducing pollution to meet air quality goals.

While AQMs are the best tools currently available for evaluating proposed ozone control strategies, it is very important to recognize that uncertainties in the model components and in the input data used by the models can have a serious impact on the model predictions. Significant progress has been made on uncertainty analysis, particularly with regard to uncertainty reduction in reactivity-based analysis methods, however some serious concerns remain regarding the implementation of reactivity-based policy.

The following section gives an overview of the general components of AQMs, and discusses the uncertainties in model parameters and inputs and the diagnostic methods used to examine their effects. Then, current models used to examine reactivity are summarized, and model performance evaluation is discussed. Finally, the selection and definition of scenario conditions for reactivity studies are presented.

## MODEL COMPONENTS

### Governing Equations

Meteorological models can be used to solve the equations of hydrodynamics to predict air density ( $\rho$ ), wind velocity vector ( $\mathbf{V}$ ), energy ( $E$ ), and pressure ( $P$ ). The governing equations are provided by the laws of conservation of mass, energy, and momentum, and the ideal gas law. Conservation of mass provides the mass continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{V}\rho = 0 \quad (1)$$

We can neglect molecular diffusion in Equation (1) because advective processes are much larger than molecular diffusive processes in the troposphere and stratosphere.

Because trace species in the atmosphere (excluding water) have concentrations at or below the part per million (ppm) level, they do not affect the solution of the equations for the wind fields. This provides an important simplification for AQMs because it allows the mass continuity equations for trace species to be solved independently of the continuity equations for air. Thus, wind fields generated by meteorological models can simply be read as inputs for an AQM.

For the purposes of AQMs, we can write the mass continuity equation for each trace species as:

$$\frac{\partial C}{\partial t} + \nabla \cdot \mathbf{V}C = 0 \quad (2)$$

where  $C$  represents either the concentration (mass/volume) or number density (molecules/volume) of the trace species. Equation (2) is called the flux form, or conservation form, because it is written in terms of the mass flux ( $\mathbf{V}C$ ).

We can rewrite Equation (2) in the advective form:

$$\frac{\partial C}{\partial t} + \mathbf{V} \cdot \nabla C = -C \cdot \nabla \mathbf{V} \quad (3)$$

where the right hand side of Equation (3) would be zero in pressure based coordinate systems or if divergence and convergence of air masses were considered negligible. We can also define a dimensionless quantity called the mixing ratio of the trace species as:

$$u \equiv C/\rho \quad (4)$$

Substituting Equation (4) into Equation (3) and rearranging provides:

$$\frac{\partial u}{\partial t} + \mathbf{V} \cdot \nabla u = -\frac{u}{\rho} \left( \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{V} \rho \right) = 0 \quad (5)$$

From Equation (1) we see that the right side of Equation (5) is zero, so the flux and advective forms of the continuity equation are equivalent when written in terms of mixing ratio.

We can solve the continuity equation in terms of number density using either the flux form or in the advective form using mixing ratio, whichever is most convenient. Rood (1987) has discussed the advantages of solving the continuity equation in the flux form and advective form. It may be easier to avoid instability and to ensure conservation of mass with number density in the flux form. It is simpler to treat divergence and vertical transport in the advective form because the mixing ratio is not affected by changes in pressure or temperature. Byun (1998a&b) has examined the solution of the continuity equations and conservation of mass using generalized coordinate systems.

The various forms of the advection equation discussed above represent the instantaneous continuity equation. Air motions, however, are generally turbulent. We can write the instantaneous number density and velocity as the sums of mean components and turbulent fluctuation components:

$$C = \bar{C} + C' \quad (6)$$

$$\mathbf{V} = \bar{\mathbf{V}} + \mathbf{V}' \quad (7)$$

and the mean flux can be written as:

$$\overline{\mathbf{V}C} = \bar{\mathbf{V}} \cdot \bar{C} + \overline{\mathbf{V}'C'} \quad (8)$$

Substituting the mean expressions into Equation (2) gives us the mean continuity equation:

$$\frac{\partial \bar{C}}{\partial t} + \nabla \cdot (\bar{\mathbf{V}}\bar{C}) = -\nabla \cdot (\overline{\mathbf{V}'C'}) \quad (9)$$

where the right-hand side of Equation (9) represents dispersion caused by both small and large scale turbulent processes, or eddies. Turbulent dispersion introduces additional unknowns into the continuity equation. Closure theory is the large body of work which attempts to “close” the continuity equation by finding various theoretical or observational relations in turbulence to solve for the additional unknowns. One common approach is to treat eddy dispersion analogously to molecular diffusion by defining an eddy diffusivity coefficient (**D**). More

sophisticated approaches such as transillience theory () attempt to represent the transport between non-adjacent grid cells caused by large scale eddies. Using the eddy diffusivity approach, and dropping the bars for the mean values, we obtain the familiar form of the advection-dispersion equation:

$$\frac{\partial C}{\partial t} + \nabla \cdot \mathbf{V}C = -\nabla \cdot \mathbf{D}\nabla C \quad (10)$$

Finally, trace species can be produced and consumed by chemical reactions, where the production rate ( $P$ ) and loss frequency ( $L$ ) of a given species may be non-linear and also vary as a function of the concentrations of other species within the system. Species concentrations may also be affected by other sink and source terms ( $S$ ) such as emissions and deposition. Thus, an advection-dispersion-reaction (ADR) equation can be written for each species  $i$ :

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \mathbf{V}C_i = -\nabla \cdot \mathbf{D}\nabla C_i + P_i(\mathbf{C}) - L_i(\mathbf{C})C_i + S_i \quad \text{for } i = 1, N \quad (11)$$

where  $N$  is the number of species represented in the photochemical mechanism. Equation (11) produces a system of  $N$  non-linear, partial differential equations (PDE) that are coupled by the species concentration vector ( $\mathbf{C}$ ). Equation (11) cannot be solved analytically, but various numerical methods can be used to obtain approximate solutions. Numerical methods can be divided into two main categories: Lagrangian approaches and Eulerian approaches.

Lagrangian models are often referred to as trajectory models because they simulate photochemistry in parcels of air that follow the wind trajectory. The frame of reference is defined relative to the wind vector, so the advection term drops out of Equation (11). If turbulent dispersion is also ignored, Equation (11) reduces to a system of ordinary differential equation (ODE):

$$\frac{dC_i}{dt} = P_i(\mathbf{C}) - L_i(\mathbf{C})C_i + S_i \quad \text{for } i = 1, N \quad (12)$$

and the problem reduces to the solution of a system of stiff ODEs. This greatly simplifies the numerical solution of the model because accurate, efficient GEAR solvers are available for systems of stiff ODEs (Gear, 1971). These are discussed below. Strengths and weaknesses of Lagrangian models are discussed below.

Eulerian approaches divide the problem domain into a grid of discrete elements or cells. Operator splitting and various numerical methods are then used to solve Equation (11) over the full domain. Components of grid models are summarized below and specific grid models are described below.

## Domain, Grid Structure and Resolution

The first Eulerian AQMs were limited to the urban scale and used grid resolutions on the order of 4 km.. The realization that long-range transport of pollutants and their precursors can impact local control strategies and the need to study regional impacts (as well as rapidly increasing computational resources) led to the use of coarse-grid regional scale models (e.g., RADM, ROM) to define boundary conditions for urban scale AQMs.

More recently, multi-scale models have been developed that nest several levels of increasingly refined grids within a single modeling system (e.g., MAQSIP, CMAQ). The simplest and most commonly used nesting approach is to define a set of uniform, rectangular grids over the model domain. This approach is still impractical to adequately resolve the fine scale structure in species distributions caused by intense point source emissions. Fine scale resolution of point source plumes has been achieved using nested plume-in-grid (PiG) modules.

The simple nested-grid approach used in AQMs is relatively inefficient compared to other approaches widely used in computational fluid dynamics. Sophisticated systems exist for automatically creating and refining irregular grid systems using finite element methods. These approaches have not been widely used in AQMs, although one notable exception, the Urban-to-Regional Multiscale (URM) Model (Odman and Russel, 1991; Kumar and Russell, 1996), is discussed below.. It is possible to use relatively simple (albeit inefficient) rectangular grids in AQMs because the domain of interest is well defined and species concentrations are relatively well behaved (*i.e.*, no sharp fronts typical of ground water problems or shock waves typical of physics problems).

Grid resolution can affect model predictions by introducing artificial dilution caused by averaging point source emissions into coarse grids and by increased numerical dispersion in advection solvers on coarse grids. Increased artificial dilution would be expected to cause lower precursor and O<sub>3</sub> peak levels but higher regional levels (Sillman et al., 1990). It is not clear what effect artificial dilution would have on calculations of reactivity. The response is difficult to predict because VOC/NO<sub>x</sub> ratios and predicted peak O<sub>3</sub> concentrations would likely increase in some cells and decrease in others. Additional investigation is required to determine the effects of grid resolution on model-simulated reactivity applications.

While urban scale domains may be adequate for rapidly reacting VOC, reactivity calculations for long lived species should be simulated on model domains sufficiently large to simulate the chemistry over a period of several days. Simulated incremental reactivity of NO<sub>x</sub> may be especially sensitive to grid resolution and the use of plume-in-grid modules.

## Initial and Boundary Conditions

When a grid-based photochemical model is applied to simulate a pollution episode, it is necessary to specify concentration fields of all the species computed by the model at the beginning of the simulation. These concentration fields are called the initial conditions.

Throughout the simulation it is necessary to specify the species concentrations, called the boundary conditions, in the air entering the three-dimensional geographic domain.

Three general approaches for specifying initial and boundary conditions for urban-scale applications can be identified: 1) use the output from a regional or global scale photochemical model; 2) use objective or interpolative techniques with ambient observational data; or 3) use default background values and expand the area that is modeled and lengthen the simulation period to minimize the uncertainties due to lack of measurements. The third technique is useful for areas sufficiently isolated from significant upwind sources.

In the ideal case, observed data would provide information about the concentrations at the model's boundaries. In practice, however, few useful data are generally available- a result of the difficulty in making measurements aloft and the fact that monitoring stations tend to be in places where air quality standards are expected to be violated. An alternative approach is to use regional or global models to set boundary and initial conditions. This is, in fact, preferred when changes in these conditions are to be forecast. In any event, simulation studies should use boundaries that are far enough from the major source areas of the modeled region that concentrations approaching background values can be used for the upwind boundary conditions.

Simulations of a multi-day pollution episode, beginning at night, when concentrations of ozone precursors are the lowest, minimize the influence of initial conditions on ozone concentrations predicted 2 and 3 days hence. Initial conditions are determined mainly with ambient measurements, either from routinely collected data or from special studies. Where spatial coverage with data is sparse, interpolation can be used to distribute the surface ambient measurements. Because few measurements of air-quality data are made aloft, it is generally assumed that species concentrations are initially uniform in the mixed layer.

The effect of uncertainties in boundary conditions on determinations of reactivity may be very important if the balance of NO<sub>x</sub> in the modeled region depends substantially on the influx of total reactive nitrogen from outside the region. Likewise, the total supply of radicals in the modeled region may depend critically on ozone advected downwards from the upper boundary, as discussed in the chapter on Environmental Conditions. Uncertainties in initial conditions, on the other hand, are not as likely to significantly impact estimates of reactivity compared to uncertainties in boundary conditions.

## **Emissions**

A key use of air quality models is to determine how pollutant concentrations respond to emissions inputs, and accurate emissions inputs are key to good model performance. Emissions inputs are developed to be compatible with the chemical mechanism used in the model, and with the model resolution (both vertically and horizontally). Typically, this would include hourly, spatially gridded estimates of the emissions of CO, NO, NO<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub> and the various primary VOCs in the mechanism.

As discussed in the NARSTO summary, such emissions estimates are developed using emissions models, and like air quality models, they combine descriptions of various processes.

For example, such models may combine estimates of process rates (e.g., the amount of chemical produced in a plant) and emissions factors (e.g., tons of emissions per ton of processed chemical) to produce an estimate of the emissions from a single industrial facility. Another calculation may use the mileage traveled along a road in conjunction with the emissions per mile (accounting for the vehicle ages in the fleet, vehicle speeds and temperature), while a third would resolve the emissions associated with residential living (space heating) with the population distribution. Biogenic emissions are estimated from the type of vegetation and the emissions from that type of plant as a function of sunlight and temperature. Emissions inventories contain considerably more chemical detail than is typically used in condensed photochemical mechanisms so, as discussed below, the VOC emissions are lumped into the appropriate chemical mechanism categories. On the other hand, the available emissions information is often less detailed spatially than a model could use, being gathered on a county or state/province basis in many cases. In this case, the estimates must then be assigned to each grid using an appropriate surrogate (e.g., population weighting). The dominant emissions inventory preparation programs include the Flexible Regional Emissions Data System (FREDS) (Modica *et al.*, 1985) and Emissions Modeling System-1995 (EMS-95) (Wilkinson *et al.*, 1994) and the emissions preprocessor system (EPS).

It is generally believed that emissions are one of, if not the most, uncertain inputs into air quality models. For example, results from the Southern California Air Quality Study suggest that the mobile source VOC exhaust emissions estimates may be low by a factor of two to four (Pierson *et al.*, 1990). Biogenic emissions (of both VOCs and NO<sub>x</sub>) are believed to be very uncertain as well, often suggesting an uncertainty of a factor of three or more (e.g., Geron *et al.*, 1994; Simson *et al.*, 1995). Many other sources would also be susceptible to significant uncertainty, but have been less well studied. On the other hand, emissions of NO<sub>x</sub> should be much better understood; many utility boilers, one of the two dominant sources, have continuous emissions monitors (CEMs, that can also provide SO<sub>2</sub>), and the studies indicate that for the other dominant source, automobiles, NO<sub>x</sub> is better estimated than VOCs (e.g., Pierson *et al.*, 1990). Biogenic NO<sub>x</sub> emissions estimates are still being developed, and may be important in some areas. Given the sensitivity of the air quality models to emissions, these uncertainties appear to be the dominating limitation in our current ability to accurately predict the dynamics of ozone over urban and regional scales.

### **Emissions Processing Methods**

Emissions processing is a critical step in preparing inputs for air quality models. The emissions model converts the point, area, mobile source emissions to hourly emissions of model species in each grid cell. The conversion procedure is completed in a sequence of steps called temporization, speciation, and gridding. In many cases, emissions models have computational requirements that exceed those requirements for the chemistry transport model. Point sources are defined for emissions processing in terms of their county, process, plant, and stack. Area sources represent emissions of a potential type in a specific region. Mobile sources emissions are based on the Vehicle-Miles-Traveled (VMT) which are converted to inventory pollutant emissions using emissions factors created by running MOBILE5 model.

The standard procedures for emission processes include the Emission Preprocessor System 2.0 (EPS 2.0) (EPA, 1993), the Flexible Regional Emissions Data System (FREDS) (Modica et al., 1989), and the Emissions Modeling System -95 (EMS-95, formerly GEMAP) (Radian, 1993). These models utilize a lookup procedure in which at each stage a given processor tries to find the properties of each source (e.g. state/county code, process code) in a cross-reference table, which lists the source properties with an associated profile number until a match is found. The profile number is used as an index into a profile table, which provides conversion factors to be used for the source. The lookup process is computationally slow and consists of many redundant steps. MAQSIP uses a fast emissions modeling system; the Sparse Matrix Operating Kernel Emissions (Coats, 1996; Coats and Houyoux, 1996). SMOKE modeling system formulates emissions modeling operations in terms of the mathematics of operator theory. Controls and projection, speciation, and gridding are represented by sparse matrices. The SMOKE computational approach increases computational efficiency enormously. SMOKE uses BEIS-2 biogenic emissions (Pierce et al., 1990) and interacts with MOBILE5 for the calculation of mobile source emissions. A case study using a five day scenario based on the OTAG 1990 inventory (Houyoux et al., 1997) indicates that SMOKE requires 32 times less CPU resources than required by EMS-95.

## **Meteorological Inputs**

AQMs generally require as inputs the hourly, vertically and horizontally resolved wind fields, as well as hourly temperature, humidity, mixing depth and solar insolation fields. Some AQMs also use the vertical diffusivities, cloud characteristics (liquid water content, droplet size, cloud size, etc.) and rain fall developed from meteorological models. Early studies, as well as many current ones, used objective analysis to interpolate relatively sparse meteorological observations over the modeling domain. Recent AQM applications have found it desirable (because of the sparseness of the data) to use dynamic, or prognostic, meteorological models. Most recently, non-hydrostatic models are being employed. One issue now facing air quality modeling is to assure that the fields developed by the more comprehensive non-hydrostatic meteorological models do not lead to mass inconsistencies when used by the AQMs, and is discussed below. The various types of meteorological models are reviewed by Seaman (this issue), and the discussion here is to highlight the link between the two model types and the effect of various meteorological modeling approaches on air quality model results.

For air pollution modeling, the equations governing air motion are generally assumed to be independent of those describing the chemical pollutant dynamics. This is because for problems like smog, it is assumed that the response of pollutant concentrations to emissions controls is so small that they do not significantly impact radiative transfer and cloud formation, and hence weather. Thus, most current air quality models take the emissions and meteorology as inputs derived by techniques that are separate from the air quality model itself. (The emissions preparation techniques do include meteorological effects.) This is the *off-line* approach (Hansen et al., 1994). When testing control strategies, the meteorological inputs are held fixed to show the response to the emissions changes alone. However, large changes in anthropogenic emissions of some species (e.g., SO<sub>2</sub>) can lead to increased or decreased aerosol formation impacting cloud formation and light transmission, possibly affecting the meteorology. If such an

impact were large, the feedback may be non-negligible. However, studies conducted up to this point where a combined model has been used show relatively little impact (e.g., Jacobson, 1997). A drawback of a combined model is that to test emissions strategies, it is necessary to solve for both the meteorological fields (again) as well as how the pollutant concentration fields respond to emissions changes. Given the sensitivity of the meteorological models to inputs, one could even see that there could be an artificial change in the meteorological fields, thus inhibiting the analysis of the control strategy effectiveness.

## **Photolysis Rates**

Photolysis is one of the most important drivers of tropospheric ozone chemistry. Without photolysis of nitrogen dioxide, there would be no significant production of tropospheric ozone. Likewise, without photolysis of ozone and carbonyls in the troposphere, there would be no production of hydroxyl radicals, and consequently the reactivity of VOCs would be zero. The physical processes which determine the amount of photolysis are: the incidence of sunlight at the top of the atmosphere at a particular zenith angle, molecular absorption of solar radiation by atmospheric constituents, reflection of solar radiation by clouds, aerosols, and by the surface, and scattering of solar radiation by cloud and aerosol droplets and by atmospheric molecules (Madronich, 1987).

Although photolysis is critical to determining the reactivities of organic species near the surface, for current determinations of reactivity in urban airsheds (e.g., Carter, 1994), only a relatively simple procedure involving the assumption of clear skies is used to determine photolysis rates. While this may be sufficient to describe the production of ozone during large smog episodes in urban areas, it is insufficient to describe long-range ozone formation over large regions, where clouds invariably affect the photolysis of atmospheric constituents. Even in urban airsheds, the inclusion of clouds can have significant impacts on VOC reactivity, as has been demonstrated by the study of Bergin et al. (1995), which showed significant differences in single-day reactivities of photoreactive species computed using the EKMA box/trajectory model assuming clear skies compared to multi-day reactivities computed by a 3-D Eulerian model assuming cloudy skies. In general, such significant differences in reactivity did not occur for non-photoreactive compounds.

Another argument for a more advanced treatment of photolysis in models for reactivity is the significant impact of vertical structure in the overhead ozone column on photolysis in the 290 nm to 320 nm (UV-B) wavelength region, due to multiple scattering (Bruehl and Crutzen, 1989). A number of chemical species apart from ozone have significant molecular absorption in the UV-B region, including several aldehydes and ketones (Martinez et al., 1992) and organic nitrates (Roberts and Fajer, 1989).

Sophisticated methods for treating multiple scattering in models, such as the adding method (Lacis and Hansen, 1974) combined with the delta-Eddington or similar two-stream techniques (King and Harshvardhan, 1986; Filyushkin et al., 1994) have been known for many years, but the computational demands of such methods have until now discouraged their on-line use in air quality models, which have traditionally employed table look-up procedures. Even

with the on-line use of advanced methods, there would still be some uncertainty in photolysis rates due to the difficulty of specifying cloud parameters, such as optical depth and scattering asymmetry.

An example of a current model which uses look-up tables to compute photolysis rates is MAQSIP. Photolysis rates in MAQSIP are computed prior to a simulation following Chang et al. (1989). In this approach, clear sky actinic fluxes are pre-calculated using a delta-Eddington radiative transfer model at specific latitudes and selected hours of the day. A climatological ozone profile is prescribed based on a US standard atmosphere and varies by season and latitude. Aerosol profiles are based on a single profile of aerosol number density (Elterman, 1968), whereas surface albedos are based on values given by Demerjian et al. (1980). The calculated clear-sky actinic fluxes are corrected for cloud effects, and the actual model photolysis rates are then linearly interpolated based on the specific time and grid point location. Future versions of MAQSIP may calculate 4-D photolysis rates by solving the radiative transfer equation for the column atmosphere at each grid point and time step.

## **Gas Phase Chemical Mechanisms**

Photochemical mechanisms specify the chemical reactions, product yields and kinetics data needed to simulate the photochemical decay of VOC and the production of secondary pollutants. Much of the computational effort in AQMs is required for the numerical solution of the gas phase chemistry, and both computational and memory costs increase rapidly as the number of chemical species increases. As a result, highly simplified condensed mechanisms have been developed for use in AQMs. A number of “lumping” approaches have been developed to represent the hundreds of VOC found in ambient air using a minimal number of “mechanistic entities”. One example is the carbon-bond method (Gery et al., 1989) in which functional lumping is used to represent all single carbon bonds in dozens of different VOC as a single mechanistic entity called PAR. Other mechanisms such as SAPRC90 (Carter, 1990) and RADM2 (Stockwell et al., 1990) used molecular lumping so that a single mechanistic entity can represent large classes of similar VOC.

The procedures used to convert real world VOC into the mechanistic entities are integral components of the photochemical mechanisms. A consequence of this is that reactivities of the VOC entities simulated in the condensed mechanism may not translate directly to reactivities of real world compounds. This also presents a considerable challenge in comparing VOC reactivities between mechanisms because superficially similar mechanistic entities may have different properties. For example, the “toluene” entity in different mechanisms might have different reactivities not only due to basic kinetics and product yield differences, but also because the “toluene” may represent different subsets of real world aromatic compounds.

One approach is to augment the condensed mechanisms with explicit chemistry for a particular VOC of interest. This circumvents the complex emissions processing that would be needed to represent the target VOC using the mechanistic entities of the different condensed mechanisms. Even when condensed mechanisms represent explicitly the chemistry of a particular primary VOC, the complex chemistry of subsequently produced intermediates is still

represented with the highly condensed chemistry using a small set of generic organic intermediates. Thus, the simulation of the reactivity of particular VOCs on multi-day time scales may require more explicit treatment of the intermediate organic chemistry as well. The effect of simplified or explicit intermediate chemistry could be investigated in multi-day trajectory models to compare condensed and explicit mechanisms. Detailed representation of intermediate products is still limited, however, by incomplete knowledge of the products formed.

The difficulties inherent in the use of condensed mechanisms could be avoided by using explicit photochemical mechanisms. While fully explicit mechanisms do exist (Derwent et al., 1998; Kerr and Calvert, 1985), there remains considerable uncertainty in the photochemistry of many of the VOC represented in those mechanism. Further, these complex mechanisms are not practical for use in grid models due to their high computational cost.

Hales et al. (1993) discussed the use of photochemical mechanisms for reactivity calculations. They listed the following criteria based on mechanism formulation and operational considerations:

- The mechanism should be designed primarily for applications on the urban scale for oxidant-forming scenarios involving a complicated mixture of VOCs.
- The mechanism should be consistent with current, consensus kinetics values such as rate constants and product yields.
- The accuracy of the mechanism should be demonstrated by comparing calculated chemical change with the results of existing smog chamber experiments.
- The mechanism should not resort to mathematical contrivance to explain basic chemical features.
- Sufficient documentation should be available for data sources, development process, operational guidance, and perceived limitations and uncertainties.
- The mechanism should not be so condensed as to ignore significant differences between unlike VOCs.
- Conversely, the mechanism should not be so large as to be overly expensive or computationally demanding.
- Clear and complete information should be available to explain conversion of all real world VOC compounds to the reactive entities of the mechanism.
- The solution algorithm designed to implement the mechanism in a model should be compatible with the above mechanism attributes and capable of representing all necessary chemical detail.
- The mechanism should be implemented in models capable of performing incremental reactivity calculations, including both grid models and trajectory models.

Hales et al. (1993) used these criteria to develop a crude ranking scheme for evaluating photochemical mechanisms. They applied this ranking scheme to the CB4, RADM2 and

SAPRC90 mechanisms and concluded that SAPRC90 rated barely above adequate, while CB4 and RADM2 were slightly less than adequate for reactivity calculations.

Improvements and kinetic updates made to these mechanisms since 1993 may have improved their suitability for reactivity calculations. In addition, several new mechanisms have been developed or are in the process of development. These include the updated SAPRC97, the Regional Acid Chemistry Mechanism (Stockwell et al, 1997), the morphecule mechanism (under development by Harvey Jeffries at UNC) and a new mechanism under development at Environment Canadian (Makar et al., 1998).

An important need for the RRWG is to re-asses the criteria proposed by Hales et al. (1993) for evaluating mechanisms, and to conduct detailed reviews of the more recent mechanisms to determine if they are suitable for use in reactivity studies.

### **Mechanism Inter-Comparisons.**

Comparisons of incremental reactivities using different chemical mechanisms constitute an important component of the uncertainty analysis in the use of reactivity scales (Bergin et al., 1999). Comparisons between mechanisms should be performed in a given model with other model inputs fixed. Such comparisons have been performed in box models (Carter, 1994) and trajectory models (Jeffries and Crouse, 1991). Further, it is necessary to investigate and explain the causes of any differences between mechanisms. Process analysis has been used both to compare mechanisms (Jeffries and Tonnesen, 1994) and to explain differences in incremental reactivities between mechanisms (Jeffries and Crouse, 1991; Bowman and Seinfeld, 1994).

As new mechanisms are developed and used in models to simulate reactivity, it is important that comprehensive comparisons should be performed both to explain differences in the mechanisms routine functioning and in their predictions of incremental reactivity. Such comparisons should be performed for a variety of scenario conditions, for a wide range of VOC and NO<sub>x</sub> emissions levels, and should include comparisons of species concentrations, process diagnostics, and indicator ratios.

### **Clouds and Aqueous Chemistry**

Cloud and fog droplets can affect gas phase species concentrations by attenuating actinic flux as discussed above, or by scavenging species from the gas phase and mediating the formation of secondary products in aqueous or heterogeneous reactions (Jacob, 1998). For example, NO<sub>2</sub> may react on acid/water surfaces to produce HONO. In addition to important effects on PM and water soluble species, aqueous chemistry can affect the gas phase concentrations of O<sub>3</sub>, and radical species (Lelieveld and Crutzen, 1990). Russell and Dennis (1998) summarize treatment of aqueous chemistry in AQMs:

Aqueous phase chemical mechanisms have been implemented in those models where a major focus was acid deposition (e.g., ADOM, RADM, and STEM-II), and are important components of their cloud modules, as well as those following the evolution of aerosols (e.g., Pandis and Seinfeld, 1989; Jacob and Gottlieb,

1989). Operating multidimensional photochemical models that include aqueous phase chemistry have anywhere from 5 to 100 additional species and 10 to 200 additional reactions. In most cases, the emphasis is on sulfur oxidation routes, and relatively small mechanisms are added. In this case, the added reactions account for the transport of hydrogen peroxide, sulfur dioxide and ozone transport to the droplets, and the resulting sulfur oxidation (e.g., Berkowitz, 1991). More detailed aqueous phase chemical mechanisms exist (see Jacob, [NARSTO]), but they have seen limited implementation in photochemical models due to the tremendous increase in computational requirements (McNair, 1995), and minor impact on model predictions for most gas phase species (Jacob; [NARSTO]).

To the extent that heterogeneous chemistry affects radical budgets, it may especially affect the reactivity of VOC species such as HCHO which function primarily as sources of radical initiation. Heterogeneous chemistry is less likely to affect O<sub>3</sub> production on the typically sunny, high pressure days most conducive to high O<sub>3</sub>, but even in that case, night time aqueous chemistry and scavenging may still affect the termination of NO<sub>x</sub> (Dimitropoulou and Marsh, 1997; Dentener and Crutzen, 1993) and the concentrations of other water soluble species used to evaluate the model. While there is large uncertainty in heterogeneous chemistry, its effects should be considered in uncertainty analysis, and clouds and heterogeneous chemistry must be represented if models are used to simulate particulate incremental reactivities

## Aerosol Dynamics Routines

Deterministically following aerosol dynamics, much like gas phase pollutants are in present models, adds an extra set of physico-chemical processes to simulate. These equations account for the continuous distribution of sizes and composition of the aerosol. Physical processes affecting aerosols include coagulation, evaporation, growth by condensation, formation by nucleation, and deposition by sedimentation. In addition, chemical reactions may take place both in, and on, the aerosol particles.

Deterministic simulation of aerosol processes within an air quality model begins with the fundamental equation of aerosol dynamics which describes aerosol transport (term 2), growth (term 3), coagulation (terms 4 and 5), and sedimentation (term 6) (e.g., Friedlander, 1977):

$$\frac{\partial n}{\partial t} = \nabla \cdot \overline{Un} + \frac{\partial I}{\partial v} = \frac{1}{2} \int_0^v \beta(\bar{v}, v - \bar{v}) n(\bar{v}) n(v - \bar{v}) d\bar{v} - \int_0^{\infty} \beta(\bar{v}, v) n(\bar{v}) n(v) d\bar{v} - \nabla \cdot Cn$$

Eq. (13)

where  $n$  is the particle distribution function (which can be a function of time, space, particle size and chemical composition);  $\overline{U}$  is the fluid velocity;  $I$  is the droplet current that describes particle growth and nucleation due to gas-to-particle conversion;  $v$  is the particle volume;  $\beta$  is the rate of particle coagulation; and  $C$  is the sedimentation velocity. One way of modeling the formation and growth of aerosols is done by sectioning the size distribution,  $n$ , into discrete size ranges (e.g., Gelbard and Seinfeld, 1980). Then the size and chemical composition of an aerosol is followed as it evolves by condensation, coagulation, sedimentation, and nucleation. Another

method involves using a functional size distribution, instead of discrete bins (e.g., Whitby *et al.*, 1991). This approach is prompted by the modal structure of the aerosol size distribution. This latter technique is computationally faster, though is less flexible and current implementations do not account for the differences in the thermodynamics and chemistry for aerosols of different sizes. The latter technique has been used in the Regional Particulate Model (RPM) to study aerosol transport and deposition in the United States (Binkowski and Shankar, 1995). Both the discrete and modal approaches require a means to figure out how to “grow” the aerosol due to gas-to-particle conversion. In turn, that calculation requires determining the partial pressure of the condensing species above the aerosol. While this has been done in reasonable detail for inorganic compounds, the theory for mixtures of organic compounds is under development as explained in the section on aerosol reactivity.

### **Vertical Transport and Diffusion**

AQMs attempt to simulate atmospheric processes in the troposphere which extends from the ground up to an average altitude of 11 km. The troposphere consists of the planetary boundary layer (PBL) which is defined as the lower levels of the troposphere that are directly affected by the earth's surface and respond to surface forcing (frictional drag, heat transfer, emissions, terrain flow, evaporation and transpiration) with a time scale of about an hour or less, and the free troposphere which is above the PBL. The PBL thickness varies in time and space, ranging from hundreds of meters to a few kilometers (Stull, 1988). Therefore, a successful AQM must simulate vertical motions both in the PBL and the free troposphere.

In the real atmosphere, wind can be separated in three categories: mean wind, turbulence, and waves. The transport of heat, momentum, moisture, and pollutants is dominated by the mean wind in the horizontal direction (horizontal advection) and turbulence in the vertical (vertical diffusion). Vertical mean wind velocities are usually much smaller than horizontal wind velocities (2 to 10 ms<sup>-1</sup>) and are on the order of millimeters to centimeters per second. Waves are frequently observed in the nighttime boundary layer and are generated locally by mean-wind shear or by mean flow over obstacles. The waves transport little pollutants, moisture and heat.

Turbulence can be visualized as consisting of irregular swirls of motion called eddies. Usually turbulence consists of many different size eddies superimposed on each other. Much of the boundary layer turbulence is generated by forcing due to surface effects. The size of the largest boundary layer eddies is roughly equal to the boundary layer height and is several orders of magnitude greater than molecular diffusivity.

A common approach to study turbulence is to split variables (wind, temperature, etc.) into a mean part and a perturbation part. By applying such a technique to the equations, a number of new terms are created and some of the terms consist of products of perturbation variables and describe the nonlinear interactions between variables. The terms are associated with turbulence in the boundary layer. Unfortunately, after applying the splitting technique, the number of unknowns in the set of equations for turbulent flow is larger than the number of equations. Therefore, the description of turbulence is not closed.

To treat the closure problem, one approach is to use only a finite number of equations and then approximate the remaining unknowns in terms of known quantities. Two major schools of turbulence closure have appeared in the literature: local and non-local closure. Neither methods are exact and can alter the reactivity of the model significantly. For local closure, an unknown quantity at any point in space is parameterized by values and/or gradients of known quantities at the same adjacent point. Local closure thus assumes that turbulence is analogous to molecular diffusion. For non-local closure, the unknown quantity at one point is parameterized by values of known quantities at many points in space. This assumes that turbulence is a superposition of eddies, each of which transport fluid like an advection process.

In Eulerian air quality models, the most widely used local closure method is the K-theory. The concept of K-theory is that turbulence can be simulated in an analogous way to molecular diffusion. It is one of the simplest parameterizations and is used both in the boundary layer and the free troposphere. However, it is valid only over small distances and can be a very poor representation when larger-size eddies are present in the flow. Furthermore, the K-theory can not simulate counter-gradient flows where a turbulent flux flows up the gradient (e.g. from cold to hot). Thus, K-theory is not recommended for use in convective mixed layers (Stull, 1988).

The most frequently used non-local closure method is the Asymmetrical Convective Model (Pleim and Chang, 1992). The Asymmetrical Convective Model simulates the effects of convective plumes by mixing material directly from the surface layer to every other layer in the convective boundary layer. Downward mixing however, occurs only between adjacent levels in a cascading manner and is simulated by a local closure method such as eddy diffusion. With this approach, a more realistic simulation of vertical transport within the convective boundary layer is obtained. However, since this method mixes the same amount of mass to every vertical layer in the boundary layer, it has the potential to remove mass much too quickly out of the surface layer. This method also fails to account for the upward mixing in layers higher than the surface layer. This method is applied only to the convective boundary layer.

Another non-local closure method is the turbulent transilient theory. This method is based upon the turbulent kinetic energy equation and allows large eddies to transport fluid across finite distances before being mixed with the rest of the environment by the smaller eddies. It provides a framework for considering the ensemble-average effect of many eddies of different sizes on the net non-local mixing in the vertical.

Wang (1998) compared three different vertical transport methods: a semi-implicit K-theory scheme (SIK) with local-closure, and asymmetrical convective method (ACM) and turbulent transilient theory (T3) schemes with non-local closure. Of the three schemes, SIK diffused mass most slowly in the vertical direction and maintained the highest amount of ozone precursors in the surface layer. ACM moved mass most rapidly out of the surface layer into other vertical levels. T3 was intermediate between the SIK and the ACM schemes in terms of the rate at which mass was mixed between different layers.

O<sub>3</sub> is a secondary pollutant and the rate of its formation depends on the amount of available precursors in the system. Even with identical initial condition and input files, different vertical

diffusion schemes can affect the rate at which emitted precursors are diffused between vertical layers, which in turn affects the rate and efficiency of O<sub>3</sub> production in each grid cell. As a result, O<sub>3</sub> reactivity in a given cell can differ significantly depending on the scheme used to represent vertical mixing. A grid cell may even change between being NO<sub>x</sub>-limited or VOC-limited by changing the vertical diffusion scheme. The O<sub>3</sub> produced and transported in the model will differ spatially and temporally. In some cases, the differences can be as large as twenty to thirty ppb (Wang, 1998).

The vertical diffusion scheme interacts non-linearly with other physical and chemical processes in the model, and its impact will change from grid cell to grid cell and from case to case. Much more study is needed to better understand its full impact on model simulations of reactivity based substitution strategies.

## Chemical Solvers

Using operator splitting on the chemistry terms, we can reduce the ADR equation to the form:

$$\frac{dC_{i,k}}{dt} = P_{i,k} - LC_{i,k} \quad \text{for } i = 1, N \quad (12)$$

where we have one ordinary differential equation (ODE) for each species  $i$ , and  $N$  is the number of species in the chemical mechanism. Subscript  $k$  represents each of the grid cells air parcels in the model.  $P_{i,j}$  is the rate of production of  $C_{i,j}$  found by summing production in all reactions, and  $L_{i,j}$  is the loss frequency of  $C_{i,j}$ . Equation (1) represents a system of coupled, first-order, non-linear, ODE's for each cell  $k$ . The ODE's are coupled by the terms  $P_{i,j}$  and  $L_{i,j}$ , which are non-linear functions of time and  $C_{1...N}$ .

We can solve for the species mixing ratios independently in each cell of the grid. Solution of the chemistry term requires approximately a factor of ten more time than the other terms in the continuity equation. Thus, the greatest potential for reducing the computational cost of the chemical tracer model (CTM) is in reducing the number of cells needed to represent the domain and in improving the efficiency of the chemical solver.

The time constant of species  $i$ , defined as  $\tau_i = 1/L_i$ , is a measure of how quickly  $C_i$  would tend to approach its equilibrium value. The system of coupled ODEs defined by (12) is *stiff* because the species time constants vary by several orders of magnitude. Systems of stiff ODEs and numerical methods for their solution are discussed in Byrne and Hindmarsh (1987). A system of equations is said to be stiff if the real component of its eigenvalues ( $\lambda$ ) are negative, the ratio of the maximum to the minimum eigenvalue is large, and  $C$  does not undergo rapid oscillations [McRae *et al.*, 1982]. While the time constant and the eigenvalues are not identical, for many short-lived species  $\tau_i \approx \lambda$ , so the stiffness of a system can be approximated as:  $\sigma = \tau_{max} / \tau_{min}$ .

A system is mildly stiff for  $\sigma \approx 10^2$  and stiff for  $\sigma > 10^4$ . Photochemical mechanisms typically produce systems with  $\sigma \approx 10^{11}$  so these systems are very stiff. Stiff systems are very

stable, but they are not efficiently solved using traditional ODE solvers because the time step is limited by the species with the fastest time constants. Non-traditional, computationally expensive methods are required to solve stiff systems.

### **The GEAR Solver**

Gear's method (Gear, 1971) has become the standard against which other methods are compared. The Gear solver is an implicit, backwards difference algorithm in which concentrations from previous time steps are used to predict the concentration at the current time. The algorithm automatically adjusts the size of the time step and the order (the number of previous time steps used) to optimize the solution. The algorithm also estimates the error in the numerical solution at each time step, and the user can specify an error tolerance that constrains the accuracy of the solution.

Gear solvers are computationally expensive. Importantly, much of the computation time is required in the first few minutes of a simulation while the order and time step are increasing. If the species sink and source functions are relatively smooth, the integration proceeds very rapidly, typically with  $\Delta t = 10$  minutes once a high order has been achieved. Thus, the Gear method works well for box models or trajectory models in which chemistry is solved continuously for a single cell.

In a grid models where operator splitting is used, the solver must be restarted at each step of the splitting, and traditional Gear solvers becomes prohibitively expensive due to their high start-up cost. *Jacobson and Turco (1994)* have developed an optimized matrix algorithm that significantly speeds up the Gear solver for vectorized computers. Although this approach is limited to vectorized supercomputers, it has been implemented in a regional scale AQM (Models3) and can be used for critical applications or as a standard to evaluate other chemical solvers.

Saylor and Ford (1996) and Chock *et al.* (1994) suggest that Gear methods can be competitive in terms of speed and accuracy for global modeling where the advection time step is on the order of one hour (as opposed to about 10 minutes for urban and regional scale AQMs). Sandu *et al.* (1997) further investigated chemical integrators and found that optimized Gear-type solvers performed best, when considering both accuracy and computational effort, again using chemical integration steps of one hour. This suggests that if one can use large time steps, the advances in optimized Gear-type solvers make that approach very attractive as compared to the hybrid and QSSA solvers currently being used in a variety of models. This may suggest that nested models may benefit from using one type of solver (e.g., Gear-type) for the coarse mesh calculations where the time step may be large, and less accurate, more efficient methods (discussed below) for the fine mesh.

### **Lower Accuracy Methods**

Accuracy tests of both the chemical kinetics solvers and the transport algorithms indicate that the methods used to integrate the chemistry introduce little error as compared to the advection algorithms (e.g., Odman *et al.*, 1992; Dabdub and Seinfeld, 1994), and it may be

possible to speed up model execution with a small impact on total numerical error by optimization of the relative amount of error introduced by the advection and chemical integration algorithms.

In general,  $P_i$  and  $L_i$  are time varying and depend on concentrations of other compounds. Even though species  $i$  might react very rapidly,  $P_i$  and  $L_i$  are rather constant over periods of a minute or so. Thus, analytical solutions to the uncoupled Equation (11) can be used to develop efficient, approximate numerical solutions to Equation (11). Such techniques have been shown to be sufficiently accurate and are an order of magnitude faster than traditional Gear solvers. The two most popular methods for use in photochemical models are the Quasi-steady state approximation (QSSA, Hestveldt *et al.*, 1978) and the Hybrid method (Young and Boris, 1977). Saylor and Ford (1996) and Chock *et al.* (1994) found that the hybrid method is generally better than QSSA.

### Mathematical and Computational Implementation

There is no known analytical solution to the general ADR equation given in Equation (11). Instead, numerical approaches are used to solve a discretized version. Numerical solution of the complex systems of partial differential equations governing both the evolution of pollutant concentrations requires specialized mathematical techniques, some of them similar to those used in meteorological models.

The ADR equation can be dissected into terms describing bulk flow (term 2), turbulent diffusion (term 3) and other processes (e.g., emission sources or chemical reactions, term 4), each having an impact on the time evolution of the transported property (term 1):

$$\frac{\partial \mathbf{c}}{\partial t} = \underbrace{[-\bar{\mathbf{U}}\nabla \cdot \mathbf{c} + \nabla \mathbf{K} \nabla \mathbf{c}]}_{\text{Convective terms}} + \underbrace{[\mathbf{R}(\mathbf{c}, t) + \mathbf{S}]}_{\text{Source Terms}} \quad (13)$$

**Response**      **Convective terms**      **Source Terms**

In AQMs, the processes have very different time scales (e.g., between species lifetimes, source emissions, and transport). They can be viewed as being relatively independent over a short period of time. This allows the equation to be "split" into separate operators, and is done to greatly shorten solution times (McRae *et al.*, 1982), and improve numerical accuracy. The solution sequence is:

$$\left. \frac{\partial \mathbf{c}}{\partial t} \right|_{\mathbf{H}} = -\bar{\mathbf{U}}\nabla \cdot \mathbf{c} + \nabla \mathbf{K} \nabla \mathbf{c} = \mathbf{L}_{\mathbf{H}}(\mathbf{c}) \quad (14)$$

$$\left. \frac{\partial \mathbf{c}}{\partial t} \right|_{\mathbf{V}} = -\mathbf{w} \frac{\partial \mathbf{c}}{\partial z} + \frac{\partial}{\partial z} \mathbf{K} \frac{\partial \mathbf{c}}{\partial z} = \mathbf{L}_{\mathbf{V}}(\mathbf{c}) \quad (15)$$

$$\left. \frac{\partial \mathbf{c}}{\partial t} \right|_{\mathbf{S}} = [\mathbf{R}(\mathbf{c}, \mathbf{t}) + \mathbf{S}] = \mathbf{L}_{\mathbf{S}}(\mathbf{c}) \quad (16)$$

$$\left. \frac{\partial \mathbf{c}}{\partial t} \right|_{\text{Total}} = (\mathbf{L}_{\mathbf{H}} + \mathbf{L}_{\mathbf{V}} + \mathbf{L}_{\mathbf{S}})(\mathbf{c}) \quad (17)$$

where  $\mathbf{L}_{\mathbf{H}}$  is the horizontal transport operator,  $\mathbf{L}_{\mathbf{V}}$  is the vertical transport operator and  $\mathbf{L}_{\mathbf{S}}$  is the operator describing other processes, such as chemistry and source emissions. Numerical accuracy is improved and computational times reduced because splitting allows use of solution techniques that are designed to effectively describe specific processes. For example, in a photochemical air quality model, one routine is used for horizontal transport due to bulk winds, and another for vertical motions, which are generally diffusive processes, and a third for the chemistry.

Historically, numerical schemes used to calculate the rate of transport have been based on finite difference, then finite element and, more recently, finite volume techniques. Spectral methods have also shown promise, but nonlinear chemical effects tend to degrade solution accuracy in some tests (Hov *et al.*, 1990; Chock, 1985; Odman *et al.*, 1996). Some of the more widely used schemes include: *Smolarkiewicz*, a finite difference method (Smolarkiewicz, 1983); *Bott*, a finite difference method (Bott, 1989); chapeau function finite element (McRae *et al.*, 1982); and *ASD* (Accurate Space Derivative) a pseudo-spectral method (Chock and Winkler, 1994). More recently, Lagrangian approaches have shown promise as well (Chock, 1995; Pudykiewicz *et al.*, 1997). These Lagrangian approaches should not be confused with Lagrangian trajectory models.

A problem with numerical solutions of the ADR equations is that the spatial discretization of the modeling region leads to artificial numerical dispersion, which is manifested by the formation of spurious waves and by pollutant peaks being spread out. A number of studies have evaluated the performance of advection solvers to identify their strengths and weaknesses, both alone and in air quality models (Hov *et al.*, 1990; Odman *et al.*, 1996; Chock and Winkler, 1994).

As discussed by Byun (1997a&b), meteorological models do not always solve, explicitly, the mass conservation equation, though air quality models usually assume that the three dimensional fields supplied do conserve mass, both globally and locally, using the same discretization methods. If not, the numerical routines in the AQMs will not conserve the mass of the trace species. This has been found to be a problem in the MM5-RADM link. Another problem that can develop is the time discretization of meteorological fields being supplied to the AQM can also lead to mass conservation inconsistencies, or if the various models are not using the same grids interpolation inaccuracies can also lead to problems.

In addition to the numerical method being employed, it is important to make sure that there is a consistent treatment of the velocity field between the meteorological model and the air quality model. The advection equation being solved is an expression of mass conservation, and

is an important requirement in air quality modeling. For an accurate study of source-receptor relationships the models must maintain mass of pollutants emitted into the atmosphere. However, there are several factors that may lead to violation of mass conservation in current air quality modeling practice. The physical law of mass conservation is expressed by the continuity equation. Some meteorological models (e.g., MM5) do not explicitly use the continuity equation in their governing equations set and they diagnose air density (which is a primitive variable in continuity equation) from pressure and temperature using the ideal gas law. If the meteorological model is not conserving energy for some reason (i.e., irreversible effects) this would also affect mass conservation. There are some efforts to include continuity equation in the equations list of meteorological models that are going to be used for air quality modeling (e.g., Byun 1997a) however, this is not going to entirely solve the mass conservation problem as discussed below.

The output of meteorological models is stored at a certain interval (e.g., 1 hr) that is usually much larger than the air quality model's time step (e.g., 5 min). It is common to interpolate the stored data and obtain meteorological data for each time step. Since the continuity equation is linear, some people suggest that linear interpolation of density and momentum components would yield a mass conserving set of variables if the originally stored variables (those densities and momenta coming from the meteorological model) satisfied continuity. However, it should be realized that the output from a meteorological model is not the exact solution to the continuity equation, which expresses mass conservation in a continuum. The meteorological model treats the continuum as a discrete set of points at discrete instants separated by a finite time step. Mass conservation in a meteorological model means the satisfaction of some discrete form of the continuity equation. Also, the terms in the continuity equation are not the variables themselves but the rate of change of density and the gradient of momentum. While linear interpolation of the rate of change of density and gradient of momentum would guarantee satisfaction of the discrete conservation equation, interpolation of density and momentum does not. To reconstruct the rate of change and the gradient from the variables requires knowledge of what discretization formulae were used in the meteorological model. In addition, knowledge of the grid (this is not a requirement when the air quality model and the meteorological model use the same grid), time steps during the time interval and some additional data (e.g., the rate of change of a variable is usually expressed as the difference between the values at the current and next time steps divided by the time step and, usually, the value at the next time step is not stored) is required. Meteorological models may use much more complex discrete forms than those used in the air quality models. For example, while explicit single-step methods are preferred in air quality models, stability considerations in meteorological models may favor the use of implicit methods, sometimes with multiple time steps.

Mass conservation is guaranteed if the mass continuity equation (Equation (1)) is discretized in the flux-form (or strong conservation form). For reasons explained above, the velocity and density fields output by the meteorological model may not necessarily satisfy the discretized form of the continuity equation as assumed by the AQM. As a solution to this problem, the vertical velocity may be recomputed (e.g., Flatoy, 1994). In this approach, the AQM would interpolate density and horizontal flux components linearly in time and solve Equation (1) for vertical flux and ignore the vertical velocity component coming from the meteorological model. The solution to the species continuity equation (Equation (11)) in the

AQM should also be discretized in the flux form, this time to conserve pollutant mass. The solution technique used for equation (11) should be consistent with the discretization used to satisfy Equation (1). Russell and Lerner (1981) and Easter (1993) describe “advection schemes” that are consistent with the solution of the continuity equation. The problems noted above suggest that the links between various meteorological models should be understood, and the resulting fields investigated, to assure that no spurious increases (or decreases) in mass occurs during the air quality modeling.

## **UNCERTAINTIES IN MODEL INPUTS: IMPLICATIONS FOR MODEL RELIABILITY**

It is important to recognize that uncertainties in model components and in model inputs may have a serious impact on model predictions. Given the uncertainty in model simulations, what is the probability that a model would suggest an inappropriate strategy? This question gets at the heart of assessing and comparing emissions control strategies. While we are not yet able to answer this question in detail, significant efforts have been made to quantify the effects on both ozone prediction and control strategy evaluation caused by uncertainties in model components (e.g. the chemical mechanism, wind field generation) and in input data (e.g. emissions rates, wind fields), and from the computational methods applied (e.g. grid size, numerical scheme).

Evaluation of model uncertainty presents a challenging problem in part due to the large number of inputs – current chemical mechanisms may include hundreds of chemical reactions. Each of these reactions has a number of parameters governing the production and destruction of chemical compounds, including kinetics data and product stoichiometry that vary as a function of sunlight and temperature. While certain reactions and products are known to be more important than others, it is difficult to determine which of these to eliminate in advance from the uncertainty analysis – a relatively unimportant reaction with a highly uncertain rate constant may have a similar effect on final model predictions as a crucial reaction with a much better understood rate constant. This complexity presents two crucial steps in evaluating the effects of uncertainty on AQM predictions:

- Selection of which input parameters and data fields to examine – the effect of uncertainty in every parameter and data field characteristic used in a three-dimensional photochemical atmospheric model can not realistically be estimated, so a subset of important parameters must be selected, and
- Estimation of uncertainty in these identified items – parameter and data uncertainties must be estimated by either quantitative analysis such as data with-holding computational experiments or by expert estimation.

While, unfortunately, the uncertainty in most inputs and parameters for large atmospheric models are unknown and are not discussed in literature, a few such studies have been published. These include expert reviews of chemical reaction rate constants and product yields (DeMore et al., 1990, 1994, 1997; Stockwell et al., 1994; Atkinson et al., 1989, 1992) and a data withholding

analysis of wind field uncertainty due to wind speed and direction measurements (e.g., Noblet et al., 1998; Bergin et al., 1999). Sensitivity analysis or uncertainty analysis using less complex models (such as a box model) can be applied in an iterative approach to reduce the set of uncertain parameters for further, more detailed analysis.

After the parameter set has been selected, and the uncertainty in each item has been estimated, a number of analysis methods are available for use. The method selected for an uncertainty analysis depends on the number of parameters to be evaluated, the computational requirements of the model, and the detail of information desired. The most common methods used are sensitivity analysis and Monte Carlo analysis.

Four types of sensitivity analysis can be defined:

- Stand-alone tests of the effects of a particular parameterization within a module or mechanism,
- Response of the model outcome variables to changes in process parameterizations, model structure/numerics, or input variables,
- Alteration of outcome variable response to an emissions change due to modification of the model or input variables, and
- Alteration in the emissions control strategy necessary for attainment of an air quality standard.

To date, most studies have assessed how changing model inputs would impact predictions of a single outcome variable, O<sub>3</sub> concentration (type 1 and type 2). While this is a necessary first step, it is insufficient because outcome variables may not always be accurate measures of system changes. In the classic example, sensitivity simulations showed that biogenic emissions had relatively small effects on peak O<sub>3</sub> but had very large effects on the control strategy effectiveness (Chameidies et al., 1988). Thus, a more rigorous uncertainty analysis should also evaluate effects of model input certainty using type 3 and type 4 analyses. For example, Tonnesen (1998) evaluated the effects of uncertainty in an important rate constant on O<sub>3</sub> concentration, O<sub>3</sub> sensitivity to emissions changes, and changes in O<sub>3</sub> attainment strategies. Uncertainty studies can also be extended by considering effects on component model processes in addition to outcome variables (Dennis et al., 1998).

The most widely used sensitivity approach is parametric analysis, in which the outputs of a base case are compared to outputs from additional simulations with parameter values changed one at a time (OAT) (Bergin et al., 1998a, 1998b). This approach is valuable when the number of parameters of interest is limited and the computational requirements of the model are very high. Systematic sensitivity analysis techniques, including local techniques such as the direct decoupled method (Dunker, 1984) and Green's function methods (Hwang et al., 1978), and global techniques such as the Fourier amplitude sensitivity test (Koda et al., 1979), represent more efficient means of calculating sensitivities to large numbers of parameters. These systematic methods have been used primarily to study atmospheric chemistry in box model simulations (Falls et al., 1979; Pandis et al., 1989; Milford et al., 1992), but in a few cases have been applied to three-dimensional (3-D) models (Dunker, 1981; Yang et al., 1997).

This OAT approach may be inadequate in AQMs, however, in which there exist strong non-linear dependencies among the input parameters. Global sensitivity methods such as Monte Carlo techniques are used to propagate probability distributions through the model to estimate uncertainties in output concentrations. Even when using an efficient sampling method such as Latin Hypercube Sampling (Iman and Shortencarier, 1984), Monte Carlo methods can require large sets of simulations to represent uncertainty distributions and can therefore be computationally intensive. This approach has been applied to evaluate descriptions of gas-phase tropospheric chemistry (Thompson et al., 1991; Yang et al., 1995; Gao et al., 1996), uncertainties in a Gaussian plume model (Freeman et al., 1986), and single-cell trajectory models of O<sub>3</sub> formation (Derwent and Hov, 1988). An analysis has been performed using a trajectory version of the CIT AQM (Bergin et al., 1999) to evaluate both secondary pollutant predictions and ozone control strategy evaluation. Preliminary Monte Carlo uncertainty analysis have been performed for three-dimensional photochemical models by Hanna et al. (1998) for a large number of parameters with a sampling size of 50 to study ozone formation, and by Yang et al., (1999) with sample size of 50 to study uncertainties in ozone predictions, control strategy effectiveness and VOC reactivity. The recent AQM and reactivity uncertainty analysis studies are described in Table 1U.

After identifying the uncertainties and sources of uncertainty in AQMs, this knowledge should be used to increase reliability in model predictions of air quality and of control strategy efficiency. The most direct method for doing so is to better quantify those parameters identified as contributing most uncertainty. Also, as computational limitations diminish, the more sophisticated statistical approaches can be applied to the complex models to account for interactions between a greater number of parameters. A preliminary study is underway (Bergin and Milford, 1999) that applies a Bayesian technique to the results of a previous Monte Carlo study in order to incorporate pollutant measurements into model predictions for a more reliable estimate of uncertainty. Techniques such as this may allow better characterization of uncertainty as well as increasing (or decreasing) confidence in model predictions.

## DIAGNOSTIC METHODS

### Brute Force Sensitivity

The simplest and most common approach to sensitivity studies is a “brute force” method in which a base case simulation is performed, and then the simulation is repeated using a change in some model input. A common sensitivity study is to investigate O<sub>3</sub> sensitivity to precursor emissions by, for example, reducing VOC or NO<sub>x</sub> emissions by 50% or some other level representative of a control scenario.

Incremental reactivity is defined as the derivative of O<sub>3</sub> with respect to precursor emissions and this can be approximated in a brute force sensitivity study by using a small, finite change in precursor emissions and calculating the difference in ozone concentration ([O<sub>3</sub>]) between two simulations:

$$\frac{d[\text{O}_3]}{dE_i} \approx \frac{\Delta[\text{O}_3]}{\Delta E_i} = \frac{[\text{O}_3]_{new} - [\text{O}_3]_{base}}{E_{i,new} - E_{i,base}} \quad (18)$$

where  $E_j$  represents base case emissions of some precursor  $j$ , and  $E_{j,new}$  represents simulation with emissions increased or decreased by some small amount.

The accuracy and stability of results calculated with Eq 4.1 vary with the choice of chemical solver and user specified error tolerance levels. To date, the primary concern in evaluating the accuracy of chemical solvers has been the accuracy with which they predict species concentrations, particularly  $\text{O}_3$ . Numerical errors of less than  $\pm 1\%$  are generally acceptable because uncertainty in measured  $\text{O}_3$  is much larger, and because such small errors have little effect on conclusions drawn from typical modeling studies.

When models are used to estimate incremental reactivity, however, numerical error can be large relative to the small changes in  $\text{O}_3$  resulting from small emissions changes. Thus, error tolerances that were acceptable for  $\text{O}_3$  can become unacceptably larger for small increments in emissions and  $\Delta[\text{O}_3]$ . To illustrate this, Figure 1(top) shows model predicted  $\Delta[\text{O}_3]$  for three different Gear error tolerances in simulations where  $\text{NO}_x$  emissions were incremented in a range from  $-2\%$  to  $+2\%$ . An error tolerance of  $3 \times 10^{-3}$  (which is the default EKMA setting) produces errors of less than  $\pm 0.2$  ppb relative to the most stringent error tolerance of  $10^{-5}$ . Figure 1(bottom) shows that these small errors in  $\Delta[\text{O}_3]$  translate to large errors in  $\Delta[\text{O}_3]/\Delta E_{\text{NO}_x}$ .

Thus, care must be exercised in simulating incremental reactivity to ensure that the emissions increment is large enough so that numerical error does not overwhelm the  $\text{O}_3$  response. If the emissions increment is too large, however, it does not provide a good approximation of the derivative because the  $\text{O}_3$  response is non-linear with the size of the emissions increment. Figure 2 illustrates this for formaldehyde (HCHO) incremental reactivity where HCHO incremental reactivity can vary between 0.34 and 0.53 depending on the size of the emissions increment. A more accurate estimate of incremental reactivity can be calculated using the centered-difference with positive and negative changes in precursor emissions:

$$\frac{d[\text{O}_3]}{dE_i} \approx \frac{\Delta[\text{O}_3]}{\Delta E_i} = \frac{[\text{O}_3]_{+2\%} - [\text{O}_3]_{-2\%}}{E_{i,+2\%} - E_{i,-2\%}} \quad (19)$$

where, for example, precursor emissions are incremented by  $\pm 2\%$ . Using Eq 4.2 the brute force method can provide accurate estimates of incremental reactivity for  $\Delta[\text{O}_3]$  values as low as a  $\pm 0.1$  ppb using a Gear solver with a strict error tolerance in a trajectory model, using single precision variables. In grid models, greater numerical error is introduced due to low order accuracy chemical solvers and numerical error in transport solvers. Tonnesen et al. (1998) found numerical error of less than  $\pm 0.5$  ppb in brute force sensitivity runs in a grid model. Careful study is required to determine the size of emissions increments which should be used and the accuracy with which incremental reactivity can be calculated in particular grid models.

An advantage of the brute-force approach is its simplicity of implementation. It is also useful for sensitivity studies designed to evaluate the effects for large changes in precursor

emissions. In these cases it is necessary to consider the non-linear dependence of the O<sub>3</sub> response on the size of the emissions change.

The brute force method cannot, however, be used to determine sensitivity to small emissions changes for which the O<sub>3</sub> response is overwhelmed by numerical error. A highly accurate and efficient method for calculating incremental reactivity for very small increments (thereby avoiding the limitations in the brute force approach) is discussed next.

### Direct Sensitivity Analysis

Direct sensitivity analysis is another technique to better understand model response. In this case, sensitivity parameters are found as the partial derivative of the predicted concentrations to specified model inputs or parameters:

$$S_{ij} = \frac{\partial c_i}{\partial P_j} \cong \frac{c(P_j + \Delta P_j) - c(P_j)}{\Delta P_j} \quad (20)$$

where  $S_{ij}$  is the sensitivity coefficient of the concentration of the  $i$ 'th species to the  $j$ 'th parameter,  $P_j$  is the  $j$ 'th model parameter (or input) and  $\Delta P_j$  is a small perturbation in the parameter. This can be found in either via a "brute force" approach as described above, or a more formal method. Brute force is conceptually the simplest but has several significant limitations. First, if the number of sensitivity coefficients desired is large, this becomes overly burdensome and computationally inefficient. Second, given the numerical noise in model calculation (e.g., due to the transport algorithms), if the parameter is not perturbed significantly, it can be difficult to accurately calculate the model response. Formal sensitivity techniques, such as the Decoupled Direct Method (DDM) and the Adjoint approach, can alleviate some of the limitations. Application of DDM in air quality modeling was pioneered by Dunker (1980, 1984). Yang et al., (1997) more recently implemented it in the CIT model to show how the model responded to various emissions and a number of model parameters. It has proven to be a computationally effective method to find model sensitivities, perform uncertainty analysis, conduct source apportionment and quantify VOC reactivities. DDM is particularly powerful for conducting reactivity analysis. The sensitivity coefficient of O<sub>3</sub> to the emissions of a particular species is that species reactivity. Thus, a single simulation where, say, 20 sensitivity coefficients of ozone to emissions of different VOCs are found, provides, directly, the 20 VOC species' reactivities. Another advantage of this method over a brute force approach for this type of calculation is that it reduces the numerical noise.

Studies using DDM to quantify reactivity include Yang et al. (1996) using a box model and Yang et al., (1998) and Kahn et al. (1998) using three-dimensional airshed models. Because of its computational efficiency, use of DDM makes it possible to conduct reactivity analysis at regional scales (e.g., Kahn et al., 1998). These studies found that using DDM provided very similar results as compared to the brute force approach, and were computationally more efficient. As discussed elsewhere, DDM has been used in a Monte Carlo analysis of reactivity uncertainty (Kahn et al., 1998).

## Process Analysis

Process analysis is a technique for explaining a model simulation – it stores the integrated rates of species changes due to individual chemical reactions and other sink and source processes (Jeffries and Tonnesen, 1994). AQMs typically operate by using the species rates of changes to predict the temporal evolution of species concentrations, but information regarding the particular reactions and processes that cause that evolution are not saved or evaluated. By integrating these rates over time and outputting them at hourly intervals, process analysis provides valuable diagnostics that can be used to explain a model simulation in terms of the budgets of radical initiation, propagation and termination, production and loss of odd oxygen and O<sub>3</sub>, and conversion of NO<sub>x</sub> to inert forms, as well as the effects of transport and other sink and source terms.

While process analysis can provide an improved understanding of cause and effect in a model simulation, it does not necessarily have predictive ability, *i.e.*, it does not predict the reactivity of VOCs. Process analysis can, however, be used to explain reactivity by explaining how O<sub>3</sub> was produced in the base case scenario and explaining exactly what changed in the sensitivity simulation.

Similarly, incremental reactivity has predictive power, but it does not necessarily have explanatory power – it can be difficult to interpret on the basis of sensitivity simulations alone why a VOC exhibits a particular reactivity. Thus, incremental reactivity and process analysis are complementary approaches that can be combined to more fully characterize the system. For example, process analysis has been used to explain the incremental reactivity of a given VOC by explaining its effects on radical initiation, NO<sub>x</sub> termination, and the changes in the amount of other VOC that react (Jeffries and Crouse, 1991; Bowman and Seinfeld, 1994).

Process analysis has been implemented in grid models (Jang et al, 1995). In addition, algorithms have been developed to track mass transport in grid models to explain how emissions in a given cell affect species downwind (Lo and Jeffries, 1997). A limitation of these approaches in grid models is that they can require large resources for storage and post-processing of integrated reaction and process rates. These limitations have been circumvented by performing processing of the integrated rates within the model and outputting a limited set of process diagnostics (Tonnesen and Dennis, 1998a) or by providing a flexible user interface to select particular process diagnostics as in Models3/CMAQ. These diagnostics are then immediately available to be analyzed in conjunction with species concentrations fields.

It remains difficult, however, to fully characterize the chemical budgets of particular precursor emissions sources in grid models because the Eulerian grid structure is not conducive to evaluating the transformations in air parcels being transported across the grid. A tracer approach that addresses this problem is described in the next section.

## Ozone Source Apportionment Technology

Source-receptor analysis is fairly easy to study in Lagrangian models, although the simplistic Lagrangian treatment of transport raises uncertainty about the results of these studies. Source-receptor relationships are much more difficult to study in Eulerian models because it is computationally expensive to maintain a record of the mass transport between cells. Eulerian models typically use the calculated rate of mass flux to update the concentration in each cell but do not compute or output the actual mass fluxes between grid cells.

The CAMx model (ENVIRON, 1997) employs a system of tracers to determine the emissions source regions which affect O<sub>3</sub> production throughout the model domain. OSAT also maintains a record of whether O<sub>3</sub> production occurred under NO<sub>x</sub>- or VOC-limited conditions (Yarwood et al., 1996). OSAT appears to be a combination of the sensitivity approach and the process analysis approach, and it is intended to provide guidance in identifying effective precursor control measures.

Mass tracking and tracer analyses are potentially useful in model studies of reactivity because: (1) they further elucidate at a process level the factors which contribute to high O<sub>3</sub>. (2) they provide detailed information regarding source-receptor relationship. Continued development and application of these diagnostic tools will be useful in model studies of reactivity.

## Indicator Ratios

Ratios of particular combinations of species have been proposed to be useful as indicators of O<sub>3</sub> sensitivity to changes in precursor emissions (Milford et al. 1994; Sillman 1995, 1998). Several indicators have been proposed using a steady state analysis of radical budgets (Sillman, 1995; Kleinman, 1994; Kleinman et al., 1998). Tonnesen and Dennis (1998a&b) have distinguished between indicators of local odd oxygen production (P(O<sub>x</sub>)) and O<sub>3</sub> concentration ([O<sub>3</sub>]) sensitivity and have analyzed indicators in terms of radical propagation efficiency. Following on the work of Johnson (1984), Blanchard et al. (1993) and Chang et al. (1997) have developed an indicator based the extent to which the available NO<sub>x</sub> has been utilized to achieve maximum potential [O<sub>3</sub>].

In theory, indicators could be used to estimate P(O<sub>x</sub>) and [O<sub>3</sub>] sensitivity to precursor emissions independently of models. Tonnesen and Dennis (1998b), however, found in modeling studies that indicators of [O<sub>3</sub>] sensitivity successfully distinguished the extreme NO<sub>x</sub>-limited and VOC-limited conditions, but were less useful for distinguishing less extreme conditions. Lu and Chang (1998) found that values of the indicator of [O<sub>3</sub>] sensitivity calculated in a model in the San Joaquin Valley differed from the values reported in other studies. Nevertheless, indicators should still provide a powerful diagnostic test to evaluate models. Sillman et al.(1995, 1997a&b) have used measurements of indicators to evaluate model applications and to identify model scenarios that failed to match observations. Local indicators of P(O<sub>x</sub>) sensitivity (Tonnesen and Dennis, 1998a) may better discriminate between NO<sub>x</sub>- and VOC-limited conditions than do the long-lived indicators. Measurements of these indicators could be useful in reactivity substitution

strategies as a means for determining whether particular regions are NO<sub>x</sub>-limited or VOC-limited, or at conditions of MIR, MOR, or some other state.

To date, the usefulness of indicators for predicting O<sub>3</sub> sensitivity has only been simulated in model sensitivity runs. Before the indicators concept or particular values of indicator ratios can be used with confidence, this predictive ability must be experimentally tested in controlled experiments. Such experimental testing could be conducted in environmental chambers or in other well defined conditions in which P(O<sub>x</sub>) and [O<sub>3</sub>] response to emissions changes can be carefully measured.

## TYPES OF MODELS

### Trajectory and Box Models

In trajectory models the continuity equation is solved using the wind field as the reference frame. In box models the advection and dispersion terms are considered to be negligible. In practical terms these two approaches are quite similar as each reduces the ADR equation to the simpler form of Equation (12).

Because of their simplicity and efficiency, trajectory models have several advantages relative to grid model:

- They are easier to code and operate compared to grid models;
- It is easy to specify model inputs and to vary inputs in sensitivity simulations;
- Large numbers of simulations can be rapidly performed for sensitivity studies.
- They can include large, explicit chemical mechanisms which would be prohibitively expensive in grid models.
- Easy to modify mechanisms to include explicit chemistry for particular VOCs.
- Trajectory models can be used to evaluate chemical effects in isolation from meteorology
- The Lagrangian reference frame facilitates evaluation of source-receptor relationships.
- Their numerical efficiency allows for simulation of climatological outcomes (*i.e.*, simulations over seasons or years).

Disadvantages of trajectory models include the following:

- They have overly simplistic representation of transport and turbulent dispersion potentially causing them to underestimate dispersion and overestimate species concentrations.

- Difficult to represent multi-day scenarios, especially those with complex mixing including stagnation, re-circulation and re-entrainment of polluted air from above the PBL.
- They provide poor temporal-spatial resolution – output is defined only at a limited set of points and times along the parcel trajectory. This makes it difficult to evaluate reactivity effects integrated over a geographical area or integrated over time at a given site.

To address this last deficiency, trajectory models have been defined using multiple air parcels moving through a fixed grid with the ensemble average of parcels within grid cells used to calculate species concentrations on the grid (Simpson et al., 1992). These approaches have also been useful in global scale chemical tracer models (CTM) for which it is still impractical to solve complex photochemistry on an adequately resolved grid (Derwent, 1998). Multiple-parcel trajectory models are also useful in cases where there is particular concern for attributing species to their source regions (Simpson, 1997). For example, the European EMEP modeling program is particularly concerned with creating “blame matrices” to determine which sources contribute to high pollutant levels.

Here, we describe several trajectory or box models that have been used in reactivity studies.

### **OZIP/EKMA**

There exist several versions of the U.S. EPA's OZIPP (Ozone Isopleth Plotting Package) computer modeling program (e.g., OZIPM-4, Hogo and Gery, 1988). The OZIPP programs employ a trajectory-based air quality simulation model, in conjunction with the Empirical Kinetics Modeling Approach (EKMA), to relate ozone concentrations to levels of VOC and NO<sub>x</sub> emissions. Early OZIPP versions were designed to provide a rigid structure within which State Implementation Plans (SIPs) could be formulated. OZIPR (Gery and Crouse, 1990) is a research-oriented version that was created to provide a more flexible and functional research tool. Its structure is similar to OZIPM-4, however, so the published user's guide (Hogo and Gery, 1988) for that program serves as a reference for the development and inherent structure of OZIPR.

OZIPR simulates complex chemical and physical processes of the lower atmosphere through use of a trajectory model. The physical representation is a well-mixed column of air extending from the ground to the top of the mixed layer. This idealized air column moves with the wind (along the wind trajectory), but cannot expand horizontally. Emissions from the surface are included as the air column passes over different emission sources, and air from above the column is mixed in as the planetary boundary layer (PBL) height rises during the day. OZIPR provides a flexible interface that can read complex chemical mechanisms, initial and boundary conditions, and diurnally varying times series of precursor emissions, temperature, humidity, and deposition velocities. It also allows default or user defined specifications of the temporal evolution of the planetary boundary layer height. A Gear method is used to solve the photochemistry. Emissions and deposition are represented as first-order reaction rates and are solved simultaneously with the chemistry.

An important limitation of OZIPR is that it does not simulate dilution of the species in the box caused by horizontal advection and dispersion. In addition, multiple day simulations are difficult to perform, and it does not represent the chemistry and transport of trace species above the mixed layer.

A key feature of OZIPR is that it is automated to perform a large set of simulations at specified intervals of VOC and NO<sub>x</sub> precursor levels. This facilitates the creation of response surface plots showing model output variables as a function of initial precursors levels. The most familiar such response surface plot is the O<sub>3</sub> isopleth diagram (U.S. EPA, 1983), but OZIPR is also automated to create response surfaces for other model species, for a large set of process diagnostics, and for the incremental reactivity of NO<sub>x</sub>, the VOC mixture, and the individual VOC species. OZIPR also outputs integrated reaction rates for the full mechanism, and an associated post-processing program can be used to perform a process analysis that describes the contribution of individual VOC to important process rates such as radical initiation, NO<sub>x</sub> termination and O<sub>3</sub> production (Jeffries and Tonnesen, 1994; Tonnesen and Jeffries, 1994).

### **The Harwell Trajectory Model**

The Harwell model is a single layer trajectory with an aloft layer in the free troposphere (Derwent et al., 1998). It is a regional scale model that uses 300 back-track air mass trajectories each of 96 hours duration, arriving at a grid of 60 arrival points across the British Isles on 5 ozone episode days during 1993 and 1994. Features of the model are listed below:

- diurnal variations in boundary layer depth, temperature and humidity are fully treated.
- 120 emitted VOCs are treated from 36 emission source categories and emissions of SO<sub>2</sub>, NO<sub>x</sub>, CO, methane and isoprene from 11 source categories on a 10km x 10km emissions grid over the United Kingdom and 50km x 50km over the rest of Europe.
- the model uses a Master Chemical Mechanism which contains 2410 chemical species and 7100 chemical reactions which can be viewed at:  
<http://chem.leeds.ac.uk:80/Atmospheric/MCM/mcmproj.html>
- the inorganic chemical reactions of the simple atoms and radicals containing oxygen, hydrogen, nitrogen and sulfur and those of CO, employ evaluated rate coefficients with their full temperature and pressure dependencies from the IUPAC and JPL evaluations.
- the 1300 photolysis reactions of the photochemically-labile species are given a full time-of-day dependence using a two-stream sixth-order code which includes treatment of the stratospheric ozone amount, surface albedo and the background aerosol.
- the model contains a treatment of the dry deposition of O<sub>3</sub>, SO<sub>2</sub>, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and 101 peroxyacetylnitrate analogues.
- the system of stiff differential equations describing the chemical development of the 2510 species is integrated with a Gear's method integrator with no assumption of photochemical steady states (even for O<sub>1</sub>D) with automatic accuracy control to 0.1%.

## **AES Box Model**

Ongoing research at the Atmospheric Environment Service (P. Makar, personal communication, 1998) has combined a gas-phase tropospheric reaction mechanism, a 1-D radiative transfer model, and a standard Gear-type and the Canadian National Air Pollution Surveillance (NAPS) measurement data to determine ozone sensitivities to initial NO<sub>x</sub> and VOC mixing ratios. Measurement records at 15 sites across Canada were extracted from the database and were used to generate one-hour ozone forecasts. The initial mixing ratios of NO<sub>x</sub> and anthropogenic VOCs were increased and decreased by 25% to determine the effect of changes in the ambient concentrations of these variables on local ozone production. VOCs were varied individually and as a group, to determine the net VOC effect and the effect of individual classes of VOCs on ozone.

The results of these simulations were used to construct finite difference sensitivities (O<sub>3</sub>/sensitivity variable), and were expressed as (ppbv change in O<sub>3</sub> per % change in variable), to allow local effect comparisons between sites. Results showed both differences and similarities across regions. Industrial Ontario areas had negative sensitivities to the initial NO concentration, indicating that decreases in NO would lead to increases in O<sub>3</sub> (due to reduced NO<sub>x</sub> titration), while Greater Vancouver sites had minimal NO sensitivity. Ontario sites had positive sensitivities for net VOCs; reductions would lead to decreases in O<sub>3</sub>; Vancouver again had a smaller effect. Site-by-site examination of individual VOC sensitivities showed that the greatest sensitivity of VOC classes was for internally bonded alkenes at most sites. The next most reactive classes varied from site to site, with either end-bond alkenes or higher aromatics having the next most important effect after internal alkenes. Magnitudes of the sensitivities showed a large variation of effects even within the same region or industrial area (Figure 3 shows sensitivities for model VOCs and NO at five Ontario sites). The study's results to date indicate that region- and VOC-class-specific VOC reductions may have the greatest impact on ozone concentrations. The study is currently being revised to include sensitivities towards biogenic hydrocarbon mixing ratios.

## **EMEP Trajectory Model**

The EMEP photochemical trajectory model provides another example, in addition to OZIP/EKMA, of a trajectory model with a long history of regulatory and policy use. The EMEP model has been used extensively in Europe to develop source-receptor relationships for O<sub>3</sub>, acid deposition, and eutrophication (Simpson et al., 1995a&b). Extensive model scenarios have been run to develop seasonal or climatological averages (Simpson, 1992, 1997). While the EMEP model has the same limitations of other trajectory model, it provides a means to evaluate two areas that may be of interest in studies of reactivity: source-receptor effects and climatological effects.

## **Urban/Regional/Multi-Scale Grid Models**

Eulerian models solve Equation (11) for a gridded domain using operator splitting as described above. Advantages of grid models include the following:

- They contain detailed descriptions of meteorological and transport processes.
- Model predicted species concentrations are defined over the full geographical and temporal domain.
- Designed to simulate multi-day scenarios.

Disadvantages of grid models:

- Expensive to maintain and run.
- Large inputs and output data sets make it difficult to perform and evaluate large numbers of sensitivity simulations.
- Difficult to determine cause and effect because of the complexity of interaction between model components.
- Limited to condensed chemical mechanisms which are typically hard-coded and difficult to change.

Table 1 (from Russell and Dennis, 1998) summarizes aspects of some of the Eulerian AQMs that are in current or recent use. Due to the large number of grid models that have been used, we will not provide detailed comments on individual models, although we will comment on several noteworthy models that were not included in Table 1.

A new regional scale chemical tracer model (CHRONOS) has been developed at the Canadian Atmospheric Environment Service (Pudykiewicz et al., 1997). While this model uses an innovative semi-Lagrangian advection solver, it also employs the somewhat dated ADOM chemical mechanism.

Environ Corporation has developed an multiscale Comprehensive Air Quality Model with extensions (CAMx) (Reynolds and Roth, 1997) that uses an extensive system of tracers (Yarwood et al., 1996) that was described above.

The Urban-to-Regional Multiscale Model (which is listed in Table 1) is noteworthy because it allows for an irregular, multiscale, spatially varying grid resolution, similar to the approach used in computational fluid dynamics. Unlike nesting, the transport algorithm allows for arbitrary grid structures, and can minimize the number of computational nodes needed to have a fine grid over a non-rectangular region (e.g., the coastline of the eastern United States). The Urban-to-Regional Multiscale has been applied to Southern California (Odman et al., 1994), the Northeastern United States (Kumar and Russell, 1996) and the eastern United States, covering a domain similar to the OTAG region. URM has been used to conduct control strategy analyses for ozone, aerosols and acid deposition, and using the direct differential method (DDM, described below), has been used for reactivity assessment.

The Multiscale Air Quality Simulation Platform (MAQSIP) is the air quality modeling framework within the Environmental Decision Support System (EDSS) which was developed as a prototype for the EPA Models-3 system. MAQSIP provides a base for the next generation, modular Eulerian air quality models. The modular design and flexibility utilized in MAQSIP

allow it to retain its state-of-the-science over time with future development and implementation of new science modules as appropriate. The MAQSIP has been driven by meteorological inputs provided by the Penn State/NCAR Mesoscale Model (MM5) (Grell et al., 1994). The emission model SMOKE provides processing of emission inventories from different sources including the NAPAP emissions. MAQSIP applications include 120 day simulation developed for the Seasonal Model for Regional Air Quality (SMRAQ) performed for the SouthEastern States Air Resources Managers (SESARM). MAQSIP configuration for the SMRAQ seasonal runs uses a modified version of the Carbon Bond IV (Gery et al., 1989) chemical mechanism, a flux-form advection scheme (Bott, 1989), a K-theory scheme for turbulent vertical redistribution of pollutants (Alapaty et al., 1997), and a dry deposition scheme (Walcek et al., 1986). Clear-sky photolysis rates are calculated following Madronich (1987). The cloud package include the deep convective parameterization scheme employed in the MM5 (Kain and Frisch, 1993).

## **Global Models**

Concerns over tropospheric ozone have expanded within the last decade to include not only the prevention of intense smog episodes in urban areas, but also the alleviation of chronic human exposure at lower ozone doses, the protection of crops, and the mitigation of global warming. As ozone standards fall closer to global background values in response to these concerns, there is a corresponding rise in the need to model the formation and transport of tropospheric ozone throughout the entire world.

The global modeling of tropospheric ozone requires spatial and temporal resolution that can best be achieved only with three-dimensional chemical transport models (CTMs). Although two-dimensional, zonally (i.e., longitudinally) averaged CTMs with realistic photochemical schemes have been used to assess global tropospheric ozone impacts (e.g., Isaksen and Hov, 1987; Hough and Derwent, 1990), they fail to account for continent-ocean differences in emissions, for zonal transport, and for the nonlinear dependence of ozone production on NO<sub>x</sub> (Kanakidou and Crutzen, 1993). On the other hand, 3-D CTMs are computationally intensive, and require less detailed treatment of chemistry than in many urban and regional models in order to produce tractable simulations (Houweling et al., 1998). Moreover, their lack of resolution on regional and urban scales limits their ability to simulate the impacts of intense pollution plumes associated with concentrated industrial sources, which may represent an important nonlinear chemical processing of NO<sub>x</sub> emissions (Sillman et al., 1990).

An important issue in the design of 3-D global CTMs is the temporal resolution of the input meteorological fields. In order to conserve computational resources, some CTMs obtain these fields as monthly averaged data from general circulation models (GCMs) used in climate studies. An intercomparison of models by the IPCC (1994) revealed, however, that the use of monthly averaged circulations significantly distorts the transport of global tracers compared to the use of daily varying circulations. More recently, 3-D CTMs have been developed which either use more temporally-resolved GCM output (Wang et al., 1998), or combine the predictive capability of a GCM with a 3-D CTM, resulting in a hybrid chemistry-climate model. (e.g., Roelofs et al., 1997). The hybrid models can not only avoid the inaccuracies associated with lack of temporal resolution in meteorology, but can also simulate feedbacks involving radiative-

chemical-dynamical coupling, a potentially important issue in climate studies. Their formulation based on the primitive equations of dynamic meteorology, however, can result in an overly large computational burden. An alternative to primitive equation hybrid models is provided by global balance chemistry-climate models (Tie et al., 1991; Olaguer, 1998), which employ a lower order version of the hydrodynamic equations to lessen computational demand. 3-D global CTMs or chemistry-climate models can be useful in the context of reactivity studies as a means of specifying boundary conditions for regional models, or for determining very long range reactivities related to background ozone. They can also be used to study global collateral impacts, such as persistence, global warming, and stratospheric ozone depletion, especially for short-lived compounds which degrade into longer-lived intermediates. Their usefulness would be tremendously improved if regional models were nested into them in limited areas of the globe, where intense anthropogenic emissions of ozone precursors warrant more spatial resolution.

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## TABLES

**Table 1U. Recent uncertainty analysis studies of air quality models and of reactivity quantification.**

<b>Air Quality Model</b>	<b>Chemical Mechanism</b>	<b>Uncertain Output Evaluated</b>	<b>Parameters Evaluated</b>	<b>Analysis Approach</b>	<b>Ref.</b>
UAM three-dimensional	CB-IV (Gery et al., 1989)	O <sub>3</sub>	23 variables related to emissions, boundary conditions, and meteorological conditions; 86 chemical rate constant variables. Total: 109 parameters.	Uncertainty estimates through survey of 10 modeling experts. Uncertainty analysis of ozone prediction performed using 50 Monte Carlo simulations.	Hanna et al., 1998
CIT trajectory version	SAPRC93 (Carter, 1995)	O <sub>3</sub> , HCHO, HNO <sub>3</sub> , PAN, NO <sub>y</sub> , and motor vehicle emissions reduction scenarios	Trajectory path, reflecting uncertainties in wind speed and direction; 29 chemical rate constant variables, 3 deposition affinities, 11 mixing height periods, the atmospheric stability class, and 6 classes of emissions. Total: 51 parameters.	Uncertainty estimates through published review (chemistry), sensitivity studies, data withholding analysis, and subjective estimates. Uncertainty analysis of ozone and other secondary pollutant predictions and of ozone control strategy evaluation performed using sets of 200 Monte Carlo simulations.	Bergin et al., 1998a
CIT three-dimensional	SAPRC90 (Carter, 1990)	O <sub>3</sub> and VOC reactivity quantification	12 reaction rate constants, emissions, mixing heights.	Studied uncertainties in VOC reactivity quantification, ozone predictions and control strategy effectiveness extending the work of Bergin et al., (1998, 1999).	Yang et al., 1999
CIT three-dimensional	SAPRC90	O <sub>3</sub> and VOC reactivity quantification	9 reaction rate constants.	Uncertainty estimates extending previous box model study (Yang et al., 1994). Sensitivity analysis of chemical mechanism rate constant uncertainties on reactivity quantification for 26 organic compounds and carbon monoxide.	Bergin et al., 1998c
Box model	RADM2 (Stockwell et al., 1990)	O <sub>3</sub> , HCHO, H <sub>2</sub> O <sub>2</sub> , and PAN; ozone control strategies	Reaction rate constants and product yields.	Uncertainty estimates from previous published study. Global Monte Carlo calculations of secondary pollutant formation and ozone	48, 14 Gao et al, 1996; Yang et al, 1996b

				control strategies.	
Box model	SAPRC90	O <sub>3</sub> and VOC incremental reactivity quantification	73 rate parameters	Uncertainties estimated through expert and published review. Initial first order sensitivity analysis of 201 compounds using the Direct Decoupled Method (DDM; ref). Uncertainties in incremental reactivities calculated using sets of 100 Monte Carlo simulations.	Yang et al., 1995
Box model	SAPRC90	Reactivity Adjustment Factors from alternative fuels	34 organic compound incremental reactivities and emissions composition of 8 fuels	Uncertainties from previous published studies. Analysis using 300 Monte Carlo simulations.	Yang et al., 1996a
CIT Three-dimensional	SAPRC90	O <sub>3</sub> and Reactivity Adjustment Factors from 5 alternative fuels	11 reaction rate constants and one product yield parameter.	Uncertainties from Yang et al., 1996a. Sensitivity analysis of chemical mechanism rate constant and product yield uncertainties on quantification of Reactivity Adjustment Factors for CNG, LPG, Ph2 gasoline, M85, and E85.	Bergin et al., 1996

**Table 1. Current Photochemical Air Quality Models and Attributes. The list is meant to be instructive as to the variety and history of photochemical models, and is not exhaustive.\***

a. Urban Scale

Model	Full Name/ Reference	Model Type	Chemical Mechanism (often used: most can use a variety of mechanisms)	Grid size, Features, Comments	Typical Applications (Location/ Pollutant/ research and/or policy focus)
UAM-IV	Urban Airshed Model, version IV (Reynolds et al., 1973)	Eulerian, multilayer, non-nested grid	CB-IV	Variable horizontal grid size (typically about 5 km).	North America., Europe/ U.S. Regulatory Model
CIT	California/Ca rnegie Institute of Technology Model (Harley et al., 1992)	Eulerian, multilayer, non-nested grid (Trajectory form available.)	SAPRC90/93 (readily changed)	variable grid (typically about 4-5 km.), cloud processes, dry dep, aerosol dynamics, sensitivity anal.	U.S, Europe, Asia, Australia/Ozon e, PM & deposition & Ozone/ Policy & research
CALGRID	California Air Resources Board Grid Model (Yamartino et al., 1992)	Eulerian, multilayer, non-nested grid	CB4, SAPRC90/93 (readily changed)	variable grid (typically about 4-5 km.), cloud processes, dry dep,	U.S, /Ozone, PM & deposition & Ozone/ Policy & research
EKMA	Empirical Kinetics Modeling Approach (NRC, 1991)	Box Model (including trajectory form)	Variable (CB4, SAPRC, RADM, etc.)	Little physical detail. Used for chemical kinetics investigatio n	Historical model used early in U.S. for policy and research. Used for studies focussing on chemistry

\* Table is taken from Russell and Dennis (1998).

b. Regional Scale\*

Model	Full Name/ Reference	Model Type	Chemical Mechanism (often used: most can use a variety of mechanisms)	Grid size, Features, Comments	Typical Applications (Location/ Pollutant/ research and/or policy focus)
STEM/ STEM II	Sulfur Transport and Emissions Model (Carmichael et al., 1991)	Eulerian, multilayer, non-nested grid	Atkinson et al. (1992)	Variable horizontal grid size (typically about 50 km.), cloud process, wet and dry deposition	U.S. and Asia/ Acid deposition/ Research
RADM	Regional Acid Deposition Model (Chang et al., 1987)	Eulerian, multilayer, non-nested grid	RADM2 (Stockwell et al., 1990)	variable grid (typically about 80 km.), cloud processes, wet and dry dep.	U.S./Acid deposition & Ozone/ Policy & research
ROM	Regional Oxidant Model (Lamb, 1983)	Eulerian, 3 layer, non- nested grid	CB-IV (Gery et al., 1989)	Typical horiz. grid about 18 km.	U.S./ Ozone/ Policy & research
EMEP Sulfur Model	European Monitoring and Evaluation Programme Sulfur Model (Eliassen et al., 1982)	Lagrangian, 1 Layer	EMEP		Europe/Ozo ne/ Policy & research
EMEP Ozone Model	European Monitoring and Evaluation Programme Oxidant	Lagrangian, 1 Layer	EMEP	150 km resolution.	Europe/Ozo ne/ Policy & research

\* Table is taken from Russell and Dennis (1998).

	Model (Simpson, 1992)				
EURAD	European Air Dispersion Model (Hass, 1991)	Eulerian, multilayer, nesting possible	RADM2	Similar to RADM/SAQ M	Europe/Acid deposition and ozone/ Research
LOTOS	Long Term Ozone Simulation Model (Bultjes et al., 1988)	Eulerian, 3 layer, non- nested grid	CBM-IV	Grid 0.5° Lat x 1.0° Lon.	Europe/Ozo ne/ Research
Harvard Model	(Sillman et al., 1990a)	Eulerian, Multilayer	Harvard		U.S./Ozone/ Research

Table 1 (cont.). Current Photochemical Air Quality Models and Attributes

NOAA	National Oceanic and Atmospheric Administration (McKeen et al., 1991a)	Eulerian, Multilayer	NOAA		U.S./Ozone/Research
REM-3	Regional Eulerian Model with 3 chemistry schemes (Stern, 1994)	Eulerian, 3 layers	CB-IV, SAPRC-90, Harwell	Grid 0.25° Lat x 0.5° Lon.	Europe/Ozone/Policy & Research
ADOM	Acid Deposition and Oxidant Model (Venkatram et al., 1988)	Eulerian, Multilayer	Atkinson et al. (1992)	Variable grid size	North America Ozone/Policy

c. Multiscale/Nested Models\*

Model	Full Name/Reference	Model Type	Chemical Mechanism (often used: most can use a variety of mechanisms)	Grid size, Features, Comments	Typical Applications (Location/Pollutant/research and/or policy focus)
SAQM	SARMAP Air Quality Model (Chang et al., 1997)	Eulerian, multilayer, nested grid	CBM-IV	Grid size from 4-80+ km.	U.S./Ozone/Policy
MAQSIP	Multiscale Air Quality Simulation Program (Odman and Ingram,	Eulerian, multilayer, nested grid	CBM-IV	Grid size from 4-80+ km.	(New model)

\* Table is taken from Russell and Dennis (1998).

	1996)				
EURAD	European Air Dispersion Model (Hass, 1991)	Eulerian, multilayer, nesting possible	RADM2	Similar to RADM/SAQM	Europe/Acid deposition and ozone/ Research
UAM-V	Urban Airshed Model-Variable (Morris, et al., 1991)	Eulerian, multilayer, nested grid	CB-IV	Grid sizes range from 4-50+km., Plume-in-grid	U.S./Ozone/ Policy
URM	Urban-to-Regional Multiscale Model (Kumar et al., 1994)	Eulerian, multilayer, multiscale	SAPRC (e.g., Carter, 1990)	Grid sizes from 4-200km, Plume-in-Grid, aerosol dynamics	U.S./Ozone/ Research and Policy

d. Photochemical models with aerosol dynamics routines.\*

Model	Full Name/ Reference	Aerosol Treatment
UAM-AERO (See UAM description above)	Urban Airshed Model, Aerosol (Lurmann et al., 1997)	Sectional approach
CIT-AERO (See CIT description above)	CIT Aerosol	Sectional approach
RPM (Based on RADM, described above)	Regional Particulate Model (Binkowski and Shankar, 1995)	Modal approach
SAQM-AERO (Based on SAQM, described above)	SAQM, Aerosol	Sectional approach
URM (See URM description above)	Urban-to-regional Multiscale (Kumar et al., 1994)	Sectional approach

\* Table provided by Robin Dennis, personal communication (1998).

# FIGURES

Figure 1. Non-Linearity and error in [O3] and d[O3]/dENox with size of emissions increment.

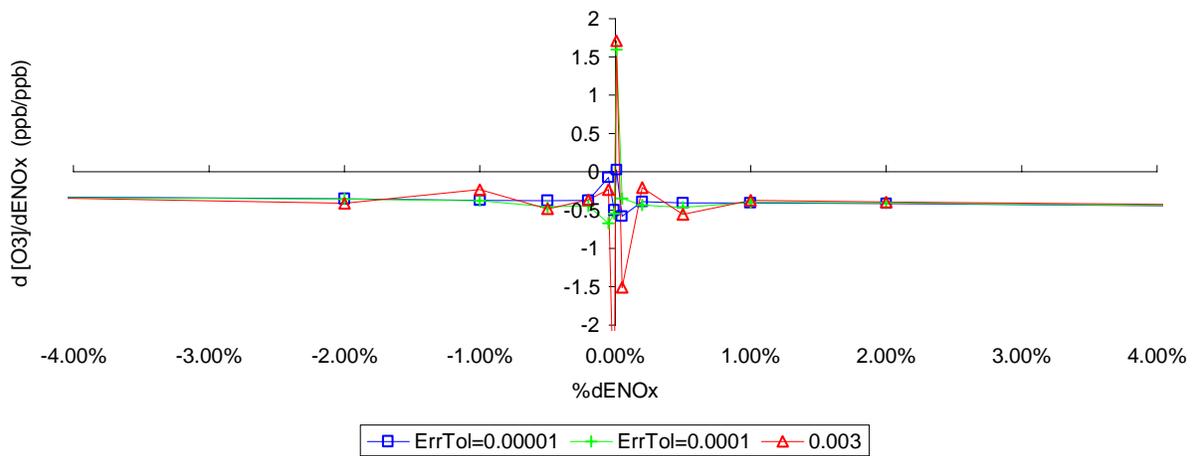
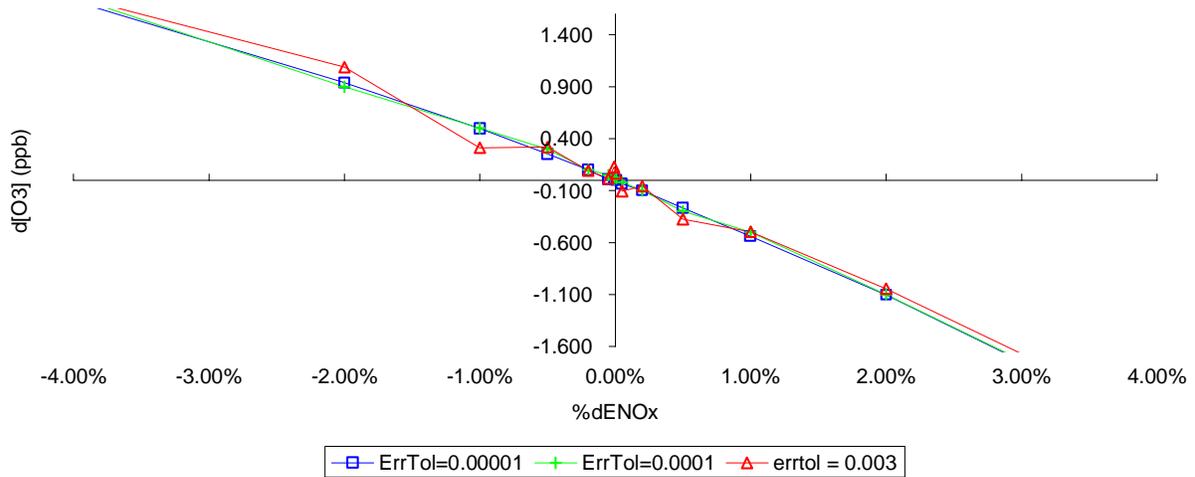


Figure 2. Non-linearity in HCHO incremental reactivity as a function of emissions increment.

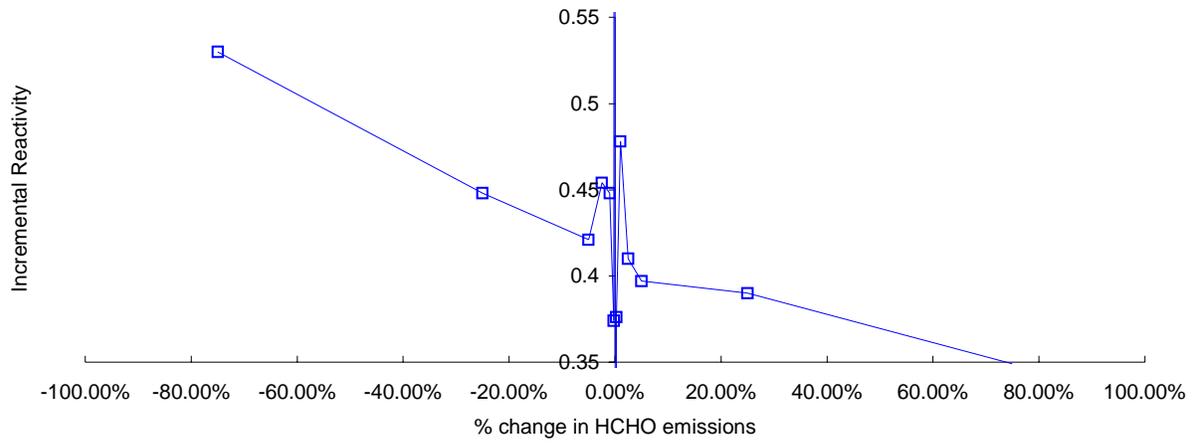
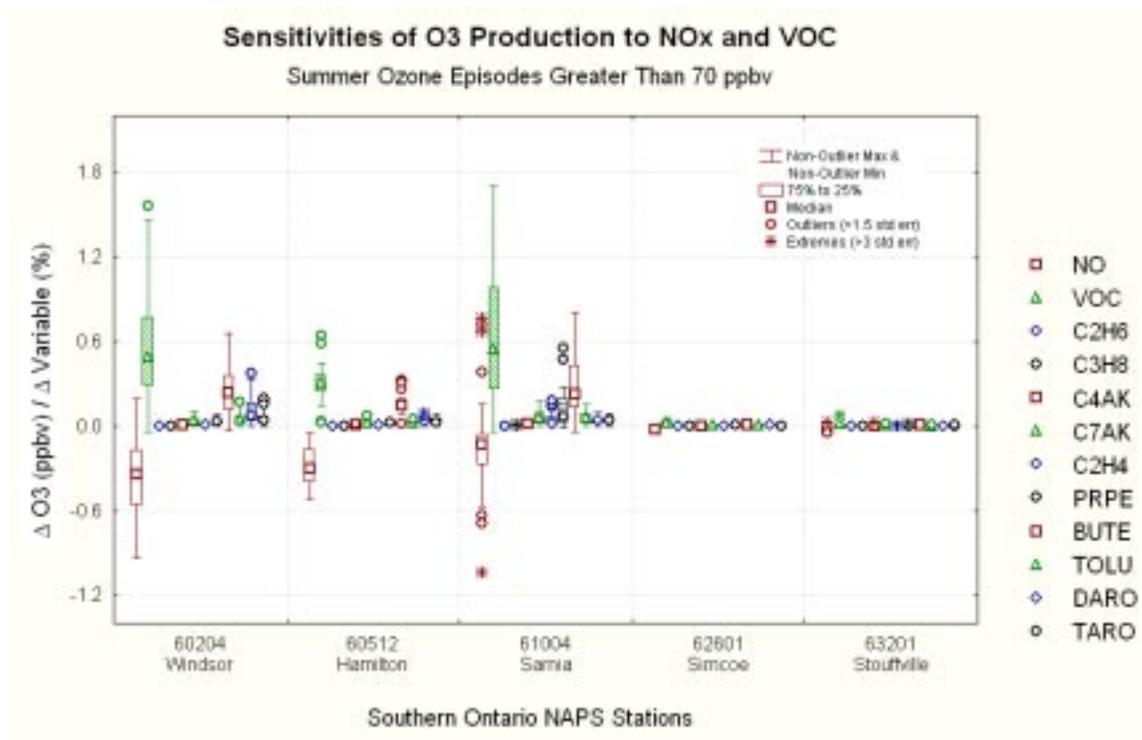


Figure 3. Sensitivities of O<sub>3</sub> Production to NO and VOC mixing ratios.



Results expressed in ppbv change in O<sub>3</sub> / percent change in initial concentration.