REACTIVITY ASSESSMENTS

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Note:

Much of the text on Quantification of VOC Reactivity and Variability in Reactivity Scales is from Bergin et al. (1998).

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QUANTIFICATION OF VOC REACTIVITY

A number of possible methods to quantify the impact of a VOC on ozone formation have been examined. Early reactivity experiments were based on amounts of ozone formed when the VOC is irradiated in the presence of NO_x in environmental chambers (e.g., Wilson and Doyle, 1970; Altshuller and Bufalini, 1982; Laity et al, 1973). However, individual VOCs are not emitted in the absence of other reactive organics, so such experiments cannot be expected to represent atmospheric conditions. Furthermore, there are chamber wall and background effects which affect the results of such experiments, particularly if the compound reacts slowly or has radical sinks in its mechanism (Carter and Lurmann, 1990, 1991; Carter et al, 1982; Bufalini et al, 1977; Joshi et al, 1973; Jeffries and Sexton, 1993). An alternative measure that has been proposed is comparison of the OH radical rate constants between VOCs (e.g., Darnall et al, 1976; CARB, 1989; Chameides et al, 1992). The EPA has for the most part has used the OH rate constant (with ethane as the boundary) for exempting compounds from VOC regulations

(Dimitriades, 1996). Although not strictly a measure of ozone formation, for most compounds reaction with OH is the main process that initiates the VOC's ozone-forming reactions. This approach has the significant advantage that the OH rate constants are known or can be estimated for essentially all VOCs of relevance to most regulatory applications (Atkinson, 1987, 1989, 1990, 1994), and the OH rate constants are properties only of the VOC, and not the environment where the VOC is emitted (other than small temperature dependencies.) However, a significant number of compounds also react nonnegligibly with ozone, NO_3 radicals or by direct photolysis, and also this method does not account for the significant differences in the subsequent reaction pathways of the initial products, which can affect how much ozone is formed after the VOC-OH reaction OH (Carter and Atkinson, 1989; Carter, 1994).

In particular, model calculations have shown that incremental reactivities of VOCs depend not only on how fast the VOC reacts, but also on the tendency of the VOC to enhance or inhibit radical levels, the tendency of the VOC to remove NO_x from the system, and the reactivity of the VOC's major products (Atkinson, 1990; Carter and Atkinson, 1989; Bowman and Seinfeld, 1994a, 1995). For example, aromatics, which have strong NO_x sinks and radical sources in their mechanisms, are predicted to have relatively high reactivities under low VOC/NO_x conditions, but are predicted to have negative reactivities when the VOC/NO_x ratio was sufficiently high. For this reason, the OH radical rate constant has been shown to correlate poorly with other measures of ozone formation potential, particularly for the more rapidly reacting VOCs (e.g., Dodge, 1994, Carter, 1991).

Because of the limitations of the OH radical rate constant scale, Weir et al. (1988), and Carter (1991) argued that a scale based on *incremental reactivities* would provide a more comprehensive measure of the effect of a VOC on actual ozone formation. This is defined as the change in ozone caused by a change in the emissions of a VOC in a specific air pollution episode. To remove the dependence on the amount of VOC added, incremental reactivity is defined by Equation 1 as the limit as the amount of VOC added approaches zero, i.e., as the *derivative* of ozone with respect to VOC (as shown on the lower plots of Figure 1):

$$IR_i = \frac{\partial[O_3]}{\partial[VOC_i]} \tag{1}$$

Here, IR_i is the incremental reactivity and the subscript i denotes the VOC being examined. This reactivity definition takes into account the effects of all aspects of the organic's reaction mechanism and the effects of the environment where the VOC is emitted. However, model calculations (Dodge, 1977; Carter, 1991, 1994; Chang and Rudy, 1990) and environmental chamber experiments (Carter et al, 1995a) have shown that changes in environmental conditions can significantly affect incremental reactivities, both in a relative and in an absolute sense. Therefore, the incremental reactivity is a function of the episode as well as the VOC. This presents obvious problems in developing reactivity scales for use in VOC control regulations that will be applicable under all conditions. Methods for dealing with this episode dependence are discussed in the section on variability below.

The incremental reactivity of a VOC under true ambient conditions cannot be measured directly—other than by changing emissions and then observing the resulting changes of air quality for enough years to factor out effects of meteorological variability—but can be estimated either by computer model calculations or by suitably designed environmental chamber experiments. Both types of estimation approaches have their limitations. In the case of model calculations, uncertainties and approximations in the model for airshed conditions, in the model formulation, and in the chemical mechanism cause uncertainties in the predicted ozone impacts, as discussed further below. In the case of experiments, it is difficult for the conditions of the experiment to simulate ambient conditions, so the results do not have general applicability. For these reasons, modeling and experimental measurements are used in conjunction for examining reactivity.

In an early model simulation, Dodge (1984) showed that, when adding a given amount of a VOC to the other VOC inputs in EKMA model simulations, the calculated change in ozone varied widely among different VOCs at low VOC/NO_x ratios, but were lower and less variable under high VOC/NO_x conditions. Carter and Atkinson (1989) showed that while the VOC/NO_x ratio was probably the most important single environmental factor affecting reactivity, other factors are important as well. Simulations of environmental chamber experiments resulted in different incremental reactivities (both absolute and relative) than simulations of atmospheric conditions, indicating that incremental reactivities measured in chamber experiments should not be used to assess atmospheric reactivities without the benefit of model calculations to account for the differences between chamber and airshed conditions. In addition, Carter and Atkinson (1989) showed that the number of days in the pollution episode and the nature of the other VOCs present also had a non-negligible effect on VOC reactivities. Carter (1994) showed that there was still some variability in relative reactivities among different one-day airshed model scenarios even after NO_x inputs in the scenarios were adjusted to yield consistent conditions of NO_x availability.

Jeffries and Crouse (1991) and Bowman and Seinfeld (1994a,b, 1995) looked at the factors affecting reactivity from the perspective of the chemical reactions actually responsible for ozone formation. The result was that the relative contribution of VOCs to the reactions that are directly responsible for ozone could be quite different than the relative incremental reactivities of those VOCs. This is because many VOCs have high (or negative) incremental reactivities—not because of the ozone formed by their own reactions, but because their reactions affect how much ozone is formed from other VOCs. For example, if the reactions of a VOC significantly affect radical levels they will affect how much O_3 is formed from the reactions of other VOCs, and for many VOCs this indirect effect on reactivity makes a larger contribution to its incremental reactivity than the ozone formed by the VOC's direct reactions (Bowman and Seinfeld, 1994a,b, 1995). This result has also been shown from an analysis of the results of incremental reactivity experiments carried out under maximum reactivity conditions (Carter et al, 1993, 1995b).

A general scale that ranks the reactivities of VOCs would clearly aid the development of regulatory applications that take differences in VOC reactivity into account. However, because incremental reactivities depend on environmental conditions, no incremental reactivity scale will correctly predict relative ozone impacts under all conditions (even if there were no uncertainties in the models, the chemical mechanism, and the airshed conditions.) This can be partially

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accounted for through the use of a relative, rather than absolute, comparison of reactivities. In other words, we do not compare the absolute amount of ozone formed per amount of VOC added, but the amount of ozone formed relative to other VOCs. This concept is applied to sources as well as compounds. For example, if one is comparing the reactivity of emissions from a gasoline-fueled vehicle to that from a compressed natural gas (CNG) vehicle, what is most important is not that the gasoline-fueled exhaust has a reactivity of 1.00 gram of ozone per gram of exhaust VOC, and CNG exhaust has a reactivity of 0.20 grams of ozone per gram exhaust VOC. These quantities are dependent on location and time. What is of greater interest is that the CNG exhaust is 5 times less reactive, so the CNG vehicle can emit about five times as much VOC in any area and still have a similar impact on ozone levels. Defining reactivity in reference to other reactivity values rather than to absolute ozone formation allows reactivity values to be more readily evaluated and compared. To calculate relative compound reactivities, we quantify the reactivity of individual VOCs as compared to a reference compound or, better, a VOC mixture (i.e., the reactivities are normalized). When these normalized compound reactivities are quantified in a relative sense, the set of reactivities is referred to as a relative reactivity scale.

While the use of a reactivity scale reduces the effect of reactivity variability, it cannot completely account for environmental effects. Nevertheless, the only practical alternative to using a general reactivity scale is regulating all compounds as if they were either reactive or unreactive, i.e., using an implicit reactivity scale where all compounds have reactivities of either 0 or 1. This method has obvious shortcomings. For these reasons, a number of reactivity scales have been developed, and are summarized in Table 1.

Modeling-based Assessments of VOC Reactivity

Two methods are traditionally used to assess VOC reactivity: experiments using smog chambers and computationally using air quality models. Both have limitations. Smog chambers do not realistically represent the physics of pollutant transport and impact of fresh emissions, and are generally carried out at higher pollutant levels than generally occur in the atmosphere. Therefore, the conditions inside a smog chamber do not reflect those conditions found in the ambient air. Given the sensitivity of a compounds impact (and hence reactivity) to the environment, this limits the applicability of smog chamber experiments for reactivity quantification. In addition, chamber wall effects can also impair such experiments, particularly if the compound reacts slowly or has radical sinks in its mechanism (e.g., Carter and Lurmann, 1991). Models also have limitations. All models suffer from a limited knowledge in the chemistry of specific compounds, and this directly impacts one's ability to quantify the reactivity of that compound. For many compounds, the chemical mechanism is not well known. A second limitation is that other uncertainties lead to uncertainties in how a model treats the dynamics of various compounds. However, the models have been developed to accurately represent the various physical and chemical processes that impact the dynamics of trace gases in the atmosphere, so they provide a method to quantify reactivity in the atmosphere. Computational modeling has been the approach taken in most recent reactivity quantification studies (e.g., Carter and Atkinson, 1989; Carter, 1994; Derwent and Jenkins, 1991; Bowman and Seinfeld, 1995; McNair et al., 1992; Yang et al., 1995; Bergin et al., 1995).

The various types of model's used for reactivity assessments include box, trajectory and three-dimensional models (also called airshed models). The differences in these models are described in the section on modeling. The three-dimensional models have the fewest limitations in their formulation, and can also provide spatial information, e.g., how compound reactivities change over an airshed. Thus, they are the most powerful approach. On the other hand, they are the most computationally intensive and until recently could not be used with the more detailed chemical mechanisms which are required for reactivity assessment. In addition, the input data usually have major uncertainties, and if the input data are incorrect the model predictions may be no more accurate than those using simpler models. The simpler models (e.g., box and trajectory models) permit a wider variety of scenarios and more cases to be examined, in greater chemical detail and at lower cost. Simpler models were used for the first reactivity assessments, and the more recent assessments were conducted using multidimensional models applied at urban and regional scales. Both types of models, because of their individual strengths, continue to have a role in reactivity quantification. A list of model-based reactivity assessments is given in Table 1.

Trajectory Model Reactivity Assessments

The first set of reactivity assessments were conducted using single cell trajectory models so that a detailed chemical mechanism could be used and the model could be applied to a number of areas. Using this approach, Carter (1994) developed a total of 18 reactivity scales, all calculated using the SAPRC-90 chemical mechanism. Subsequent versions of these scales have been calculated by Carter using the updated (SAPRC-98) version of the mechanism (Carter, 1998), but the scenarios and reactivity assessment methods were not changed.

The Carter scales represent the average results from 39 modeled trajectories, each representing a single day episode in an urban area with varying, though low, VOC-to-NO_x ratios. Averaging reactivities across these trajectories accounts for some of the variability caused by environmental conditions, as discussed further below. The 18 reactivity scales were derived using nine different approaches for dealing with the dependence of reactivity on environmental conditions and on two methods for quantifying ozone impacts. A summary of these scales is presented in Table 2. Of those 18 scales, the *Maximum Ozone Incremental Reactivity* (MOIR) scale and the *Maximum Incremental Reactivity* (MIR) scale were found to be reasonably representative of the full set, and are discussed in more detail below. The MIR scale reflects primarily the effect of the VOC on ozone formation rates. The MOIR, Equal Benefit Incremental Reactivity (EBIR), and the base-case average ratio ozone yield scales are more sensitive to the effect of the VOC on ultimate O_3 yields in NO_x-limited conditions. Scales based on integrated O_3 are sensitive to both factors, but tend to be more similar to MIR than MOIR (see also the discussion in following sections.) Scales sensitive to effects of VOCs on ozone formation rates generally give higher relative reactivities for aromatics, and lower relative reactivities for alkanes, than those based on ultimate O_3 yields in NO_x-limited conditions.

More recently, Carter (unpublished results) calculated reactivity scales based on the effect of the VOC on maximum 8-hour average ozone levels, which is more representative of

the new Federal ozone standard. The reactivities were similar to those calculated using the integrated ozone scale.

Two of the above scales that have been most seriously considered for regulatory use are the MOIR scale and the MIR scale. The MOIR is based on incremental reactivities for NOx conditions which are most favorable to ozone formation, as indicated by the "MOR" point on the bottom-left plot in Figure 1. The MIR is based on the incremental reactivities of VOCs under relatively high NO_x conditions where the VOCs have their highest incremental reactivity, as is also shown on the bottom-left plot of Figure 1. Carter and co-workers (Weir et al, 1988; Carter, 1994) proposed using the MIR scale for regulatory applications because the MIR scale reflects reactivities under environmental conditions which are most sensitive to effects of VOC controls. The MIR scale may be less accurate than others in predicting O_3 effects under lower NO_x conditions; however, because of the lower sensitivity of O_3 under those conditions, the practical impact of those inaccuracies is less than would be the case for the conditions where the scale is designed to apply. The MIR scale was also found to correlate well to scales based on integrated O_3 yields, even in lower NO_x scenarios. It can also be argued that this scale is appropriate when used in conjunction with a NO_x control program, which provides the most effective ozone control under low NO_x conditions.

Nevertheless, the MOIR scale is attractive because it is more representative of the "worst case" ozone formation conditions in various airsheds, and also because it tends to be more conservative in predicting substitution benefits for most alternative fuels. The MIR scale tends to predict larger reactivity benefits for slowly reacting compounds than may be appropriate, because the higher NO_x levels of MIR scenarios cause suppressed radical levels, which decrease the amount that slower reacting compounds react in the scenarios. Ultimately, CARB concluded that the MIR was a superior method to the OH scale for assessing reactivity, and used the scale as a basis for deriving Reactivity Adjustment Factors (RAFs) in California's LEV/CF regulations (CARB, 1991). RAFs are discussed further below. The MIR scale is now also widely used as a means for comparing reactivities of vehicle emissions during various driving cycles as well as with the use of alternative fuels (e.g., AQIRP, 1993).

An alternative approach that may have the best features of both the MIR and MOIR would be to use a scale based on integrated ozone or maximum 8-hour average ozone under base-case or maximum ozone conditions. This has the advantage of the MIR scale in that it performs well in predicting reactivity effects under high NOx conditions that are most sensitive to VOCs (because it correlates reasonably well to MIR for most VOCs), while also being based on conditions of scenarios that are more representative of worst case O_3 pollution episodes. Furthermore, in the context of Eulerian model simulations where ozone impacts vary with both time and space, integrated ozone throughout the full air basin and time period of the episode is arguably a more robust measure of the exposure of the environment to ozone than the peak ozone concentration, which might be highly localized in time and place. Comparisons of Eulerian model predictions with the MIR and MOIR scales are discussed below.

An alternative series of reactivity scales derived using a trajectory model are the *Photochemical Ozone Creation Potential* (POCP) scales, also shown on Table 1, which were calculated by Derwent and other researchers in Europe (e.g., Derwent and Jenkin, 1991;

Andersson-Skold et al, 1992) using updated versions of the Derwent and Hov (1979) chemical mechanism (see Atmospheric Chemistry section) and a two-layer Lagrangian model representing various multi-day trajectories across Europe. The reactivities are calculated from the change in mid-afternoon ozone for each day in the trajectory resulting from removing the test VOC from the emissions, divided by the integrated emissions of the test VOC up to the time of the ozone observation. Different POCP scales were calculated using different trajectories, and unlike the Carter approach no scales were derived to represent multiple conditions. Most of the POCP scenarios probably represent low NO_x conditions.

A comparison of MIR, MOIR, and POCP reactivities for selected VOCs is shown on Figure 2. The MIR and MOIR scales give very similar relative reactivities for most compounds, and are consistent in predictions of which compounds are highly reactive and which are not. However, for reasons indicated above, the MOIR scale gives lower relative reactivities for aromatics, and also predicts lower relative reactivities for radical initiators such as formaldehyde, which have larger effects on rates of ozone formation than on ultimate ozone yields. The MIR, MOIR, and POCP relative reactivities generally predict similar orderings of reactivities (relative reactivities), but some significant differences are observed. The largest differences, particularly for the alkanes and methyl ethyl ketone (MEK) are probably due primarily to differences in the chemical mechanisms employed, rather than the types of scenarios employed. The mechanisms used to develop the POCP reactivities are chemically detailed and intended to be explicit, but unlike the SAPRC and Carbon Bond mechanisms have not been evaluated against chamber data, and may not adequately represent the large NO_x sink processes in the aromatic photooxidations that give them low or negative reactivities under low NO_x conditions (see Atmospheric Chemistry section). The relatively low reactivity predictions for the higher alkanes by the SAPRC mechanisms have been verified by environmental chamber experiments (Carter and Lurmann, 1991; Carter et al, 1993, 1995b, 1997; Carter, 1995). Effects of differences and uncertainties in chemical mechanisms on reactivity scales are discussed in more detail in a later section.

Jiang et al. (1996) also used a trajectory model to evaluate reactivity. This study used the SAPRC-90 chemical mechanism in the Ozone Isopleth Plotting Research version (OZIPR) trajectory model (Gery and Crouse, 1989) to predict the reactivity of 17 VOCs and methane in the Lower Fraser Valley of Canada. This study designated nine VOCs as significant contributors to the ozone concentrations, seven of which represent lumped compound groups. The greatest contributor to ozone formation was found to be ARO2, a lumped model species used to represent the xylenes and other fast reacting aromatics.

Eulerian Model Reactivity Assessment

A serious concern about the regulatory application of scales such as MIR and MOIR is that they are all based on the single cell (Lagrangian) model simulations of single-day pollution episodes. MIRs have been developed based on 10-hour simulations, whereas some organic compounds may remain in an urban airshed for 2 to 3 days, and even longer when considering regional ozone. Further, trajectory models lack the physical detail (e.g., wind shear, venting to/from the free troposphere), the spatial and temporal detail of emissions and resulting

pollutants, and the multi-day pollution effects that can be represented in Eulerian models. For that reason, it is important that the scales derived using trajectory models be evaluated using more detailed models with the same chemical mechanism. Initial studies applying three-dimensional air quality models to assess reactivity have been carried out by Russell and co-workers (e.g. McNair et al, 1992; Bergin et al,1996,1998; Kahn et al, 1998a,b; Yang et al., 1998). Those studies primarily employed the Carnegie/California Institute of Technology (CIT) Model (Mc. Rae et al, 1982; Harley et al, 1993) applied to a 3-day air pollution episode in the Los Angeles air basin (Harley et al., 1994), or the Urban-to-Regional Multiscale (URM) model (Odman et al., 1994). In addition to Los Angeles-based studies, Kahn et al. (1998a) also applied the CIT model to the Swiss Plateau and Mexico City to study the use of reactivity over domains with greatly different levels of VOC and NO_x, and Kahn et al. (1998b) studied reactivity variations over a regional domain, looking at the U.S.-Mexico border region. Two of these studies (Kahn et al. 1998b and Yang et al., 1998) incorporated the Direct Decoupled Method (DDM) for computational efficiency.

A challenge in comparing VOC reactivity using results between box and grid modeling studies is the difference between quantification measures, or metrics, that can be defined from each analysis method. Differences in the spatial and temporal representation of emissions can also make the comparison of results difficult. In the Eulerian reactivity studies, incremental emissions of the test compound were modeled by increasing the test VOC proportionally to the spatial and temporal distribution of the base organic species emissions. The rates of all organic species emissions in each modeling cell for each hour were used to determine the rate of the test species emission in that cell. This is represented mathematically by Equation 2, where, at time t in model cell x, y, z, the perturbed emission (E^p) of test species i is calculated as the base emission of that species (E_i^b) plus a fraction, (α), of the sum of the total base level emissions of reactive organic gases . Index j refers to each represented explicit or lumped emitted VOC. This modeling method accounts for the effect of emissions variation, transport, and multi-day reactions.

$$E^p_i(x,y,z,t) = E^b_i(x,y,z,t) + \alpha\Sigma_j E^b_j(x,y,z,t) \qquad (2)$$

In addition to different representation of emissions by trajectory and three-dimensional models, results from three-dimensional modeling can be described in a number of ways. Three of the most useful metrics are the difference between peak ozone concentrations predicted using the base and perturbed inventories, and population- and exposure-weighted exposure to ozone levels exceeding a threshold value. Further description of these metrics are presented elsewhere (McNair, et al. 1992, Bergin, et al., 1995). Eulerian model results can also be compared across different parts of the modeled domain, which have varying VOC to NO_x ratios because of pollutant emissions and transport, as well as variation in incident radiation caused by cloud cover (Bergin et al, 1995).

In an initial application of a three-dimensional model for reactivity analysis, McNair et al. (1992) used the CIT air quality model with a relatively highly lumped chemical mechanism, the Lurmann, Carter, Coyner (1987) mechanism (LCC), to quantify the reactivity of 11

individual and lumped VOCs. This study allowed comparison with single-cell model reactivity studies by others, and also between different metrics of ozone impact, including how the species impact the peak ozone as well as ozone exposure. The results showed that the MIR reactivities did not perform well in predicting peak ozone sensitivities for the model species, but performed reasonably well in predicting effects of model species on integrated ozone exposures over the air quality standard. The MOIR scale did not compare as well as MIR to airshed model derived results for either the impacts on peak ozone or on ozone exposures over the air quality standard. The comparisons of McNair et al. (1992) are complicated somewhat by the fact that the study utilized the LCC chemical mechanism, which does not correspond directly with SAPRC-90 mechanism species used in calculating the MIR and MOIR scales. However, agreement between the MIR scale and the McNair et al. (1992) ozone exposure predictions is remarkably good considering the difference in the mechanisms, models, and ozone impact quantification techniques employed. It was noted in this study that much of the variability found could be ascribed to using a single species (CO in this case) for normalization, which is discussed further below.

Subsequent to the study of McNair et al. (1992), the SAPRC-90 mechanism was implemented in the CIT model (referred to as the CIT-S90) by Bergin et al. for more direct comparison with the MIR and MOIR reactivity scales (Bergin et al, 1995, 1998). Here, reactivities are normalized to a mixture of VOCs representative of exhaust emissions, as in the reactivity studies of Carter (1994) and Yang et al. (1995). Some differences were found which are believed to be due to multi-day pollutant carryover and cloud cover represented in the CIT model, which are not accounted for by box models. The CIT-S90 was also used to investigate effects of environmental variabilities and of chemical mechanism uncertainties on reactivities (discussed in the variability and uncertainty sections, respectively, below.) A more detailed comparison of the CIT-S90 study results and the MIR and MOIR are also presented below.

One other three-dimensional model study of reactivity is that of Kahn et al. (1998a,b), who conducted a reactivity study on VOC solvents having a wide range of reactivities. The SAPRC-90 chemical mechanism was used for this study, assuming rate constants of similarly reacting compounds for those solvents for which chamber studies have not been performed. The solvents studied included m-xylene (the most reactive), parachlorobenzotriflouride (PCBTF, a halogenated aromatic which is the least reactive), benzotriflouride (BTF), acetone, ethanol and isobutane. These compounds not only have a wide range of reactivities, but also represent a number of different types of VOCs. Using a box model to quantify the MIR and MOIR reactivities, as seen in Figure 3, they found reasonable agreement between the normalized MIR and MOIR reactivities, though the absolute reactivities differed by a factor of two. These results, along with others (Carter, 1994a; Bergin et al., 1995, 1997; Russell et al., 1995), suggest that normalizing reactivity (i.e., using relative reactivities) removes much of the environmental variation, though species reactivities do vary in regions of low NO_x availability or very high VOC levels. Further, the VOC reactivity assessment for the U.S.-Mexico border region shows that it is currently possible to conduct reactivity assessments regionally, particularly when using a tool such as DDM. A further study (Yang et al., 1998) used a three-dimensional model to analyze both the uncertainties in relative reactivities and the spatial variability in the southern California area. That study is further discussed in the applicable sections, below.

The above studies deal primarily with assessing the reactivities of individual VOC species. In addition, a series of studies have looked at quantifying the reactivity of source emissions, e.g., how the reactivity of a mixture of VOCs emitted by a source might be affected by the methods employed, the location, and the metric of interest. A sampling of such studies is listed in Table 3.

VARIABILITY IN REACTIVITY SCALES

One of the stronger debates on the use of reactivity quantification for determining the potential impact of VOCs on ozone is that the absolute amount of ozone formed from a given quantity of VOC is heavily dependent on the local ambient conditions, including the meteorology (wind speed, temperature, mixing height and humidity), pollutant transport (the residence time of emissions in an urban area), distribution of emissions sources (e.g., proportion of biogenic, mobile source, and other emissions), and background pollutant concentrations (e.g., the VOC/NO_x ratio and the absolute levels of VOCs and NO_x). This dependence on variable conditions was discussed above when presenting various reactivity scales and experimental results.

One effect of variable conditions is that, in the extreme, a compound can go from being fairly reactive under certain conditions to having a negative reactivity under others (e.g. toluene). This dependence may make the use of generalized reactivity weighting and the development of reactivity-based control strategies problematic. However, one should also recognize that for most of the organics, those that are highly reactive relative to the other VOCs under one set of conditions remain highly reactive under other conditions. Likewise, the less reactive VOCs remain less reactive. Compounds that vary widely, such as toluene, are the exception rather than the rule. As discussed above, this variation can be reduced by the use of normalizing and relative ranking in the reactivity quantification of VOCs.

For example, in 1990, CARB (1991, 1993) adopted the LEV/CF regulations, where vehicle exhaust emissions standards used "Reactivity Adjustment Factors" (RAFs), which are ratios of reactivities of the alternatively fueled to conventionally fueled exhausts, to account for the reactivity differences of these exhausts. The impact of environmental condition variability on RAFs was investigated by Russell et al. (1995), who calculated both the absolute reactivities and the RAFs of exhaust from vehicles operated on six fuels along each of the 39 trajectories used in developing the MIRs. The results are shown by box plots in Figure 4. The variation in absolute ozone forming potentials across cities is substantial. However, in the case of the RAFs, where the reactivities of the exhausts are normalized by the reactivity of standard gasoline exhaust, variation among cities is sharply diminished (Figure 4B). Again, it is the relative ozone impact that is of greatest concern. Such a marked decrease may not be found for source types emitting fewer compounds.

A second issue in the analysis of variability in reactivity with environmental conditions is the effect of NO_x and VOC background concentrations. The MIR scale was derived using conditions relatively high in NO_x, as might be experienced in areas with a high density of NO_x emissions (e.g., areas highly impacted by traffic or local industries with significant combustion sources).

MOIR conditions occur at lower NO_x levels, but the ROG/NO_x ratios are still lower than what might be found in rural areas. Reactivity simulation conditions used by Derwent and co-workers (1991) have even less NO_x, which represents conditions where VOC controls and reactivity weighting are relatively ineffective (as discussed below). So the question arises as to how well a measure of reactivity quantification can represent many areas, given the possible range of environmental conditions under which ozone formation occurs. This was, in part, addressed above when comparing the MIR, MOIR, and POCP scales, and is addressed further below.

The impact of environmental conditions on reactivity should be discussed at two levels. First, how it affects the reactivity of individual VOCs; and second, how it would likely affect the reactivity of emissions from a source whose composition is made up of a large number of VOCs. As suggested above, the absolute amount of ozone formed from any VOC is highly dependent on the environmental conditions. In an area already rich in VOCs (i.e., a NO_x-limited regime), the small addition of an individual VOC has a lower impact than if that same increment of VOC emissions occurs in an area rich in NO_x (where ozone formation is VOC-limited). As shown by Carter (1994), the average absolute reactivity of a suite of VOCs using the MIR scale is about twice that when using the MOIR scale. Further, there are those few compounds that can go from having relatively high reactivities to low or negative reactivities. This would appear to inhibit the use of reactivity weighting in regulatory applications.

An interesting exercise that addresses the impact of environmental variabilities is a comparison between trajectory model results and three-dimensional model results. By their nature, the three-dimensional models cover domains with a wide range of environmental conditions, going from NO_x-rich conditions in urban centers to VOC-rich conditions downwind. Further, they can follow the transport of pollutants over long distances. In the Bergin et al. (1995, 1998) modeling studies described previously, the spatially and temporally resolved ozone impacts were used to calculate impacts on the peak ozone, the potential population-weighted ozone exposure, and the spatial-weighted ozone exposure. From those calculations, the corresponding compound reactivities were quantified, normalized to the reactivity of a mixture of VOCs (so the results are relative reactivities.) As shown in Figure 5, the results from the MIR and MOIR box model calculations (Carter, 1994a), conducted for 39 cities, agreed well with related metric results from the airshed calculations for the Los Angeles, California area (as described further below).

In interpreting the results of the comparison between the two modeling approaches, and the differences found between the three metrics defined for the airshed model results, it is important to understand the ozone and population patterns in the region. The peak ozone is found in the eastern basin, in an area with relatively little NO_x, and thus has a high VOC/NO_x ratio. On the other hand, the population is concentrated more in the western basin, in areas with more dense emissions, and in particular NO_x-rich mobile source emissions, and thus having a low VOC/NO_x ratio. Also, the peak ozone is found downwind of the urban area, after the pollutants have had a chance to age, again in contrast to the more densely populated regions that experience fresh emissions. Further, the meteorology (e.g., temperatures and mixing heights) in the two portions of the basin is different. Because of these differences, contrasting the population-weighted ozone impact with the peak ozone impact can help capture the level of difference found

from environmental variability. The spatial-exposure metric is expected to give results with characteristics of each of the other metrics.

As shown in Figure 5, the airshed model-derived spatial and population density weighted results behave similarly to MIRs. The greatest differences are found for formaldehyde and other compounds whose reactivities are highly dependent on photolytic reactions. This may be explained by the use of a reduced photolysis rate in the airshed modeling to account for the observed cloud cover. The box model used clear sky conditions. The reductions in the reactivities are consistent with the sensitivity to the rate constants for the photolytic reactions (Yang et al, 1995), as addressed in the uncertainty section below. In general, airshed model results for Los Angeles agree well with MIRs, and further show that individual organics have very different ozone impacts. Such a study has not been conducted for other regions.

Russell et al. (1995), Bergin et al. (1995), and Kahn et al. (1998) compared several reactivity metrics for the box and grid models for some two dozen plus compounds including some half dozen aromatics. In general, aromatics turn out to be significantly less reactive or negative, on a relative basis, for some metrics. Since the EPA is moving to an 8 hour ozone standard, this should be the primary metric of choice. It appears as if additional work is needed to look at aromatics under several different conditions. Eastern transport conditions should also be examined in a multiday scenario. A number of the aromatics, important for industrial emissions, may be different on a relative basis.

To further compare the trajectory and airshed model results, regression analysis was performed between the box model reactivities and the airshed reactivities. As shown in Table 4, Carter's MIR scale corresponded well with the population exposure-based reactivities, and the MOIR scale agreed well with the CIT-S90 peak-ozone sensitivity. In these two cases, the slope of the regression line is virtually 1 (showing little bias as reactivities increase), and the correlation is high. The CIT-S90 spatial exposure metric correlates well with both the MIR and MOIR scales, but shows some bias in the comparison with the MOIR scale, indicating that the spatial exposure metric finds the less reactive compounds to be relatively more reactive than does the MOIR scale.

As seen from Figure 5, there are significant similarities between the CIT-S90 metrics as well, though some differences are evident. Differences were quantified by calculating the normalized bias (a value of 1 would indicate a 100% bias) and standard deviation between the scales (Table 5). These differences between potential metrics for reactivity quantification within a modeling study also introduce variability.

A similar issue in regards to the role that environmental variability plays in reactivity quantification is how various meteorological characteristics can affect reactivities. Russell et al. (1995) studied the variability in reactivities as found using the results of the box model of Carter under differing conditions, a similar box model (Yang et al, 1995), and a three-dimensional model (Bergin et al, 1995). First, using just the results of the box model calculations of Carter (1994), they quantified the inter-city variability in the absolute species reactivities along the 39 trajectories, and the inter-city variability in the relative reactivities of the individual VOCs along those same trajectories. Normalized MIRs were calculated by dividing each species city-specific

MIR by the geometric mean reactivity of all the species reactivities for that city, and multiplying by the geometric mean reactivity of the 39-city average MIRs. This alleviates the problem that VOCs are generally less reactive, in an absolute sense, in one city versus another. A sample of their results is given below in Table 6. As seen, the variability in the relative reactivity is significantly reduced between the different trajectories when the relative reactivities are used. Use of relative reactivity generally reduced variability by almost a factor of two, from about 20% to 12%.

More recently, Kahn et al. (1998a,b), Qi et al. (1998) and Yang et al. (1988) also studied spatial variability in VOC reactivity. Kahn et al., (1998a) approached this by applying a three dimensional model to different domains (Los Angeles, Mexico City and Switzerland) that experience very different levels of ozone precursors. Los Angeles has relatively high levels of NOx in most of the domain, and moderate levels of VOC. Switzerland has lower NOx and VOC levels. Mexico City has high NOx levels, and very high VOC levels. While the Los Angeles and Switzerland reactivity results were similar, the Mexico City reactivities varied, suggesting that having a large amount of VOC has a greater impact on compound reactivity than does the level of NO_x. This was further indicated in the Yang et al., (1998a) study, discussed above, which found that the sensitivity of the <u>relative</u> reactivities to the uncertainties in the VOC emission level was greater than to those in the NO_x level. Yang et al. (1998), also plotted the spatial variation in the VOC reactivities in the Los Angeles basin. Not surprisingly, the relative reactivities do vary (Figure 6). Formaldehyde has its greatest relative reactivity in the source regions since it reacts quickly and is a strong radical source, further increasing VOC oxidation in a NOx-rich environment. The slower reacting compounds (e.g., pentane) have a proportionally higher relative reactivity downwind. VOCs that can become significant NO_x sinks (e.g., toluene) have the greatest variation in reactivity, going from being positive in the source region to negative far downwind. This spatial variability suggests that it is important to define the end-point of interest: e.g., peak ozone, ozone exposure, and to calculate the corresponding relative reactivity.

Kahn et al. (1999b) applied the CIT model using the 3-D Direct Decoupled Method (DDM3D) to the U.S.-Mexico border region. This study looked at both the use of direct sensitivity analysis for reactivity assessment, as well as spatial variation in relative reactivity. The use of DDM3D produced similar results to the brute force approach with less computational noise and effort.

In the study by Yang et al., (1998), Monte Carlo analysis was applied with the CIT/DDM3D model, to quantify how influential rate constants, VOC and NOx emissions and meteorology (i.e., mixing height) impacted the relative reactivity of 11 VOCs. Figure 6 also shows the spatial variability in the coefficient of variation of the HCHO relative reactivity. The uncertainty is relatively uniform at about 35% over the middle of the domain. In addition, multiple linear regression was used to find how individual species' reactivities depended upon model parameters (e.g., rate constants) and inputs (emissions of VOC and NOx, and mixing heights). For example, the relative reactivities for the ozone exposure to HCHO and pentane were found to be:

$$RR_{HCHO} = 3.0 - 1.5F_{NO_2+h\nu} + 1.4F_{VOC_e} + 2.1F_{HCHO+h\nu} - 0.43F_{PAN-decomp} -$$
$$1.1F_{O_3+h\nu\rightarrow O^1D} + 0.9F_{NO_2+HO}$$
$$RR_{pentane} = 0.4 - 0.09F_{O_3+h\nu\rightarrow O^1D} - 0.02F_{VOC_e} - 0.003F_{AFG2+h\nu} -$$
$$0.046F_{NO_2+HO} + 0.11F_{AAR2+HO} - 0.058F_{OSD+H_2O}$$

The independent variables, the F's, represent the ratio of the variable of interest to the default value, the VOC_e subscript represents the amount that the total VOC emissions were changed, and the other subscripts (e.g., HCHO+hν) represent the corresponding reaction rates. Only the six most important parameters are given. The correlation coefficients in both cases are about 0.80. Both regression and uncertainty analyses suggest that the most influential variables were the formaldehyde photolysis rate, ozone photolysis to O^1D, the NO2-HO reaction and the VOC emission rate. On the other hand, the mixing height and NO_x emission rate had relatively less impact. It should be noted that these results may be specific to the domain modeled, and should not be generalized to being true for other areas. In fact, it might be suspected that the sensitivity to the VOC emissions rate may be particular to area like Los Angeles, and that would not be the case for a location like Mexico City (high VOC area) or much of the less-urbanized United States (low NO_x), or areas with a larger influence of ozone precursors being transported into the region. This is an obvious area for further exploration.

CHEMICAL MECHANISM UNCERTAINTY

As discussed in the Atmospheric Chemistry section, the chemical mechanisms used in the models to calculate the reactivities of the VOCs have significant uncertainties, which causes a corresponding uncertainty in results of reactivity assessments Measurement errors in laboratory kinetic and product studies contribute to a minimum level of uncertainty in the mechanisms of even the best studied VOCs, and the reactions of many of the organic compounds emitted into urban atmospheres have never been studied in controlled experiments. Their representation in chemical mechanisms is based on analogy to compounds of similar structure, creating added uncertainty, which is difficult to quantify. At issue is the extent to which the uncertainties in the chemistry impact the calculation of the reactivities for organic compounds.

One way to assess the effects of chemical mechanism uncertainty is to compare reactivity predictions using different mechanisms which represent the same state of the art but which incorporate differing assumptions concerning unknown areas of the chemistry and differing condensation approaches. As discussed above, the SAPRC-90 mechanism was used for calculation of the MIR, MOIR and other reactivity scales because of the number of VOCs it can explicitly represent. The RADM-II mechanism employs assumptions similar to SAPRC-90 concerning uncertain portions of the aromatics and other mechanisms, and would be expected to give similar reactivities for the species that the condensed mechanisms are designed to represent. However, this may not be the case for the Carbon Bond IV (CB4) mechanism, which employs differing assumptions concerning some of the uncertainties in the aromatics mechanisms, and

uses different methods for treating alkane and alkene reactions (Gery et al., 1988). Table 7 shows a comparison of MIR and MOIR (relative to the total base case emissions) calculated with the SAPRC-90 and with a recent version of the CB4 (with minor updates concerning peroxy radical reactions that do not significantly affect ozone predictions (Yarwood, 1994; Carter, 1994b). Other than the mechanism, the scenarios and the calculation methodology are the same (Carter, 1994b). Note that the only compounds shown are those that are either represented explicitly in CB4 or are represented by model species developed based on mechanisms of very similar compounds, so the differences reflect primarily differences in representation of the actual reactions, rather than condensation effects. Note also that the SAPRC-90 and the CB4 mechanisms were developed around the same time, so they are both based on approximately the same data base of kinetic, mechanistic, and environmental chamber results.

The most conspicuous difference on Table 7 is for toluene, for which the developers of the CB4 added a speculative reaction so model simulations could accurately predict the relatively low maximum ozone yields in some toluene-NO_x outdoor chamber experiments (Gery et al., 1988). This reaction is not included in the SAPRC-90 mechanism, nor is it in the CB4 mechanism for xylenes. This causes somewhat lower MIR reactivities for toluene and causes toluene to be negatively reactive at the lower NO_x levels where maximum ozone formation occurs. (The SAPRC-90 mechanism also predicts that toluene becomes negatively reactive at low NO_x levels, but the NO_x levels must be much lower than is the case with CB4.) In the case of xylenes, where the CB4 lacks this speculative reaction, the MIR and MOIR relative reactivities agree quite well. The somewhat higher CB4 formaldehyde reactivity is believed to be caused primarily by a greater sensitivity of the CB4 mechanism to radical input processes, rather than by differences in the formaldehyde mechanism itself.

Another way to assess the effects of mechanism uncertainty is to examine changes in calculated reactivities that result when mechanisms are updated. Since SAPRC-90 was developed there has been new kinetic and mechanistic data concerning a number of relevant reactions, and environmental chamber studies of a number of compounds. The effects of two rounds of updates to the SAPRC mechanism on MIR's for selected compounds are shown on Table 8. The SAPRC-97 mechanism is an updated version of SAPRC-90 which incorporates significant updates in PAN kinetics, major modifications to alkene and aromatic reactions and mechanisms for other individual VOCs resulting from new mechanistic and environmental chamber data (Carter et al, 1997). The SAPRC-98 represents a complete update to the rate constants of the inorganic and common product reactions, somewhat more detailed representation of reactive organic products, revised estimation methods for OH + alkanes and oxygenates, and re-evaluations against the chamber data (see Carter, 1998 and the Atmospheric Chemistry section.)

Table 8 shows that updates to the base mechanism can cause a relative MIR change on the order of ~15% even for explicitly represented compounds whose mechanisms were not changed. In the case of going from SAPRC-90 to SAPRC-97, the changes for some of the aromatic isomers is due to new environmental chamber data, and the changes for acetylene and methyl isobutyrate are due to changes in the estimated, unverified mechanisms. (Differences between SAPRC-90 and SAPRC-97 are discussed further below.) In the case of going from SAPRC-97 to SAPRC-98, the relatively large increases in MIR for the higher alkanes, 2-(2-

ethoxyethoxy), ethanol and other compounds is due largely to the use of a more reactive model species to represent more reactive non-aldehyde oxygenated products, the changes for acetylene and methyl isobutyrate are due to mechanism revisions resulting from new chamber data, and in the case of the higher ketones the change is due to representing these compounds explicitly rather than by MEK. It can be seen that changes of up to a factor of 3 have occurred for compounds with unverified mechanisms.

More systematic studies of the effects of mechanism uncertainties have been carried out using airshed and box models to explore to what degree uncertainties in chemical rate parameters affect the calculated compound reactivities (Yang et al., 1995; 1996a,b; Bergin et al., 1996; 1997; Wang and Milford, 1998). Figure 7 compares results from box model uncertainty analysis studies conducted by Yang et al. (1996b) using the SAPRC-90 chemical mechanism and by Wang and Milford (1998) using the SAPRC-97 mechanism. Both studies used Monte Carlo analysis with Latin Hypercube Sampling to calculate the uncertainties in MIRs and MOIRs. Computational requirements were reduced by using a single set of trajectory conditions designed by Carter (1994a) to give incremental reactivities close to the average from the 39 trajectories used in developing his scales. Uncertainty estimates for parameters in the SAPRC-90 mechanism were compiled by Stockwell et al. (1994), largely from concurrent reviews of kinetic data (DeMore et al., 1990; Atkinson et al., 1989). For the SAPRC-97 mechanism, the uncertainty estimates were updated using more recent reviews (DeMore et al., 1994; 1997). In addition, Wang and Milford (1998) rectified a shortcoming of the earlier study by developing original estimates of uncertainties in aromatics oxidation parameters. Aromatics oxidation chemistry is highly uncertain, and the parameters used in chemical mechanisms are estimated by fitting ozone production due to aromatics oxidation in environmental chamber experiments. Accordingly, the uncertainty estimates that Yang et al. (1996a) used for these parameters were very large and highly subjective. Wang and Milford (1998) applied stochastic parameter estimation techniques to the aromatics database from the University of California at Riverside environmental chambers, to objectively assess the uncertainty in the aromatics oxidation parameters.

As shown in Figure 7, mean MIR estimates calculated with SAPRC-97 are generally higher than those calculated with SAPRC-90, reflecting revisions to the mechanism. One exception is the MIR for 1,2,4-trimethylbenzene, which has been adjusted downward based on recent chamber experiments. Yang et al.'s (1996) uncertainty estimates for MIRs ranged from about 30% to 50% of the mean MIR values, for most compounds. Uncertainty estimates for most aromatic compounds fell at the upper end of that range. The recent uncertainty estimates for MIRs made by Wang and Milford (1998) are somewhat lower, ranging from 25% to 35% in most cases. Reduced uncertainty estimates for aromatic compound reactivities suggest that the chamber data effectively constrain the uncertainty in these values. Both studies indicate that uncertainties in MOIRs are somewhat higher than those for MIRs. For SAPRC-97, Wang et al. estimate that uncertainties in MOIRs range from about 30% to 50% for most compounds.

As noted by Yang et al. (1995, 1996b) uncertainties in many rate parameters have similar effects on the reactivities of various compounds, so the resulting incremental reactivities are strongly correlated. For example, an increase in the photolysis rate for NO2 increases the reactivity of most species by about the same proportion. Thus, the relative reactivity of one

species compared to another is not affected as much as the absolute incremental reactivities by chemical parameter uncertainties.

Bergin et al. (1997) extended the box-model rate constant uncertainty studies to a three-dimensional model uncertainty study. After the most influential rate parameters were identified by Yang et al. through Monte Carlo simulations, described above, those values in the CIT-S90 model were varied by twice the estimated uncertainty, and the compound reactivity simulations were then recalculated. Results of one metric studied (spatial exposure) are shown in Figure 8. This analysis, again, found that relative reactivities have relatively low sensitivities to rate constant uncertainties. The implication of this result is further demonstrated by considering uncertainties in source reactivity quantification and RAFs. Further analysis of uncertainties using a three-dimensional model was conducted by Yang et al., (1998). As shown in Table 9, the uncertainties in the local relative reactivity were about 30%, accounting for uncertainties in 14 of the most influential rate constants, VOC and NOx emissions, and mixing height. Table 9 rank orders the sources of uncertainty. They found that the major source of uncertainty in quantifying most of the VOC reactivities were the NO2+HO reaction rate and the VOC emissions rate.

REFERENCES

Altshuller, A. P. and Bufalini, J. J. (1971). *Environ. Sci. Technol, 5:* 39.

Andersson-Skold, Y.; Grenfelt, P.; and Pleije, K. (1992). *J. Air Waste Mgmt. Assoc.*, 42:1152–1158.

AQIRP (1993). *Reactivity Estimates for Reformulated Gasolines and Methanol/Gasoline Blends in Prototype Flexible/Variable Fuel Vehicles,* Technical Bulletin No. 7, Auto/Oil Air Quality Improvement Research Program. Available from the Coordinating Research Council, Atlanta, GA.

Atkinson, R. (1987). *Int. J. Chem. Kinet.,* 19:799–828Atkinson, R. (1990). *Atmos. Environ.,* 24A:1–24

Atkinson, R. (1989). *J. Phys. Chem. Ref. Data,* Monograph No 1.Atkinson, R. (1994). *J. Phys. Chem. Ref. Data,* Monograph No. 2.

Bergin, M.S.; Russell, A.G.; and Milford, J.B. (1995). *Environ. Sci. & Tech.,* 29(12):3029–3037.

Bergin, M.S.; Russell, A.G.; and Milford, J.B. (1998). *Environ. Sci. & Tech.,* 32(5):694–703.

Bowman, F.M. and Seinfeld, J.H. (1994a). *J. Geophys. Res.,* 99:5309–5324.

Bowman, F. M. and Seinfeld, J.H. (1994b). *Atmos. Environ.,* 28:3359–3368.

Bowman, F. M. and Seinfeld, J.H. (1995). *Prog. in Energy and Comb. Sci.* 21:87–417.

Bufalini, J. J.; Walter, T.A.; and Bufalini, M.M. (1977). *Environ. Sci. Technol.,* 11:1181–1185.

CARB. (1989). *Definition of a Low-Emission Motor Vehicle in Compliance with the Mandates of Health and Safety Code Section 39037.05 (Assembly Bill 234, Leonard, 1987),* Report by Mobile Sources Division, California Air Resources Board, El Monte, CA.

CARB. (1990). *Proposed Regulations for Low-Emission Vehicles and Clean Fuels—Staff Report and Technical Support Document,* Sacramento, CA, August 13. See also Appendix VIII of *California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light Duty Trucks and Medium Duty Vehicles,* as last amended September 22, 1993. Incorporated by reference in Section 1960.1 (k) of Title 13, California Code of Regulations.

CARB. (1991). *Proposed Reactivity Adjustment Factors for Transitional Low-Emissions Vehicles—Staff Report and Technical Support Document,* Sacramento, CA, September 27. Andersson-Skold, Y.; Grenfelt, P.; and Pleije, K. (1992). *J. Air Waste Mgmt. Assoc.*, 42:1152–1158.

Carter, W.P.L. (1990). *Atmos. Environ.,* 24A:481–518.

Carter, W.P.L. (1991). *Development of Ozone Reactivity Scales for Volatile Organic Compounds,* EPA 600/3-91-050. U.S. Environmental Protection Agency, Research Triangle Park, NC (August).

Carter, W.P.L. (1994a). *J. Air and Waste Mgmt. Assoc.,* 44:881–899.

Carter, W.P.L. (1994b). *Calculation of Reactivity Scales Using an Updated Carbon Bond IV Mechanism,* Report prepared for Systems Applications International under funding from the Auto/Oil Air Quality Improvement Research Program.

Carter, W.P.L. (1995). *Atmos. Environ.,* 29:2513–2517.

Carter, W.P.L. (1998): "Updated Maximum Incremental Reactivity Scale for Regulatory Applications," Preliminary Report to California Air Resources BoardContract No. 95-308. See http://cert.ucr.edu/~carter/r98tab.htm.

Carter, W.P.L.; Atkinson, R.; Winer, A.M.; and Pitts, J.N. Jr. (1982). *Int. J. Chem. Kinet.,* 14:1071.

Carter, W.P.L. and Atkinson, R. (1989). *Environ. Sci. and Technol.,* 23:864.

Carter, W.P.L. and Lurmann, F.W. (1990). *Evaluation of the RADM Gas-Phase Chemical Mechanism,* Final Report, EPA-600/3-90-001.

Carter, W.P.L. and Lurmann, F.W. (1991). *Atmos. Environ.,* 25A:2771–2806.

Carter, W.P.L.; Pierce, J.A.; Malkina, L; Luo, D.; and Long, W.D. (1993). *Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds,* Report to Coordinating Research Council, Project No. ME-9, California Air Resources Board Contract No. A032-0692; South Coast Air Quality Management District Contract No. C91323, United States Environmental Protection Agency Cooperative Agreement No. CR-814396-01-0, University Corporation for Atmospheric Research Contract No. 59166, and Dow Corning Corporation (April 1).

Carter, W.P.L.; Luo, D.; Malkina, I.L.; and Pierce, J.A. (1995a). *Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying ROG Surrogate and NOx.* Final report to Coordinating Research Council, Inc., Project ME-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323 (March 24).

Carter, W.P.L.; Pierce, J.A.; Luo, D.; and Malkina, I.L. (1995b). *Atmos. Environ.,* 29:2499–2511.

Carter, W. P. L., D. Luo, and I. L. Malkina (1997): "Environmental Chamber Studies for Development of an Updated Photochemical Mechanism for VOC Reactivity Assessment," final report to California Air Resources Board Contract 92-345, Coordinating Research Council Project M-9, and National Renewable Energy Laboratory Contract ZF-2-12252-07. November 26.

Chameides, W.L.; Fehsenfeld, F.; Rodgers, M.O.; Cardelino, C.; Martinez, J.; Parrish, D.; Chang, T.Y. and Rudy, S.J. (1990). *Atmos. Environ.* 24A(9):2421-2430.

Chang, T.Y.; Rudy, S.J.; Kuntasal, G.; Gorse, R.A., Jr. (1989). Atmos. Environ. 23(8):1629–1644.

Darnall, K.R.; Lloyd, A.C.; Winer, A.M.; Pitts, J.N. Jr. (1976). *Environ. Sci. Technol.*, 10:692.

Derwent, R.G. and A.M. Hov. (1979). *Computer Modeling Studies of Photochemical Air Pollution Formation in North West Europe*, AERE R 9434, Harwell Laboratory, Oxfordshire, England.

Derwent, R.G. and Jenkin, M.E. (1991). *Atmos. Environ.,* 25(A):1661-1673

Dimitriades, B. (1996): "Scientific Basis for the VOC Reactivity Issues Raised by Section 183(e) of the Clean Air Act Amendments of 1990," J. Air Waste Manage. Assoc. 46, 963-970.

Dodge, M.C. (1977) "Combined Use of Modeling Techniques and Smog Chamber Data to Drive Ozone-Precursor Relationships" in Proceedings, International Conference on Photochemical Oxidant and Its Control, Research Triangle Park, North Carolina, EPA-600/3-80-028a. Carter, W.P.L. (1990). Atmos. Environ., 24A:481–518.

Dodge, M.C. (1984). *Atmos. Environ.*, 18:1657. In B. Dimitriades, ed., *International Conference on Photochemical Oxidant Pollution and Its Control—Proceedings: Volume II, September 1976*. Research Triangle Park, NC.

Gery, M.W. and Crouse, R.R. (1989). *User's Guide for Executing OZIPR* . Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Jeffries, H.E. and Sexton, K.G. (1993). *The Relative Ozone Forming Potential of Methanol Fueled Vehicle Emissions and Gasoline-Fueled Vehicle Emissions in Outdoor Smog Chambers,* Draft Final Report to the Coordinating Research Council, Project No. ME-1 (September).

Jeffries, H.E. and Crouse, R. (1991). *Scientific and Technical Issues Related to the Application of Incremental Reactivity. Part H: Explaining Mechanism Differences,* Report prepared for Western States Petroleum Association, Glendale, CA (October).

Jiang, W.; Singleton, D.L.; Hedley, M.; and McLaren, R. (1996) *Atmos. Environ.* 31(4):627-638.

Joshi, S.B.; Dodge, M.C.; and Bufalini, J.J. (1982). *Atmos. Environ.,* 16:1301–1310.

Kahn, M.; Yang, YJ; and Russell, A.G. (1997). "Reactivities of Organic Solvents: Comparison between Urban and Regional Domains," Paper No. WA-97-!1540. Presented at the A&WMA Annual Meeting, Toronto, Canada. June. Air & Waste Management Association, Pittsburgh, PA.

Kahn, M., Yang, YJ and Russell, A.G.., (1999 a) "Photochemical reactivities of common solvents: comparison between urban and regional domains," Atmos. Env. (in press)

Kahn, M.; Qi , L.; Yang, YJ and Russell, A.G.(1999b) "Regional assessment of realtive reactivities using a decoupled, direct method for sensitivity analysis" (to be submitted)

Laity, J.L.; Burstain, F.G.; and Appel, B.R. (1973). In R.W. Tess, ed., *Solvents Theory and Practice,* Adv. Chem. Series, 124:95.

Lonneman, W.; Lawson, D.R.; Rasmussen, R.A.; Zimmerman, P.; Greenburg, J.; Middleton, P.; and Wang, T. (1992). *J. Geophys. Res.*, 97:6037.

Lurmann, F.W.; Carter, W.P.L.; and Coyner, R.A. (1987). *A Surrogate Species Chemical Reaction Mechanism for Urban-Scale Air Quality Simulation Models. Volume I - Adaptation of the Mechanism,* EPA-600/3-87-014a.

McNair, L.; Russell, A.; and Odman, M.T. (1992). *J. Air Waste Mgmt. Assoc.,* 42:174.

Odman et al., 1994 (URM model)Russell, A.; Milford, J.; Bergin, M.S.; McBride, S.; McNair, L.; Yang, Y.; Stockwell, W.R.; and Croes, B. (1995). *Science* 269:491–495Russell, A.G.; St. Pierre, D.; and Milford, J.B. (1990). Science 247:201–205.

Russell, A.G.; Milford, J.; Bergin, M.; McNair, L.; Yang, YJ.; and Stockwell, W. (1995) Science, 269:491-495.

Trijonis, J.C. and Arledge, K.W. (1976). Utility of Reactivity Criteria in Organic Emission Control Strategies: Application to the Los Angeles Atmosphere, EPA/600/3-78/019; TRW/Environmental Services: Redondo Beach, CA.

Weir, B.R.; Rosenbaum, A.S.; Gardner, L.A.; Whitten, G.Z.; and Carter, W. (1988). *Architectural Coatings in the South Coast Air Basin: Survey, Reactivity, and Toxicity Evaluation,* Final Report to the South Coast Management District, SYSAPP-88/137, Systems Applications, Inc., San Rafael, CA (December).

Wilson, K.W. and Doyle, G.J. (1970). *Investigation of Photochemical Reactivities of Organic Solvents,* Final Report, SRI Project PSU-8029, Stanford Research Institute, Irvine, CA (September).

Yang, Y.-J.; Das, M.; Milford, J.B.; Bergin, M.S.; Russell, A.G.; and Stockwell, W.R. (1994). *Quantification of Organic Compound Reactivities and Effects of Uncertainties in Rate Parameters. An Integrated Approach Using Formal Sensitivity and Uncertainty Analysis and Three Dimensional Air Quality Modeling.* Report prepared for the Auto/Oil Air Quality Improvement Research Program (August).

Yang, Y-J.; Stockwell, W.R.; and Milford, J.B. (1995). *Environ. Sci. & Tech.,* 29(5):1336–1345.

Yang, YJ.; Khan, M.; Wilkinson, J.; and Russell, A.G. (1999) "Spatial uncertainty assessment of relative reactivities" (in preparation)

Yarwood, G. (1994): System Applications, Inc., San Rafael, CA, personal communication with W.P.L. Carter.

TABLES

Table 1: Summary of compound reactivity modeling studies

Reference	Model Type	Mechanism	Application
Derwent and Jenkin (1991)	trajectory	Harwell	Two-layer multi-day trajectory simulations of reactivity. Referred to as POCP scales.
McNair et al. (1992)	three-dimensional (CIT)	LCC	Calculation of 3 reactivity scales for 11 lumped compounds. Simulations were performed for a three-day period in the Los Angeles area (the SCAQS episode).
Carter (1994a)	trajectory	SAPRC-90	Development of 18 reactivity scales (including the MIR and MOIR) for 117 compounds. Results are the average of 39 trajectory simulations for 10-hour periods.
Yang et al. (1994)	trajectory and three-D (CIT)	SAPRC-90	Review of rate constant uncertainties and also portions of (Yang et al, 1995; Bergin et al, 1995, 1998). Report.
Yang et al. (1995)	trajectory	SAPRC-90	Rate constant uncertainty calculations for the reactivities of 26 compounds under MIR- and MOIR-type conditions. One averaged trajectory was used rather than the 39 used in the Carter MIR and MOIR calculations.
Bergin et al. (1995)	three-dimensional (CIT)	SAPRC-90	Calculation of 3 reactivity scales for 27 compounds. Simulations were performed for the SCAQS episode.
Jiang et al. (1996)	trajectory	SAPRC-90	Calculation of the contributions of eighteen compounds to ozone concentrations in the Lower Fraser Valley.
Bergin et al. (1997)	three-dimensional (CIT)	SAPRC-90	Rate constant uncertainty calculations for the scales and compounds in the Bergin et al. (1995) study above.
Kahn et al. (1999a)	trajectory and three-dimensional	SAPRC-90	Calculation of solvent reactivities using box and airshed modeling in multiple domains.
Carter (1998)	trajectory	SAPRC-98	Update of Carter (1994)
Kahn et al., (1999b)	three-dimensional	SAPRC-90 (with updates)	Regional uncertainty analysis and use of direct sensitivity method
Yang et al. (1999)	three-dimensional	SAPRC-90 (with updates to 97)	Spatial uncertainty analysis of reactivities

Table 2. Summary of major characteristics of Carter (1994) reactivity scales.

Scale	Type of Scenarios used	Derivation of scale from individual scenario reactivities	Ozone quantification	Reflects effect of VOC on:
Maximum Incremental Reactivity (MIR)	Low ROG/NO$_x$ conditions where O$_3$ is most sensitive to VOC changes	Averages of incremental reactivities in the MIR scenarios	Maximum ozone	Ozone formation rates
Maximum Ozone Incremental Reactivity (MOIR)	Moderate ROG/NO$_x$ conditions where highest O$_3$ yields are formed	Averages of incremental reactivities in the MOIR scenarios	Maximum ozone	Ultimate ozone yield
Equal Benefit Incremental Reactivity (EBIR)	Higher ROG/NO$_x$ conditions where VOC and NO$_x$ control are equally effective in reducing O$_3$	Averages of incremental reactivities in the EBIR scenarios	Maximum ozone	Ultimate ozone yield
Base-Case Average Ratio: O$_3$ Yield	Base case conditions (ROG/NO$_x$ conditions are as observed for the individual scenarios)	Averages of incremental reactivities in the base case scenarios	Maximum ozone	Ultimate ozone yield
Base-Case Least Squares Error: O$_3$ yield.	Base-Case	Minimizes change in ozone if a "null test" substitution were made using the scale[a]	Maximum ozone	Depends on the variability of scenario conditions[b]
Base-Case Average Ratio: Integrated O$_3$	Base-Case	Averages of incremental reactivities in the base case scenarios	Integrated ozone	Ozone formation rate and ultimate yield
Base-Case Least Squares Error—Integrated O$_3$	Base-Case	Same as base case least squares error — O$_3$ yield.[b]	Integrated ozone	Ozone formation rate

[a] A "null test" substitution based on a reactivity scale consists of substituting VOC emissions such that the scale predicts there would be no change in ozone.

[b] Depends on effect on O$_3$ formation rate if scenarios are highly varied in ROG/NO$_x$ conditions .

Table 3. Summary of source emissions reactivity modeling studies

Reference	Model Type	Mechanism	Application
Trijonis and Arledge (1976)	calculated (not modeled)	EPA Smog Chamber Data	Estimated major source reactivities for metropolitan Los Angeles.
Chang et al. (1989)	trajectory	LCC	Methanol fuel vehicle impacts with respect to conventionally fueled vehicles.
Russell et al. (1990)	three-dimensional (CIT)	LCC	Potential methanol fuel vehicle impacts for the SCAQS episode (compared to equal mass emissions from conventional vehicles).
McNair et al. (1994) (100)	three-dimensional (CIT)	LCC	Calculations of RAFs for 4 fuels. Simulations were performed for the SCAQS episode.
Yang et al. (1996) (101, 102)	trajectory	SAPRC-90	Rate constant and exhaust composition uncertainty calculations for the RAFs from reformulated gasolines and methanol.
Bergin et al. (1996) (103)	trajectory and three-dimensional (CIT)	SAPRC-90	Report on box model study described above (101, 102) and a 3D study of the effects of rate constant and product yield uncertainties on predicted ozone impacts of 5 alternative fuel RAFs.
Russell et al. (1995) (96)	trajectory and three-dimensional (CIT)	SAPRC-90	Evaluation of combined results of most previous studies (82, 84, 85, 100, 101, 103). An economic analysis was also performed.
Guthrie et al. (1996) (104)	three-dimensional (UAM)	CB4	Modeling of potential impacts of the use of three alternative fuels (CNG, M85, and RFG) in two urban areas. Report.

Table 4. Regression results for airshed model exposure vs. MIR and airshed peak ozone vs. MOIR measures (Bergin et al., 1996, 1998)

Comparison	R^2	Slope	Intercept
Population Exposure to MIR	0.81	0.88	0.04
Spatial Exposure to MIR	0.97	0.98	0.04
Peak to MOIR	0.80	1.01	0.05
Spatial Exposure to MOIR	0.96	1.09	-0.06

Table 5. Normalized bias and standard deviation between reactivity metrics calculated using the CIT-S90 airshed model (Bergin et al., 1996, 1998)

Comparison	Bias	Standard
Population to Spatial Exposure	-0.21	0.22
Peak Ozone to Spatial Exposure	0.22	.052
Peak Ozone to Population Exposure	0.39	0.67

Table 6. Example MIRs and variations between locations (mean and standard deviation) (Russell et al., 1995)

Compound	Mean reactivities across 39 cities (Non-normalized/Normalized)	Standard deviation (Non-normalized/Normalized)
HCHO	7.2/7.1	1.0/0.58
Methanol	0.56/0.55	0.11/0.064
Ethane	0.25/0.24	0.070/0.045
Toluene	2.7/2.7	0.52/0.28
Pentene	6.2/6.1	1.2/0.64

Table 7. Comparision of relative reactivities calculated using the SAPRC90 and the Carbon Bond 4 mechanisms.

| Compound | Reactivity relative to base ROG mixture (mass basis) | | | | | |
| | MIR | | | MOIR | | |
	S-90	CB4	Diff	S-90	CB4	Diff
n-Hexane	0.31	0.35	10%	0.53	0.57	7%
Ethene	2.31	2.42	5%	2.61	2.76	6%
Propene	2.98	3.48	14%	3.11	3.66	15%
trans-2-Butene	3.15	3.13	-1%	3.10	3.28	5%
Toluene	0.86	0.57	-52%	0.52	-0.19	378%
m-Xylene	2.58	2.62	1%	2.02	2.04	1%
Formaldehyde	2.26	2.81	19%	1.72	2.21	22%
Acetaldehyde	1.75	1.99	12%	1.79	2.09	14%
Methylethy ketone	0.37	0.28	-35%	0.45	0.46	1%
Methanol	0.18	0.19	5%	0.23	0.23	2%
Ethanol	0.42	0.42	-1%	0.60	0.61	2%

Table 8. Effect of SAPRC mechanism updates on calculated MIR's.

Compound	Reactivity relative to base ROG mixture (mass basis) SAPRC Version			Change		
	90	97	98	90->97	90->98	97->98
Ethane	0.08	0.08	0.09	0%	15%	15%
n-Octane	0.19	0.17	0.32	-12%	63%	84%
n-Pentadecane	0.09	0.09	0.15	-8%	58%	71%
2,4-Dimethyl Heptane	0.42	0.44	0.51	5%	20%	15%
Ethene	2.31	2.05	2.53	-11%	9%	23%
Propene	2.98	2.72	3.18	-9%	7%	17%
1-Hexene	1.40	1.40	1.61	0%	15%	15%
trans-2-Butene	3.15	3.24	3.76	3%	19%	16%
Isoprene	2.87	2.30	2.93	-20%	2%	27%
a-Pinene	1.04	0.96	1.29	-8%	24%	35%
Toluene	0.86	1.26	1.06	46%	23%	-16%
p-Xylene	2.09	0.71	1.12	-66%	-46%	58%
m-Xylene	2.58	3.49	2.82	35%	9%	-19%
1,3,5-Trimethyl Benzene	3.20	3.37	2.83	5%	-12%	-16%
1,2,4-Trimethyl Benzene	2.80	1.31	1.90	-53%	-32%	45%
Naphthalene	0.37	0.31	0.78	-17%	109%	150%
Acetylene	0.16	0.09	0.31	-45%	94%	256%
Ethanol	0.42	0.42	0.49	-1%	15%	15%
Propylene Glycol	0.49	0.61	0.67	24%	38%	11%
Methyl t-Butyl Ether	0.20	0.18	0.34	-10%	72%	91%
2-(2-Ethoxyethoxy) EtOH	0.41	0.59	0.99	43%	139%	67%
Methyl Isobutyrate	0.06	0.18	0.11	196%	72%	-42%
Formaldehyde	2.26	1.62	2.33	-28%	3%	44%
C3 Aldehydes	2.07	1.85	2.13	-11%	3%	15%
Acetone	0.18	0.12	0.12	-33%	-31%	2%
C6 Ketones	0.27	0.23	0.94	-13%	251%	304%

Table 9. Rank ordering and source attribution of uncertainty in relative reactivities for airshed modeling of Los Angeles.

Parameter	Relative Reactivity, Uncertainty and Contributions to Relative Reactivity Uncertainty		
	HCHO	Pentane	Average over 11 VOCs
Overall Relative Reactivity/ uncertainty/COV	5.76/1.05/0.26	0.42/0.051/0.12	$COV_{average}$=0.19+/-0.09
Paramter	**Uncertainty Contributions**		
NO2+hv	0.085	0.024	0.03
O3+NO	0.016	0.019	0.01
O3+hv-->O^{1}D	0.084	0.19	0.05
O^{1}D+H2O	0.011	0.076	0.03
O^{1}D+M	0.043	0.043	0.02
HO +NO2	0.079	0.173	0.19
HO2+NO	0.006	0.022	0.01
RO2R+NO	0.005	0.006	0.02
AFG2+hv	0.009	0.057	0.12
CCO+NO	0.039	0.035	0.12
CCO+NO2	0.034	0.038	0.08
PAN decomposition	0.073	0.022	0.08
HCHO+hv	0.276	0.11	0.13
AAR2+HO	0.044	0.035	0.01
NOx Emissions	0.004	0.002	0.006
VOC Emissions	0.182	0.051	0.08
Mixing Height	0.011	0.094	0.04

FIGURES

Constant ozone isopleths

Constant VOC = 10 m.mol/m^2

Constant NOx = 2.5 m.mol/m^2
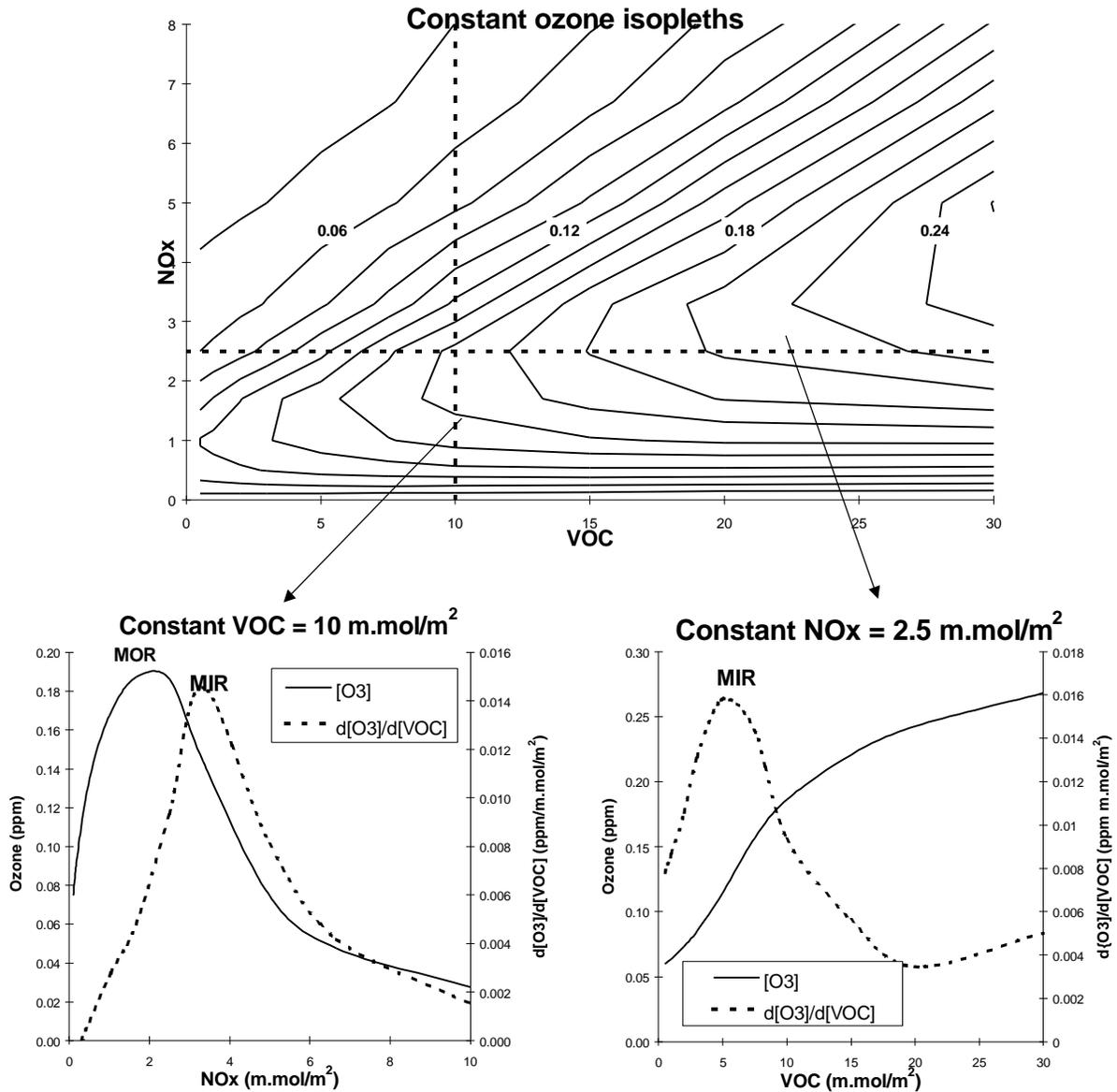
[1]MOR, maximum ozone reactivity, also referred to as maximum ozone incremental reactivity (MOIR); MIR, maxium incremenmtal reactivity.
One day maximum ozone concentrations calculated in a one-day box model simulation using the "averaged conditions" scenario of Carter (1994) and the SAPRC-93 chemical mechanism.

Figure 1. Dependence of peak ozone and d[O3]/d[VOC] on VOC and NOx

Figure 2. Comparison of MIR, MOIR, and POCP relative reactivities
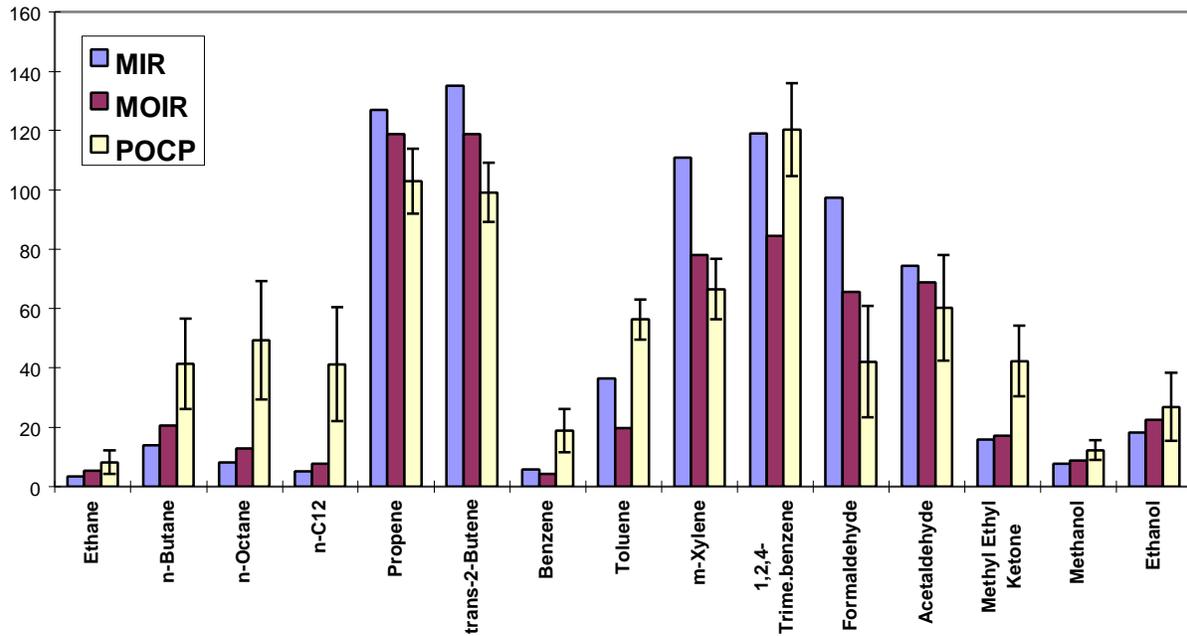
[1] **Incremental reactivities (ozone per gram) are shown relative to ethene = 100. MIR and MOIR reactivities from Carter (23). POCP reactivities are averages for various trajectories calculated by Derwent and Jenkin (81), with the error bars being the standard deviation of the averages.**

Figure 3. Relative (normalized) N-MIR and N-MOIR reactivities for six solvents (Kahn et al, 1997)
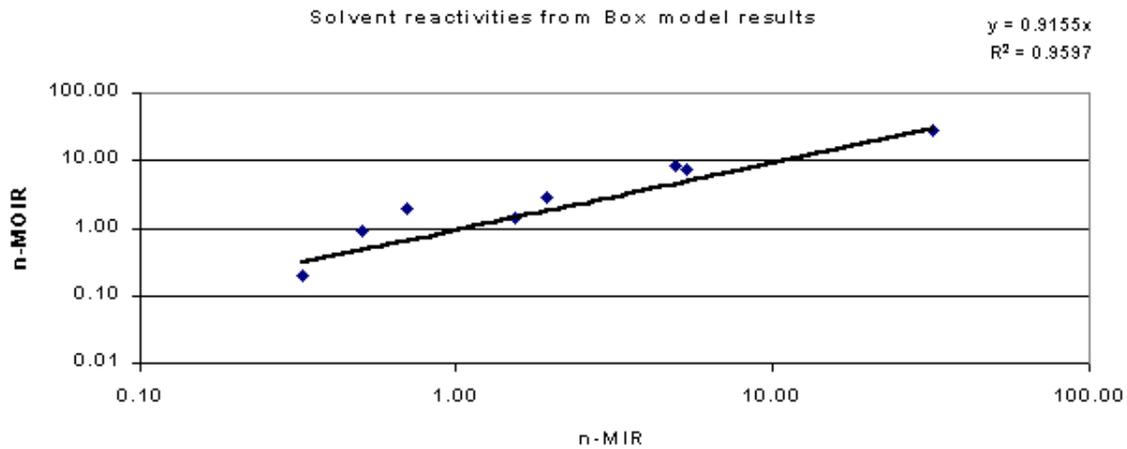
Figure 4. Box plots of the calculated (A) net reactivities (NRs) and (B) normalized reactivities (RAFs) across cities (Russell et al., 1995)
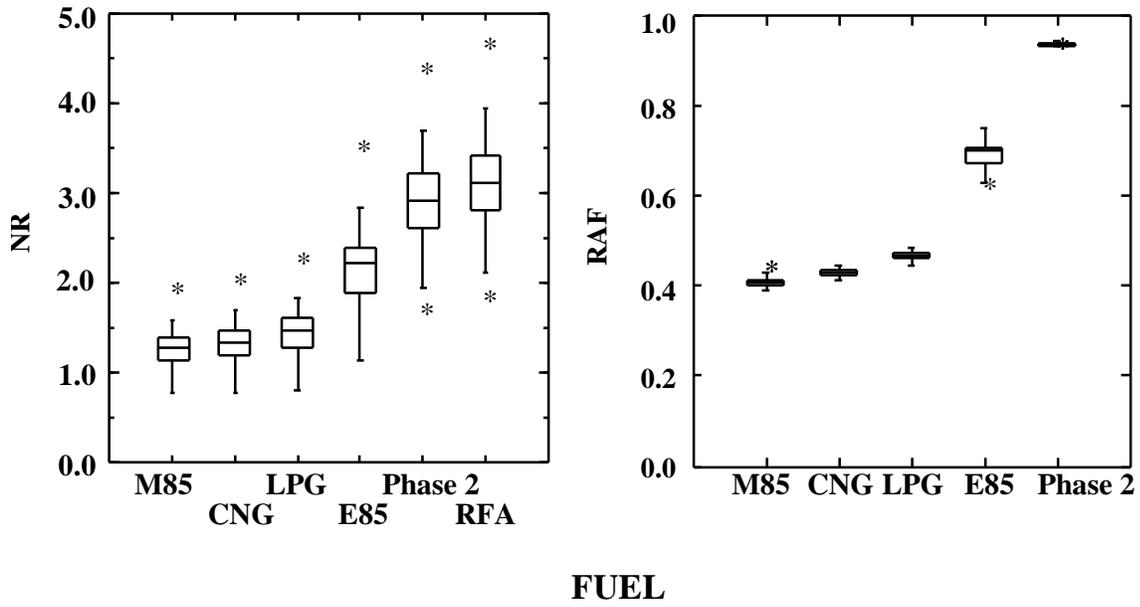
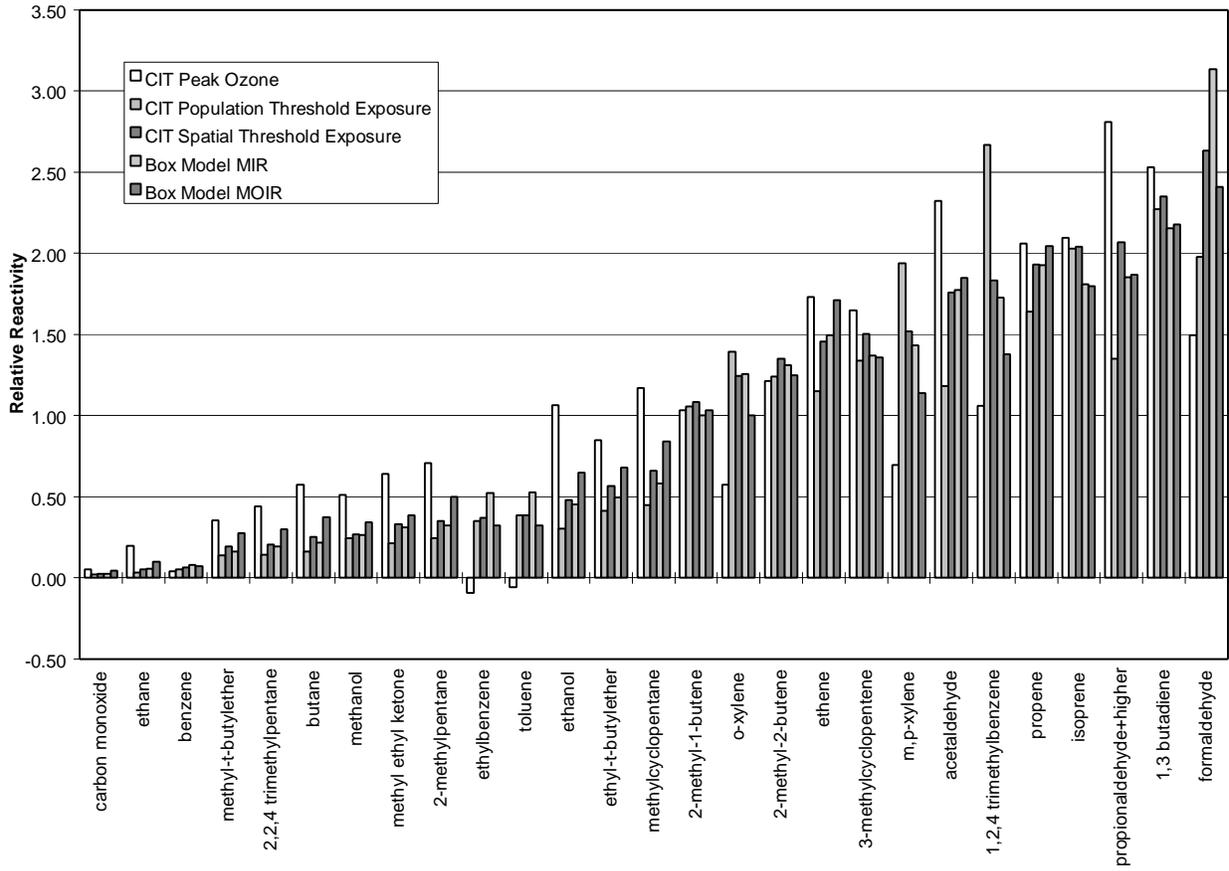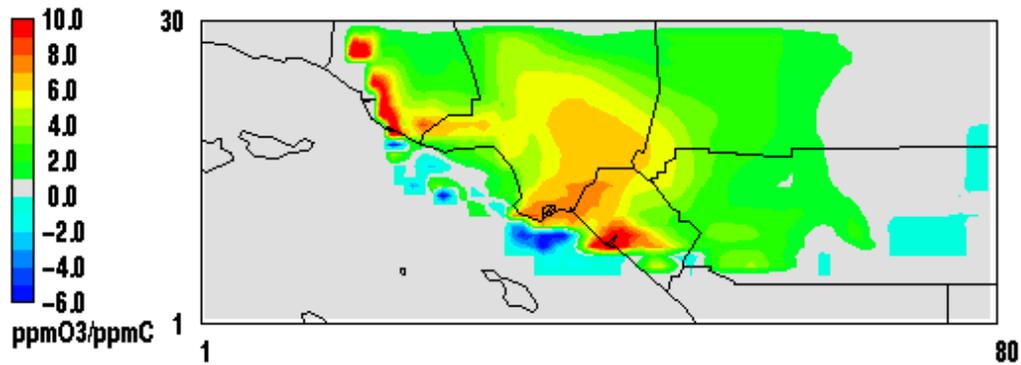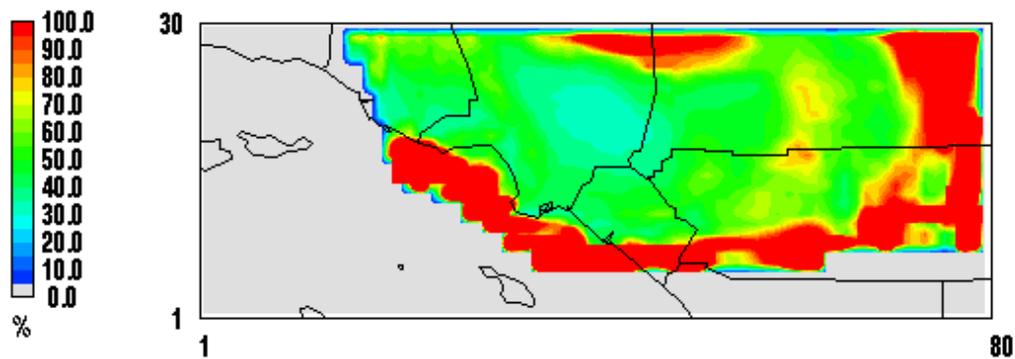**Figure 5. Comparison of three-dimensional and trajectory modeled relative reactivities**

Figure 6. Spatial distribution of relative reactivities (Yang et al., 1999)
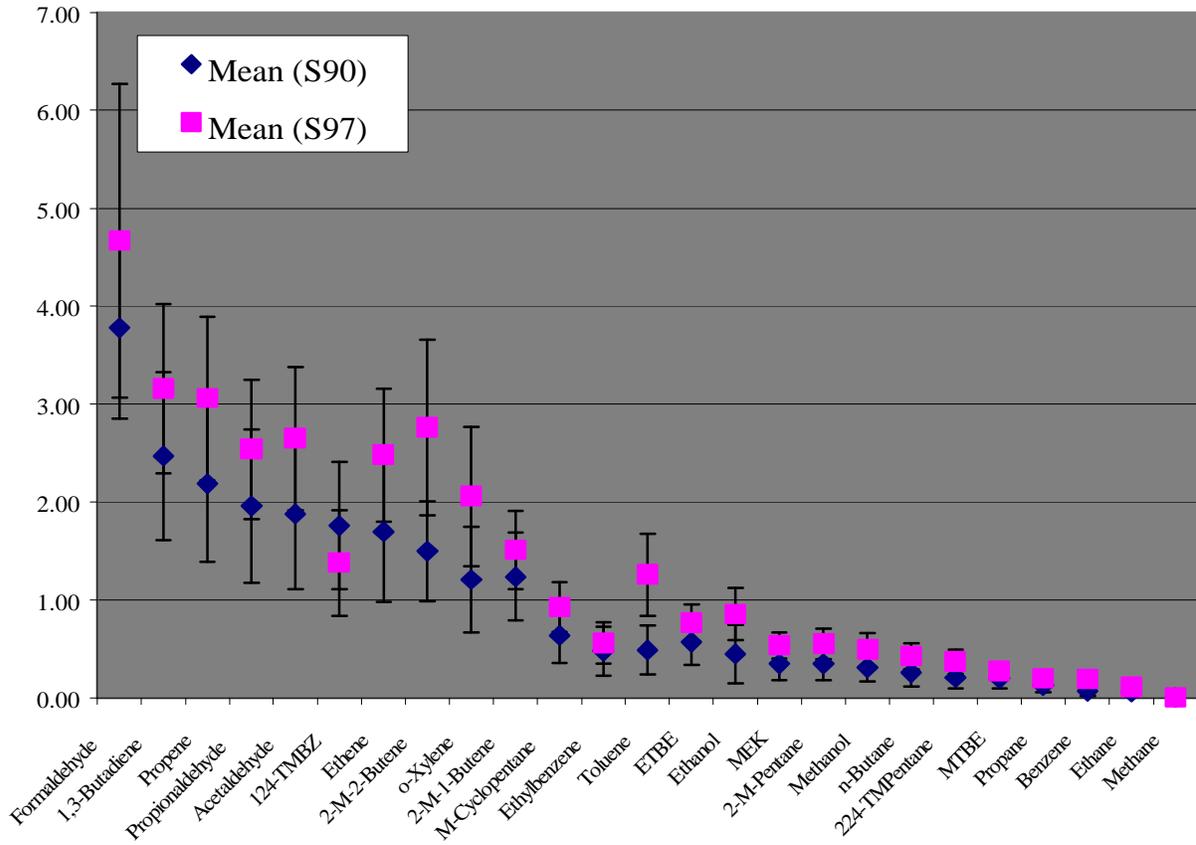

a. Normalized HCHO Relative Reactivity (ppmO3/ppmC) at 1400 hour, August 29, 1987 in the Los Angeles, CA area.

b. Coefficient of variation (relative uncertainty) (%) of the HCHO Relative Reactivity at 1400 hour, August 29, 1987.

Figure 7.

Mean values and 1s uncertainties of MIRs for selected organic compounds, calculated with the SAPRC90 and SAPRC97 mechanisms

Figure 8. Spatial exposure normalized reactivity predictions from rate constant uncertainty adjustments (Bergin et al., 1998)