

RECENT RESEARCH ON VOC OZONE REACTIVITY

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Presented at the Workshop on Ozone and Particles: Policy and Science – Recent Developments and Controversial Issues (Regional and Urban Air Pollution)
Bad Breisig, Germany
October 7-11, 2002

Introduction

Control policies that take into account differences among VOCs in their relative effects on O₃ formation have been adopted in California and are being considered by the United States EPA. These require a means to quantitatively rank VOCs by reactivity, which has policy and scientific difficulties. Among the policy issues is the fact that relative effects of VOCs on O₃ depends on ambient conditions, and decisions must be made on how to take this into account when a single scale is required. The scientific difficulties come from the fact that the predictions of the models needed to estimate effects of VOCs on ambient ozone are no more reliable than the chemical mechanisms and the model for airshed conditions they employ. The mechanisms of the hundreds of types of emitted VOCs are complex and uncertain, and environmental chamber data, which have a number of limitations, are necessary to test their predictive capabilities. The large grid-based models that are considered to be the most accurate for simulating ozone formation over wide regions have employed highly condensed mechanisms, and current reactivity scales, and until recently most studies of VOC reactivity effects, are based on use of trajectory or box models designed to represent urban conditions. There is a concern that such models may not accurately predict relative VOC reactivities in multi-day or long-range transport scenarios, where O₃ formation is also of concern.

This presentation will focus on two areas of research at our laboratories. In the first section, we will briefly summarize progress in developing a new environmental chamber facility at our laboratories for more comprehensive mechanism evaluation at lower pollutant concentrations than has previously been possible. This project was a focus of the previous US/German workshop that was held in Riverside, California in October, 1999. Although the project was initiated in 1999, because of delays and difficulties the new facility has just been completed and characterization is now underway. Current research plans and anticipated future uses for the facility will be discussed.

Most of the presentation will focus on results of an initial study of VOC reactivity effects using an existing regional model of the Eastern United States. This type of region is considered to be the most problematical for VOC reactivity scales because much of it is NO_x-limited, dominated by biogenic VOCs, and long-range transport over large areas is important. Various metrics or methods for deriving O₃ reactivity rankings based on the varying regional impacts are compared, and their advantages and disadvantages for use in regulatory applications are discussed.

Development of a New Environmental Chamber Facility at the University of California at Riverside

Background

An important area of uncertainty in quantitative assessments of VOC reactivities concerns the uncertainties in chemical mechanisms used to in the models to estimate the effects of changing VOC emissions on O₃ formation. The atmospheric chemical mechanisms of all but the simplest of the emitted VOCs are highly complex and contain many estimated rate constants and branching ratios. Because of this, the ability of these mechanisms to accurately predict effects of VOCs on O₃ formation need to be evaluated by comparing model predictions against results of well-characterized environmental chamber experiments. Existing chambers have been used to develop the models now used to predict ozone formation, and are beginning to provide data concerning formation of PM. However, we have reached the limits of the capabilities of current chamber facilities, and improvements are needed if significant further progress is to be made. For example, current chambers require use of relatively high pollutant concentrations, but data at low concentrations are needed to predict how we can attain ozone and PM standards.

The limitation of the ability of current environmental chambers to provide data needed to evaluate mechanisms at lower pollutant concentration is of particular concern for the mechanisms for aromatic compounds, which because of lack of detailed knowledge of mechanisms details are represented using highly parameterized mechanisms adjusted to fit the relatively high concentration chamber data. The extrapolation of the nonlinear chemistry to lower reactant concentrations may not be correct if the parameterization used does not appropriately represent the actual mechanisms of the compounds.

Because of this, in 1999 the U.S. Congress made \$2.9 million available through the EPA for the University of California at Riverside (UCR) to develop a “next generation” chamber facility to simulate atmospheric processes under more controlled and realistic conditions than previously possible. UCR was chosen for this because of its experience in atmospheric chemistry, environmental chamber research, and VOC reactivity research.

In addition to constructing and evaluating the new facility, a research plan was developed to utilize the new facility for priority research in the following areas:

- Improving our ability to predict effects of NO_x and the major types of VOCs on O₃ and PM formation under conditions more representative of ambient and near-attainment environments than current data, with varying temperature, humidity, and pollutant levels.
- Determining how best to use ambient measurement data for predicting effects of control strategies and evaluating the reliability of ambient measurement instrumentation.
- Evaluating ozone and PM impacts of VOC emissions from specific sources such as architectural coatings and low reactivity solvents being proposed for substitutions.

The Reactivity Research Working Group (RRWG), a public-private partnership to provide an improved scientific basis for reactivity-related regulatory policies, is serving as an oversight group for assuring that the research effectively addresses regulatory priorities. Key participants are the EPA, the California Air Resources Board and other regional agencies, the American Chemistry Council, and representatives of solvents, coatings and other industry groups, and various researchers in atmospheric chemistry and airshed modeling.

The background and objectives for this project is described in more detail in the project proposal (Carter et al, 1999), and the research plan is described in detail in the first progress report for this project (Carter, 2002a).

Accomplishments to Date

Progress on this progress through the end of 2001 is described in detail in the first periodic report on this project (Carter, 2002a), with a separate report summarizing progress through August of this year. Briefly, the program was initiated with a successful international workshop held in Riverside, California concerning atmospheric chemistry and environmental chamber research, where useful input concerning this project was obtained from researchers from the United States and Europe. Near-term needs for measurement instrumentation were assessed, and equipment was purchased and evaluated. Extensive experiments were constructed using small test reactors to evaluate material for construction, to test design parameters, and to evaluate the new instrumentation. The results showed that if appropriate steps are taken it is possible to conduct experiments under NO_x conditions at least an order of magnitude lower than existing data, thereby providing results that better represents ambient air pollution. There was some skepticism when this project was proposed such low NO_x experiments might not be feasible.

Private-sector funding was obtained to finance construction of a new building needed to house the chamber facility, with the chamber located on the second floor and the laboratory and offices underneath it. The chamber consists of a 16,000 cubic ft temperature-controlled “clean room” enclosure fitted with a 300 KW argon arc light source, with space for two up to 8,000 cubic ft reactors where the reactions will be monitored. The reactors are constructed of Teflon film fitted on specially designed moveable frameworks, with an associated high volume mixing system suitable for injecting low volatility materials, and a computer-controlled sampling and calibration system for the analyses. A high capacity air purification system is used to keep the enclosure clean and provide highly purified air for the experiments. Photographs of the building and laboratory and reactor are shown on Figure 1, and a diagram of the reactor is shown on Figure 2.

The first experiment in the new facility, using a preliminary light source and reactor configuration, was carried out in February of 2002. The first experiment with the arc lights and the near-final configuration for a single reactor was conducted in July. The second reactor and the final mixing and sampling system is expected to be in place and operational by September. The initial experiments included evaluations of background effects, the performance of the light source, temperature control system, and analytical instrumentation in the current configuration. These characterization and performance evaluation studies, which are still underway, provide essential data needed for evaluating computer model predictions of the effectiveness of control strategy for reducing ozone and PM.

Current Plans

Although these accomplishments are significant, as with most groundbreaking research and development projects the time and cost required was greater than initially estimated. We had hoped to complete the facility in 2001 for about \$2 million, and use the remaining EPA funds to support operating the facility when conducting the research outlined above. However, we presently project that the Federal funds will be expended by January 2003, by which time we will have only begun conducting experiments of direct relevance to mechanism evaluation.

However, we do have funding from the California Air Resources Board (CARB) to use the new facility to assess reactivities of VOCs used in architectural coatings, and a smaller amount for general low NO_x mechanism evaluation research. We also expect to get some additional funding from Federal or other sources in the coming year. Therefore, although the funding situation will require that we cut back the

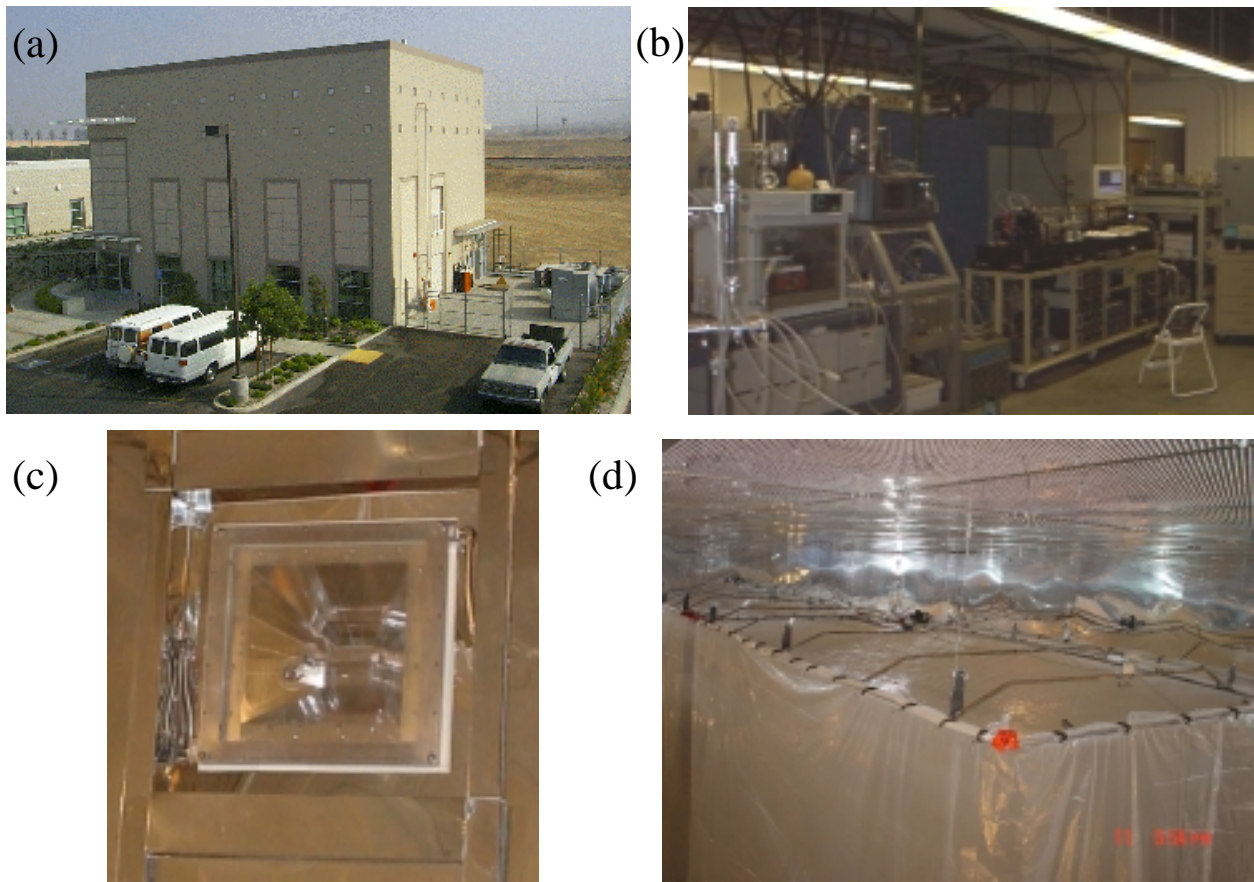


Figure 1. Photographs of the new chamber facility. (a) Outside view of building. (b) Laboratory area downstairs. (c) Argon arc light inside the chamber enclosure (d) Prototype reactor (constructed of polyethylene for engineering testing)

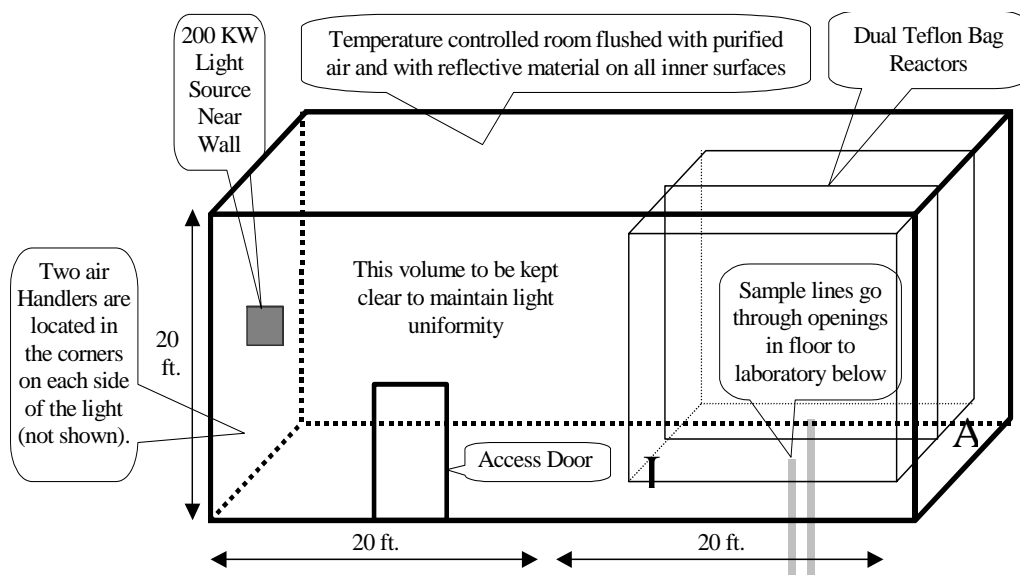


Figure 2. Schematic of the temperature-controlled enclosure housing the reactor.

research plan from that given in the original proposal and first report, significant research can still be carried out with the presently available funding.

The initial use of the new chamber once the construction and characterization is completed will be in the areas of low NO_x mechanism evaluation, temperature effect studies, and VOC reactivity assessment. Selected relatively simple chemical systems will be studied to evaluate measurement methods, models for chamber effects, and basic mechanism components. The initial focus for both the low NO_x mechanism evaluation and temperature effects studies will be on aromatics, where the low NO_x mechanism and temperature effects predictions are the most uncertain, though temperature effects and low NO_x experiments using more realistic surrogate - NO_x systems will be conducted for overall mechanism evaluation.

The initial priority for VOC reactivity assessments will be studies of selected architectural coatings constituents as required by our current CARB contract. The compounds or materials to be studied are being determined in consultation with the CARB staff and the CARB's Reactivity Research Advisory Committee, and the current priorities are 2,2,4-trimethyl-1,3-pentanediol isobutyrate (trade name Texanol®), an important component of water-based paints, and the various types of petroleum distillates. However, experiments will also be conducted for comparison with previous studies of selected VOCs, and experiments with aromatics will be conducted if the other experiments indicate mechanism problems.

The proposal and original work plan also calls for using the facility to evaluate mechanisms for effects of VOCs on secondary PM formation, and equipment for making PM measurements were acquired as part of this project. Although current funding is insufficient for comprehensive PM studies, initial experiments will be conducted using the facility to evaluate and demonstrate its capability for PM evaluation. This is needed to support planning or proposals for additional PM studies. Dr John Seinfeld of CalTech and Dr. David Cocker of UCR are collaborators on this project with regard to PM studies, and PM research in this facility will be coordinated with their separate research programs to provide complementary rather than duplicative data. In the meantime, Dr. Cocker will be using the PM equipment acquired for this project for other PM-related experiments in a separate environmental chamber.

Evaluation of Relative VOC Reactivities Using a Regional 3-D Model

Background and Objectives

Most current VOC reactivity scales are based on models with detailed chemistry but with very simplified representatives of airsheds (e.g., Carter, 1994a, 2000; Derwent and Jenkin, 1991; Derwent, 2002). Tests of reactivity scales with 3-D models are limited mainly to a few urban areas (RRWG, 1999). There is a concern that these reactivity scales may not be representative of O₃ impacts on a regional scale, particularly for long-range transport scenarios, NO_x-limited areas, and the widespread regional areas where biogenic sources dominate over anthropogenic emissions of VOCs. These concerns must be addressed before reactivity-based will be widely adopted in the United States.

To address these concerns, the Reactivity Research Working Group (RRWG) contracted UCR, in collaboration with ENVIRON international, to carry out a preliminary assessment of relative VOC reactivity effects using an existing regional model available at ENVIRON. An existing database was used to carry out the preliminary assessment at relatively rapidly and at relatively low cost. A scenario representing the eastern United States was chosen for study because of the importance of long-range transport and biogenic VOCs in this region, and because the effects of reactivity-based strategies on O₃ is the most uncertain in this type of scenario.

The overall objectives of this project were to assess relative incremental ozone impacts of different types of VOCs represented in the model with respect to

- Variation within the modeling domain
- How the results are used to derive measures of reactivity
- Comparisons with reactivities calculated using the EKMA models used to derive the Carter (1994, 2000) reactivity scales

The study also included assessing effects of selected large-scale substitutions, but this is beyond the scope of the current presentation.

Approach

The modeling database used in this study was the CRC-NARSTO database representing the July 7-15, 1995 episode in the Eastern United States. The CAMx model, version 3.01, was used (ENVIRON, 2002). A map of the domain is shown on Figure 3. As indicated there, the model used three nested grid sizes, with 36Km grids used for the entire region, and the finest grid size (4 Km) being used for the region centered around New York City and New Jersey.

For this preliminary study the version of the CAMx model with the Carbon Bond 4 (CB4) mechanism was employed (Gery et al, 1988), with some updates as discussed in the CAMx documentation (ENVIRON, 2002). Although this mechanism is not suitable for comprehensive reactivity studies because it is highly condensed and out of date it was used in this preliminary study because it is the least expensive for a preliminary assessment and because it represents most (but not all) of the major classes of the major classes of reactive VOCs. This makes it suitable at least for a qualitative initial assessment of how reactivities of different types of VOCs vary within the modeling domain.

The direct decoupled method (DDM) feature of CAMx was employed to calculate the sensitivities of ground level ozone to changes in emissions of the 8 CB4 VOC model species, CO, and ethane. The specific species for which O₃ sensitivities were calculated are listed in Table 1. In addition to these, ozone sensitivities were calculated for total NO_x emissions, total VOC (biogenic + anthropogenic) emissions, total anthropogenic VOCs, and major anthropogenic VOC source types. Various methods were used to derive reactivity scales from the distributions of sensitivities in the thousands of ground-level grid cells, as discussed below.

Reactivities of the various CB4 model species were derived relative to the ozone impacts of the mixture of total emitted anthropogenic VOCs. This is a useful definition of relative reactivity for regulatory application because it reflects the effects of regulating emissions of the one type of VOC only compared to regulating all VOCs equally. The mixture of total emitted anthropogenic VOCs is referred to as the “base ROG” mixture, and for this work its composition was derived from a recent EPA emissions database (EPA, 1998). Its composition in terms of CB4 species, weighed by both carbon number and reactivity, is shown on Figure 4. The ozone impacts of the base ROG were derived from the ozone impacts of its components. Although the composition of this mixture was not derived from the emissions input employed in this scenario, the calculated O₃ impacts of this base ROG mixture corresponded very closely to the O₃ sensitivities to the total anthropogenic VOCs that were calculated in this work.

In order to assess differences and similarities in reactivity scales derived using various O₃ impact metrics, a total of 126 separate regional reactivity scales were derived in this work. These were based on two different methods to quantify O₃ formation in a grid cell in an episode day, four different episode days, and three domain sizes, and six different methods to derive regional reactivity scales for each given episode day, domain size, and O₃ quantification method. The two O₃ quantification methods used

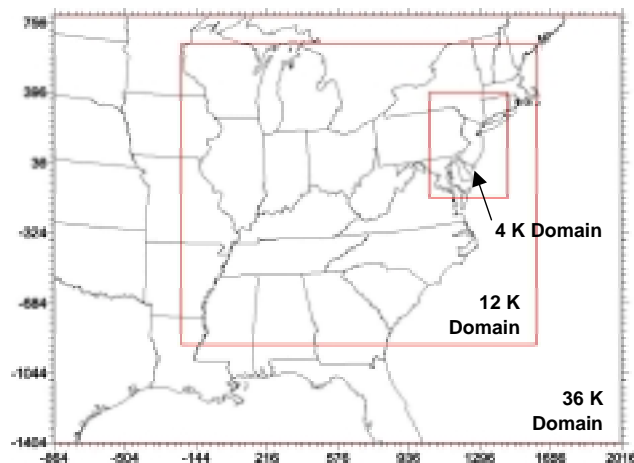


Figure 3. CRC-NARSTO modeling domain employed in this study.

Table 1. Carbon Bond model species whose ozone sensitivities were determined

Species	Approximately representative of
PAR	Carbons in C ₄ - C ₆ alkanes
ETH	Ethene (explicit)
OLE	Propene (primarily)
TOL	No specific compound. May be indicative of compounds with very NO _x sensitive reactivities (e.g., phenols, styrenes)
XYL	Xylenes
FORM	Formaldehyde (explicit)
ALD2	Acetaldehyde (explicit)
ETOH	Ethanol (explicit)
ETHA	Ethane (explicit, added for this study)
CO	Carbon monoxide (explicit)

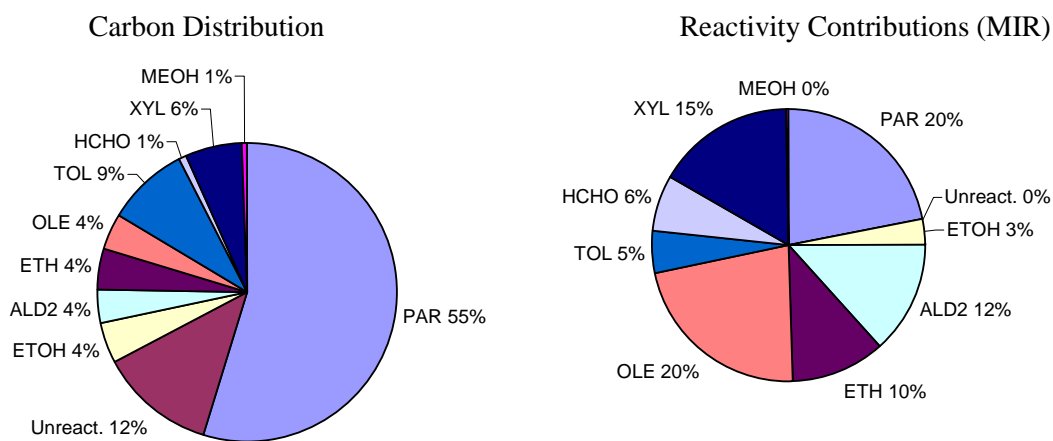


Figure 4. Relative carbon and reactivity distributions of the carbon bond species used for the base ROG surrogate used to compute relative reactivities.

consisted of effects of the VOC species on daily maximum 1-hour and daily maximum 8-hour averages, the four episode days used were July 12-15 for the 1-hour quantification and July 12-14 for the 8-hour quantification. Separate sets of scales were derived for the 36K domain, representing the full Eastern U.S. as shown on Figure 1, and for the 12K and 4K subdomains. Since the reactivities in the 12K domain were much like those in the full 36K domain, the examples shown in this report will be restricted for scales derived for the 36K and 4K domains.

The six different approaches for deriving regional reactivity scales from the effects of the VOCs on the daily O₃ impacts in the thousands of cells were as follows:

- Regional Maximum O₃: This uses the impacts of the VOC species on the domain-wide maximum O₃ concentration. This addresses the need to reduce peak O₃ concentrations but is not a true global metric because it reflects impacts at only a single location. As discussed below, impacts using this metric are highly variable because the chemical characteristics of the cell with the peak ozone varies significantly with domain and episode day.
- Regional Maximum Incremental Reactivity (Regional MIR): This uses impacts of the VOC species on daily maximum O₃ concentration at the location where O₃ is the most sensitive to changes in anthropogenic VOC emissions. This represents impacts on regions where O₃ is most sensitive to VOC controls and is comparable to the widely used MIR scale (Carter, 1994). However, this is also not a true global metric because it represents impacts at only one location, though it is not as variable as the regional maximum O₃ scales because the chemical characteristics of MIR regions tend to be comparable from day to day.
- Regional MIR to MOIR: This uses effects on the VOC species on averages of the daily maximum O₃ in all ground-level cells in the episode day where O₃ has a positive sensitivity to total anthropogenic VOCs and a negative sensitivity to total NO_x emissions. This reflects impacts in the relatively high NO_x areas near source areas where only VOC controls will reduce O₃. This also represents chemical conditions used to derive the MIR to MOIR scales, since O₃ sensitivities to NO_x are always negative in scenarios with the highest VOC sensitivities, and by definition O₃ sensitivities to NO_x are zero in MOIR scenarios, since they are defined as scenarios where any changes in NO_x emissions will reduce O₃ formation. Thus, these scales represent a refinement to the regional MIR scale in that it reflects impacts on multiple cells in the domain. Approximately 4-7% of the cells in the episode days in the full 36K East Coast Domain employed in this study represent MIR to MOIR conditions.
- Regional Average O₃: This uses the effects of the VOC species on the average of the daily maximum 1-hour average O₃ for all the ground-level cells in the domain under consideration. Thus this is a truly global metric that weighs O₃ sensitivities at each location equally, regardless of the O₃ concentration or the sensitivity to VOC emissions. This gives urban O₃ impacts the least weight of all the metrics considered in this work.
- Regional Average O₃ Over the Standard: This is a modification of the regional average O₃ scale where only those cells where the O₃ level is over the air quality standards of 0.12 ppm (for 1-hour daily maximum O₃) or 0.08 ppm (for the 8-hour quantification) are used in the average. This is a global metric that reflects impacts on regions where O₃ air quality standards are not met, but not on regions where O₃ levels are not a concern. However, it does not address impacts in areas where standards are met but slight O₃ increases may result in exceedences.
- Minimum Substitution Error: This method involves finding the relative reactivities of the VOC species that minimizes the sum-of-squares changes in O₃ concentrations in a null test substitution of the base ROG for the VOC species. A “null test” substitution is one that the reactivity scale predicts will not change O₃. For example, if the “PAR” species has a relative reactivity of 0.5 on a carbon basis in a particular scale, that scale would predict that replacing all PAR emissions with the base ROG on an equal carbon basis would yield the same O₃. Since impacts vary from cell to

cell, such “null” substitutions would cause O₃ to increase in some areas and decrease in others, and the sum of squares of this O₃ change is referred to as the “substitution error”. Mathematically, the minimum substitution error relative reactivities can be determined by finding the slope, forced through zero, of plots of the O₃ sensitivity of the species against the O₃ sensitivity of the base ROG mixture for the various cells (examples of such plots are presented below). This is a truly global metric that weighs effects of VOCs on O₃ in the high O₃ and most VOC-sensitive areas most highly while taking effects of VOCs on O₃ in all regions into account.

As indicated above, one of the objectives of this project was to compare regional reactivity scales with those using the one-day urban EKMA scenarios used to derive the Carter (1994, 2000) reactivity scales. However, the Carter scales cannot be compared to those derived in this work because a different chemical mechanism was employed. Therefore, in order to obtain more comparable data, the same set of 39 1-day EKMA model scenarios used to derive EKMA reactivity scales for the version of the CB4 mechanism employed in the regional model calculations. Analogous methods were used to derive the scales as used with the regional model, with the EKMA MIR scale consisting of averages of O₃ sensitivities to the scenarios where NO_x inputs are adjusted to yield maximum base ROG reactivity, and the EKMA average O₃ scale consisted of averages of the O₃ sensitivities for the 39 base case (unadjusted NO_x) scenarios.

It should be noted that the 39 EKMA scenarios used by Carter (1994, 2000) are out of date and predict far greater O₃ levels than is currently observed in the 39 U.S. cities they are designed to represent. This is another factor that may cause differences in reactivity scales compared to those using the more up-to-date regional model.

Results and Discussion

Figure 5 shows maps of the high O₃ and VOC sensitive regions for the representative episode days July 12 and July 14. It can be seen that these days differ in terms of the locations of the peak O₃ concentrations and (to a somewhat lesser extent) the location of the most VOC sensitive regions. This indicates that the different episode days represent somewhat different meteorological conditions and, to the extent that such conditions affect reactivity, may give different reactivity results. Not also that the most VOC sensitive regions are not necessarily the same as the regions where the highest O₃ concentrations occur.

Figure 6 shows plots of the sensitivities of the maximum 1-hour average O₃ concentrations in all the cells in the total 36K domain for each of the 4 episode days to total VOC against their sensitivities to total NO_x emissions. The lines and comments on the plot show reactivity characteristics in terms of NO_x conditions according to the definitions used by Carter (1994), with the term “ZBIR” added to refer to conditions where O₃ has no sensitivity to VOCs. It can be seen that most of the cells in this domain are highly NO_x sensitive, with O₃ being more sensitive to changes in NO_x emissions than to changes in VOC in ~85% of the cells, as indicated by the number of points below the “EBIR” line on the plot. Only about 15% of the cells are more sensitive to VOC than NO_x emissions. This tendency of most of the regional domain to be NO_x sensitive has been known for some time, so this result is as expected.

Figure 7 shows plots of the daily maximum 1-hour average O₃ sensitivities of selected VOC model species against those for the base ROG for all the ground-level cells in each of the episode days. As with Figure 6, each point represents a separate 36K cell for one of the four episode days. The distances of the points from the origin indicate the magnitude of the absolute sensitivities of O₃ to changes in VOC emissions, which can be seen to be variable. If the relative reactivities of the VOC species were the same in each cell, then all points would lie on the same line, with a zero intercept. As it is, the relative reactivities are variable, with the variability being different for different types of species. The lines on the

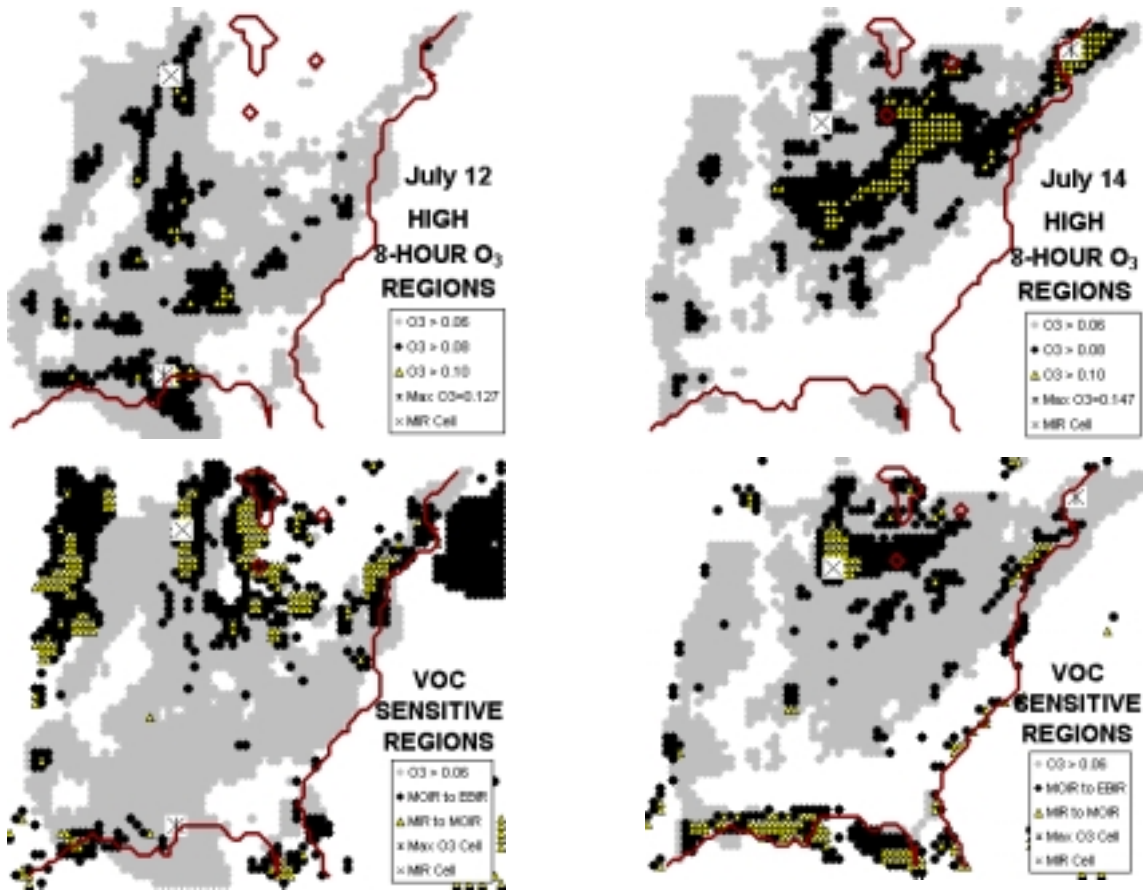


Figure 5. Distribution of high O₃ and VOC sensitive regions for the July 12 and July 14 episode days.

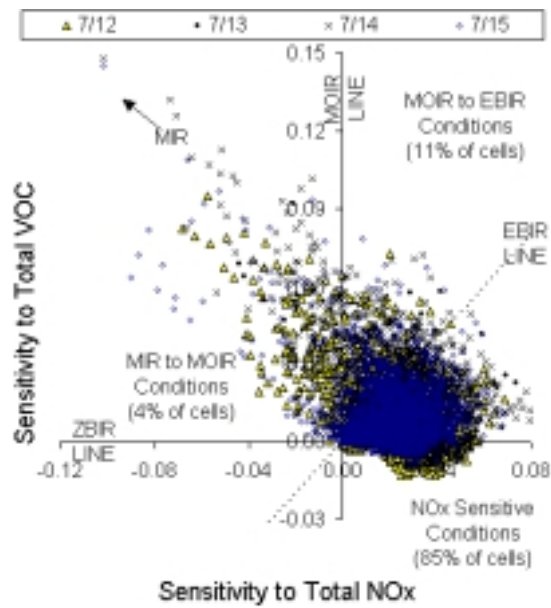


Figure 6. Sensitivities of maximum 1-hour average O₃ to total VOC and total NO_x

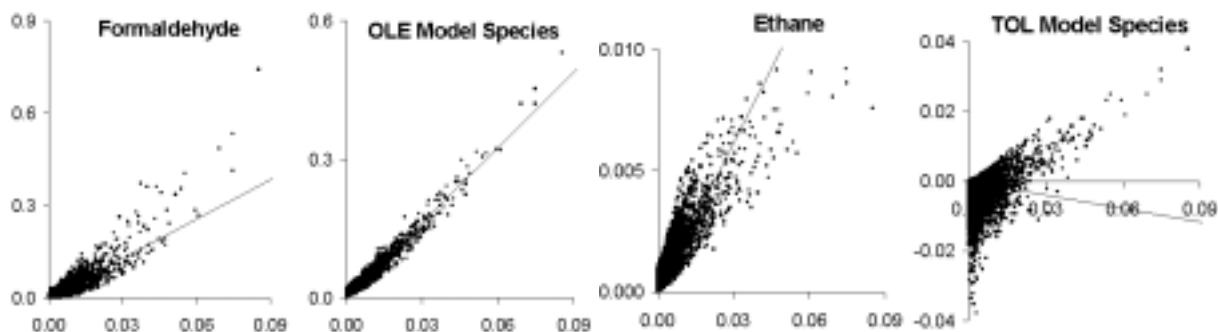


Figure 7. Plots of maximum 1-hour average O₃ sensitivities of representative model species against the sensitivities to the base ROG mixture for the 4 episode days in the 36K domain. The lines shown are the least squares fit lines, forced through zero, whose slopes are the minimum substitution error reactivities.

plots are the least squares fit lines forced through zero, whose slopes are the minimum substitution error relative reactivities. The OLE model species has the least variable relative reactivities, while the TOL species, whose O₃ sensitivities are highly dependent on NO_x conditions, has the most variable reactivities. In particular, it has very negative impacts in the NO_x-limited cells where the base ROG impacts tend to be relatively low, while it has positive impacts in the higher NO_x cells where the base ROG impacts are higher. This is due to the unusually large NO_x sinks in the mechanism for the CB4 TOL model species.

Figure 8 shows the comparisons of the various reactivity metrics for the selected model species whose data are shown in Figure 7. Relative reactivities derived from the EKMA scenarios are also shown. Formaldehyde is chosen as representative of highly reactive radical initiating compounds, ethane is chosen as representative of slowly reacting, low reactivity compounds, and OLE and TOL model species are chosen because they have respectively the least and the most variable reactivities of the species studied. Plots comparing selected pairs of relative reactivity scales showing all the model species, episode days, and domains are shown on Figure 9.

These figures show that there is indeed variability in the relative reactivities depending on how the scale is derived from the regional model results. As suggested by the data on Figure 7, the greatest variability is for the TOL model species, which has large negative reactivities for the metrics that give most weight to ozone impacts in the many NO_x-limited cells and positive reactivities for the MIR and other metrics that give most weight to the VOC-sensitive regions. Formaldehyde and ethane also have variable reactivities depending on the metric, by up to a factor of 3 depending on the metric used. Generally, the metrics that tend to have the highest relative reactivities for formaldehyde tend to have the lowest relative reactivities for ethane, and vice-versa. This is discussed further below.

Although the reactivity metrics are variable depending on how they are derived, with the exception of the highly variable TOL model species all the metrics tend to give the same general reactivity ranking for the various types of VOCs. For example, ethane is always less reactive than formaldehyde on a carbon basis regardless of the metric used, and the same can be said about most other pairs of species. For example, Figure 9a shows a comparison of the relative reactivities in the regional average O₃ scale, which reflects O₃ impacts over the entire domain, compared to the minimum substitution error scale, which is more dominated by urban impacts, and although all the points do not fall on the same line, they are highly correlated. This is true when most other pairs of scales are compared.

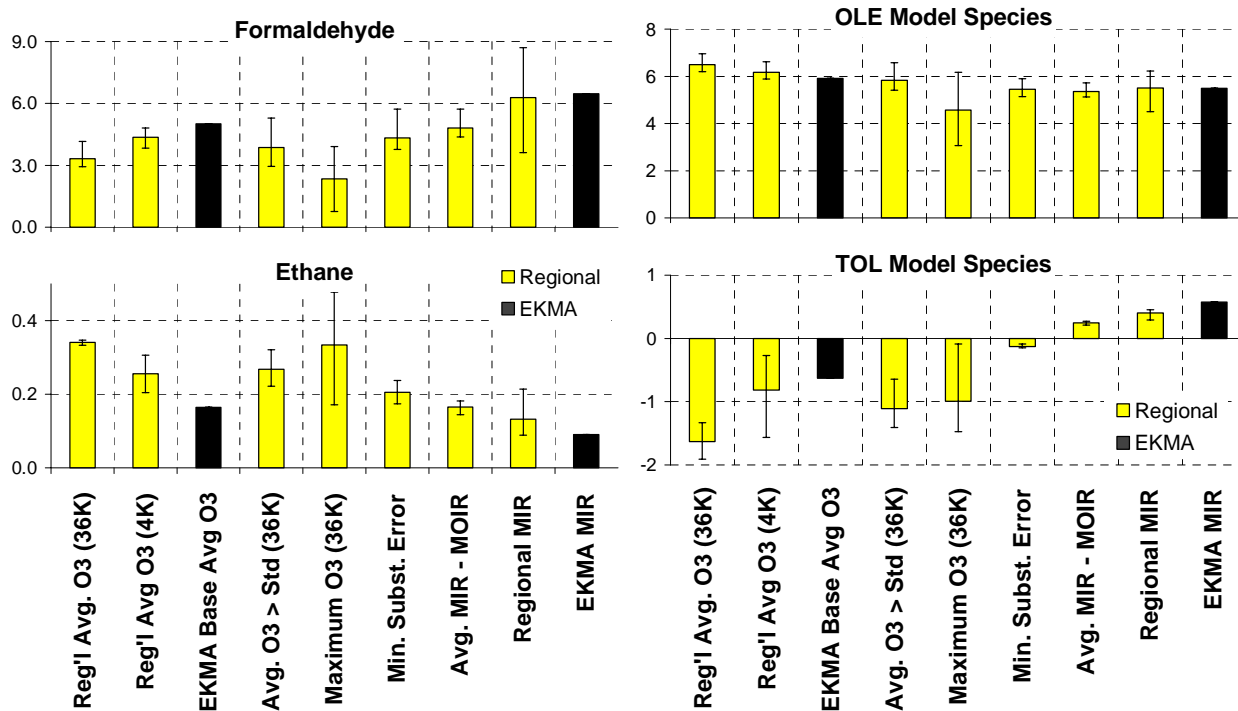


Figure 8. Comparisons of relative reactivity metrics for selected model species.

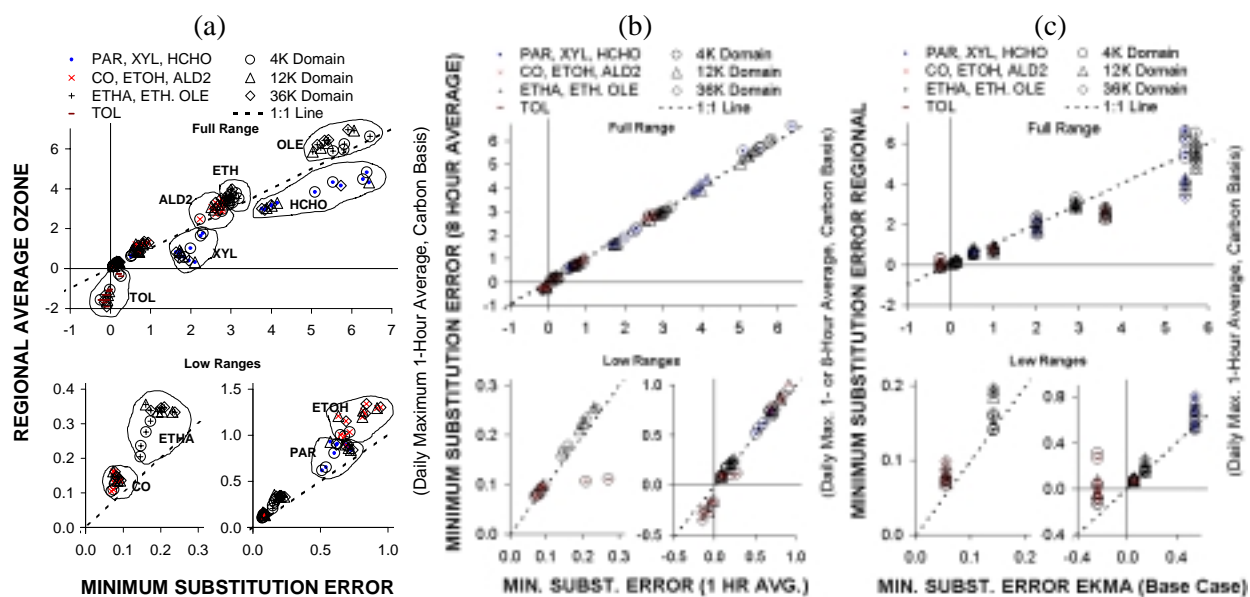


Figure 9. Comparisons of selected pairs of relative reactivity scales for all the episode days and domains. (a) Regional Average O_3 vs. Minimum Substitution Error; (b) Relative reactivities for 8-hour average O_3 vs. 1-hour average O_3 for the Minimum Substitution Error method; (c) Regional vs. Base Case EKMA for the Minimum Substitution Error method.

Figure 9b shows a comparison of scales derived using the daily maximum 8-hour average O₃ quantification with the corresponding scale derived using the 1-hour average O₃. The results of other pairs of scales that reflect impacts on the same regions are similar. This indicates that the averaging time does not significantly affect relative VOC O₃ impacts.

Comparisons of relative reactivities derived using the EKMA models with those derived using the regional model can be seen on Figure 8 and Figure 9c. Although there are differences, it is interesting to note that the EKMA relative reactivities correspond remarkably closely to the regional model relative reactivities derived using analogous methods. This is despite the significant differences between the EKMA and the regional models in terms realism in representing complexities of transport and meteorology, and the fact that most of the EKMA scenarios much higher O₃ conditions than occur even in the urban areas in the regional model. There may be a tendency for the EKMA models to predict lower relative reactivities of the slowly reacting species because of the shorter reaction time (1-day compared to the multiple day regional simulation), but this tendency is not large.

As shown on Figure 5, above, the various episode days in the regional scenario used in this study have differing meteorological conditions and locations of high O₃ and VOC sensitive areas, and this would be expected to cause some day-to-day variability in relative reactivity scales. This day-to-day variability is indicated by the error bars on Figure 8 and the scatter in the points for the different episode days on Figure 9 for the regional relative reactivities. The error bars on Figure 8 suggest that the different types of metrics have differing degrees of day-to-day variability. This is shown on Figure 10, which gives averages of fractional standard deviations for all model species (except the highly variable TOL species) for various types of metrics.

It can be seen that the reactivity scales derived using the truly global average O₃ or minimum substitution methods, or those representing large numbers of cells with similar chemical conditions such as the average MIR-MOIR methods have the least amount of day-to-day variability. The greatest variability is for the metrics representing impacts in only a single cell, with the regional MIR scale being less variable than the regional maximum O₃ scale because MIR regions tend to have similar chemical conditions, while conditions of cells with the highest O₃ level can vary from day to day, depending on

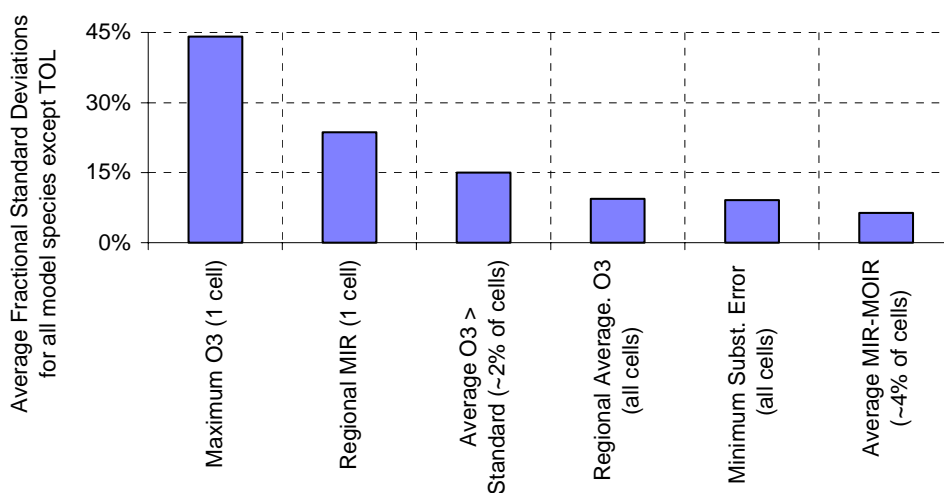


Figure 10. Day to day variability of regional reactivity metrics. Data are shown for the 1-hour O₃ quantification. Results for the 8-hour O₃ quantification are similar.

meteorology, transport, etc. In general, the regional maximum O₃ scale is too variable to be a suitable metric for VOC reactivity comparisons, and is not considered in the discussion of classification of reactivity scales in the following section.

Classification of Reactivity Scales by Effective Range

An important characteristic of a reactivity scale from a policy perspective is its effective range, i.e., the range of reactivities from the least reactive compound that is of relevance to ozone control to the most reactive. The magnitude of this range measures the maximum effectiveness of a reactivity-based regulatory policy when applied to compounds that would otherwise be regulated on a mass basis, and affects the incentive to substitute to low reactivity compounds should a reactivity-based policy be adopted. Using a reactivity scale with an inappropriately low effective range may be insufficient to encourage beneficial substitutions, while using one with too high a range may result in increased O₃ by encouraging substitutions that are less beneficial than the scale implies.

Since the actual ozone impacts of compounds will range from zero for compounds that do not react at all to some finite value for reactive compounds, strictly speaking the effective range of any reactivity scale is infinite. However, the current informal policy adopted by the U.S. EPA is to exempt from VOC regulations compounds with lower reactivity as ethane (Dimitriades, 1999), which makes the relative reactivity of that compound a reasonable choice for defining the lower end of the effective range. On a carbon basis, the most consistently reactive CB4 model species in most metrics is OLE, so that is chosen as defining the high end of the effective range. Therefore, the OLE/ethane reactivity ratio (on a carbon basis) is used as definition of the effective range for the purpose of comparing the reactivity scales developed in this work.

It turns out that the effective range as measured by the OLE/ethane reactivity ratio is a good indicator of relative reactivities of other species. This is shown on Figure 11 which shows plots of relative reactivities of the other model species against the OLE/ethane reactivity ratio for most of the regional and EKMA reactivity scales developed in this work. (Data for the highly variable regional maximum O₃ scale are not shown.) It can be seen that in essentially all cases the regional model relative reactivities are highly correlated with the effective ranges, and change monotonically with the effective range, with the relative reactivities of the more reactive species increasing and those of the less reactive species decreasing as the range increases. Even the reactivities of the highly variable TOL model species correspond reasonably well with the effective ranges, being negative in the scales with low effective range and high in scales with high ranges. This is because scales with low effective ranges tend to weigh the low NO_x conditions more highly, while scales with high effective ranges represent MIR-like conditions where TOL tends to have positive reactivities.

Figure 11 also shows that in most cases the relationships between relative reactivities and effective ranges are the same for EKMA-derived reactivity scales as they are with the reactivity scales derived from the regional model calculation. The exceptions appear to be acetaldehyde and ethanol, where the EKMA relative reactivities tend to be somewhat higher than regional model relative reactivities with similar effective ranges. The reason why ethanol and acetaldehyde are different in this regard is unclear at the present time. However, this difference is not large compared to the variability of the data.

Figure 12 shows a summary of the effective ranges for the representative regional and EKMA reactivity scales developed in this work. The MIR and MIR-MOIR reactivity scales that reflect primarily the more VOC-sensitive regions tend to have the highest effective ranges, while the regional average O₃ scales that are more sensitive to impacts in the many NO_x-limited cells tend to have the lowest ranges, with the difference between the extremes being about a factor of 3. Note also that the reactivity scales derived using the data for the more urban-dominated 4K domain tend to have higher effective ranges than

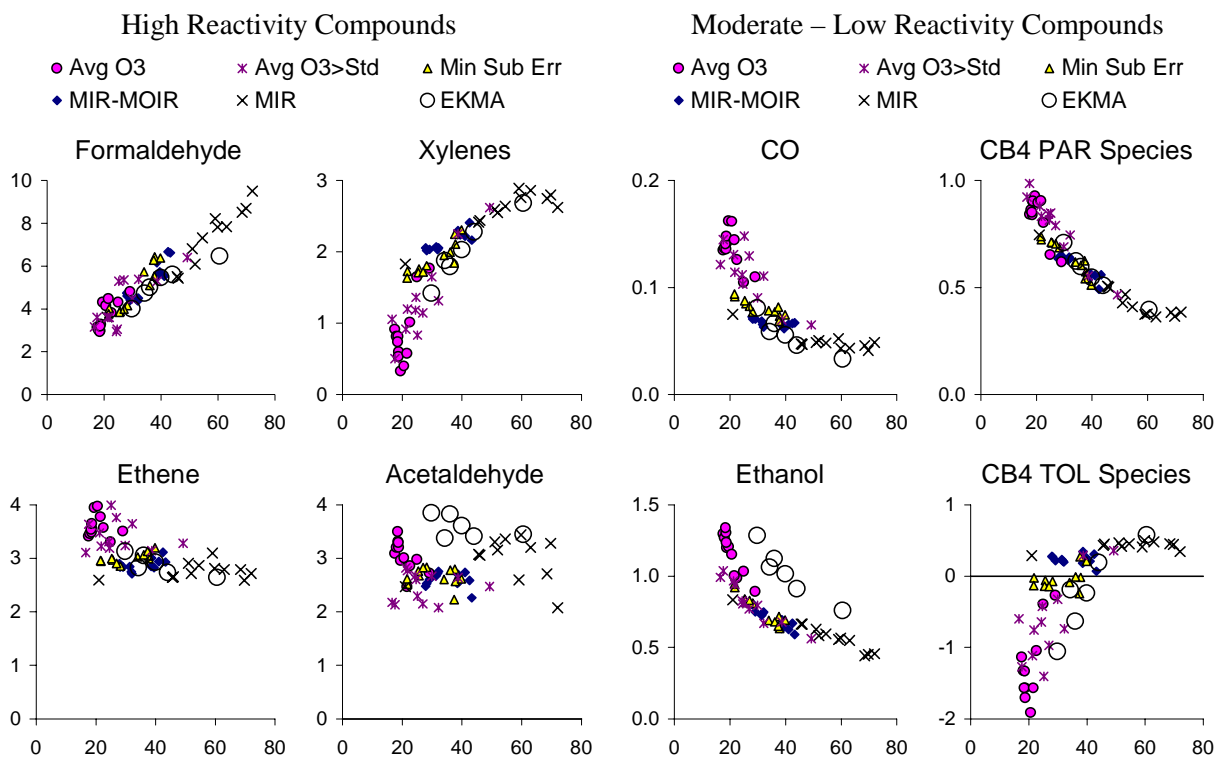


Figure 11. Plots of relative reactivities of the model species against the effective ranges. Relative reactivities shown on a carbon basis.

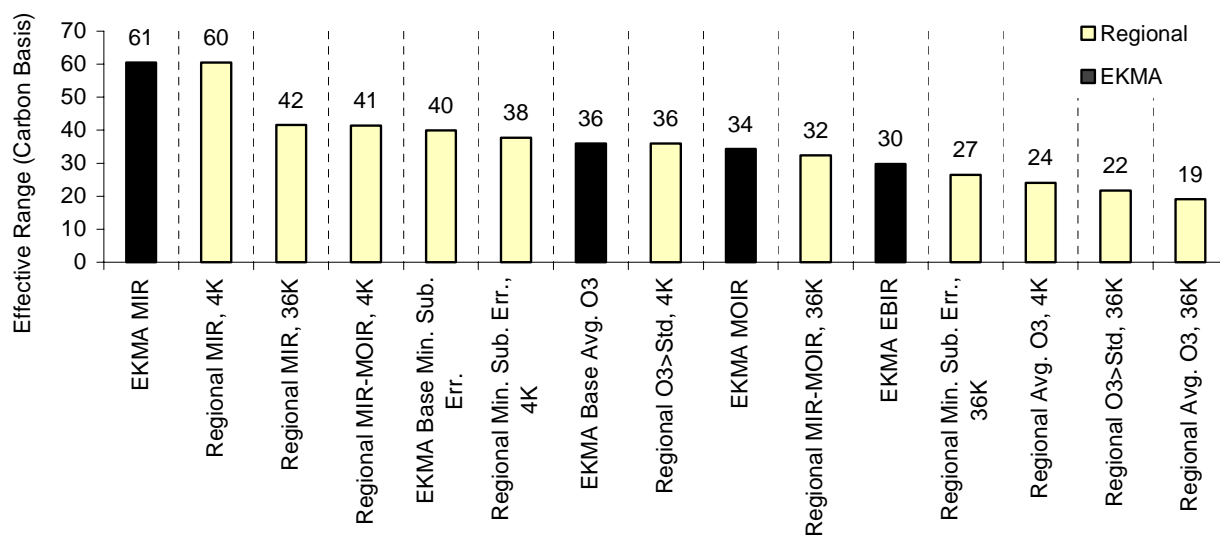


Figure 12. Summary of effective ranges for regional and EKMA reactivity scales

those derived using the entire 36K region. This is because the more urban regions tend to have more relatively high NO_x areas that resemble MIR to MOIR conditions. The EKMA-derived reactivity scales tend to have very similar effective ranges as the regional model scales derived using comparable methods.

Conclusions and Recommendations

This project has achieved its primary objectives of providing modeling data that addresses the concern that relative reactivities of VOCs towards ozone formation may be sufficiently different on a regional scale than indicated by previous modeling studies of urban scenarios to present problems should reactivity-based VOC controls be adopted. Although there are some differences between urban and regional-scale relative reactivities, regional and EKMA models give directionally consistent reactivity rankings by most metrics for the major types of reactive VOCs. This suggests that it should be possible to develop reactivity scales that appropriately represent both urban and regional impacts. Averaging time for the daily maximum O₃ does not significantly affect relative reactivities, so the averaging time used in the O₃ standards should not be an important factor affecting the optimum reactivity scales. However, choices will have to be made concerning which types of model and reactivity metrics are most appropriate to use when developing reactivity scales for regulatory applications

The effective range provides a useful means to classify relative reactivity scales, since it reflects predicted maximum benefits of reactivity-based substitutions (and the maximum incentives of reactivity-based regulations), and is correlated to relative reactivities for most species. The effective ranges of scales can vary by up to a factor of ~3 depending on how impacts in different types of regions are weighed. Scales dominated by urban or VOC-sensitive regions give the highest effective ranges (up to ~60 on a carbon basis for CB4 scales based on the OLE/ethane ratio), while scales weighting impacts throughout large regions more equally give the lowest ranges (down to ~20 for CB4 scales). However, even with the lowest effective range scales there is still a significant difference in O₃ impacts between the highest and lowest reactivity VOCs, indicating it is probably not correct to conclude that all VOCs become nearly equal in O₃ impacts if a sufficiently large regional domain is considered.

This preliminary study certainly does not represent a definitive evaluation of relative VOC reactivity on regional scales because of the limitations of the CB4 mechanism and the fact that only a single episode was modeled. However, information should now be sufficient for policy decisions to be made concerning whether reactivity based regulations are worth the complexities involved, how to weigh regional vs. urban effects when deriving a regulatory scale, and whether it is best to use a scale with a low or high effective range. Such decisions are necessary to guide priorities for subsequent research.

Assuming the policy decision is to proceed with reactivity-based regulations, the modeling research should focus on how best to derive regulatory reactivity scales for the hundreds of types of emitted VOCs. Up-to-date, experimentally tested, and *detailed* chemical mechanisms are required for this purpose – CB4 is clearly unsuitable for this application. The models used must represent the full range of relevant chemical conditions, and should be based on modeling other regions and episodes than just the one considered here. Until recently calculating reactivity scales for the hundreds of different types of VOCs using multi-cell regional models has not been possible, and even with the improvements in the computers and modeling software becoming available is still difficult and has not yet been done. The results of this project suggest that use of appropriate EKMA models may give very similar reactivity scales as comprehensive regional models, and thus use of this approach in the near term may not be inappropriate. However, the EKMA scenarios used for the Carter (1994, 2000) scales are out-of-date, poorly documented, do not represent current urban conditions, and are not suitable for representing non-urban areas. Research in improving EKMA scenarios is clearly appropriate if they are to continue to be used for reactivity assessment.

Finally, as discussed in the first part of this presentation, no matter how representative and comprehensive the model is for urban and regional scenarios, relative reactivity predictions are still no better than the chemical mechanism that is implemented in the model. Basic chemical mechanistic studies are still needed to reduce the fundamental uncertainties, and well-characterized environmental chamber experiments are needed to evaluate and improve the predictive capabilities of the mechanisms. Such data are needed to reduce uncertainties in reactivity predictions for even the most well studied VOCs. In addition, there are many types of VOCs that have not been adequately studied, and introduction of new types of VOCs is expected in the future as new solvents and processes are developed. The priority and incentives for such research will only increase should reactivity-regulations become more widely adopted.

Acknowledgements and Disclaimer

The development of the environmental chamber facility discussed in the first section was funded by the United States Environmental Protection Agency through cooperative agreement CR-827331-01-0. The California Air Resources Board projects that will be supporting work in this chamber are contracts 00-333 and 01-305. The major work in developing this facility was carried out by Dennis Fitz, Kurt Bumiller, Chuck Bufalino, Irina Malkina, John Pisano, Claudia Sauer and others at CE-CERT, and support by Dr. Joseph Norbeck, director of CE-CERT is also acknowledged.

The regional model VOC reactivity project discussed in the second section was funded by the American Chemistry Council through contract SC-20.0-UCR-VOC-RRWG as a part of its contribution to the research program of the Reactivity Research Working Group. Collaborators on this project were Gail Tonnesen of CE-CERT, who assisted in the data processing and analysis, and Greg Yarwood of ENVIRON international, who prepared the model inputs and carried out the model calculations.

The conclusions and opinions expressed in this presentation are entirely those of the author, and do not necessarily reflect those of the funding agencies or collaborators. Mention of trade names does not constitute endorsement or recommendation for use.

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