

INVESTIGATION OF VOC REACTIVITY EFFECTS USING EXISTING REGIONAL AIR QUALITY MODELS

Progress Report to the
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Summary

Results to date on an ongoing project to assess VOC reactivity effects in the Eastern United States using the CRC-NARSTO database representing the July-5, 1995 episode and the Carbon Bond mechanism are described. The Direct Decoupled Method (DDM) as implemented in the CAMx model was used to calculate the incremental ozone impacts of 8 Carbon Bond VOC species, CO and ethane, and various methods were used to quantify ozone impacts and derive regional reactivity metrics based on them. The results indicated that relative ozone impacts of the modeled species varied significantly throughout the domain, but for most model species except for TOL reasonably consistent results are obtained if “minimum substitution error” or “regional maximum incremental reactivity” metrics are used. There were no large differences in regional relative reactivities derived based on maximum 8-hour ozone averages compared to those based on 1-hour averages. Metrics based on the regional maximum ozone concentration were found not to give consistent results. The regional reactivity results are similar to the reactivity scales derived using the Carbon Bond mechanism with the scenarios and methods of Carter (1994a) but some differences are observed. Although the large scale reactivity-based substitution calculations called for this project have not yet been conducted, a preliminary analysis of calculations where all anthropogenic VOCs are removed or replaced by ethane indicate that with a few exceptions their results are reasonably consistent with what is predicted by incremental reactivity analysis based on these DDM results. Preliminary conclusions obtained from the project thus far are summarized.

Disclaimer

This report describes work on an ongoing project, and all data, analyses and conclusions should be considered to be preliminary. This report reflects the analyses and conclusions of the first author (W.P.L. Carter) only, and although it incorporate the substantial contributions of the other investigators it has not been reviewed by them. This report is for the internal use of the American Chemistry Council (ACC) and the Reactivity Research Working Group (RRWG) members only, and should not be distributed beyond their participating organizations or cited without permission from the authors.

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Introduction

The objective of this project is to use an existing regional modeling database to assess VOC reactivity effects to assess VOC reactivity effects in the eastern half of the United States. Use of an eastern U.S. scenario is chosen for this initial study because transport is believed to be important in this region, because the effectiveness of reactivity-based substitutions in such scenarios has not been adequately assessed and is considered to be quite uncertain. The specific objectives include the following:

- Assessing the extent to which relative ozone impacts of various types of VOCs vary within the regional modeling domain, which includes a wide variation of source and receptor areas.
- Assessing the effects of using different reactivity metrics when quantifying regional ozone impacts. This includes assessing effects of using different methods to quantify ozone impacts at a given location, and using different methods to derive a single reactivity measure that appropriately reflects the multiple impacts in multiple locations.
- Comparison of relative ozone impacts of various types of VOCs derived for this regional modeling domain with their impacts calculated using the EKMA models used to derive the Carter (1994a) reactivity scales.
- Assessing the effects of selected large-scale reactivity based VOC substitutions and the extent to which the effects of large-scale substitutions can be predicted by incremental reactivity scales.
- Assessing alternative approaches for deriving a general reactivity scale representing regional ozone impacts.

This report describes the results of this project to date, which includes primarily work on incremental reactivity calculations analyzed using the coarse grid results. Although fine scale reactivity results are also available and preliminary results using them were presented at the RRWG meeting on February 16-17, 2002, there was insufficient time to analyze them using the metrics currently employed, and these results will be presented and compared with the coarse grid results in a later report. Most of the large scale substitution calculations to be carried out for this project have not yet been conducted, though some preliminary results obtained using 100% anthropogenic VOC reduction or ethane substitution scenarios are briefly discussed.

Modeling Database

The modeling database used for this study was the CRC-NARSTO database for the July 7-15, 1995 episode in the Eastern United States. The CRC-NARSTO episode was developed by ENVIRON and is being used in studies sponsored by the Coordinating Research Council. It is not a SIP model, but it has the advantages of having higher resolution than the corresponding SIP models and offering the SAPRC97 mechanism as an alternative to CB4 (though only CB4 has thus far been used in the current study). The database uses 36, 12, and 4-kilometer grids, with the highest resolution grids being centered on New Jersey and the New York Metropolitan area. The emissions data were prepared using EPA Net96 and the meteorological data were prepared using MM5. The model domain indicating the grid sizes employed is indicated on Figure 1.

Because of the way the model was initialized, the model did not simulate the highest resolution grids until the simulation of July 11. Therefore, for consistency in treatment of different episode days, the reactivity analyses in this report were conducted for days prior to July 11. In addition, we have not yet completed the analysis of the high-resolution data, so the results discussed in this report will incorporate the high-resolution data only as averages in the 36-kilometer grids. data from the 36-kilometer grids only. Analysis of the results for the full domain shown on Figure 1 was given priority because it represents the

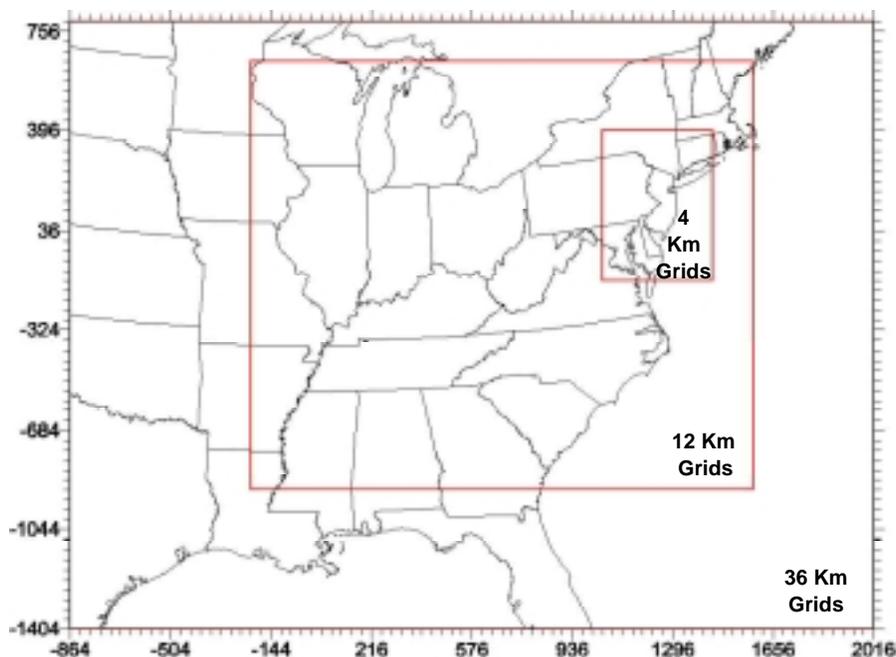


Figure 1. CRC-NARSTO modeling domain used for this study for the July 17, 1995 episode.

widest range of conditions for the purpose of assessing variability of VOC reactivity. Incorporating the high-resolution results as averages in low resolution grids probably will not introduce significant inaccuracies in most regions, especially since the results are being aggregated to obtain global metrics in any case. However, the effects of averaging out finer structure in the data may be non-negligible in some urban or large source areas. This will be examined by conducting a more complete analysis of the fine grid data later in this project.

Chemical Mechanism

Although the database and CAMx model for this episode can support use of either the SAPRC-99 or CB4 mechanism, it was decided that calculations for the initial phase of this project the CB4 mechanism because of the lower cost and because CB4 has been widely used in other scenarios. It represents most (though not all) of the important classes of reactive VOCs, allowing reactivity trends for the major classes to be assessed with the minimum number of species and computational overhead.

However, use of the Carbon Bond mechanism does have some disadvantages that must be taken into account when assessing the results of this study. It was developed in the late 1980's (Gery et al, 1988) so it does not represent the current state of knowledge of atmospheric chemistry. Some modifications were made to correct for problems in its representation of peroxy + peroxy reactions at low NO_x conditions, and to update the isoprene mechanism to be consistent with the isoprene mechanism of Carter (1996) (Environ, 1998). It is highly condensed, which means that it cannot be used to predict the impacts of most individual VOCs, except in a highly approximate manner. It has inappropriate or no representation of some important types of VOCs, as discussed below. In addition, comparison of box model reactivity results suggest that the Carbon Bond mechanism may be more sensitive to radical initiation and termination effects than current mechanisms (Jeffries and Crouse, 1991; Hales et al, 1993), which may affect the spatial variability of the reactivity results.

Nevertheless, the CB4 mechanism considered to be suitable for at least an initial and qualitative assessment of variability of reactivity effects within a regional modeling domain, which is a major objective of this study. Calculations to verify the reactivity trends using this mechanism can be conducted using the more up-to-date and chemically detailed mechanisms in a later phase of this project, if appropriate, or by comparison with results of SAPRC-99 simulations of this same episode being carried out by Russell and co-workers for other RRWG projects.

Because of the importance of ethane in the current EPA reactivity policy (Dimitriades, 1999), a model species representing this compound explicitly was added to this mechanism for this work. The ethane mechanism is based on that used in the SAPRC-99 mechanism, using the appropriate CB4 species, ALD2, to represent the formation of acetaldehyde, its major photooxidation product.

Table 1 lists the model species in the version of the CB4 mechanism used in this project, and the types of compounds whose reactivity characteristics they represent. The table also indicates the types of compounds that are not represented or (in our opinion) not appropriately represented in the current version of the mechanism. It also indicates the distribution of species used to represent the base ROG composition for the purpose of relative reactivity assessment, as discussed later in this report.

Table 1 indicates that the Carbon Bond 4 mechanism represents the major classes of reactive VOCs that must be considered when modeling ozone formation, though with two major exceptions. These are internal alkenes, whose emissions are represented only by the emissions of their reactive products, and radical inhibiting compounds, which are not represented at all. These omissions are probably not significant when representing entire emissions because the initial reactions of the internal alkenes are probably not as important in terms of overall impacts as the reactions of their products, and because the overall contribution of radical inhibiting compounds in current emissions profiles is relatively small. However, this means that the reactivity characteristics of these types of compounds are not represented in the model simulations in this work.

Toluene is an important compound in the emissions, and the TOL model species used to represent it is also used for other monoalkylbenzenes and lower reactivity aromatics. As also indicated on Table 1, we do not believe that the TOL model species in the current mechanism appropriately represents the reactivity characteristics of these compounds. In particular, the CB4 TOL model species is calculated to have O₃ reactivities that are much more sensitive to NO_x conditions than is calculated for toluene in the SAPRC or other current mechanisms (Jeffries and Crouse, 1991; Hales et al, 1993). This is probably primarily because the CB4 mechanism uses a very high (36%) cresol yield, while currently accepted product data indicate that the yield is more likely in the ~20% range (Carter, 2000a and references therein). However, other mechanism differences may also contribute to the significantly different reactivity characteristics predicted for toluene compared to current state-of-the-science mechanisms.

It is probable that the reactivity characteristics of toluene in terms of dependences on environmental conditions is better represented by those predicted by CB4 XYL (xylene) model species, though the magnitude of the impacts would be greater than is the case for toluene because of the greater reaction rate and higher yields of radical initiators for xylenes compared to toluene. The reactivity characteristics of the CB4 TOL model species is probably more indicative of those of styrenes or phenols, whose reactivities are calculated to be highly dependent on NO_x conditions in the SAPRC-99 mechanism (Carter, 2000a). Since a comprehensive reactivity assessment should include considerations of such compounds, the reactivity characteristics calculated for the TOL model species is still of interest in this study.

Table 1. List of Carbon Bond 4 VOC model species, indicating those whose ozone sensitivities were studied for this project. The types of compounds whose reactivity characteristics that are not represented by this mechanism are also indicated.

Species	Compounds Represented	Base ROG contribution (millimole/mole C)
<u>CB4 species whose ozone sensitivities were calculated</u>		
PAR	C ₄ – C ₆ alkanes (one PAR for each carbon). Used in the model to represent extra carbons on other molecules. (1 carbon)	547
ETH	Ethene (represented explicitly) (2 carbons)	21
OLE	Propene (primarily) (2 carbons)	20
TOL	Used to represent toluene and monoalkylbenzenes in emissions, but gives reactivity results that are considered to be inappropriate for these compounds. Reactivity characteristics may be indicative of those for styrenes and phenols. See text. (7 carbons)	12
XYL	Xylenes (8 carbons)	8
FORM	Formaldehyde (represented explicitly) (1 carbon)	10
ALD2	Acetaldehyde (represented explicitly) (2 carbons)	19
ETOH	Ethanol (represented explicitly) (2 carbons)	21
ETHA	Ethane (represented explicitly). Not represented in the standard CB4 mechanism but added for the purpose of this study. (2 carbons)	
CO	Carbon Bond (explicitly represented) (1 carbon)	
<u>CB4 species whose ozone sensitivities were not calculated (reactivity contribution to the base ROG neglected)</u>		
ISOP	Isoprene (represented explicitly)	0.4
MEOH	Methanol (represented explicitly)	5
MTBE	Methyl 2-butyl ether (represented explicitly) (Expected to have similar reactivity characteristics as PAR)	0.2
UNR	Unreactive compounds (has reactivities of zero by definition).	124
<u>Chemical Compounds not adequately represented by available CB4 species</u>		
Internal alkenes. (Only their products are represented; effects of initial OH and O ₃ reactions are ignored.)		
Toluene. (Reactivity characteristics of the TOL model species not considered to be representative of this compound. See text.)		
Radical inhibiting VOCs such as benzaldehyde or high molecular weight alkanes. (No model species in the mechanism with string radical inhibiting characteristics.)		

Base ROG Mixture

The impacts of VOCs on ozone formation are known to be highly dependent on environmental conditions, particularly availability of NO_x (Carter and Atkinson, 1989, RRWG, 1999 and references therein). However, the purpose of this project is assess the effects of policies that encourage VOC substitutions, the quantities of interest in this study are *relative* reactivities, i.e., ratios of incremental reactivities of the VOCs to some standard compound or VOC mixture. These would be expected to be less variable with conditions because the effects of variability of sensitivities of O_3 to VOCs in general are factored out. It is the variability of the relative reactivities that must be considered when assessing impacts of reactivity-based VOC substitution policies.

In this work, relative reactivity is defined as the ratio of the incremental reactivity of the compound or model species to the incremental reactivity of a standard mixture designed to represent the composition of anthropogenic VOC emissions from all sources. This is referred to as the “base ROG mixture” in the subsequent discussion. Defining relative reactivity in terms of base ROG mixture is useful definition from a policy perspective because it gives a measure of the relative benefit (or disbenefit) of regulating or increasing emissions of this compound alone compared to regulating or increasing emissions from all VOC sources equally. For example, if a compound has a relative reactivity of 2 it means that a control strategy that reduces emission of that compound alone will have twice the O_3 reduction of a control strategy that reduces all VOC emissions by the same amount.

The base ROG mixture should approximate the composition of the total mixture of all non-methane anthropogenic VOC emissions into the models. Although the total emissions composition should be generally be very similar for current regional models using the same generation of emissions inventories, there may be slight differences among the modeling databases used in the RRWG studies. For model intercomparison purposes it is more important that the same mixture be used as the standard than that they necessarily exactly represent the emissions inventory used in each simulation, which may differ in some respects among the models, provided that the standard mixture is reasonably representative.

Because the RRWG modeling studies are national in scope, the base ROG mixture to be used for this study consists of the mixture of VOCs from the total emissions profile that was provided by the EPA to represent total anthropogenic emissions into regional models (EPA, 1998). This composition was used to derive the fixed parameter version of the SAPRC-99 mechanism for Models-3 (Carter, 2000b). Although this may not be exactly the same as the composition of the total anthropogenic emissions profiles used in the specific model in this study, and may not necessarily reflect the current state of the EPA’s emissions databases (see comments in the EPA, 1998 reference), it is considered to be a sufficiently close approximation for the purpose of this study.

The composition of the base ROG is specified in terms of moles of model species per mole carbon of base ROG. The data provided by the EPA (1998) were provided in terms of mass emissions of EPA SAROAD classes. Methane was removed from the mixture, and the non-methane composition was converted into molar emissions of SAPRC-99 and other mechanism model species using emissions assignments made for use with a comprehensive emissions database that is in preparation (Carter, 2002). Note that some of the compounds that were not assigned to SAPRC-99 species have assignments to carbon bond species, either from previous emissions assignments or made by Carter (2002). Approximately 99% of the mass of the emitted non-methane organics in the EPA emissions profile could be assigned to Carbon Bond species using this approach. The emissions were normalized to give moles of model species per mole carbon of base ROG.

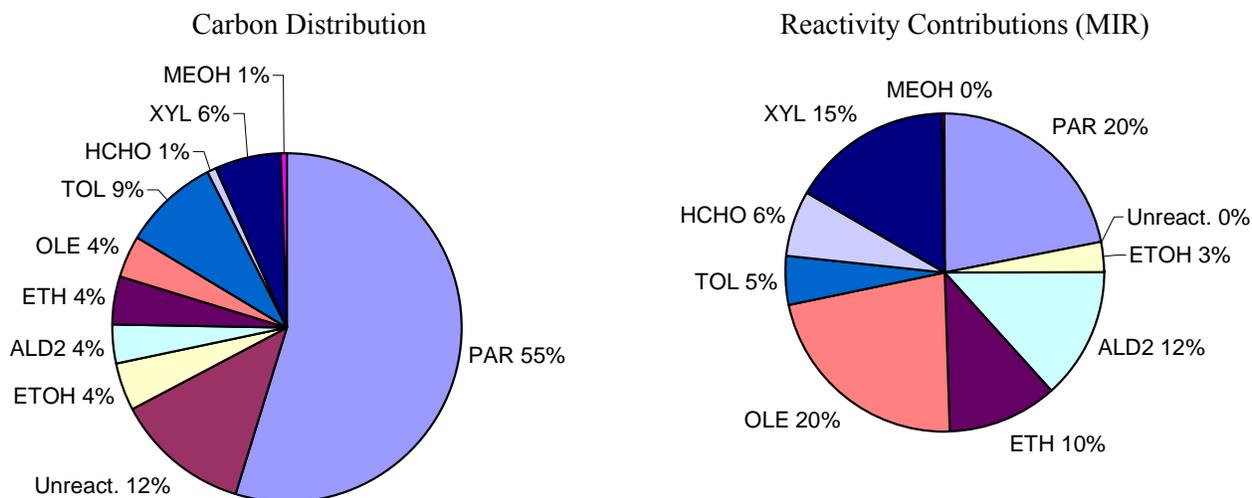


Figure 2. Relative carbon and reactivity distributions of the carbon bond species used for the base ROG surrogate used to compute relative reactivities.

The base ROG composition in terms of moles carbon bond species is given on Table 2, and Figure 2 shows the distributions in terms of carbon and reactivity. The reactivity distributions were derived using EKMA MIR scale, derived for this version of the Carbon Bond mechanism as discussed below. In terms of carbon distributions (which approximates mass), more than half of the base ROG is PAR and approximately 2/3 are PAR + unreactive VOCs, about 15% are aromatic species and the remainder are the various other species. When weighted by reactivity contribution, the various reactive species become more comparable in their contributions, with no single species contributing more 20% of the overall ozone impact as estimated using the MIR scale.

DDM Calculations

For the current phase of this project, the changes in ozone formation caused by incremental changes of various types of model species were calculated using the decoupled direct method (DDM) as implemented in CAMx. These sensitivities were calculated as a function of time and space and output as hourly averages for all the ground level cells. Two separate DDM calculations were carried out, using the same episode as the base case. Sensitivities of other model species besides O_3 to changes in the emissions were also calculated, but in this work we will consider O_3 sensitivities.

Note that even though the discussion here characterizes the DDM simulations as calculating the effects of changes of emissions, technically the DDM simulations do not involve actually changing any emissions. Instead, the DDM method involves calculating derivatives with respect to emissions or other inputs by appropriate manipulation of the kinetic differential equations (Dunker, 1980; Dunker et al, 2000). However, since the results should be the same as one would obtain by actually varying emissions (and test calculations have shown this to be the case), for simplicity this is how they will be referred to in the discussion in this report.

In the first DDM calculation, the sensitivities to changes in total VOC and NO_x emissions were computed. The results gave ppm changes in O_3 per fractional changes in emissions, e.g., a total VOC or NO_x sensitivity of 0.1 means that a 10% change in all VOC or NO_x emissions would cause a 10 ppb

change in ozone. Note that the VOC emissions that were varied in this calculation included biogenic as well as anthropogenic VOCs, so the results of the VOC sensitivity calculations were not the same as the results of the base ROG sensitivity calculations, which represent variations in anthropogenic emissions derived from the second DDM calculation. This is discussed further below.

In the second DDM calculation, the sensitivities to changes in surface emissions to CO and the VOC model species listed in Table 1 were calculated. The emissions varied had the same time and space distribution of the total anthropogenic VOCs. Note that this is different than the time and space variation of the total VOC used in the first DDM calculation because biogenics were not included in the second calculation. The results give the ppb changes in ozone relative to fractional changes in total anthropogenic VOC emissions, with the added anthropogenic VOC emissions represented by the single model species with the same number of carbons. For example, a sensitivity coefficient of 0.1 for OLE means that increasing the total anthropogenic VOC emissions by 10%, and representing all of this increase by the same number of carbons of OLE, will cause O₃ to increase by 10 ppb. Note that because OLE has two carbons the number of moles of OLE added to cause this change is half as much as the number of carbons, which means that the impact on a molar basis is twice as much (since the amount added is in the denominator). This method gave the sensitivities of ozone to the model species to the model species on a per carbon basis. These were multiplied by the carbon numbers of the model species to get the sensitivities on a mole basis, which are the units used in this report. Table 1 indicates the carbon numbers that were used for this purpose.

These DDM sensitivities of ozone with respect to the model species as derived in the second calculation as the *incremental reactivities* of these species, which is defined as the change in O₃ caused by adding the model species to the emissions, divided by the amount added. The amount added is relative to the total anthropogenic VOC emissions, which is the same for all of the VOC model species. Since in this work we are concerned with relative reactivities only, no attempt was made to convert these into absolute incremental reactivity units such as moles O₃ per mole of model species. This is because the conversion factor of the molar DDM sensitivities to absolute incremental reactivities is the same for all species, so it cancels out when computing relative reactivities.

The incremental reactivities of the base ROG mixture that was used as the basis of deriving the relative reactivities was calculated from the incremental reactivities of the model species and the molar concentrations of the model species to one mole carbon of the base ROG, as given on Table 1, i.e.,

$$\text{IR}(\text{Base ROG}) = 0.547 \text{ IR}(\text{PAR}) + 0.021 \text{ IR}(\text{ETH}) + 0.020 \text{ IR}(\text{OLE}) + 0.012 \text{ IR}(\text{TOL}) + \\ 0.008 \text{ IR}(\text{XYL}) + 0.010 \text{ IR}(\text{FORM}) + 0.019 \text{ IR}(\text{ALD2}) + 0.021 \text{ IR}(\text{ETOH})$$

where IR(Base ROG) incremental reactivity of the base ROG in terms of ozone formed per carbon of base ROG mixture, IR(PAR) is the incremental reactivity of the PAR species in terms of ozone formed per mole PAR, etc.

As indicated on Table 1, DDM sensitivities and therefore incremental reactivities were not calculated for all CB4 species used to represent the base ROG. The contributions of these species were not counted when computing the base ROG reactivity. As indicated on Figure 1, the contributions of these species are negligible, so neglecting them should have no significant effect.

Reactivity Metrics Used

In order to derive reactivity quantifications using regional models, it is necessary to specify the time period being covered, the portions of the domain that are included in the analysis, the method used to

quantify the ozone impact in a given cell, and the method used to derive a single reactivity metric from the results throughout the domain. The specific approaches employed in this study are described below.

Episode Days Used

For the purpose of this study, each 24-hour period of the multi-day simulation is treated as a separate “episode” for the purpose of deriving a regional reactivity metric using the various ozone impact and multi-cell reactivity quantification methods. This is appropriate because even though the ozone a given day are affected by ozone formed on previous days, the meteorology, and thus the transport phenomena and the resulting spatial pattern of where the highest ozone occurrences, are quite different on each day. The episode day is defined as being from midnight to midnight, Eastern Standard Time. Since the data from the calculations are stored as 1-hour averages given for the ending hour, this means that the data used for a given day are the hourly averages associated with 1 AM to midnight. Note that the “midnight” (Hour 24) data go with the day that ended and not the day that is beginning because it is the average for the previous hour. The

As indicated above, because of the desire to remove the influences of initial and boundary conditions, the results from the first two days of the simulation (July 7 and 8) are not used in the analysis, and also the data for July 9 and 10 are not used because high-resolution data were not computed for those days. In addition, the CAMx simulations ended at 1800 EST on July 15, so July 15 could not be used because it was not a full day and therefore not comparable to the previous days of the episodes. Therefore, the episode days considered in this study were July 11, 12, 13, and 14. As shown below each of these days had significant differences in ozone spatial patterns, indicating that they represent different conditions of meteorology and transport.

Quantification of Ozone Impact in a Cell

Ozone impacts can be quantified in a number of ways, and the most appropriate method depends on the objectives of the analysis. Since the RRWG studies are ultimately aimed at guiding policies aimed at achieving the ambient air quality standards for ozone, the most appropriate quantification is probably in terms of the quantification used in the standards. These are daily maximum 1-hour and 8-hour ozone levels. Since effects of VOCs on 8-hour averages may be different than affects on 1-hour levels, both methods are considered in this study.

The 1-hour ozone impact metrics were derived by determining the hour in the simulated day that had the highest average ozone for that hour, and using the DDM sensitivities for that hour to derive the incremental reactivities of the model species and the base ROG associated with this cell for this episode day. These give the relative impacts of the VOCs on the peak 1-hour ozone concentration in that cell.

Likewise, the 8-hour ozone impact metrics were derived by determining the hour in the simulated day that had the highest 8-hour average associated with it, and using the averages of the DDM sensitivities for those 8 hours to determine the incremental reactivities for that cell and episode day. (The averages of the DDM sensitivities reflect the sensitivities for the average because averages are essentially sums, and derivatives of sums are sums of derivatives.) Since the regulatory definition of 8-hour averages associates the average with the *beginning* hour of the averaged data, for this study the 8-hour averages associated with a given hour are derived by averaging the data for that hour and the 7 following hours. Note that the 8-hour averages assigned to hours after 1600 involve averaging in data for the following day. Therefore the morning data for July 15 were used when computing the 8-hour average metrics for July 14, the last day for which reactivity metrics were computed.

Computation of Global Reactivity Metrics

The procedures discussed above will in effect give thousands or relative reactivity scales for each of the two impact metrics, one for each grid cell for each day. This provides useful information on how reactivities by these metrics vary with location for the different types of episode days, which addresses one of the objectives of this study. However, most types of quantitative reactivity-based analyses require derivation of a single scale (or at least a manageable number of scales) that appropriately represents the distribution of impacts throughout the episode. There are many alternative approaches that can be used to derive such a global reactivity metric, and four alternative approaches, which are only a subset of the many other possibilities that might be considered, are utilized in this study. These are discussed below.

Least Squares Substitution Error: Base ROG for VOC

One of the applications of reactivity-based regulatory policies would be to use reactivity scales to predict effects of substitution of one type of VOC for another. If a global reactivity scale were perfect, i.e., if relative ozone impacts of VOCs were the same in all cells and the scale used reflected these impacts, then a substitution of one type of VOC for another using an appropriate reactivity adjustment would result in no change in ozone in any of the cells. Since relative impacts indeed vary, any substitution, no matter what weighting factor is used, would cause ozone changes in at least some of the cells. The total ozone change in all the cells, quantified by some appropriate method, is referred to as the “substitution error” in this discussion. The best one could hope for would be to obtain optimum weighting factors that minimize substitution errors that result when reactivity-based substitutions are made. The reactivity scale that yields these optimum weighting factors are referred to as minimum substitution error scales.

A useful way to quantify substitution errors is the sum of squares of the ozone change in all the cells being considered. Sum of squares is appropriate because it counts positive and negative errors equally, and weighs larger errors more than smaller ones by increasing factors. It is generally the approach used in optimizations such as line fits, etc.

The substitution errors will depend on the type of substitution being considered. Since we are interested in relative reactivities, the relevant substitutions are replacing the VOC by the base ROG, or vice-versa. It turns out that in general different results are obtained depending on which is being substituted for what, so alternative global metrics are derived based on the two possibilities. In the first option, we consider the effect of removing the test species and replacing it by the base ROG by a factor equal to the amount of species removed times the relative reactivity of the compound. Since the relative reactivity of the compound is the ratio of the change in O₃ caused by adding the VOC to that caused by adding the base ROG, the net change in O₃ in a cell caused by this substitution should be zero if the appropriate relative reactivity value were employed. For all the cells, the sum of squares substitution error would be given by

$$\text{Sum of Squares Substitution Error} = \sum_{\text{cell}} [\text{RR}(\text{Species}) \cdot \text{IR}_{\text{cell}}(\text{Base ROG}) - \text{IR}_{\text{cell}}(\text{Species})]^2 \quad (\text{I})$$

where RR(Species) is the relative reactivity of the species the global reactivity scale, -IR_{cell}(Species) is the ozone reduction in the cell caused by removing one unit of the species from the emissions, and RR(Species)·IR_{cell}(Base ROG) is the ozone increase caused by replacing it by the reactivity-adjusted amount of base ROG. Note that this is based on a linear approximation for estimating effects of substitutions from incremental reactivities, and is strictly speaking valid only for small substitutions. However, this is still appropriate because this is an incremental reactivity scale.

The value of RR(Species) that minimizes this sum of squares substitution error is given by

$$RR(\text{Species}) = [\sum_{\text{cells}} IR_{\text{cell}}(\text{Species}) IR_{\text{cell}}(\text{Base ROG})] / [\sum_{\text{cells}} IR_{\text{cell}}(\text{Base ROG})^2] \quad (\text{II})$$

Note that this is the same as the slope of a least squares fit line, forced through zero, of plots of $IR_{\text{cell}}(\text{Species})$ vs. $IR_{\text{cell}}(\text{Base ROG})$. Examples of such plots are given in the Results section, below. Note, however, that the line has no intrinsic meaning beyond the fact that its slope is mathematically equivalent to the least squares substitution error relative reactivity.

Least Squares Substitution Error: VOC for Base ROG

Although substituting the VOC for the base ROG may be considered as a rough analogue to reactivity-based strategies aimed at reducing emissions of highly reactive compounds, much of the interest in reactivity-based controls in recent years has been on substituting current emissions with VOCs with low reactivity. A better analogue to this would be substituting the VOC for the base ROG. An appropriate reactivity scale for this type of substitution may be one based on minimizing the substitution error caused by removing the base ROG and replacing it by the test compound by an appropriate reactivity adjusted factor. This factor would be the ratio of the ozone formed by the base ROG to the ozone formed by the test compound, which is the reciprocal of its relative reactivity. Under this scenario, the sum of squares substitution error is given by

$$\text{Sum of Squares Substitution Error} = \sum_{\text{cells}} [IR_{\text{cell}}(\text{Base ROG}) - IR_{\text{cell}}(\text{Species})/RR(\text{Species})]^2 \quad (\text{III})$$

and the $RR(\text{Species})$ that minimizes this is given by

$$RR(\text{Species}) = [\sum_{\text{cells}} IR_{\text{cell}}(\text{Species})^2] / [\sum_{\text{cells}} IR_{\text{cell}}(\text{Species}) IR_{\text{cell}}(\text{Base ROG})] \quad (\text{IV})$$

Note that in this case it is the same as the slope of a least squares fit line, forced through zero, of plots of $IR_{\text{cell}}(\text{Base ROG})$ vs. $IR_{\text{cell}}(\text{Species})$. This is *not* necessarily the same thing as the $RR(\text{Species})$ that minimizes the base ROG for VOC substitution error, though they are close if the data are well fit by a line forced through zero.

Although in some respects this aggregation approach seems like a more realistic type of substitution upon which to base a reactivity scale (for low reactivity VOCs, at least), in practice it does not give well-defined values for VOCs whose reactivities are zero or scattered around zero, i.e., are negative in some conditions and positive in others. Relative reactivities cannot be derived if the incremental reactivity of the species is zero because it is in the denominator in Equation (III), and mathematical instability occurs the species incremental reactivities are scattered around zero. This problem can be seen in the results obtained for the TOL model species, which has this characteristic.

Regional Maximum O₃ Metric

An alternative metric that was employed in the regional reactivity modeling studies carried out by Russell and co-workers (e.g., Hakami et al, 2002) is to base the global metric on the impacts of the VOCs on the maximum ozone concentration throughout the domain. If each episode day is treated separately, this would involve finding the hour and cell that has the highest maximum O₃ concentration (either 1-hour or 8-hour averages, depending on the quantification used), and using the relative reactivities in that hour in that cell as the global reactivity metric. This may be an appropriate approach if the policy is to reduce the highest O₃ levels, though it should be noted that this is not a true global metric because it reflects impacts in only a single cell. However, comparing maximum ozone reactivities on different days give an indication of how ozone impacts are affected in different regions, since the location of the ozone maximum, and the meteorological conditions giving rise to it, are different in the different episode days.

Hakami et al (2002) refer to this metric as the “3-D MOIR,” since it refers to conditions where the maximum ozone occurs. However, it should be pointed out that the cell where the O₃ maximum occurs may not necessarily represent MOIR conditions according to the definition used by Carter (1994a) when deriving the MOIR scale. Carter (1994a) defines MOIR conditions where NO_x levels are optimum for ozone formation, which means that a true MOIR cell is one where either increasing or decreasing NO_x emissions would reduce the O₃ concentration. This is mathematically equivalent to the cell having a local NO_x sensitivity (derivative) of zero. In fact the results of our calculations indicate that the maximum ozone concentration usually (but not always) occurred in quite NO_x sensitive cells, as indicated by relatively large and positive sensitivities to NO_x emissions. This may be due to the highest O₃ being formed as a result of long-range transport through NO_x limited regions.

Regional MIR Metric

A second alternative metric that was derived in the regional reactivity modeling studies of Russell and co-workers (e.g., Hakami et al, 2002) is to base the global metric on the impacts of the VOC in the cell where the VOC has the highest incremental reactivity. This would involve first finding for each cell the time of the peak O₃ levels (either as 1-hour or 8-hour averages), determining the incremental reactivities for the times of the ozone peaks in each cell, and then using the relative reactivities in the cell that has the highest incremental reactivity of the base ROG as the global metric. This is of interest because it is an analogue to the widely-used MIR scale of Carter (1994a), which is based on quantifying ozone impacts for conditions that are most sensitive to VOC emissions, as measured by the base ROG incremental reactivity. Again this is not a true global metric because it is based on relative impacts in only a single cell. However, the results of this study indicate that relative impacts under MIR or near-MIR conditions tend not to be highly variable, so the relative impacts in this single cell should give a fair approximation to the impacts in other cells with approximately MIR-like conditions.

Excluded Cells

Although an obvious approach in deriving global reactivity metrics is to aggregate impacts in all cells in the modeling domain, an argument can be made that it may be appropriate not to include all cells in this aggregation. In particular, if one is less concerned with impacts in a certain type of cell compared to others, it may not be appropriate to include them when deriving global metrics such as least squares substitution error scales. If cells are included in the aggregation where the impacts are of lesser concern and if the reactivity characteristics are different than the case in most of the domain of major interest, the global reactivity metric may not necessarily reflect the optimum scale for consideration.

For example, from a policy perspective it may not matter particularly if a substitution causes a small ozone change in a cell where the ozone is already well below the level of concern. Reactivity characteristics in very low ozone cells may be quite different in those where the O₃ level approaches or exceeds the ambient air quality standards, and it may not be appropriate to bias the results by optimizing to fit impacts that are not of primary concern. On the other hand, it is probably not appropriate to ignore reactivity effects in cells that may be in compliance with the standard in the base case but may become out of compliance if a substitution is made that causes moderate ozone increases in that area. If cells with low O₃ are excluded from the aggregation, the cutoff level should be sufficiently below the standard that moderate increases above that level are not likely to be concern.

For the purpose of this study, after discussions with members of the EPA policy group and other input, we (somewhat arbitrarily) chose the O₃ cutoff at 80 ppb when computing metrics based on the 1-hour maximum, and 60 ppb when computing metrics based on the 8-hour average. These are respectively 40 and 20 ppb lower than the current standards of 120 and 80 ppb, and appear to be

reasonable margin for the purpose of this analysis. Thus, cells with peak 1-hour average O₃ less than 80 ppb are not included when deriving the least squares substitution error metrics or finding the cell to derive the MIR metric for the scales using the 1-hour average quantification. Likewise cells with peak 8-hour average O₃ below 60 ppb are excluded when deriving the corresponding 8-hour average aggregated scales. Obviously, this restriction has no effect on determinations of regional O₃ maximum metrics.

In addition, almost 1/3 of this modeling domain consists of cells over the ocean or large lakes, which have no receptors of significant concern. A preliminary analysis indicates that many of these cells have quite different distributions of ozone sensitivities than cells over the ground, presumably because of the lack of local emissions. For this reason, we believe that it is appropriate to exclude such cells from the domain when deriving aggregated reactivity scales. Since we currently have no geographical information about the cells in the present database, we zero anthropogenic NO or PAR emissions as the indicator of cells over water. An examination of maps of such cells (shown in some of the figures in the Results section) indicates that this is a reasonable approximation.

It is important to point out that excluding over-water cells when deriving aggregated reactivity scales does *not* mean that we are ignoring effects of ozone transport over water, which may be significant in some cases. The cells are not removed from the modeling domain that is used to do the actual calculations of the formation of ozone from the emissions, or of the sensitivity coefficients for the effects of changing the emissions on this process. If ozone over a particular land cell is affected by processes occurring over water, then the effects the emissions changes on these processes are being represented in the sensitivity results calculated for that cell, which are not being excluded if the ozone is sufficiently high.

EKMA Reactivity Scales

For comparison purposes, incremental reactivities of the Carbon Bond model species were also calculated using the modeling approach and scenarios employed by Carter (1994a) to derive the MIR and the other box model, NO_x-adjusted incremental reactivity scales. The scenarios and methods employed were as discussed by Carter (1994a), with some minor modifications to the methodology as described by Carter (2000a). The only difference was that the Carbon Bond mechanism as implemented in the CAMx model used in this study was employed, and reactivities were calculated only for the Carbon Bond model species. The approach was essentially the same as used by Carter (1994b) when deriving these scales for an earlier version of the Carbon Bond mechanism.

These scales are referred to as “EKMA” reactivity scales to refer to the fact that EKMA-type box models were used rather than a regional model such as discussed in the rest of this report. The starting point was 39 EKMA scenarios developed by the EPA (Baugues, 1990). As discussed by Carter (1994a,b), some reactivity scales were derived based on averages of incremental reactivities of the carbon bond model species in the 39 scenarios with NO_x inputs adjusted to yield specified reactivity characteristics, and others were derived based on results of the base case (i.e., unadjusted NO_x) scenarios. The specific scales used in this study were as follows:

- The MIR scale was derived by adjusting the NO_x inputs in the 39 EKMA scenarios to yield the highest incremental reactivity of the base ROG. The base ROG used for this purpose was actually based on a somewhat different composition (see Carter, 1994b), but this should have minor or essentially no effect on the MIR scenarios that were derived. This represents the relatively high NO_x conditions where O₃ is most sensitive to VOCs, and where NO_x has a negative effect on O₃ formation.

- The MOIR scale was derived by adjusting the NO_x inputs to yield the highest peak ozone concentration. This represents NO_x conditions that are optimum for ozone formation.
- Two minimum substitution error scales were derived using incremental reactivities in the 39 base case, using the same approaches as employed when deriving regional model minimum substitution error scales, except in this case each base case EKMA scenario was treated as a separate cell.

In all these cases, the incremental reactivities are derived in terms of the effects of the VOC species on the peak O₃ concentration, which, because of the nature of the box models, was the final O₃ level in the one day simulations. This makes them comparable to the calculations using the maximum 1-hour average O₃ quantification.

Note that the relative reactivities in the EKMA reactivity scales are relative to the same base ROG mixture as employed for the regional reactivity scales, whose composition is given in Table 1. This is somewhat different than the mixture used as the base ROG when calculating the EKMA reactivities or determining the NO_x inputs for the MIR scale, which based on the mixture employed in the original calculations of Carter (1994a,b), but is employed in this study for direct comparability with the regional reactivity results.

Large Scale Substitution Calculations

Although the major large-scale substitution calculations called for in the statement of work for this project have not yet been carried out, two relatively simple such calculations were carried out for initial evaluation purposes. In the first calculation, all anthropogenic VOCs were removed, with emissions of NO_x, biogenic VOCs, and all other model inputs unchanged. In the second calculation, all the anthropogenic VOCs were replaced by ethane, on an equal carbon basis. Again, NO_x, biogenic VOC and other inputs were not changed. The latter calculation can be thought of as representing a mass-based substitution strategy where all anthropogenic VOCs are replaced by a borderline exempt compound, while the first provides a useful basis for comparison with the ethane substitution results.

Results

Reactivity Characteristics of Episodes

Figure 3 shows maps of the modeling domain used in this study, showing the spatial distribution of the cells where the maximum 1-hour average ozone exceeded the cutoff of 80 ppb, and also showing the cells with the highest peak 1-hour average ozone concentration and the highest base ROG maximum incremental reactivities are shown. The light shaded areas show the portions of the domain that had non-zero emissions, which are taken as the land cells that were used in the reactivity aggregation analysis. The diamonds indicate those cells where O₃ is higher than the cutoff that are calculated to be more sensitive to VOC than NO_x emissions based on the analysis discussed below. Figure 4 shows similar maps for the 8-hour ozone quantification method. Various reactivity-related statistics for the episode days are summarized on Table 2. These are discussed further below.

The results indicate differences in the episode days, particularly July 11 and 12 where the peak O₃ levels were in the South, compared to July 13 and 14, where the peak O₃ tended to be in the Midwest (see Figure 3 and Figure 4). The results also indicate differences in the extent of cells where the 8-hour O₃ exceeded the cutoff levels were greater than was the case for the 1-hour O₃, despite the fact that the ratio of the cutoff level to the air quality standard level was higher for the 8-hour average. This is consistent

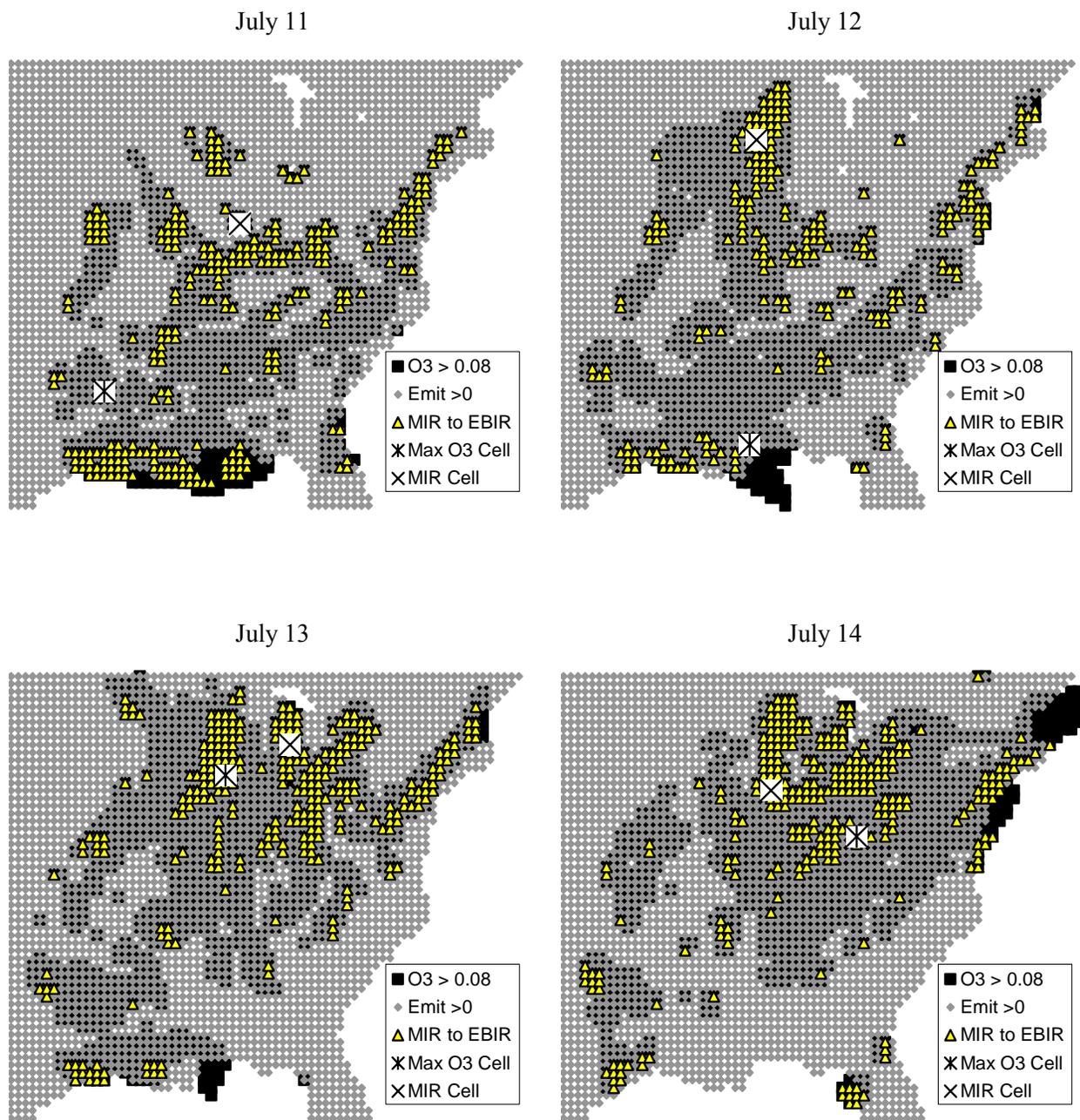


Figure 3. Maps of model domain for the four episode days considered, showing regions of high ozone, cells where O_3 is more sensitive to VOC than NO_x emissions, and the locations of the maximum O_3 and maximum incremental reactivity (MIR) points. Data based on maximum 1-hour average ozone quantification method

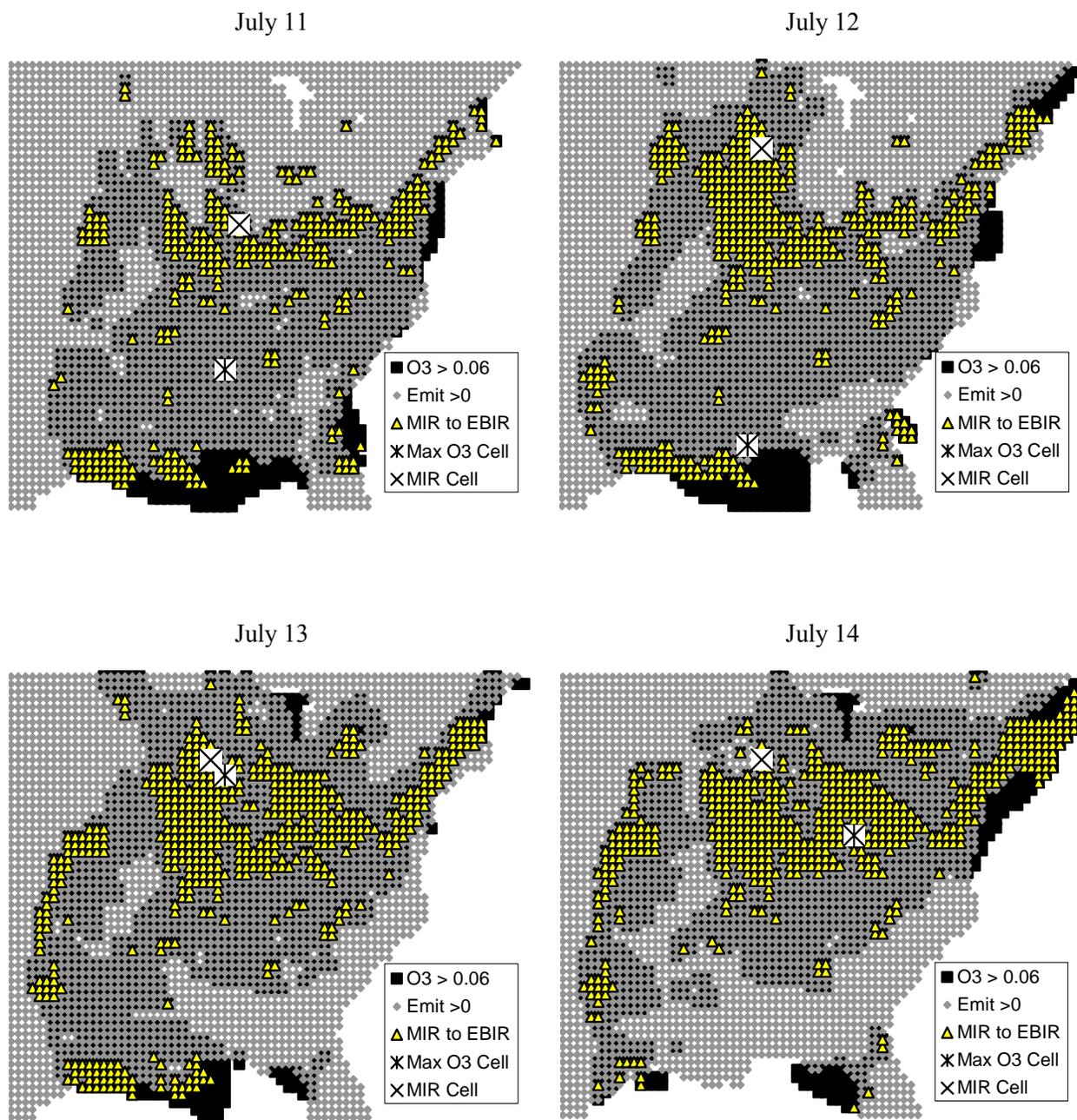


Figure 4. Maps of model domain for the four episode days considered, showing regions of high ozone, cells where O_3 is more sensitive to VOC than NO_x emissions, and the locations of the maximum O_3 and maximum incremental reactivity (MIR) points. Data based on maximum 8-hour average ozone quantification method

Table 2. Summary of overall reactivity characteristics of the episode days considered in this study.

Episode Day	7/11	7/12	7/13	7/14	Overall
Overall Domain-Wide Ozone Maxima (ppb)					
1-Hour Average	165	162	187	175	187
8-Hour Average	127	126	139	139	139
Fraction of Cells Exceeding Given O ₃ Levels					
1-hour average > 80 ppb	18%	22%	25%	25%	23%
1-hour average > 120 ppb	1%	1%	2%	4%	2%
8-hour average > 60 ppb	32%	37%	38%	36%	36%
8-hour average > 80 ppb	7%	7%	10%	12%	9%
Fraction of Cells in Various NO _x Conditions (1 Hr Avg. O ₃ Quantification) (Only cells with O ₃ > 80 ppb and nonzero NO emissions)					
MIR to MOIR	9%	4%	5%	6%	6%
MOIR to EBIR	24%	19%	21%	19%	21%
EBIR to ZBIR [a]	62%	71%	70%	72%	69%
ZBIR to NIR [b]	6%	5%	3%	3%	4%
Fraction of Cells in Various NO _x Conditions (8 Hr Avg. O ₃ Quantification) (Only cells with O ₃ > 60 ppb and nonzero NO emissions)					
MIR to MOIR	6%	12%	15%	9%	10%
MOIR to EBIR	19%	17%	18%	15%	17%
EBIR to ZBIR [a]	68%	62%	56%	65%	63%
ZBIR to NIR [b]	8%	8%	11%	10%	10%
O ₃ Sensitivity to total VOC (ppb O ₃ per fractional change in total VOC emissions) (1-Hour maximum O ₃ quantification)					
Maximum	0.10	0.09	0.15	0.17	0.17
Minimum	-0.01	-0.01	-0.02	-0.01	-0.02
MIR Cell [c]	0.08	0.09	0.15	0.13	
Maximum O ₃ Cell	0.02	0.05	0.12	0.07	
O ₃ Sensitivity to Base ROG (ppb O ₃ per fractional change in anthro. VOC emissions) (1-hour maximum O ₃ quantification)					
Maximum (MIR Cell)	0.050	0.040	0.047	0.075	
Maximum O ₃ Cell	-0.000	0.008	0.034	0.005	
O ₃ Sensitivity to total NO _x (ppb O ₃ per fractional change in total NO _x emissions) (1-Hour maximum O ₃ quantification)					
Maximum	0.08	0.07	0.07	0.07	0.08
Minimum	-0.07	-0.06	-0.10	-0.15	-0.15
MIR Cell	-0.06	-0.06	-0.07	-0.07	
Maximum O ₃ Cell	0.08	0.05	-0.01	0.03	

[a] ZBIR refers to conditions where the ozone sensitivity to total VOC emissions is zero, but the ozone sensitivity to NO_x is positive.

[b] NIR refers to conditions where the ozone sensitivity to total VOC emissions is negative.

[c] This is not necessarily the maximum because the MIR cell is the cell with the maximum sensitivity to the base ROG, which is different from the sensitivity to total VOC (see text).

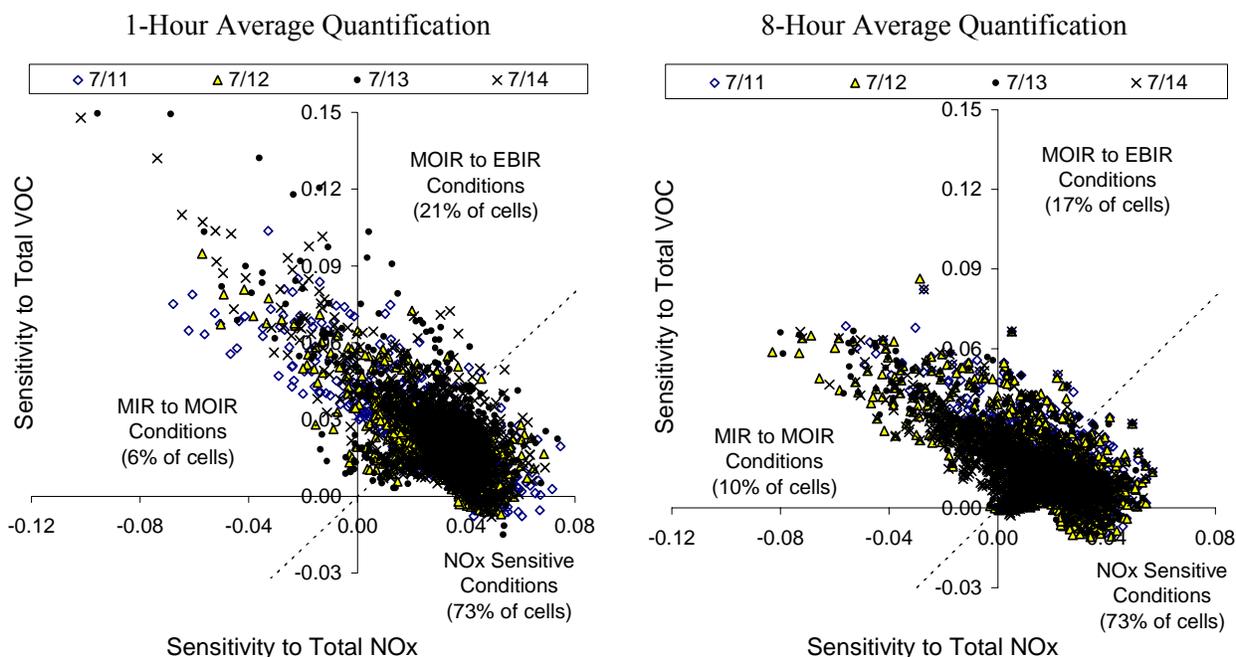


Figure 5. Plots of sensitivities of daily maximum 1-hour or 8-hour average O_3 to changes in total NO_x and VOC emissions. The dotted lines show the conditions where O_3 formation is equally sensitive to VOC and NO_x controls. Note that the data plotted are only for the cells where there were nonzero emissions and where the peak O_3 exceeded the cutoff levels of 80 ppb or 60 ppb for 1-hour or 8-hour quantifications, respectively.

with the fact that the current 8-hour standard is considered to be more difficult to obtain than the 1-hour standard.

Figure 5 shows plots of sensitivities of daily maximum 1-hour or 8-hour average ozone levels to changes in total NO_x and VOC emissions. Each point indicates the sensitivities for a single cell for a given episode day. Note that according to the episode reactivity classifications given by Carter (1994a), cells with NO_x sensitivities of zero (i.e., cells along the “y” axis) represent MOIR conditions, and cells with negative NO_x sensitivities represent MOIR to MIR or higher NO_x conditions. The dotted line on the plots shows the conditions where O_3 formation is equally sensitive to VOC as NO_x controls, referred to by Carter (1994a) as EBIR conditions. Points to the left of this line represent conditions where O_3 is either more sensitive to VOC controls than NO_x controls or where NO_x controls make ozone worse, while points to the right of this line represent NO_x sensitive conditions where NO_x control is more effective in reducing ozone. Note that there is a tendency for VOC sensitivity to increase with decreasing NO_x sensitivity, which is consistent with the fact that in general O_3 sensitivities to VOCs tend to increase, while O_3 sensitivity to NO_x tends to decrease, as NO_x levels are increased. The fact that the points do not all fall on the same line indicates that other variable conditions in the domain also affect these O_3 sensitivity factors.

Figure 5 also indicates the percentages of the total number of high O_3 cells with nonzero emissions in the four days that fall into the various NO_x conditions according to the classifications of Carter (1994a). The distributions for the individual days is shown on Table 2, which indicates some day-to-day variation, especially in the relative number of MIR to MOIR cells. (The distribution for all cells is not significantly different, though the relative number of NO_x sensitive cells is somewhat higher.) It can

be seen that over 75% of the cells are under NO_x sensitive conditions, reflecting the fact that most of the area in Eastern U.S. are non-urban areas away from large NO_x sources. However, more than a quarter of the cells in these episodes are more sensitive to VOC controls than NO_x controls, indicating the importance of VOCs in affecting regional ozone. Approximately 5% of the cells represent MIR to MOIR conditions where 1-hour maximum ozone levels are adversely affected by NO_x controls and where VOC control is most effective. The number of such cells is approximately twice as much when considering effects on maximum 8-hour average ozone levels.

As discussed above and also indicated on Table 2, the incremental reactivity of the base ROG mixture is not the same as the sensitivity of the O_3 to the total VOC emissions, because the former was derived by varying only anthropogenic VOCs, while the latter was derived by varying all VOCs, including biogenics. The differences between these two are illustrated on Figure 6, which shows plots of the sensitivities of ozone to the base ROG to the sensitivities to the total NO_x emissions. It can be seen that they are indeed correlated but that there is considerable scatter, and also variability from day to day. This is true even in the cells with high VOC and base ROG sensitivity, which reflect relatively high NO_x conditions that are expected in source areas. This indicates the importance of biogenic VOCs in affecting overall ozone sensitivities.

Another indication of the importance of the biogenic VOCs can be obtained by comparing the magnitudes of the sensitivities of O_3 to the base ROG compared to the sensitivity to total VOCs. Although the sensitivity to varying only anthropogenic VOCs was not calculated directly (and probably should be as part of this project or follow-on work), the sensitivity to the base ROG should give an approximation of it. The quality of the approximation depends on the extent to which the compositions of the anthropogenic VOC emissions vary throughout the domain, and the extent to which these compositions represent that used for the base ROG. The distribution of the ratios of the sensitivity of the 1-hour maximum O_3 to the base ROG relative to total VOC emissions for all the episode days is shown on Figure 7. Cells with very low sensitivity to VOC emissions are excluded. It can be seen that the sensitivity of the maximum 1-hour average O_3 to the base ROG is less than 25% the sensitivity to total VOC emissions in most of the cells, and only about 1% of the cells have a base ROG sensitivity greater than 50% of the sensitivity to total VOC. This indicates that anthropogenic VOC emissions are relatively unimportant in affecting O_3 levels compared to biogenics in most of this modeling domain.

Regional Relative Reactivities

Figure 8 through Figure 11 show plots of the ozone sensitivities (incremental reactivities) of all the model species against the incremental of the base ROG mixture for the nonzero emissions cells where the O_3 maximum was above the cutoff level for each of the four episode days and two ozone quantification methods. (The relatively small number of points where the incremental reactivities of the base ROG are negative are not shown – in all cases the distribution of points are very similar to those with zero base ROG reactivity.) The lines on the plots show the least squares fit lines, forced through zero, for the data for all four days. These are of interest because their slopes give the minimum substitution error reactivities for the four episode days combined. The solid lines show the fits for the ROG for VOC substitution, while the dotted lines show the fits for the VOC to ROG substitution. Note that the regional MIR relative reactivity would be indicated by the slope of lines (not shown on the plots) from the point between the farthest to the right on each plot (i.e., the point with the highest base case ROG reactivity) and the origin. In most (but not all) cases these MIR lines would be very close to the least squares fit lines that are shown.

It can be seen that for most model species the incremental reactivities correlate quite well to the incremental reactivities of the base ROG throughout most of the modeling domain, except for those cells where the sensitivity to anthropogenic VOCs is very low. The main exception is the TOL model species,

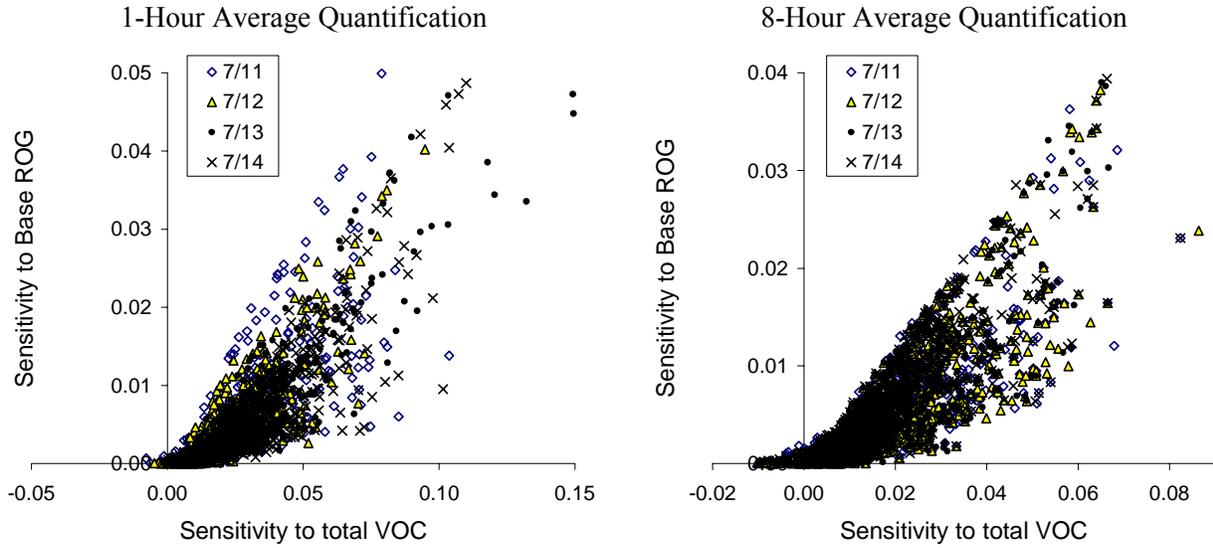


Figure 6. Plots of sensitivities of daily maximum ozone concentrations to variations in anthropogenic emissions with the base ROG composition against variations in total VOC emissions.

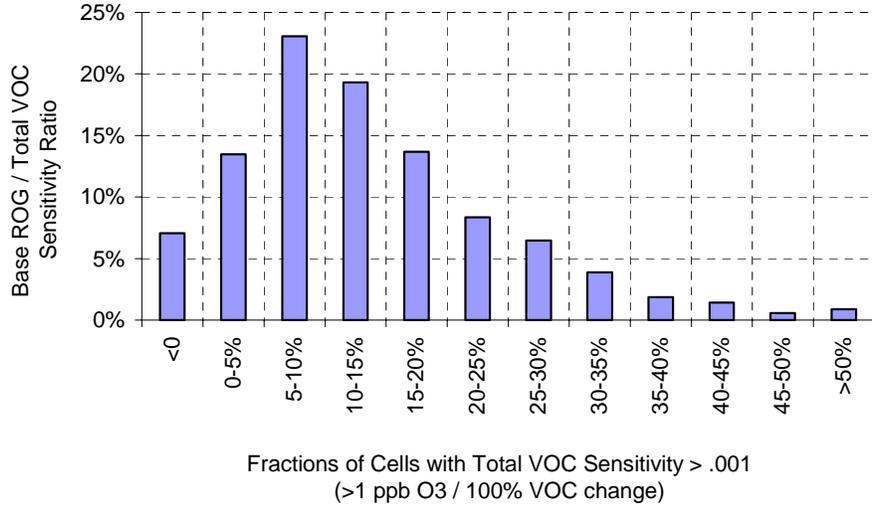


Figure 7. Distribution of the ratio of the sensitivity of the daily 1-hour maximum ozone to the base ROG to its sensitivity to total VOC emissions for all four of the episode days considered in this study.

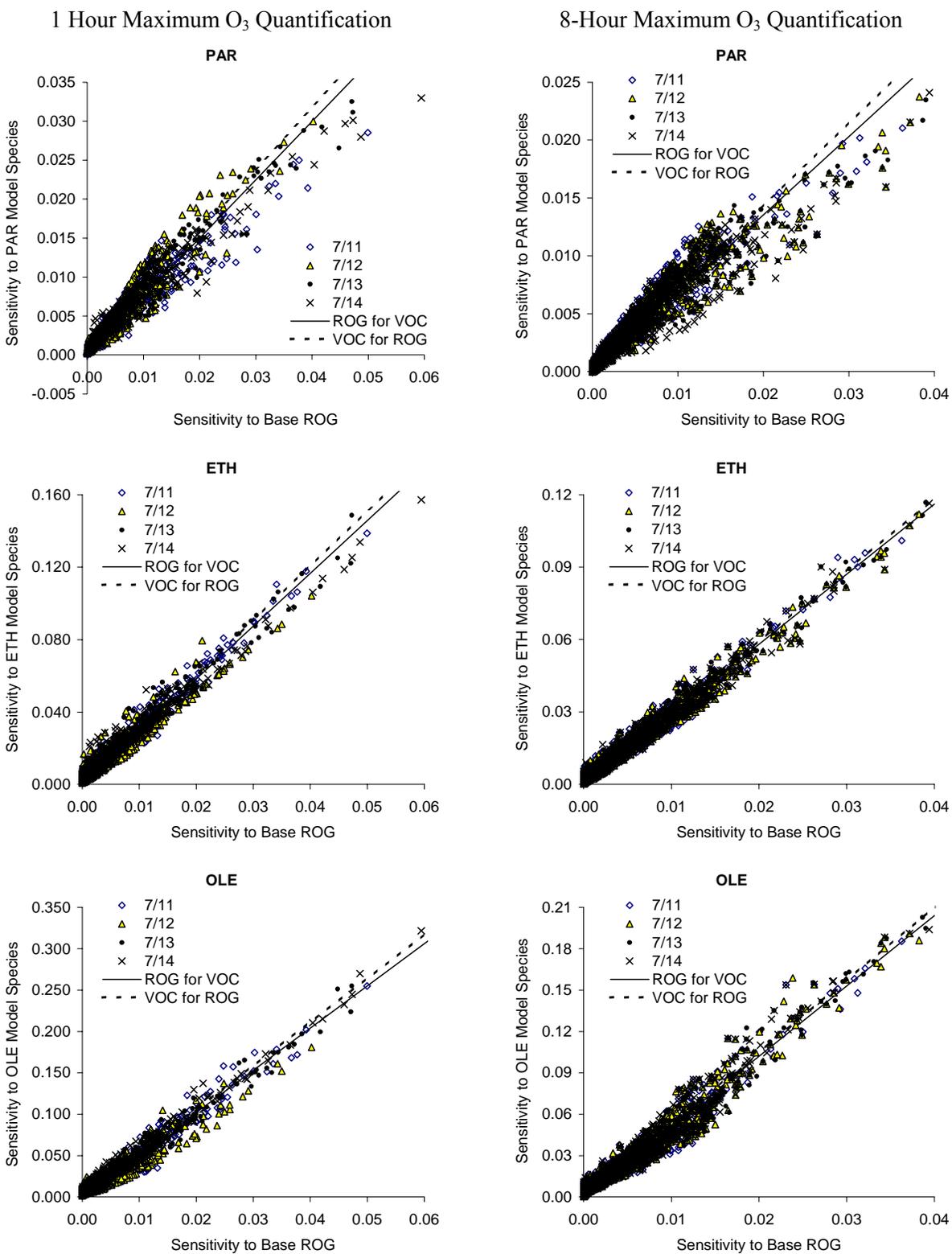


Figure 8. Plots of incremental reactivities of the PAR, ETH, and OLE model species against the incremental reactivities of the base ROG mixture. Reactivities shown are on a carbon basis.

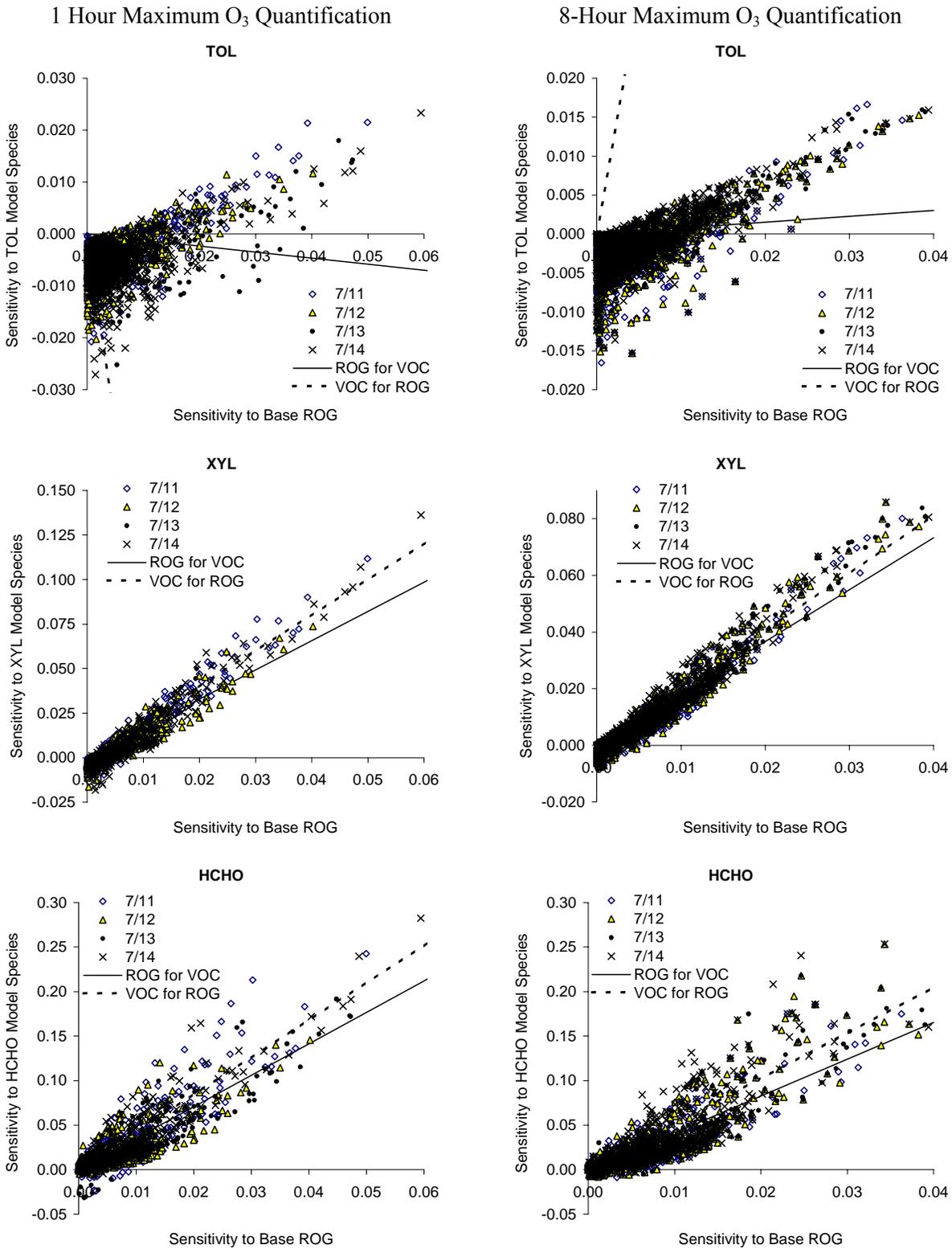


Figure 9. Plots of incremental reactivities of the TOL, XYL, and HCHO model species against the incremental reactivities of the base ROG mixture. Reactivities shown are on a carbon basis.

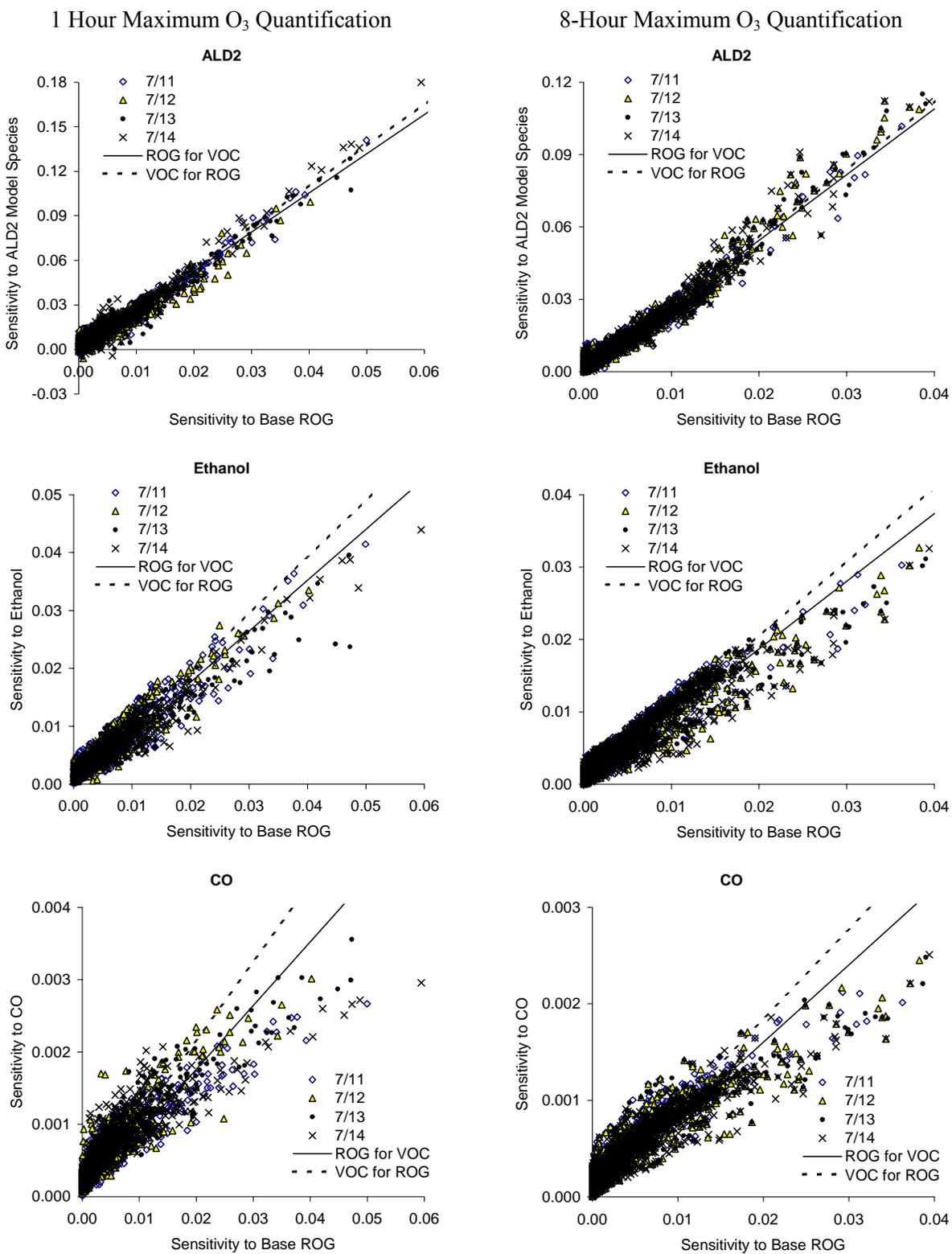


Figure 10. Plots of incremental reactivities of the ALD2, Ethanol, and CO model species against the incremental reactivities of the base ROG mixture. Reactivities shown are on a carbon basis.

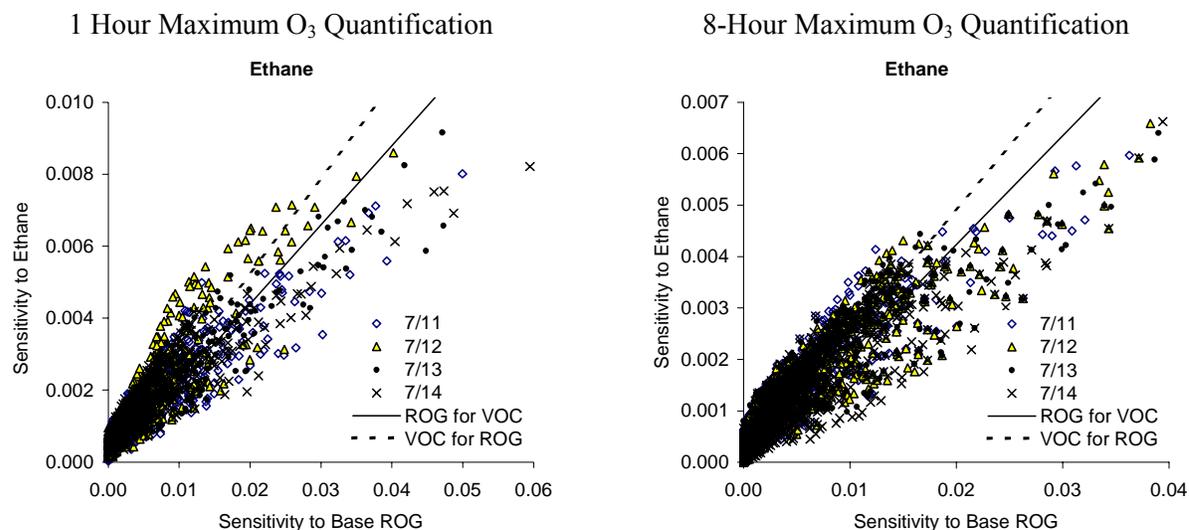


Figure 11. Plots of incremental reactivities of ethane against the incremental reactivities of the base ROG mixture. Reactivities shown are on a carbon basis.

which is discussed below. The species with the best correlation to the base ROG are ETH, OLE, ALD2 and XYL, and those with the most scatter (excluding TOL) are formaldehyde, CO, and ethane. There is no large difference in the degree of scatter of the data for the 8-hour compared to the 1-hour quantification data, though the scatter may be very slightly less in the case of the 8-hour data, especially for XYL.

The high degree of scatter for the TOL model species is due to its extreme sensitivity to NO_x conditions, due to peculiarities in its mechanism as discussed above. In particular, it tends to have moderately high positive reactivity under higher NO_x conditions because of its radical initiating characteristics, but very negative reactivities in moderate or low NO_x conditions because its mechanism has strong NO_x sinks. Although as discussed above this is probably not a very good representation for toluene, its qualitative reactivity characteristics are probably similar to compounds such as styrenes, phenols, or alkyl bromides, whose reactivities tend to exhibit this type of strong dependence on NO_x conditions (Carter, 2000a, Carter et al, 1997). The reactivity characteristics of toluene itself are probably better represented by the XYL model species, except with lower magnitudes because of its lower rate constant (Carter, 2000a).

The relative reactivity of the formaldehyde, CO, ethane and (to a lesser extent) the PAR model species are quite variable in the various cells, though nowhere near the extent that is the case for the TOL species. In the case of formaldehyde, this is probably due to variations throughout the domain in sensitivities to radical initiators, which tend to be more important in high NO_x conditions than when NO_x is limited. The variation is less than for TOL because although the formaldehyde relative reactivity tends to decline in lower NO_x conditions, it does not generally become negative. In the case of CO, ethane, and (to a lesser extent) PAR, the variability may reflect different sensitivities throughout the domain to relatively slowly reacting species. The ozone impact of slowly reacting species is expected to dependent on details of transport conditions. For example, if it such species are transported out of the source area only to NO_x limited regions where little additional O_3 formation can occur it will have a relative lower

impact than would the case if they were transported over other source areas, where fresh NO_x emissions would permit its reactions to form additional O_3 .

Based on these considerations, one would expect reactivities of slowly reacting species to correlate better to each other than to the base ROG, since the dependences of their impact on conditions should be similar. This is shown on Figure 12, which gives plots of the reactivities of ethane and CO vs. PAR. It can be seen that the scatter is significantly less in the case of ethane, and somewhat less in the case of CO. The lesser improvement in correlation in the case of CO is probably due to at least in part to the fact that this has the lowest rate constant, but could also be due to other differences in its mechanism compared to other model species, such as lack of radical sources and NO_x sinks.

Table 3 gives a summary of the numerical reactivity results, including the regional maximum ozone and EKMA reactivity results. The numerical reactivity results are compared graphically on Figure 13 through Figure 15, where the differences and similarities between the various metrics may be more evident.

In general, except for the TOL model species, the regional relative reactivities derived using the minimum substitution error and the regional MIR methods tend to agree quite well, with no significant or consistent differences between scales derived using the 1-hour and 8-hour metrics. Because of the variation with conditions and the different meteorologies on the different days there is variability among these scales, but this variation is small compared to the relative reactivity differences among the VOCs. In particular, the standard deviation of the averages for the regional minimum substitution error and MIR scales are less than 25% of the averages in all cases except for TOL, and are less than 10% of the averages for ETH, OLE, and ALD2.

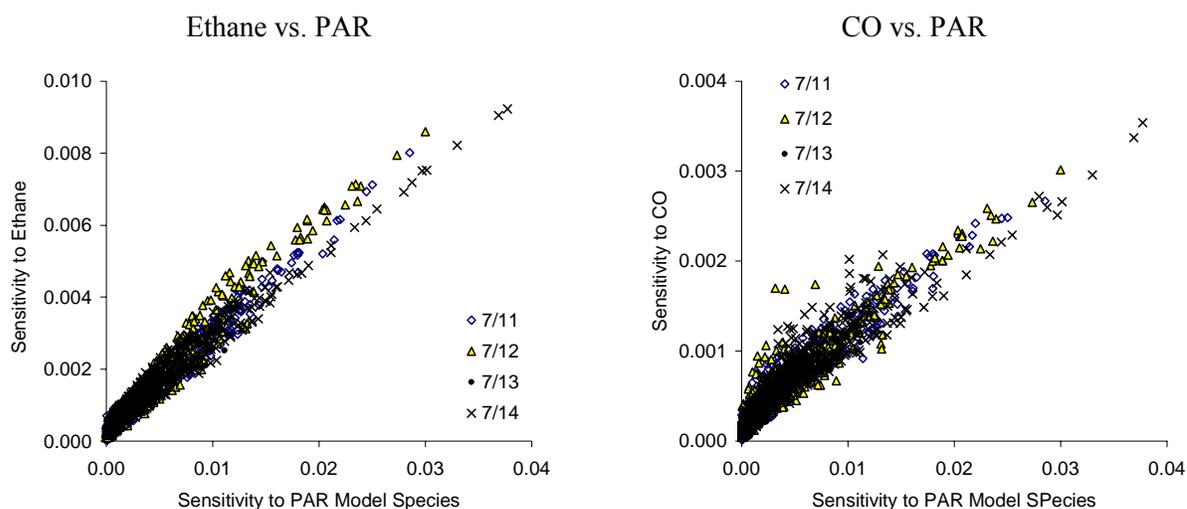


Figure 12. Plots of incremental reactivities of ethane and CO against those of the PAR model species. Reactivities are shown for the 1-hour maximum O_3 quantification and are on a carbon basis.

Table 3 (continued)

Aggregation Method	Relative Reactivity (Mole Basis for species, Carbon basis for base ROG)								
	EKMA Model	Regional Model							
		1-Hour Average Quantification				8-Hour Average Quantification			
		7/11	7/12	7/13	7/14	7/11	7/12	7/13	7/14
Ethanol									
Min. Err. ROG / VOC Subst.	2.0	1.8	2.0	1.7	1.7	2.0	1.9	1.8	1.8
Min. Err. VOC / ROG Subst.	2.2	2.0	2.2	1.9	1.8	2.2	2.1	2.0	2.0
MIR or Regional MIR	1.5	1.7	1.7	1.0	1.5	1.7	1.7	1.6	1.7
MOIR or Regional Max O3	2.1	-7.5	1.5	1.3	2.8	2.6	1.7	2.4	2.2
CO									
Min. Err. ROG / VOC Subst.	0.056	0.083	0.102	0.093	0.080	0.089	0.079	0.077	0.079
Min. Err. VOC / ROG Subst.	0.065	0.098	0.121	0.110	0.107	0.105	0.091	0.088	0.089
MIR or Regional MIR	0.033	0.053	0.075	0.075	0.055	0.056	0.064	0.064	0.064
MOIR or Regional Max O3	0.059	-1.173	0.153	0.088	0.172	0.212	0.138	0.132	0.093
Ethane									
Min. Err. ROG / VOC Subst.	0.29	0.42	0.54	0.44	0.40	0.46	0.43	0.41	0.41
Min. Err. VOC / ROG Subst.	0.32	0.48	0.63	0.52	0.49	0.55	0.50	0.47	0.47
MIR or Regional MIR	0.18	0.32	0.43	0.28	0.30	0.33	0.34	0.33	0.34
MOIR or Regional Max O3	0.31	-3.17	0.53	0.34	0.84	0.68	0.52	0.53	0.52

As indicated above, the VOC for ROG minimum substitution error method does not give numerically stable results if the incremental reactivity of the model species is scattered around zero. Since this is the case for the TOL model species, the aggregated reactivities derived using this method are extreme in magnitude and variability and probably should be considered to be meaningless. Even the more mathematically robust ROG for VOC minimum substitution error method gives highly scattered results for TOL, with the sign varying from day to day, though at least the magnitudes appear to be representative of the distribution with conditions. By this quantification, the only thing that can be concluded is that the minimum substitution error relative reactivity of TOL is 0 ± 1 on a mole basis. On the other hand, the TOL reactivities by the regional MIR method are quite consistent, with the average having a standard deviation of only 15%. This is because the regional MIR points all represent very chemically similar, high NO_x conditions in all of the episode days.

It is interesting to note that for most of the model species the regional MIR reactivities are not significantly different than the reactivities derived by the minimum substitution error methods, despite the fact that probably no more than ~5% of the cells approximately represent MIR conditions. This may be due in part to the fact that the least squares optimization methods tend to weigh the cells with higher impacts more, but given the relatively small number of MIR cells it unlikely that they would be completely dominating the results. As shown on Figure 8 through Figure 11, for most model species the relative reactivities in the lower reactivity cells tend not to be consistently different than the relative reactivities seen in the MIR or near-MIR cells. The main exceptions to this (besides TOL, which was discussed above) are ethane and CO, both slowly reacting species, where the MIR's are about 30% lower than the minimum substitution error reactivities. This may be due to the higher NO_x conditions in MIR

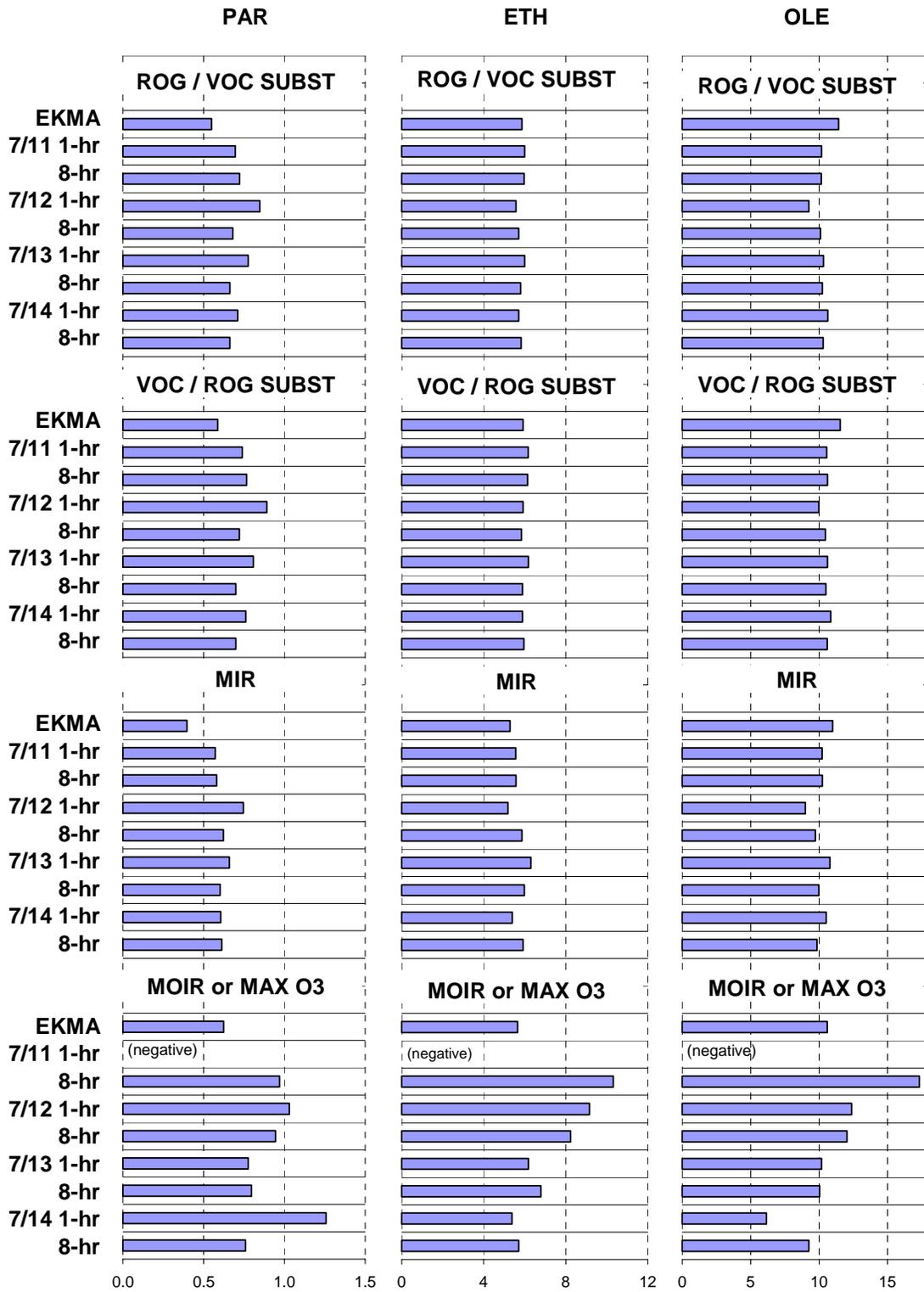


Figure 13. Plots of relative reactivity results in various scales for PAR, ETH, and OLE model species. Data are shown on a mole basis for the VOC and a carbon basis for the base ROG.

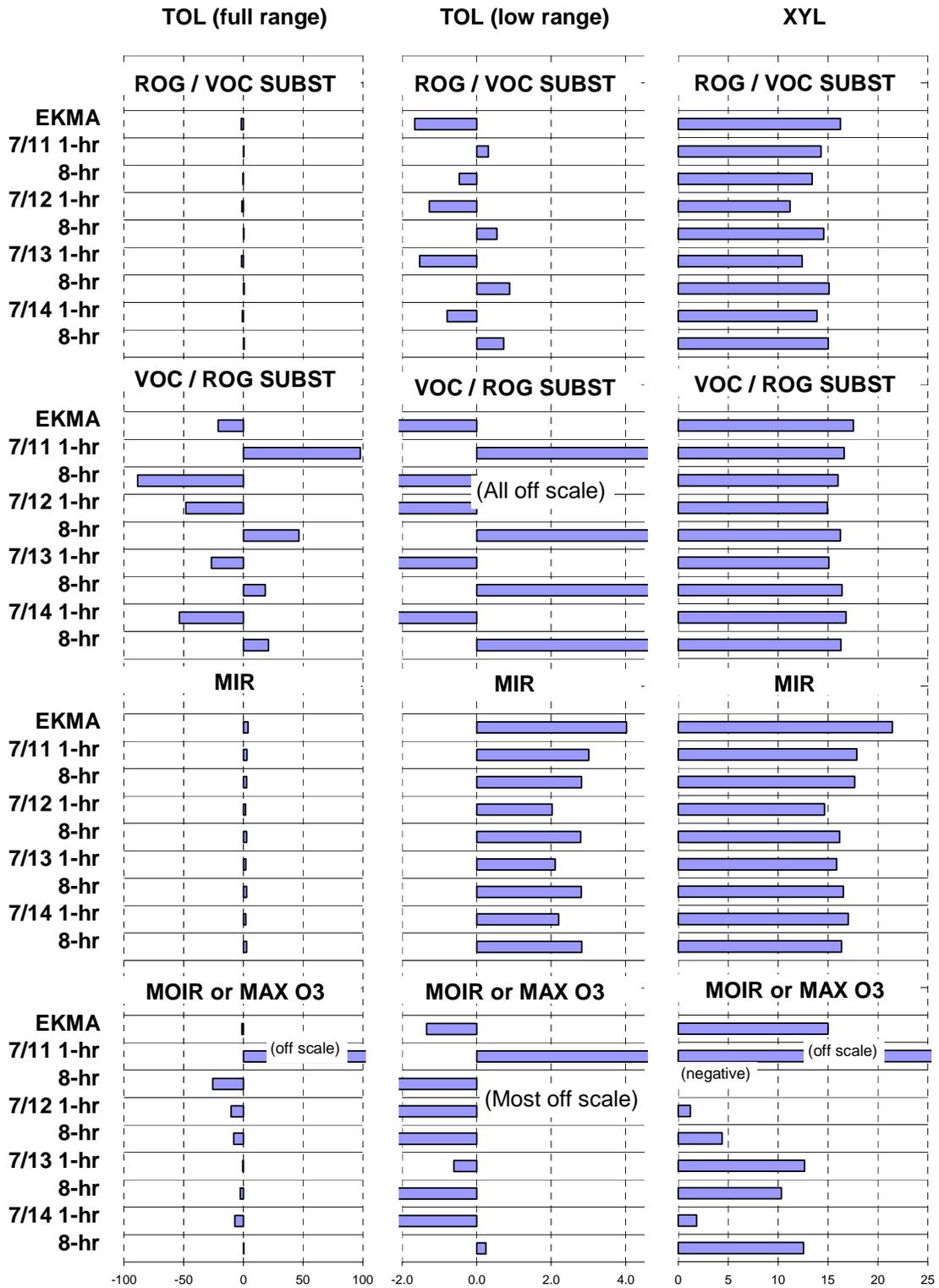


Figure 14. Plots of relative reactivity results in various scales for TOL and XYL model species. Data are shown on a mole basis for the VOC and a carbon basis for the base ROG.

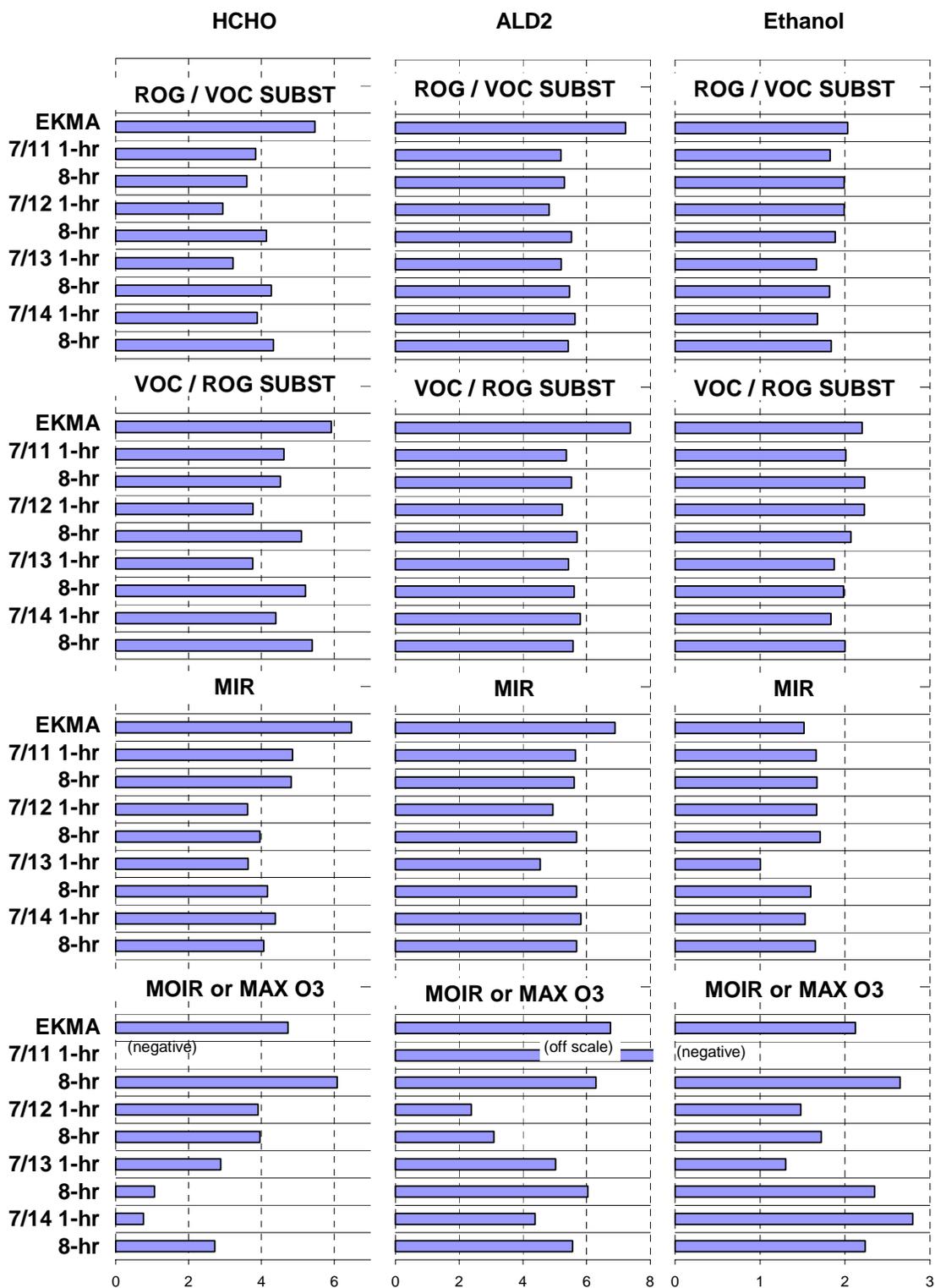


Figure 15. Plots of relative reactivity results in various scales for HCHO and ALD2 model species and ethanol. Data are shown on a mole basis for the VOC and a carbon basis for the base ROG.

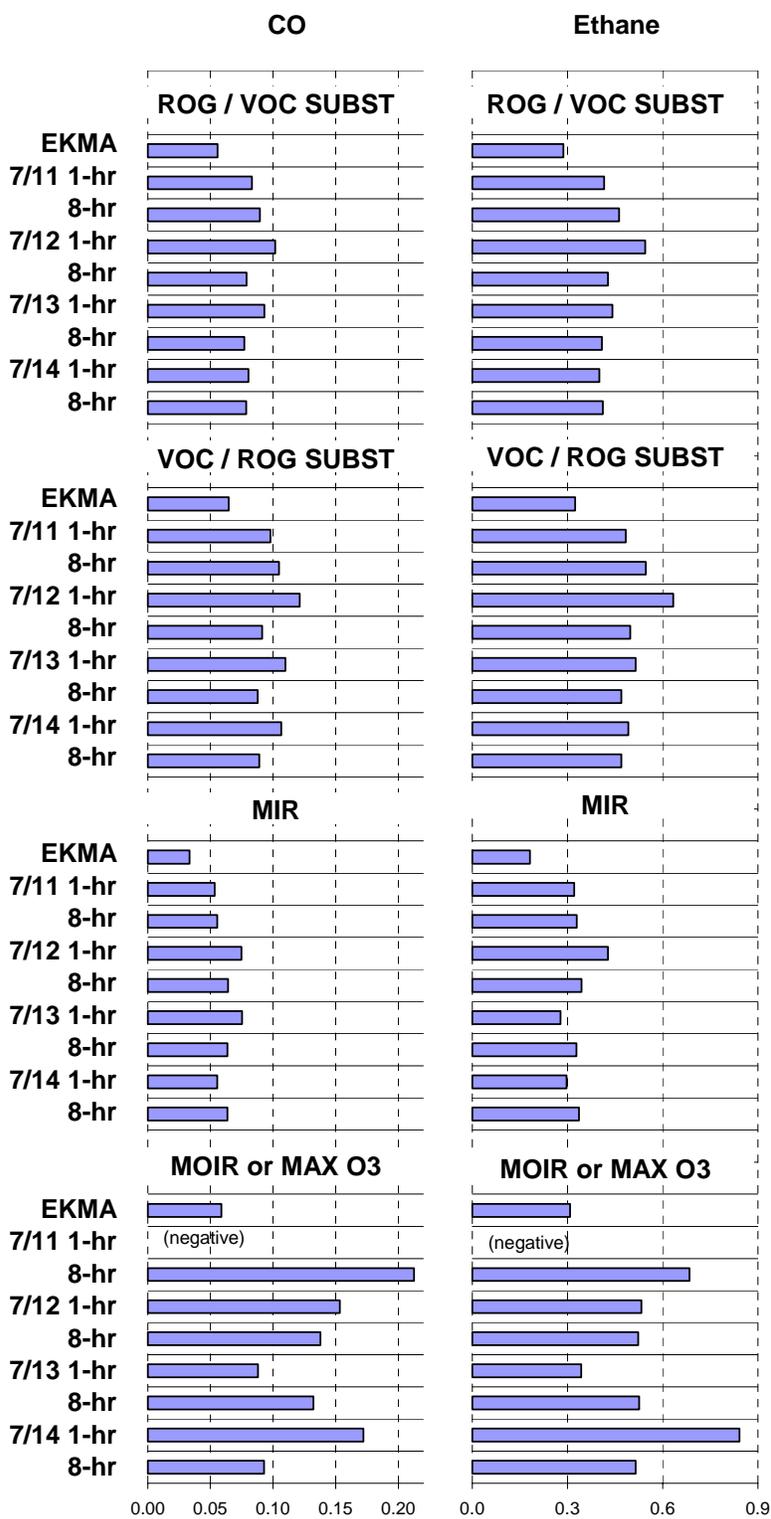


Figure 16. Plots of relative reactivity results in various scales for CO and ethane. Data are shown on a mole basis for the VOC and a carbon basis for the base ROG.

cells inhibiting radicals due to the OH + NO₂ reaction, thus reducing the amounts of these slower reacting species that react. However, a process analysis may be necessary to fully evaluate this.

Table 2 and Figure 13 through Figure 16 show that the regional maximum O₃ method gives much more scattered reactivity metrics than any of the other regional quantification methods examined in this work. As discussed above, the cells with the regional maximum O₃ do not necessarily represent MOIR conditions as defined by Carter (1994a), which refers to cells where NO_x levels are optimum for O₃ formation. Although the highest O₃ cells all have high O₃ levels, this does not mean that changes in NO_x emissions may not make O₃ even higher. In particular, in three of the four episode days the cells with the highest 1-hour average O₃ levels had quite high positive NO_x sensitivities, indicating that they were quite NO_x limited, while for the other day (July 13) the highest 1-hour O₃ cell had a slightly negative NO_x sensitivity, indicating that it represented MIR to MOIR conditions. Clearly, a combination of factors must be involved in causing a particular cell to have the highest O₃ level, with multi-day transport probably playing a significant role in most cases. Because of the variability of these factors, there is variability in the ozone sensitivity results.

For example, it can be seen that the regional maximum O₃ reactivity quantification method essentially fails for the 1-hour ozone quantification for the July 11 episode day, which gave negative relative reactivities for species that had positive reactivities by all other metrics, and extreme and unrepresentative values in other cases. This is because where incremental reactivity of the base ROG in the maximum ozone cell for that day was negative and very close to zero. That cell had the closest to the highest NO_x sensitivity for that episode day, indicating that it was highly NO_x limited. The only way it could have achieved such a high O₃ level would have been long-range transport from other cells. The very low base ROG sensitivity indicated that the ozone formation processes that lead to the high O₃ in that cell were apparently dominated by biogenics.

Comparison of Regional a EKMA Relative Reactivities

Table 2 and Figure 13 through Figure 16 also show the relative reactivities derived using the 1-day EKMA scenarios and reactivity aggregation methodologies used by Carter (1994a) to derive the MIR and other scales, only using the same Carbon Bond chemical mechanism as employed in these CAMx simulation. For most model species the results are surprisingly close to the comparable regional reactivity metrics given the significant differences in the types of scenarios employed. Even for TOL the EKMA reactivities are within the scatter of the data for the various regional reactivity metrics, though the EKMA MIR is ~50% higher than the average of the regional MIRs, which is outside the range of their scatter. For species other than TOL, the average of all the EKMA metrics differ from the averages of all the regional metrics except maximum O₃ by less than 40%, with the difference being less than 25% for about half the species.

However, there is a consistent bias for the EKMA scales towards predicting lower relative reactivities for the slower reacting species, and lower relative reactivities for aldehydes. A bias in the EKMA model towards underpredicting reactivities in slowly reacting species is expected because the slower reacting compounds have less of a chance to react in the one day EKMA scenarios than they would in multi-day regional model simulations. This is shown in Figure 17, which gives plots of the ratios of the EKMA to regional reactivity results using the two most robust metrics against the fraction of the model species that reacts (the kinetic reactivity) in the EKMA MOIR scale. It can be seen that the differences for the species with kinetic reactivities less than 0.5 become consistently greater as the rate of reaction decreases. Note that the species with the kinetic reactivity around 0.5 where the EKMA and regional are in good agreement is ethanol, which has a very similar mechanism as ethane other than its lower OH rate constant. Therefore, the differences between ethanol and ethane are clearly due to their differences in reaction rate.

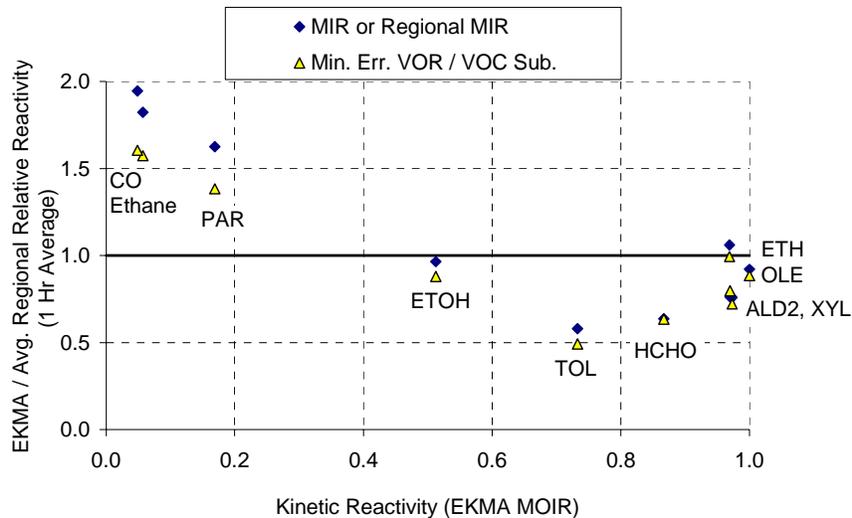


Figure 17. Plots of ratios of regional model to EKMA reactivities against MOIR kinetic reactivities for the least squares ROG for VOC substitution error and the MIR aggregation methods. The reactivity ratios shown are based on the maximum 1-hour average quantification method.

The reason for the bias in the case of the aldehydes and aromatics is less clear, but may be due to EKMA models having greater sensitivity to radical initiation processes than regional models. This would also be consistent with the lower regional reactivity of TOL in the MIR scale

Preliminary Results of Large-Scale Substitution Calculations

Because the processing of the data are not complete, results of the large-scale substitution calculations will be presented for July 13 and 14 only, and only for the maximum 1-hour ozone quantification method. As with the reactivity results, data will also be presented only for the full domain with 36 kilometer grids, with the results for the finer grids being averaged into coarser grid for the purpose of this analysis.

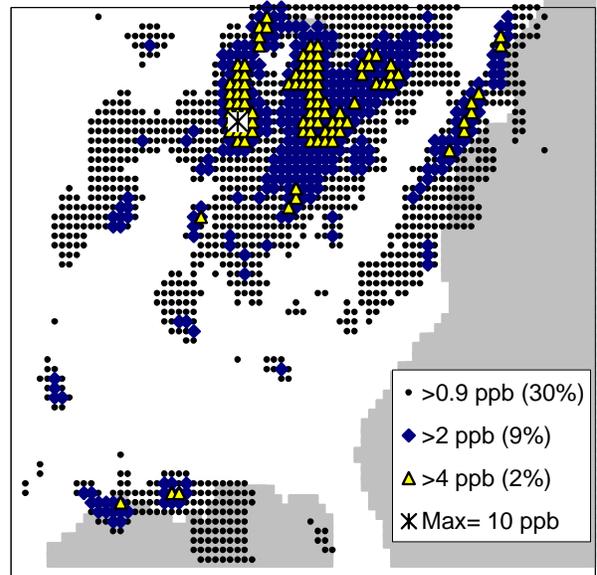
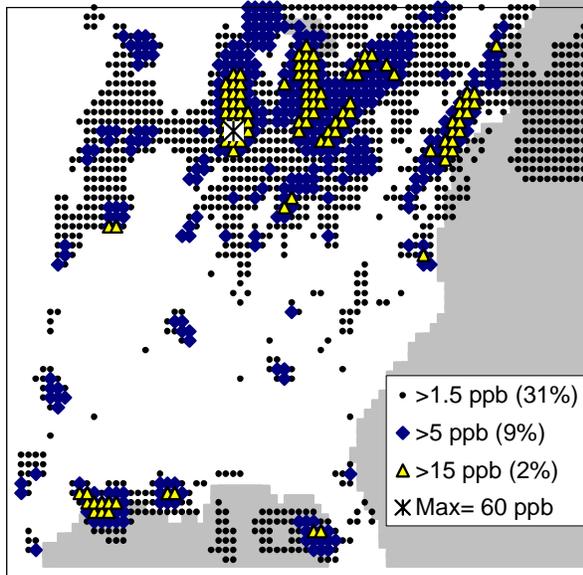
Figure 18 shows maps of maximum 1-hour average ozone changes resulting first from removing the anthropogenic VOCs, then by replacing the anthropogenic VOCs by ethane, on an equal carbon basis as the amount that was removed. The ranges used on the plots were chosen so that in each case a given symbol would represent approximately the same number of cells, i.e., 30-33%, 9%, and 2% of the total cells for the symbols for the low, medium, and high range, respectively.

It can be seen that both of these two episode days were quite similar in their effects of the changes to the anthropogenic VOC emissions. The spatial pattern will probably be different for the other two episode days, based on the plots shown on Figure 2 and Figure 3. Note that these calculations indicate that the anthropogenic VOCs have a relatively small effect on the maximum 1-hour average O_3 throughout most of the domain, with only about 10% of the cells having a greater ozone change than 5 ppb on both days. This indicates the importance of the biogenic VOCs, as indicated by the relative sensitivity of O_3 to the base ROG to the total of all VOC emissions, as discussed above and shown on Figure 7.

O₃ Reduction from Removing Anthropogenic VOCs

O₃ Increase from Adding Ethane After Anthropogenic VOCs Are Removed

July 13



July 14

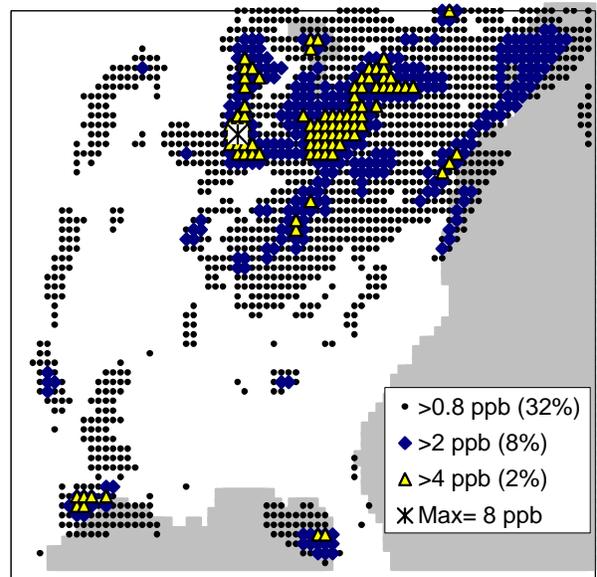
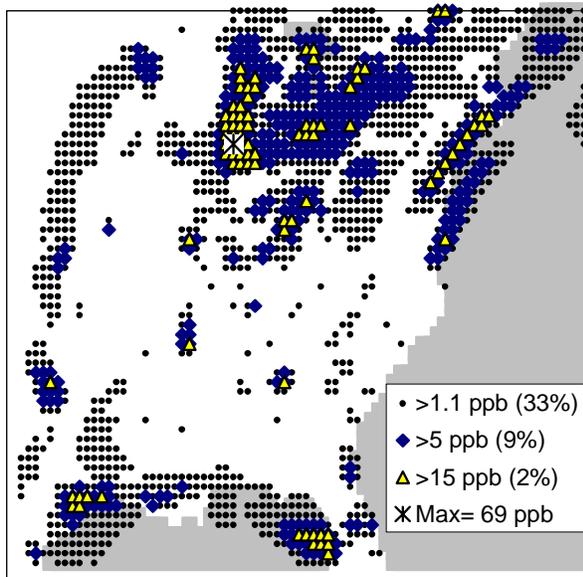


Figure 18. Predicted changes in maximum 1-hour ozone caused by first by removing anthropogenic VOCs and then by replacing the removed anthropogenic VOCs by ethane on a carbon basis. Numbers in parentheses indicate the fraction of cells where the ozone change is in the indicated range.

As expected, replacing the removed anthropogenic VOCs by an equal carbon amount (i.e., approximately equal mass) of ethane causes O₃ increases in about the same spatial pattern as the reductions caused by removing the anthropogenic VOCs. Also as expected given the relatively low reactivity of ethane, the amount of O₃ increased is less than the amount of reduction caused by removing the anthropogenic VOCs. Based on the minimum substitution error relative reactivities of ethane, one would expect the ozone increase caused by adding back the ethane to be about 20-25% of the ozone reduction caused by removing the anthropogenic VOCs. In fact, the increases in the most sensitive cells were somewhat less than that, while those in the less sensitive cells were more. This can be seen by the ratio of O₃ changes in the highest 30%, 9%, and 2% of the cells as shown on Figure 18.

One of the objectives of this project is to determine how well (or poorly) the incremental reactivities such as obtained from these DDM calculations can predict effects of large scale substitution calculations. One would think that they may perform reasonably well in predicting substitutions of moderate fractions of the inventory, but the performance would deteriorate with the magnitude of the change, and not perform well at all in predicting effects of entire removal or replacements of anthropogenic VOCs. However, as indicated above, because of the large biogenic VOC emissions the anthropogenic VOCs contribute only a fraction of the total VOC sensitivity in most of the cells. This suggests that complete anthropogenic VOC substitution or removal may not be as poorly approximated by incremental reactivity analyses as one might initially think.

The ability of the DDM calculations to predict the effect of the removal of all anthropogenic VOCs for these two episode days is shown on Figure 19, which gives plots of 1-hour maximum ozone change observed in the direct calculation against the change predicted from the DDM calculation of the base ROG reactivity. It can be seen that the prediction is remarkably good in most of the cells, except for a small subset of cells where the DDM analysis significantly underpredicts the directly calculated ozone change. Figure 20 shows the location of those cells, which are primarily along the Northeast coast on both simulated days. The reason that the results are so different in those particular cells is not clear, but it is interesting to note that there is a direct relationship between the performance of the DDM analysis in predicting the anthropogenic VOC removal and the incremental reactivity of the base ROG. This is shown on Figure 21, which gives plots of the directly calculated / DDM-predicted ozone change against base ROG reactivity. It can be seen that the DDM predictions perform quite well when the base ROG reactivity is high, but become increasingly biased low when the base ROG sensitivity declines below a predicted ozone change of 5 ppb.

The ability of the DDM-calculated incremental reactivity of ethane to predict the effect of adding the ethane to the no-anthropogenic VOC simulation is shown on Figure 22. The performance is actually quite good in this case, especially considering that the “base case” in this simulation is the no-anthropogenic-VOC case, which is different than the 100% anthropogenic VOC simulation that was actually used to derive the ethane reactivities. Although the data are scattered, the cell-to-cell scatter is not really all that much more than the scatter in the DDM relative reactivities for ethane itself, as shown on Figure 11. There is a bias for the DDM analysis to underpredict somewhat the effect of the ethane addition. It is interesting to note, however, that there is no set of cells where the bias is clearly different than the range observed in the other cells, contrary to the prediction of the anthropogenic removal case.

Conclusions and Remaining Work

This project is still ongoing, so the final conclusions resulting from this work will not be made until it is completed. Nevertheless, some tentative conclusions can be made based on the results obtained to date. These are briefly summarized below.

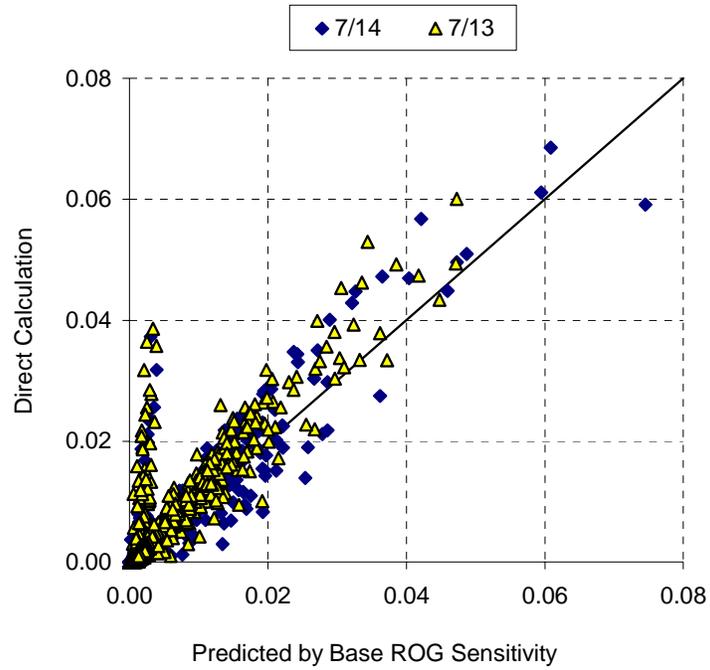


Figure 19. Plots of changes in daily 1-hour maximum ozone concentrations calculated by removing all anthropogenic VOC emissions against the changes predicted by the DDM calculation of the base ROG incremental reactivity.

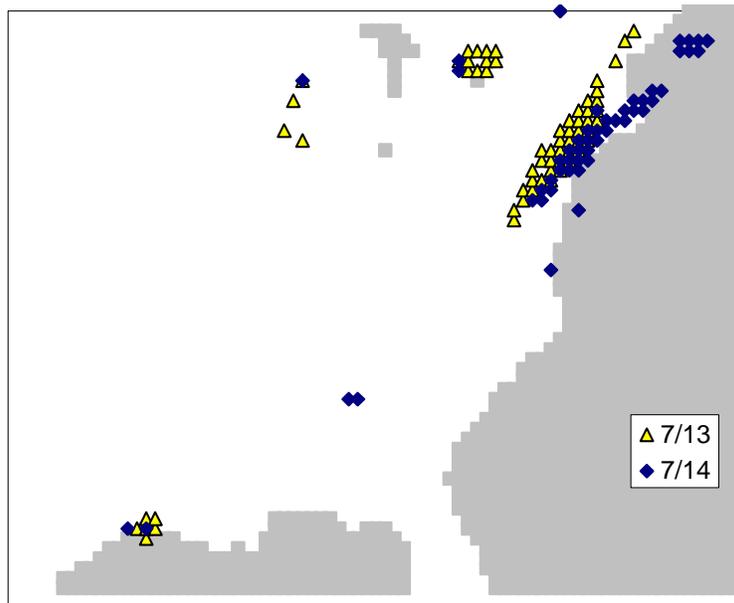


Figure 20. Cells where the DDM calculation underpredicted the daily 1-hour maximum ozone concentration caused by removing all anthropogenic emissions by more than a factor of 1.5.

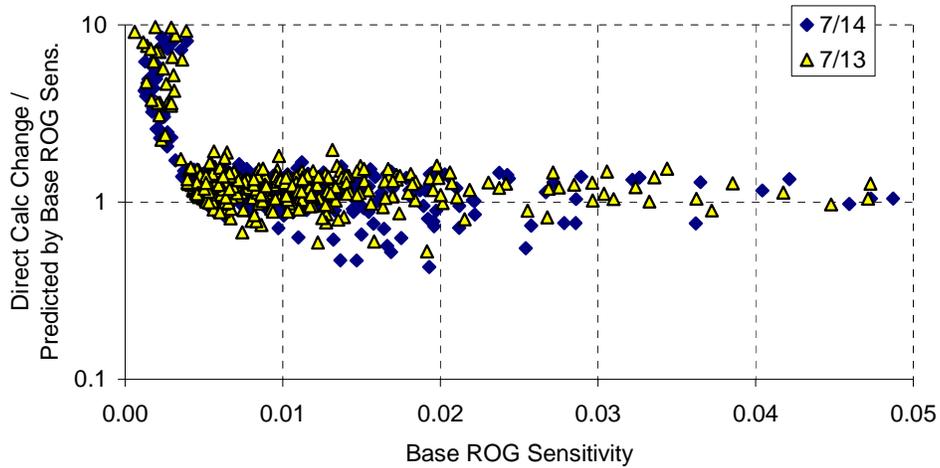


Figure 21. Plots of the ratio of the directly calculated change in the daily 1-hour maximum ozone caused by removing the anthropogenic VOCs against the change predicted from the DDM calculations against the DDM-calculated sensitivity of the base ROG mixture.

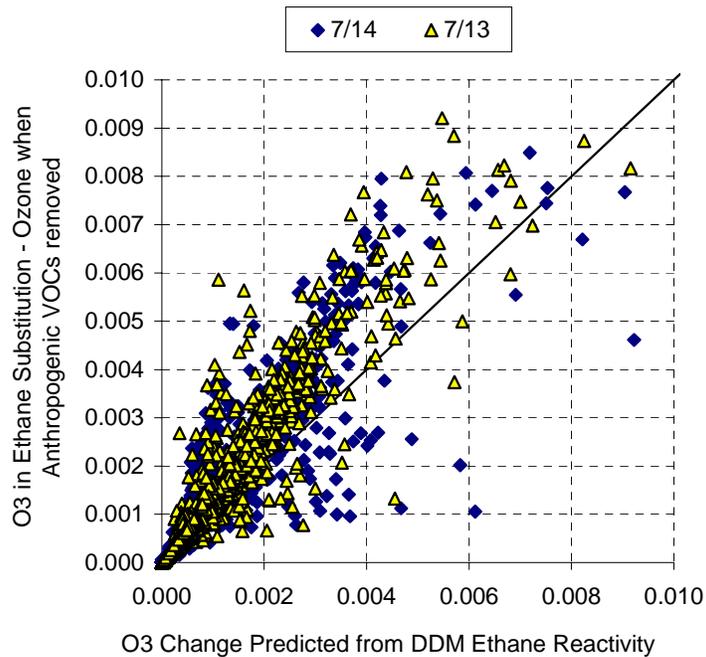


Figure 22. Plots of changes in daily 1-hour maximum ozone concentrations calculated by adding ethane to replace the anthropogenic VOCs in the simulation where they were removed against the changes predicted by the DDM calculation of ethane incremental reactivity

- Most of the East Coast domain simulated in this study is NO_x limited and VOC controls would be much less effective than NO_x controls.
- Biogenic emissions dominate over anthropogenic VOCs in most cells in this episode. Removing all anthropogenic VOCs while holding NO_x constant causes only relatively modest O₃ reductions in most of the domain.
- Relative reactivities of VOCs vary from cell to cell, though the variability is less in the more VOC sensitive cells.
- The minimum substitution error method provides a means to derive a regional reactivity metric based on varying ozone impacts throughout the modeling domain.
- The minimum substitution error and regional maximum incremental reactivity metrics give reasonably consistent results for all Carbon Bond model species except for the highly NO_x – sensitive TOL species.
- The regional maximum ozone reactivity metric does not provide a consistent basis for deriving a regional reactivity scale, and its continued use is not recommended.
- The regional relative reactivities based on effects on the maximum 8-hour average O₃ are not significantly different than those based on maximum 1-hour averages.
- Reactivity scales derived using the EKMA models and reactivity analysis approach of Carter (1994a) are surprisingly consistent with the more robust regional reactivity metrics, though there are some biases.
- The EKMA-based relative reactivity scales appear to consistently underpredict reactivities of slowly reacting species, probably because of the shorter time scale of the reaction.
- The EKMA-based relative reactivity scales appear to overestimate the reactivities of aldehydes and aromatics, though this needs to be verified using more up-to-date mechanisms. This is because the Carbon Bond mechanism has been shown to be more sensitive to radical initiation effects than other mechanisms (Jeffries and Crouse, 1991; Hales et al, 1993).
- With some exceptions that need to be investigated, the DDM approach predicted the effects of complete removal of all anthropogenic VOCs and massive substitutions of all anthropogenic VOCs with ethane surprisingly well. This is probably because the biogenic VOCs tend to dominate over the anthropogenic VOCs in most of the model domain, so removing all anthropogenic VOCs is not as large a perturbation on the overall system as one might think. This suggests that incremental reactivity analyses may be a useful means to predict more realistic substitution scenarios.

The work remaining on this project consists of completing the analysis of the DDM results using the higher resolution data and conducting additional large scale substitution calculations to further assess reactivity effects. A proposal to extend this program to analyze the regional reactivity results using chemical process has been submitted to the American Chemistry Council. Further discussion of these areas is beyond the scope of this report.

References

Baugues, K. (1990): “Preliminary Planning Information for Updating the Ozone Regulatory Impact Analysis Version of EKMA,” Draft Document, Source Receptor Analysis Branch, Technical Support Division, U. S. Environmental Protection Agency, Research Triangle Park, NC, January.

- Carter, W. P. L. (1994a): "Development of Ozone Reactivity Scales for Volatile Organic Compounds," *J. Air & Waste Manage. 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, April 12.
- Carter, W. P. L. (1996): "Condensed Atmospheric Photooxidation Mechanisms for Isoprene," *Atmos. Environ.*, 30, 4275-4290.
- Carter, W. P. L. and R. Atkinson (1989): "A Computer Modeling Study of Incremental Hydrocarbon Reactivity", *Environ. Sci. Technol.*, 23, 864.
- Carter, W. P. L. (2000a): "Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment," Report to the California Air Resources Board, Contracts 92-329 and 95-308, May 8. Available at <http://www.cert.ucr.edu/~carter/reactdat.htm>.
- Carter, W. P. L. (2000b): "Implementation of the SAPRC-99 Chemical Mechanism into the Models-3 Framework," Report to the United States Environmental Protection Agency, January 29. Available at <http://www.cert.ucr.edu/~carter/absts.htm#s99mod3>.
- Carter, W. P. L. (2002): Emissions database work in progress under contract for the University of Houston.
- Carter, W. P. L., D. Luo, and I. L. Malkina (1997): "Investigation of the Atmospheric Ozone Formation Potential of Selected Alkyl Bromides," Report to Albemarle Corporation, November 10. Available at <http://www.cert.ucr.edu/~carter/absts.htm#alkbr>.
- Dimitriades, B. (1999): "Scientific Basis of an Improved EPA Policy on Control of Organic Emissions for Ambient Ozone Reduction," *J. Air & Waste Manage. Assoc.* 49, 831-838
- Dunker, A. M. (1980). "The Response of an Atmospheric Reaction-Transport Model to Changes in Input Functions." *Atm. Env.* 14, 671-679.
- Dunker, A. M., G. Yarwood, J. Ortmann, and G. M. Wilson (2000). "Implementation of the Decoupled Direct Method for Sensitivity Analysis in a Detailed Air Quality Model," Institute for Mathematics and Its Applications, Workshop on Atmospheric Modeling, University of Minnesota, March 15-19.
- ENVIRON (1998). "User's Guide to the Comprehensive Air Quality Model with Extensions, Version 2.00," available at <http://www.camx.com>.
- EPA (1998). Emissions received by email from Deborah Luecken of EPA on Thu, 31 Dec 1998. The email message indicated that the data were forwarded from nmm@hpcc.epa.gov on 12/30/98 06:58:57 PM. The message also included the following text: "These ASCII files contain SAROAD emission totals for Benjyey's 36km evaluation grid. These attached files ...are based on the 1995-NET EPA US inventory. These files contain the emission summaries for the US part of the grid." The comments also note that the emissions have not been completely reviewed and should be regarded as preliminary. Separate totals were given for area and point source totals. These were summed up to get the total emissions.
- Gery, M. W., G. Z. Whitten, and J. P. Killus (1988): "Development and Testing of the CBM-IV For Urban and Regional Modeling," EPA-600/ 3-88-012, January.
- Jeffries, H. E. and Crouse, R. (1991): "Scientific and Technical Issues Related to the Application of Incremental Reactivity, Part II: Explaining Mechanism Differences," Final report to the Western States Petroleum Association, Los Angeles, CA.

- Hakami, A., R. A. Harley, J. B. Milford, M. T. Odman and A. G. Russell (2002): "Regional, Three-Dimensional Reactivity Assessment of Organic Compounds," Manuscript in preparation. (Personal communication to W. P. L. Carter, April, 2002).
- Hales, J. M., M. W. Gery, and Crouse, R. (1993): "VOC Reactivity and its Application for Emission Regulation," Report submitted to the American Petroleum Institute, March.
- RRWG (1999): "VOC Reactivity Science Assessment", Prepared by the Reactivity Research Working Group Science Team, May 5, Available at <http://www.cgenv.com/Narsto/reactinfo.html>.