Effects of Chemical Mechanism Uncertainties on the Reactivity Quantification of Volatile Organic Compounds Using a Three-Dimensional Air Quality Model

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Accurate quantification of the ozone-forming potential, termed "reactivity", of voltaile organic compounds (VOCs) is critical for correctly assessing the impacts of emissions on air quality. As reactivity-based regulations are being more carefully considered for urban ozone control strategies, the uncertainties in our ability to quantify reactivity are gaining importance. This study utilized a three-dimensional air quality model to examine the uncertainty in reactivity quantification resulting from a set of reaction rate constant uncertainties. A previous study identified the set of rate constants that were most critical for single-cell model ozone predictions. With the detailed airshed model, uncertainties in rate constants for aldehyde photolysis, nitric acid formation, and decomposition of peroxy acetyl nitrate (PAN) and peroxy propionyl nitrate plus higher PAN analogues (PPN) exhibited the greatest impact on relative compound reactivity values. For the compounds and reactions examined, the combined responses to 2σ changes in reaction rate constants were approximately 15% of the predicted relative reactivity values, with the reactivities of ethylbenzene and toluene exhibiting the greatest response. The choice of reactivity quantification measures and the air quality models used had a greater impact on relative reactivity predictions than did the rate constant uncertainties.

Introduction

The atmospheric chemistry of urban ozone precursors, oxides of nitrogen (NO$_x$), and volatile organic compounds (VOCs) is nonlinear and is influenced by local meteorology and ambient conditions, which makes ozone behavior difficult to predict and control. Despite great efforts in ozone control, many major urban areas continue to exceed the National Ambient Air Quality Standard (NAAQS) for tropospheric ozone (*1*). In response, regulatory control strategies are becoming increasingly stringent and costly. Previous studies have shown that in many areas the ozone NAAQS cannot be met without significant reductions of both NO$_x$ and VOC emissions. The ability to identify which emissions reductions would most effectively reduce pollution would help in minimizing costs. VOCs have historically been regulated as a single class of compounds, i.e., by limiting the total mass of VOC emitted, regardless of the composition. Research has shown that the hundreds of individual species included in the VOC class (mostly hydrocarbons and oxygenated hydrocarbons) can each have substantially differing effects on ozone formation (*2–4*). Thus, more direct use of the ozone-forming potential of VOCs, termed "reactivity", is rapidly gaining attention because potentially more effective control strategies could be developed by incorporating these reactivity values into regulatory policy (*4–6*).

One such reactivity-based policy is part of the California Clean Fuels/Low Emissions Vehicles Regulations (*7*). In these regulations, a reactivity scale based on a maximum incremental reactivity (MIR) (*7, 8*) value for compounds or compound classes is used to calculate the total reactivity of alternative fuel vehicle emissions. This scale was developed over a wide range of meteorological inputs and background concentrations using a detailed chemical mechanism, the Statewide Air Pollution Research Center 1990 (SAPRC90) mechanism (*9*), incorporated into a single-cell or "box" air quality model.

The use of the MIR scale in regulations led to a number of concerns about the quantification of compound reactivity. One such concern addressed the level of physical detail accounted for by the box model in the quantification of reactivity. To examine this issue, two reactivity studies have been conducted (*10, 11*) using a comprehensive three-dimensional (3D) urban air quality model: the Carnegie/California Institute of Technology (CIT) model (*12, 13*), which accounts for a high degree of physical complexity. One of these studies (*11*) incorporated the SAPRC90 mechanism in the CIT model so the results could be directly compared to the regulatory MIR scale. The resulting version of the CIT model is referred to as the CIT-S90.

A second serious concern about VOC reactivity quantification is that uncertainties, particularly in the chemical mechanism, may have significant effects on the calculation of reactivity values. As experimental methods evolve, more refined parameters become available for modeling purposes. For example, a recent study by Donahue et al. (*14*) suggests that estimates of the rate constant for NO$_2$ + OH → HNO$_3$ used for modeling of the lower troposphere are overestimated by approximately 30%. The findings of the Donahue et al. study exemplify the importance of examining the effects of chemical mechanism uncertainty on ozone and incremental reactivity predictions. Identification of which parameters have the greatest impact allows efforts to focus on refining the measurements of those parameters and will provide a measure of confidence in the interpretation of current model predictions.

The study described here extends the prior CIT-S90 reactivity study and presents the results of an uncertainty analysis performed on the chemical mechanism for the three reactivity scales developed during the previously described study. A box model was used in a previous formal uncertainty analysis to identify those rate constants that contributed the greatest amount of uncertainty to the ozone formation predictions (*15*). The CIT-S90 model was then used to examine the impact of those critical rate constant uncertainties on reactivity quantification using a 3D model. There are

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TABLE 1. SAPRC90 Mechanism Characteristics, As Implemented with the CIT Model for Reactivity Studies

chemical species	
transported	71
steady-state	15
constant	5
explicit VOCs	33
total	91
reactions	
photolytic	20
total	203

fundamental differences between box and 3D models that could strongly impact the effect of chemical mechanism uncertainties on ozone predictions. Box models can be applied to a large number of scenario conditions and used with detailed statistical methods, while a 3D model accounts for a much higher degree of physical detail (i.e., effects of multiday transport, spatial and temporal variations of emissions, and cloud cover) and provides more detailed metrics for evaluation.

A key limitation of the uncertainty analysis performed here is that it was confined to uncertainties in rate parameters in the SAPRC mechanism, neglecting other mechanism uncertainties such as those in product yields and, more broadly, in mechanism formulation (e.g., degree of explicitness or omission of important reactions or species). Only reaction rate constants were examined in this study because they are believed to be the source of the largest fraction of identifiable uncertainty in the mechanism (*16*). Beyond the chemical mechanism, the study did not attempt to treat uncertainties in the simulation conditions or the emissions estimates for which reactivities are calculated. Additionally, it is likely that uncertainties in input conditions for individual scenarios, particularly emissions and meteorology fields, have an impact on compound reactivity quantification, especially on those affected by photolysis rates. However, how this might effect the *relative* ranking of reactivity has been less clear.

Methods

The CIT air quality model (*12, 13*) follows the evolution of chemical species in the atmosphere, providing spatial and temporal predictions of pollutant concentrations for given conditions over a specified time interval. Input data required by the model include local meteorological conditions such as wind, temperature, and solar radiation; the domain topography; initial and boundary conditions of species concentrations; and anthropogenic and biogenic species emissions. Some of the main model components include calculations for advection, turbulent diffusion, and deposition and a chemical reaction mechanism that calculates the production and destruction of species.

For the previous CIT-S90 reactivity study (*11*) and this uncertainty study, the chemical mechanism used, SAPRC90, was made explicit for 33 VOCs. The basic mechanism characteristics are shown in Table 1. The model was applied to the Los Angeles air basin for both studies because of the serious ozone problem there, the quality of input data available, and the application of the MIR scale in California for regulatory use. Data inputs such as meteorology and emissions were adopted from the August 1987 episode of the South Coast Air Quality Study (*17, 18*). Although it is generally acknowledged that the mobile source organic emissions are underpredicted in this data set (*13*), the inventory was not enhanced for this study. It has been previously shown that the use of two inventories with very different levels of VOC and NO_x leads to similar reactivity quantification results (*19*).

In the previous reactivity study (*11*), the model was used to calculate incremental reactivities for 26 organic compounds plus carbon monoxide. Species reactivity was determined by first modeling ozone formation using a base emission inventory and then simulating the effects of increasing the emissions of one species. Emissions of most organic species were increased by 20% of the total emitted VOCs (on a molar basis) in each grid cell each hour to account for the spatial and temporal variations in emissions. Carbon monoxide was increased by 100% of the VOCs. These two sets of ozone predictions, base and perturbed, are then compared to calculate the reactivity of that species, which can be defined in a number of ways. One benefit of using a 3D model rather than a box model is that a variety of air quality impacts can be examined. This provides a more realistic and comprehensive analysis of the atmospheric response to the spatial and temporal variations of emissions, multiday effects, and spatial distribution of pollutant impacts. With a 3D model, these impacts can also be correlated with the human population distribution (e.g., as a measure of exposure impact).

In this study, as in previous similar studies (*10, 11*), several reactivity measures were examined including effect on peak ozone, population-weighted potential exposure, and spatial exposure. Peak ozone is defined simply as the maximum ozone concentration in parts per million (ppm) predicted in the modeling domain using each emissions inventory. The predicted peak ozone forms relatively far downwind of Los Angeles in an area with a relatively high ratio of VOC to NO_x concentrations, which is therefore not as sensitive to VOC emissions as is most of the urban basin. Population-weighted exposure is calculated as the population residing in the modeling grid location times the ozone concentration, summed for each hour that the concentration is over the threshold value (i.e., 0.09 or 0.12 ppm for ozone). The two threshold results are then averaged. Spatial exposure is the summation of the grid cells with ozone concentrations exceeding the threshold value times the concentration for each hour over the threshold. The units are ppm·grid·h, or km²·ppm·h (one grid is 25 km² in area). The two threshold results are also averaged for this metric. A more detailed description of these reactivity measures is presented elsewhere (*11*).

To present reactivity measures in a more relative sense and to better compare measures between the zero- and three-dimensional model results, reactivities were normalized to that of a suite of compounds representative of exhaust emissions from motor vehicles operated on industry-average gasoline. The use of a suite of compounds for normalization rather than a single compound reduces the possible bias that can result if the normalizing species does not respond in a way representative of most compounds and also reduces the uncertainty in the calculation of the relative reactivities (*4, 20*). A further advantage is that it allows direct comparison of the reactivity of each compound to that of emissions from a major source.

In this study, the normalized reactivity for each species, NR_i, is defined as

$$NR_i = \frac{R_i}{R_{\text{composite}}} = \frac{(P_i - P_{\text{base}})/C_i}{\sum_j \left[\frac{f_j}{C_j}(P_j - P_{\text{base}}) \right]} \quad (1)$$

Here, NR_i is the normalized reactivity of species i; R is the carbon-based reactivity of species i or the normalizing composite; P is the air quality metric of interest (e.g., peak ozone or an exposure value) corresponding to emissions of species i, of composite species j, or of the base case; C_i is the

TABLE 2. Composite Composition Used for Normalizing Reactivities and Airshed Calculated Reactivities

species	no. of Carbons	fraction in composite (ppmC per ppmC)	normalized relative reactivity		
			peak O$_3$	av threshold exposure	
				population-weighted	spatial
carbon monoxide	1	0.000	0.05	0.02	0.03
ethane	2	0.126	0.20	0.03	0.05
benzene	6	0.000	0.04	0.05	0.06
methyl *tert*-butyl ether	5	0.052	0.35	0.14	0.19
2,2,4-trimethylpentane	8	0.000	0.44	0.14	0.20
butane	4	0.003	0.57	0.16	0.25
methanol	1	0.000	0.51	0.24	0.27
methyl ethyl ketone	4	0.004	0.64	0.21	0.33
2-methylpentane	6	0.000	0.71	0.24	0.35
ethanol	2	0.056	1.06	0.30	0.48
ethyl *tert*-butyl ether	6	0.010	0.85	0.41	0.56
toluene	7	0.060	−0.10	0.35	0.37
ethylbenzene	8	0.047	−0.06	0.38	0.38
methylcyclopentane	6	0.141	1.17	0.45	0.66
2-methyl−1-butene	5	0.009	1.03	1.05	1.08
o-xylene	8	0.039	0.57	1.39	1.24
2-methyl−2-butene	5	0.055	1.21	1.24	1.35
3-methylcyclopentene	6	0.001	1.65	1.34	1.50
m,p-xylene	8	0.121	0.69	1.94	1.52
ethene	2	0.109	1.73	1.15	1.45
1,2,4-trimethylbenzene	9	0.035	1.06	2.67	1.83
acetaldehyde	2	0.012	2.32	1.18	1.76
isoprene	5	0.000	2.09	2.03	2.04
propionaldehyde + higher aldehydes	3	0.006	2.81	1.35	2.07
propene	3	0.009	2.06	1.64	1.93
1,3-butadiene	4	0.096	2.53	2.27	2.35
formaldehyde	1	0.011	1.50	1.98	2.63

TABLE 3. Normalized Bias and Standard Deviation between Metrics for Each Model

		bias(NB)	SD
CIT Model	population, spatial	−0.21	0.22
	peak, spatial	0.22	0.52
	peak, popululation	0.39	0.67
box model	MIR, LA MIR	0.07	0.12
	MIR, MOIR	−0.15	0.27
	MOIR, LA MIR	0.22	0.37

TABLE 4. Normalized Bias and Standard Deviation between Metrics and Models

box model	CIT model					
	population exposure		spatial exposure		peak ozone	
	bias(NB)	SD	bias(NB)	SD	bias(NB)	SD
MIR	−0.16	0.24	0.05	0.09	0.26	0.56
LA MIR	−0.09	0.20	0.12	0.17	0.32	0.65
MOIR	−0.3	0.42	−0.10	0.24	0.12	0.35

number of carbon atoms in a molecule of species *i*; and *f$_j$* is the carbon fraction of species *j* in the composite mixture. The composition of the normalizing mixture is given in Table 2.

Table 2 also shows three reactivity scales predicted for the 27 compounds examined. In the prior CIT-S90 reactivity study (*11*), two photolytic rate constants were calculated using transposed cross sections and yields. For this reason, the reactivity scales and scale comparisons were recalculated and are presented here. The two rate constants represent the photolytic decomposition of two classes of unknown aromatic fragmentation products: AFG1, formed from benzene, tetralin, and naphthalenes; and AFG2, formed from aromatics containing alkyl groups. These reactions mainly affect predictions of the chemical behavior of aromatic compounds.

TABLE 5. Regression Results for the Exposure versus MIR and Peak Ozone versus MOIR Measures

	R^2	slope	intercept
population to MIR	0.81	0.88	0.04
MIR to population		0.92	0.15
population to MOIR	0.74	0.95	−0.02
MOIR to population		0.78	0.27
spatial to MIR	0.97	0.98	0.04
MIR to spatial		0.99	−0.01
spatial to MOIR	0.96	1.09	−0.06
MOIR to spatial		0.88	0.10
peak to MIR	0.60	0.78	0.26
MIR to peak		0.77	0.19
peak to MOIR	0.80	1.01	0.05
MOIR to peak		0.79	0.16
MIR to MOIR	0.94	1.09	−0.08
MOIR to MIR		0.86	0.13

As in previous studies conducted with airshed models (*10, 11*) as well as box models (*2, 8, 15*), species reactivities are found to differ by over an order of magnitude. Tables 3−5 show the recalculated relationships between airshed and box model reactivity predictions. In these tables, three box model scales (*8*) are shown for comparison. MIR denotes the average maximum incremental reactivity scale developed from calculations of 39 scenarios developed for different cities, and MOIR denotes a similar 39 scenario-average scale for maximum ozone incremental reactivity, which is based on peak ozone. LA MIR denotes a maximum incremental reactivity scale developed for conditions in Los Angeles (one of the 39 scenarios). In Tables 3 and 4, the normalized bias between metrics *x* and *y* (from either model), NB$_{x,y}$, was calculated as

$$NB_{x,y} = \frac{1}{25}\sum_{i=1}^{25}RR_{i,x,y} = \frac{1}{25}\sum_{i=1}^{25}2\left(\frac{R_{i,x} - R_{i,y}}{R_{i,x} + R_{i,y}}\right) \quad (2)$$

TABLE 6. SAPRC90 Reaction Sets Considered in Uncertainty Analysis [% of Total Uncertainty and σ/k from Box Model Study (20)]

influential reaction	% of total uncertainty	σ/k^a	description	set
$NO_2 + OH \rightarrow HNO_3$	32.1	0.265	$NO_2 + HO$	1
$NO_2 + h\nu \rightarrow NO + O$	10	0.265	NO_2 Photolysis	2
$O_3 + NO \rightarrow NO_2 + O_2$	5.1	0.193	$O_3 + NO$	3
$RCHO + h\nu \rightarrow CCHO + RO_2\text{-}R + RO_2 + CO + HO_2$	0.9	0.343	aldehyde photolysis	4
$HCHO + h\nu \rightarrow 2HO_2 + CO$	9.7	0.342		
$CCO\text{-}O_2 + NO \rightarrow CO_2 + NO_2 + HCHO + RO_2\text{-}R + RO_2$	7.1	0.764	peroxyacyl + NO	5
$C_2CO + NO \rightarrow CCHO + RO_2\text{-}R + CO_2 + NO_2 + RO_2$	1.5	0.764		
$CCO\text{-}O_2 + NO_2 \rightarrow PAN$	5.4	0.671	peroxyacyl + NO_2	6
$C_2CO\text{-}O_2 + NO_2 \rightarrow \_PPN$	1.6	0.671		
$PAN \rightarrow CCO\text{-}O_2 + NO_2 + RCO_3$	5.0	0.696	PAN, PPN decomposition	7
$PPN \rightarrow C_2CO\text{-}O_2 + NO_2 + RCO_3$	1.2	0.696		
$AFG1 + h\nu \rightarrow HO_2 + HCOCO\text{-}O_2$		1.332	AFG1/AFG2 photolysis	8
$AFG2 + h\nu \rightarrow HO_2 + CO + CCO\text{-}O_2 + RCO_3$	6.3	1.332		
$MEOH + OH \rightarrow HO_2 + HCHO$	0	0.481	methanol + OH	9

^{a} Normalized uncertainty, σ/k, where σ is the 1σ uncertainty of rate constant k. ^{b} AFG1 represents unknown aromatic fragmentation products formed from benzene, tetralin, and naphthlenes. AFG2 represents unknown aromatic fragmentation products formed from aromatics containing alkyl groups.
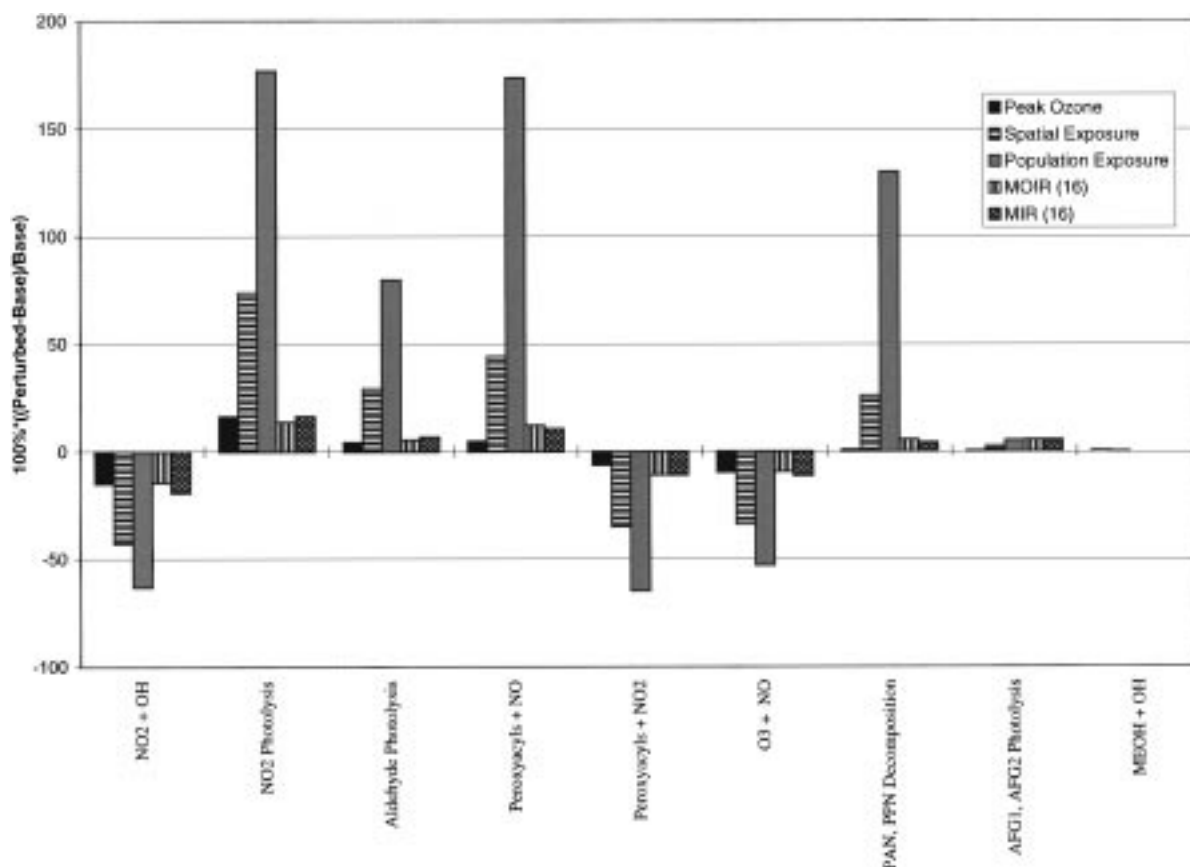

FIGURE 1. Percent change in base ozone predictions from rate constant uncertainty tests.

Here, $RR_{i,x,y}$, the reactivity ratio, is a function of the predicted reactivity, R, for species i from the metrics x and y. $NB_{x,y}$ is the average of these reactivity ratios predicted by the metrics for 25 of the 27 species (ethylbenzene and toluene values are omitted in this comparison because their negative reactivities cause the denominator to approach zero). In both the previous reactivity analysis and the recalculated analysis, the normalized bias is generally low and the correlation for the 27 species, shown in Table 5, between the box model reactivities and those calculated with the airshed model is high. Airshed reactivities based on spatial exposure show a strong correlation with the box model MIR scale as well as the strongest airshed metric correlation with the box model MOIR scale. Airshed reactivities based on peak ozone sensitivity are significantly different from those based on exposure metrics and from the box model MIRs, although they show similar trends. Peak ozone-based reactivities are well correlated with the box model peak ozone reactivities (MOIR). For a more complete description of the CIT model application and metric comparison, please refer to Bergin et
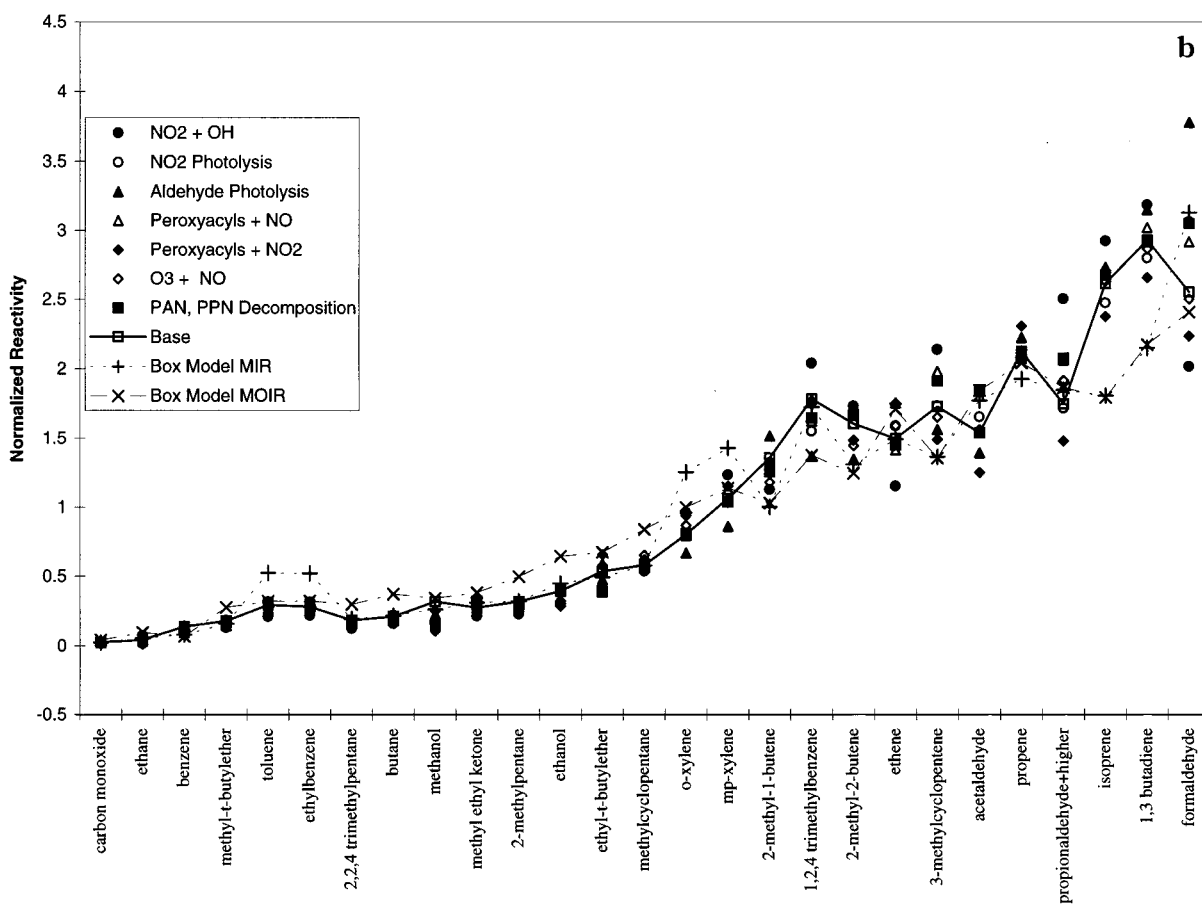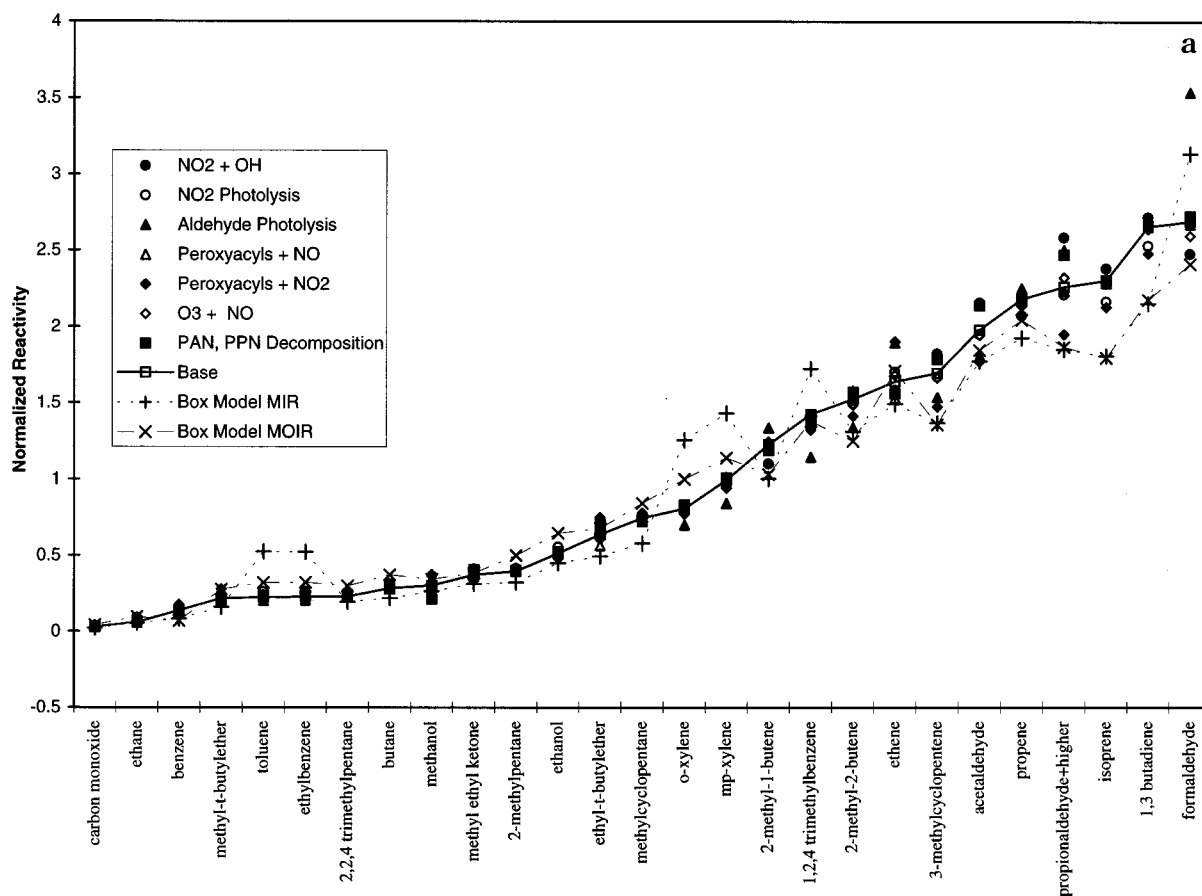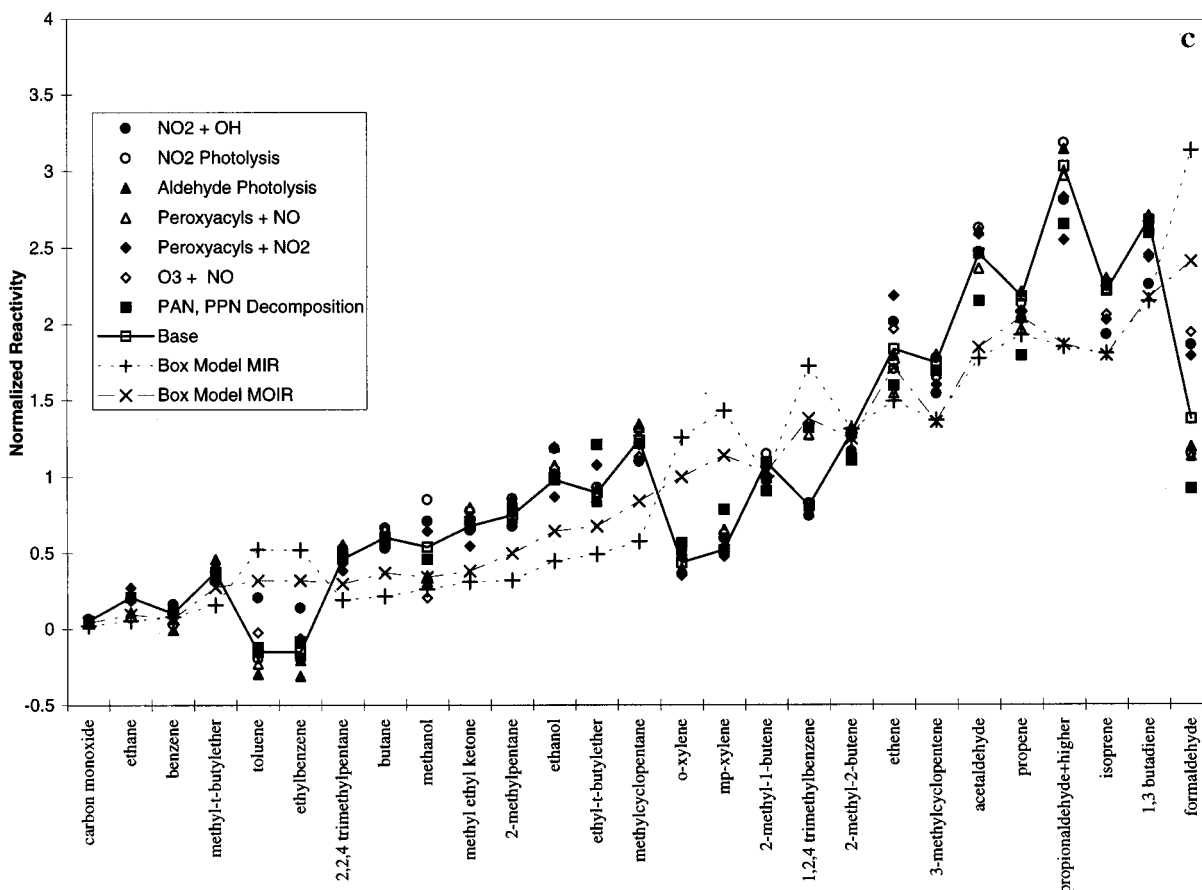
FIGURE 2. (a) Effect of 2σ rate constant perturbations on normalized reactivities based on spatial exposure. (b) Effect of 2σ rate constant perturbations on normalized reactivities based on population exposure. (c) Effect of 2σ rate constant perturbations on normalized reactivities based on peak ozone.

al. 1995 (*11*).

Identification of Critical Rate Constants

Major sources of uncertainty in the reactivity scales presented above, as well as in the MIR and MOIR scales, include reaction rate constants and speciation product parameters used in the chemical mechanism. The effect of uncertainty in reaction rate constants on reactivity quantification was targeted for a formal sensitivity study (*15*), using a box model with the SAPRC90 chemical mechanism to simulate the average of the 39 modeling scenarios that were used to create the MIR and MOIR scales. A Monte Carlo analysis with Latin Hypercube Sampling was applied to examine the effects of uncertainties in the rate parameters of the SAPRC90 mechanism on ozone formation predictions and on incremental reactivities of selected organic species. The results of this box model study were used to identify a reduced set of critical rate parameters for uncertainty analysis with the CIT-S90 model. This approach takes advantage of both the formal sensitivity analysis made practical by the lower computational requirements of a box model and the greater physical and temporal representation made possible by the 3D model, allowing us to examine in detail the potential uncertainty impacts in reactivity quantification on a specific real-world pollution episode.

Estimates of uncertainty in the rate parameters of the SAPRC mechanism were compiled (*21*) largely from reviews by NASA (*22*) and IUPAC (*23*) panels. Because these estimates are subjective, the larger of the NASA or IUPAC uncertainty estimates was adopted if the panels disagreed. Possible correlation between uncertainties in some parameters was neglected in the box model study, as uncertainties were

assumed to be independent across parameters. For example, the peroxyacyl + NO and the peroxyacyl + NO_2 rate constants were measured as a ratio for development of the chemical mechanism. However, because they are not perfectly correlated, they were treated independently in the uncertainty study. It should be noted that this is a conservative approach, and the prediction sensitivities to these rate constant uncertainties would likely decrease if these reactions were coupled during the uncertainty test. Further details on the uncertainty compilation and box model simulations are available elsewhere (*15, 20*).

Rate constants of 12 of the 203 mechanism reactions were found in the box model study to be responsible for approximately 86% of the total uncertainty caused by rate constants in predicted ozone concentrations (*15*). The same set of rate constants also accounts for much of the estimated uncertainty in MIR and MOIR values (*15*). Some of the 12 reactions behave very similarly and so were grouped for this study, resulting in eight sets of reactions to be examined in this uncertainty analysis. Table 6 provides a listing of these reactions, first-order estimates of their uncertainty contribution to total ozone predictions (% of total uncertainty), the assumed normalized rate constant uncertainty (σ/k) from the box model study, and the reaction set description used here. In addition to these 12 rate constants, which were influential on compound reactivities in general, rate constants for the primary oxidation reactions of individual organic compounds were found to be influential for the reactivity of that particular compound (*15*). For example, the rate constant of the reaction for methanol with the hydroxyl radical is influential on the calculation of the reactivity of methanol. Reactivities of the more slowly reacting organic

compounds, such as methanol, were shown by the box model study to be especially sensitive to the rate constants for their initial oxidation reactions. To keep computational requirements reasonable, initial oxidation parameter affects on reactivities were calculated with the CIT-S90 only for the illustrative case of methanol, which is also listed in Table 6.

Effects of Rate Constant Uncertainties on Reactivity Quantification

To examine the effect of rate constant uncertainty, reactivity scales were developed for perturbations in each of the first seven targeted rate constant sets in Table 6, which can then be compared to the nominal reactivity scales. Sensitivity of reactivity quantification of six aromatics to the uncertainty in the lumped aromatic ring fragment destruction reactions (AFG1/AFG2 photolysis) is also examined, as is the sensitivity of methanol reactivity quantification to the methanol + OH rate constant. The methanol uncertainty effect was included in the sensitivity study because of methanol's importance to alternative fuels discussions. However, because methanol is not a common compound in the emissions inventory, is relatively unreactive, and is not a reaction product of other species, the sensitivity of the reactivities of the other 26 species to the methanol + OH rate constant was not examined.

The effect of rate constant uncertainty was calculated by increasing the nominal rate constant(s) of interest by twice the reported uncertainty, resulting in the "perturbed" rate constant(s):

$$k_{per} = (2(\sigma/k) + 1)k_{nom}$$

where k_{per} is the perturbed rate constant, σ/k = normalized rate constant uncertainty (shown in Table 3), and k_{nom} is the nominal rate constant.

Of note, the previously mentioned study by Donahue et al. (14) suggests that the current recommended values, including those used in SAPRC90, overestimated the NO_2 + OH rate constant by approximately 30% for standard temperature and pressure conditions in the lower troposphere.

After modification to the chemical mechanism of each specific rate constant(s), a 3-day model simulation was conducted with the base inventory and each of the 27 perturbed emissions inventories (which have an incremental amount of the VOC of interest added to the base inventory). The results from the simulations using the perturbed inventories and the base inventory were then used to calculate new compound reactivities, which were normalized to the compound suite described above. A comparison was then made between the predicted reactivity scales calculated using the nominal rate constants versus the perturbed rate constants, for each set of rate constants and for each of the three reactivity measures considered. Thus, seven sets of sensitivity simulations were used to recalculate the reactivities of all 27 species being studied, one additional set of sensitivity simulations was used to recalculate the reactivities of the six aromatic species being studied, and one additional set of simulations was conducted for methanol. Of note, even with the reduced set of parameters, this type of analysis is computationally intensive.

Airshed Model Uncertainty Analysis Results and Discussion

Before examining the effects of rate constant uncertainty on VOC reactivity values, the effects on base ozone predictions are examined. Figure 1 shows the percent change in base ozone predictions caused by the targeted rate constant uncertainties, as measured by peak ozone, population exposure, and spatial exposure. For example, when the model is run with nominal reaction parameters (i.e., the base run), resulting predicted peak ozone is 0.179 ppm. After increasing the NO_2 + OH rate constant by twice the estimated uncertainty [$2(\sigma/k)$ as defined above], predicted peak ozone is 0.153 ppm, a 14.7% decrease. The impact of the transposed photolysis rates was examined for two of the reaction sets: NO_2 photolysis and AFG1/AFG2 photolysis. The percent change in base ozone predictions from the same targeted rate constant uncertainties previously calculated using a box model for MIR and MOIR conditions (16) are shown for comparison.

As can be seen in Figure 1, population exposure is the metric that is most sensitive to the rate constant uncertainties, followed by spatial exposure, the box model metrics, and then peak ozone. In particular, as measured by population exposure, NO_2 photolysis, peroxyacyl + NO, and PAN and PPN decomposition rate constant uncertainties caused more than a 100% increase in ozone exposure predictions over the base run. Most uncertainties caused at least a 50% change from the base predictions of population exposure. The probable reason for this metric sensitivity is that these rate changes cause ozone formation to occur earlier in the simulation, while the polluted air mass is still in very populated areas, rather than further downwind where the population is relatively sparse. A slight spatial shift can lead to a large difference in population exposure. The sensitivity of the spatial exposure metric is likely due to slight changes in ozone levels in grid cells that are very near the threshold concentrations (0.12 and 0.09 ppm). The largest change for this metric is in response to the NO_2 photolysis rate constant uncertainty, which caused a 75% increase in the predicted exposed area. All the other rate constant uncertainties examined caused less than a 50% change in the spatial exposure predicted value. The responses of the two box model metrics, MIR and MOIR, generally fall between the grid model spatial exposure and peak ozone metrics, more closely aligning with peak ozone. Peak ozone is clearly the least sensitive grid model measure to the targeted rate constant uncertainties, with the largest impact being less than 20%. Overall, the NO_2 photolysis rate constant had the largest effect on ozone prediction for all grid model metrics, while NO_2 + OH had the largest impact on box model metrics. The reaction sets lead to the same directional changes in ozone predictions for all metrics (decreases for NO_2 + OH, peroxyacyls + NO_2, and O_3 + NO; increases for all others.) It is important to note that, while the uncertainty effects on base ozone predictions is an absolute measure; the effects on relative comparisons of compound reactivity may be quite different.

For the set of 27 VOCs examined, Figure 2a−c compares normalized reactivity predictions from the base case run, each rate constant perturbation run, and the box model MIR and/or MOIR scales discussed previously. Figure 3a−c compares the same information for the six aromatics with the AFG photolysis uncertainty runs. Species on the y-axis are listed in order of increasing base reactivity as measured by spatial exposure. Figure 2a,b, the spatial and population exposure predictions respectively, show the best general agreement with the box model scales. Figure 3a−c exhibit essentially the same relative reactivity rankings for each metric with both the box and airshed models.

The rate constants to which the reactivities of most compounds are the most sensitive appear to be dependent on the metric examined. Both exposure measures (Figure 2a,b) appear to be most sensitive to the change in aldehyde photolysis rates, with some compounds showing sensitivity to changes in the NO_2 + OH and the peroxyacyls + NO_2 rate constants. Looking at reactivities based on peak ozone (Figure 2c), rate constants for PAN and PPN decomposition, NO_2 photolysis, peroxyacyls + NO_2, and the NO_2 + OH
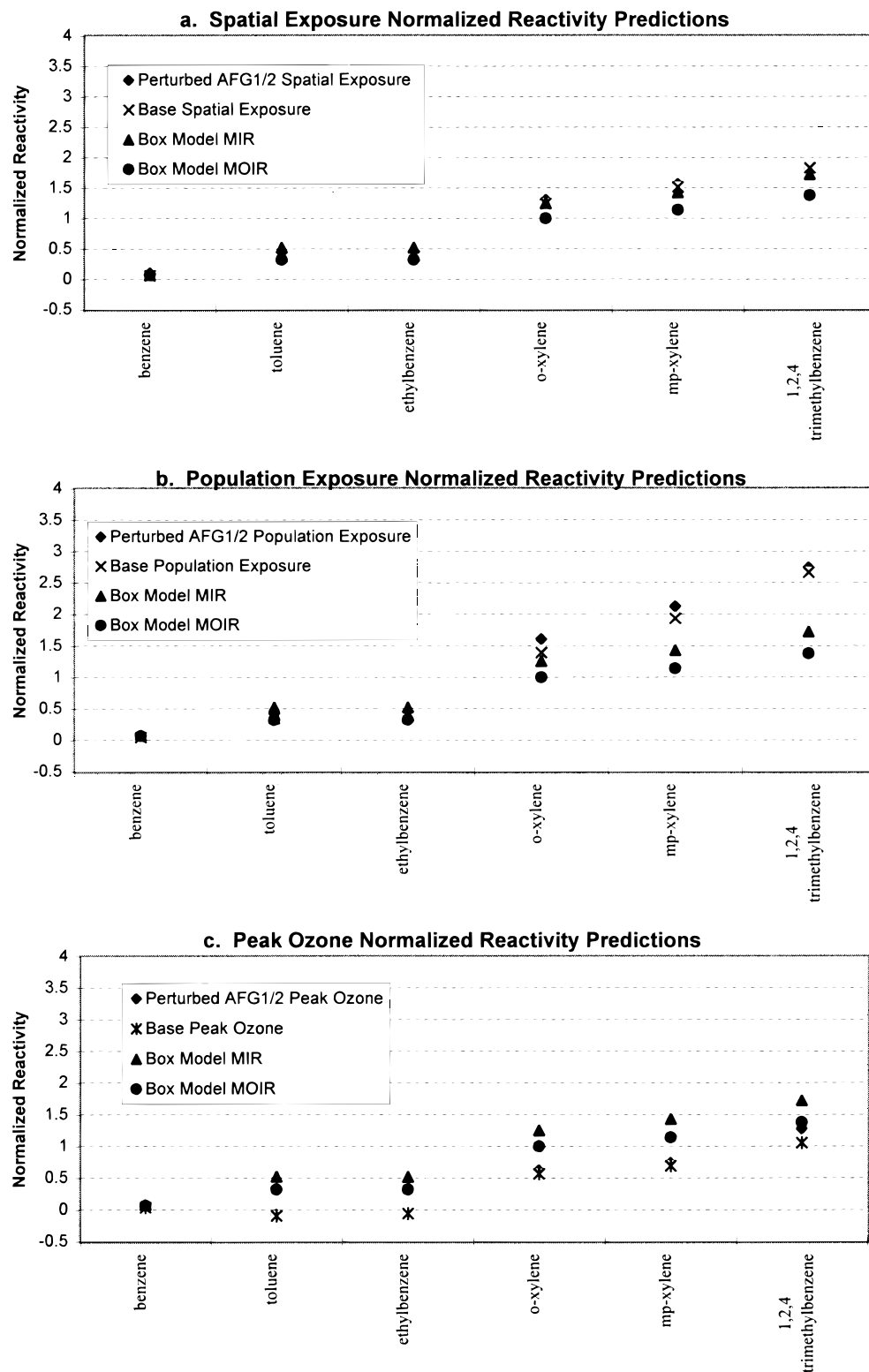
a. Spatial Exposure Normalized Reactivity Predictions

Legend:
- ◆ Perturbed AFG1/2 Spatial Exposure
- ✕ Base Spatial Exposure
- ▲ Box Model MIR
- ● Box Model MOIR

X-axis: benzene, toluene, ethylbenzene, o-xylene, mp-xylene, 1,2,4 trimethylbenzene

Y-axis: Normalized Reactivity

b. Population Exposure Normalized Reactivity Predictions

Legend:
- ◆ Perturbed AFG1/2 Population Exposure
- ✕ Base Population Exposure
- ▲ Box Model MIR
- ● Box Model MOIR

X-axis: benzene, toluene, ethylbenzene, o-xylene, mp-xylene, 1,2,4 trimethylbenzene

Y-axis: Normalized Reactivity

c. Peak Ozone Normalized Reactivity Predictions

Legend:
- ◆ Perturbed AFG1/2 Peak Ozone
- ✻ Base Peak Ozone
- ▲ Box Model MIR
- ● Box Model MOIR

X-axis: benzene, toluene, ethylbenzene, o-xylene, mp-xylene, 1,2,4 trimethylbenzene

Y-axis: Normalized Reactivity

FIGURE 3. Normalized reactivity impact of AFG1/AFG2 photolysis uncertainty.

reactions all appear to have some effect. Comparing Figure 2, panels a–c, it can be seen that the overall range of reactivities from the rate constant uncertainty calculations is often smaller than the differences in reactivity between metrics, particularly between the exposure metrics and the peak metric. Another interesting feature to note in these figures is that the MIR and MOIR reactivities for many compounds fall outside of the rate constant uncertainty range of the CIT-S90 metrics; however, the relative ranking is similar.

Formaldehyde exhibits the highest reactivity sensitivity to uncertainty of all the tested compounds as measured by each metric.

To summarize the uncertainty results, Figure 4 shows the normalized standard deviation (NSD) of the calculated reactivities for each compound and metric. NSD is defined here as the standard deviation of the reactivity values predicted from each rate constant uncertainty run divided by the base-predicted reactivity value, multiplied by 100%.
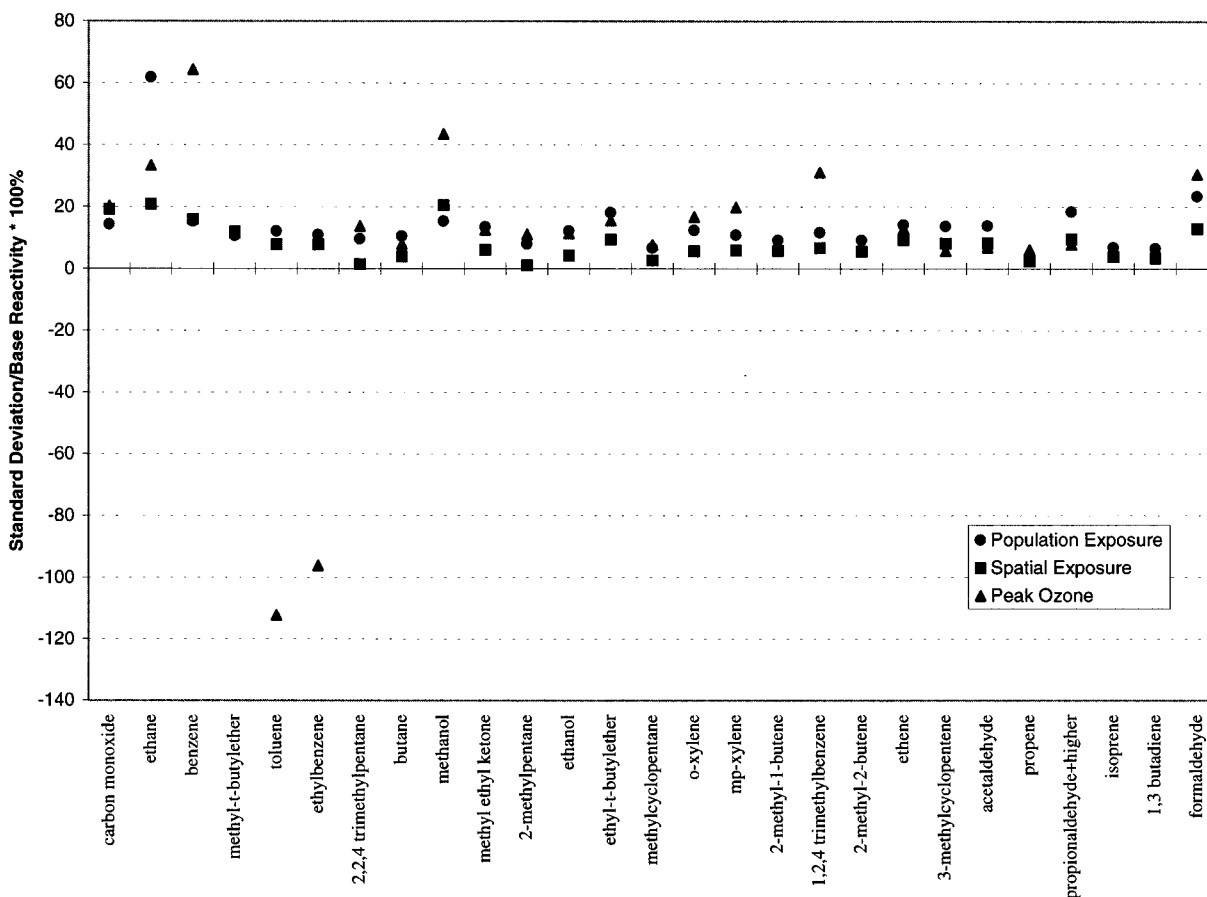
FIGURE 4. Effect of 2σ rate constant perturbations on normalized reactivities for CIT metrics.

It should be noted that the $2(\sigma/k)$ rate constant changes were all positive, so the spread of reactivity predictions for the rate constants tested is represented in this figure, not the direction of response. As shown in Figure 4, only a few compounds exhibit NSD values greater than 20%, a low response to $2(\sigma/k)$ changes in the rate constants studied. For peak ozone, two aromatics—ethylbenzene and toluene—exhibit unusually high NSDs, -89% and -104%, respectively. This is caused by the $NO_2 + OH$ reaction rate constant uncertainty, as can be seen in Figure 2c, and is magnified because the compound reactivities are close to zero. These two compounds also respond differently when comparing reactivities between models and metrics. One reason for this is that the impacts of the organic nitrates (PAN and PPN) formed by these compounds are affected by the spatial representation of pollutant distributions in the model used, which is different between single-cell and airshed models. For example, the peak ozone metric predicts slightly negative reactivities for these compounds, but the exposure metrics predict slightly positive reactivities. Other compounds with high NSDs for some metrics include 1,2,4-trimethylbenzene, which is fairly reactive and also an aromatic; ethane and benzene, which have very low reactivities; and methanol and formaldehyde, for which the key rate constant estimates have recently been improved (24).

In summary, results indicate that the use of different metrics in determining compound reactivities as well as the differences between single-cell and airshed model predictions have a larger impact on relative reactivity predictions than do rate constant uncertainties for the compounds and reactions examined. Compound reactivity values as calculated using the three metrics explored here responded differently to rate constant uncertainties. The population-weighted metrics respond more to changes that impact ozone

in the most densely populated areas, which are also in the more dense source regions. For example, the $NO_2 + OH$ rate constant is important in this region due to the high NO_2 concentrations as well as to the OH limitation in oxidizing VOC. Further downwind, other reactions start to have an increasing impact, e.g., radical–radical reactions and the PAN decomposition/formation rates. The peak ozone metric is more sensitive to those uncertainties but also is impacted by numerical limitations (due to the advection solver) since, often, the change found was very small and the brute-force differencing loses accuracy. Additionally, our uncertainty analysis results indicate that a rather small set of rate constants are influential, presenting a limited number of specific opportunities for increasing confidence in gas-phase chemical mechanisms. One significant step is revisions recently made to the SAPRC mechanism to incorporate new recommendations for PAN chemistry and HCHO photolysis reactions (24). Also, a small number of compounds exhibited large responses to the rate constant uncertainties, in particular ethylbenzene and toluene. Because toluene and ethylbenzene lead to organic nitrate formation, these compounds may increase *or* decrease ozone concentration predictions, depending on the metric examined, the nominal rate constant value, and the local conditions. Changes in ozone predictions as measured by different metrics and the responses of these metrics to rate constant uncertainties are critical when considering how to measure ozone impacts for evaluating potential control strategies and in assigning federal standards.

Acknowledgments

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