Assessment of Research Studies in Addressing Key Reactivity Policy-Relevant Questions

Question	UCR -- Carter	GT -- Russell	MCNC -- Arunachulam	Reviewer's Comments
1 What is the hypothesis that we want to test?	It is possible to develop a means to quantify differences in ozone impacts of the major classes of emitted VOCs sufficiently well that these relative ozone impact quantifications can be effectively used in VOC regulations to reduce ambient ozone levels. For this to be the case, it is necessary to show the following: ► That VOC regulations, either by themselves or on conjunction with NOx controls, are effective in reducing ground level ozone at least in some regions that are of concern to policy makers; ► That relative ozone impacts of the major classes of VOCs are not so variable over time and space that it is not possible to derive a meaningful relative ozone impact quantification; and ► That differences in ozone impacts among the major classes of VOCs are sufficient to make the effort of researching and implementing reactivity-based regulations worthwhile.	The hypothesis is whether or not reactivity scales that are calculated through three-dimensional regional air quality modeling, can offer a quantitative measure to rank different organic species, based on their relative importance in photochemical ozone production, and if such scale could prove useful and applicable in developing and evaluating VOC-based pollution control strategies. In particular: ► Are VOC reactivity scales stable and robust? • With respect to different regions? • With respect to varying meteorologies? • With respect to changing emissions? ► Are species' reactivities different enough from each other to warrant using a regulatory mechanism to account for the variations in reactivities? ► Are multi-dimensional air quality models the appropriate tools to develop reactivity scales?	While the overall objective of this project is to generate scientific evidence in support of EPA's reactivity policy with respect to emissions controls for attainment of the air quality standards, the specific goal is to: ► Perform modeling and analyses using existing state-of-the-art systems like MAQSIP and SMOKE to provide data on the effectiveness of substituting less reactive organic emissions for more reactive ones Thus, the hypothesis that we want to test is: "Can we can develop methods and means to assess individual reactivities of volatile organic compounds (VOCs) in quantifying changes in ozone related metrics?"	
2 What would be the effect on ambient air levels of substituting low reactive compounds for highly reactive ones?	The incremental reactivities and large scale substitution calculations carried out for this project indicate that substituting low reactive compounds for highly reactive ones will reduce ozone levels, though the amount of reduction varies throughout the regional modeling domain, and the effects of the substitutions are relatively small in much of the modeling domain. The latter result is because much of the modeling domain consists of areas that are very NOx-limited or dominated by biogenic emissions. However, the areas where the substitution effects are small are also the areas where O3 is very insensitive to total anthropogenic VOC emissions. For example, replacing all anthropogenic VOC emissions with ethane was found to have O3 reductions that were ~80% those caused by removing all anthropogenic VOC emissions, with the most significant ozone reductions generally occurring in the same regions.	Our effort is aimed at quantitatively calculating the reactivity of a range of compounds from high to low reactivity. If we show that there is a wide range in reactivities from species to species, and that the reactivities are substantial, this will show that the substitution of a low reactivity compound for a high reactivity compound will lower ozone. Further, our results will show over what spatial extent this holds true. Also, it will show if this is true for different meteorologies. Our results to date suggest that the reduction in ozone concentrations due to such substitution will show a high temporal and spatial variability. The effect of substitution is more in areas that are heavily affected by anthropogenic (NOx and VOC) emissions, where high ozone concentrations are more of a concern. Since the 3D reactivities are calculated on a relative basis, a similar question is how big a substitution is required for each VOC to reach the same level of improvement in air quality.	Given that about 75% of the total VOCs in the domain are biogenic in origin, and that the various substitution scenarios modeled for this project involve the smaller portion of the anthropogenic VOC emissions (20% of total VOCs are from area and point sources), the effect of substituting low reactive compounds for higher reactive ones are not significant in such environments. The reduction in ozone (seen by various metrics identified for this project) though somewhat small in magnitude, varies by geographic region; however, majority of these reductions occur in regions of high anthropogenic VOC emissions (e.g., urban and industrial).	

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3	**Would controlling only the most reactive compounds (while exempting lower reactive compounds) have any significant impact on ambient ozone levels?**	Large scale substitution calculations to examine this probably will not be conducted for this project, but the effects can be estimated using the incremental reactivity results. Such an analysis has not yet been conducted but will be done for the final report. It is expected that the result will be qualitatively similar to the ethane substitution results; i.e., such substitutions will reduce ozone in the same areas where reducing mass emissions of anthropogenic VOCs are effective.	Our study addresses this issue directly by providing quantitative information as to how ozone will respond, on a species-by-species basis, to removing specific compounds, including highly reactive VOCs. When combined with an emissions inventory of the VOCs, one can calculate the level of expected improvement. What we have found is that, while such large-scale substitution should have a significant effect on ozone levels, the specific reduction levels for each location and time, to some degree would depend on the original emission pattern for the domain and episode. It is also important to note that the calculated reactivity values (as well as the other defined reactivity scales) are incremental. Therefore, estimating the effect of large-scale substitutions would entail inaccuracies that stem from linearity assumption for reactivities.	Based upon the substitution scenario that MCNC tested, (substituting Xylene with a Glycol Ether surrogate), we did observe some reductions in the various ozone metrics [Air Quality Index (AQI) counts, Persistence (#grid-cells exceeding a chosen threshold ozone concentration), and Severity (Sum of concentration-weighted grid-cells exceeding a chosen threshold ozone concentration)] that we identified. While these reductions were not large, the test proved that substituting low reactive compounds for high reactive compounds does have an effect on ambient ozone levels. Understandably, these impacts were seen mostly in areas with high levels of Xylene emissions in the basecase. It should also be noted that the impacts for 1-h O3 based metrics were slightly larger than those based upon 8-h O3.	
4	**How would low reactivity compounds emitted in large volume affect ambient ozone levels? Could widespread exemption of lower reactive compounds cause the ambient air quality standard to be violated in certain locations?**	As long as the "low reactivity" compounds are not inert or ozone inhibitors, increasing their emissions would necessarily cause ozone to increase in VOC-sensitive areas. Exemptions would only have an environmental benefit if they resulted in reduced emissions of more reactive compounds. The amount of reduction of more reactive VOCs that would result from an exemption will depend on the properties and cost of what is exempted and the economics and requirements of the industries or consumer activities that are affected.	The largest relative impact of low reactivity compounds is in areas where the impact of additional VOC emissions is low. But in areas near non-attainment with substantial NOx emissions, further emissions of large amounts of low reactivity compounds could lead to violations. Also some compounds that appear to be of lower reactivity in box modeling appear to have a higher reactivity when we use grid models on large regional areas. Furthermore, extrapolating the results from incremental reactivities to large-scale substitution may not be very accurate. Such large change in emission characteristics can cause non-linear response in terms of reactivities. However, relative reactivities are fairly insensitive to such non-linearities. Evaluation of the effect of large volume of low reactivity compounds is beyond the objective of this project, but the findings suggest that if the increase in low reactivity VOC emissions is more or less coupled with respective decrease in the emissions of highly reactive compounds, the ozone levels will decrease in most places.	To test a higher species exemption, we simulated a strategy where 15% of all VOCs from area and point sources were substituted with MEK. While this strategy does not exactly address the first part of this question, the results from this scenario are somewhat relevant here. The results from various metrics for this scenario showed some improvements with this substitution, showing that large volume of low reactive compounds still contribute to ozone, but not as much as with more reactive VOCs in the base mixture. To explicitly answer this question, we need to perform another simulation where the low reactive compounds are allowed to increase along with the substitutions.	

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5 **What is the geographical validity of reactivity scales? Are scales valid over the whole country or only in certain locations? If not, how large are variations? What would be the cause of the variations?**	Geographical variability of relative reactivities is expected because relative reactivities are known to depend on environmental factors such as relative NOx levels, availability of radical sources and sinks, the presence of other pollutants, etc. A major objective of this and most of the other Task 1579.1 projects is to assess this issue. The results to date indicate that scales are only valid in areas where there is at least some minimum sensitivity of O3 to anthropogenic VOCs. However, VOC regulation is not relevant to reducing O3 in areas where this is not the case, so a VOC reactivity scale would be equally irrelevant in such areas. There is variability in the relative reactivities in the VOC-sensitive areas, but for most of the major types of VOCs the variability is small compared to the differences between the highest and lowest reactivity classes.	This is a major portion of our study. We are calculating the spatial reactivities of compounds, and comparing those reactivities to studies conducted for other parts of the country. The scales that are developed as part of this project are relative scales. While absolute reactivities show a great deal of spatial variability, relative scales are fairly constant. These scales for different regions (remote NOx-limited, or urban VOC-limited, or high biogenic areas), different episodes (with high or low ozone levels), different control scenarios, and different domains (Western or Eastern US) are similar, although some notable differences exist (e.g., the significant difference in formaldehyde reactivity in the East and West). The variability in the reactivity scales is mainly due to different emission pattern, chemical regimes, and meteorology.	Reactivity scales for the various substitution scenarios do vary geographically, especially from NOx-limited to VOC-limited environments. In a VOC-limited environment, the VOC reactivity scales do vary depending on the original VOC/NOx ratios in a particular area. We performed VOC substitution scenarios in two different domains, the Eastern US and the Southeastern US (over Texas). Overall, the effects on many of the metrics computed over the Eastern US were larger than those in the Texas modeling domain. For more detailed analysis we need to look at sub-domains. These sub-domains could be identified in a simplistic manner, like urban versus rural, or by computing VOC/NOx ratios and categorizing different grid-cells based upon specific cut-offs. Using the latter approach, we found the largest ozone reductions in the VOC-limited grid-cells, and the reductions decreased as the grid cells shifted from VOC-limited to NOx-limited. We also saw ozone increases for some substitution scenarios; the cause for these increases is being investigated.	
6 **How do initial conditions affect reactivity scales (i.e., VOC/NOx ratios)?**	The effects of initial conditions such as VOC/NOx ratios on reactivity are most directly examined by using box model calculations, and a number of such studies have already been carried out. The regional models also indicate the effects of variabilities on conditions, since the variable conditions are what cause the geographical variability as discussed above. The technical reasons for why certain conditions affect reactivities have been assessed and discussed previously, though process analysis can be used to elucidate this further, if needed.	We are applying our models over multiple days both to address this issue and make sure that our results are less susceptible. Our previous tests show that ozone sensitivity to initial ozone, NOx, or VOC fades away fairly fast (2-3 days) into the simulation. As the first two days are considered ramp-up period, the effect of initial conditions is considered minimal. On the other hand, boundary conditions of NOx/VOC may have a more significant effect on the absolute reactivity levels, but relative reactivity scales remain fairly insensitive.	▸ ***Initial conditions based upon VOC/NOx ratios*** The reactivity scales are quite dependent upon the VOC/NOx ratio prevalent to begin with, and the impact that we can see for a substitution scenario depends on whether the cell is VOC-limited or NOx-limited in the base case. ▸ ***Initial conditions for ozone*** The initial conditions for ozone we used in the base case modeling for the Eastern U.S. were derived from a gridded global ozonesonde database. This results in somewhat higher initial conditions for ozone within the boundary layer. To test the ‘impact of IC specification’, we performed additional sensitivity simulations by initializing ozone within the first 2 km of the vertical modeled domain to 35 ppb. Similar vertical profiles were also used for the lateral boundary conditions. Overall, the relative reductions seen in the second set of simulations with reduced ICs were comparable to those calculated in the first set.	

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7	**How does meteorology affect scales?**	Meteorology will affect reactivity scales through at least two mechanisms. Meteorology affects emperature and light intensities, which affects rates of essentially all the ozone formation reactions. A less favorable meteorology for reaction rates (lower temperature or light intensity or duration) will have a similar effect as reducing VOC/NOx ratios and may tend to increase the extent of the domain that is VOC sensitive, even though it would decrease ozone levels. Meteorology also affects the transport of pollutants from one area to another, which in effect changes the nature of the physical and chemical scenario being examined. Different transport patterns in different meteorological episodes can result in significant variability in geographical distributions in ozone and reactivity in the same region. Thus, reactivities can vary from day to day in any given location, just as they vary from location to location in any given day.	We are modeling two different episodes, both with about 8 days each. For the July 1995 meteorology, ozone levels were high over part of the period, but not all. The May 1995 period had more moderate levels. The range of conditions over the periods is very large, so we can assess how meteorology impacts results. Meteorology is one of the major sources of variability in absolute reactivity scales. Meteorology can affect the chemical dynamics of the atmosphere (temperature, sunlight, and humidity are all very important factors in ozone production), but more importantly it defines the emission distribution pattern (through transport) of the pollutants in the domain. For this reason, modeling different episodes and days is important. Relative reactivity scales for most species show low day-to-day variability, while some other species (e.g. formaldehyde) appear more sensitive to meteorological regime.	The reactivity impact metrics considered in this analysis generally vary from day-to-day depending upon the prevailing meteorological conditions for that episode day. The episodes that were chosen for modeling here (extreme events identified to support SIP development for ozone non-attainment areas) were already high ozone events, showing a gradual build-up of high ozone due to a combination of meteorological parameters. The scales computed from the modeling vary on a temporal as well as spatial basis. Some of the metrics computed for this project show a higher response to a substitution strategy on a high-ozone day than on a low-ozone day [e.g. the second half of the June 19-30, 1996 episode had higher ozone levels than the first half, and the response of the reactivity metrics computed are larger in the second than in the first half of the episode]. A more detailed assessment needs to be performed to study the correlation between meteorological parameters and reactivity scales.	
8	**Do reactivity scales shift if reactivity is evaluated over different lengths of time? (i.e., would a scale evaluated over 8 hours differ from a scale evaluated over 5 days?)**	The preliminary results of this project indicate that there are only very minor differences between regional reactivity metrics derived based on 8-hour averages compared to those derived based on 1-hour average data. Evaluating scales over longer periods of time have not been carried out, but could be done for periods of up to 4 days if desired. I suspect that the results would not be greatly different.	Again, we are modeling relatively long episodes from which we extract both day-by-day reactivities and averaged long-term averaged reactivities. We have evaluated different reactivity scales for 1 and 8-hour periods. For the most part, relative reactivity scales for those two averaging periods are very similar to each other.	From the metrics computed for the different substitutions scenarios modeled here, the reactivity scales are larger in the case of 1-h O_3 than for 8-h O_3. Furthermore, the choice of a threshold level seems to have influence on the extent of the reactivity impacts. Tables 1 and 2 show the episode-composite percent reductions computed for persistence and severity at thresholds of 125 and 80 ppb for 1-h O_3, and at thresholds of 85 and 60 ppb for 8-h O_3 over the 36 and 12-km domains respectively. For all the substitutions investigated here, the reductions in the case of 1-h O_3 metrics are higher than those for 8-h O_3. Also, there seems to be larger reductions at a higher threshold, indicating that most of the reductions are occurring in cells that had high ozone to begin with.	

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9	**What is sensitivity of scales to different conditions? For example, do compounds' position on the scale flip-flop with different conditions?**	The sensitivity of reactivity scales to different conditions was discussed above under questions 5 and 6, above. Many relative reactivities can "flip-flop" if we include very low VOC sensitive regions where reactivities are highly variable and often negative. However, cases of scale flip-flops are much less common among the major classes of compounds in regions where ozone has at least some sensitivity to VOCs. A few compounds such as styrenes and cresols have reactivity characteristics similar to CB4's "TOL" model species, whose reactivities relative to other VOCs can vary significantly even in VOC sensitive regions. However, these compounds are relatively few and not typical of the major groups of compounds affecting ozone formation.	As mentioned before, we are studying this issue by using two different episodes and both 1995 and 2010 emissions. Absolute reactivity values have been found to be sensitive to different environmental conditions. Domain-wide relative reactivity scales, on the other hand, are much less sensitive to factors like emissions pattern, meteorology, and chemical regime. Based on the results from different domains and episodes, the ranking of domain-wide relative reactivity scales is not greatly affected by those conditions.	Most of the high reactivities were observed only in VOC-limited regimes, and even for the same substitution strategy, some cells showed counter-benefits under NOx-limited environments. The reactivity scales that we computed for the Eastern U.S. showed different responses in the 36 and 12-km modeling domains. From our data we see that the responses in the 36-km Eastern U.S. domain were higher than those obtained in the 12-km domain centered over NC. This is likely due to the fact that the 12-km domain on the whole is relatively more NOx-limited than the 36-km domain, and the 12-km domain does not include grid-cells which showed maximum responses to the substitution scenarios (like those areas downwind of Chicago and New York which are more responsive to the substitutions).	
10	**Should we be looking at other kinds of scales than MIR scales? What other scales should we look at? Would we want to evaluate how other types of scales vary with varying conditions?**	Ultimately we should look at reactivity scales that take into account ozone impacts under the full range of conditions for which VOC control is relevant, using an appropriate method to weigh the differing impacts under the different conditions. Different regions and meteorologies should be modeled to determine the appropriate criteria and regions that should be used to derive a general regulatory reactivity scale, though for practical regions the actual scale would probably be based on only a subset of regions chosen to be representative. The choice of the best weighing criteria and most appropriate set of regions to base a reactivity scale requires policy input. Use of MIR is based on deriving a reactivity scale that represents the regions that are the most sensitive to VOCs. Obviously the impacts in these regions should be given weight, but an argument can be made that impacts in the more widespread lower NOx regions where O3 still has non-negligible sensitivity to VOCs should be considered to at least some extent.	To address this issue, we are calculating various reactivity scales and assessing their robustness and utility. We have looked at four domain-wide relative reactivity scales, i.e. MIR-3D, MOIR-3D, exposure, and least square fit. All these scales are found to be very similar. Therefore, any domain-wide relative reactivity scale should result in a fairly similar ranking for VOCs. This said, some scales have a higher significance, e.g., MOIR (because of it's direct regulatory impact), and population exposure. However, MOIR is based on results at one point, and is thus more erratic.	We have used scales other than MIR [AQI, Persistence, Severity] for evaluating the efficacies of different substitution scenarios. All these scales have been evaluated for their response under varying conditions. With additional resources, there is scope for more detailed evaluation. For instance, all these scales have been evaluated only on a domain-wide basis for each of the modeling grids. To isolate the response of the modeling system by geographic region (urban vs rural, attainment vs non-attainment areas within a given modeling domain), it is desired to subset the data on a spatial basis, and then perform the analyses. This might yield information on whether the scales are responding in areas that matter from a NAAQS perspective.	

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11	**What atmospheric model is used to evaluate validity of reactivity scales? Is this model one that is widely used and available to various independent researchers so that work can be verified and peer reviewed? Is a proprietary model of value if it is not widely accessible to everyone?**	The model used should represent the best science that has been adequately evaluated and quality assured, and the model should incorporate the appropriate level of chemical detail needed for VOC reactivity assessment . Peer review is the established means for assessing scientific quality and thus is probably essential for a model to be used for a regulatory scale. A widely-used model is more likely to be more thoroughly debugged than one that is newly developed, and should be preferred for this reason. If a new model is significantly better scientifically, sufficient time should be made available for it to be evaluated by independent groups before it is used for regulatory applications. Proprietary models should not be used unless there is no other scientifically acceptable alternative, and only then if they are accessible to independent environmental, industry, academic, as well as government groups, only if the scientific algorithms are published and thoroughly quality assured, and only if the documented source code is made available at least to peer reviewers.	Here, our results can be compared to our previous studies using two different 3-D models, and to the other two groups using two other models. We used an updated version of Urban to Regional Model (URM), which has been used in a number of previous studies and is available to all interested parties. For a similar study we have used a different model (MAQSIP) for a different domain (California). The results of the two studies are very comparable. In the future, we propose using CMAQ.	MCNC used the Multiscale Air Quality Simulation Platform (MAQSIP), a comprehensive atmospheric gas-aerosol model for this project. MAQSIP, developed at MCNC, served as the prototype for the Models-3/CMAQ modeling system, and has been applied at various scales from local to regional to global for regulatory as well as scientific research applications. MAQSIP is available freely in the public domain for the research and regulatory community to download and develop applications for their own needs. Both MAQSIP and CMAQ include state-of-the-art scientific components, and have several common features, both being flexible, modular and scalable. Applications developed using MAQSIP can be somewhat easily migrated to CMAQ if chosen at a later stage of the project. MAQSIP uses the I/O API format for inputs and outputs which make it very easy to migrate from one platform to another. A proprietary model should not be used for a project like this, since this might serve as the basis for a future regulation.	
12	**What is the sensitivity of reactivity in the model? Are all compounds lumped into a few bins? Is carbon bond IV, which lumps compounds into 11 reactivity bins, sensitive enough to evaluate reactivity scales? Is there a better way of handling reactivity in models? If so, what?**	The software and mechanisms now exist to separately represent and calculate relative ozone impacts of the ~500 or so different classes of organics with known or estimated mechanisms when using box models. Regional models can be adapted to calculate full reactivity scales. Although the computational burden using regional models for all the ~500 species would be large, it is not outside the capability of today's computers. It is almost certainly possible to estimate reactivities for the full range of species based on results of smaller numbers of calculations after research on relationships between various types of mechanisms and reactivity patterns. It may also be possible to derive a set of box models to give the same type of distribution of reactivity as one would obtain in regional models. This would permit reactivity scales to be computed and updated as readily as is now the case for MIR and the other EKMA-based scales and probably would be the best long-term solution. The Carbon Bond IV mechanism is out of date and its regulatory use should be phased out.	Our results will provide a continuous reactivity scale. Policy makers can view the results and suggest if binning is sensible and if natural breaks occur. We have calculated reactivity scales for about 30 explicit species, as well as 10 lumped VOCs, using SAPRC-99 chemical mechanism. A detailed chemical mechanism is favorable for reactivity study, and the results are more reliable.	The Carbon Bond IV (CB4) mechanism, a condensed mechanism lumping VOCs into 11 groups of modeled organic compounds, it is a good starting point in assessing reactivities for various compounds because it has been widely used in regulatory modeling. Using both CB4 and the Regional Acid Deposition Model (RADM2) mechanism, we substituted Methyl-ethyl ketone (MEK) for VOCs. While the RADM2 chemical mechanism includes a model species KET as a surrogate for MEK, we explicitly added MEK chemistry in the CB4 mechanism in MAQSIP. Although detailed chemical mechanisms might be preferred to evaluate reactivity scales, their computational burden may be a deterrent for studies involving repeated modeling simulations and analyses. To compare the effects of a condensed mechanism like CB4 and a detailed chemical mechanism like RADM2 or SAPRC99 on reactivity scales, one should make the VOC substitutions with each mechanism over the same modeling domain and time period, then compare the resulting reactivity scales and metrics.	

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13	**Are effects of grams versus moles being considered? If a certain percentage of VOC is being reduced in a model, is this by weight or by number of moles? If one compound is being substituted for another in a computer run, is this substitution being made by weight or by number of moles? How will this affect the outcome of the experiment?**	The grams vs. moles issue is not relevant to application of California-type reactivity weighting regulations because the VOCs are all compared and regulated on an estimated ozone impact basis. If regulations are based on moles, the reactivity scales should give ozone per unit mole, while if they are based on mass they would give ozone per unit mass. In either case, once the amounts are multiplied by the reactivity scale in the appropriate units the results are the same. Note that the differences between mass- or mole-based substitutions will depend on the types of compounds being substituted. For compounds with average molecular weights it will not make any difference. The average molecular weight of the EPA emissions profile used as the base ROG in our project is around 70, which is similar to that for C5 hydrocarbons, MEK, or ethylene to propylene glycol. Realistic substitution calculations should be based on our best estimates of how emissions would actually change if substitutions are carried out.	We view this as, ultimately, a non-issue. Mole-based reactivities can be converted to gram-based reactivities and vice versa. Any calculation conducted without a very, very large perturbation should see virtually no effect. The incremental reactivities are calculated based on the unit mass (grams or moles) of VOC emitted. In the calculations, and because of the linear approximation of the reactivity, gram-based or mole-based perturbations give identical results. Of course, for each unit a different value for relative reactivity scales are calculated. The choice of the units, is mainly a regulatory decision.	MCNC made its VOC substitutions and performed its analyses on a gram-, a mole-, and a molC-basis. When VOC emission reductions are made across-the-board by a certain percentage, the distinction between gram-based and mole-based reduction is irrelevant because both yield the same amount of reduction. When a specific VOC species is substituted with another, it is important to distinguish between gram-based, mole-based or molC-based substitution, although stoichiometric calculations are based upon species reacting on a molar basis. Also the distinction will vary depending on the types of compounds being substituted and the type of substitution implemented (e.g., fraction of total VOC, or fraction of individual, or group of compounds). Low molecular weight species will respond differently than high molecular weight species, and the net mass after substitution might be more or less than the original mass of emissions. For our MEK substitutions, the responses in ozone metrics were higher in the case of grams-based substitution than with mole-based or molC-based substitutions.	