

Technical Challenges Involved in Implementation of VOC Reactivity-Based Control of Ozone

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Controlling VOC emissions on the basis of their individual contribution to ozone formation has been subject to extensive discussion and research in past years, and the concept has gained some acceptance in the air pollution community for certain product categories and industrial operations. Despite its potential to decrease ozone formation, there are some technical challenges that still remain before we can confidently apply the concept of reactivity in the most beneficial manner to reduce ozone concentrations. The goal of this paper is to (1) assess how existing science in this area supports the use of reactivity, particularly, the maximum incremental reactivity, for VOC control under a national policy application and (2) identify where uncertainties exist that could affect such a policy. Box model and air quality model results are used to show that there are ways to describe a chemical's reactivity that are relatively robust across large geographic areas. Modeling results also indicate that the choice of metric is important in determining the potential benefits and detriments of a reactivity-based emission control policy.

Introduction

In the air pollution community, "reactivity" describes a chemical's potential to produce a pollutant of interest. For ozone formation from volatile organic compound (VOC) emissions, reactivity quantifies a VOC's potential to produce ozone. Different VOCs can produce vastly different amounts of ozone. Ethene (C₂H₄), for example, can produce over 14 times more ozone than ethane (C₂H₆) under the same conditions (1). Because of these chemical differences among VOCs, ozone control efforts might be more efficient and cost-effective if they focus first on emissions of high ozone producers rather than decreasing all VOCs equally or allowing disproportionate decreases in low-reactivity compounds.

There have been many analyses and studies on using the range of VOC reactivities to improve air quality (2–5), including much work compiled by and sponsored by the California Air Resources Board (CARB) (listed at <http://www.arb.ca.gov/research/reactivity/reactivityresearch.htm>) and the Reactivity Research Working Group (listed at <http://www.narsto.org/section.src?SID=10>).

Despite the substantial research in this area, reactivity has so far been used to a limited extent for regulatory

purposes. CARB first used the concept of reactivity as a regulatory tool in 1990 for their Low Emission Vehicle/Clean Fuels Regulation (6). A later rule used the maximum incremental reactivity (MIR) to calculate VOC limits for aerosol coatings, such that the reduction of ozone formation would be equivalent to a much larger and more technically infeasible VOC mass reduction (7). This action was approved as a pilot project by the United States (U.S.) Environmental Protection Agency (EPA) in 2005 (8). Texas has used MIRs in cap-and-trade programs for high-reactive VOCs in the Houston/Galveston/Brazoria ozone nonattainment area (9). In these cases, the regulatory uses of reactivity were approved for restricted VOC categories and limited geographical areas.

There is interest in expanding the use of reactivity for other VOC-emitting industrial operations and in other states. The EPA issued guidance encouraging use of VOC reactivity information in the development of ozone control measures (10), and recently finalized national regulations using the MIR to regulate VOC content in aerosol coatings (11). Although research indicates that a reactivity-based VOC control policy has potential for larger decreases in ozone than indiscriminate VOC mass-based reductions (5, 12–15), there are some technical challenges in utilizing the concept of reactivity in other applications and regions. This paper poses four technical challenges that must be addressed before we may confidently apply reactivity-based VOC controls for national applications and discusses how the available literature has addressed them. The discussion is put in the context of a practical application to VOCs in aerosol coatings.

Representing Ozone Formation from Individual VOCs.

The first challenge is accurately representing total ozone production that results from emissions of an individual VOC. This is a multistep process that depends on both the physical (i.e., temperature, sunlight) and chemical (other chemicals with which it interacts) environments and considers ozone formed from all reactive products until either a stable product is formed or the chemical and its products are removed from the atmosphere. Chemical mechanisms describing these reactions have been evaluated under controlled conditions in smog chambers and have been found to reproduce behavior over a large range of VOC and NO_x concentrations (16). There is some evidence for overall ozone underprediction at low VOC/NO_x ratios, where reactivity-based VOC controls are of most interest (16).

Reactivity applications require success in calculating both overall ozone concentrations and ozone formation from each individual VOC. While much is known about the general chemical reactions of the most-abundant VOCs in the atmosphere, there is still some uncertainty concerning the chemistry of many, less-abundant VOCs, including their exact chemical products and subsequent reactions of these products. Approximately 87% of the nearly 800 explicit compounds for which reactivities are available are estimated as being "uncertain" (17). As an example, Table 1 illustrates the range of uncertainty categories for 29 chemicals that are major components of aerosol coatings or their proposed replacements. For these chemicals, estimated uncertainties are largely category 1 or 2, with some exceptions. Dichloromethane is category 6, and an upper limit is suggested to account for this uncertainty (17). Table 1 also shows how updates to the chemistry can change the reactivities: for example, compare MIRs from the SAPRC-99 mechanism with those from an updated version, SAPRC-07 (18). The changes resulting from this update range from a 40% decrease (dichloromethane) to a 38% increase (*p*-xylene) in the predicted MIRs for these compounds. Previous studies have

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TABLE 1. Examples of Uncertainty Categories and Scales Reported by Carter (17) for 29 Chemicals That Are Common Components of or Potential Replacements in Aerosol Coatings^a

compound	uncertainty category ^b	SAPRC-99			SAPRC-07
		MIR	MOIR	EBIR	MIR
propane	1	0.56	0.36	0.26	0.47
<i>n</i> -butane	1	1.32	0.82	0.58	1.10
<i>n</i> -octane	2	1.09	0.70	0.40	0.82
isobutane	1	1.34	0.80	0.57	1.20
isopentane	2	1.67	1.01	0.72	1.38
3-methylpentane	2	2.06	1.20	0.83	1.72
branched C6 alkanes	3	1.52	0.90	0.62	1.25
branched C10 alkanes	3	1.07	0.64	0.35	0.85
branched C11 alkanes	3	0.84	0.52	0.27	0.64
cyclopentane	2	2.67	1.51	1.02	2.28
cyclohexane	2	1.44	0.89	0.56	1.16
toluene	2	3.97	1.17	0.35	3.99
<i>m</i> -xylene	2	10.61	3.19	1.54	9.83
<i>o</i> -xylene	2	7.48	2.46	1.22	7.67
<i>p</i> -xylene	2	4.24	1.36	0.53	5.85
methyl ethyl ketone	1	1.48	0.65	0.42	1.47
dichloromethane	6	0.07	0.04	0.03	0.04
acetone	1	0.43	0.17	0.11	0.36
methanol	1	0.69	0.33	0.21	0.67
ethanol	1	1.69	0.93	0.65	1.47
dimethyl ether	1	0.93	0.58	0.45	0.78
2-butoxyethanol	1	2.88	1.27	0.83	2.83
ethyl-3-ethoxy propionate	3	3.59	1.45	0.91	3.54
methyl acetate	1	0.07	0.05	0.04	0.07
ethyl acetate	1	0.64	0.36	0.26	0.60
propyl acetate	3	0.86	0.51	0.36	0.74
isopropyl acetate	2	1.12	0.62	0.43	1.05
<i>n</i> -butyl acetate	2	0.88	0.53	0.36	0.79
amyl acetate	3	0.94	0.58	0.38	0.78

^a Averages are computed over 39 cities and units are (ozone (g)/VOC (g)). The uncertainty increases with category value. ^b These categories are summarized from ref 17 as follows: (1) reactivity is not expected to change significantly, (2) mechanism may change somewhat if refined, but reactivity changes are expected to be less than a factor of 2; (3) value is uncertain, with possible changes up to a factor of 2; and (6) mechanism is probably incorrect, but biases in reactivity predictions are uncertain. More details on the uncertainty can be found in Carter (17).

reported that although uncertainties in mechanism parameters can change calculated reactivities (19, 20), they generally change reactivities for all VOCs similarly so that relative reactivities do not change substantially.

Defining Reactivity. The next challenge is to define reactivity appropriately. The most commonly used description is from Carter (1) who applied a one-dimensional box model with the SAPRC-90 chemical mechanism, for a 1-day scenario, to develop reactivity scales for a large number of chemicals. Carter (1) defined several metrics, including the MIR, the maximum ozone incremental reactivity (MOIR), and the equal benefit incremental reactivity (EBIR). The MIR represents conditions when ozone is most sensitive to VOC concentrations, the MOIR represents conditions when ozone is maximized, and the EBIR represents conditions when ozone is equally sensitive to changes in VOC or in nitrogen dioxide plus nitric oxide, collectively referred to as NO_x.

Past regulatory uses of reactivity have focused on the MIR metric. To create an MIR scale, NO_x concentrations are adjusted such that an incremental change in VOC produces the maximum change in ozone, under meteorological and chemical conditions representing 39 U.S. cities (1). The MIR does not represent average or common conditions, but times

and areas where ozone is highly sensitive to VOC emissions. Under NO_x-sensitive conditions, controlling VOC emissions will have little effect on ozone, and the incremental reactivity will be lower than the MIR. The average VOC/NO_x ratio used to calculate the MIR is 3.1 ppbC/ppb (17). While a few parts of the country, mainly urban areas, are predicted to have many hours with a ratio this low, many are always predicted to have higher VOC/NO_x ratios, especially in summer, because of high VOC levels. Figure 1a shows the fraction of hours during July, 2001, with a predicted ozone concentration greater than or equal to 50 ppb and a VOC/NO_x ratio less than 3.1. These values were simulated using the community multiscale air quality (CMAQ) modeling system with a 12 km resolution (21). A smaller grid resolution would not dilute emissions as much and would result in more grid cells with smaller ratios, but it would also result in more grids with larger ratios. There are grids around some urban areas, including Houston and Chicago, where ratios less than 3.1 occur often, but most nonurban grids are never this low. When the VOC/NO_x ratio criterion is raised to 6.4, the average EBIR ratio (Figure 1b), many more grid cells are represented. Figure 2 illustrates the distribution of VOC/NO_x ratios for 3600 km² areas (25 model grid cells) around Chicago, Houston, and Atlanta. MIR conditions (ratio less than 3.1) are represented more often in some urban areas than others, but MOIR (less than 4.5) and EBIR (less than 6.4) conditions are more likely to occur. Since MOIR and EBIR metrics do not maximize reactivity, they produce smaller values for reactivity scales than the MIR, as shown in Table 1.

The appropriateness of calculating MIRs from a 1 day episode has been questioned because reactivity differences between compounds decrease when calculated over multiple days (22). It is unclear whether using a one-dimensional box model, which has difficulty accounting for regional-scale chemistry and transport over multiple days, biases the calculated MIR values. To address these concerns, several studies (5, 14, 15, 23, 24) have attempted to determine whether reactivity scales and relative rankings might change when a more realistic, three-dimensional air quality model (AQM) is used in a multiday simulation.

With AQMs, additional metrics can be used to describe reactivity, including seven different three-dimensional metrics representing a range of conditions, such as average conditions, high ozone concentrations, and those relying on least-squares summaries of the data (15) (Supporting Information). In general, most metrics correlated well with each other and rank chemicals similarly by their reactivity. Several metrics, including the minimum substitution error method 1 (MSE1), the regional MIR to MOIR (M2M), and the regional MIR, were found to be robust over large areas with more spatial and temporal consistency than others (25). Figure 3 shows correlations between one robust three-dimensional metric, the M2M, calculated from three different AQMs and box model MIRs, with all metrics normalized to the reactivity of the base (ambient) VOC mixture. The values in these figures are from the CMAQ modeling system, the urban-to-regional multiscale model (URM) previously reported by Hakami et al. (24), and the CAMx model, previously reported by Carter et al. (15) (see Supporting Information). The number of species is limited because these AQMs use condensed chemical mechanisms.

The CMAQ and URM models predict similar values, despite differences in model domain, resolution, episode, and emissions inventory. The CAMx values are similar, but slightly higher for OLE (primarily representative of propene) and FORM (formaldehyde). The M2M metric generally correlates well with the box model-based MIR, but the latter gives smaller values for slower-reacting species and higher values for faster-reacting species. There is more scatter with other metrics that are more broadly averaged than the M2M.

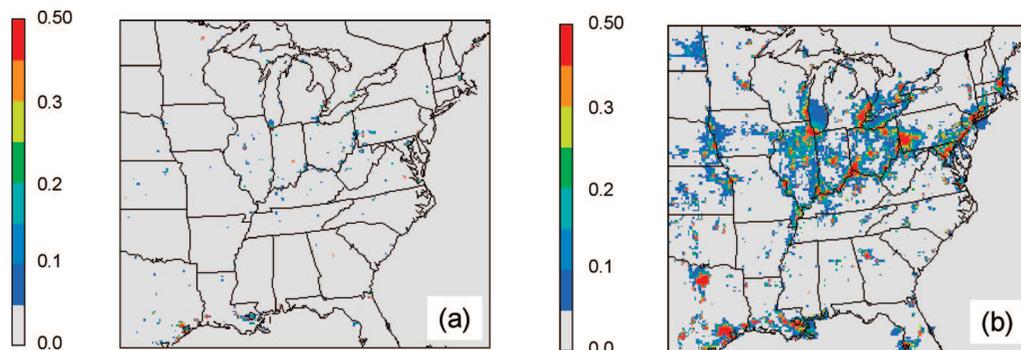


FIGURE 1. Fraction of hours during July, 2001, with predicted ozone concentrations of ≥ 50 ppb and (a) $\text{VOC}/\text{NO}_x \leq 3.1$ or (b) $\text{VOC}/\text{NO}_x \leq 6.4$.

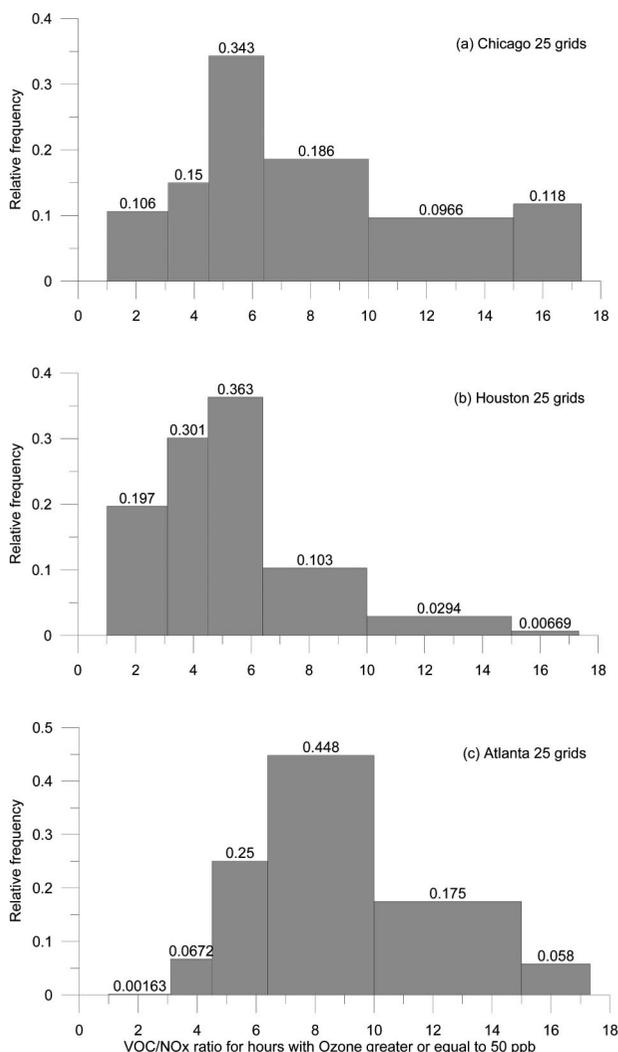


FIGURE 2. Histograms showing VOC/NO_x distributions for 25 grid cells (approximately 3600 km²) around selected cities for all hours in July 2001 with 1 h of ozone greater than or equal to 50 ppb. The leftmost box represents MIR conditions; the next, MOIR; and the next, EBIR.

Carter et al. (15) also show good correlations between one-dimensional MIR values and several other three-dimensional metrics.

The strong correlations among metrics from three different AQMs indicate that choice of model and chemical mechanism does not significantly change the reactivity scales. Good correlations between the realistic, robust three-dimensional metrics and the one-dimensional MIR scale indicate that many features that are important in regional

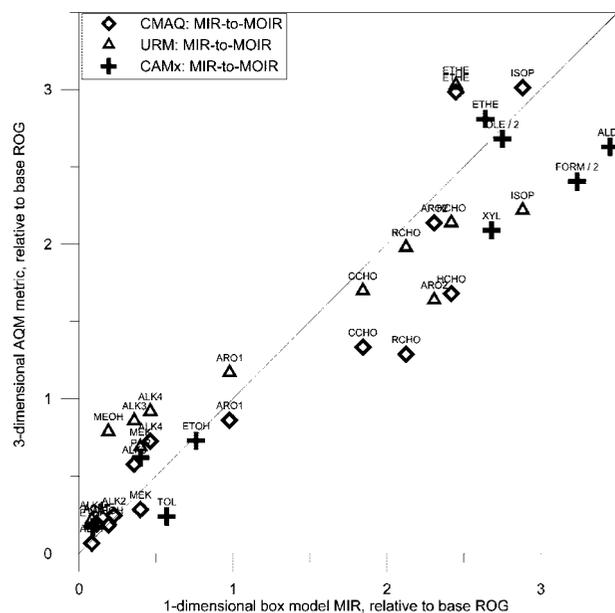


FIGURE 3. Comparison of the three-dimensional MIR-to-MOIR metric for different chemical compounds calculated using the CMAQ model and the values previously reported from the URM (24) and CAMx (15) models, versus the corresponding one-dimensional MIR values from Carter (1). All values are normalized by the reactivity of the base VOC mixture. Chemical species labels are model species names, and the values for CAMx CB4 species FORM and OLE are divided by 2 for scaling purposes.

ozone formation are captured by both AQMs and box models, to the extent that they are represented by the MIR.

Derwent et al. (13, 26) calculated IRs using a detailed chemical mechanism in an air-parcel trajectory model that accounted for multiday, long-range transport, and their scale correlated well ($R^2 = 0.9$) with the one-dimensional MIR scale. Other scales, such as population exposure weighted scales, have also been evaluated and found to be reasonably consistent with box-model scales (5, 20, 23).

While different metrics are generally consistent, the choice of metric is important because the effective range, defined as the spread of reactivities between the most- and least-reactive VOCs, varies widely among metrics. Carter et al. (15) report that carbon bond (CB4) (27) model species OLE is between 19 and 61 times more reactive than ethane, depending on the metric. The use of the aerosol coatings example and the box model results shows that ozone formation from 1.0 g of *o*-xylene is equal to anywhere from 3.4 to 8.5 g of *n*-butyl acetate (Table 1), depending on the metric used. A metric with a larger effective range would allow a greater mass of less-reactive compounds to be emitted, relative to one with a smaller effective range and

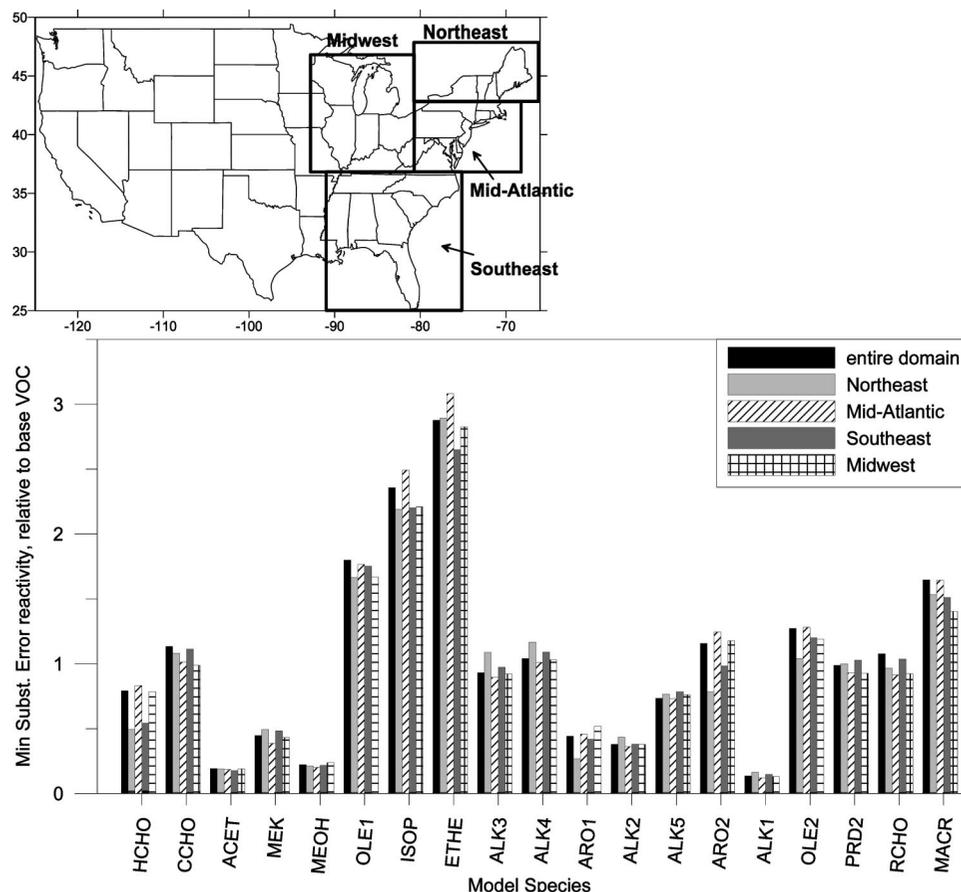


FIGURE 4. Relative reactivities for the entire domain and four different areas of the Eastern U.S. The metric shown is the MSE1, normalized by the reactivity of the base (ambient) VOC mix, for an episode in July, 1999. The labels are SAPRC99 model species which include both explicit and lumped model species.

provides more incentive for manufacturers to substitute high-reactivity VOCs with lower-reactivity VOCs. Reduction of the most-reactive VOCs in aerosol coatings (xylenes and toluene) would provide a multipollutant benefit because these compounds are also hazardous air pollutants (HAPs) and aerosol precursors. Unless specifically prohibited, as in the CARB regulation (7) but not in the EPA rule (11), reactivity-based criteria could provide incentive to increase another HAP, dichloromethane, whose low relative reactivity make it attractive, barring other considerations. In practical application, such countervailing forces as other regulations and raw material costs for greater solvent mass may intervene. While choice of metric affects the degree of substitution and calculation of ozone-equivalent emissions, the application of a reactivity factor results in a more representative comparison regarding ozone formation than considering mass only.

Spatial Variations in Reactivity Scales. Because ozone production depends on the physical and chemical environment, VOCs will produce different amounts of ozone at different areas and times. The third challenge for use of reactivity in a national rule is to determine if reactivity scales are sufficiently constant throughout the entire country and ozone season.

Box model-based MIR values (1) used in previous regulations are averages of calculations over 39 cities whose city-specific MIR values vary significantly. Previous studies have shown that calculating MIRs relative to a base mixture reduces city-to-city variability (5). Because relative values are similar for all cities, using average MIRs will give the same general substitution for solvent mixtures, such as aerosol coatings, as city-specific values (Supporting Information).

AQMs can be used to examine spatial variations in metrics over the U.S. Metrics from the CMAQ model were geographically stratified by dividing the Eastern U.S. into four regions and recalculating the scales for each region separately. Figure 4 shows results for the MSE1 scale and illustrates that the values do not change much from region to region for this metric. CMAQ shows similar regional agreement for the M2M and regional average ozone metrics. Hakami et al. (24) showed similar results in regional comparisons for the Eastern U.S. and California, providing evidence that a properly defined metric does not have significant regional variability. One scale, if formulated appropriately, could therefore be used for the entire country.

Effects of Replacement of Higher-Reactivity Chemicals with Lower-Reactivity Chemicals. Another challenge is to maximize ozone benefits while minimizing unintended, adverse consequences of a reactivity policy. Previous studies have confirmed that when a high-reactivity VOC is replaced by a lower-reactivity chemical on an equal-carbon or equal-molar basis, ozone formation is predicted to decrease (13–15), although ozone changes in NO_x-limited areas or for small substitutions may be insignificant (14). When substitutions are done on an equal-reactivity basis, a larger mass of low-reacting VOC might replace a smaller mass of high-reacting VOC, with the amount based on the metric. For example, 8.5 g of *n*-butyl acetate could replace 1.0 g of *o*-xylene using the MIR (Table 1). Although this substitution is theoretically an equal-ozone substitution, it is possible that ozone may decrease in some areas (close to sources) and increase in others (downwind of sources).

Carter et al. (15) simulated equal-ozone substitutions by substitution of all anthropogenic VOCs emitted in the Eastern

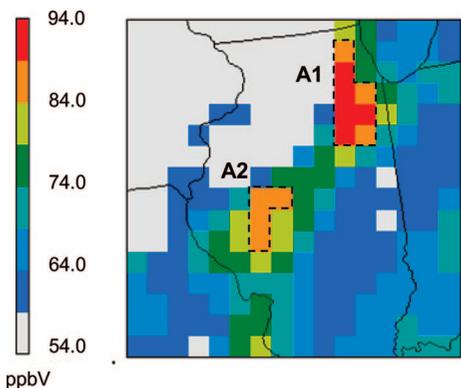


FIGURE 5. Maximum 8-h average ozone concentrations for the 3 day downwind episode. The two areas of potential ozone exceedances are marked by the orange and red areas inside A1 and A2.

U.S. with 5.1 times more ethane, based on the MSE1 scale. Ozone decreased in VOC-sensitive cells but increased in NO_x-sensitive cells, where the relative reactivity of ethane was higher than the value used to calculate the substitution factor. While more grid cells had ozone increases than decreases, the decreases were larger than the increases.

To further examine potential downwind reaction of additional VOC mass, the CMAQ modeling system was used to track ozone sensitivity to VOC emissions in Chicago, IL, represented by eight grid cells covering Cook County, for a 3 day episode (July 10–12, 1999) with well-defined southwest transport. This episode was chosen for its relative simplicity in transport characteristics and the small influence of upwind biogenic and anthropogenic ozone precursors. By using an AQM, we account for the other processes (formation of stable products, dry and wet deposition) that act on VOCs as they are transported downwind, removing them from further ozone formation.

The relative sensitivities of ozone in each grid cell to VOC emissions from Chicago were used to estimate the effect of replacing a highly reactive VOC with a lower-reactive VOC. These ozone production sensitivities were first calculated for equal-mass reductions and are useful for examination of the relative effects of substitution scenarios. The absolute change would depend on the amount of mass substituted, location, and other factors.

For this simulation, there were two areas with predicted 8 h ozone concentrations above 84 ppb, as shown in Figure 5. One area is around Chicago (area A1, consisting of 8 grid cells, with a peak of 100 ppb), and one downwind, around Springfield (area A2, 4 grid cells, with a peak of 86.9 ppb). Over the peak ozone period and area, the spatial distribution of ozone sensitivity to different VOCs varied. For example, ozone sensitivity to SAPRC-99 species ARO2 (mostly xylenes and trimethylbenzenes) emissions has a high gradient, centered on Chicago, because it reacts quickly close to the source. The slower-reacting species ALK1 (representing ethane) has a lower-gradient extending farther from the source, with values close to 20% of the peak almost across the state.

To identify areas of ozone increase and decrease, we focus on the ratio of ozone sensitivity of ARO2 emissions in Chicago to that of ozone sensitivity to lower-reactivity ethane and acetone multiplied by a substitution factor. Where the ratio equals 1, the higher-reactivity ARO2 can be replaced with a larger amount (substitution factor) of lower-reactivity compounds, with no net effect on ozone. Where the ratio is larger than one, substitution of ARO2 with a larger amount of ethane or acetone predicts a beneficial ozone decrease. Ratios less than 1 indicate areas where the reactivity substitutions actually increase ozone relative to that formed from the

original ARO2 emissions. The magnitude of ozone change is proportional to the ratio, hence a ratio of 1.25 would indicate a 25% ozone decrease from this VOC under the substitution.

Since the proposed national rule for aerosol coatings is based on box model-derived MIRs and an approximately 19.4% reduction in VOC mass emissions (11), these parameters were used to define ozone-equivalent substitutions. The ARO2 box model MIR is 8.62 (based on weighted values of xylenes and trimethylbenzenes); the acetone MIR is 0.43, and the ethane MIR is 0.31 (17). An ozone-equivalent substitution ratio, using these MIRs and a 19.4% emission reduction, would result in a substitution ratio of 21.8 for ethane and 16.1 for acetone.

For an ethane substitution ratio of 21.8, as presented in Figure 6a, the sensitivity ratios in area A1 ranged from 1 to 2.9, indicating ozone benefits, with a value of 2.1 at the peak ozone grid cell. In Figure 6, all cells with sensitivities less than 10% of the peak value are screened out of the analysis and shown as gray to focus on the most meaningful ratios. The corresponding ratios in A2 ranged from 0.6 to 0.9, indicating ozone disbenefits, with 0.8 at the peak ozone grid. Not only did the benefits occur where concentrations were highest (A1), but the benefits were larger than the disbenefits and occurred where the sensitivities were highest.

When the substitution ratio is lowered to 13.9 (Figure 6b), a value between the MIR and the box model emission-reduced MOIR, all ratios in the domain are greater than 1, indicating ozone benefits everywhere and larger benefits in area A1.

The behavior for acetone is slightly different. When substituted at the MIR ratio of 16.1 (Figure 6c), disbenefits occur in most of the sensitive grids, although many cells in A1 are close to ozone equivalence (near 0.9). Disbenefits in A2 are substantial, ranging from 0.5 to 0.6. As the substitution ratio is lowered to 9.8, on the basis of the EBIR (Figure 6d), there are only benefits in A1 (ranging from 1.1 to 1.6), but there are some disbenefits in A2. The substitution ratio must be lowered to 7.3 to predict a benefit in every grid.

This sensitivity study looked at substitutions only in Chicago, and downwind ozone increased most in another urban area, as transported emissions were added to fresh NO_x emissions. In practical applications, VOC reactivity substitutions would occur in all areas simultaneously, so transported VOCs would be added to a downwind mixture with a lowered VOC reactivity. Conclusions based on simulations in Chicago may not be applicable to the rest of the country; for example, different chemical mechanisms show different behavior in this area than in most of the U.S. (21). In addition, the small influence of biogenic compounds in this scenario would make this substitution more VOC sensitive than more common scenarios.

Although the DDM substitutions give relative potential changes in ozone, they do not quantify ozone changes under a realistic substitution scenario. If the ozone produced from a VOC in a solvent is very small, an increase or decrease of 100% because of substitution results in very small changes in ozone. Although other simulations (15) provide upper limit estimates on ozone changes under large-scale VOC substitutions, these scenarios would not be implemented in practical applications. The CARB aerosol coating limits provide realistic scenarios, but the category is limited and the resulting changes will be small, making it difficult to see subsequent ozone changes. While we do not know how ozone would respond if reactivity-based substitutions were implemented for a large number of emission categories, a beneficial result is likely, based on our estimates, if an appropriate substitution ratio is used.

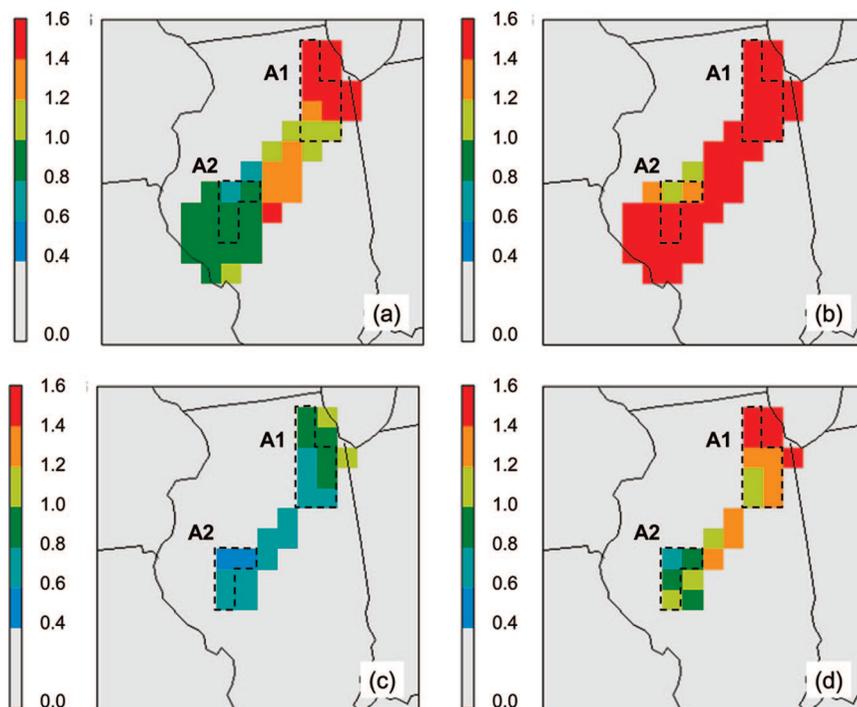


FIGURE 6. Predicted ozone change ratio resulting from replacement of ARO2 with (a) ethane at ratio of 21.8, (b) ethane at ratio of 13.9, (c) acetone at ratio of 16.1, and (d) acetone at ratio of 9.8. Values are the sum over the 8 h of July 12 during which the maximum ozone is predicted. All cells in grey (values less than 0.4) are screened out of the analysis because of low sensitivity. Values of >1.0 indicate ozone decreases (benefits), and values of <1.0 indicate ozone increases.

Discussion

The scientific community has developed a large body of research to support the development of reactivity-based strategies for controlling VOC emissions. Box model-based MIRs have been used for regulatory applications of reactivity, but they are not exempt from questions about their appropriateness. They represent chemical behavior at VOC/NO_x ratios that are lower than typically occur during periods of high-ozone formation in many parts of the U.S., so it is not clear that they are always the best way to represent effects of VOCs over large areas of the country. The box model-based MIR also has the largest effective range of all metrics, which provides the largest mass of substitutions between low- and high-reactivity compounds. If the intent is to quantify ozone formation in areas that are VOC-sensitive or to provide maximum incentives for use of low-reactivity chemicals, then the large effective range of the MIR is appropriate. Other advantages of the MIR scale include the long history of use and analysis and ease of updating scales as more scientific information becomes available and new chemicals are added. A disadvantage of the large effective range of the MIR is the larger potential for ozone increases compared to metrics with smaller ranges. The choice of an appropriate reactivity metric clearly requires a balance between maximizing ozone benefits while minimizing disbenefits.

In addition to box models, three-dimensional AQMs can be used to calculate reactivity metrics. AQMs are more representative of multiday episodes and long-range transport and allow a better characterization of ozone formation over large areas. AQM metrics, particularly the M2M and MSE1, are more scientifically justifiable and robust than box model MIRs, but there are no detailed reactivity scales yet available, for most industrial chemicals, using AQMs. Because of this, we cannot apply three-dimensional metrics for current policy applications; the simpler box model metrics are the only sufficiently comprehensive scales available now.

Additional research is needed to develop robust reactivity scales that use the latest scientific knowledge implemented in three-dimensional AQMs. Metrics and scales for a limited number of chemicals have been developed using AQMs, but these must be extended to develop comprehensive scales for the large number of chemicals used by industry. Additional analyses of alternatives to the box model MIR should be performed to determine which metric best characterizes ozone formation throughout the U.S.

Any reactivity-based substitutions could allow larger overall mass to be emitted than an equal-ozone mass-restricted solvent, and downwind increases in ozone from increased mass of low-reacting compounds are possible. Current studies have only looked at extreme cases (i.e., substitution of all VOCs with ethane, substitutions in Chicago). While these simulations showed some ozone increases, the reduction of maximum ozone was also significant, especially near urban areas. The degree of potential benefit and disbenefit depends on the substitution ratio, which depends on the metric. If reactivity-based VOC controls are limited to the aerosol-coatings category, changes in overall emissions and downwind effects would likely be small, especially in NO_x-sensitive areas, where additional VOCs do not affect ozone. If VOC reactivity-based controls are extended to many emission categories, it is possible that ozone may increase in downwind areas. Several additional factors must be considered in judging the significance of potential ozone increases. If areas with ozone exceedances decrease while areas with ozone increases remain in compliance, there is an overall regulatory benefit. If ozone decreases occur in areas with high population density while increases occur in minimally populated areas, the population-weighted ozone exposure would be improved. We note that current strategies for mass-based control of VOCs, which do not discriminate among different VOCs, could result in lower mass emissions but higher overall ozone-forming potential.

One outstanding technical issue, therefore, is whether or not realistic reactivity-based changes in VOC formulation might result in ozone increases downwind. Detailed and realistic studies are needed to identify the potential for ozone increases, especially if reactivity-based regulations are applied to additional emission categories. Developing realistic, complex emission scenarios is one area that needs to be explored in more detail through collaboration between industry, academia, and government. Implementing these scenarios in AQMs to evaluate impacts of reactivity policies is essential to develop appropriate substitution ratios and evaluate benefits of reactivity-based VOC control.

A benefit of current and proposed reactivity rules is that they require ozone reductions equivalent to additional VOC mass reductions; the allowed reactivity of the total mixture is reduced, resulting in smaller ozone formation potentials than prerule mixtures. In addition, a reactivity-based rule makes the concept of exempt compounds obsolete because a continuous scale more accurately describes reactivity than simply judging a VOC as either reactive or nonreactive (2). Rather than allowing unlimited emissions of exempt compounds, a reactivity-based rule would count them in total VOC emissions. For the example of aerosol coatings, the previously exempt compound acetone could be a substantial portion of total VOC mass.

We note that ozone formation potential is only one of several properties of a VOC that can affect air quality. While reactivity-based regulations would control VOCs based on their ozone formation potential, they would not consider other adverse effects of the VOC, such as its potential to produce particulate matter, its toxicity or potential to produce HAPs, or its global warming potential. These properties much also be taken into account when VOC emissions are evaluated for their total effect on human health and the environment.

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Supporting Information Available

Descriptions of additional reactivity metrics that can be calculated from AQMs, examples of city-to-city variation of MIR values from box models, and more details on the calculations of ozone sensitivity to emissions from the Chicago CMAQ simulation. This material is available free of charge via the Internet at <https://pubs.acs.org>.

Literature Cited

- (1) Carter, W. P. L. Development of ozone reactivity scales for organic gases. *J. Air Waste Manage. Assoc.* **1994**, *44*, 881–899.
- (2) Dimitriades, B. Scientific basis for the VOC reactivity issues raised by Section 183(e) of the Clean Air Amendments of 1990. *J. Air Waste Manage. Assoc.* **1996**, *46*, 963–970.
- (3) Avery, R. J. Reactivity-based VOC control for solvent products: More efficient ozone reduction strategies. *Environ. Sci. Technol.* **2006**, *40*, 4845–4850.

- (4) Croes, B.; Holmes, J. R. Reactivity-based hydrocarbon controls: Scientific issues and potential regulatory applications. *J. Air Waste Manage. Assoc.* **1992**, *42*, 657–661.
- (5) Russell, A.; Milford, J.; Bergin, M. S.; McBride, S.; McNair, L.; Yang, Y.; Stockwell, W. R.; Croes, B. Urban ozone control and atmospheric reactivity of organic gases. *Science* **1995**, *269*, 491–495.
- (6) California Air Resources Board. The California Low-Emission Vehicle Regulations. 2007. Available at http://www.arb.ca.gov/msprog/levprog/cleandoc/cleancomplete_lev_ghg_regs_with_evap2006.pdf.
- (7) California Air Resources Board. Final Regulation Order for Reducing the Ozone Formed From Aerosol Coating Product Emissions. 2001. <http://www.arb.ca.gov/regact/conspro/aerocoat/finreg.pdf>.
- (8) Revisions to the CA state implementation plan and revision to the definition of volatile organic compounds (VOC)—Removal of VOC exemptions for CA's aerosol coating products reactivity-based regulation. *Fed. Regist.* **2005**, *70*, 53930–53935.
- (9) Approval and promulgation of state implementation plans; Texas; Highly reactive volatile organic compound emissions cap and trade program for the Houston/Galveston/Brazoria ozone nonattainment area. *Fed. Regist.* **2006**, *71*, 52659–52664.
- (10) Interim guidance on control of volatile organic compounds in ozone state implementation plans. *Fed. Regist.* **2005**, *70*, 54046–54051.
- (11) U.S. EPA. National volatile organic compound emission standards for aerosol coatings: Proposed rule. *Fed. Regist.* **2007**, *72*, 38952–38991.
- (12) McBride, S. J.; Oravetz, M. A.; Russell, A. G. Cost-benefit and uncertainty issues in using organic reactivity to regulate urban ozone. *Environ. Sci. Technol.* **1997**, *31*, 238A–244A.
- (13) Derwent, R. G.; Jenkin, M. E.; Passant, N. R.; Pilling, M. J. Reactivity-based strategies for photochemical ozone control in Europe. *Environ. Sci. Pol.* **2007**, in press.
- (14) Arunachalam, S.; Mathur, R.; Holland, A.; Lee, M.; Olerud, D.; Jeffries, H. *Investigation of VOC Reactivity Assessment with Comprehensive Air Quality Modeling*. U.S. Environmental Protection Agency: Research Triangle Park, NC, 2003; http://www.narsto.org/files/files/RRWG_FinalReport_CEP.pdf.
- (15) Carter, W. P. L.; Tonnesen, G.; Yarwood, G. *Investigation of VOC Reactivity Effects Using Existing Regional Air Quality Models*. Report to American Chemistry Council SC-20.0-UCRVOCRRWG; 2003; http://www.narsto.org/files/files/carter_final.pdf.
- (16) Carter, W. P. L.; Cocker, D. R., III; Fitz, D. R.; Malkina, I. L.; Bumiller, K.; Sauer, C. G.; Pisano, J. T.; Bufalino, C.; Song, C. A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation. *Atmos. Environ.* **2005**, *39*, 7768–7788.
- (17) Carter, W. P. L. Documentation of the SAPRC-99 chemical mechanism for VOC reactivity assessment; Report to the CA Air Resources Board, Contracts No. 92–329 and 95–308, <http://pah.cert.ucr.edu/~carter/reactdat.htm>, 2000.
- (18) Carter, W. P. L. Documentation of the SAPRC-07 chemical mechanism and updated ozone reactivity scales. Final Report to the CA Air Resources Board, Contract No. 03–318, <http://pah.cert.ucr.edu/~carter/SAPRC/saprc07.doc>, 2007.
- (19) Yang, Y.; Stockwell, W. B.; Milford, J. B. Uncertainties in incremental reactivities of volatile organic compounds. *Environ. Sci. Technol.* **1995**, *29*, 1336–1345.
- (20) Bergin, M. S.; Russell, A. G.; Milford, J. B. Effects of chemical mechanism uncertainties on the reactivity quantification of volatile organic compounds using a three-dimensional air quality model. *Environ. Sci. Technol.* **1998**, *32*, 694–703.
- (21) Luecken, D.; Phillips, S.; Sarwar, G.; Jang, C. Effects of using the CB05 versus SAPRC99 versus CB4 chemical mechanism on model predictions: ozone and gas-phase photochemical precursor concentrations. *Atmos. Environ.* **2008**, in press.
- (22) Stockwell, W. R.; Geiger, H.; Becker, K. H. Estimation of incremental reactivities for multiple day scenarios: An application to ethane and dimethoxymethane. *Atmos. Environ.* **2001**, *35*, 929–939.
- (23) Hakami, A.; Harley, R. A.; Milford, J. B.; Odman, M. T.; Russell, A. G. Regional, three-dimensional assessment of the ozone formation potential of organic compounds. *Atmos. Environ.* **2004**, *38*, 121–134.
- (24) Hakami, A.; Bergin, M. S.; Russell, A. G. Ozone formation potential of organic compounds in the Eastern United States: A comparison of episodes, inventories, and domains. *Environ. Sci. Technol.* **2004**, *38*, 6748–6759.
- (25) Hakami, A.; Arhami, M.; Russell, A. G. *Further Analysis of VOC Reactivity Metrics and Scales*. U.S. Environmental Protection

- Agency: Research Triangle Park, NC, 2004; http://www.narsto.org/files/files/Hakami_report2_final.pdf.
- (26) Derwent, R. G.; Jenkin, M. E.; Saunders, S. M.; Pilling, M. J. Characterization of the reactivities of volatile organic compounds using a master chemical mechanism. *J. Air Waste Manage. Assoc.* **2001**, *51*, 699–707.
- (27) Gery, M. W.; Whitten, G. Z.; Killus, J. P.; Dodge, M. C. A photochemical kinetics mechanism for urban and regional scale computer modeling. *J. Geophys. Res.* **1989**, *94* (D10), 12925–12956.

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