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Urban Ozone Control and Atmospheric Reactivity of Organic Gases

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Control strategies for urban ozone traditionally have been based on mass reductions in volatile organic compounds (VOCs). Studies show, however, that some organic gas species (such as alkanes and alcohols) form an order of magnitude less ozone than equal mass emissions of others (such as alkenes and aldehydes). Chemically detailed photochemical models are used to assess uncertainty and variability in reactivity quantification. VOC control strategies based on relative reactivity appear to be robust with respect to nationwide variations in environmental conditions and uncertainties in the atmospheric chemistry. Control of selective organic gas species on the basis of reactivity can offer cost savings over traditional strategies.

Tropospheric ozone, formed from nonlinear reactions between VOCs and nitrogen oxides (NO_x), is a primary constituent of urban smog (*1*). Estimates of VOC control costs needed to attain the National Ambient Air Quality Standard (NAAQS) for ozone of 0.12 parts per million are on the order of billions of dollars per year, and in the most severely impacted regions, the necessary control technologies have not been identified completely (*2, 3*). Despite considerable resource investment since the promulgation of the NAAQS, most large cities do not meet this standard. A variety of new directions are being explored to find more effective control strategies. One path, controlling NO_x emissions instead of VOC emissions, appears to be most effective for regional transport problems, in rural areas, and in urban areas with high biogenic VOC emissions. However, in the largest urban areas with the worst ozone problems, reducing VOC emissions also appears to be effective (*1, 2, 4*). Currently, control strategies and air quality regulations are based on reducing the total mass of VOCs emitted (excluding methane).

There are a number of reasons to consider incorporating specific information about the individual VOC species emitted in designing more effective control strategies. Of the hundreds of different VOC compounds emitted, each has a different impact on ozone levels. The relative ozone-forming potentials of individual VOCs, or "reactivity," can differ by more than an order of magnitude from one compound to another. For example, in a typical urban atmosphere, 1 kg of ethane will form about two orders of magnitude less ozone than 1 kg of formaldehyde. Ignoring the reactivity of emissions when regulations are developed may lead to ineffective, inefficient control strategies and possibly even lead to measures that worsen air quality. Consideration of reactivity focuses control efforts on those emissions with the greatest impacts on urban ozone. Other compelling reasons to consider reactivity-based strategies include providing strong incentives for accurate determination of emissions compositions, for pollution prevention through product redesign or reformulation, and the potential for large reductions in emissions control costs (*5*). We have examined the scientific basis for reactivity-based VOC regulations by quantifying the variability and uncertainties in reactivity estimates. We suggest that estimates of the relative impacts of individual VOCs on ozone can be incorporated into control strategies in order to refine control efforts nationwide.

Here we describe the analysis procedures used to quantify VOC reactivity, with particular attention to the reactivity scale used for automobile emission regulations in California (*6*). Although reactivity-based regulations are currently used in California, the potential environmental and economic advantages of this approach and the adoption of California vehicle regulations elsewhere (notably the Northeast) broaden the need to understand the scientific foundations, criticisms, benefits, and outstanding research issues associated with reactivity weighting (*7*). We examine the dependence of reactivity measures on (i) environmental conditions, particularly meteorology and precursor ratios; (ii) the level of chemical and physical detail and uncertainty in the models used for quantifying reactivity; and (iii) the uncertainties in emissions compositions. Our analysis shows that the relative reactivity of emissions mixtures, such as exhaust from alternatively fueled vehicles normalized to emissions from a base case fuel, is not very sensitive to any of these three factors. In conclusion, we present the results of an economic analysis which shows that strategies that use reactivity-based controls are not only more effective than those relying on mass-based controls but can also be less expensive.

We used photochemical air quality models and a variety of analysis methods. The two classes of photochemical models that have been used most extensively are chemically detailed but physically simplified zero-dimensional box models (*8–13*) and more comprehensive, physically detailed, three-dimensional (3D) airshed models (*10, 11, 14–17*). The method currently used for reactivity quantification in California was developed by Carter (*8*), who used a box model, and is based on the SAPRC90 chemical mechanism (*18*) to quantify how an incremental change in the emissions of a specific VOC would affect ozone. In addition to examining results from Carter's studies, we have also developed and applied both a box model (*10–12*) and a chemically detailed 3D model (*16, 17, 19*) for studying reactivity issues. For both models, atmospheric chemistry is treated using a version of SAPRC90 with 91 species (27 detailed organics) and 203 reactions. The box model is used for statistical analysis of reactivity quantification and uncertainty estimation over a wide range of variables. The more comprehensive 3D model is used to examine the dominant uncertainties identified through use of the box model while accounting for transport and multiday effects, and for estimation of pollutant exposure metrics. A linear optimization cost analysis model is developed to examine economic impacts of explicitly accounting for reactivity in control strategy design.

To illustrate the use of reactivity in the development of control strategies and regulations, we consider the reactivity scale used in California's Low Emission Vehicle (LEV) and Clean Fuels Regulations (*20*). Recently, Carter (*9*) used a chemically detailed, photochemical trajectory model to quantify the ozone formed from 180 differ-

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ent VOCs in 39 cities across the United States. Eighteen reactivity scales were developed from those model calculations. The scales differ in the assumptions about the levels of NO_x and the measure of ozone impact (such as impact on the peak ozone versus integrated impact over time). One scale, the maximum incremental reactivity (MIR) scale, has been chosen for regulatory application in California. MIRs for individual VOCs are calculated in 10-hour box model simulations and are defined as the maximum sensitivity of the peak ozone concentration ($[O_3]_p$) to a small increase in the initial conditions and emissions of the VOC (E_i). The MIRs are found for the input ratio of VOCs to NO_x that leads to the maximum sensitivity to VOCs:

$$MIR_i = \max\left(\frac{\partial[O_3]_p}{\partial E_i}\right) \text{ for all VOC/NO}_x \quad (1)$$

Examples of MIRs are given in Table 1, which shows both their averages and standard deviations across 39 sets of simulation conditions representing different cities. Typically, MIRs are observed at relatively low VOC/NO_x ratios (about 4 to 6 ppm C:1 ppm NO_x), as might be expected in dense source regions. This indicates that the MIR scale will be more applicable to urban core conditions, where VOC control is most effective, than to rural conditions where ratios are usually higher (and NO_x controls are more effective). Thus, the use of the MIR scale is meant to complement, not replace, NO_x controls. To determine the ozone formed per unit mass of emissions from a specific source [that is, the net reactivity (NR_j) for source j], the MIR of each compound is multiplied by the mass fraction of the compound in the emissions (f_{ji}), and the weighted emissions fractions are then summed:

$$NR_j = \sum_{i=1}^{n} f_{ji} MIR_i \quad (2)$$

For application in California, the MIR scale is used to quantify the reactivity of the exhaust emissions from alternatively fueled vehicles, scaled to the reactivity of exhaust emissions from a vehicle using standard gasoline (NR_j). The ratio of the reactivity of the alternative fuel to that of standard gasoline is called the reactivity adjustment factor (RAF) and is used to modify the allowable mass emissions rate from alternatively fueled vehicles:

$$RAF_j = \frac{\sum_{i=1}^{n} f_{ji} MIR_i}{\sum_{i=1}^{n} f_{bi} MIR_i} = \frac{NR_j}{NR_b} \quad (3)$$

RAFs calculated for exhaust emissions for five fuels, (i) standard gasoline (as the base, b), (ii) phase II reformulated gasoline, (iii) 85% methanol–15% gasoline blend (M85), (iv) liquefied petroleum gas (LPG), and (v) compressed natural gas (CNG), are given in Table 2. For example, the RAF for M85-fueled vehicle emissions indicates that on a mass-weighted basis, those emissions should produce about 37% as much ozone as the same mass emitted from a gasoline-fueled vehicle under urban conditions. Under the California regulations, M85-fueled vehicles could then emit 2.7 times as much mass, leading to an equivalent ozone impact.

One of the most widely noted criticisms of using VOC reactivity for developing control strategies is the possible large variation of individual compound reactivities between locations as a result of both the change in atmospheric conditions as well as the change in the relative abundance of VOC and NO_x (7). Although such variation might appear to complicate the use of a single reactivity weighting scheme across regions, box and airshed modeling results indicate that the variation in relative reactivities is not so severe. In the MIR scale, compound reactivities are an average of those quantified for conditions in 39 cities. The absolute MIRs of individual compounds vary significantly between locations (9), as demonstrated by the SDs of the reactivities across the cities (Table 1). On average, the SDs are about 22% of the mean reactivity values. However, the intercity variation is much lower for RAFs or when the MIR is normalized. Normalized MIRs are calculated by dividing each specie's city-specific MIR by the geometric mean reactivity of all the species reactivities for that city, and multiplying by the geometric mean reactivity of the 39-city average MIRs. As shown in Table 1, the SDs of the normalized reactivities are significantly less. The NRs of exhaust from vehicles operated on six fuels (6) are shown by box plots in Fig. 1A, indicating the variation in the calculated MIR values across the 39 cities. The variation in absolute ozone-forming potentials across cities is substantial. However, when the reactivities of exhaust from alternatively fueled vehicles are normalized by the reactivity of standard gasoline exhaust (that is, the RAF is calculated), variation among cities is sharply diminished (Fig. 1B). The important point here is not the absolute magnitude of the RAF, which will change as the composition is modified by control technology changes, but that the RAF is relatively invariant across the cities. This variation does not include the uncertainty due to the emissions composition, which is presented below.

Another issue of concern associated with environmental variability is that the relative abundance of VOCs and NO_x can differ markedly between locations, but the MIR scale was developed for conditions of relatively high NO_x that are most typical of urban areas. In California, the MIR scale was chosen intentionally to complement NO_x control. At lower NO_x levels, it is expected that the absolute level of ozone production of any individual VOC will be less than under MIR conditions (the level of NO_x, not VOCs, becomes the limiting factor). This effect is investigated in two

Table 1. Examples of MIRs and variations between locations (mean and SD).

Compound	Mean reactivities across cities (nonnormalized/normalized)	SD (nonnormalized/normalized)
HCHO	7.2/7.1	1.0/0.58
Methanol	0.56/0.55	0.11/0.064
Ethane	0.25/0.24	0.070/0.045
Toluene	2.7/2.7	0.52/0.28
Pentene	6.2/6.1	1.2/0.64

Table 2. Exhaust reactivity adjustment factors (*6, 14*).

Fuel	MIR-RAF	MOIR-RAF
Base	1.00	1.00
Phase II	0.94	0.97
M85	0.37	0.38
LPG	0.47	0.57
CNG	0.43	0.49

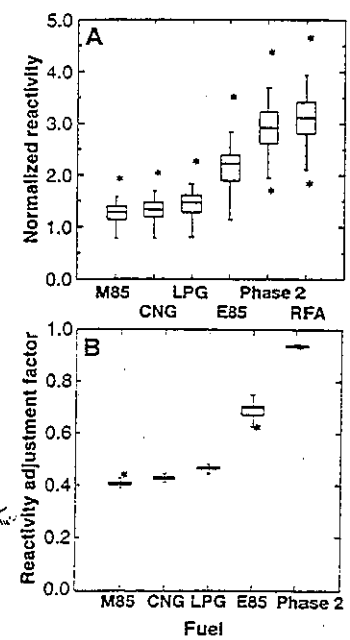

Fig. 1. Boxplots of the calculated (**A**) net reactivities (NRs) and (**B**) normalized reactivities (RAFs) across cities. The median is represented by a horizontal line. The edges of the boxes represent rough quantiles in the data. Horizontal lines represent the extremes of the data, and outliers are represented by stars.

ways. First, Carter developed an alternative scale, the maximum ozone incremental reactivity (MOIR) scale, which is similar to the MIR scale, except that the sensitivity is evaluated for initial VOC/NO_x conditions leading to the maximum ozone level (instead of conditions for which the sensitivity is greatest):

$$\mathrm{MOIR}_i = \frac{\partial \max([O_3]_p)}{\partial E_i} \qquad (4)$$

Conditions leading to the MOIR are calculated to occur at higher VOC/NO_x levels (about 7 to 8:1) than those associated with the MIR scale. MOIR-based RAFs [Table 2 and (*6*, *14*)] are similar to those calculated with MIR values. Carter (*9*) also examined how using other measures of ozone sensitivity (such as the effect on time-integrated concentrations instead of peak concentrations) would affect RAF values, and found relatively little variation. In a second test of how changes in the relative abundance of VOC and NO_x affect reactivity weighting, two emissions inventories, differing in their VOC/NO_x ratios by about a factor of 2, were used in an airshed modeling study to test the efficacy of reactivity weighting of exhaust emissions (*15*). Reactivity weighting led to nearly equivalent ozone impacts when either inventory was used. That study also considered two ozone episodes with significantly different meteorological conditions. Reactivity weighting of emissions, again, led to similar ozone impacts for both episodes (within an uncertainty of about 10%).

A second concern frequently raised with the use of reactivity weighting is the effects of uncertainties and level of detail in the physical and chemical representation used for quantifying reactivity. A specific concern regarding the physical level of detail stems from the MIR scale being developed with the use of a zero-dimensional model. Such simplified models lack realistic treatment of pollutant transport and mixing, which could lead to poor characterization of reaction rates and consequently of reactivities. Moreover, MIRs have been developed on the basis of 10-hour simulations, whereas some organic compounds may remain in an urban airshed for 2 to 3 days. To investigate these issues, we applied an advanced, 3D photochemical model with the SAPRC90 mechanism to the Los Angeles basin (*16*, *17*). Detailed source emissions and meteorology for a 3-day period (27 to 29 August 1987) were used (*21*). This is one of the periods for which the model has been extensively evaluated. Ozone impacts, on a per carbon basis, of an incremental increase in the emissions of 28 VOCs were calculated relative to a base mixture representing gasoline vehicle exhaust. Use of the airshed model allows quantification of the impact of emission changes and reactivity on population-weighted ozone levels and spatial ozone impacts, as well as peak ozone levels (*22*).

Correspondence between two of the airshed metrics and the box model MIR (*9*) scales is shown in Fig. 2. The airshed model–derived spatial and population density–weighted results behave similarly to MIRs. The greatest differences are found for formaldehyde and other compounds whose reactivities are highly dependent on photolytic reactions. This is explained by the use of a reduced photolysis rate in the airshed modeling to account for the observed cloud cover. The box model used clear sky conditions. The reductions in the reactivities are consistent with the sensitivity to the rate constants for the photolytic reactions (*10*). In general, airshed model results for Los Angeles agree well with MIRs and further show that individual organics have very different ozone impacts. Similar studies should be considered for other regions (such as the Ozone Transport Region of the northeastern United States).

A third concern often raised is that the quantification of compound reactivities is limited by uncertainties in our knowledge of atmospheric chemistry and its representation through chemical mechanisms. Measurement errors in laboratory kinetic and product studies contribute to uncertainty in the chemical mechanisms used to calculate incremental reactivities. Moreover, the reactions of many of the organic compounds emitted into urban atmospheres have never been studied in controlled experiments. Their representation in chemical mechanisms is based on analogy to compounds of similar structure, creating added uncertainty. At issue is whether the uncertainties in the chemistry significantly impact the calculation of the reactivities for organic compounds. We used both the box model (*10*, *12*) and airshed model (*17*) to explore the extent to which uncertainties in chemical rate parameters impact the calculated reactivities.

Uncertainties in calculated reactivities are estimated from box model simulations through use of Monte Carlo analysis with Latin hypercube sampling. To reduce computational requirements, the simulations are conducted for a single set of trajectory conditions, which was designed by Carter (*9*) to give results close to the average MIRs from the 39 trajectories nationwide. Uncertainty estimates were compiled (*23*) for all of the rate parameters of the SAPRC90 mechanism, largely from concurrent reviews of kinetic data (*24*, *25*). Rate parameters are treated as lognormally distributed, independent random variables. Results are shown in Fig. 3.

Uncertainty estimates (1σ) range from 30 to 50% of the mean MIR values, for most compounds. The estimated uncertainty in the predicted peak ozone concentration for the average MIR simulation conditions was about 30%, relative to a mean prediction of ~0.15 ppm. For predicted O_3 and MIRs, the most influential uncertainties are those in rate parameters that control the availability of NO_x and radicals (*12*). For MIRs, uncertainties in the rate parameters of primary oxidation reactions, or reactions of stable intermediates, are also influential. Uncertainties in many rate parameters have similar effects on the reactivities of various compounds, so the resulting MIRs are strongly correlated. For example, an increase in the photolysis rate for NO_2 increases the reactivity of most species by about the same proportion. Thus, the relative reactivity of one species compared to

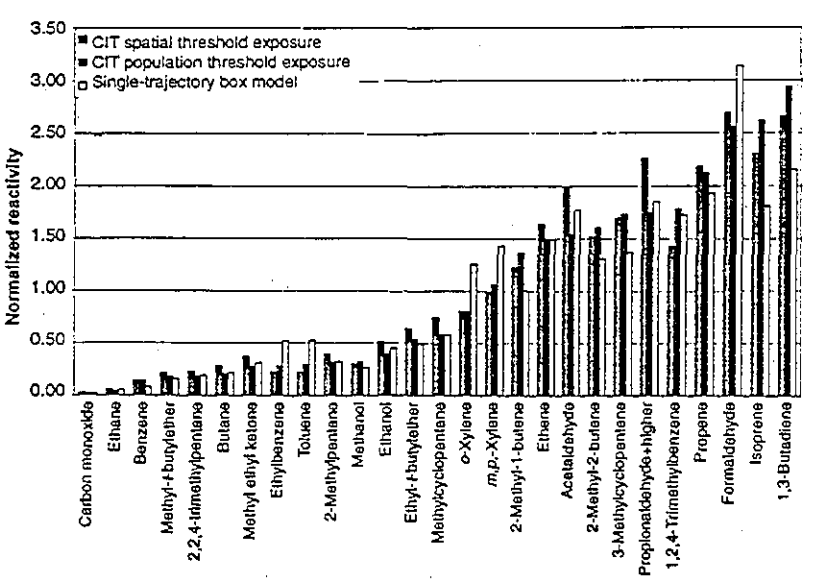

Fig. 2. Results and comparison of reactivity metrics for reactivity quantification.

another is not affected as much as the absolute MIRs by uncertainties in rate constants. After the most influential rate parameters are identified by Monte Carlo simulations, their values are varied, one at a time, in 3D airshed model simulations (*17*). This analysis confirmed the low sensitivity of relative reactivities to uncertainties in rate constants. The implication of this result is clearly shown by the following analysis of uncertainties in RAFs.

For exhaust emissions from selected fuel-vehicle combinations tested in the Auto/Oil Air Quality Improvement Research Program (AQIRP) (*26*), we calculated RAFs and associated uncertainties (*10*). Monte Carlo simulations with Latin hypercube sampling are used for this analysis, treating both chemical rate parameters and exhaust compositions as random variables. Uncertainties in the exhaust compositions were estimated from the variance and covariance of emissions of each compound across the vehicles that the AQIRP study tested on a given fuel. Emissions of each compound were then treated as correlated, normally distributed random variables. No attempt was made for this analysis to estimate uncertainties associated with whether the test vehicles were representative of vehicles on the road.

Results of RAF uncertainty calculations are shown in Fig. 4 for exhaust emissions from prototype flexible- and variable-fueled vehicles operated on M85 compared to exhaust emissions from passenger cars operated on industry average gasoline. The mass-based RAF for the AQIRP M85 exhaust composition has a mean value of 0.49 with an uncertainty of 17% (1σ relative to the mean). Compared to the degree of uncertainty in the MIRs for HCHO (32%) and MeOH (48%), the RAF uncertainty is significantly reduced as a result of interspecies correlation. This reduction in uncertainty is even more pronounced for RAFs of fuels such as reformulated gasoline that have exhaust compositions closer to that associated with conventional gasoline.

Further treatment of uncertainties should account for product yields and correlation among some rate parameters for the chemical mechanism used to calculate MIRs. Preliminary results have indicated that uncertainties in product yields also have a small effect on relative reactivities (*27*), but this question is being examined further with the airshed model for specific application to alternative fuels (*19*).

Uncertainties in emissions composition have been cited as confounding factors in the use of reactivity weighting for ozone control. We have previously addressed this issue through the combined reactivity-composition uncertainty estimate for M85 fuel discussed above. To examine the role of variation in emissions composition across fuels, variances of RAFs were calculated with the use of exhaust composition data (*6*) for four alternative fuels and standard gasoline. The data consisted of mass fractions of VOC exhaust from transitional low-emission vehicles (TLEVs) for each exhaust type and the SD associated with that fraction. Variances of the RAFs for each fuel are calculated by the Delta Method (*28*). Each fuel's RAF was calculated as the ratio of two normally distributed random variables, the MIR of the alternative fuel divided by the MIR of standard gasoline. MIR values were calculated on the basis of the average MIR scale. The results are shown in Fig. 5, which displays the 5th, mean, and 95th percentiles of each fuel's RAF value. Comparison of Fig. 5, which has only one degree of uncertainty, with Fig. 4 suggests that much of the uncertainty results from the composition. Exhaust emission compositions are derived from a small number of tests on a small number of vehicles, particularly for the alternatively fueled vehicles (*6*). Further, there is relatively little information on the effect of deterioration on the species emitted. More tests across a wide range of vehicles are required to better characterize the impact of uncertainty in fuel composition on calculation of RAFs.

Source emissions are usually not as well characterized as those from automobiles. Although lack of detailed knowledge on the emissions compositions of different sources, automotive and others, does add uncertainty to control strategy design, regulations that explicitly credit industry for using less-reactive compounds could add a valuable economic incentive to more completely characterize source emissions, particularly for the largest emitters. This has already been the case for automotive emissions. This information would be useful for better identifying the efficacy of controls and for other studies that depend on an accurate knowledge of emissions compositions (such as a basis for receptor modeling studies to help determine emissions inventories).

Although the results presented above suggest that relative reactivity scales are robust with respect to uncertainties in chemistry, environmental conditions, and emissions, and hence support accounting for VOC reactivity in developing strategies to control ozone, the economic consequences of doing so also warrant consideration. A mixed-integer programming approach to optimization of ozone control strategies across cost, tons of VOC emissions, and reactivities of VOCs indicates that there is potential for cost savings with the adoption of reactivity-based regulations (*5*). Using emission compositions and costs for the Los Angeles air basin, economically optimized VOC-based control strategies are determined on the basis of two approaches, one neglecting and one accounting for the reactivity differences of the emissions. In the first case, an optimized mass-based strategy is simulated such that the total VOC mass reductions are maximized at each cost level. Second, a reactivity-based scheme is assumed in which the reactivity of each source's emissions is calculated and the ozone reductions are maximized at each cost level. Results from the two approaches

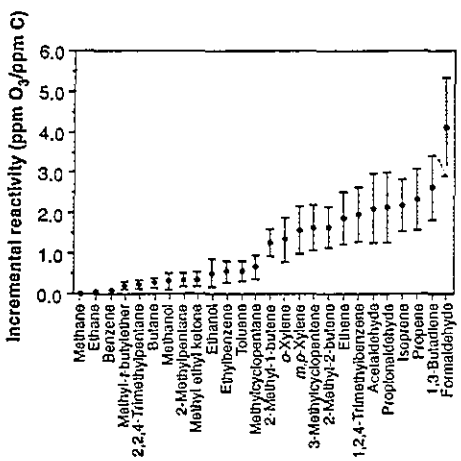

Fig. 3. Mean values and 1σ uncertainties of MIRs for selected organic compounds, as calculated from uncertainties in kinetic parameters.

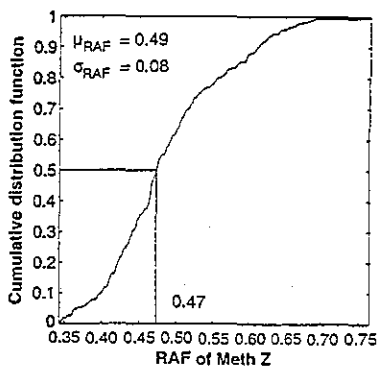

Fig. 4. Cumulative distribution function of the uncertainty in the RAF of prototype flexible-fueled M85 vehicles.

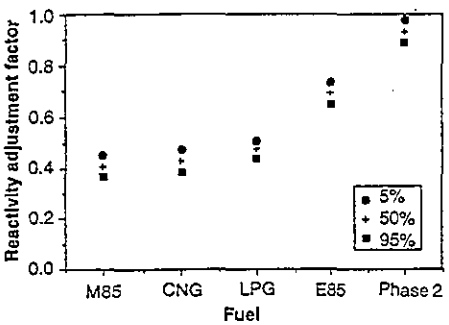

Fig. 5. Variation in RAFs due to exhaust composition for four alternative fuels (5th, 50th, 95th percentiles shown).

are compared in Fig. 6 for ozone reduction at a given expenditure level.

Figure 6 depicts the results for the optimization model across different levels of total cost. Optimal reductions for mass- and reactivity-based systems are scaled according to source reactivities. From this graph, it is clear that on an annual basis the reactivity-based system achieves the same ozone reductions at a lower total cost than the mass-based system. For example, at control costs of $15 million per year, the ozone reduction achieved with a reactivity-based scheme is about two times that achieved under the mass-based scheme. As control costs escalate, the two methods converge, because a greater proportion of all sources will be controlled in both cases. Up to control levels of about 25% of the total controllable emissions, the reactivity-based scheme gives greater ozone reductions for the same cost. The graph does not converge at zero because of the inclusion of a category with a negative cost-effectiveness. A negative value of cost-effectiveness is estimated in this case because of anticipated savings from the reformulation of a particular coatings process. Further economic benefits beyond those found below can accrue over time as control technologies are developed specifically for reactivity adjustment. Cities that can best utilize such strategies include those areas where ozone formation is VOC-limited, as is suggested for the coastal California cities, Phoenix and Chicago. Another application of reactivity quantification to lower total control costs is as a basis for VOC emissions trading between sources. Without a sound foundation for quantifying the impact of one source's emissions compared to another, it is difficult to ensure that a VOC trade would not adversely impact air quality. This issue was of primary concern in the RECLAIM trading program in southern California where VOCs are not included in the program (*2*).

The use of reactivity adjustments in control strategy design allows a new avenue for air quality improvement. Reactivity-based control strategies include economic incentives which would ensure that reformulation would lower reactive VOCs and improve air quality. Present mass-based regulations credit industry for reducing tons of all VOCs, rather than for reducing the most reactive compounds. A hidden problem in reformulation regulations, familiar to the surface coating and consumer products industries, is that while the reformulated product may emit a smaller mass of VOCs, the composition of the emissions may lead to greater ozone formation. Thus, the cost of reformulating may not necessarily yield improved air quality. By creating a regulatory structure that would promote selective control of VOCs with higher reactivity, reformulation and other control technologies can be evaluated and developed with respect to trade-offs between reactivity and mass of emissions, leading to pollution prevention through a more cost-effective process and product design.

Although there are still some uncertainties, this analysis suggests that both scientific understanding and potential economic benefits support the consideration of VOC reactivity weighting in ozone control strategies. Many of the uncertainties and criticisms previously raised about quantification of reactivities are found to be less pronounced when relative reactivity is used, as would be the case in regulatory practice. There are significant differences between individual compound impacts even when the uncertainties are considered. Additional benefits of accounting for reactivity include increased incentives for industry to fully characterize its emissions and for pollution prevention through product reformulation.

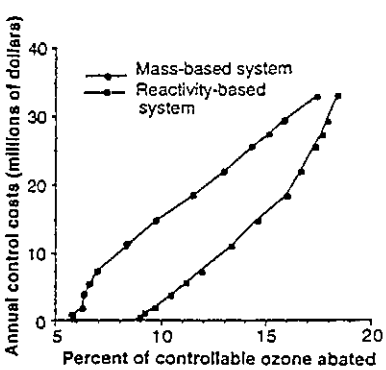

Fig. 6. Percent of controllable ozone abated at different levels of total control cost.

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