

# Evaluation of Atmospheric Processes for Ozone Formation from Vehicle Emissions

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## ABSTRACT

The factors involved in evaluations of effects of volatile organic compound (VOC) and oxides of nitrogen emissions from motor vehicles on ground-level ozone are reviewed. The chemical basis for ozone formation, the computer models and chemical mechanisms used for predicting ozone impacts, and methods for quantifying differences among VOCs in their ozone impacts, are discussed. It is recommended that evaluations of effects of changing fuel and vehicle technology on ozone include an analysis of the effects of uncertainties in the model calculations and of the variability of ozone impacts with atmospheric conditions. Other related research needs are summarized.

## INTRODUCTION

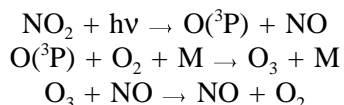
Motor vehicles emit oxides of nitrogen ( $\text{NO}_x$ ), carbon monoxide, and a variety of volatile organic compounds (VOCs) into the atmosphere. These emissions adversely affect air quality in a number of ways. Carbon monoxide and some types of VOC emissions from vehicles (e.g., benzene, formaldehyde and 1,3-butadiene) are directly toxic. Oxides of nitrogen oxidize react to form nitric acid, which can contribute to acid deposition, or to form aerosol nitrates, which contribute to atmospheric haze and particulate loading in the atmosphere. But the air quality impact of most serious concern is the fact that  $\text{NO}_x$  and VOCs react with sunlight in the atmosphere to form ground-level ozone, the principal component of the photochemical "smog" which plagues many areas. Vehicle emissions are thought to contribute approximately half of the VOC and  $\text{NO}_x$  emitted into the Los Angeles and other regions, and their contribution to the VOC inventory may be understated. Other urban areas are probably similar. Because of this, reducing the ozone forming potential of vehicle emissions one of the major objectives in the development and assessment of new fuel and vehicle technologies

The evaluation of alternative methods to reduce the impact of vehicle emissions on ozone requires an ability to predict how changes in VOC and  $\text{NO}_x$  emissions will affect photochemical ozone. This is not a simple problem for a number of reasons. The photochemical reactions involved in ozone formation are complex and nonlinear, and the effects of changes in VOC and  $\text{NO}_x$  emissions can vary significantly with environmental conditions [1]. Furthermore, different types of VOCs can differ significantly in their "reactivities" towards ozone formation [2]. Because of this, simply comparing VOC emissions by mass is not adequate when assessing ozone impacts of alternative vehicle VOC emissions which have

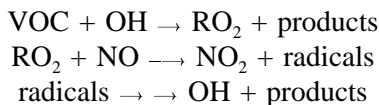
significantly different chemical compositions, as is the case with many alternative fuels. Being able to assess how different vehicle or fuel technologies will affect ozone requires an understanding and ability to predictively model the reactivities of individual VOCs and NO<sub>x</sub> in the atmosphere, which in turn requires an understanding and ability to predictively model the atmospheric processes responsible for ozone formation. In addition, it also requires an ability to make judgements on the relative merits of various fuel or vehicle alternatives given the variability of ozone impacts with environmental conditions. In this paper, we will discuss the various factors which need to be considered, and approaches which have been or could be used in such evaluations.

## CHEMICAL BASIS OF OZONE FORMATION

The only significant process forming O<sub>3</sub> in the lower atmosphere is the photolysis of NO<sub>2</sub>, which is reversed by the rapid reaction of O<sub>3</sub> with NO.



This results in O<sub>3</sub> being in a photostationary state dictated by the NO<sub>2</sub> photolysis rate and the [NO<sub>2</sub>]/[NO] ratio. If reactive VOCs were not present, then significant amounts of O<sub>3</sub> would not be formed. When VOCs are present, they react to form radicals which either consume NO or convert NO to NO<sub>2</sub>, which, because of the photostationary state relationship, causes O<sub>3</sub> to increase. Although many types of reactions are involved [3], the major processes can be summarized as follows:



The rate of ozone increase caused by these processes is dependent on the amounts of VOCs present, the rate constants for the VOC's initial reactions, and the level of OH radicals and other species with which the VOCs might react. Ozone production continues as long as sufficient NO<sub>x</sub> is present that reactions of peroxy radicals (RO<sub>2</sub>) with NO<sub>x</sub> compete effectively with their reactions with other peroxy radicals.

Note that the OH radical levels are particularly important in affecting the O<sub>3</sub> formation rate in the presence of NO<sub>x</sub> because reaction with OH is a major (and in many cases the only) process causing most VOCs to react. Thus if a VOC reacts in such a way that it initiates radical levels (or forms a product which does), then it would enhance the rate of ozone formation from all VOCs present. This would result in the VOC having a high impact on ozone formation compared to other VOCs which react at the same rate. If the VOC has radical termination process when it reacts in the presence of NO<sub>x</sub>, it will cause all VOCs to react slower and form less O<sub>3</sub>. In some cases this reduced O<sub>3</sub> formation from other VOCs may be more than enough to counter the ozone formation from the VOC's direct reactions, resulting in the VOC having a net negative effect on ozone formation [2,4].

Ozone formation stops once NO<sub>x</sub> is consumed to sufficiently low levels. Because NO<sub>x</sub> is removed from the atmosphere more rapidly than VOCs, this means that NO<sub>x</sub> availability ultimately limits O<sub>3</sub> formation. If the NO<sub>x</sub> levels are high enough that it is not consumed before the end of the day, then it is mainly the rate of the VOC's reactions, and their effects on OH radicals, which affect ozone levels. Indeed, high levels of NO<sub>x</sub> inhibits O<sub>3</sub> because reaction of OH with NO<sub>2</sub> reduces OH levels. If, however, NO<sub>x</sub> is consumed before the end of the day, then O<sub>3</sub> is NO<sub>x</sub>-limited, and increasing NO<sub>x</sub> would cause increased O<sub>3</sub> formation. Under such conditions, if a VOC's reactions caused NO<sub>x</sub> to be removed more

rapidly than if the VOC were absent (such as, for example, by forming nitrogen-containing products such as PAN's from aldehydes and nitrophenols from aromatics), then this would have a negative effect on O<sub>3</sub> yields, and tend to reduce the amount of O<sub>3</sub> formation resulting from the VOC's reactions. Under highly NO<sub>x</sub>-limited scenarios, this becomes sufficiently important that the emissions of a VOC with significant NO<sub>x</sub> sinks in its mechanism has a net negative effect on the amount of O<sub>3</sub> formed. This can be true even for those VOCs which may have highly positive effects on O<sub>3</sub> under conditions where NO<sub>x</sub> is plentiful.

Thus NO<sub>x</sub> conditions are a major factor determining the impact of VOC emissions on ozone. However, other conditions will also affect VOC reactivity, by affecting how rapidly NO<sub>x</sub> is removed, by affecting overall radical levels and thus how rapidly NO<sub>x</sub> and VOCs react, and by affecting other factors determining the efficiency of ozone formation. This results in variations of VOC reactivities among the different airshed conditions, even those with similar NO<sub>x</sub> levels [2,4,5].

## AIRSHED MODELS

Airshed models are computerized representations of the atmospheric processes responsible for ozone formation which can be used to predict how VOC and NO<sub>x</sub> emissions affect ozone in various environmental conditions. The models currently in use vary considerably in complexity and structure, but from the perspective of O<sub>3</sub> predictions, they have two major components: the model for the chemical transformations involved in ozone formation (the chemical mechanism), and the model for airshed conditions (the pollution scenario). The chemical mechanism is discussed below. The model for airshed conditions can vary greatly in complexity and the amount of input data they require. Simple "box" models represent the polluted atmosphere by discrete air parcel which moves over the air basin and receives emissions which then react in the single well-mixed parcel. Complex "grid" models divide the air mass into multiple vertical and horizontal cells where the chemical reactions and (where applicable) emissions occur, and represent transport and diffusion of the pollutants between the cells. The grid models provide the most physically realistic representation of any airshed and provide the only means to predict observed pollution levels in real-world pollution episodes.

However, the most complex models have large input data requirements and much of the input information they require is highly uncertain. For this reason, their O<sub>3</sub> predictions may be no more reliable than predictions of much more simplified box models. Furthermore, their large demands on computer and analysis time severely limits the number of cases which can be examined. This is a significant impediment to assessing multiple options, to evaluating how impacts vary with environmental conditions, and to conducting the sensitivity calculations necessary to understand how various factors affect the results. Although box models oversimplify the transport and diffusion, and provide limited information on spacial variability, they can represent the chemical transformations in greater detail, and are more than adequate for representing the wide range of *chemical* conditions which affect how changes in VOC and NO<sub>x</sub> emissions will affect ozone formation. They have the major advantage that ozone impacts under a large number of conditions can be systematically examined. A comprehensive set of simple model scenarios will provide more information concerning the range of relative ozone impacts for variable environmental conditions than can be obtained with a much more limited number of more complex model simulations.

## CHEMICAL MECHANISM

The chemical mechanism is the portion of the airshed model which represents how O<sub>3</sub> is formed from the reactions of NO<sub>x</sub> and the various types of VOCs. It must be able to take all the chemical factors affecting ozone formation appropriately into account if the ozone predictions of the model are to be credible. However, current chemical mechanisms have many uncertainties. Several hundred different types of organic compounds have been identified in speciated emissions inventories, and they all have

differing reaction rates, amounts of NO oxidation caused by the radicals they form, effects on OH radical and NO<sub>x</sub> levels, and reactivities of their products. Laboratory and environmental chamber data are available to develop and test the mechanisms for only a subset of these, and there are gaps in our understanding of important details of the atmospheric reactions of all but the simplest VOCs. For this reason, even some of the most extensively studied VOCs are represented in airshed models using parameterized mechanisms which are adjusted to fit environmental chamber data. For the other VOCs, their reactions are either derived by analogy with mechanisms for compounds which have been studied, or they are represented as if they reacted the same way as the other compound.

Because of these uncertainties, before any chemical mechanism is incorporated in an airshed model it is essential that it be shown that it can predict at least the major features of the VOC-NO<sub>x</sub>-air photooxidation process. This can be tested by conducting environmental chamber experiments and then determining whether the results are consistent with the predictions of the mechanism. Irradiations of single VOCs in the presence of NO<sub>x</sub> in air test the mechanisms for the individual compounds, NO<sub>x</sub>-air irradiations of more complex mixtures test the performance of the model as a whole, and experiments where the effect of adding single VOCs to irradiations of NO<sub>x</sub> and complex mixtures test model predictions of the VOC's reactivity. Evaluation of chemical mechanisms with chamber data is complicated by uncertainties in chamber effects, and separate characterization experiments are needed to evaluate models for these effects which are used when evaluating the mechanism of interest [6,7,8]. Although this introduces uncertainties in such evaluations, the uncertainties in evaluating chemical mechanisms using chamber data are far less than the uncertainties in attempting to evaluate mechanisms using the full airshed model and ambient air data.

Nevertheless, the rate constants for at least the initial atmospheric reactions of almost all important VOCs have been measured or can be estimated with a reasonable level of confidence [3]. Mechanistic data and environmental chamber results are available for a sufficient number of representative compounds to allow parameterized mechanisms to be developed to represent reactions of over 100 different types of VOC's [9]. Such a mechanism has been incorporated in a box model and used to estimate the ozone reactivities of most VOCs measured from vehicle emissions [4,5]. This mechanism still uses a highly simplified representation of the subsequent reactions of these species, designed mainly to represent the overall photooxidation and ozone formation processes. Box models can potentially incorporate much more complex mechanisms than this, but given the current state of knowledge of atmospheric reactions of VOCs, any additional complexity would be largely speculation which would not necessarily improve the model's predictive capability.

Grid models are very computationally intensive, and most of the computer time is taken up in processing the chemistry. Because of this, such models must have highly condensed chemical mechanisms. For example, Carbon Bond IV mechanism in the UAM model (the most widely used model in regulatory applications) uses only 11 model species to represent the hundreds of types of VOCs emitted [10]. Such mechanisms were developed and optimized to simulate current ambient mixtures, and were not designed for use for evaluating scenarios where the emissions speciation may change significantly.

## QUANTIFICATION OF VOC REACTIVITY

The most direct measure of ozone reactivity of a VOC is the change in ozone caused by changing the emissions of the VOC in an air pollution episode. Model calculations and environmental chamber experiments have shown that environmental conditions can significantly affect how a change in VOC emissions affects ozone formation, both in a relative and an absolute sense [2,4,5]. The effect of a VOC emissions change on ambient ozone formation cannot be measured directly — other than by changing emissions and then observing the resulting changes of air quality for enough years to factor out effects

of meteorological variability — but can be estimated by computer model calculations or by suitable designed environmental chamber experiments. Both types of estimation approaches have their limitations. In the case of model calculations, uncertainties and approximations in the chemical mechanism and the model for airshed conditions, as well as the model formulation itself, cause uncertainties in the predicted ozone impacts. The impacts of these uncertainties on model predictions need to be understood before the results of such calculations can be used for decision making. In the case of experiments, one does not necessarily know whether the conditions of the experiment are a sufficiently close approximation to ambient conditions that the results have general applicability. The only way to assess this is by modeling the conditions of the experiments and comparing the results with model simulations of the atmosphere. This has its own set of uncertainties. Such calculations indicate that results of appropriately designed experiments should correlate fairly well with atmospheric reactivities under high  $\text{NO}_x$  conditions, but not under conditions where ozone is  $\text{NO}_x$  limited [4]. For this reason, airshed model calculations is considered to be the most useful general approach for assessing reactivity, with the principal utility of experimental reactivity measurements being to verify the mechanisms' predictions.

Two general types of types of approaches can be used in model simulations for assessing ozone impacts of VOCs: conducting scenario-specific assessments or developing general VOC reactivity scales. A scenario-specific assessment is a model simulation whose objective is to estimate, as accurately as possible given the limitations of the available data and the type of model employed, the air quality impacts of some specific emissions change in a specific airshed scenario. If the objective is to evaluate atmospheric impacts of vehicle emissions, it would involve assuming specific degree of penetration of a specific new fuel or vehicle technology in a specific air pollution episode. A distinguishing characteristic of such studies is an attempt to make the emissions change being modeled a realistic representation of what might actually occur if the particular new fuel or vehicle technology were to become widely used. This type of study potentially provides the most accurate assessment given the limitations and uncertainties in the data and the model. However, such studies provide relatively limited useful information about other fuel options or new technologies, or about what might happen if the emissions from the fuels or technology being considered were significantly different than what is assumed in the study. Thus they are most useful for assessing options which are in the advanced stages of being considered, and whose emissions impacts are relatively well understood.

A general scale ranking reactivities of VOCs would clearly be useful in assessing and comparing multiple fuel options, especially if reactivities of the mixtures can be obtained by linear summation of reactivities of the components. While scenario-specific assessments provide the best estimate of effects of any particular substitution, they are of limited utility for screening many options, and may not necessarily be superior to a more general scale when estimating relative ozone impacts for a wide variety of conditions. A reactivity scale directly relating VOCs to ozone would allow emissions with quite different VOC compositions to be directly compared on an ozone impact basis.

The author has proposed utilizing the "incremental reactivity" of VOCs as a basis for deriving reactivity scales [4,5]. The incremental reactivity of a VOC in a pollution scenario is defined as the change in ozone caused by adding a small amount of the VOC to the emissions in the scenario, divided by the amount of VOC added. Although strictly measuring only effects of small VOC changes, calculations have shown that the incremental reactivity of a VOC can provide a reasonably good approximation of the effects of larger VOC emissions changes, up to ~25% or more of the total VOC emissions. However, like VOC reactivity in general, the incremental reactivity of a VOC varies significantly with  $\text{NO}_x$  levels and other environmental conditions, and for many types of VOCs ratios of incremental are also quite variable.

The fact that incremental reactivities depend on environmental conditions means that no single scale can predict incremental reactivities, or even ratios of incremental reactivities, under all conditions. Thus the concept of a "reactivity scale" oversimplifies the complexities of the effects of VOC emissions on ozone formation. But an appropriate set of reactivity scales could address this problem by bracketing the range of environmental conditions relevant to ozone formation. This could also permit a systematic assessment of the variability of relative ozone impacts of different types of VOCs or VOC emissions mixtures. For some applications, such as setting VOC emissions standards, the only practical choice is between using some reactivity scale or ignoring reactivity altogether. The latter would be the appropriate choice if reactivities were so variable that all VOCs could be considered to be the same to within this variability. If this is not the case, and if the policy is adopted to use a reactivity scale, the issue becomes how one would develop a scale whose use would result in the greatest overall air quality improvement for the range of conditions where it will be applied.

In an investigation of alternative reactivity scales, the author calculated a number of different scales, based on different types of environmental conditions, and on various methods for quantifying ozone impacts [4]. These include: the Maximum Incremental Reactivity (MIR) scale, derived from impacts of the VOCs on peak ozone concentrations under high  $\text{NO}_x$  conditions where  $\text{O}_3$  is most sensitive to VOC emissions; the Maximum Ozone Incremental Reactivity (MOIR) scale, derived from impacts of VOCs on peak ozone concentrations under lower  $\text{NO}_x$  conditions most favorable for  $\text{O}_3$  formation; and various "base case" scales derived from incremental reactivities in various  $\text{O}_3$  non-attainment areas throughout the United States. Alternative base scales can be derived based on effects of VOCs on integrated ozone and integrated ozone over the standard as well as from effects on peak ozone concentrations. Although there are a number of different scales, to a large extent the choice boils down to use of a scale which, like MIR, reflects primarily the effect of the VOC on ozone formation rates, a scale which, like MOIR and the base case scales based on peak ozone concentrations, is more sensitive to the effect of the VOC on ultimate  $\text{O}_3$  yields in  $\text{NO}_x$ -limited conditions, or scales based on integrated  $\text{O}_3$ , which tend to be sensitive to both factors. Scales sensitive to effects of VOCs on ozone formation rates tend to give higher relative reactivities for aromatics, and lower relative reactivities for alkanes, than those based on ultimate  $\text{O}_3$  yields in  $\text{NO}_x$ -limited conditions.

Although a single reactivity scale may be necessary for some applications such as reactivity-based emissions standards, it is clearly preferable to use multiple scales, representing different types of environmental conditions and different methods for quantifying  $\text{O}_3$  impacts, when evaluating ozone impacts of alternative fuel and vehicle technologies. This approach is in fact being used in the analysis of vehicle emissions data from the Auto/Oil Air Quality Improvement Program, where different mixtures are compared using both the MOIR and the MIR scales. We suggest that other scales, such as the base case scales and scales based on integrated ozone, also be used. Use of multiple scales may not give a single relative ozone impact number, but, if the set of scales is appropriately chosen, would give an answer with an associated uncertainty range, which is (or should be) much more valuable to the decision-maker. If the set of reactivity scales is sufficiently comprehensive, then the results of any detailed scenario-specific assessment should be within the error bounds of the multiple-scale assessment.

In fact, the different reactivity scales have been found to give remarkably similar ratios of incremental reactivities for most of the alternative fuel options currently being considered [4], so the uncertainty range in this regard is not as large as one may expect based on variabilities of reactivities of individual compounds. This is because most exhausts are complex mixtures, and variabilities for reactivities of individual compounds tend to cancel out. Note, however, that the uncertainty range reflects only the effect of uncertainties of variabilities in atmospheric conditions, and not the uncertainties in the representativeness of the scenarios used to derive the scales, nor any systematic uncertainties in the chemical mechanism or other aspects of the model formulation. Reactivity calculations using other

chemical mechanisms, incorporating alternative assumptions concerning uncertain aspects of the VOCs' ozone forming reactions, and derived using different types of model formulations, and derived using different sets of scenarios, are necessary to get a handle on the magnitude of this source of uncertainty. The limited amount of work carried out thus far in this area is not sufficient for a reliable assessment of this source of uncertainty.

#### NEED FOR SYSTEMATIC UNCERTAINTY ANALYSES

Our principal recommendation for the evaluation effects of changes in vehicle and fuel technology on ozone formation is to conduct a comprehensive analysis of the propagation of uncertainties throughout the entire system. The overall uncertainty of the analysis is obviously important from a policy perspective. From a research perspective, is important to know which of the many of the many uncertainties are the most important in affecting the ozone impact prediction, and where research resources need to be directed to reduce this uncertainty. Some sources of uncertainty are much easier to quantify than others, and an obvious first step is to conduct an analysis of the effects of these uncertainties. This will at least give a lower-limit uncertainty range to the final result. For example, vehicle exhaust emissions are variable, and a sufficiently large exhaust data set would allow the impact of this source of uncertainty to be analyzed. With regard to atmospheric processes, the use of multiple reactivity scales will provide an analysis of the impact of the variability of reactivity with atmospheric conditions on overall ozone impact analyses. Other sources of uncertainty which are more difficult to quantify include uncertainties in vehicle emissions models and the atmospheric process and airshed model uncertainties which were discussed above. Probably the best approach to assess these is to develop alternative models or chemical mechanisms with reasonable assumptions and determine the extent to which their use gives different ozone impact answers. For example, the author is under contract to the CARB to develop alternative chemical mechanisms for evaluating how their use might affect model predictions of effects of NO<sub>x</sub> controls, and such mechanisms could well be used for deriving alternative reactivity scales for mechanism uncertainty analysis.

It should be pointed out that because of their resource requirements the complex grid models, while best suited for scenario-specific analyses, are of only limited utility for systematic uncertainty analysis. Because of the many variables which need to be examined in any comprehensive propagation of error analysis, the use of such complex, highly computer intensive, models would not be practical. Thus atmospheric processes would necessarily have to be represented using box models or reactivity scales calculated by box models. However, the complex grid models have an important supporting role in assuring that the reactivity results from the simpler models span the range of results that would be obtained using more complex grid models, and in developing an appropriate set of model scenarios representing the range of conditions occurring in real atmospheres. Ultimately, results with the box models would need to be verified using the more comprehensive models, with the box model results guiding which complex model simulations would provide the most useful results. However, without the results of the uncertainty analysis using the simpler models, we suspect that the complex models are not being used as productively as they could.

#### ATMOSPHERIC PROCESS RESEARCH NEEDS

In the long run, the most valuable research for improving our ability to predictively model ozone formation from vehicle emissions will be that aimed at improving our understanding of the fundamental processes involved. With regards to atmospheric chemistry, this includes elucidating the reaction pathways and products formed in the oxidations of VOC species, such as aromatics, which are currently represented in the model with parameterized mechanisms. Currently available environmental chamber data allow development of parameterized mechanisms, but have chamber effects which makes the applications of the mechanisms to the atmosphere uncertain, and even the adjusted mechanism do not fit all the available chamber data satisfactorily [6,11,12,13]. For example, current chemical mechanisms do not satisfactorily

predict the dependence of ozone formation on temperature as observed in chamber studies [12,13]. However, the current chamber data base in this regard is inadequate, and more well-characterized data and systematic studies are needed. Improved environmental chamber methods and technology are necessary to reduce the uncertainties in the evaluations and (where necessary) parameterizations of chemical mechanisms. There are also a number of long-term research needs regarding our airshed conditions. The greatest concern at present is the need to improve the quality of the emissions inventory, but model inputs, particularly for the most complex grid models, are also highly uncertain. Research is also needed to improve model formulation and computational efficiency, so more physically realistic models can be more widely used for examinations of multiple scenarios and sensitivity studies. There is also concern that errors in numerical approximation methods may be non-negligible in the current generation of the most complex models.

In the shorter term, the most valuable research would be focused on improving our ability to quantify the many uncertainties involved in evaluations of ozone impacts of vehicle emissions, and to understand how these uncertainties affect the overall results. This was discussed in the previous section. The use of airshed models simulating multiple scenarios representing the range of atmospheric conditions where O<sub>3</sub> pollution is a concern is an important component of this analysis. This requires research into what is an appropriate distribution of airshed conditions which should be represented in such an analysis. The scenarios used by the author in calculating the current MIR, MOIR and other reactivity scales were developed using a protocol which is not totally appropriate for this purpose. The chemical mechanisms currently used in airshed models are all out of date in some respects, and are inconsistent in some respects with the available data base of environmental chamber experiments, including more recent experiments which have not been used previously in their evaluations. The development of alternative mechanisms which are equally consistent with the laboratory experiments and theoretical and laboratory results need to be carried out in conjunction with the updates of the current mechanisms, to allow the importance of the remaining mechanistic uncertainties to be assessed. The priorities for medium- and longer-term research can then be set based on the results of this uncertainty analysis.

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