

# VOC REACTIVITY SCIENCE ASSESSMENT: EXECUTIVE SUMMARY

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## BACKGROUND

When volatile organic compounds (VOCs) are emitted into the atmosphere, they can undergo photochemical reactions that may contribute to the formation of ground-level ozone, which exceeds air quality standards in many areas. For that reason, emissions of VOCs have been subject to controls for a number of years, and significant additional controls are believed to be necessary before air quality standards can be met. Certain VOCs may also contribute to the formation of atmospheric particulate matter (PM), form toxic oxidation products, or have other impacts on the environment. The emissions of certain VOCs are regulated or banned because

they are highly toxic or deplete the stratospheric ozone layer. However, other than this, the need to reduce ozone has been the main factor driving the regulation of VOC emissions in the United States.

It has been realized for a number of years that not all VOCs are equal in their effects on ground-level ozone formation. Some VOCs react so slowly they have almost no effect on ozone pollution episodes, others not only form ozone themselves but also enhance ozone formation from other VOCs, and others actually inhibit ozone formation. In recognition of this, the U.S. EPA has had a policy of exempting from VOC regulations compounds that react extremely slowly or, more recently, compounds which have been shown to be ozone inhibitors. However, the vast majority of VOCs have been regulated as if they all had the same effect on ozone, even though this is known not to be the case.

The impact of a VOC on formation of ozone or other measures of air quality is referred to as its atmospheric “reactivity”. VOC regulations that take into account differences in VOC reactivity have the potential of being much more cost-effective than present policy, and would eliminate the need for the arbitrary dividing line in the current exemption policy. However, there are significant uncertainties on how VOC reactivities should be quantified and determined, and there are major unresolved policy issues that affect what scientific research is most needed. In view of this, the EPA and other regulatory agencies joined with industry groups and interested researchers to form the Reactivity Research Working Group (RRWG), to coordinate policy-relevant research related to VOC reactivity. The RRWG mission statement is as follows:

Our mission is to provide an improved scientific basis for reactivity-related regulatory policies. That will be accomplished by bringing together all parties actively interested in sponsoring, planning, performing or assessing policy-relevant scientific research on the reactivities of organic compounds emitted to ambient air, as related to the formation of ozone, PM<sub>2.5</sub>, and regional haze. This is for the purposes of coordinating such research and defining potential applications, while continuously involving key policy makers.

One of the first tasks of the RRWG is to produce assessments of policy and scientific issues related to reactivity. This document gives the result of the assessment of the scientific issues. Its objective of this assessment is to summarize the current state of the science related to quantifying VOC impacts in the atmosphere, and to summarize the critical research areas most needed to reduce the uncertainties involved. Contributors include many of the scientists who have conducting research in these areas, as well as other interested participants in the RRWG. This document, together with the RRWG policy issues document, will then be used as a basis for formulating a research plan to provide an improved scientific basis for reactivity-related regulatory policies.

## ASSESSMENT OF SCIENTIFIC ISSUES

There are many factors that affect the impact of a VOC on the atmosphere. These include how much is emitted into the gas phase, how rapidly it reacts, how its reactions affect ozone and other impacts, how environmental conditions affect how rapidly it reacts and the impacts of its reactions, and the volatilities, reactivities and impacts of its oxidation products. Because it is difficult to duplicate in the laboratory all the environmental factors that affect VOC reactivity, the only practical way to quantify a VOC's impact in the atmosphere is to calculate it using computer airshed models. This requires a mechanism for the VOC's relevant atmospheric reactions, and a model for the environment where the VOC is reacting. If either is incorrect, then the model predictions for the VOC's impact in that environment will also be incorrect, at least to some extent. Furthermore, since the VOC's impact depends on the environment, the choice of the environment to carry out the assessment will affect the results. Since environmental conditions are highly variable, knowledge of the distribution of environmental conditions is important for determining the most appropriate reactivity scale to use in regulations affecting large regions or the entire United States.

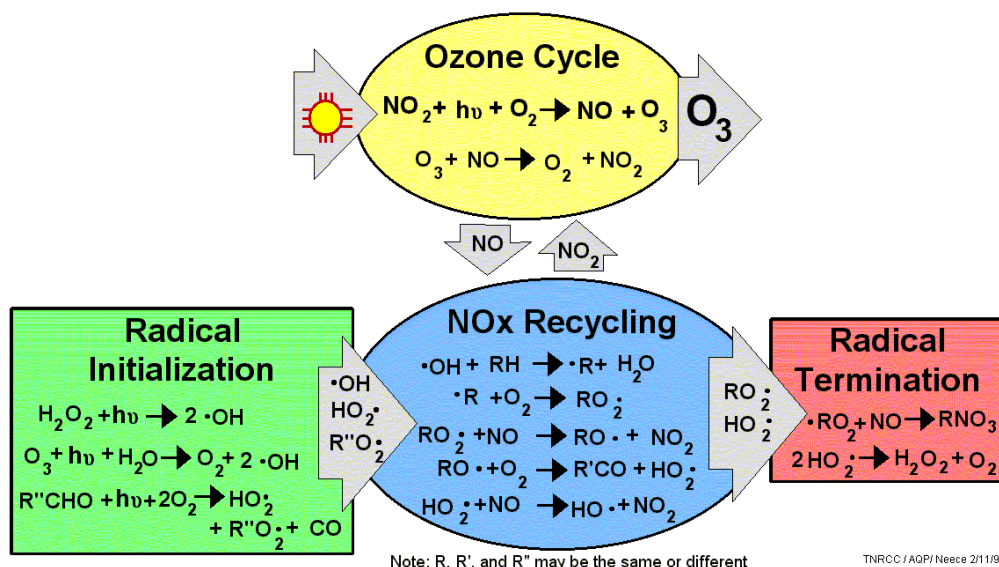
Clearly, there are many scientific issues and research areas involved in the quantification of VOC reactivity. For the purpose of this assessment, these have been divided into seven different areas, which are discussed in separate chapters of this assessment document. These are briefly summarized below.

### **Atmospheric Chemistry**

Model predictions of a VOC's impact can be no more reliable than the chemical mechanism used in the model to represent its atmospheric reactions. Although the rate constants for initial reaction consuming most VOCs in the atmosphere are known or can be estimated, the subsequent reactions for most VOCs are complex and incompletely understood. Furthermore, many of the oxidation products formed are unknown or uncertain. Nevertheless, significant progress has been made in recent years in improving our knowledge of and ability to predictively model the ozone formation potentials of many VOCs. However, ozone predictions for many other VOCs are still highly uncertain, and predictions of other impacts besides ozone require knowledge of much more of the details of the mechanisms which remain highly uncertain for most VOCs.

The current state of knowledge of atmospheric chemistry as it relates to VOC reactivity is summarized below, and discussed in more detail in the "Atmospheric Chemistry" chapter in this assessment. The chemical mechanisms currently used or being developed for VOC reactivity are then summarized, and our ability to model ozone reactivities of various VOCs are discussed. Although both gas-phase and heterogeneous processes are discussed, the focus of this discussion is mainly mechanisms for prediction of ozone and other gas-phase products, since discussion of mechanisms for predictions of aerosol formation potential is given in a separate section, as discussed below.

Figure EX-1. Diagram of processes affecting the rate of ozone formation.



The basic gas phase chemistry important in photochemical smog has been the subject of much study over the last fifty years. The oxidation of hydrocarbons begins with the abstraction of a proton by the hydroxyl radical (OH). In the presence of NO<sub>x</sub> (NO<sub>x</sub> = NO + NO<sub>2</sub>), the subsequent reactions result in the conversion of molecular oxygen to ozone. Ozone production continues as long as sufficient NO<sub>x</sub> is present so that reactions of peroxy radicals (RO<sub>2</sub>) with NO compete effectively with their reactions with other peroxy radicals. Ozone formation stops once NO<sub>x</sub> is consumed to sufficiently low levels. Conversely, high levels of NO<sub>x</sub> also inhibit O<sub>3</sub> because reaction of OH with NO<sub>2</sub> reduces OH levels. A diagram of the processes involved in ozone formation is shown in Figure EX-1.

Another factor affecting the behavior of VOCs and NO<sub>x</sub> in ozone formation is competition for the hydroxyl radical. Although higher VOC concentrations generally lead to more ozone formation, increasing NO<sub>x</sub> for a given VOC concentration may increase or decrease ozone, depending on the prevailing VOC-to-NO<sub>x</sub> ratio. As a result, the rate of ozone production is not simply proportional to the amount of NO<sub>x</sub> present. The reader is referred to the “Atmospheric Chemistry” chapter for further details.

The reactions that participate in smog formation can be divided into two groups: those that involve inorganic (non-carbon-containing) molecules such as OH and NO<sub>2</sub>, and reactions that involve VOCs and other organic species. Inorganic atmospheric reactions have been studied for many years, and the available laboratory data is evaluated on a regular basis. The reference documents produced by the NASA Stratospheric Data Panel (NASA, 1997) and the IUPAC Panel (Atkinson et al., 1997) are widely used as sources for the rate constants and other values

needed for modeling ozone formation. In general, gas-phase reactions of inorganic species are well characterized, but some are still under study to reduce the uncertainty associated with key interactions. The dominant area of remaining uncertainty with respect to inorganic species is that of reactions between gases and liquid or solid species. These heterogeneous reactions affect laboratory and atmospheric systems differently, and thus their characterization under both conditions is crucial to the extrapolation of smog chamber studies to the real atmosphere.

In contrast to the subset of inorganic reactions, the organic reactions that contribute to local air quality are complex and still highly uncertain. The least uncertain aspect of these reactions is the initial rates of VOC reactions with OH or NO<sub>3</sub> radicals or with ozone. Modern rate constant measurements are often precise, and where individual rate constants have been measured they are often known fairly well. Nevertheless, the stated uncertainties in rate constants in the compilations are almost always 25% or greater. For most compounds it is usually not particularly difficult or costly to obtain these rate constants if no data are available. While methods exist for estimating rate constants for the reactions of VOCs with OH and NO<sub>3</sub> radicals when data are not available, these estimates are probably only good to a factor of two for most VOCs.

Much of the complexity in organic photooxidation mechanisms comes from the variety of reactions in which the intermediate alkoxy radicals can participate. Absolute rate constants have been measured for only a few of the simplest alkoxy radical reactions, and most of the other available data concerns ratios of rate constants which can be inferred from results of product studies. This type of information is becoming available for an increasing number of systems because of ongoing product studies, though these branching ratios still need to be estimated for the large majority of VOCs emitted into the atmosphere.

In recent years the development of theoretical methods for the calculation of potential energy surfaces allows the direct computation of some rate constants. These have not yet been exploited to any significant extent in the uncertain areas of atmospheric chemistry, and the time seems right for a serious theoretical look at many of these processes. Estimates of heats of reaction are also used in many of the estimation methods, and often can be used to rule out chemically unreasonable reaction schemes. Theoretical calculations could potentially be very useful in providing the data needed to support application of thermochemically-based estimation methods.

The combined knowledge of atmospheric chemical processes can be used to estimate ozone production from a given release of VOCs. To do so, a chemical mechanism is developed and incorporated into an airshed model. Because of the large number of compounds emitted or formed in the polluted troposphere and the large numbers of reactions they, and their reactive products, can undergo, these mechanisms must necessarily contain significant simplifications and approximations. Furthermore, because of limitations in our knowledge, these mechanisms must contain assumptions and extrapolations to represent processes that are important but whose details are unknown. Different mechanism developers can apply different approaches to simplify or “condense” the mechanism to make it tractable and can use different assumptions and extrapolation methods when representing the main areas of uncertainty.

Different methods for mechanism compression include those based on reactivity, concentration weighting, and reactivity across carbon bonds within the molecules of each individual species. One alternate approach is to compress the mechanism in a transient fashion; the detailed speciation is retained until chemical integration is required, then the mechanism is compressed for the purposes of integration. After integration, the original information may be recovered. The development of these methods will allow increased hydrocarbon speciation in future modeling of reactivity. At the same time, increased model speciation in the absence of laboratory-based mechanistic or kinetic data will add little confidence to model results. The extent to which the use of detailed, temporarily compressed mechanisms improves ozone simulations has yet to be determined and would be an area worthy of further study.

Most, though not all, of the mechanisms used in the current generation of models have been summarized by Bergin et al. (1997) and Dodge (1999). The major mechanisms relevant to current reactivity assessments are discussed in the “Atmospheric Chemistry” chapter. The Carbon Bond IV mechanism is important because it is widely used in regulatory models. Its rate constants and reaction schemes represent the state of knowledge as of approximately 1987, although some important rate constants have been updated since then. The RADM-2 mechanism developed by Stockwell et al. (1990) is used in the EPA’s Regional Acid Deposition (RADM) model and is the only mechanism currently incorporated in the EPA’s Models-3 system. This mechanism was recently updated, expanded, and renamed RACM (“Regional Atmospheric Chemistry Mechanism”). It is the most updated of the published mechanisms in terms of its rate constants and the mechanisms for its explicit reactions.

The SAPRC mechanisms are important because they are designed specifically for VOC reactivity assessment and have been employed to generate reactivity scales that have been or are being considered for use in regulatory applications. The SAPRC-90 mechanism has been evaluated against results of ~500 smog chamber experiments and in most cases fits the ozone data to within  $\pm 30\%$ . Alternatives to the SAPRC mechanism (e.g., the Master Chemical Mechanism (MCM) of Derwent and co-workers) are being developed and applied by researchers in Europe. These mechanisms are not used in the United States because model software is not adapted to mechanisms of this size. Also, they have not yet (to our knowledge) been evaluated against results of environmental chamber experiments.

In Canada, the ADOM-II mechanism is currently used for reactivity simulations, and a new mechanism is under development for gas-phase and particulate modeling in the AURAMS model. Tests to date have shown that the new mechanism provides a significant improvement in the ability to predict chamber data compared to the ADOM-II mechanism.

Before any chemical mechanism is incorporated into an airshed model, it must be demonstrated to predict at least the major features of the VOC-NO<sub>x</sub>-air photooxidation process. The only practical means for doing this is to conduct experiments using an environmental chamber, also called a smog chamber, where the chemical processes of interest occur under controlled and well-characterized conditions. Although there are really no practical alternatives at the present time, use of environmental chambers for mechanism evaluation is not without significant problems. Some shortcomings of chamber experiments include the high VOC concentrations at which most experiments must be conducted, the occurrence of reactions on

chamber walls, the inability to track most intermediate products, the difficulty of characterizing illumination inside the chamber, and the lack of multi-day experiments representative of conditions downwind of pollution events.

In summary, recent years have seen significant progress in our understanding and ability to model the gas-phase reactions of pollutants in the troposphere. Nevertheless, there remain major gaps in our knowledge of the details of these gas-phase reactions, and our understanding of potentially significant heterogeneous processes is even less complete. Many of the mechanisms used to predict ozone are highly parameterized and simplified, with empirical adjustments to fit chamber data, and with no reliable ability to predict impacts other than on ozone and perhaps overall OH radical levels.

Ongoing improvements in airshed model hardware and software permit use of more detailed atmospheric mechanisms, which have the potential to give more accurate and comprehensive predictions for any VOC of interest. However, without knowledge of the mechanistic details, any predictions made using these detailed mechanisms may be no more reliable than those of the simplified and parameterized mechanisms currently in use. Therefore, the main factors limiting the chemical accuracy of current and future airshed models are limitations in our knowledge of atmospheric chemistry and limitations in the environmental chamber database needed to verify the accuracy of model predictions.

### **Aerosol Forming Potential**

Urban fine particulate matter is comprised of a complex mixture of both primary and secondary organic and inorganic compounds and emanates from a wide variety of sources. An important component that can significantly contribute to the fine particulate burden, especially during severe urban smog episodes, is secondary organic aerosol (SOA). Like ozone, secondary organic aerosol results from the atmospheric oxidation of VOCs, but it is generally formed only from the oxidation of VOCs comprised of six or more carbon atoms. This is because oxidation products must have vapor pressures that are sufficiently low to enable them to partition into the aerosol phase.

The atmospheric chemical reaction pathways of VOC molecules sufficiently large to lead to SOA are complex, and resulting oxidation products are both numerous and difficult to quantify analytically. As a result, it is currently not possible to determine the aerosol formation potential of individual VOCs strictly on the basis of atmospheric chemical reaction mechanisms. This means that SOA yields must be determined experimentally.

As discussed in the “Aerosol Formation Potential” chapter of this assessment, SOA yields have been determined experimentally for many individual VOCs. The data obtained indicate SOA yields vary widely with conditions, which means that, as with ozone reactivity, no single aerosol formation potential can be associated with any given VOC. However, Odum et al (1996) found that the California Institute of Technology (Caltech) environmental chamber data could be fit by a semi-empirical gas/aerosol partitioning model which assumes that the mix of semi-volatile oxidation products from a VOC can be represented by two empirical products,

characterized by parameters  $\alpha_1$ ,  $K_1$ , and  $\alpha_2$ ,  $K_2$ . Here, the  $\alpha$ 's refer to the yields of the products, and the  $K$ 's refer to their gas-aerosol partitioning coefficient, which is a function of the molecular weight, vapor pressure, and the activity coefficient of the product in the aerosol phase mixture. Such parameters have been derived for a variety of aromatic hydrocarbons and biogenic terpenes.

This gas/aerosol partitioning model can be used to predict SOA yields in a chamber experiment or in the atmosphere from

$$Y = \Delta M_o \sum_{i=1}^N \frac{a_i K_i}{1 + K_i \Delta M_o}$$

where  $Y$  is the aerosol mass formed from the VOC (in terms of mass aerosol formed per mass VOC reacted),  $\Delta M_o$  is the mass of aerosol present, and  $N$  is the number of semi-volatile products, which is assumed to be 2 in the semi-empirical model.

It must be noted that this theory assumes that secondary products are unable to form a solution with existing inorganic seed aerosol. Furthermore, most of the experimentally determined SOA yields have been measured at relative humidity (RH) less than 5%. At this level of RH the seed aerosol is dry and the resulting organic aerosol is water-free. Because organic products will likely be most soluble in their own liquids, SOA yields measured at essentially 0% RH can be expected to represent an upper limit to the aerosol partitioning that will result. Experiments are presently underway at the Caltech to measure SOA yields as a fraction of RH over realistic ambient RH ranges.

Because of the difficulties in characterizing SOA on a molecular basis and considering the significant uncertainties associated with model input data, the treatment of SOA in current air quality models is limited. Seigneur *et al.* (1998) recently reviewed the treatment of SOA formation in current regulatory and research-grade air quality models, and the results are summarized in the "Aerosol Formation Potential" chapter of this assessment.

Of the eight models that treat SOA formation, six use an approach assuming a single SOA yield from each VOC, which as indicated above is not consistent with chamber data. The GATOR model (Jacobson, 1997) describes gas-particle partitioning of about ten condensable and soluble organic species that, however, are not directly representative of ambient condensable reaction products. In the CIT model, SOA is modeled by mass transport between gas and particulate phases, which is governed by the same formulation as that for inorganic volatile compounds. Recent work by Strader *et al.* (1998) combines the organic-phase absorption approach of Odum *et al.* (1996, 1997a,b) with recent experimental data on saturation vapor pressures of organic compounds, and derived a model with six condensable products, with yield parameters determined on the basis of Caltech chamber data. This approach has been incorporated in the revised version of the UAM-AERO air quality model. This approach differs from that of Odum *et al.* in that the partitioning coefficient parameters,  $K_i$ , were derived from theory rather than fits to chamber data. However, at present both methods rely on empirical data to determine the partition parameters.



The “Aerosol Forming Potential” chapter also discusses data on ambient aerosol composition. Although the available data provide some information on the magnitude and structure of secondary organic aerosol, this information is incomplete and requires that significant assumptions be made in interpreting the ambient data. Our understanding of the chemical nature and sources of secondary organics would be significantly improved by the identification of suitable molecular tracers of organic aerosol formation pathways.

Atmospheric chemical reaction mechanisms currently included in urban-and regional-scale models were designed for accurate prediction of ozone formation chemistry. Generally, these mechanisms do not account for the chemistry of organics in sufficient detail to predict the generation of semi-volatile products. Many of the higher molecular weight organics that are not important in ozone formation, but are sources of secondary organic aerosol, are not represented in current mechanisms. To predict SOA formation, chemical reaction mechanisms need to be expanded to include all the important SOA-forming organics and to include, to the extent known, a representation of the semi-volatile products formed from each parent compound. Evaluation of the organics that need to be included will be based on available chamber data, on estimated atmospheric oxidation mechanisms, and on the estimated vapor pressures of the oxidation products. While this expansion may not lead to substantially improved ozone prediction, it is essential to prediction of SOA formation.

## **Emissions Data**

The emissions from the multitude of sources in the environment are critically important inputs in the airshed models that must be used to assess impacts or reactivities of VOCs. The amount of emissions determines the nature of the chemical environment in which the VOC reacts, and thus affects not only the absolute amount of ozone and other secondary pollutants formed, but also the incremental effects of any additional VOC on the formation of those pollutants (i.e., the VOC reactivities). Emissions data also impact directly on government policy. Changes in emissions levels over time reflect the effectiveness of government regulations, as well as changes in activity level. The accuracy and completeness of emissions databases are therefore of great importance.

The creation of an emissions database takes place in several stages, with each stage having associated errors and uncertainties. From sources such as Moody et al (1995), the SPECIATE web site (Ryan, 1998), Moran et al (1997), and the AP-42 database (EPA, 1995), typical stages for determining anthropogenic emissions are as follows:

- Source profiles (which provide a breakdown of the total VOC emitted from a given source type into a detailed VOC fractionation) are constructed from measurements. A limited number of profiles are currently available (e.g. about 300 used in SPECIATE).
- Source types are categorized using Source Classification Codes (SCC), Area Mobile Source codes (AMS) and Standard Industrial Classification codes (SIC). Typical emissions processing systems have thousands of source classifications (Ryan, 1998).
- Each classified source type is assigned a source profile from the set of available profiles.

- The total annual VOC emission for each source type is determined from the product of the appropriate emission factor, activity rate, and control factors (AP-42; EPA, 1995).
- Individual sources from the database are assigned total annual VOC emissions, source classification codes, and source profiles.
- The total annual VOC emission rates may be multiplied by meteorological factors (e.g. to include dependence of emissions on ambient temperatures).
- The source profiles, linked to the individual sources in (5), are used to convert the total annual VOC emission into a speciated annual VOC emission.
- The detailed speciation is lumped into a smaller number of species for modeling purposes (e.g. Middleton et al., 1990).
- Temporal allocation occurs; temporal factors are applied to the model species annual emissions to create seasonal, daily, then hourly emissions estimates.
- Spatial allocation factors are used to create the spatial distribution of area sources. Smaller point sources are sometimes included with the area sources.

For biogenic emissions, the processing differs somewhat:

- Spatially varying biomass factors (mass of emitting foliage / unit horizontal area) are linked with monthly frost/seasonal variation factors and a database of vegetation categories.
- Net vegetation standard emission rates (30°C, 1000  $\mu\text{mol}/\text{m}^2/\text{sec}$  photo-synthetically active radiation (PAR)) are calculated for each part of the vegetation grid.
- Temperature and / or PAR corrections are applied for the meteorology at the site.

For both forms of emissions, regridding from the database spatial grid to the model grid is often required.

Each of the stages listed above has uncertainties, many of which have not been characterized in a quantitative way. The limited number of source profiles compared to SCC, SIC, or AMS codes is an example. The extent to which the available source profiles adequately represent the much larger set of source classifications is unknown. The source profiles themselves are the result of a relatively small number of measurement studies; in some cases a single study is used to represent the emissions from an entire industry. Errors in the total annual VOC emission rates are usually not estimated. Similarly, errors in temporal emission factor estimates are usually not estimated. For the biogenic emissions, the existence of detailed vegetation databases is required; these are not always available with sufficiently fine spatial detail for adequate resolution of emitting regions.

Some of the sources of uncertainty have been characterized. The effect of lumping detailed speciation emissions into model speciation has been examined by Middleton et al (1990) - comparisons there and in later work (Kuhn et al., 1998; see also “Lumping” in the Atmospheric Chemistry chapter of this assessment) indicate that the effects of speciation in model ozone

production may be a smaller source of error than other model approximations. Similarly, the procedures for determining standard emission rates for specific vegetation types are well established and the uncertainties associated with these measurements are known (c.f. Guenther et al., 1996).

From the standpoint of VOC reactivity and ozone formation, it is essential to determine which emissions-related uncertainties have the biggest impact on the predicted reactivity of the atmosphere. This in turn could be used to design measurement initiatives directed at reducing the most significant uncertainties. Sensitivity studies of model results associated with errors in the temporal factors, source profile assignment and total VOC emission rates should be directed towards determining which aspects of the emissions system have the biggest impact on reactivity. A few preliminary studies of this nature are discussed in the “Emissions Uncertainty” section of the “Emissions Data” chapter of the assessment. Emissions uncertainties can contribute 30 to 50% of the overall uncertainty in O<sub>3</sub> predictions, while the contribution to uncertainty in VOC reactivity may be smaller (8%).

Certain aspects of anthropogenic emission factor calculation are described in the “Status of Anthropogenic Emissions” section of the emissions data chapter. There it is noted that all available data for point sources should be taken into account, for both minor and major emitters. In addition, time factors and other parameters have typically been estimated based on episode days; non-episode, non-attainment days may therefore be incorrectly represented in emissions databases. Biogenic hydrocarbon emissions are described in a separate section of the chapter on emissions data. Note that the need for improved vegetation databases is given as the most significant need for further research.

Emission reduction effects such as volatility suggest that some AP-42 emissions estimates may not adequately describe the amounts of VOCs that ultimately enter the atmosphere. These arguments are discussed below and in the “Emissions and Volatility” chapter of this assessment, since they are relevant to assessing reactivities of individual VOCs as well as the quality of the overall emissions inventory.

## **Volatility and Fate**

The formation of tropospheric ozone from a volatile compound is a dynamic multi-step kinetic process that is highly dependent upon the relative concentrations of NO<sub>x</sub> and the VOC. The tropospheric concentration of a VOC is likewise affected by both the rate and extent of release from an emission source and by the rate of removal through a variety of competing processes (photooxidation, deposition, horizontal and vertical transport, aerosol formation) (Mackay et al, 1996). The latter considerations are clearly important in assessing effects of VOCs on formation of ozone and other impacts which involve the VOC reacting in the gas phase. These are discussed in more detail in the “Volatility and Fate” chapter of this assessment, and are summarized below.

Consideration of equilibrium vapor pressures and partition between gas phase and aerosols suggests that many low-vapor-pressure (LVP) VOC will be present predominately in the gas phase. However, this conclusion may not be entirely correct in view of those studies

indicating alternate fates for the VOCs contained in consumer, commercial, and agricultural products (Rapaport, 1988; Bennett et al, 1998). There are many ways that compounds of low volatility, especially those that are hydrophilic, may be prevented from entering the atmosphere or removed once they enter, but quantitative assessments are rare.

The rate of volatilization may dictate the overall rate of ozone formation for a particular VOC. Under some circumstances, the rate of release of a VOC to the environment may be the rate-limiting step in ozone production, thereby restricting its relative importance and overall contribution. Although, research has shown that the rate of volatilization from wastewater's and agricultural lands can affect airborne exposures to VOCs, there has been no systematic study of the volatilization rates from complex mixtures such as coatings, composites, and consumer products (Bianchi and Varney, 1977; Sharma and Overcamp, 1996). The overall impact of VOCs from these emission categories can be affected by the nature of matrix in which there are dissolved with lower rates of volatilization occurring when water soluble compounds are dissolved in an aqueous matrices (Lyons, 1990). Another important aspect of the volatilization issue is the role of competing removal processes. When volatilization rates are low, there is time for competing processes to remove the VOC by alternate routes (Watson et al, 1998). New research is needed to examine the issue of volatilization rate and to the develop models that can incorporate all that that is known about a chemical's tropospheric fate and removal.

Because LVPs fall outside normal analytical methods, little is known about the ambient air concentration of semi-volatile compounds. Difficulties with source apportionment by chemical mass balance and analytical determination hinder any reliable estimation of the emissions rate for low volatility compounds. The total emissions of these compounds is not known with certainty, and the contribution from coatings and commercial products may be much lower than the proportions attributed to these sources in current emissions inventories (Watson et al, 1998).

## **Air Quality Models**

As indicated above, because a VOC's impacts on air quality depend on the environment where it is emitted, use of airshed models provides the only practical means to predict the VOC's impact in an actual environment. Air quality models (AQMs) are computerized representations of the atmospheric processes responsible for air pollution, including ozone formation. The models simulate the atmosphere in varying degree of detail by mathematically representing emissions; initial and boundary concentrations; chemical reactions of emitted species and their products; and local meteorology such as sunlight, wind, and temperature. In this way, an understanding of the atmosphere's chemistry and meteorology is combined with estimates of source emissions to predict the possible effects of control strategies. AQMs are also an important tool in gaining understanding about the behavior of various compounds in the atmosphere, such as the reactivity of VOCs, and AQM simulations can be used to develop attainment strategies that minimize the costs of control strategy implementation. These models are essential for evaluating control strategies aimed at meeting air quality goals.

While AQMs are the best tools currently available for evaluating proposed ozone control strategies, it is important to recognize that the uncertainties in model components and in input data used by the models might have a serious impact on the model predictions. Significant progress has been made on uncertainty analysis, particularly with regard to uncertainty reduction in reactivity-based analysis methods. However, some serious concerns remain regarding the implementation of reactivity-based policy.

Important issues in the application of AQMs for control strategy evaluation and reactivity quantification are as follows:

- Although serious questions still exist about the validity of models for the simulation of particular scenarios, it can be argued that we may have greater confidence in their ability to predict relative changes, such as for reactivity quantification.
- Box models and trajectory models are useful for calculating preliminary reactivity scales and for detailed uncertainty and sensitivity analysis. Box/trajectory models, however, are overly simplistic for evaluating reactivity-based substitution strategies and regional or national reactivity scales. Grid models should be used for these purposes. (This is discussed further in the “Environmental Conditions” section.)
- The traditional model evaluation criteria currently in use by the U.S. EPA are inadequate for determining the fitness of a model simulation for assessing control strategies. Various diagnostic approaches exist that may be useful in improving model evaluation, and these approaches should be considered in developing new criteria for model evaluation. For applications of models to reactivity scales, it is particularly important to develop diagnostic tests that validate model representation of odd nitrogen and radical budgets.
- As discussed in the “Environmental Conditions” chapter, the representation of transport and dispersion affects precursor concentrations and O<sub>3</sub> concentrations. This can also affect VOC to NO<sub>x</sub> ratios and O<sub>3</sub> sensitivity to precursors. While box models have overly simplistic dispersion schemes, the more physically complete grid models still have large uncertainties in their representation of vertical dispersion and horizontal advection. Uncertainty in transport processes such as nocturnal jets could significantly affect model predictions of reactivity. Sensitivity studies are needed to examine the possible effects of uncertainty in the meteorology on simulations of reactivity-based substitution strategies.
- Uncertainty and sensitivity analysis of model performance and reactivity prediction is crucial. Four types of sensitivity analyses are typically applied:
  1. Stand alone analysis of the effect of inputs or model formulation.
  2. Evaluation of outcome variable responses caused by a change in the process parameterizations, model structure/numerics, or input variables (e.g., the effect of a change in meteorology on O<sub>3</sub> concentration predictions.)
  3. Evaluation of the change in outcome variable sensitivity to precursor emissions caused by a change in inputs (e.g., the effect of a change in meteorology on O<sub>3</sub> sensitivity to VOC reductions.)
  4. Evaluation of the change in an emissions control strategy (magnitude or type) needed to attain an air quality standard.

- It is necessary to determine the adequacy of each of these types of analyses in assessing reactivity-based substitution strategies. Additional analysis tools should be explored and current techniques should be applied to a wider range of parameters.

## **Environmental Conditions**

Even if there were no uncertainty in the chemical mechanism or the airshed model when applied to a particular episode, the reactivity calculated for the VOC will be applicable only for that episode, and may not accurately represent impact in another area, or under different meteorological conditions. Nevertheless, most practical reactivity-based regulatory strategies being proposed involve using a single reactivity scale that will be applied on a national or at least regional basis. At best, the distribution of VOC reactivities in an appropriate ensemble of environmental conditions can be used as the basis for the regulatory decision. In either case, an assessment of the most appropriate type of reactivity scale, or set of scales, for regulatory applications requires knowledge of the distribution of environmental conditions relevant to the application of the regulation.

In the “Environmental Conditions” chapter of this assessment, the environmental factors affecting reactivity, atmospheric structure, and potential impacts of long range transport, and variability in current reactivity scales are discussed. As discussed there and in the “Reactivity Assessments” chapter (see below), current urban reactivity scales presume that air near the surface moves slowly and is confined to the boundary layer and do not adequately consider long range transport mechanisms involving the coupling of the boundary layer to the free troposphere. For example, in many instances ozone and its precursors are rapidly vented aloft and quickly transported downwind of the mid-latitude jet stream, where they can be re-entrained into the boundary layer.

It can be argued that reactivity scales that do not adequately account for long range transport mechanisms may not be appropriate for assessments relevant to the new ozone standard of 80 ppb averaged over 8 hours. Long-range transport of ozone and ozone precursors via the free troposphere has the potential to influence the level of radicals in remote urban and rural areas, thereby influencing the local reactivities of VOCs in those areas. Transport of ozone precursors has the potential to influence the NO<sub>x</sub> budget in remote rural areas, through reservoir species such as PAN and other organic nitrates that do not easily rain out of the atmosphere. It also has the potential to produce significant quantities of ozone in remote urban and rural areas when compared to the difference between the new federal ozone standard (80 ppb) and the level of background tropospheric ozone (30 ppb). Regional, 3-D Eulerian models that adequately resolve both the boundary layer and the free troposphere are presently the only tools that are believed to properly account for long-range transport mechanisms involving boundary layer-free troposphere coupling. Therefore, it is recommended that use of such models in reactivity assessments be expanded. This is discussed further in the following section.

## Reactivity Assessments

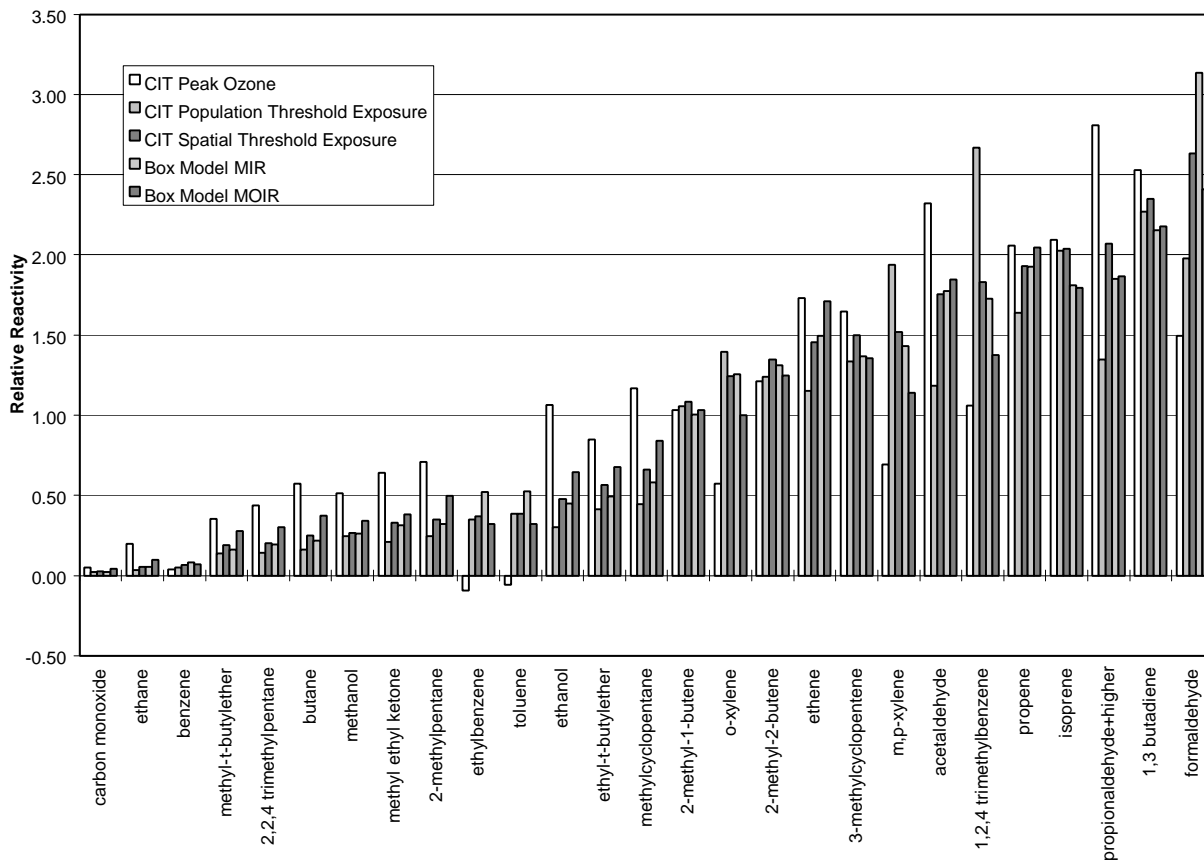
Over the past decade, studies have been performed to assess the reactivity of organics and the viability of using VOC relative reactivity rankings in emissions regulations. Both experimental and modeling based approaches have shown a wide range of reactivities, and, to a lesser extent, increased the availability of tools to quantify reactivity. While the early studies utilized smog chambers and box/trajectory model calculations, more recent studies have included three-dimensional photochemical modeling and applied uncertainty analyses to both box model and three dimensional assessments.

The first studies conducted by Carter (e.g., Carter, 1994) showed that there is a wide variation in the ozone forming potential of VOCs and that the absolute amount of ozone formed per mass of VOC emissions differed significantly depending upon ambient conditions. For example, the absolute amount of ozone formed for virtually all species was found to decrease when NO<sub>x</sub> availability was reduced (e.g., MOIR vs. MIR conditions). However, the relative amount of ozone formed (e.g., the amount of ozone formed from 1 kg of emissions of the target species compared with the amount of ozone formed from 1 kg of a base mixture) was found to be a more stable and robust measure of VOC reactivity than an absolute measure, regardless of ambient conditions. As shown in Figure ES-2, the “relative reactivity” is also reasonably consistent regardless of modeling methods or quantification metric. Indeed, studies using both box and airshed models indicate that relative reactivity is significantly less sensitive to model uncertainties and environmental variabilities than are absolute measures. Uncertainties and variabilities led to relative reactivity coefficients of variation of 10-30% in most cases, suggesting that relative reactivity is viable beyond single airsheds or states. This hypothesis should be further investigated.

At present, reactivity studies can be performed at both regional and urban scales. Three-dimensional models, using advanced chemical mechanisms and sensitivity analysis techniques, have been applied to the areas of Los Angeles and the Texas-Mexico border to quantify and assess the spatial variability of relative reactivities of various VOCs. Similar modeling approaches have been applied at larger scales, e.g., the eastern United States and part of southeastern Canada, though not to quantify VOC reactivity. Such a spatial extension would be straightforward and could be used to further understand regional reactivity issues.

As discussed in the “Atmospheric Chemistry” chapter, one issue that contributes significantly to the uncertainty in reactivity quantification is that chemical oxidation pathways are well known for only a relatively small number of compounds. Most of the VOC reaction paths are estimated. Reactivity estimates for novel compounds would be subject to high levels of uncertainty until their chemistry was elucidated. However, current Monte Carlo and sensitivity analysis techniques can establish bounds on reactivity estimates and aid in identifying the most important areas for further investigation. Studies to date suggest that, for the most part, the major uncertainty in relative reactivities is from uncertainty in the initial reaction rate constants (e.g., the reaction of the VOC with the hydroxyl radical).

Figure ES-2. Comparison of three-dimensional and trajectory modeled relative reactivities. Relative reactivity is defined as the ratio of the incremental reactivity of the VOC divided by the incremental reactivity of the mixture used to represent reactive VOC emissions from all sources.



A strong foundation for understanding VOC reactivity issues has been developed, and the appropriate tools exist with which to further this understanding. Specific research projects should be identified to:

- enable the development of reactivity scales for use at the national levels (e.g., in the U.S., Canada, or Mexico)
- further define appropriate metrics for reactivity assessment
- apply prediction and analysis tools at larger scales and in a greater variety of locations and conditions, and
- further investigate the sources and impacts of uncertainties.



## **Persistent Organic Pollutants**

Persistent Organic Pollutants (POPs) are under increasing international scrutiny due to their potential for long-range transport and because of their possible impacts on the global environment. It has been proposed that organic compounds with even modest atmospheric lifetimes may accumulate in remote regions after being emitted into the air, through successive deposition to and re-volatilization from soil and water. On the other hand, slowly reacting compounds tend to have the least adverse impact near the environment where they are emitted, and reactivity-based control strategies may tend to encourage the use of such compounds. Since slowly reacting compounds tend to be the most persistent, this is an obvious concern when implementing such policies.

A discussion of persistent organic pollutants and related issues is beyond the scope of the present assessment. It is recommended that an assessment of the current state of knowledge in this area be included as part of a comprehensive overall assessment of VOC reactivity. Appropriate independent expert(s) will need to be identified to carry out this assessment.

## SUMMARY OF RECOMMENDATIONS

The recommendations for research in the various areas covered by this assessment are summarized in this section. They are given for the various subject areas discussed above, though a number of recommendations span several of these areas. Note that there has been no attempt at this point to prioritize these research needs. This will be done when the overall RRWG research plan is formulated, which will take into account the results of the assessment of the relevant policy issues as well as the results of this science assessment.

### Atmospheric Chemistry

Recommendations for research in the area of Atmospheric Chemistry and Chemical Mechanisms fall into three broad categories: laboratory studies to provide a more complete understanding of the processes which must be included in models of tropospheric reactivity, theoretical calculations and model improvements to allow for maximum use of our knowledge and performance of reactivity assessments, and environmental chamber improvements and validation experiments to provide a high-quality data base against which to test airshed and reactivity models. These are summarized below.

#### Laboratory Studies

- Rate constants and mechanisms for reactions of peroxy radicals with NO, HO<sub>2</sub>, other RO<sub>2</sub>, and NO<sub>3</sub> radicals need to be studied. This would include additional data for nitrate yields from peroxy + NO reactions, particularly for non-hydrocarbon reactions.
- Branching ratios for the competing reactions of alkoxy radicals, particularly those not formed from alkanes and alkenes, need to be studied.
- Details of the reactions of ozone with alkenes and other VOCs containing double bonds *under atmospheric conditions* need to be elucidated. Total radical yields are particularly important in model simulations of VOC reactivity.
- More information is needed concerning the tropospheric chemistry of the oxygenated products formed in the photooxidation of VOCs.
- Laboratory and ambient air measurements need to be carried out to determine the atmospheric fate of potentially reactive oxygenated species, particularly those with a high OH reactivity (or expected high OH reactivity) and a known or expected low volatility.
- Further study of heterogeneous reactions in the atmosphere and in environmental chambers are needed. This includes, but is not limited to, reactions involving HONO formation, N<sub>2</sub>O<sub>5</sub> hydrolysis, and reactions involved in secondary aerosol formation.
- Studies are needed to improve our understanding of reactions on smog chamber walls. Such information will reduce uncertainties and sources of errors when using environmental chamber data to evaluate and develop chemical mechanisms.

- More information is needed concerning heterogeneous processes in aqueous media. Needed studies include improved characterization of aerosol phase and composition, heterogeneous chemistry of peroxy radicals, HONO as an early morning HO<sub>x</sub> source in urban areas, temperature dependence of aqueous phase reactions, and compilation of data for modeling atmospheric aqueous phase chemistry.
- Information is needed concerning possible reduction of HNO<sub>3</sub> to NO<sub>x</sub> on soot or sulfate aerosol. Reactivity of O<sub>3</sub> on soot, mineral dust, and organic carbon aerosols is also poorly known at this time.
- Mechanisms and products of the reactions of OH-aromatic adducts with O<sub>2</sub> and NO<sub>3</sub> remain highly uncertain. *Quantitative* yield information and studies of the reactions (including photolyses) of these aromatic products are especially needed.
- Thermal decompositions and other atmospherically important reactions of the higher PAN analogues, such as that formed from methacrolein and isoprene, need to be studied.
- Information concerning the reactions of radicals formed from halogen-containing compounds, amines, and other nitrogen-containing compounds is needed before reactivities of such compounds can be assessed with any accuracy.

#### **Computational and Modeling Techniques**

- The computation of rate constants using ab initio, transition state, and other theoretical methods needs to be applied to atmospherically-relevant systems. These techniques should be tested through comparison to known processes, then applied towards predicting mechanisms and reaction rates which are currently unknown.
- The methods used to estimate mechanisms of VOCs for which there are no data need to be improved. For many classes of compounds no reliable estimation methods yet exist. Theoretical calculations of the most uncertain reactions and targeted experimental studies to establish or evaluate relationships are needed.
- Sensitivity analysis should be applied to the mechanisms to help decide which processes will be most important to study in the future. This requires quantifying the uncertainties involved, not only in the elementary rate constants, but also in parameterization methods in mechanisms adjusted to fit chamber or other data.
- Work is needed to assess the optimum level of detail for atmospheric chemical mechanisms, given the modeling application and knowledge of the processes being represented. The minimum list of inorganic reactions required for photochemical reactivity calculations, including the pressure and water vapor dependent pathways of HO<sub>2</sub>, needs to be determined. A model comparison of highly speciated versus lumped versus temporarily compressed mechanisms should be performed for a realistic atmospheric conditions to determine the relative merits of model speciation in reactivity estimates.

- The implementation of the Morphecule approach needs to be completed, and its advantages over alternative methods for representing chemical detail in models need to be assessed.

### **Smog Chamber Studies**

- Improved facilities are needed to evaluate mechanisms under lower pollutant conditions than is currently possible, and improved instrumentation is needed to monitor trace species and intermediates and VOC reaction products.
- Methodologies need to be developed to screen or assess reactivity more readily and at lower cost than is currently possible.

### **Aerosol Formation Potential**

Research recommendations concerning assessment of aerosol forming potentials of VOCs can be summarized as follows:

- Aerosol formation yields need to be measured for the full variety of VOCs of interest. Such measurements need to be made under a sufficient variety of conditions to determine all relevant parameters that will affect SOA yields in the atmosphere, including temperature and humidity.
- The environmental chamber systems used to determine SOA yields need to be improved so that conditions affecting aerosol formation, particularly temperature and humidity, can be controlled and systematically varied.
- Experimental data are needed under controlled conditions to test theories and models for SOA formation.
- The treatment of SOA formation in models needs to be improved. At a minimum, the treatment must be consistent with available environmental chamber data.
- Gas-Phase atmospheric chemical reaction mechanisms need to be adapted to predict formation of semi-volatile products from the major classes of emitted VOCs and to appropriately represent their reactions.
- The types of semi-volatile products formed from the reactions of the major classes of emitted VOCs need to be determined, and their vapor pressures and other parameters affecting their partitioning into the vapor phase need to be determined.
- More information is needed concerning the chemical composition of the organic components in ambient aerosol, and of organic aerosol formed from VOCs in environmental chamber experiments.

## **Emissions Data**

The following recommendations are made concerning the problem of reducing the uncertainty of the emissions data which are used as inputs to the air quality models used for reactivity assessment:

- The impact of the uncertainties and approximations used in the emissions assignment process on the results of models used for reactivity calculations needs to be determined. Sensitivity analyses should be conducted to identify the effect of uncertainties and approximations in temporal factors, source profile assignment and total annual VOC emission rates on model reactivity estimates.
- The biogenic emissions data are particularly uncertain, and these uncertainties may significantly affect reactivity assessments in regional scenarios. There is a need for the improvement of the vegetation land-use database and area average factors used in biogenic emissions estimates to reduce their uncertainty. Other significant data gaps include lack of factors genetic variability within species and for wounding of vegetation, inadequate characterization of emission underestimates due to chemical losses, and the need for refinement of emission activity and escape efficiency parameters.
- EIIP procedures, operational information, and stack sampling should be used to ensure adequate speciation of anthropogenic VOCs, with the encouragement of industry participation.
- Time factors for apportionment of VOCs on non-episode days need to be designed, as well as appropriate changes to engineering and VOC composition parameters to reflect non-episode emissions days.
- Updates to the limited set of speciation profiles are essential for improvement to the emissions databases.

## **Volatility and Fate**

The following research recommendations are made concerning the issue of the extent to which individual VOCs are emitted into the gas phase and undergo the gas-phase reactions involved in the formation of ozone, SOA, and other secondary pollutants.

- Alternative Fate factors for Partitioning need to be designed, to account for alternative fates such as losses to waste-water, chemical transformations, adsorption onto sinks
- Volatility factors need to be designed to account for the effects of volatility on net emissions.
- More validation data are needed for fate and transport models.
- Methods need to be developed to incorporate the possibility of alternative fates besides gas-phase reaction in the models used to assess VOC reactivity. These are not represented in the EKMA models used to develop the MIR and other scales, and the Eulerian models generally only represent deposition of compounds in the mixed layer.

- Fate and transport models need to be enhanced to incorporate gas-phase atmospheric reactions.
- The principal physicochemical properties used in environmental fate analysis need to be determined for a wider variety of VOCs. These include Henry's law constant, octanol-water partition coefficient, air-octanol partition coefficient, and vapor pressure at 25 °C. These parameters are generally available for common volatile compounds, but the values for low-vapor-pressure compounds are often undetermined and must be estimated.
- Methodologies for the ambient air measurements need to be improved so a wider variety of VOCs, particularly semi-volatile oxygenated compounds, can be monitored in the gas phase. The list of commonly measured substances in ambient air does not include semi-volatile oxygenated compounds which are in the emissions inventory. More research on VOC monitoring methods is needed to ensure data reliability.
- Field studies designed to measure the emitted species are required to test any modeled hypothesis regarding atmospheric fate of emitted species,. These are a necessary last step in determining the accuracy of both the emissions profiles and the assumptions made with regards to the relationship between usage, emissions and ambient air concentrations. Experimental costs may require the generalization of a limited number of measurements to a larger class of compounds or emissions types.
- Sensitivity Analysis studies are needed to examine how the ozone yield from VOCs can be affected by factors affecting the VOC volatilization and removal from the troposphere. These studies are needed using urban, regional, and global models that include state of the science chemical mechanisms for VOC photooxidation.

### **Air Quality Models**

Recommendations for future research concerning the air quality models used to determine VOC impacts in ambient environments are as follows:

- Appropriate model evaluation criteria need to be developed for examining reactivity and other control strategies.
- The available tools for sensitivity, uncertainty, and reactivity analyses need to be evaluated, and more appropriate tools may need to be developed. Methods need to be developed to aid in incorporating available measurement data into models, to reduce uncertainty in reactivity predictions.
- Studies are needed to examine the possible effects of uncertainties on three-dimensional simulations of reactivity-based substitution strategies.

### **Environmental Conditions**

The following research areas are recommended to address the issues raised in the assessment of the representation of environmental conditions. Note that some of these

recommendations involve improvements in airshed model formulation, reactivity assessment methods, or in the chemical mechanisms, and thus could have been included in those sections.

- The role of upper and lateral boundary conditions for ozone and ozone precursors in determining the reactivities of VOCs in urban and rural airsheds needs to be investigated.
- Models with improved representations of convective, mesoscale, and synoptic-scale transport in large-scale reactivity models, including deep convection, frontal motions, and tropopause folding events need to be used in reactivity assessments
- Chemical mechanisms used in reactivity assessment models need a more complete representation of radical source, including chlorine radicals from sea salt in coastal airsheds.
- Chemical mechanisms used in reactivity assessments need better resolution of organic nitrates, including both soluble multi-functional organic nitrates that may deplete  $\text{NO}_x$  from polluted air masses and non-soluble organic nitrates that can deliver  $\text{NO}_x$  to remote rural environments.
- Rigorous measurements of the total reactive nitrogen budget need to be made in urban and rural areas within the United States to provide more extensive ground truth for both chemical mechanisms and airshed models.
- More emphasis on evaluating export-oriented approaches to reactivity is needed.
- Large-scale 3-D modeling assessments of the effectiveness of existing and alternative reactivity-based control strategies are needed. This is discussed further below.

## **Reactivity Assessments**

In addition to the above recommendations concerning improved models and chemical mechanisms, the following recommendations can be made concerning reactivity assessments in general.

- Assessment of Relative Reactivity need to be made on a regional scale. To date, studies have primarily concentrated on using three-dimensional models to assess VOC reactivity at the urban (Los Angeles) and small regional (e.g., Texas) scales. This type of study should be expanded to assess reactivities at large regional scales (e.g., eastern United States, Eastern Canada). Further, the spatial variability in reactivity should be quantified for important VOCs.
- Determination Appropriate Reactivity Scale Metrics need to be determined. To date, there has been little investigation on the variety of reactivity scales that can be defined. This may involve assessments of health effects, economic impacts, and other policy-related issues.

## **Persistent Organic Pollutants**

No specific recommendations are made concerning research areas related to persistent organic pollutants except that assessment of the current state of knowledge in the area of persistent organic pollutants as it relates to VOC reactivity needs to be carried out.



## REFERENCES

- AP-42 database on Air Chief 4.0 CD-ROM, EFIG/EMAD/OAQPS/EPA, USEPA, 1995
- Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe (1997): "Evaluated Kinetic, Photochemical and Heterogeneous Data for Atmospheric Chemistry: Supplement V., IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry," *J. Phys. Chem. Ref. Data*, **26**, 521-1011.
- Bennett, D. H., T.E. McKone, M. Matthies, and W.E. Kastenberg (1998). General formulation of characteristic travel distance for semivolatile organic chemicals in a multimedia environment. *Environ. Sci. Technol.* **32**, 4023.
- Bergin, M.S., Russell, A.G., Carter, W.P.L., Croes, B., and Seinfeld, J.H. "VOC Reactivity and Urban Ozone Control." *Encyclopedia of Environmental Analysis and Remediation*, pp.3355-3383. J. Wiley & Sons, New York, NY.; 1998.
- Bianchi, A. P. and M.S. Varney (1997). Volatilisation processes in wastewater treatment plants as a source of potential exposure to VOCs *Ann. Occup.Hyg.* **41**, 437.
- Carter, W.P.L. (1994). *J. Air and Waste Mgmt. Assoc.*, 44:881–899.
- Dodge M.C., (1999): Chemical oxidant mechanisms for air quality modeling: Critical review paper for 1998 ozone assessment (to be submitted to Atmospheric Environment, Available at [http://narsto.owt.com/Narsto/assess\\_activities.html](http://narsto.owt.com/Narsto/assess_activities.html).)
- Guenther, A., W. Baugh, K. Davis, G. Hampton, P. Harley, L. Klinger, L. Vierling, P. Zimmerman, E. Allwine, S. Dilts, B. Lamb, H. Westburg, D. Baldocchi, C. Geron and T. Pierce, "Isoprene fluxes measured by enclosure, relaxed eddy accumulation, surface layer gradient, mixed layer gradient, and mixed layer mass balance techniques", *J. Geophys. Res.*, **101**, 18555-18567, 1996.
- Jacobson, M. Z. (1997): Development and application of a new air pollution modeling system. Part II: Aerosol module structure and design, *Atmos. Environ.*, **31**, 131-144.
- Kuhn, M., P.J.H. Builtjes, D. Poppe, D. Simpson, W.R. Stockwell, Y. Andersson-Skold, A. Baart, M. Das, F. Fiedler, O. Hov, F. Kirchner, P.A. Makar, J.B. Milford, M.G.M. Roemer, R. Ruhnke, A. Strand, B. Vogel, and H. Vogel, Intercomparison of the gas-phase chemistry in several chemistry and transport models, *Atm. Env.*, **32**, 693-709, 1998.
- Lyons, D. (1990). Computer modelling of solvent blends. *J. Oil Colour Chemists Assoc.* **73**, 82.
- Mackay, D, A. Di Guardo, S. Paterson, G. Kicsi, and CE. Cowan. (1996). Assessing the fate of new and existing chemicals: A five-stage process. *Environ. Toxicol. Chem.* **15**, 1618.

- Middleton, P., W.R. Stockwell, and W.P.L. Carter, Aggregation and analysis of volatile compound emissions for regional modelling, *Atm. Env.*, 24, 1107-1123, 1990.
- Moody, T., J.D. Winkler, T. Wilson, S. Kersteter, "The development and improvement of temporal allocation factor files", EPA report EPA-600/R-95-004, USEPA Office of Research and Development, Washington, D.C. 20460, 1995.
- Moran, M.D., M.T. Scholtz, C.F. Slama, A. Dorkalam, A. Taylor, N.S. Ting, D.Davies, P.A. Makar, and S. Venkatesh, 1997. An overview of CEPS1.0: Version 1.0 of the Canadian Emissions Processing System for regional-scale air quality models. *Proc. 7<sup>th</sup> AWMA Emission Inventory Symp.*, Oct. 28-30, Research Triangle Park, North Carolina, Air & Waste Management Association, Pittsburgh
- NASA (1997): "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 12," JPL Publication 97-4, Jet Propulsion Laboratory, Pasadena, California, January.
- Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H. (1996) Gas/particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.*, **30**, 2580-2585.
- Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H. (1997a), Aromatics, reformulated gasoline, and atmospheric organic aerosol formation, *Environ. Sci. Technol.*, **31**, 1890-1897 (1997).
- Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Flagan, R. C., and Seinfeld, J. H. (1997b) The atmospheric aerosol-forming potential of whole gasoline vapor. *Science*, **276**, 96-99.
- Rapaport, R. A. (1988). Prediction of consumer product chemical concentrations as a function of publicly owned treatment works treatment type and riverine dilution. *Environ. Toxicol. Chem.* **7**, 107.
- Ryan, R., EPA Website [<http://www.pes.com/testarea/speciate>], accessed Nov 23, 1998.
- Sharma, M. and T.J. Overcamp (1996). Air emissions of volatile liquids spilled on sands. *Environ. Prog.* **15**, 229.
- Seigneur, C., Pai, P., Louis, J. F., Hopke, P., and Grosjean, D. (1998) Review of three-dimensional air quality models for particulate matter, Report No. 4669, American Petroleum Institute, Washington, D.C.
- Stockwell, W. R., P. Middleton, J. S. Chang, and X. Tang (1990): "The Second Generation Regional Acid Deposition Model Chemical Mechanism for Regional Air Quality Modeling," *J. Geophys. Res.* 95, 16343- 16376.

Strader, R., Gurciullo, C., Pandis, S., Kumar, N., and Lurmann, F. W. (1998) Development of gas-phase chemistry, secondary organic aerosol, and aqueous-phase chemistry modules for PM modeling, 1998. Draft Final Report STI-99510-1822-DFR, Coordinating Research Council, Atlanta, Georgia.

Watson, J. G., J.C. Chow, and E.M. Fujita (1998). Review of volatile organic compound source apportionment by chemical mass balance. 1998 Ozone Assessment - Critical Review Paper, North Atlantic Research Strategy for Tropospheric Ozone, Pasco, WA.

## LIST OF CONTRIBUTORS

Given below is the list of people who contributed to the various sections of this draft of the assessment, along with their affiliations and the sections to which they contributed. The persons taking the lead in compiling the various sections are also indicated. Participants are listed in alphabetical order.

D.Allen (University of Texas, Austin): Aerosol Potential

M. Bergin (Originally at University of Colorado, now at Georgia Institute of Technology, Atlanta): Air Quality Models; Reactivity Assessments (co-leader)

D. W. Byun (NOAA): Environmental Conditions

W. P. L. Carter (University of California, Riverside): Overall team leader; Executive Summary; Atmospheric Chemistry; Reactivity Assessments

D. R. Crosley (SRI International): Atmospheric Chemistry

J. A. Dege (Dupont Co.): Environmental Conditions

R. Derwent (Meteorological Office, Bracknell, UK): Air Quality Models

D. M. Golden (SRI International): Atmospheric Chemistry

R.W.. Hamilton (Amway Co.): Emissions and Volatility

A. Hanna (MCNC): Air Quality Models

L. T. Iraci (SRI International): Atmospheric Chemistry

J. C. Johnston (SRI International): Atmospheric Chemistry

J. J. Kurland (Union Carbide Co.): Emissions and Volatility

P. A. Makar (Atmospheric Environment Service, Ontario, Canada): Atmospheric Chemistry; Air Quality Models; Emissions and Volatility (leader),

J. Milford (University of Colorado): Reactivity Assessments

M. D. Moran (Atmospheric Environment Service, Ontario, Canada): Emissions and Volatility

D. A. Morgott (Eastman Kodak Co.): Emissions and Volatility

- J. D. Neece (Texas Natural Resource Conservation Commission): Reaction diagram in Executive Summary
- E. P. Olaguer (Dow Chemical Co.): Air Quality Models; Environmental Conditions (leader); Persistent Organic Pollutants
- P. J. Ostrowski (Occidental Chemical Co): Reactivity Assessments; Environmental Conditions.
- P. Pai (AER, San Ramon, CA): Aerosol Potential
- A. Russell (Georgia Institute of Technology, Atlanta): Reactivity Assessments (co-leader); Emissions and Volatility, Air Quality Models
- J. H. Seinfeld (California Institute of Technology): Aerosol Potential (leader)
- G. Sistla (New York State Department of Environmental Conservation): Emissions and Volatility
- G. Tonnesen (U.S. EPA): Air Quality Models (leader)
- Z. Wang (University of North Carolina at Chapel Hill): Air Quality Models.