

**TEXAS** environmental improvement  
**ENVIRONMENTAL**  
**RESEARCH** through research  
and science  
**CONSORTIUM**

# Strategic Research Plan 2007-2009

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## INTRODUCTION

Over 10 million Texans live in the Houston-Galveston-Brazoria and Dallas-Ft. Worth metropolitan areas. These regions account for more than half of the State's economy and employment levels. Reducing air pollution, to comply with Federal air quality mandates, is one of the most pressing public policy challenges facing these regions today. Economic analyses suggest that failure to meet federal mandates will result in billions of dollars in lost economic development for the State (Perryman Group, 2002).

In response to this air quality challenge, government, business and community leaders in the Houston-Galveston-Brazoria and Dallas-Ft. Worth regions in 2002 established a non-profit organization, the Texas Environmental Research Consortium (TERC), **to improve the scientific basis for air quality decision-making**. TERC researches crucial scientific issues to help policymakers find cost-effective solutions to Texas' air quality challenges.

TERC's original mission was to address the ozone problem in the Houston-Galveston-Brazoria area, which violates the federal standard for that pollutant. Its scope soon broadened to include the 9-county Dallas-Fort Worth area, which also violates the ozone standard, plus much of eastern Texas. This expanded geographical scope facilitates transfer of air quality modeling improvements and scientific understanding of ozone formation among regions. In addition, the Consortium has expanded its efforts to a broader range of air pollutants than just ozone. Specifically, the Consortium has expanded its charge to include fine particulate matter and hazardous air pollutants, to ensure that air quality strategies for multiple pollutants are consistent and complementary. **Thus, TERC now sponsors research to address the problems of ozone, particulate matter, and hazardous air pollutions in the Houston-Galveston-Brazoria area, Dallas-Fort Worth area, and eastern Texas.**

The Charter of the Consortium<sup>1</sup> calls for the development of a Strategic Research Plan (SRP) to guide decisions on research supported by TERC. The plan is prepared and updated in consultation with the TERC Science Advisory Committee (SAC), the Texas Commission on Environmental Quality (TCEQ), and the U.S. Environmental Protection Agency (EPA). In addition, other stakeholders are afforded the opportunity to review and offer comments on the plan. The first version of the SRP was issued in August 2002, and the second version in November 2004. This updated Strategic Research Plan identifies important research needs for TERC to address over the next two years. It should be stressed that all research considered in this Strategic Research Plan will be evaluated and further refined to maximize utility for the State Implementation Plan (SIP) as well as improvements to the health of Texas citizens.

This Strategic Research Plan identifies Texas' research needs in the following areas:

1. Emissions Characterization and Inventories
2. Meteorology/Transport
3. Chemistry and Physics of Atmospheric Constituents
4. Ambient Measurement/Monitoring
5. Analysis of Air Quality Data
6. Air Quality Modeling
7. Human Exposure
8. Policy/Controls.

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<sup>1</sup> <http://www.harc.edu/harc/Projects/AirQuality/Information/Background/Charter.aspx>.

# 1 EMISSIONS CHARACTERIZATION AND INVENTORIES

## 1.1 Introduction

Complete and accurate emission inventories are essential to analyze and comprehend the wealth of data and information collected during the recent Texas Air Quality Study II (TexAQS II). This was one of the critical lessons learned in the original TexAQS 2000 field study. The TexAQS II Rapid Science Synthesis Team (RSST) final report (Cowling et al., 2007) devoted many recommendations to preparing, improving, and clarifying emission inventories and emission estimates. Therefore, the TCEQ has launched an unprecedented effort to collect data for a special emission inventory for the intensive period of the field study. This Special 2006 Emission Inventory includes temporal (hourly) and spatial (grid level) emission estimates for point, area, mobile, and biogenic sources across the study domain. Much work, however, remains to be done to capitalize on this newly available data. Recommendations for additional research activities follow below.

## 1.2 General Recommendations

Continued improvements in emission inventories are needed. In particular, TexAQS II revealed that various volatile organic compounds (VOCs) and highly reactive VOCs (HRVOCs) are still understated in the existing inventories. Many of these compounds are not only ozone precursors, but also Hazardous Air Pollutants (HAPs), so that improving their emission inventories will benefit not only the Texas SIP, but also contribute to better understanding of human exposure to air toxics.

Compilation of emission inventories is primarily the responsibility of the TCEQ, and care must be taken so as not to duplicate ongoing work by the agency. However, TERC and its Principal Investigators should support development of emission inventories based on TexAQS II data and significant findings, as it is critical to development of the Texas SIP and implementation of appropriate emission reduction control strategies for attaining the air quality standards in Texas.

It is vitally important that a comprehensive emission inventory, including all source categories and pollutants, be compiled and quality assured so that all projects and investigators conducting air quality modeling and data analysis activities can have access to the best (and consistent) emission data for the TexAQS II study period. Furthermore, the base emission inventory data for each source and source category as well as the processed emission data for modeling, including spatial, temporal, and species allocation, need to be easily accessible by the user community.

Evaluation activities should be conducted to determine the areas of the inventory which need increased attention and areas where confidence is high. The ground-level and aircraft measurements obtained from past field studies will be invaluable in this regard. In addition, an assessment should be conducted of whether pending issues from TexAQS 2000 have been resolved by TexAQS II findings.

Research is especially needed to improve the spatial and temporal resolution of emission estimates. Moreover, attention should be devoted to appropriate forecasting techniques for various inventory sources, in order to “grow” the base emission inventory to the SIP attainment demonstration year. Different source categories will likely require different forecasting techniques. Currently, the process for forecasting emissions is not adequately documented.

### 1.3 Point Sources

Further refinement of the hourly point source estimates from the largest industrial sources is needed. These estimates include emissions of sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), and carbon monoxide (CO), as well as individual VOC and particulate matter (PM) species. In addition to normal emissions from routine operations, the estimates should include emissions from start-ups, shut-downs, malfunctions, and fugitive releases. An emission inventory with this degree of detail from point sources has never been compiled previously and is expected to help explain many of the monitoring observations.

Investigators should enhance the database by improving estimates of emissions of HRVOCs, formaldehyde, and NO<sub>x</sub> from myriad sources such as power plants, petrochemical facilities (storage tanks, cooling towers, flares, valves/flanges, cat crackers, wastewater treatment systems, loading/unloading operations, etc.), including cokers used in refineries, which may possibly emit large amounts of uncounted HRVOCs/VOCs, and other industrial facilities. Improved speciation profiles for petrochemical sources are also needed for support of air quality modeling and source attribution modeling. In addition, better characterization of stochastic emission events in the Ship Channel is needed (these events seem to be responsible for the narrow plumes that were seen during day and night-time periods). This might require "top-down" analyses of the VOC signatures seen at TCEQ's auto-GC monitoring stations and at Houston Regional Monitoring (HRM) sites. Analyses of these data would also be valuable for evaluating the inventories and perhaps narrowing the list of possible emitters.

Data obtained from the Solar Occultation Flux (SOF) experiment should also be examined to determine its usefulness for supplementing and/or evaluating the validity of point source emission inventories. Top-down verification of the SOF data using aircraft measurements and Lagrangian Reactive Plume Model (LRPM) analyses will help to establish confidence in the results of the SOF experiment. The SOF data set should also be examined to determine its usefulness for determining the relative importance of primary and secondary formaldehyde (HCHO) to ozone formation in pollution plumes.

### 1.4 Area Sources

The multitude of area source categories should also receive special attention. This should include characterization of wildfires and prescribed fires that are essential to simulating aerosol levels. Large construction sites should be located and fugitive dust emissions should be enhanced or moderated, depending on the degree of dry or wet conditions. Chlorine sources may also require special assessment.

A potential area source category that might be considered for scientific assessment and regulatory attention is solvents, such as those used in paints and coatings and consumer products. Solvents and other widely used VOCs may be important not only because of their local emissions and air quality impacts, but also because of their regional ozone formation potentials and role in ozone and precursor transport.

The results of TERC Project H51C (Hendler et al., 2006) should be evaluated further, and a follow-up scientific assessment of VOC emissions related to upstream oil and gas production and the corresponding impact on the HGB airshed should be conducted.

### 1.5 Mobile Sources

Special attention should be given to mobile sources since they contribute a large portion of NO<sub>x</sub> and VOC emissions. Close consultation with the TCEQ is recommended to avoid duplication of effort in this area, given the in-house activities within the agency.

Hourly vehicle miles traveled (VMT) and speed data on major thoroughfares (from bottom-up travel demand models or top-down Highway Performance Monitoring System, or HPMS, procedures, where appropriate) and the latest 2006 information (including post hoc data) should be used as inputs to EPA's MOBILE6 emission factor model to produce temporally and spatially varying on-road emission estimates for NO<sub>x</sub>, VOC (including various air toxics), CO, and PM. Major traffic congestion and major congregation of traffic such as sporting and entertainment events should be incorporated.

TexAQS II researchers should coordinate their efforts with those responsible for preparing the on-road emission inventories to reconcile differences between observationally inferred and modeled emission estimates (as indicated in RSST Finding D2). Any findings in this regard should be reported to the appropriate national or local agency responsible for mobile emissions or travel demand model development, including the developers of the new MOVES model at the EPA.

Off-road emissions should also receive special attention due to relaxed federal engine standards. Higher quality spatial and temporal inventories are needed for all off-road sources, primarily locomotives, but also aircraft, lawn and garden equipment, construction equipment, and recreational boating. Estimates should include temperature and humidity effects on heavy duty diesel emissions.

If not already addressed elsewhere, nitrous acid (HONO) and formaldehyde (HCHO) emissions from mobile sources should be more accurately characterized. HONO from mobile sources would tend to correlate with HONO from multiphase reactions, with both processes producing build-up during the night and early morning. Photolysis of both HONO and HCHO may contribute substantially to radical production during the morning hours.

### 1.6 Biogenic Sources

Temperature and moisture effects on biogenic emissions should be addressed. Assessment of estimates by BEIS, MEGAN, GloBEIS, and other algorithms should be conducted. More refined data on crops and other vegetation cover should be compiled. Moreover, the latest land use/land cover data based on satellite and other information should be incorporated into models of biogenic emissions, including the results of TERC Project H55 (Wells and Howard, 2007).

### 1.7 Source Attribution

A number of source attribution techniques are available to examine various geographical and source category contributions to ozone exceedances. Techniques based on 3-D Chemistry-Transport Models (CTMs) include Anthropogenic Precursor Culpability Assessment (APCA), the Direct Decoupled Method (DDM), Higher-order DDM (HDDM), and the 4D Variational (4DVar) method. APCA is a tracer technique, whereas DDM, HDDM, and 4DVar are automated sensitivity techniques. DDM and HDDM are source-oriented, whereas 4DVar is receptor-oriented. Application of HDDM or 4DVar may be useful in isolating the contribution of HCHO or other targeted species to ozone formation. However, simpler trajectory or Lagrangian plume analyses may provide initial answers and guide future work. "Fingerprint" techniques, such as Principal Component Analysis and Positive Matrix Factorization, and emissions ratio studies are additional methods that can be used to determine the relative importance of various sources.

A Lagrangian Reactive Plume Model (LRPM) could be used to identify potential sources of HCHO directly emitted into the Houston nighttime boundary layer. Data from formaldehyde monitors at Moody Tower and meteorological data (including profiler data) from Moody Tower, La Porte Airport, and other sources, together with observations of other nighttime species (including vertical gradient information from differential optical absorption spectroscopy, or DOAS), can be used to constrain the LRPM. In conjunction with an analysis of industrial processes, a constrained LRPM analysis would enable better

identification of potential source areas and possible emitters of HCHO. The LRPM can also be applied to daytime plumes to compare the relative contributions of primary and secondary HCHO. Daytime flight information from the Baylor Aircraft, which also employed a Hantzsch reaction fluorescence instrument similar to the one deployed at Moody Tower to measure HCHO, may be especially useful in this regard.

Aerosol source apportionment analyses will be needed, especially if there are issues related to non-attainment of PM<sub>2.5</sub> standards in Houston. These analyses might also provide some insight into the sources of ozone precursors. Analyses of long integration time filter samples of aerosol composition and high time resolution measurements of aerosol optical and microphysical properties should both be used to address these issues. In addition, and to the extent possible, data for gas phase composition and relevant chemical reactions should be incorporated. In addition to commonly used methods such as Chemical Mass Balance, Positive Matrix Factorization, other statistical techniques (e.g., Potential Source Contribution Functions) and data mining should also be employed using data from TCEQ and HRM sites.

## **2 METEOROLOGY/TRANSPORT**

### 2.1 Introduction

The wealth of data acquired from the TexAQS II field campaign provides an opportunity to add to our understanding of the meteorological environment in East Texas and its role in air quality. The primary issues that need to be addressed in the context of the 8-hour ozone standard and anticipated concerns about Particulate Matter (PM) are: 1) compilation and analysis of comprehensive meteorological data sets, 2) investigation of vertical exchange processes, 3) assessment of regional scale transport, and 4) assistance of TCEQ in the development of new meteorological episodes. This is because ozone, ozone precursors and PM can be exchanged into the Planetary Boundary Layer (PBL) from above as well as mixed within the PBL, and can be transported from distant regions. Data should be compiled and analyzed to serve as the basis for improved treatments of vertical mixing and long-range transport, and these data and improved treatments need to be incorporated into simulations of meteorological episodes for use in SIP modeling. Relevant research addressing these issues is described below.

### 2.2 Compilation and Analysis of Comprehensive Data Sets

A comprehensive meteorological overview incorporating data from as many platforms and sites as possible is needed. It would be worthwhile to include data on vertical profiles from: balloons and ozonesondes, LIDAR data, profiler data, data from research aircraft (including the P3 and Aztec), and ACARS measurements from commercial aircraft. These data can be used to extend and augment the work previously done in the Vertical Mixing Experiment (VME). They would include characterizations of the stability and shear environments and their relationship to chemical species distributions.

Available surface data from TexAQS II could be integrated into analyses using operational (routine) weather observations. Data from sites in the Houston Triangle, Moody Tower, and other fixed installations can be used to refine and augment the final operational analyses. What is recommended here is the preparation of graphical and descriptive products, not a full assimilation of the supplemental data. All of these analyses should be contrasted with operational and post-analysis model products, at the surface and at significant levels aloft, and with a special emphasis on vertical profiles.

Continued special measurements using rawinsondes and ozonesondes are highly desirable to supplement past data collection efforts and to provide useful information for model evaluation and data assimilation, especially for real-time forecasts.

### 2.3 Vertical Mixing

The Vertical Mixing Experiment (VME) conducted at Moody Tower provides a unique and excellent opportunity to evaluate and improve the representation of vertical exchange processes in models. A first step in this regard would be to determine the ability of different methods for parameterizing small scale vertical mixing such as eddy diffusion and/or the Asymmetric Convective Mixing (ACM2) model to explain the observed concentrations and vertical gradients of CO, O<sub>3</sub>, VOC (including HCHO), and NO<sub>y</sub>. Such studies would guide the development of operational Chemistry-Transport Models (CTMs) by improving the physical basis of vertical mixing in these models. Previous modeling exercises (e.g., TERC Project H12.8HRB; Jeffries et al., 2005) have shown that predictions of ozone and other important species are very sensitive to the vertical mixing scheme used in the PBL. Similar studies could be done using vertical profile data.

A project is needed that makes use of a comprehensive meteorological dataset for TexAQS II, the physical insights derived from analysis of the VME data, and the Ensemble Kalman Filter (EnKF) method to develop meteorological simulations for the TexAQS II intensive period. The EnKF data assimilation scheme may especially be applied to determine the optimal choice of parameterization schemes and parameter values for vertical mixing in an operational context. The meteorological data assimilation could perhaps be coupled to the assimilation of tracer data, such as for CO, using a simple tracer advection model.

Data from TexAQS II also provide an opportunity to test current understanding of the dynamics of the PBL in a coastal zone, including the evolution of the sea breeze and its influence on PBL height and vertical mixing. The development of more advanced boundary layer parameterizations should be encouraged, and reasons for discrepancies between the current suite of meteorological models and observations (e.g., for the spatial and temporal patterns of PBL height) should be determined. Assimilating satellite data for sea surface temperatures may be helpful in improving simulations of PBL height and vertical mixing over Galveston Bay and the Gulf of Mexico.

Zhang and Tilley (2001) showed that soil moisture influences atmospheric circulation over a wide range of spatio-temporal scales. Surface (skin) temperature is most sensitive to soil moisture during the mid-morning hours. Skin temperature errors could be minimized by adjusting soil moisture using the technique adopted in Zhang and Tilley (2001).

Some effort should also be made to incorporate improvements in the spatial resolution (both vertical and horizontal) of meteorological models for Houston. Such studies might include the testing of the urban canopy module developed by National Oceanic & Atmospheric Administration (NOAA)/EPA.

### 2.4 Long-Range Transport

Flow conditions associated with frontal passages and associated large-scale pressure systems played a major role in producing high ozone on several days during the TexAQS II intensive, in both DFW and Houston. Studies investigating the dynamics and tracer transport associated with such conditions should be conducted to improve the performance of both forecast and retrospective simulations. This includes simulating the meteorological and chemical conditions observed by the Baylor Aztec during the passage of a stationary front through the DFW region during TexAQS II. Attention should be paid to both conditions at the surface and processes aloft, including the free troposphere.

The role of night-time horizontal flushing of pollutants and their subsequent influence on regional concentrations of ozone and precursors should be examined. For this reason, the dynamics of the nocturnal jet should be explored in greater detail.

Successful simulation of the transport of pollutants depends on accurate specification of initial and boundary conditions in models. The recent incorporation of the 4DVar data assimilation method into the Community Multiscale Air Quality (CMAQ) model should be exploited as a means of improving model initial conditions for atmospheric constituents. Coupling between air quality models and larger-scale models such as the Regional Air Quality Model (RAQM) and MOZART should also be pursued to improve model boundary conditions.

Given the potential lowering of the federal ozone standard, more attention should be paid to transport mechanisms involving the free troposphere. Accurately simulating transport in this region and exchange with the PBL will require better treatments of such processes as stratosphere-troposphere exchange, convective venting of pollution from the PBL, subsidence and entrainment from the free troposphere into the PBL, and the physics and chemistry of lightning generation of NO<sub>x</sub>. The use of satellite data may be especially helpful in improving the understanding and simulation of transport in the free troposphere. For example, satellite data for CO vertical profiles in the free troposphere may be used to supplement PBL observational data (e.g., from aircraft and surface measurements) and model results in studying transport mechanisms involving the free troposphere, especially along frontal boundaries.

### 2.5 Development of New Episodes

A prerequisite to the development of operational air quality models for attainment demonstrations is the simulation of meteorological conditions during past ozone episodes. Analyses of this sort carried out in TERC Project H60 for the DFW area using 2005 episodes (Kemball-Cook et al., 2006) should be repeated for the 2006 ozone season, especially during the TexAQS II intensive period. Progress in developing the EnKF data assimilation capability (TERC Project H24; Nielsen-Gammon et al., 2004), which can be used not only to tune the parameters of a meteorological model, but also to determine the optimal selection of parameterization schemes, should be exploited.

Recent attempts at simulating the meteorological conditions associated with the TexAQS II intensive period have revealed the difficulty of properly simulating the dynamics of convection and the associated precipitation and wind flows. False thunderstorm activity can easily be generated in meteorological models. The resulting air circulation and precipitation, when fed into air quality models, may obscure the real ozone production that might otherwise occur. This problem should be the focus of intense investigation, to enable more high ozone days to be successfully simulated.

Clouds have important influences on both winds and the photolysis of atmospheric constituents. Errors in simulated cloudiness can result in significant biases in ozone, due to both transport and photolysis. Previous research for the Texas SIP has focused on assimilating Geostationary Operational Environmental Satellites (GOES) data for clouds into air quality models. Future research should determine physically consistent ways to assimilate cloud and precipitation data in both meteorological and air quality models. In addition, radiative transfer models for computing actinic flux under cloudy conditions should be updated to reflect the most recent developments.

Previous TERC research (e.g., Project H55) contributed to the development of new data sets (e.g., from satellites) that more accurately represent physical land surface characteristics. These data sets should be deployed in land surface and meteorological models.

## 3 CHEMISTRY AND PHYSICS OF ATMOSPHERIC CONSTITUENTS

### 3.1 Introduction

In order to develop effective control strategies to reduce secondary pollutants such as ozone, secondary particulate matter (PM) and secondary air toxics, it is necessary to understand, and predictively model, the chemical and physical processes involved in their formation from primary emissions. Many of the processes involved are complex and nonlinear, and if the models used to develop State Implementation Plans (SIPs) do not take them properly into account, the SIP control strategies so developed may not be as effective as predicted, or may even have unintended consequences. The considerations of chemistry and physics for ozone, secondary PM and secondary air toxics are somewhat different, though they also have features in common. These are discussed below.

### 3.2 Ozone

Ozone is formed from gas-phase reactions of emitted volatile organic compounds (VOCs) and oxides of nitrogen ( $\text{NO}_x$ ). These reactions, which are complex and nonlinear and have many uncertainties, are represented in air quality models using "chemical mechanisms" that necessarily contain simplifications and approximations of the actual chemistry that occurs. Important areas of uncertainty include, but are not limited to, predictions of radical initiation processes, heterogeneous processes affecting gas-phase species, atmospheric reactions of aromatics, and appropriate representation of the complex, and often atypical, mixtures of VOCs that occur in Houston. Note that formation of ozone in Houston has been found to be particularly sensitive to mechanism uncertainties, so research in this area is particularly relevant to Houston. Prediction of ozone formation in  $\text{NO}_x$ -limited areas such as DFW tend to be somewhat less sensitive to mechanism uncertainties, though uncertainties concerning  $\text{NO}_x$  sources and sinks are a concern in models for such areas.

Areas of near- and mid-term research specifically relevant to reducing uncertainties in chemical mechanisms used for ozone prediction include the following:

- Determine the extent to which mechanisms used in models for Texas are consistent with available environmental chamber data, and assess the implications of any inconsistencies. Areas of inconsistency are already known to exist. A project to do this has already been funded by the TCEQ, but follow-up work, and possibly new chamber data, may be needed.
- Determine the extent to which mechanisms used in models for Texas are consistent with available ambient data, but only under conditions where appropriate measurements have reduced uncertainties in pollutant input (e.g., emissions) and transport sufficiently that the major uncertainties concern the chemical transformations. Particularly useful in the Houston context would be measurements relevant to model predictions of radical initiation processes and ozone productivity. Simultaneous measurements of as many species as possible is necessary to give good tests for mechanisms and reduce uncertainties in inputs. Examples of types of projects are discussed further in the "ambient measurements" section.
- Conduct systematic model sensitivity studies under conditions known to be sensitive to mechanism differences (e.g., Houston). This would include assessing uncertainties in rate constants known to be important in  $\text{O}_3$  models (e.g.,  $\text{OH} + \text{NO}_2$  and those for PAN reactions), as well as uncertainties in initiation processes and mechanisms for different types of VOCs (e.g., aromatics). Simply comparing existing mechanisms is not adequate, since up-to-date mechanisms tend to use the same body of data and evaluations, and comparing old with new mechanisms only shows effects of changes in what we

think is occurring, and the causes of any differences that are found are usually not clear. This should include sensitivities to control strategy predictions as well as to absolute O<sub>3</sub> levels.

- Examine heterogeneous processes involving HONO formation and NO<sub>x</sub> sinks (e.g., N<sub>2</sub>O<sub>5</sub> hydrolysis) as part of the ambient and model sensitivity studies discussed above, and also in appropriate laboratory and chamber studies.

The results of the chamber and ambient evaluation studies will undoubtedly indicate where improvements are needed to existing chemical mechanisms and where basic mechanistic studies are needed to support these improvements. Any strategic research plan should necessarily include support for chemical mechanism development and associated laboratory studies. Support for laboratory studies should be based on chemical mechanism development needs.

In recent years, California has taken the leadership in chemical mechanism related research in the United States because of the severity of the ozone problem there and the interest in evaluating control strategies taking relative VOC reactivities into account. However, chemical mechanism issues are probably even more important in addressing the problems in Houston than in California, and Texas needs to take greater leadership in this area. In any case, the chemical mechanism research program should be coordinated with related research efforts elsewhere, perhaps by forming joint working groups.

The physics of ozone formation involves appropriate specification of temperature and actinic flux that affect the rates of chemical reactions. It also requires appropriately characterizing the heterogeneous processes that may affect the gas-phase reactions, such as HONO formation and NO<sub>x</sub> sinks on various types of surfaces (e.g., sticking coefficients, particulate morphology, radiative properties). The former is associated with characterizing ambient conditions for modeling, while the latter must be considered in developing more complete treatments of ozone formation mechanisms.

The physics of ozone formation on regional scales includes processes related to the production of NO<sub>x</sub> by lightning. Little work has been done to incorporate such processes into SIP models, while the strong possibility exists that the federal ozone standard will be lowered significantly so as to make regional ozone an even bigger component of ozone exceedances in Texas. The latest methodologies and datasets pertaining to lightning frequency, and the physics and chemistry of associated NO<sub>x</sub> formation, should be the subject of research to increase the accuracy of regional ozone simulations in SIP models.

### 3.3 Secondary PM Formation

Particulate matter (PM) comes from a number of sources, both primary and secondary. In order to derive appropriate control strategies to achieve air quality standards for PM, it is necessary to conduct analysis of ambient PM to determine the contribution of various types of sources. This would include chemical characterization and source apportionment studies. Developing control strategies for primary PM is mainly a matter of assessing emissions and transport, though chemical and physical transformations and loss processes of the emitted PM may also need to be studied. Developing control strategies for secondary PM also requires characterizing, and predictively modeling, the chemical and physical processes by which non-volatile compounds are formed from emitted gas-phase species. Information to date indicates that secondary PM, including secondary organic aerosol (SOA) formation, is an important contributor to the total PM problem, particularly to the smallest particles that have the greatest health impacts.

Model prediction of secondary PM and SOA requires use of chemical mechanisms that are designed and evaluated for this purpose. Current models use mechanisms designed primarily for O<sub>3</sub> formation, but use ad-hoc parameterized add-on mechanisms for predicting secondary PM that have not been adequately evaluated. Therefore, predictions of secondary PM formation, and their evolution as emissions are

changed as a result of ozone control strategies, are not very reliable. Research is needed to reduce the uncertainty of these predictions. Chemical and physical mechanisms need to be developed that are capable of predicting SOA formation and that are also computationally efficient. Such mechanisms need to take into account formation rates of low-volatility precursors, gas-to-particle partitioning processes, and condensed-phase reactions. Because of the complexity and uncertainty of the processes involved, developing comprehensive mechanisms will require longer-term research and basic laboratory studies.

Near- and medium-term research priorities should be determined after forming a working group of experts in the chemistry and physics of PM formation. PM related research programs carried out elsewhere need to be assessed to take full advantage of ongoing work in areas where PM control has been given greater priority. It is expected that the research might include the following elements:

- Characterizing the chemical composition of PM in areas of PM exceedances to determine the relative importance of various sources that need to be controlled, and the chemical characteristics of secondary PM.
- Evaluating sensitivities of uncertain model parameters and inputs in model predictions of PM for conditions in Texas, in order to prioritize research.
- Including measurements relevant to PM formation and chemical characterization of PM as part of field studies in Texas. The ambient characterization data used for evaluating O<sub>3</sub> models will also be necessary for evaluating models for secondary PM. Using these results to evaluate the predictive capability of PM models in existing models will be useful in determining areas of needed research.
- Evaluating PM modules used in existing models for consistency with available environmental chamber data on PM formation, where available, in a manner analogous to that discussed above for O<sub>3</sub> mechanisms. This will require a survey of relevant data and eventually designing and conducting new experiments to simulate relevant conditions in Texas.
- Developing improved PM modules for models that better reflect the actual chemistry and physics occurring and that are consistent with available environmental chamber and ambient data. This effort will include determining priorities for laboratory, environmental chamber, and field measurements, and obtaining the data most needed.
- Exploring methods to increase the computational efficiency of PM models, such as the use of adaptive chemical mechanisms and other innovative numerical techniques.
- Evaluating SAPRC, CB05, and other chemical mechanisms as to their implications for environmental decision making, such as the sensitivity of Relative Response Factors to the choice of chemical mechanism.

Many of the general issues involved with chemical mechanism research in conjunction with prediction of O<sub>3</sub> are also applicable to modeling PM, and accurate models for O<sub>3</sub> are necessary (though certainly not sufficient) for reliably modeling PM. The main difference is that the science of PM formation is more complex and less evolved than is the case for ozone, and more research is needed. An example of an issue with important implications for both ozone and PM chemistry is the role of heterogeneous formation of HONO on particulates in determining the budget of atmospheric radicals.

### 3.4 Air Toxics/Hazardous Air Pollutants

Concern over exposure to primary HAPs near source areas makes investigations of emissions and transport, discussed elsewhere in this document, major priorities for air toxics research. However, atmospheric sink processes, and perhaps absorption onto and subsequent re-emission from surfaces, may also be important for certain types of primary toxic emissions. Environmental fate models need to be applied to determine the extent to which atmospheric concentrations of these species are sensitive to such processes. If sufficient sensitivity is found, then models for these processes need to be reviewed, evaluated and, if necessary, improved.

Chemical mechanisms developed for predictions of O<sub>3</sub> and even PM formation are in general too condensed to be useful for predicting concentrations of most types of toxic species. However, adding the necessary species to the model for representing selected primary toxic compounds is relatively straightforward (though adding them to the emission inventories so that they can be appropriately modeled may not be), so in principle O<sub>3</sub> and PM models could also track appropriate toxic species. However, sink and absorption/evaporation processes may need to be better represented in the models in some cases, as indicated above. Such models should be evaluated using ambient data; the most cost-effective way to do this would be as part of ongoing field projects.

The possibility of exposure to unacceptable levels of secondary air toxics also needs to be assessed. Oxidation products for many VOCs are often much more toxic than the parent compound, though generally their atmospheric concentrations are not as high as primary compounds near the source areas because of dilution prior to reaction. An assessment of toxic oxidation products of known pollutants (particularly rapidly reacting compounds that may form oxidation products before they are fully diluted) needs to be assessed in terms of their predicted ambient concentrations compared to their known or lower limit toxic levels. Atmospheric measurements that can detect toxic oxidized species (not just hydrocarbons) would be useful in this regard, and should be included as part of field projects.

If necessary, chemical mechanisms may need to be enhanced to predict concentrations of secondary toxics that may be of concern. The general research issues involved in these cases are similar to those discussed above for O<sub>3</sub> and PM. Note that such mechanisms may need to be much more chemically detailed than the highly condensed mechanisms currently used for O<sub>3</sub> modeling.

## **4 AMBIENT MEASUREMENT/MONITORING**

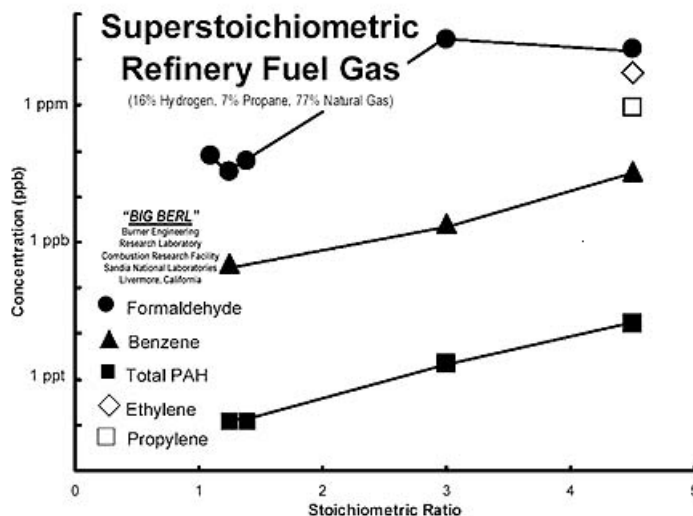
### 4.1 Introduction

Direct measurements of atmospheric trace gases and aerosols in and around Texas are essential to understand and control air pollution. Ambient measurement and monitoring serves to:

- Test emission inventories;
- Evaluate chemical transport model predictions;
- Enable enforcement of air quality regulations;
- Assess progress in attaining federal air quality standards;
- Contribute to Weight of Evidence approaches in the SIP (e.g., trend indication); and
- Improve our fundamental understanding of the chemistry of air pollution.

## 4.2 Aldehydes

It has been suggested that formaldehyde (HCHO) is a major source of radicals in the Houston airshed. Model studies by Vizuete et al. (2006) show that hypothetical increases in formaldehyde emissions from flares or mobile sources could increase peak ozone in Houston by up to 30 ppb. Direct measurements of refinery fuel gas emissions from a controlled burner under super-stoichiometric conditions showed 1 ppm HCHO in the flue gas, comparable to the amount of ethylene and propylene produced (Seebold et al., 2004; see Figure 1). The evidence from ambient measurements to date, however, suggests that the bulk of HCHO is secondary rather than primary. A study by scientists at Rice University (Friedfeld et al., 2002), examining statistical correlations between HCHO and CO (an indicator of primary formaldehyde) and between HCHO and ozone (an indicator of secondary formaldehyde), suggests that secondary formation accounts for about 63% of total formaldehyde in Houston. The diurnal variation observed on the NOAA Ron Brown during TexAQS II showed greatest concentrations of HCHO during daylight hours that were infrequently correlated with CO. When correlated, ambient ratios of 3-10 ppt HCHO per ppb CO were observed (Herndon et al., 2007), an order of magnitude less than indicated by diesel exhaust speciation studies (Merritt, 2003; Fanick, 2005). More research is required to determine the actual contribution of formaldehyde to ozone productivity in Houston, including direct measurements of formaldehyde emissions from operational flares and continuous monitoring of ambient formaldehyde levels.



**Figure 1.** Results of a controlled burner experiment (after Seebold et al., 2004).

Formaldehyde is only one of several aldehydes that are both radical sources and toxic species. The Houston Exposure to Air Toxics Study (HEATS) will measure personal exposure to several aldehydes and other carbonyls using specially developed portable monitors, but continuous ambient measurements of such species are lacking. Dinitrophenylhydrazine (DNPH) cartridge monitors could be deployed at various monitoring sites in Houston to provide such routine measurements.

## 4.3 Nitrogen Compounds

Multiphase reactions involving nitrogen compounds such as nitrous and nitric acid remain a major source of uncertainty in our understanding of the chemistry of ozone and PM in Texas. The recent TexAQS II experiments, however, represent a state-of-the-art investigation of these processes. The results of these experiments indicate daytime mixing ratios of nitrous acid (HONO) from several hundred ppt to a few ppb, well above the levels which can be accounted for with homogenous gas-phase chemistry. HONO

therefore represents a major source of hydroxyl radical ( $\text{OH}^\circ$ ) and potential sink for odd oxygen. Continued research into the mechanism and extent of production of HONO is called for, supported by special ambient measurements of HONO, other relevant gas-phase species such as  $\text{HNO}_3$ , and potential substrates for heterogeneous reactions, such as aerosol and soot particles.

In contrast to indications regarding the importance of HONO, recent evidence from TexAQS II indicates that  $\text{N}_2\text{O}_5$  hydrolysis on wet particles is slow, even unmeasurable, in the Houston environment (RSST Finding G6). This is most likely the result of an organic coating on aerosols. If true, less reactive nitrogen may be lost during the night, and more left over to facilitate ozone formation during the following day. This finding should be confirmed through further observation of night-to-day transition chemistry.

Reactive nitrogen compounds play a central role in smog formation, and this may be especially true for Texas. Even the most fundamental N components such as  $\text{NO}_2$  can pose an analytical challenge. One of the strengths of the TERC research program has been the deployment of multiple sensors for members of the  $\text{NO}_y$  family, and this work should continue. For example, PAN-analogue monitoring may help to determine when air masses represent fresh emissions or aged air.

#### 4.4 Fine Particulate Matter

Fine particulate matter is important in itself, and not only because of its role in ozone formation. Air quality models do not directly generate fields of fine particulate mass; rather they generate concentration fields for specific aerosol species in specific size bins. Monitoring must be performed at a sufficient number of sites where the chemical composition of aerosols is measured. The PM mass measurements can then be interpolated for comparison to models.

The optical properties of aerosols will become increasingly relevant to air pollution control in Texas due to the implementation of the regional haze rule. Nephelometers from the Automated Surface Observing System (ASOS) and the FAA inventory could be used to estimate visibility. Modeled extinctions could then be compared with ASOS products and Interagency Monitoring for Visual Environments (IMPROVE) nephelometers in Class I areas. This will provide a means to evaluate particle and gas-phase chemical processes in models and their associated biases.

Aerosols affect not only visibility, but also heating and photolysis rates that feed back into atmospheric dynamics and photochemistry. Continued observational studies on the physical and chemical properties as well as the distribution of PM are called for. Observations should include measurements of particle morphology, composition, hygroscopicity, size distribution, and radiative properties.

A special aspect of TexAQS II was the co-performance of many sophisticated in-situ measurements by aircraft in clouds, supplemented by related satellite measurements. These data, including especially detailed cloud microphysical information, constitutes a rich database related to aerosol-cloud interactions that may be useful in PM studies.

#### 4.5 Primary Pollutants

For emission inventory testing, ratios of primary pollutants ( $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{SO}_2$ , VOCs) continue to be a powerful tool. TexAQS II aircraft measurements of pollutant ratios and direct flux measurements using the Solar Occultation Flux (SOF) technique both point to the conclusion that, while VOC emissions in Houston do seem to have decreased between 2000 and 2006, they may still be underestimated by at least an order of magnitude. The use of advanced monitoring techniques over large areas, such as the combination of long-path methods (e.g., Differential Optical Absorption Spectroscopy [DOAS], Open Path Fourier Transform Infrared [OP-FTIR] Spectroscopy) and Computer-Aided Tomography (CAT),

could help to improve emission inventories of key species, especially in the Houston Ship Channel. At the facility level, sophisticated measurement techniques such as Solar Occultation Flux (SOF) and Differential Absorption Lidar (DIAL) could be deployed to better quantify emissions from specific industrial processes, such as coking and flaring.

Houston tunnel and TexAQS II aircraft studies show CO/CO<sub>2</sub> ratios substantially lower than indicated by the 1999 National Emissions Inventory (Frost, 2007) but higher than derived from roadside measurements that show molar ratios of  $6-9 \times 10^{-3}$  (NRC, 2006). Currently, measurements and models of CO are not in agreement. Because CO represents a fair fraction of the reactivity with OH° during the day, and is a useful tracer of PBL dynamics, continued work on observations and comparisons to models and emission inventories is called for. For example, new auto-zeroed trace level CO monitors could be deployed at various monitoring sites in order to study the relationship of CO to NO<sub>x</sub>, so that ambient measurements and emission inventories can be reconciled.

#### 4.6 Satellite Remote Sensing

Satellites have emerged as a useful tool in understanding the big picture of smog and haze episodes. Remote sensing can evaluate emission patterns and trends in species such as SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, and in particulate matter. The relationship of atmospheric concentrations of these species to synoptic features such as wave cyclones and fronts can also be discerned to help formulate conceptual models. Moreover, the satellite data itself can be assimilated into chemical transport models and used to explore the importance of various transport and mixing processes. Of special interest are satellites that measure vertical profiles of species and aerosols in the troposphere, such as the Tropospheric Emission Spectrometer (TES) and the Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO). TERC should position itself to take advantage of developments in satellite remote sensing by agencies including NASA, NOAA, and the European Union (EU).

#### 4.7 Halogen Chemistry

In the past, it has been speculated that halogens may be a source of radicals that could fuel ozone production. Houston's location near the Gulf may enhance reactions with halogens released from sea salt aerosols. Initial results from TexAQS II measurements of halogen chemistry (RSST Finding A4), including observations of up to 1 ppb of ClNO<sub>2</sub>, are intriguing and deserve further investigation. Appropriate monitoring instrumentation (e.g., electron capture detection gas chromatography) should be deployed in future measurement campaigns that specifically target halogens of importance to the Houston environment.

#### 4.8 Summary

In summary, it is time for definitive work to determine the relative importance of primary versus secondary formaldehyde and other radical sources such as HONO in determining ozone productivity in Houston. Recent research on multiphase reactions has been fruitful and puts TERC on the cutting edge of air pollution science. Such research should be continued, especially in the light of measurements that indicate levels of HONO that cannot be explained by gas-phase chemistry alone. Direct observations of primary pollutants, especially when analyzed as ratios, can lead to the improvement of both emission inventories and models. Coordination between chemical measurements and dynamical models can also yield insight into transport and mixing processes. Finally, satellite remote sensing and halogen chemistry have emerged as exciting new areas of investigation that may be important to Texas air quality research.

## 5 ANALYSIS OF AIR QUALITY DATA

### 5.1 Introduction

Data for atmospheric composition are collected routinely throughout Texas by ambient networks mandated by the Clean Air Act Amendments and as part of focused research efforts, such as those during TexAQS I and II. Data are collected for O<sub>3</sub>, PM, CO, SO<sub>2</sub> and NO<sub>2</sub> at over 40 sites in the Greater Houston Area, partly to fulfill requirements for determining attainment of the National Ambient Air Quality Standards. Data for the chemical composition of atmospheric particles are also collected in large urban areas as part of the (Aerosol) Speciation Trends Data Network. Data for hydrocarbons and some aldehydes and other oxygenated species are also collected at a few sites in large urban areas. All of the data collected as part of these ongoing monitoring efforts are used to help evaluate photochemical models, to evaluate human exposure to criteria pollutants (e.g., O<sub>3</sub>) and hazardous air pollutants (e.g., benzene), and to determine source contributions to pollutant concentrations. In addition to these routine efforts, data for other species of importance to air quality have been obtained as part of TexAQS I and II.

Data obtained during the intensive field campaigns are more comprehensive than those obtained by the stationary monitoring networks, but are limited by their short duration. The analysis of year round data sets from stationary monitoring networks could add further insight into the nature of the air quality problems facing Texas. A major challenge is to meld data from these two disparate sources (field campaigns and stationary monitoring networks) to yield more useful information than would have been obtained if the data sets had been analyzed separately. This rich combination of air quality data could then be analyzed with various statistical and data mining techniques to determine trends, investigate source culpability, and evaluate chemical transport model predictions.

### 5.2 General Recommendations

The following general recommendations would enable us to better use the data collected by the various air measurement programs in Texas.

- Archive, organize and merge meteorological, emissions, ground based and aircraft chemical composition data and model output in a central location.
- Characterize spatial and temporal variability of data obtained by ambient monitoring networks for criteria air pollutants, air toxics, precursors to ozone formation, and aerosol components.
- Analyze data collected by TERC programs during TexAQS II. These include:
  - the Southeast Texas Transport Study
  - the Northeast Texas Plume Study
  - the Solar Occultation Flux (SOF) Experiment
  - the Houston Triangle Experiment
  - the TexAQS II Radical Measurement Project (TRAMP)
  - the Vertical Mixing Experiment, and
  - the Baylor Aztec flights.
- Coordinate analyses of TexAQS II data collected by TERC projects with analyses of data collected by other programs.

- Analyze data collected at VOC and aerosol composition monitoring sites in terms of source contributions. These analyses could be performed using Chemical Mass Balance, Positive Matrix Factorization, the UNMIX receptor model, or data mining techniques.
- Use field study and routine monitoring data to evaluate meteorological and air quality model performance using both broad metrics (e.g., EPA performance metrics, correlation metrics) and monitor-by-monitor comparisons of observations with meteorological and chemical species predictions.
- Analyze data from the Houston Exposure to Air Toxics (HEATS) field study. The analysis should deploy a variety of methods, including data mining and comparison of observed personal exposures with the predictions of human exposure models. Results from such analyses could also be used to plan further field studies.

### 5.3 Recommendations for Specific Analyses

***Photochemical model simulation of radical sources and ozone productivity need to be reconciled with observations.***

- a. Measurements of radicals as well as their source and sink species should be compared to numerical models of radical formation and removal.
- b. The ozone production rate and ozone production efficiency should be determined using a constrained steady-state model, such as that of Kleinman et al. (2005).
- c. A comparison should be made between the  $\text{OH}^\circ$  reactivity measured directly by the Pennsylvania State University group and the  $\text{OH}^\circ$  reactivity calculated from the full suite of measurements made at Moody Tower. The role that aldehydes play in the measured and calculated  $\text{OH}^\circ$  reactivity is of special interest. The percentage of the measured reactivity from unknown  $\text{OH}^\circ$  reactions should also be estimated.
- d. Observed wind speed and direction should be used to generate back trajectories that help identify sources of high concentrations.
- e. Researchers should consider potentially important nighttime  $\text{NO}_3$  reactions leading to irreversible  $\text{NO}_x$  loss, such as with carbonyls and olefins (Brown et al., 2006). These also destroy odd oxygen and tie up VOCs that might otherwise generate  $\text{HO}_2$ , as well as transform  $\text{NO}_x$  to  $\text{RONO}_2$ . Aerosol particles may be rapidly coated with an organic layer inhibiting the multiphase reactions involving  $\text{N}_2\text{O}_5$ . Investigators should address the nighttime chemistry of  $\text{NO}_x$ ,  $\text{HO}_x$ , and VOCs, comparing for example the rate of formation of vapor phase  $\text{HNO}_3$  to numerical simulations.
- f. Photolysis rates currently used in CMAQ or CAMx should be compared to surface level measurements. Photolysis rates will be based on on-line, explicit calculations of UV and visible solar fluxes in an upcoming version of CMAQ, and these new rates should also be compared to measurements. These analyses will require data for aerosol optical properties and column aerosol optical depth to determine if the effects of aerosols on calculated solar fluxes are adequately treated.
- g. The origin of high nighttime  $\text{HO}_x$  is intriguing and should be investigated. Periods of rain should provide a test of the zero. Rainfall periods could be ascertained from archived NEXRAD, National Precipitation Analysis (NPA), and NASA/TRMM satellite data.

- h. The origin of HONO at night and during the day should be investigated. If calculated values of  $j(\text{HONO})$  are correct, then there is a substantial photochemical source of HONO as well as a multiphase nighttime source.
- i. The role of HCHO and HONO in the observed radical budget should be determined. It might be particularly interesting to observe how the radical budget changes as the wind direction shifts, thus bringing in air parcels from different parts of Houston.
- j. The sum of individual components of reactive N ( $\text{NO}$ ,  $\text{NO}_2$ , PAN,  $\text{HNO}_2$ ,  $\text{HNO}_3$ , etc.) should be compared to the measurement of total  $\text{NO}_y$ , and the relative contribution of each component species should be compared to model calculations. This evaluates analytical techniques and photochemical mechanisms. For example, does the ratio of  $\text{NO}_2$  to  $\text{NO}$  make sense in terms of  $j(\text{NO}_2)$  and the concentrations of  $\text{O}_3$  and  $\text{HO}_2$ ?
- k. Where possible, simultaneous collocated measurements should be compared with each other to evaluate analytical accuracy and agreement of standards. This should begin with species with a high level of confidence such as ozone. Do tower and aircraft measurements agree? The more challenging measurements such as  $\text{HNO}_3$ , HONO, HCHO, and other VOCs should follow.
- l. Large concentrations of ozone and PM aloft show the potential regional nature of smog in Houston. High concentrations of  $\text{NO}_y$  and  $\text{SO}_2$  above the PBL (up to 4000 m altitude) would be unusual. Rapid photochemical formation of  $\text{O}_3$  must be distinguished from rapid changes in  $\text{O}_3$  due to downward transport from the lower free troposphere. To determine the relative importance of vertical mixing and photochemistry, the Baylor aircraft data should be evaluated and compared to other measurements aloft. Moreover, in interpreting the role of vertical mixing, CO tracer studies should be considered as the chemistry of CO is simple. Measured and modeled profiles of CO should agree, or there is an error in emissions or mixing.
- m. Existing data from all platforms should be analyzed to identify sources of  $\text{HO}_x$  – this includes primary emissions of HCHO and other aldehydes, as well as multiphase formation of HONO.
- n. Measurements of VOCs and radicals at all sites and on all platforms should be coordinated with model studies to evaluate chemical mechanisms such as SAPRC, CB4, and CB05.
- o. Mixing ratios of  $\text{H}_2\text{O}_2$  should be compared to  $\text{SO}_2$  to see if  $\text{H}_2\text{O}_2$  is a potentially irreversible sink for  $\text{HO}_x$  through  $\text{H}_2\text{SO}_4$  formation, or a reservoir from which OH can be returned via photolysis.

***Multiphase processes involving aerosols need to be accounted for in photochemical models.***

The TRAMP and Houston Triangle studies provided a wealth of data for gas phase and aerosol composition. This data set gives us the opportunity to test the processes used in models. Some effort should be made to incorporate and test the effects of multiphase processes, in particular those that might affect the abundance of free radicals, in atmospheric models. The formation of HONO by multiphase processes is an example of the types of analyses that could be done. As a first step, simulations could be performed in a box model framework. Data from the TRAMP study also indicated the formation of new particles in nucleation bursts. Studies relating these events to precursors would provide valuable information about the interactions between gaseous precursors and secondary aerosol formation in Houston. The role of these particles as cloud condensation nuclei in Houston could also be investigated.

## 6 AIR QUALITY MODELING

### 6.1 Introduction

Most of the unresolved fundamental science issues affecting the validity and performance of air quality models used in connection with the State Implementation Plan (SIP) have been discussed in preceding sections of this document. Rather than simply repeat them, it is more useful to present a framework of policy-relevant issues that may help to prioritize specific research needs. This framework is influenced by the results of prior TERC research, as well as by the consensus drawn from the recently concluded TexAQS II Principal Findings Data Analysis Workshop and TRAMP Data Analysis Workshop. The framework issues are as follows:

- The ozone productivity of the Houston SIP model may be low due to insufficient **new radical sources**. This depresses simulated control strategy effectiveness.
- **Transport** of ozone and precursors may in the future be more critical to ozone exceedances in Texas, especially if the federal ozone standard is lowered by EPA.
- The emission inventory for Houston may still undercount **VOC/HRVOC emissions**. Their simulated local ozone impact may be raised if radical sources are increased in models. In addition, their transport effects may not be adequately mitigated by regulations.
- **New episodes** for the Houston-Galveston-Brazoria (HGB) and Dallas-Ft. Worth (DFW) ozone non-attainment areas may respond differently to control strategies than previous episodes due to meteorology and lower NO<sub>x</sub> emissions.

### 6.2 New Radical Sources

Preliminary box model simulations of the Houston radical budget constrained by ancillary observations of primary species were performed as part of the analysis of TRAMP data (University of Houston, 2007). The results indicated a possible deficit of radical sources such that simulated HO<sub>x</sub> concentrations were only half of the observed levels. When a HONO mixing ratio of 1 ppb was imposed, most of the radical underprediction disappeared, indicating the importance of fast-photolyzing new radical sources in determining the reactivity of the Houston airshed. This is supported by the results of TERC Project H60 (Vizueté et al., 2006), which showed that: 1) much of the current inventory of HRVOCs and other VOCs for Houston could not be initially reacted in the CAMx model due to insufficient levels of new OH<sup>°</sup> radicals (rather than internal radicals generated after the initial reaction of primary VOCs); and 2) hypothetical, but plausible, extra emissions of formaldehyde (HCHO) from either flares or mobile sources boosted peak ozone in Houston by as much as 30 ppb. If such new radical sources were confirmed and incorporated into the HGB SIP model, either through adjustments to the HCHO or higher aldehyde emission inventory, or through heterogeneous HONO formation, control strategy effectiveness might be enhanced significantly due to increased ozone productivity of the airshed.

### 6.3 Transport

Estimates of the local versus background ozone contributions based on aircraft observations around Houston during TexAQS II confirm the findings of TERC Project H12.8HRA, which showed that background ozone is a substantial portion of many ozone exceedances in Texas. The EPA has recently proposed lowering the 8-hour ozone standard, perhaps to around 70 ppb, which would make transport of background ozone even more important from a regulatory standpoint.

#### 6.4 HRVOC/VOC Emissions

Results of the TERC-funded SOF experiment and of ambient ratio studies based on data collected by the NOAA P3 aircraft during TexAQS II indicate that, although HRVOC/VOC emissions in Houston have substantially declined since 2000, current emission inventories may still underestimate their true levels, possibly by an order of magnitude or more. Missing sources of VOCs may include refinery cokers, which are not completely accounted for in emissions reported by industrial facilities. Although the apparent insufficiency of radical sources in the Houston SIP model may make VOC control strategies insensitive to this shortfall, the true impacts of VOC emissions in Houston may be underappreciated. This applies not only to the local ozone impacts of VOCs, but also to their longer-range impacts through transport of primary VOCs and of critical secondary by-products such as formaldehyde and PAN. For example, TERC Project H59 (Sandu et al., 2006) demonstrated using the adjoint sensitivity method that ground-level ozone in the DFW area may at times be significantly influenced by formaldehyde originating from the Gulf Coast. Given that additional NO<sub>x</sub> controls may be more difficult to obtain than in the past, additional VOC controls may be an attractive option if there are higher levels of VOCs to reduce than currently estimated, and if the effectiveness of such controls is greater than anticipated.

#### 6.5 New Episodes

The TCEQ is committed to developing new model episodes for the HGB SIP based on the wealth of data obtained during TexAQS II. There is an obvious advantage to this in that model performance can be better gauged based on a greater number of observations. There is also the added advantage that emission reductions already achieved since the previous episode year of 2000 would be accounted for in a 2006 episode. Lower emissions lead to lower observed ozone design values. Moreover, because of the nonlinearity of ozone chemistry, lower NO<sub>x</sub> emissions may enhance the ozone production efficiency of the airshed, offsetting the impact of a shorter time period for reduction on the Relative Response Factors. The combination of these elements may make it easier for Texas to demonstrate ozone attainment.

#### 6.6 Recommendations

- Combine bottom-up and top-down modeling approaches to improve formaldehyde, HRVOC, and other VOC emission inventories. For example, combustion models can be used to investigate the emissions of formaldehyde, HRVOCs, and other VOCs from flares based on speciated process flows as a function of facility type. This can be complemented by inverse modeling (e.g., 4DVar) using an Eulerian air quality model based on monitoring observations.
- Compile literature values of HCHO/CO ratios for motor vehicle fuels (e.g., TexLED, CNG, ethanol, biodiesel), and perform air quality model sensitivity studies for various fleet composition and fuel scenarios to determine ambient formaldehyde and ozone impacts associated with each scenario.
- Conduct air quality model sensitivity studies to investigate HONO impacts on Houston ozone productivity. This includes: 1) setting HONO levels to observed concentrations for a 2006 retrospective simulation and comparing the model radical and ozone predictions to measured values during TexAQS II; and 2) conducting mechanistic HONO experiments involving various heterogeneous formation pathways, such as those involving soot and aerosol substrates.
- Investigate the regional ozone formation potentials of biogenic and anthropogenic VOCs, accounting for nocturnal transport and secondary by-products such as PAN and formaldehyde.

- Perform inverse modeling to improve HRVOC/VOC emission inventories based on TexAQS II observations.
- Assist the TCEQ in developing summer 2006 episodes for HGB with improvements in:
  - specification of initial (e.g., 4DVar) and boundary (e.g., RAQM) conditions for chemical species
  - chemical mechanism (e.g. CB05 or SAPRC)
  - heterogeneous chemistry (e.g., HONO formation)
  - liquid partitioning, deposition and re-volatilization of soluble species (e.g., HNO<sub>3</sub>)
  - treatment of clouds and photolysis (e.g., assimilation of GOES data)
  - sub-grid scale chemical processing (e.g., plume-in-grid chemistry or parameterizations derived from a Large Eddy Simulation model with chemistry)
  - vertical mixing (e.g., ACM2) and resolution
  - physics of the free troposphere (e.g., lightning NO<sub>x</sub>, stratosphere-troposphere exchange, convective venting from the PBL, subsidence and entrainment into the PBL)
  - meteorological data assimilation (e.g., EnKF, skin and sea surface temperatures).
- Continue real-time meteorological and air quality forecasting to evaluate the effectiveness of model improvements over a long time period.
- Apply the 2005 DFW episode developed in Project H60 to investigate control strategies for the DFW ozone non-attainment area.

## 7 HUMAN EXPOSURE

### 7.1 Introduction

TERC's mandate, while not extending to the investigation of human health impacts, allows for the technical assessment of human exposure to air pollutants. Measurements of human exposure are essential for understanding the effectiveness of control measures designed to protect human health. Residents in the Greater Houston Area (GHA) are potentially exposed to high levels of a large number of toxic air pollutants from the concentrated petrochemical facilities in the Ship Channel, as well as from mobile sources. In contrast, human exposure to hazardous air pollutants in other regions in East Texas (Dallas-Fort Worth, Tyler-Longview, Austin, San Antonio, etc.) results from mobile sources, rich-burn compressor engines, power plants, and cement kilns, to name a few.

Most attention has been paid to non-attainment of National Ambient Air Quality Standards (NAAQS) for criteria pollutants (O<sub>3</sub>, PM, CO, SO<sub>2</sub>, NO<sub>2</sub>), in particular for O<sub>3</sub>. Levels of toxic air pollutants in the GHA, in particular, diesel exhaust particles, benzene, toluene, o-, m-, and p- xylene, acrolein and perhaps formaldehyde have already been shown by Sexton et al. (2007) to result in unacceptably high cancer risks from chronic exposures.

Field and modeling studies are needed to adequately assess the risks to public health from criteria air pollutants and from EPA's list of Hazardous Air Pollutants (HAPs). Atmospheric chemistry in the GHA is exceedingly complex and many potentially toxic components cannot be measured and therefore the toxicity of the atmospheric mixture cannot be adequately assessed. The large size of the GHA combined with the large number of sources and pollutants makes it impractical to rely on field measurements alone in assessing personal exposure across the GHA. Instead, predictive models of human exposure need to be further developed to make best use of the field data.

## 7.2 Recommendations

The following recommendations could enable us to better assess human exposure to criteria pollutants and air toxics:

- Develop techniques for monitoring and assessing personal exposures to air toxics and criteria air pollutants.
- Perform innovative field studies that allow a better characterization of personal exposures to pollutants from different sources in the GHA.
- Develop bio-indicators based on chemical analysis of various metabolic products that could be used as markers of exposures to particular pollutants.
- Support the development of techniques that could be used to determine the potential adverse effects of pollutant mixtures, such as the use of cultured lung cells.
- Analyze data from the Houston Exposure to Air Toxics (HEATS) field study. The analysis should deploy a variety of methods, including data mining and comparison of observed personal exposures with the predictions of human exposure models. Results from such analyses could also be used to plan further field studies.
- Collaborate with the Texas Medical Center research community in applying air quality models, observations, and data analysis tools to the development of Epidemiological Surveillance Systems based on human exposure.
- Support modeling studies to improve the accuracy of neighborhood exposure estimates, especially close to sources.
- Combine neighborhood scale models with urban and regional scale models to account for transport of long-lived primary and secondary air toxics.
- Combine air quality and human exposure models with data assimilation tools to improve human exposure assessment based on limited observations.
- Deploy a model for spatial analysis of air pollution and a land use regression model, including the use of Geographical Information System (GIS) and ancillary variables, to predict VOC and NO<sub>2</sub> levels at unmonitored sites.
- Expand chemical mechanisms used in air quality models to include more toxic species.
- Develop and apply multi-media fate and transport models to assess indirect exposure and better evaluate chronic risk due to air toxics.
- Improve human exposure models by developing more accurate representations of local human activity patterns appropriate for the general population, with emphasis on susceptible sub-groups.

## 8 POLICY/CONTROLS

### 8.1 Policy Issues

Addressing the key scientific issues identified in this plan will improve the understanding of ozone and fine particulate matter formation and transport in Texas. However, improving understanding in each of the key areas, then synthesizing that information and evaluating air quality improvement strategies, is a long-term process. While it is essential that this process proceed, there is also a compelling need to address a number of questions related to policy decisions. These questions are:

- What emission reductions lead to the greatest reductions in ozone concentrations? For example, is it more effective to focus on highly reactive and other VOCs from industry or regional NO<sub>x</sub> controls?
- How would reductions in ozone concentrations in Houston affect the peak ozone levels in Dallas-Fort Worth, Beaumont-Port Arthur, and Central and East Texas? How would reductions in ozone concentrations in East Texas affect the peak ozone levels in Dallas-Fort Worth? Researching these questions can lead to a true “State” Implementation Plan.
- What is the impact of long range (U.S. and international) transport of air pollutants on Texas’ ozone and fine particulate matter concentrations? Researching this question can lead to a multi-State plan, as recommended by the National Academy of Sciences.

In addition, the TERC SRP timeline will fall within the State of Texas 81<sup>st</sup> Legislative Session. TERC efforts should be timely in order to provide necessary technical details to support legislative changes that will result in implementing quantified, cost-effective control strategies.

In addition to providing useful information to policy makers consistent with short-term deadlines imposed by the regulatory process, long term analysis of emission reductions is necessary in light of possibly more stringent standards, increased population, and resulting changes in commercial and residential development.

### 8.2 Control Strategies/Technologies

Control strategies and technologies are judged by their cost and effectiveness. Evaluating effectiveness must account for both reduced emissions and improved ambient pollutant levels. Control strategy research projects should be prioritized as listed below. Those projects with the potential to provide the greatest improvement in ambient pollutant levels for the lowest cost should be given the highest priority.

1. In order of priority, survey and evaluate available new technologies and process modifications for
  - a. reducing NO<sub>x</sub> emissions,
  - b. reducing emissions of VOCs, focusing on highly reactive VOCs, and
  - c. reducing emissions of primary particulate and emissions of particulate precursors such as sulfur compounds.
2. Develop new control measures and identify ways to improve the effectiveness of existing control measures for area, point, non-road mobile, and on-road mobile sources, including improving the accuracy of emissions estimates for these source categories.
3. Evaluate the appropriate spatial and temporal effect of control strategies.
4. Identify where estimated emission estimates may be considered to be double counted based on assumptions in the model. Seek solutions to resolve this issue.

5. In addition to near term (attainment date) quantification, analysis should also include long term emission reduction benefits due to future maintenance plans, area reclassification, new stringent NAAQS, etc.

In all cases, surveys and evaluation of new technologies should be preceded by a thorough review of currently available research.

Because of the breadth of issues considered in this SRP and the limited resources at hand, priority should be given, as in the past, to core issues related to the Texas SIP, particularly when funds from the State Legislature are used. Proven and inexpensive control strategies such as low sulfur fuels and PM traps should be given a chance to address particulate matter (PM) concerns until PM non-attainment becomes a reality in Texas.

Some research issues identified in this SRP are so fundamental (e.g., radical chemistry, transport) that successfully tackling them may make it possible to discover new and/or more effective control strategies, such as: 1) controls on formaldehyde emissions from flares, 2) new fuel regulations targeting emissions of radical sources such as HONO and formaldehyde from motor vehicles, 3) chemical treatments of man-made surfaces to limit HONO production on the urban canopy, 4) demonstrably effective new reductions in HRVOC/VOC emissions from cokers and other undercounted emission sources, and 5) new approaches to controlling regional background ozone, such as solvent controls based on regional reactivity and more statewide approaches to NO<sub>x</sub> control. TERC should cooperate closely with the TCEQ to ensure that any new knowledge generated translates into effective actions to reduce pollution in Texas.

## CONCLUSION

The recently concluded TexAQS II campaign offers an immense opportunity to improve the practice of air quality modeling and help Texas more easily demonstrate attainment of the 8-hour ozone standard. While many improvements are necessary, two in particular stand out as pressing needs for the State Implementation Plan:

- Incorporating multi-phase radical chemistry and enhanced sources of new radicals in air quality models; and
- Accurately representing the physical and chemical details governing long-range transport of pollution.

These research issues are so fundamental that successfully tackling them will benefit not only the ozone SIP, but also future compliance with federal and State regulations governing regional haze, particulate matter, and air toxics. In addition, progress on these two fronts may make it possible to discover new and/or more effective control strategies.

On a more practical level, progress must also be accomplished in:

- Improving the accuracy of emission inventories, including their spatial and temporal resolution, especially for highly reactive and other VOCs; and
- Developing new SIP model episodes based on the wealth of new data obtained from TexAQS II.

TERC recognizes that it must work collaboratively with numerous partner institutions, most especially with the TCEQ, to successfully contribute to the solution of air quality problems in Texas. This Strategic

Research Plan provides a framework to guide TERC decision making over the next two years, with the aim of channeling research funds to the most productive projects that will generate lasting benefits for Texas citizens in years to come.

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