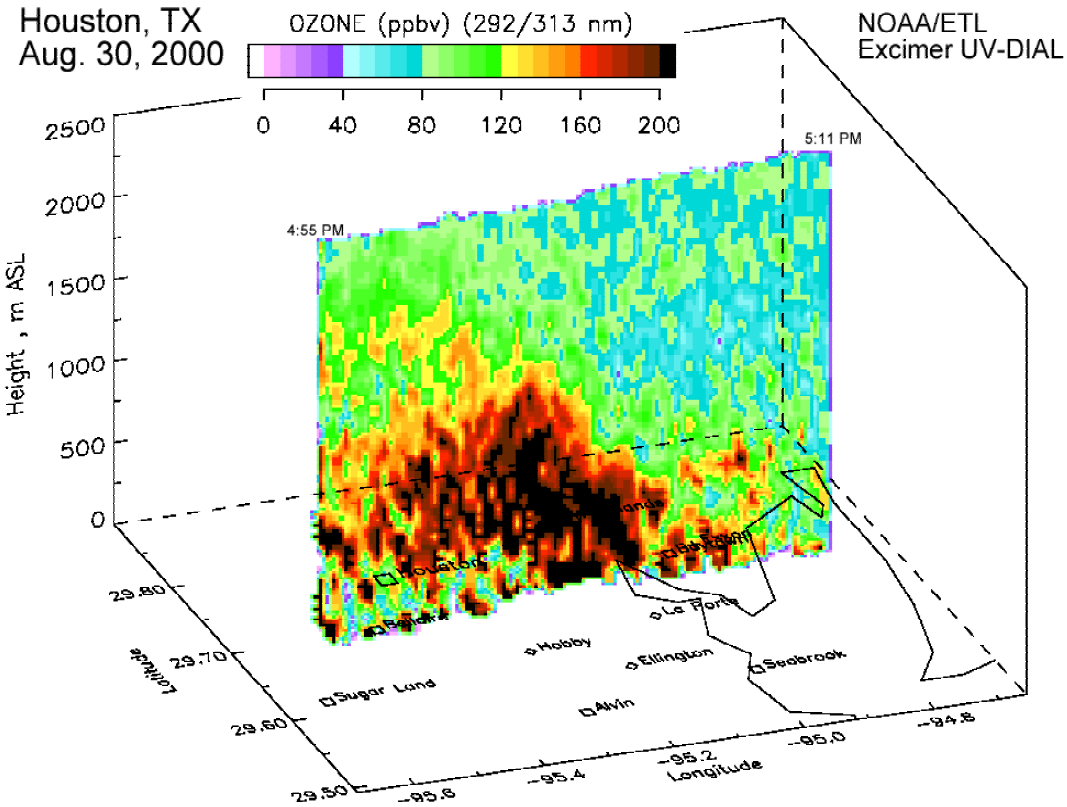
ACCELERATED SCIENCE EVALUATION of OZONE FORMATION IN THE HOUSTON-GALVESTON AREA

SUMMARY



Science Synthesis Committee

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The Texas Commission on Environmental Quality, the scientific community, the environmental community, and the business community are jointly assessing scientific data on ozone formation in the Houston-Galveston area emerging from one of the largest and most successful air quality studies ever undertaken. This field program, referred to as the Texas Air Quality Study, was conducted during the summer of 2000 (TexAQS-2000). The scientific assessment of these data is being accelerated, compared to the normal pace of scientific review and publication of findings, in order to provide critical scientific information on ozone formation to decision-makers who are evaluating air quality management plans in the Houston-Galveston area. The goals of this Accelerated Science Evaluation are to examine the causes of rapid and efficient ozone formation in the Houston-Galveston Area and to provide guidance on the relative sensitivities of the ozone concentrations to reductions in the emissions of reactive hydrocarbons and oxides of nitrogen.

A previous summary of the findings of the Accelerated Science Evaluation was prepared in February 2002. Findings numbered 1-8 in this document are refined versions of the Findings presented in February. The refinements reflect additional insights provided by on-going data analyses. Also provided in this summary are additional findings that have emerged from data analyses conducted after February 28. These are numbered 9-11. All of the findings presented in this summary are supported by other documents associated with the Accelerated Science Evaluation (Accelerated Science Evaluation, 2002a,b,c,d,e).

Issue 1: What are the likely causes of rapid ozone formation events?

During the Texas Air Quality Study, conducted between August 15 and September 15, 2000, a number of episodes with high ozone concentrations occurred. These episodes were characterized by at least two distinctly different sets of meteorological conditions and the episodes are believed to be representative of conditions that have historically led to high ozone concentrations in the Houston-Galveston area. Measurements made during the episodes have led to the following findings regarding ozone formation in the Houston-Galveston area.

Finding 1: Almost without exception, air parcels with very high ozone concentrations, observed by aircraft during the Texas Air Quality Study, had back trajectories that indicated a substantial contribution of emissions from industrial source regions. These air parcels also had chemical compositions that were representative of industrial sources, rather than typical urban sources.

The ozone formation associated with industrial plumes is more rapid and more efficient than ozone formation in the urban plumes. The rate of ozone formation, expressed in units of ppb/hr, has been estimated based on measurements made by aircraft.

Finding 2: The rate of ozone production in and around the industrial source dominated areas in Houston can be very high; ozone formation rates ranging between 50 ppb/hr and 150 ppb/hr were measured on multiple days during the

month long Texas Air Quality Study. These rates of ozone production are much higher than those observed in other urban areas, which are almost always less than 40 ppb/hr.

The efficiency of ozone formation in the Houston-Galveston area was also measured by aircraft. The efficiency is typically reported as molecules of ozone formed per molecule of NO_x reacted.

Finding 3: The efficiency of ozone production in and downwind of the industrial source dominated areas in Houston can be very high, ranging from 10-20 molecules of ozone per molecule of reacted NO_x. These efficiencies of ozone formation are much higher than those observed in other urban areas (typically 3-5), those observed in the Houston urban plume (approximately 5), or those observed in the plume of an isolated power plant in the region (approximately 2). This finding suggests that NO_x emissions in different source regions within the Houston-Galveston area can have very different impacts on ozone formation.

Finding 4: Ozone production in the Houston urban plume was found to be slower and less efficient than in the composite industrial plume from the Ship Channel region and in plumes from isolated petrochemical facilities. The ozone production observed in the urban plume may lead to ozone concentrations in excess of the National Ambient Air Quality Standard; however, the ozone formation observed in the urban plumes was significantly slower and less efficient than the rates observed in the industrial plumes. The ozone formation rates and efficiencies observed in the Houston urban plume were similar to rates observed in other urban areas.

Finding 5: The high rates and high efficiencies of ozone production in the industrial plumes are driven by high concentrations of reactive hydrocarbons in the presence of NO_x. The concentrations of hydrocarbons observed in the industrial source areas, both by aircraft and by ground-based monitors, are much higher than concentrations observed in comparable studies in Dallas-Fort Worth, Atlanta, Nashville, New York, Philadelphia and Phoenix. The composition of the excess hydrocarbons is consistent with the composition from industrial sources. The mass of the excess hydrocarbons is dominated by low molecular weight hydrocarbons (alkanes, alkenes and aromatics); the reactivity of the excess hydrocarbons during the Texas Air Quality Study was most often dominated by low molecular weight alkenes; however, at times, aromatics and alkanes dominated contributions to reactivity; biogenic emissions did not contribute significantly to the reactivity of the plumes examined during the Texas Air Quality Study.

The high efficiency and the high rate of ozone formation in the industrial plumes are caused by very high concentrations of reactive hydrocarbons. Reducing concentrations of reactive hydrocarbons would reduce efficiencies, however the peak ozone concentration obtained in a plume will also depend on the availability of NO_x. Quantitatively examining the response of ozone concentrations in the industrial plumes to VOC and NO_x emission reductions requires the use of computational models; however, the accuracy and reliability of the models depends on accurate input data on emissions and meteorology. Findings from the Texas Air Quality Study suggest that current

emission inventory data will not lead to accurate estimates of the rate and efficiency of ozone production in industrial plumes.

Finding 6: Industrial hydrocarbon emissions are significantly underestimated. Measurements of the ratios of hydrocarbons to NO_x in the industrial plumes were consistently factors of 2-15, and in some isolated instances even a factor of 50 or more higher, than the ratios reported in the inventories. Mass balance calculations suggest that the NO_x inventory is in reasonable agreement with observations and that the main reason for the high ratios is underestimation of hydrocarbon emissions. Estimates of the emissions of alkanes, alkenes and aromatics all appear to be low. In most observations, alkenes contribute the bulk of the reactivity; however, in some plumes alkanes or aromatics contribute the bulk of the reactivity.

Substantially improved emission inventory data are a prerequisite for determining the sensitivity of ozone formation to reductions in the emissions of reactive hydrocarbons and oxides of nitrogen.

Finding 7: Observations of wind fields aloft, and other meteorological phenomena during Texas Air Quality Study, support and refine the evolving conceptual model of meteorological conditions that lead to ozone formation in the Houston-Galveston area. Observations collected during the Texas Air Quality Study suggest that stagnation, wind fields that slowly rotate in direction throughout the day, the occasional presence of low level jets, and other phenomena have a significant influence on the formation and transport of ozone. Analysis and modeling of these complex features is ongoing

Issue 2: How will the rapid and efficient ozone formation observed in industrial plumes respond to VOC controls and NOx controls?

Developing alternative emission reduction strategies involves policy decisions, informed by scientific and technical decision support tools. The Accelerated Science Evaluation can provide scientific evaluations of models and other decision support tools. These tools, in turn, provide guidance on the sensitivity of ozone formation to reactive hydrocarbon and NO_x emission reductions. The State of the Science in air quality models used in the Houston-Galveston area has been summarized in other Accelerated Science Evaluation documents (Accelerated Science Evaluation 2002b,c,d,e). The information presented in those documents leads to the following findings:

Finding 8: The chemical mechanisms for ozone formation currently employed in models of air quality in the Houston-Galveston area are adequate to explain the main features of rapid and efficient ozone formation observed in industrial plumes. Additional refinements to the chemical mechanisms may improve model performance and may reveal opportunities for development and refinement of emission control strategies. Nevertheless, current chemical mechanisms of ozone formation chemistry are sufficient for describing the vast majority of the ozone formation that is observed in the region.

Finding 9: Ground observations of hydrocarbon concentrations, taken over a period of several years, and aircraft data collected during the Texas Air Quality Study, identify numerous episodes with very high hydrocarbon concentrations. While the species detected at high concentrations vary from episode to episode, most hydrocarbon species emitted from industrial sources have been detected at high concentration in at least some episodes.

The fact that the industrial emissions of all light hydrocarbon species appear to be underestimated suggests that the sources of these hydrocarbons are ubiquitous in industrial facilities. Sources that are ubiquitous are fugitive emissions, flares and cooling towers, and emissions from these sources are being investigated.

Finding 10: Measurements, made by the Baylor aircraft downwind of industrial sources in the fall of 2001, suggest that while some industrial plumes are well mixed, other plumes are spatially heterogeneous. The spatially heterogeneous plumes can contain regions with high concentrations of VOC, regions with high concentrations of NO_x and regions with high concentrations of both VOC and NO_x. Whether a plume is well mixed or heterogeneous is likely to depend on the distance from the source and atmospheric stability conditions.

Findings 9 and 10 suggest that multiple hydrocarbons may be sources of reactivity in industrial plumes and that the plumes may have a variety of VOC/NO_x ratios. Box model simulations of ozone formation can be used to identify the VOC/NO_x ratios and the hydrocarbon species that have the greatest ozone formation potentials.

Finding 11: Results from box model simulations run under conditions based on Houston's industrial regions suggest that emissions of as little as 100 pounds of light alkenes (ethylene, propylene, butenes, pentenes, butadiene) and aromatics can lead to >50 ppb enhancements of ozone concentrations over a 1 km^2 area. Ozone productivities of alkane emissions are generally significantly lower than for alkenes and aromatics. The box model simulations also indicate much higher ozone productivities under conditions that involve high concentrations of both VOC and NO_x, as opposed to conditions that involve high concentrations of VOC alone.

Although box models can be useful in providing semi-quantitative guidance on the response of ozone production to VOC and NO_x emission reductions, the results must be used with caution. Industrial plumes from different source regions are often distinct and have different VOC compositions and VOC/NO_x ratios. Even from a specific source region, temporal variations in VOC compositions and VOC/NO_x ratios can be significant. So, box model simulations and plume models incorporating detailed chemical mechanisms can provide guidance about the effectiveness of emission reductions in specific emission and plume mixing scenarios, but it could be misleading to average results across multiple plumes.

Ideally, gridded photochemical models could be used to address the limitations of box model simulations. It is encouraging that current gridded photochemical models, given

emission inputs that are consistent with observations, predict rapid ozone formation. But, the uncertainties in emission inventories continue to make evaluation of the performance of gridded photochemical models difficult.

References

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