EXECUTIVE SUMMARY

The objective of this study was to improve and quantify our understanding of ozone (O_3) and formaldehyde (HCHO) production from industrial emissions of Highly Reactive Volatile Organic Compounds (HRVOC) in the Houston area. The study took advantage of unique aircraft measurements during the National Aeronautics and Space Administration (NASA) Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC^{4}RS) project in the fall of 2013. The aircraft encountered plumes with enhanced O_3 downwind of petrochemical facilities in Houston. HRVOC, namely ethene, propene, butenes and 1,3-butadiene, cause these types of O_3 plumes but quantifying the relative contributions of individual HRVOC to O_3 formation has been difficult. Chemical compounds, called β-hydroxynitrates (βHNs), are formed when HRVOC react in the atmosphere in the presence of nitrogen oxides (NOx). Measurements of the C_2-C_5 hydroxynitrates aboard the DC-8 provide a novel means to link observed enhancements of O_3 and HCHO to reactions of specific HRVOC and isoprene.

The study objectives were accomplished by a combination of data analysis and reactive plume modeling using the SCICHEM Lagrangian puff model. QA/QC'd data (provided by Caltech) taken aboard the NASA DC-8 research aircraft during the 2013 SEAC^{4}RS project in Houston were used in the analysis. The observational analysis was conducted for 20 plumes that were encountered on 11 flights in the Houston area from August 12 to September 23, 2013. The plume modeling focused on the September 18, 2013 flight which intercepted the Houston Ship Channel (HSC) plume at downwind distances of 40, 80 and 100 km. An HRVOC tracer mechanism was developed to describe first-generation formation of β-hydroxynitrates, aldehydes and O_3 from alkenes. This mechanism was used in both the observational analysis and the plume modeling to quantify the direct contributions of HRVOC oxidation to O_3 and aldehyde formation in the intercepted plumes. Direct contribution refers to O_3 and aldehyde produced immediately following OH reacting with the HRVOC.

In the observational analysis, the direct contributions were quantified from the measured βHN concentrations. O_3 enhancements in the plume intercepts ranged from 4 to 54 ppb. The fraction of these enhancements directly attributable to HRVOC and isoprene emissions (as indicated by the O_3/βHN ratios) ranged from 6% to 24%. Isoprene contributed, on average, 35% (range of 9% to 56%) of the directly attributable O_3 enhancement. This average contribution of isoprene is approximately equal to that of ethene, the most important HRVOC from the observational analysis. The direct contributions of individual HRVOC to the anthropogenic O_3 enhancement (i.e., excluding the isoprene contribution) on average ranked in this order: ethene (49%), propene (32%), butenes (13%) and butadiene (6%). However there were wide variations in these relative contributions: ethene (24% to 72%), propene (14% to 66%), butenes (8% to 24%) and butadiene (2% to 13%). Some of these variations represent

systematic changes in contributions with downwind distance as emissions were photochemically processed, with the more rapidly reacting HRVOC contributing a larger fraction early and the contribution from the more slowly reacting ethene gradually increasing.

The base case plume modeling for the September 18, 2013 flight considered the HSC as a single large source with an initial plume width of 6 km. HRVOC emissions from the HSC were based on SOF measurements conducted in Houston in 2011. Predicted profiles of O_3, NOy, NOz, HCHO and CH_3CHO concentrations for each downwind plume intercept were compared with corresponding DC-8 measurements. The model predicted peak O_3 increments in the HSC plume accurately, but the NOz and aldehyde results showed that chemistry proceeded more slowly in the model plume than indicated from the measurements during the early stages of the plume. Much better agreement for aldehydes and NOz was obtained in a sensitivity study in which 6 smaller sources along the Ship Channel were used to model the HSC emissions. The overall effect of using multiple narrower source plumes was that the chemistry proceeded more rapidly and model performance was improved at 40 km downwind.

The modeled direct contributions of HRVOC to downwind O_3 were generally consistent with the results from the observational analysis. The base case results showed that direct formation of O_3 from the HSC HRVOC emissions explained only 12 to 22% of the O_3 increments in the plume on September 18, 2013. The sensitivity study with 6 sources attributed 23 to 25% of the O_3 enhancements directly to HRVOC. Representing the HSC emissions by multiple, narrower source plumes accelerated plume chemistry and improved model performance. Another sensitivity study showed that plume chemistry is sensitive to whether HRVOC and NOx are released together or segregated in separate plumes that interact as they disperse and overlap each other.

The observational analysis and plume modeling of HSC plume intercepts during the SEAC^{4}RS project represent a significant advance in our understanding of the role of HRVOC emissions from the HSC on O_3 concentrations in the Houston region. The results indicate the need for additional studies, discussed below.

Key Findings from Observational Analysis

- O_3 levels during the days when the aircraft sampled the HSC plume indicate that most of these days represent typical, moderate O_3 days in Houston without unusually large HRVOC emission events.
- The fraction of O_3 formation in the HSC plumes that is directly attributable to HRVOC and isoprene emissions (as indicated by the $O_3/\beta HN$ enhancement ratios) is surprisingly small, averaging only ~13% with a range from 6% to 24%.
- Isoprene contributed, on average, 35% (range of 9% to 56%) of the directly attributable O_3 enhancement, making this species' average contribution approximately equal to that of ethene, the most important HRVOC.

- The direct contributions of individual HRVOCs to the anthropogenic O_3 enhancement (i.e., excluding the isoprene contribution) on average ranked in this order: ethene (49%), propene (32%), butenes (13%) and butadiene (6%).
- The total O_3 formed downwind of HRVOC sources is larger than the sum of the direct contributions of the individual HRVOCs and isoprene derived from O_3/βHN enhancement ratios.
- The observational analysis presented here has limitations that must be fully appreciated.

Key Findings from Plume Modeling of HSC Emissions

- Modeled ozone increments in the HSC plume on September 18, 2013 are in good agreement with aircraft measurements; noting that the HSC emissions were based on ambient measurements.
- Using several sources instead of a single source to represent the HSC emissions results in a better simulation of plume reactivity and formation of products such as NOz, HCHO, and CH_3CHO.
- Direct formation of O_3 from HRVOC emissions contributes 12 to 22% of the O_3 increments in the HSC plume on September 18, 2013 with a single source versus 23 to 25% for multiple sources.
- O_3 increments in the modeled plume are not sensitive to the source configuration (single source versus 6 sources) indicating that higher direct O_3 production from HRVOC emissions with 6 sources was offset by lower indirect O_3 production.
- O_3 increments in the modeled plume are sensitive to whether VOC and NOx are co-emitted or segregated.
- Butenes and propene are the largest HRVOC contributors to O_3 formation near the HSC. Ethene contributions become more important at larger downwind distances.
- More than 50% of the HCHO increments in the HSC plume are directly attributable to HRVOC emissions, with the highest contribution being about 80% at the nearest downwind distance of 40 km.
- Direct contributions of HSC HRVOC emissions to CH_3CHO concentration increments in the plume vary from 46% at the furthest downwind distance (100 km) to 100% at the nearest downwind distance (40 km).

Recommendations

The observational analysis suggests that there may be a loss mechanism(s) for βHNs in the gas phase. If this is indeed the case, then this may have implications for the availability of NOx in the gas-phase as the plume ages, because the βHNs are formed from many VOC and represent a substantial fraction of organic nitrates. Thus, additional studies of the fate of βHNs are warranted.

The modeling and observational analysis also indicate that a substantial fraction of the O_3 in the HSC plume is formed indirectly by the interaction of HRVOC emissions with other VOCs. For example, the observational analysis showed a large contribution of (biogenic) isoprene to O_3 in the HSC plume. More studies are required to understand direct versus

indirect O_3 formation in HSC plumes and to identify and quantify the various sources (including isoprene) of indirect contributions.

The plume modeling provided a unique opportunity to study the fine-scale photochemical interaction of plumes from nearby sources and initial segregation of NOx and VOC emissions. The current study provides a first look at these effects. Future studies can use more recent measurements of HSC emissions (e.g., from AQRP Project 14-007) and investigate further how initial plume width and emissions segregation influence O_3 production from industrial sources. Results from plume model and plume-in-grid model studies can show what resolution should be used in grid models. SCICHEM is well-suited to conducting these studies because it has full chemistry and allows overlapping plumes to interact photochemically. SCICHEM is also the underlying plume model in the recent EPA release of the plume-in-grid version of CMAQ 5.0.2, referred to as CMAQ-APT (where APT stands for Advanced Plume Treatment).