FINAL REPORT

To the Texas Environmental Research Consortium on
Project H12-EE

Survey of Technological and Other Measures to Control HRVOC Event Emissions

Prepared for

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EXECUTIVE SUMMARY

Texas is at the forefront, both nationally and internationally, in considering alternative approaches and policies to control and manage emissions that are precursors to ground level ozone formation. In particular, these unprecedented activities include instituting programs that identify and control specific volatile organic compounds, referred to as Highly Reactive Volatile Organic Compounds (HRVOCs), based on their relative atmospheric reactivity, allowing trading of hydrocarbon emissions, and incorporating field data into photochemical modeling inputs. As is true for all ground-breaking work, there are numerous questions regarding the scientific bases for the policies, and no readily available answers. In response, this work examines a portion of the scientific and technical issues that must be addressed in implementing these types of control strategies.

Specifically, the project focused on three issues:

1. When emissions of HRVOCs are reduced, emissions of other compounds co-emitted with the HRVOCs will also be reduced. What are the likely co-benefits of reducing HRVOCs (i.e., what other co-emitted species might also be reduced)?

2. What impacts on ozone formation could occur as the result of capping HRVOC emissions and trading HRVOCs emissions within a facility or between facilities?

3. What regulatory strategies used elsewhere (foreign and domestic) might be used to reduce HRVOCs in the Houston area?

Co-benefits of Reducing HRVOCs

Objective:

The fraction of total volatile organic compound (VOC) emissions that come from sources in HRVOC service was quantified and the potential reductions in other VOC (OVOC) emissions that might occur due to HRVOC controls (also referred to as ancillary OVOC reductions) in the Houston/Galveston/Brazoria area was estimated. In addition, the effect of potential underestimation of the OVOC inventory on photochemical modeling results was investigated.

Key Findings:

1. Event emissions for 2003, as reported in the TCEQ event database, accounted for approximately 10% of the total mass of HRVOC emissions released in the HGB area (per the TCEQ point source database). Only 25% of the mass associated with HRVOC related events consists of OVOCs and more than half of this consists of light alkanes (particularly propane), which have relatively low reactivity. Furthermore, if event emissions of interest are limited to those released at rates greater than 1200 pounds of HRVOC per one-hour time block, the weight percent of simultaneously released OVOCs drops to 13%. In these cases, the most highly-reactive OVOCs, substituted aromatics, account for only 0.2% of the HRVOC event

emission streams. Therefore, the OVOC emission reductions likely to occur through control of HRVOC event emissions are expected to be minimal. This analysis does not, however, provide any guidance with regard to the potential benefits to controlling event emissions of OVOCs not co-emitted with HRVOCs.

2. In contrast to the situation for event emissions, where emission reductions of OVOCs due to HRVOC controls are minimal, the reduction in OVOC annual emissions that occur when HRVOC annual emissions are controlled appear to be significant. The mass of these ancillary OVOC emissions reductions are anticipated to be three times the mass of the HRVOC reductions; the reactivity of these ancillary OVOC reductions is anticipated to be 50% of the HRVOC reactivity reduction, if species are weighted by maximum incremental reactivity (MIR).

3. The composition and reactivity weighted composition of the ancillary OVOC reductions is dominated by alkanes up to C6 and substituted aromatics, especially xylenes and toluene.

4. Photochemical modeling results suggest that a reduction in OVOC emissions would reduce formation of ground-level ozone.

5. Increasing the emissions of light alkanes by a factor equivalent to the factor by which terminal olefin emissions were increased (based on ambient observations) can have a significant effect on ozone production. Depending on the other assumptions made in the simulation, daily maximum ozone concentrations can increase by more than 10 ppb (parts per billion). This increase is larger than the decrease in ozone concentrations associated with ancillary reductions of OVOCs. When the emissions of substituted aromatics are likewise increased, daily maximum ozone concentrations typically increase by several additional ppb.

<u>Recommendation:</u>

Assessments of the co-benefits of OVOC reductions are based on data on OVOC emissions. These OVOC emission inventories are subject to significant uncertainties, including uncertainties in mass emission rates and speciation profiles. Reducing these uncertainties through source testing and ambient monitoring would improve the degree of confidence in the findings of analyses such as those presented in this report.

Effects of Caps and Trading on Ozone Formation

<u>Objective:</u>

The impacts of possible responses of regulated facilities to HRVOC emission caps were examined and the impacts of possible HRVOC trading scenarios on ozone formation were assessed.

Key Findings:

1. The simplest way to perform photochemical modeling to examine the effect of an HRVOC emissions cap is to assume that all HRVOC emissions at regulated facilities are reduced by an equivalent factor. However, in response to a cap, facilities may reduce emissions first from process streams that have the highest concentrations of HRVOCs. To examine the impact of this phenomenon on ozone formation, a 'worst-case' scenario was examined. In the scenario, preferential reductions are made at HRVOC dominated sources, such that the benefits associated with ancillary reduction of OVOCs are minimized. Furthermore, the HRVOC emissions remaining at the sites (emission accounts) were placed closest to NO_X-rich point sources. Photochemical modeling of this scenario led to daily maximum ozone concentrations a few ppb larger than the simpler ('across-the-board reductions') scenario, on days that are conducive to ozone formation.

2. A facility may meet its HRVOC emission cap by eliminating emissions from streams with high mass fractions of HRVOCs. In this scenario, facilities will continue to eliminate streams until they are below the cap, and the final stream to be eliminated may place the facility at an emission rate significantly below the cap. This scenario leads to over-control of HRVOC emissions. Photochemical modeling of this scenario shows ozone production that is slightly greater than and less than (depending on the day considered) an "across-the-board" scenario.

3. Multiple scenarios for trading annual HRVOC emissions were considered that changed the location, but not the timing, of the HRVOC emissions. These scenarios were 'worst-cases' in that they assumed trades resulting in spatial concentration of HRVOC emissions. These trading scenarios have only a marginal effect (several ppb of ozone) on daily peak ozone concentrations within the Houston/Galveston/Brazoria area; changes in the spatial distribution of ozone concentrations were also minimal.

4. Trading of annual HRVOC emissions for event HRVOC emission, or other changes in the temporal pattern of HRVOC emissions resulting from trades, appears to be more complex than changing the location (but not the timing) of HRVOC emissions due to trades. This appears to especially true for trading of OVOCs for HRVOCs based on reactivity.

Recommendation:

The trading scenarios that have been developed and analyzed to date are limited in scope. Additional scenarios and corresponding photochemical modeling runs should be completed before a high level of certainty can be placed on the effects of trading on control strategies. Preliminary results, however, indicate that emissions trading is a viable option and there are no immediate "red flags" that would suggest that trading is necessarily detrimental.

4. Survey of Regulatory Strategies

Objective:

Regulatory strategies (regulations and control technologies) used in different parts of the world to reduce VOCs, and how those strategies might be used in the Houston/Galveston/Brazoria area to reduce HRVOC's, was examined.

Key Findings:

1. The current HRVOC regulations for the Houston/Galveston/Brazoria area represent the forefront of such control programs, both nationally and internationally.

2. Existing control measures target source sectors that represent by far the major actual and potential sources of HRVOCs in the region. No evidence was found to suggest the existence of any other source sectors that might represent suitable targets for additional HRVOC regulation.

Recommendations:

In addition to Texas, California and Louisiana are the two other states that have the most significant activities relative to HRVOC identification and control. California has done the most in the area of evaluating emissions in terms of MIR (maximum incremental reactivity). Louisiana has added to the list of compounds recognized as HRVOCs in Texas, including acetaldehyde, toluene, xylenes, and isoprene in its list. It is recommended that Texas keep abreast of strategies and regulations being applied in these two states; Texas should also keep abreast of emerging national and international activities in this area. Texas should also continue to examine root cause analysis of HRVOC emissions.