

FINAL REPORT

To the Texas Environmental Research Consortium on
Project H12-EE

Survey of Technological and Other Measures to Control HRVOC Event Emissions

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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.

Recommendation:

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

Objective:

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.

1. INTRODUCTION

1.1 Background

The Houston/Galveston/Brazoria (HGB) area has been designated as a severe non-attainment area due to ozone levels that frequently exceed the National Ambient Air Quality Standard (NAAQS). The area is therefore required to meet the standard of 125 parts per billion by volume (ppbv, concentrations averaged over 1 hour) on or before November 15, 2007. In addition, the area must now also begin to address the new ozone standard, with concentrations averaged over 8 hours. Although most large urban areas struggle to meet air quality standards, HGB differs in a number of ways, including its dense concentration of industrial point sources from refining and petrochemical operations. The HGB area lies within the Texas Commission on Environmental Quality (TCEQ) Region 12 and includes eight counties: Brazoria, Chambers, Fort Bend, Galveston, Harris, Liberty, Montgomery, and Waller Counties (Figure 1.1).

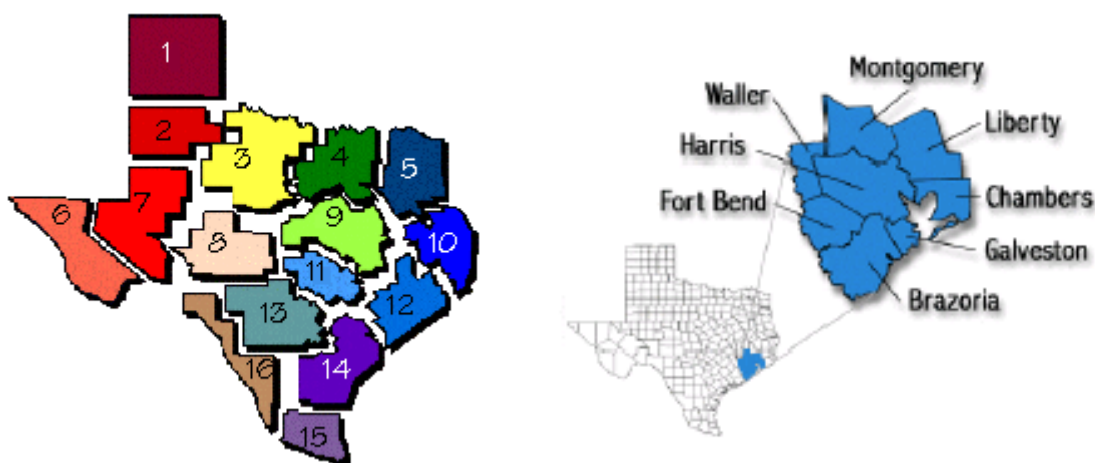


Figure 1.1. The HGB area lies within the TCEQ Region 12 and includes Brazoria, Chambers, Fort Bend, Galveston, Harris, Liberty, Montgomery, and Waller Counties.

In keeping with control strategies implemented elsewhere in the country, early versions of the State Implementation Program (SIP) for HGB targeted emissions of nitrogen oxides (NO_x), including a 90% point source reduction. Results from the TexAQS 2000 field study (Kleinman et al., 2003; Ryerson, et al., 2003), however, suggested that volatile organic compounds (VOCs) emitted by the large and numerous refining and petrochemical industrial complexes located in the HGB region play a much greater role in the formation of ground-level ozone than previously realized. Furthermore, a set of four specific compounds was identified as being the most significant in terms of mass and photochemical reactivity. These are ethene (ethylene), propene (propylene), 1,3-butadiene, and isomers of butene (butylene) and as a group are termed highly-reactive volatile organic compounds or HRVOCs. As a consequence of these findings, the SIP was revised to reduce HRVOC emissions from four key industrial sources: fugitives, flares, process vents, and cooling towers. The original approach for HRVOC control was a site-wide cap program (emissions limits by account); this was replaced by the establishment of a cap and trade program. TCEQ notes that “the HRVOC rules are performance-based, emphasizing

monitoring, recordkeeping, reporting, and enforcement, rather than establishing individual unit emission rates” (TCEQ, 2004a).

One unique aspect of refining and petrochemical operations is the occurrence of intense, short-term emissions that are released in addition to continuous emissions. Referred to as “event emissions,” these can result in extremely high emission rates of VOCs (HRVOCs in particular) relative to continuous emission rates (Murphy and Allen, 2004). Although reporting requirements for these emissions became much more stringent in early 2003, the most effective means of regulating and controlling these emissions is still being evaluated. As of December 2004, the commission adopted rule 30 TAC §115.722(c), which states that short-term HRVOC emissions must be limited to 1,200 pounds of per one-hour time-block, from any flare, vent, pressure relief valve, cooling tower, or any combination thereof, for sites that emit greater than 10 tons per year of HRVOC. In addition, the mass of these event emissions must be included in an annual cap of HRVOC emissions (TCEQ 2004b). This is currently limited to Harris County, but the commission reserves the right to extend the rules of the HRVOC emissions cap and trade program in Chapter 101, Subchapter H, Division 6 to include the surrounding seven counties (TAC, 2004).

Thus, the TCEQ has established a novel cap and trade program to limit industrial emissions of HRVOCs. Since this program is ground-breaking, it raises a number of scientific and technical issues for which there are no ready answers. The current project focuses on three of these scientific and technical issues that are discussed in the task reports that follow. These are:

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?

1.2 Methodology

The project involves the analysis of emissions from existing non-electric generating units (negu) as well as a series of photochemical grid modeling simulations for different VOC control and inventory scenarios. In order to address the issues pertinent to this project, The University of Texas developed a number of case studies with alternative control scenarios and adjustments to other VOCs (OVOCs) in the point source emissions inventory. These inventories were developed by adjusting existing emission inventories. The development of complete attainment demonstration inventories with all growth factors and detailed control strategies was beyond the scope of this work. Therefore, the emission inventories and photochemical modeling results described in this work should be considered as sensitivity studies or “what-if” analyses; they are not intended to represent actual changes in the attainment demonstration.

All photochemical modeling case studies start with the attainment demonstration files and inventories used by TCEQ. The only changes are to modify the HRVOC control package and to

modify VOC emissions in negu point source files. All other files used for the modeling simulations are left unedited. The starting negu emission inventory files include un-grown, uncontrolled emissions (regular plus imputed extra olefins). The University of Texas modified these files to represent various VOC reduction and imputation scenarios. The result is an analysis of the relative impacts of different strategies and assumptions including uniform, across-the-board-controls vs. facility caps, vs inter-facility trading of HRVOC emissions. Effects of OVOCs on ozone production for both event (short-term) emissions and continuous emissions (subject to annual cap) are considered. In the case of the event emissions, the 2000 base inventory was used instead of the attainment demonstration in order to be consistent with previous analyses performed under HARC Project H13, which examined short-term releases of VOCs in HGB and their effect on ozone formation (Murphy and Allen, 2004).

Two reference case studies were developed in order to assess the relative effects of the different scenarios. Case 1 applies uniform, across-the-board controls that simplify many of the VOC reduction strategies. This case is also the starting point from which all other case studies (scenarios) are developed. The assumptions in Case 1 are as follows:

1. Inventories were adjusted (controlled) only for those accounts (sites) slated for HRVOC cap as of June 2004 (see Appendix A).
2. All VOC emissions from sources in HRVOC service at capped facilities are controlled uniformly. There is no distinction made between fugitive and non-fugitive sources and at any one given source (emission point) there is no preferential reduction of HRVOCs over OVOCs.
3. Capped sources in Harris County are reduced by 90%; those in the surrounding seven counties are reduced by 60%.
4. All four VOC species identified as highly-reactive are controlled in all eight counties.

This set of assumptions serves to provide a uniform set of conditions and is presumed to be a best-case scenario against which the other scenarios can be evaluated.

Case 0 was created as an emulation of the attainment demonstration. Although the files used in the attainment demonstration packet are not created in this manner, the effective results are the same (see Appendix E). This case was created by zeroing out all of the HRVOC controlled sources in the regular inventories and replacing them with separate files in the same format as the extra olefins files with all VOCs included (controlled HRVOCs plus uncontrolled OVOCs). Speciation was based on the speciated inventory. All VOC fugitive emissions in the regular inventory were reduced by 64%. A comparison of this case with the attainment demonstration is presented in Appendix E and indicates that this is an appropriate emulation. The assumptions in Case 0 are as follows:

1. Inventories were adjusted (controlled) only for those accounts (sites) slated for HRVOC cap as of June 2004 (see Appendix A).

2. For non-fugitive sources, only HRVOCs at capped facilities are reduced. Sources currently classified as fugitive are reduced uniformly at all sources (emission point) by 64%; there is no preferential reduction of HRVOCs over OVOCs.
3. Capped sources in Harris County are reduced by 90%; those in the surrounding seven counties are reduced by 60%.

Case Studies Involving Continuous Emissions

All of the case study simulations in this project that examine continuous emissions (i.e., ozone season daily) are based on the fy07j.cs03_harCap emissions inventory developed by TCEQ for the Houston/Galveston/Brazoria area mid-course review, also referred to as the attainment demonstration. The files that allowed the University of Texas to run fy07j.cs03_harCap simulation were downloaded from the TCEQ website at http://www.tnrcc.state.tx.us/air/aqp/airquality_photomod.html#camx. These include the initial/boundary conditions, meteorological input, emission inventory, and other auxiliary files needed for the simulation. These files have been processed by the TCEQ and are ready to be used in CAMx (Comprehensive Air Quality Model with Extensions) photochemical modeling simulations. All controls to the inventory were applied using files that are external to the point source inventory and because the files have already processed, it is not possible to manually control the inventory by direct manipulation of emission mass on a source-by-source basis. This set of files is referred to as Case TCEQ.

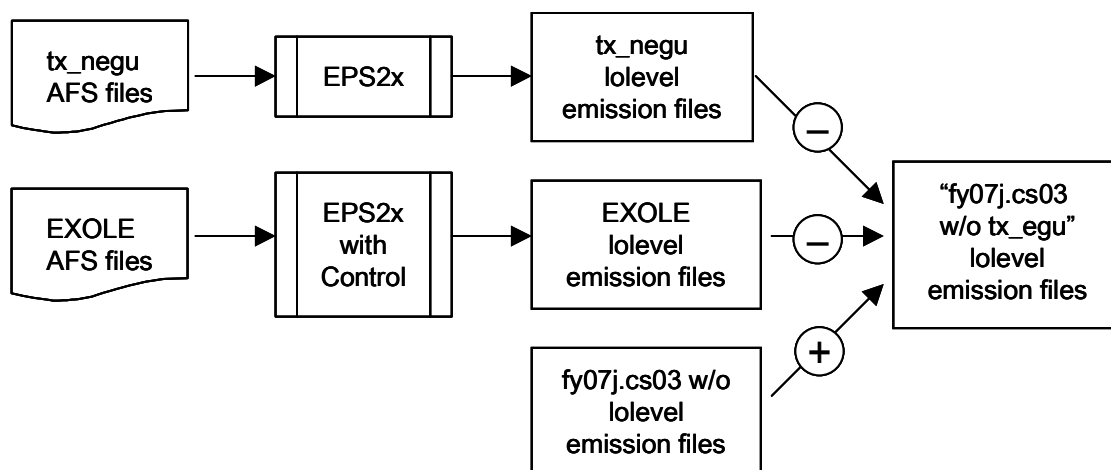
In addition to the above files, the TCEQ provided the University of Texas with the following files that made it possible to create modified inventories to emulate various control strategies by direct manipulation of the inventory on a source-by-source basis.

- AFS file for non electric generating units point sources in Texas for fy07j.cs03_harCap (tx_negu files)
- AFS file for imputed extra olefins (exole files)
- Input files specifying chemical species split factors, temporal profiles and control strategy
- Scripts and extra input files that process above into (1) low level, gridded, model-ready emission files and (2) elevated, ASCII emission files
- Elevated ASCII emission files for point sources except Texas non-egu sources or the imputed extra olefins
- Scripts that merge/process elevated ASCII emission files into elevated model-ready emission files.

Emissions Preprocessor Systems 2 (EPS2x) was used to process the emission inventory into model-ready format.

Before beginning the analyses it was necessary to prepare low-level emission files that did not have emissions from the tx_negu or exole files. The University of Texas processed air facility

system (AFS) files for these two emission categories into model-ready format. These were then subtracted from the TCEQ prepared fy03j.cs03_harCap model-ready file. Figure 1.2 shows the process schematically. After the subtraction, negative emissions, which cannot be managed in CAMx, were identified for 14 cells of the 5,395 cells within the 4-km domain. These negative emissions affected 5 different species between 11:00 pm and 6 a.m. The largest discrepancy was



for isoprene, which yielded negative emissions of 5.2 lbs/day in this small number of cells. Since the total mass and the geographic area affected is extremely small and because these negative emissions occur at night when ozone production is not expected, these numbers were reset to zero for the species at those particular hours in those particular cells.

Figure 1.2. Development of the case studies required preparation of a low level emission file “fy07j.cs03” that did not have emissions from the tx_negu or exole files.

The integrity of both the files and the processing completed at The University of Texas was verified by performing a simulation using the original AFS files without any modification and all the emission processing scripts as provided by TCEQ. This case, termed UT Base, was created in order to compare the results obtained using files processed at TCEQ, the attainment demonstration fy07j.cs03_harCap, with those processed at UT. If all of the files and processing used at UT were correct, the results should be identical. Figure 1.3 shows schematics for low level emission files processing, and Figure 1.4 shows that of elevated emission files.

For low level emissions, the process is to reverse the process of generating “without tx_negu” files. In this case, the model-ready file that is created in the previous step is added to the emissions of tx_negu and exole, which were also created in the previous step. The outcome was virtually identical to the TCEQ version of fy07j.cs03_harCap lolevel files, except for the correction to avoid negative numbers. Elevated emissions were prepared as follows. For the purposes of this project, TCEQ compiled point source emissions of all but those in the tx_negu and exole files, and processed them into one text file (an intermediate format to create model-ready file). UT processed the tx_negu and exole AFS files separately using the same format as provided by TCEQ. The three files were then merged together into one set of model-ready emission files. The quality assurance section (Appendix E) describes the comparison of the TCEQ version and UT version of fy07j.cs03_harCap.

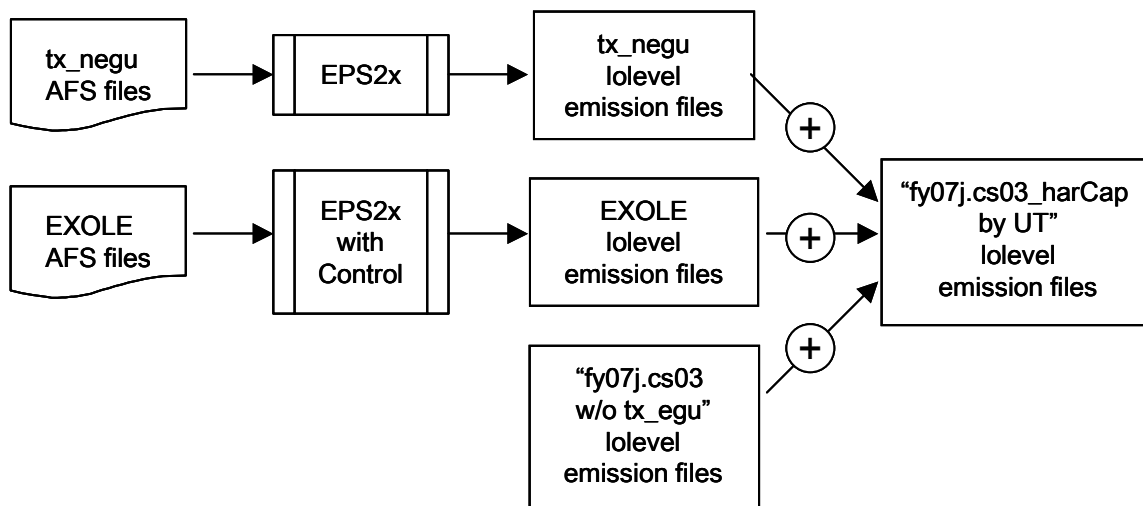


Figure 1.3. Verification of the files and processing done by UT for fy07j.cs03_harCap involved the creation of low level emission files as diagramed above.

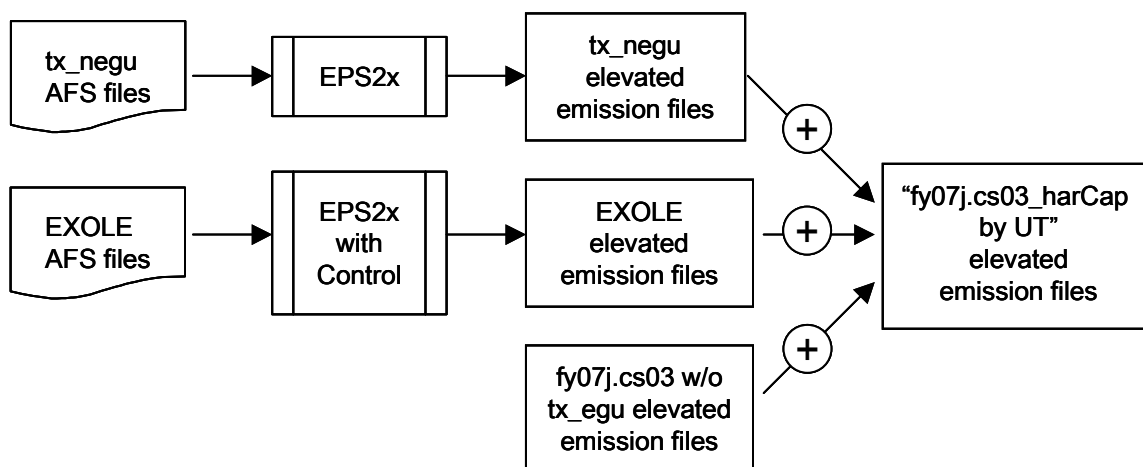


Figure 1.4. Verification of the files and processing done by UT for fy07j.cs03_harCap involved the creation of elevated emission files as diagramed above.

In order to generate emission files with direct implementation of control strategies as performed in this study, two portions of the process were changed from the standard generation of fy07j.cs03_harCap. First, the emission fields in the AFS files were modified using Excel in order to implement control strategies that were investigated in this study. A perl script was written in order to reformat the text file exported from Excel into AFS file format. Second, the EPS2 module that implements HRVOC controls in the Houston/Galveston/Brazoria area was removed, so that VOCs are not controlled twice.

VOC upset release simulations

Evaluation of the effects of interspecies trading of event emissions started with the non-imputed base year (2000) simulation generated by TCEQ. This inventory, which is sometimes referred to as base5b.regular, was selected in order to be consistent with event simulations performed under Project H13. The event emission database as well as the speciated VOC emissions inventory suggested that three classes of compounds would be of the greatest interest in considering interspecies trading. These classes were olefins, aromatics, and paraffins. Propene, n-pentane, and xylene (representing all three isomers) were chosen as the model species for each class.

A propene event released at the rate of 5819 pounds per hour was selected as a typical HRVOC emission event. This was based on aircraft measurements made on August 25th, 2000. The timing of the release was 10:00 am to noon. The rate and total amount of release of the other two species, n-pentane and xylene were adjusted using maximum incremental reactivity (MIR) (Carter, 2002) such that they satisfied the following relationship.

$$(\text{Emission rate of propene}) \times (\text{MIR of propene}) = (\text{Emission rate of OVOC}) \times (\text{MIR of OVOC})$$

Timing and length of release for the OVOCs were not modified. Table 1.1 summarizes the three simulations.

Table 1.1

Species	CB4 Species	Maximum Incremental Reactivity (MIR) (gO3/gVOC)	Release Rate (lbs/hr)	Release Period	Total Release (lbs)
Propene	1 PAR + 1 OLE	11.57	5,819.00	10:00 to noon	11,638.00
n-Pentane	5 PAR	1.53	44,004.00	10:00 to noon	88,008.00
Xylenes (1/3 of each isomer)	1 XYL	7.44 (average) 10.61 (meta-), 7.48 (ortho-), 4.24 (para-)	9,045.00	10:00 to noon	18,090.00

The calculated mass of emission was added to the model-ready binary emission file for the base5b.regular simulation. The release was added to cell (41, 44) of the 4-km resolution, low level, gridded emission file. The cell is located in the Deer Park region of Harris County. An in-house (University of Texas) program that reads and writes CAMx input emission file was used to add extra emissions in the particular cell. The CAMx simulations for August 25 and August 30 were made using the simulation output of the day before (August 24 and August 29, respectively) as the restart file.

1.3 Emissions Inventories and Other Sources of Data

Data used to create and modify negu files for annual emissions (ozone season daily) in this study were derived from 3 different TCEQ model ready files (version 5b).

Regular Texas Non-electric Generating Unit (NEGU) Inventory

The regular Texas non-electric generating unit (negu) inventory is based on the TCEQ's 2000 Point Source Database (PSDB). It includes records of the geographic location, stack parameters, and projected 2007 annual emissions of ozone precursors from non-electric

generating units (NEGUs). In addition, during TexAQS 2000, industrial facilities were asked to provide hourly emissions of ozone precursors that could be used for inter-comparison studies with aircraft and ground-based measurements, as well as for future photochemical modeling. Together these inventories formed the “NEGU inventory” used as the basis of the attainment demonstration for the region.

The regular tx_negu inventory includes the location and magnitude of all annual emissions from non-electric generating units (negus) in the TCEQ Texas point source database. Emission records are listed by account (site) and VOCs are not speciated. This file is part of the attainment demonstration packet and emission magnitudes are equivalent to 2000 EI (including the daily averaged special inventory). Growth and control factors for 2007 are applied separately during processing. In this project this file was one of the two inventory files used as the starting point for all case studies. The only changes to the file were in emission magnitudes at facilities within the 8-county HG area, per case study descriptions.

Imputed Extra Olefins Inventory

In response to ambient data collected during TexAQS 2000, which indicated that existing VOC inventories underestimate the magnitude of emissions of olefins with the double carbon bond at the end of its structure, the imputed extra olefins inventory imputes additional terminal olefins (predominantly HRVOCs) in the NEGU inventory to facilities within the eight-county HGB area. The mass added equals 4.5 times that of total HRVOCs in the regular HGA negu inventory. This file is also part of the attainment demonstration packet. In this project it was one of the two inventory files used as the starting point for all case studies. The only changes to the file were in emission magnitude per the case study descriptions.

VOC Speciated Inventory

The VOC speciated negu inventory provides VOC composition based on either company survey data or the approximately 10,000 source profiles for point sources. In the inventory, VOC composition is assigned according to Storage and Retrieval of Aerometric Data (SAROAD) codes for process and storage units (Facility Identification Numbers – FINs) and emission points (emission point numbers – EPNs) at each emission point in Texas that emits greater than 1 pound per day of VOC. This inventory is not explicitly part of the attainment demonstration packet; but it represents the speciation profiles used. In this project it was used to determine relative VOC compositions (% HRVOCs and OVOCs) at process and storage units and emission points. It was also the basis for the imputed extra OVOC files (Cases 4, 5, and 6 described in subsequent sections) and in general guided manipulation of the inventories in order to generate the different case studies.

Event Emission On-Line Reporting System

A database of emissions events was developed during Project H13 (Murphy and Allen, 2004) using reports posted on the TCEQ event emission on-line reporting system. All data used to analyze event emissions in this project were taken from this database, which includes all event emissions reported in the HGB area between January 31, 2003 (the earliest date in the reporting system) and January 30, 2004 (TCEQ, 2004c).

1.4 Acknowledgements

The authors acknowledge the Texas Advanced Computing Center (www.tacc.utexas.edu) for providing a portion of the computational resources used to complete this work. The authors also gratefully acknowledge the contributions of Texas Commission on Environmental Quality in providing the model-ready files used for photochemical modeling of the attainment demonstration and assistance in modifying the files in order to perform sensitivity analyses. The work reported on in this paper was funded by the Texas Environmental Research Consortium (TERC), through project H12EE “Survey of Technological and Other Measures to Control HRVOC Event Emissions.”

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2. 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 xylene 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.

Recommendation

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.

Report: Co-Benefits of Reducing HRVOCs

Most VOC process streams at industrial facilities located within the Houston/Galveston/Brazoria area involve a mixture of HRVOCs and OVOCs. Different species may occur together during the manufacture, use, and storage of VOCs, and consequently during their emission. Alternatively, the same equipment and release points are often used in association with different process streams at different times throughout the year, such that the annual profile might appear “mixed” even in the absence of actual physical mixing of different compounds. For example, there are 8,545 VOC process units located within Harris County; only 2,420 (28%) of these have a single VOC species associated with them. Of the 13,033 process units that emit more than 1 pound per day of VOC within the HGB area, 5167 of the units (40%) are in HRVOC service and 4586, or 89%, of these have OVOCs species in their emission streams (i.e., only 581 of the units emit only HRVOCs). In the subsections below, the changes in emissions of OVOCs that might occur as the result of HRVOC controls are considered. The effects of controls on both short-term (event) emissions and on annual (ozone daily) emissions are examined using the event emission database and the speciated VOC point source emissions inventory, both available from the TCEQ.

2.1 Event Emissions

TERC Project H13 drew attention to the importance of emission events of highly-reactive VOCs (HRVOCs) in explaining the occurrence of rapid ozone formation and transient high ozone events (THOEs) in the Houston region (Murphy and Allen, 2004). The magnitudes and variability of emission events in the Houston-Galveston area between January 31, 2003 and January 30, 2004 were examined using event reports made available through the recently developed TCEQ on-line event reporting system (TCEQ, 2004a). Total mass and flow rates (pounds per hour) of HRVOC during events were calculated and compared against annual mass and average flow rates within the region. It was found that event emissions account for approximately 10% of the total mass of HRVOC released in the HGB area and large events (those that exceed the annual average of 1,883 lbs/hr) occur on the order of almost twice a month.

The same set of data used in Project H13 were evaluated in order to determine the effect that controlling HRVOC event emissions might have on reducing emissions of OVOCs that occur in association with these events. Of the 722 HRVOC events considered, 301 (42%) had only HRVOCs in the VOC profile. The remaining 421 events were characterized by a full range of compositions in terms of the ratio of HRVOC to OVOCs (Figure 2.1). The total VOC mass associated with all 722 events is 2,273,234 pounds. Of this total, 1,702,600 lbs (or 75%) are HRVOCs. More than half of the OVOCs by mass (312, 451 pounds or 14% of the total) are light alkanes (C3 to C5), dominated by propane (150,994 lbs), which is only one-twentieth as reactive as propene (Figures 2.2 and 2.3).

As of December 23, 2004, the TCEQ adopted rule 30 TAC §115.722(c), which states that short-term HRVOC emissions must be limited to 1,200 pounds per one-hour time-block (TCEQ 2004b). If event emissions of interest are limited to those released at these rates or greater, the weight percent of simultaneously released OVOCs drops from 25% 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 benefits of controlling OVOCs only through control of HRVOC event emissions are likely to be minimal. This does not, however, provide any guidance with regard to the potential benefits to controlling event emissions of OVOCs not co-emitted with HRVOCs.

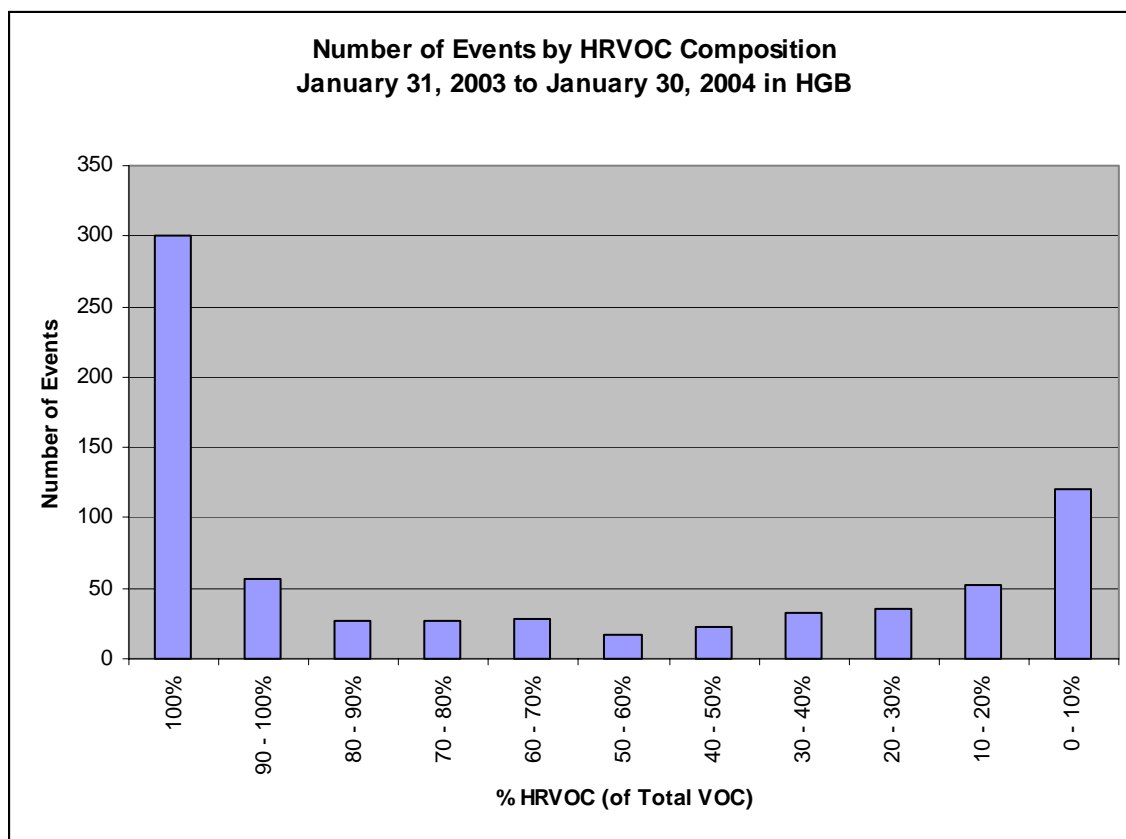
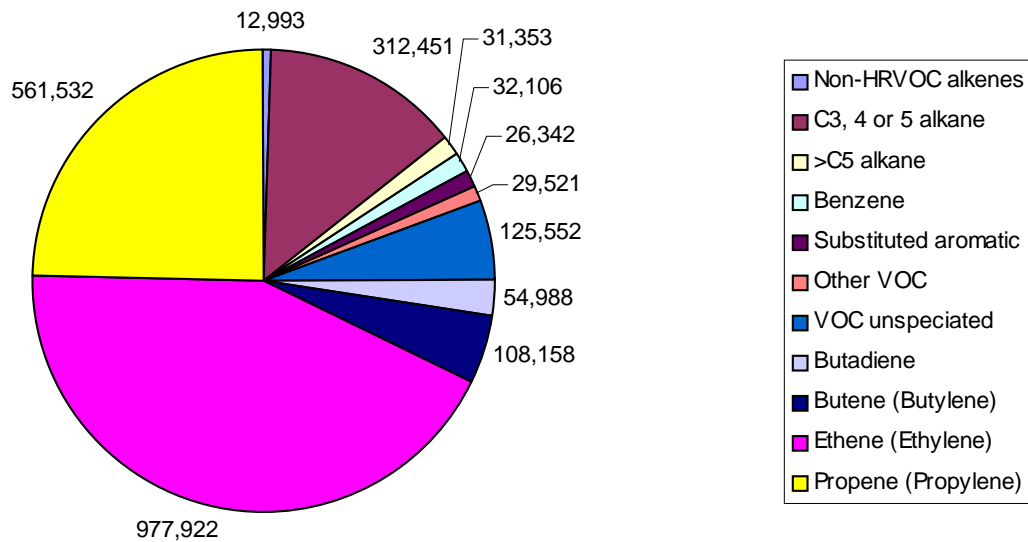


Figure 2.1. Out of 722 HRVOC events occurring in the Houston/Galveston/Brazoria area over a 12-month period, 301 (42%) contained only HRVOCs in the VOC profile. The remaining 421 events were characterized by a full range of compositions in terms of the ratio of HRVOC to OVOCs.



**Categories of VOC (lbs)
Released in HRVOC Event Emissions
Jan 2003 to Jan 2004**

Figure 2.2. 570,635 pounds of OVOC were released along with 1,702,600 pounds of HRVOC during a total of 722 HRVOC events. 312,451 pounds of OVOC consisted of light alkanes (C3, C4, and C5), half of which was propane (C3).

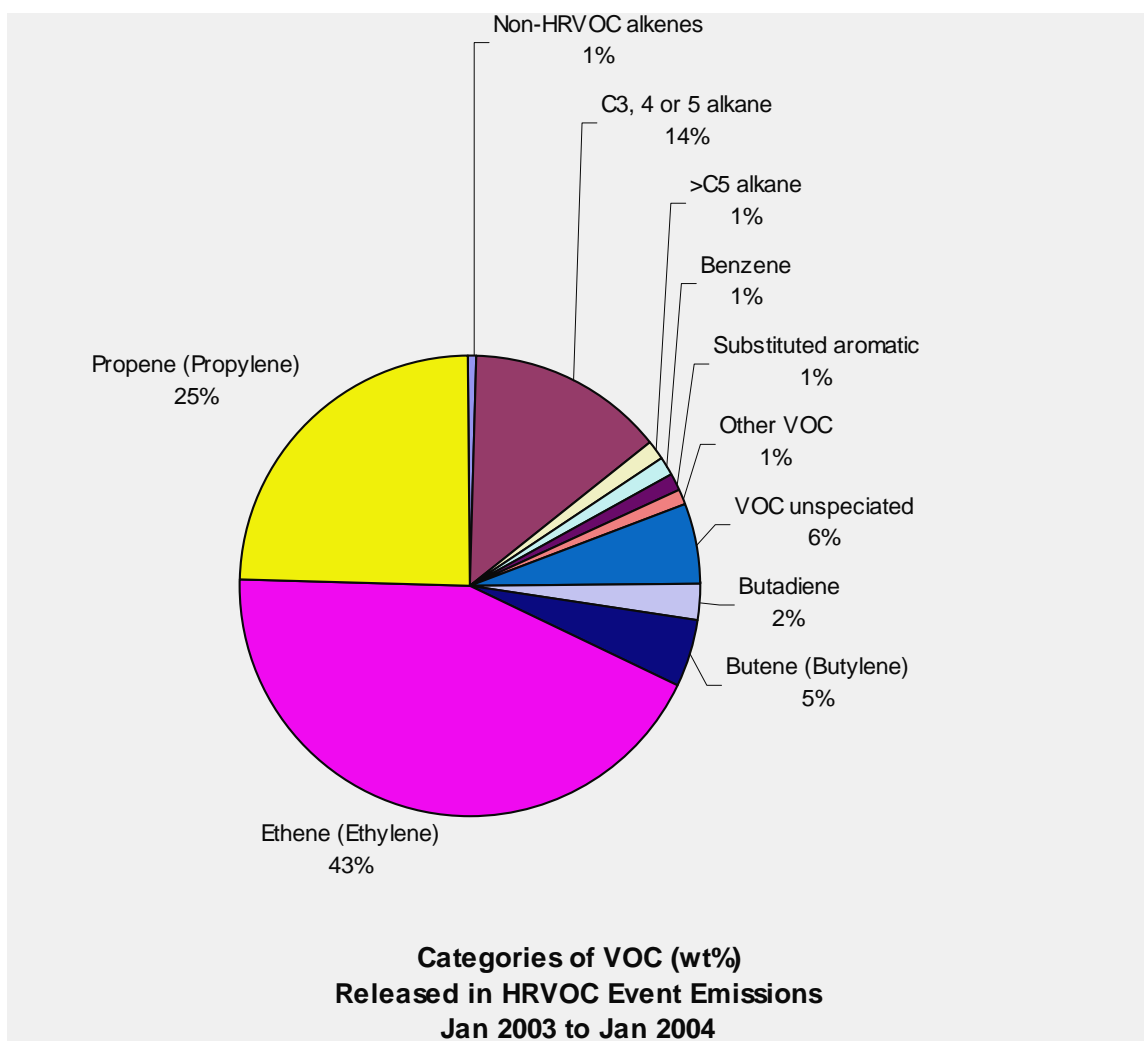


Figure 2.3. 75% by mass of the VOCs released during 722 HRVOC events consisted of HRVOCs. Substituted aromatics, which have approximately the same reactivity as HRVOCs, accounted for only 1% of the co-emitted mass.

2.2 Continuous Emissions

Most (90%) of the HRVOC mass emitted in the HGB area is due to continuous emissions rather than event emissions. Therefore, another important step in evaluating the possible co-benefits of reducing HRVOC emissions is to examine the continuous or “base” emissions as reported in the non-electric generating (negu) emissions inventory. In particular, the speciated VOC inventory, which is based on the speciation profiles included in the attainment demonstration, is used to evaluate the potential for reduction of OVOCs in conjunction with control of HRVOCs. This inventory is also used to determine if there are any inherent biases in assuming that sites would control HRVOC emissions at emission points rather than at process or storage units. The speciated inventory is available on the TCEQ website (TCEQ, 2003) along with a report that documents the creation of this inventory (Cantu, 2003).

In the speciated VOC point source emissions inventory, the specific compounds assumed to be associated with each emission stream are described explicitly in the emission inventory using Storage and Retrieval of Aerometric Data (SAROAD) codes. These assignments are based on the speciation profiles used in conjunction with the attainment demonstration emissions inventory. For the purpose of photochemical modeling, the composition of the VOC streams in most point source emissions inventories is defined indirectly through the use of such speciation profiles. Speciation profiles may be specific to a particular process unit, as determined by company survey data, but they are more commonly based on the unit's Source Category Code (SCC) and one of approximately 10,000 "typical" source profiles for point sources. For example, SCC 30600201 refers to a "Fluid Catalytic Cracking Unit." The standard speciation profile for this SCC code is 15.77% isomers of hexane, 61.90% formaldehyde, and 22.32% dimethylamine; (note that there are no HRVOCs associated with this profile). This profile is used, for example, at Sea Lion Technology in Texas City (Galveston County). In contrast, Chevron Phillips in Sweeny (Brazoria County) has supplied site-specific data; for SCC 30600201, this includes three different profiles for three different process units. For one of its crackers, the emissions are described as equal amounts of isomers of butene, propene, propane, and n-butane. In other words, 50% of the emissions associated with this unit are HRVOCs and 50% are OVOCs. Another cracker has a profile that assigns only 22.2% HRVOCs (butene and propene) and 77.8% OVOCs (equal amounts of hexane, propane, n-butane, formaldehyde, xylene, benzene, and toluene) to the unit. The third cracker has 18 different VOC species assigned to it with only two species (11%) that are categorized as HRVOCs. Thus, there can be significant amount of variability between different process units, with the same function, within the same account or site.

One of the initial concerns in developing scenarios to evaluate potential co-benefits of HRVOC reduction, was whether companies would tend to implement changes at the process or storage unit also referred to as a FIN (facility identification number) or at the actual point of release or EPN (emission point number). The goal of the case studies (constructed as part of the H12EE project) was to selectively add and/or control (reduce) OVOCs while meeting the HRVOC reduction requirements. This requires knowledge of the composition of each source stream. While the FIN (process or storage unit) and its associated speciation profile is used to define the make-up of the VOC composition at its source, there may be multiple EPNs (emission release points) each of which may service other units characterized by VOC streams of entirely different compositions. The structure of the composition information therefore involves data for both EPNs and FINs within nearly 500 separate accounts in the 8-County Houston/Galveston/Brazoria area.

The relationship between EPNs and FINs can be either quite simple or complex. Most typical is a one-to-one relationship between EPN and FIN, but relationships of up to 1-to-5 (in either direction) are common. Characterization of a single EPN requires summation of all FIN emissions being serviced by the EPN and vice versa. An example of a moderately complex relationship from Dixie Chemical is illustrated in Figure 2.4.

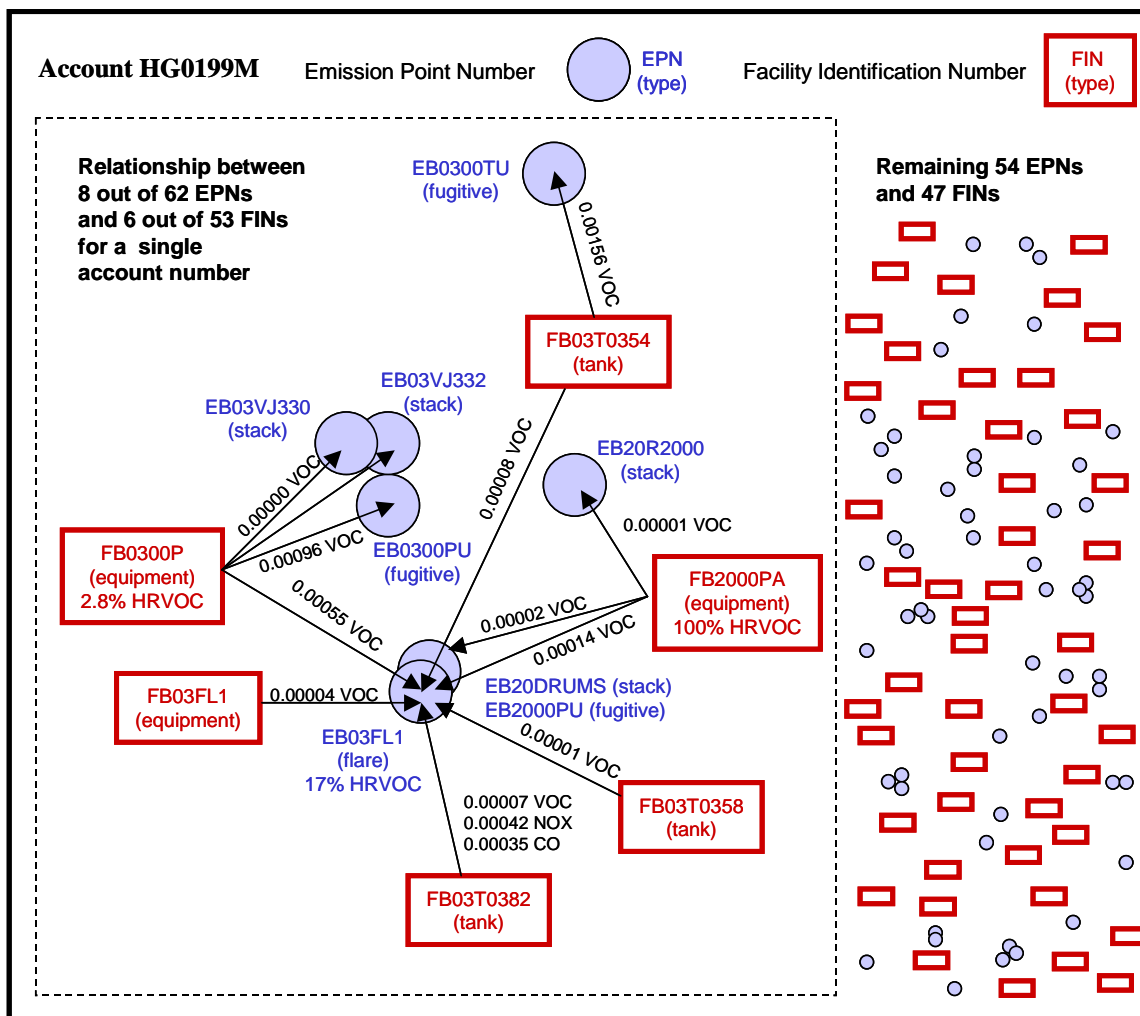


Figure 2.4. The relationship between a subset of FINs, and EPNs within a single account (site) is shown above. The facility identification number (FIN) represents a piece of equipment or a storage unit (e.g., a tank) within the account (site). Each FIN is characterized by a Source Classification Code (SCC) that is typically used to determine the speciation profile for the unit. Emission points (EPNs) are currently classified as stacks, fugitive, or flares and have specific location information associated with them. In the diagram above, each line (or arrow) connecting one FIN (in red) to one EPN (in blue) represents one record in an afs (air facility system) file used in photochemical modeling. The total mass associated with each FIN (or process unit) is summed across all EPNs servicing the unit and the total mass associated with each EPN (emission point) is summed across all FINs feeding into the emission point.

The emissions inventory files are structured in standard database format with fields and records. Each record of mass emitted, reported in units of tons per day (TPD), is characterized by three fields of interest to this project; these are account numbers (sites), FINs (process and storage units) and EPNs (emission points). Each production site (or account) is indicated by a seven-character code. This code is assigned by TCEQ and is associated with the site registration number (RN) listed in the Central Registry. Geographically, a site may cover from “square meters” to “square kilometers.” Within each site are numerous pieces of equipment or storage

devices (e.g., tanks) that are assigned an identification code by the company referred to as a FIN. FINs range from one to multiple character codes and have no regular form unless imposed by the company. Each FIN is assigned an SCC or Source Classification Code that is used to assign a default speciation profile in instances where a profile is not provided by the company. No location information, other than being associated with the geographic confines of the account (site), is embedded in the FIN. EPNs also consist of one to multiple character codes assigned by the company. Latitude and longitude or Lambert Conformal Projections (LCP) are used to describe a reasonably precise location of the point where a release to air occurs. The current classification describes release points as belonging to one of three categories: flare, stack, or fugitive. There is no speciation profile directly attributed to an EPN; it must be calculated as the weighted mass average of FINs to which the EPN is linked.

In the example shown in Figure 2.4, six different units (FINs) are serviced by a single flare (EB03FL1). The piece of equipment identified as FB0300P (its FIN), sends 0.00055 tons per day, of which 2.8% is HRVOC, to the flare; FB03FL1 sends 0.00004 tons per day, none of which is HRVOC; a third piece of equipment (FB2000PA) sends 0.00014 tons per day of 100% HRVOC to the same flare. The other three FINs are all tanks and have no HRVOCs associated with them. Together the tanks account for 0.00016 tons of VOC per day emitted by the flare. If the total emissions from this flare are summed and a cumulative speciation profile generated for this EPN, the emission stream consists of 17% HRVOC.

In order to quantify the co-reduction in OVOC emissions that might occur in this, or any other complex of EPNs and FINs, it was anticipated that it might depend on whether HRVOC controls are implemented predominantly at EPNs or at FINs. Using the example in Figure 2.4 to illustrate this concern, if emissions from the EPNs in HRVOC service (all except EB0300TU) are reduced by 90%, the total HRVOC mass emitted from the complex drops from 0.00021 TPD to 0.00002 TPD and the total OVOC mass changes from 0.00323 to 0.00173 TPD. If instead, HRVOC reductions are achieved by reducing the emissions emanating from the FINs in HRVOC service (FB2000PA and FB0300P), the total OVOC mass drops to only 0.00191 TPD, thus leaving 10% more OVOC mass. Table 2.1 illustrates these calculations and relationships. Given the large number of one-to-one relationships between EPNs and FINs, it was not anticipated that choosing to manipulate the inventory using one group or the other would cause significant bias; however, in order to eliminate that concern, an evaluation of the differences that might result was conducted in conjunction with a study to determine the types and amounts of OVOC that might be reduced as the result of HRVOC controls.

Table 2.1. Comparison of Ancillary Reductions of OVOCs with HRVOC reductions at EPNs vs. FINs

FIN	HRVOC FIN?	EPN	HRVOC EPN?	VOC TPD	% HRVOC	TPD HRVOC		TPD OVOC		
						Before reduction	90% reduction	Before reduction	90% at EPN	90% at FIN
FB03T0354	no	EB0300TU	no	0.00156	0%	0	0	0.00156	0.00156	0.00156
FB03T0354	no	EB03FL1	yes	0.00008	0%	0	0	0.00008	0.00001	0.00008
FB2000PA	yes	EB03FL1	yes	0.00014	100%	0.00014	0.00001	0	0	0
FB2000PA	yes	EB20R2000	yes	0.00001	100%	0.00001	0.00000	0	0	0
FB2000PA	yes	EB2000PU	yes	0.00002	100%	0.00002	0.00000	0	0	0
FB03T0358	no	EB03FL1	yes	0.00001	0%	0	0	0.00001	0.00000	0.00001
FB03T0382	no	EB03FL1	yes	0.00007	0%	0	0	0.00007	0.00001	0.00007
FB03FL1	no	EB03FL1	yes	0.00004	0%	0	0	0.00004	0.00000	0.00004
FB0300P	yes	EB03FL1	yes	0.00055	2.8%	0.00002	0.00000	0.00053	0.00005	0.00005
FB0300P	yes	EB0300PU	yes	0.00096	2.8%	0.00003	0.00000	0.00093	0.00009	0.00009
TOTAL						0.00021	0.00002	0.00323	0.00173	0.00191

The speciated VOC point source inventory (TCEQ, 2003) was used to analyze the proportion and composition of other volatile organic compounds (OVOCs) that are associated with emission of highly-reactive volatile organic compounds (HRVOCs). Although only about half of the approximately 27,000 FINs and 26,000 EPNs in the base inventory are included in the speciated inventory, all of those with significant emissions of VOC (more than one pound per day) are represented. This simplification results in a much more manageable data set of approximately 13,000 FINs and 12,000 EPNs with no appreciable loss of information (Cantu, 2003).

2.3 Emissions Inventory Analysis: Ancillary OVOC Reductions

The goal of this portion of the study was to examine reductions in “Other VOC” emissions (OVOCs) that may occur due to HRVOC controls (ancillary OVOC reductions). The analysis assumes that there is a uniform reduction of all VOC compounds (HRVOC and OVOC) at all HRVOC sources located within the 147 HRVOC capped facilities in 8-county HGB area. Comparisons are made between the effects on the inventory for reductions at emission points (EPNs) vs. reductions at process or storage units (FINs). The evaluation is based on the 2000 speciated VOC emissions inventory available from TCEQ (TCEQ, 2003). A full list and description of the 147 facilities in the HGB area that were expected to be subject to HRVOC caps as of June 2004 are listed in Appendix A. A summary of the accounts is presented in Table 2.2.

Figure 2.5 illustrates the mass of VOC reduction by species that could be expected for every 10% increment of HRVOC reduction at emission points (EPNs). The analysis is done in this manner because the final degree of HRVOC control may vary between counties (e.g., higher for Harris than the surrounding 7 counties) and/or between source types (e.g., lower for fugitives than for vents, flares, and cooling towers). Also note that this analysis was done using only the base 2000 inventory (i.e., excluding inputs from the special and imputed olefins inventories) so the total mass is lower than for the attainment demonstration. However, the relative masses and species of interest are expected to be similar.

Table 2.2. Summary of Accounts Subject to HRVOC Caps as of June 2004

Category	TPD HRVOC	# of Accounts	Counties (# Accounts)
Crude Petroleum and Natural Gas	0.19	16	Brazoria (3), Chambers (5), Fort Bend (3), Harris (1), Montgomery (3), Waller (1)
Industrial Gases and Inorganic Chemicals	0.32	7	Brazoria (1), Harris (6)
Plastic Materials and Synthetic Rubber	4.53	14	Brazoria (1), Chambers (1), Harris (12)
Industrial Organic Chemicals	20.91	64	Brazoria (11), Chambers (3), Fort Bend (1), Galveston (6), Harris (42), Montgomery (1)
Petroleum Refining	3.62	9	Brazoria (1), Galveston (3), Harris (5)
Storage, Petroleum Bulk Stations and Terminals	0.73	18	Brazoria (1), Chambers (2), Fort Bend (1), Galveston (1), Harris (11), Liberty (2)
Pipelines	0.68	7	Brazoria (1), Chambers (4), Harris (2)
Other Categories	0.14	12	Harris (10), Liberty (2)
TOTAL		147	

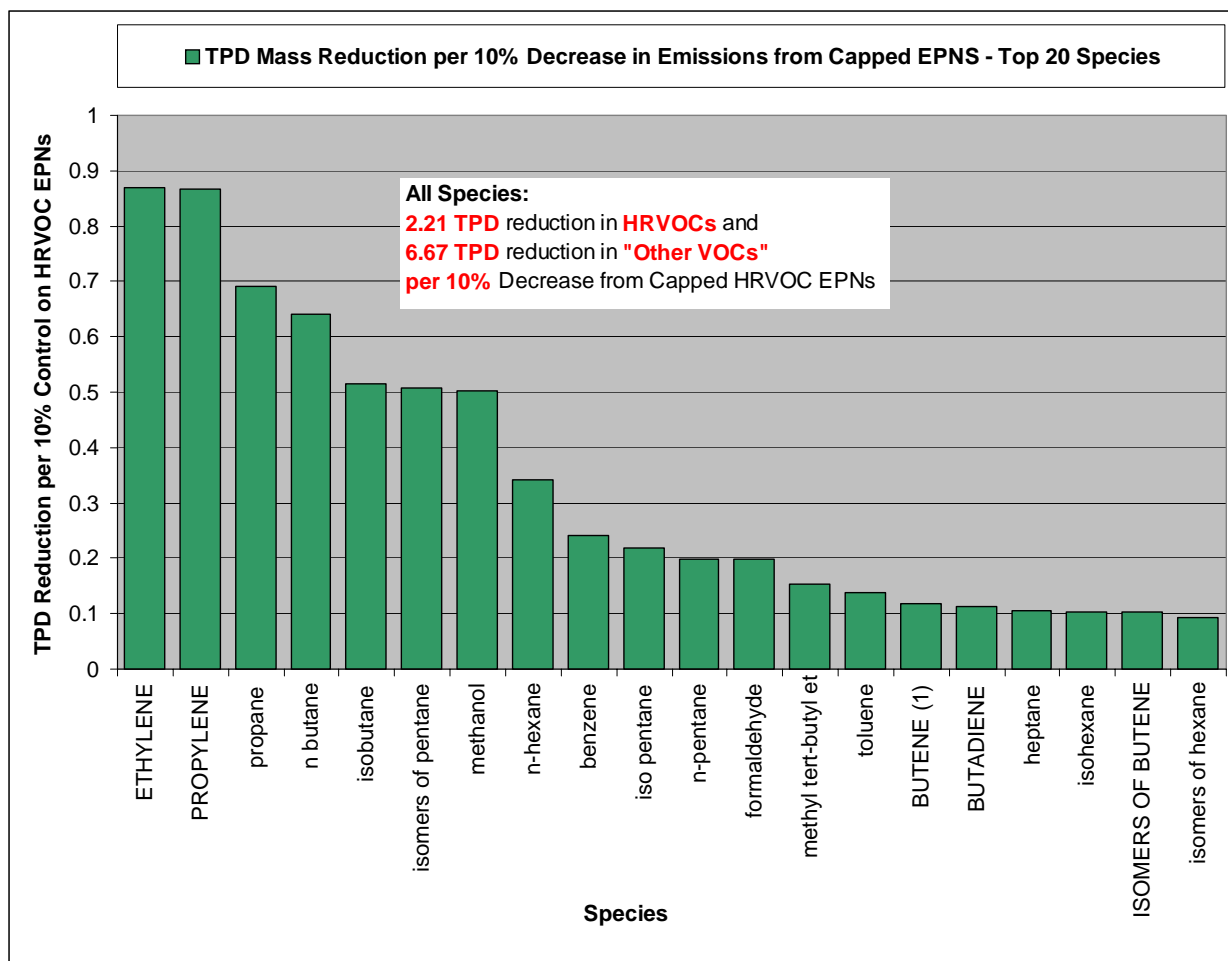


Figure 2.5. For HRVOC reductions at emission points (EPNs), three times as much OVOC mass is reduced as HRVOC mass. The most notable groups of species affected are light alkanes and aromatics.

For HRVOC reductions at emission points (EPNs), three times as much OVOC mass is reduced as HRVOC mass. The most notable groups of species affected are light alkanes and aromatics.

Figure 2.6 illustrates the mass of VOC reduction by species that could be expected for every 10% increment of HRVOC reduction at process and storage units (FINs). The analysis is done in this manner because the final degree of HRVOC control may vary between counties (e.g., higher for Harris than the surrounding 7 counties) and/or between source types (e.g., lower for fugitives than for vents, flares, and cooling towers). Also note that this analysis was done using only the base 2000 inventory (i.e., excluding inputs from the special and imputed olefins inventories) so the total mass is lower than for the attainment demonstration. However, the relative masses and species of interest are expected to be similar. As for HRVOC reductions at emission points (EPNs), three times as much OVOC mass is reduced as HRVOC mass when reductions are implemented at FINs and the most notable groups of species affected are light alkanes and aromatics.

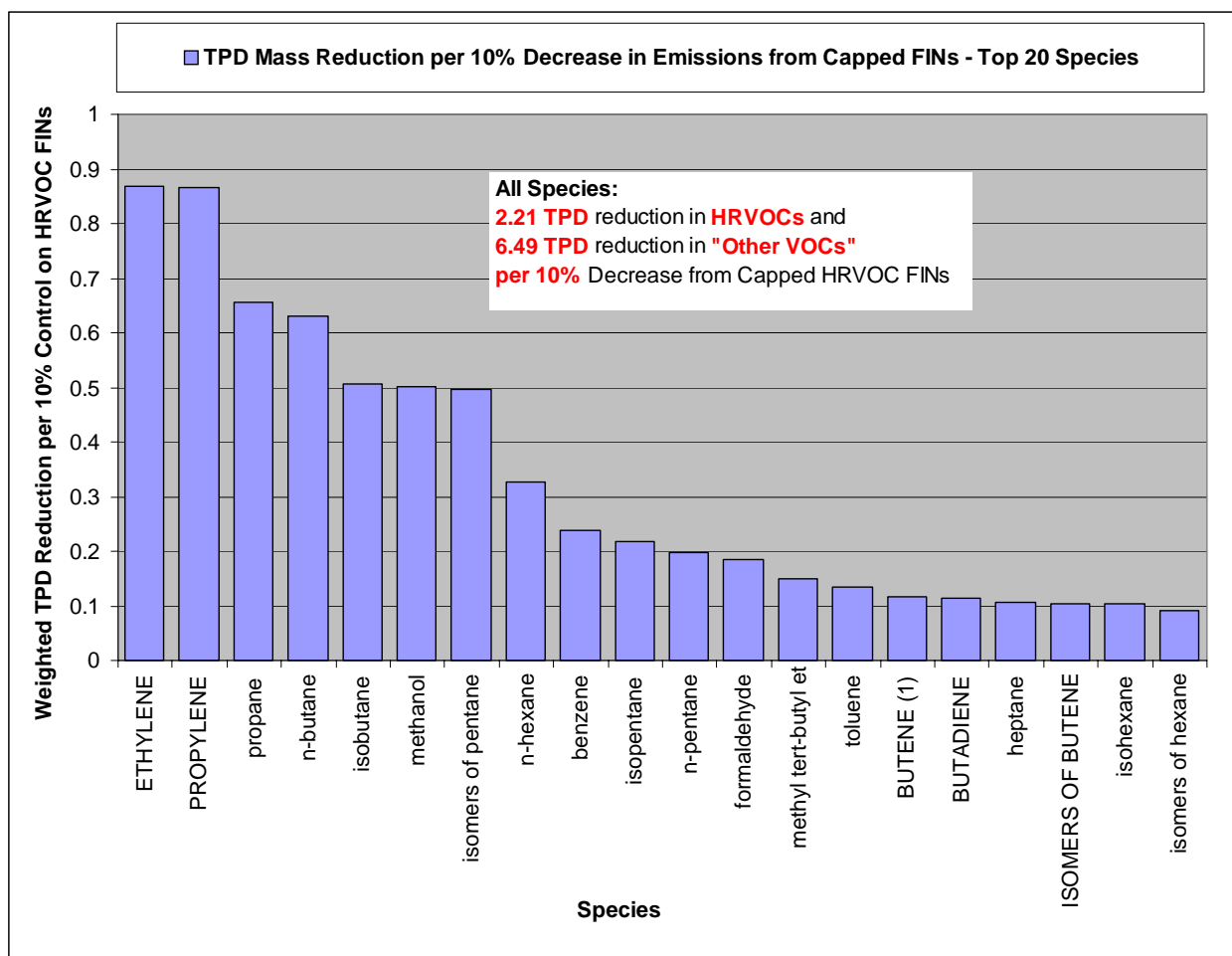


Figure 2.6. For HRVOC reductions at process and storage units (FINs), three times as much OVOC mass is reduced as HRVOC mass. The most notable groups of species affected are light alkanes and aromatics.

Performing the same analysis but weighting the mass by MIR (maximum incremental reactivity) produces similar results, in that light alkanes and substituted aromatics remain as the most significant OVOCs and there is little distinction between HRVOC controls at FINs vs. EPNs. The most significant difference is that instead of an additional 300% OVOC benefit as was seen in considering mass only, the OVOC benefit drops to a 1.5X benefit (i.e., an additional 50% over reduced HRVOCs only) when the mass is weighted by reactivity. This would still appear to be a significant co-benefit (i.e., a 60% reduction of HRVOCs plus ancillary OVOCs would be expected to result in the same reduction in ozone as a 90% reduction in HRVOCs alone.)

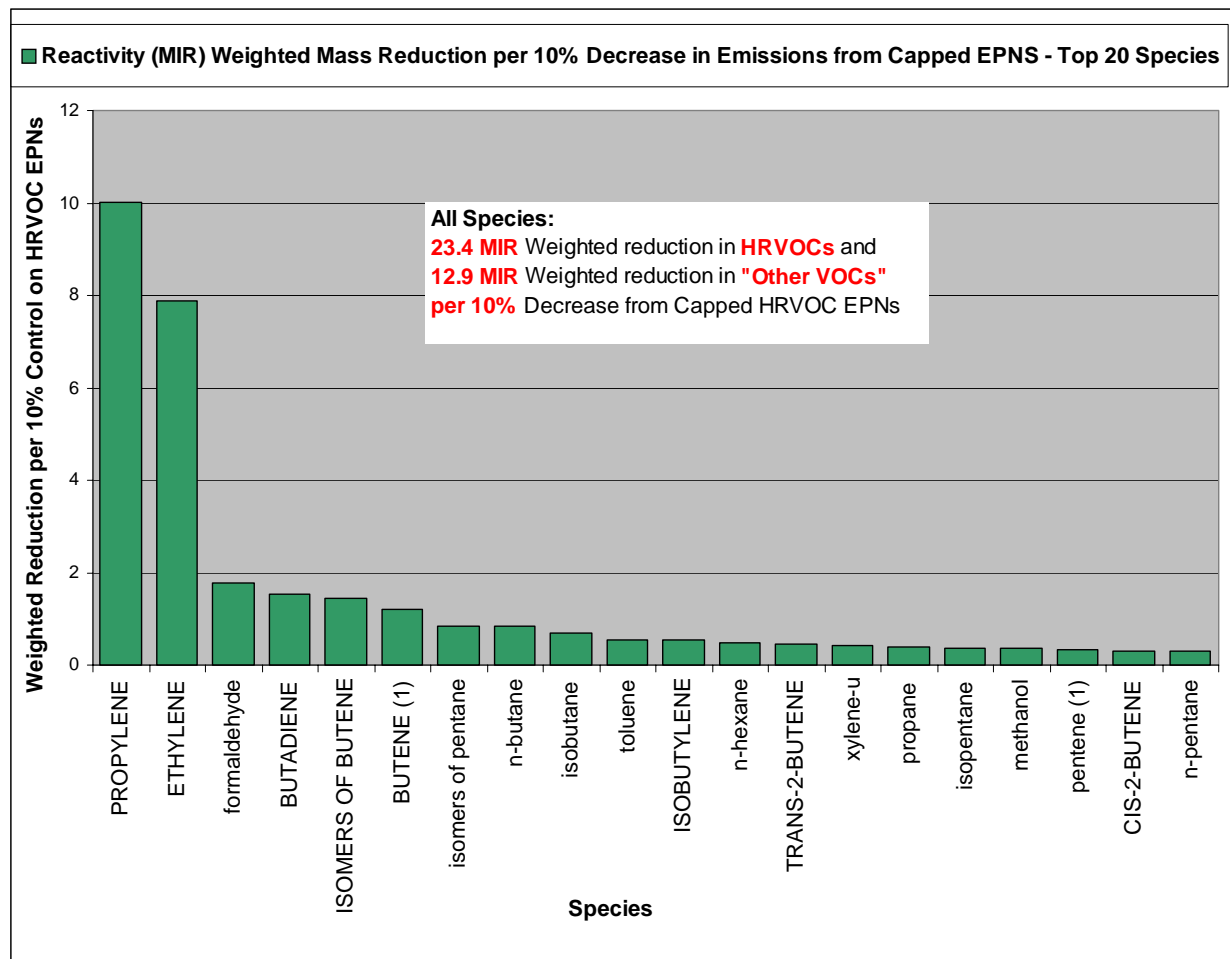


Figure 2.7. For HRVOC reductions at emission points (EPNs), half as much OVOC MIR weighted mass is reduced as HRVOC MIR weighted mass. The most notable groups of species affected are light alkanes and aromatics.

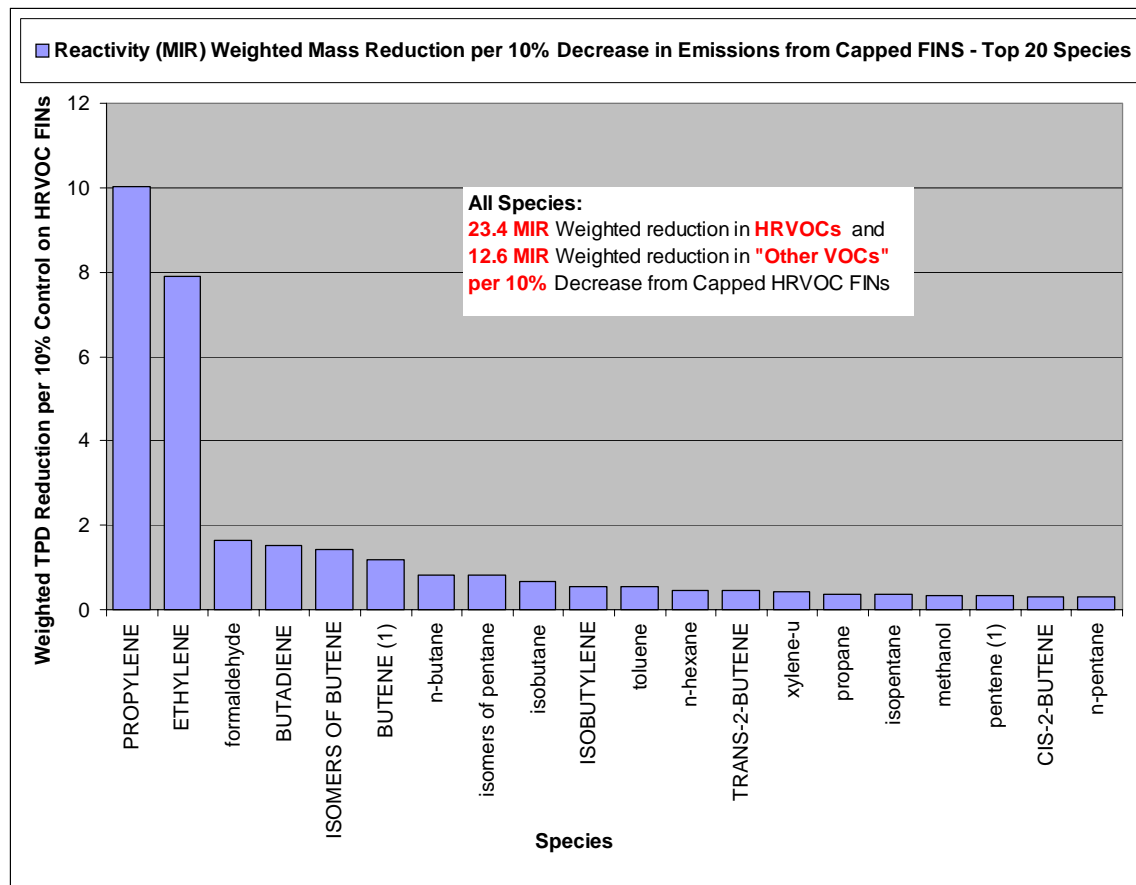


Figure 2.8. For HRVOC reductions at process and storage units (FINS), half as much OVOC MIR weighted mass is reduced as HRVOC MIR weighted mass. The most notable groups of species affected are light alkanes and aromatics.

Based on the above analyses, it is concluded that there is virtually no difference in the total mass or the species that are reduced as the result of uniform reduction of emissions from HRVOC EPNs versus FINS. In addition, the co-benefits of OVOC reduction appear to be significant with a potential mass reduction of 4X that of HRVOCs alone and a 1.5X reduction when weighted by MIR. The most important OVOCs to consider by mass and MIR include alkanes up to C6 and substituted aromatics, especially xylene and toluene. Formaldehyde and benzene (which is important by mass but not when weighted by MIR) are both controlled as hazardous air pollutants (HAPs).

The results of this task provided guidance in the design of the case studies used to perform the photochemical modeling sensitivity analyses described in the next task report. In particular, it was decided to “control” emissions in the inventory at EPNs rather than FINS, as originally proposed, as it would not greatly affect results and it permitted direct manipulation of the emissions inventory as a function of specific geographic location. The results also highlighted the need to consider the ancillary effects of OVOC reduction in conjunction with HRVOC controls. Finally, it was determined that the impacts of OVOCs on ozone formation should be investigated as both event emissions and as an overall adjustment (imputation) of the base

inventory. In particular, two categories were selected for these investigations: light alkanes (C3 to C7) and substituted aromatics (C7 to C9).

A similar but more focused study was conducted by ENVIRON (Appendix B). In an evaluation of potential co-benefits of HRVOC controls at mid-sized propylene units in Houston it was concluded through examination of the inventory that fairly significant co-benefits in the form of reduced emissions of OVOCs are likely to be achieved by measures taken to reduce propylene emissions at polypropylene production plants in the Houston area. The largest proportionate reductions would be for hexane.

2.4 Photochemical Modeling of Ancillary OVOC Reductions, Case Study 1

Volatile organic compound (VOC) emission streams from non-electric generating (negu) point sources are typically composed of a number of different species. The compounds in each stream may be a mixture of both highly-reactive VOCs (HRVOCs) and other VOCs (OVOCs). Alternatively, the same piece of equipment may be used for different streams at different times within the calendar year. In either case, improved monitoring or maintenance and repair programs are expected to result in reduced emissions of both HRVOCs and OVOCs.

Case 1, the “control” case, considers the effects of proportional reduction of all VOCs from capped HRVOC EPNs, with no distinction made between fugitive emissions and non-fugitive emissions. This case is intended to represent “real world” responses to HRVOC reductions such as increased flare efficiency and decreased leak rates from fugitives. EPNs in VOC service but not in HRVOC service experience no decrease in emissions; EPNs in HRVOC service but not at capped facilities (accounts) experience no decrease in emissions. A 90% reduction is assumed at the 81 capped accounts located in Harris County and a 60% reduction is assumed at the 66 accounts located in the surrounding seven-counties of the non-attainment area (see Appendix A for a list of accounts). For example an EPN that releases 0.8 TPD of HRVOC and 0.2 TPD of OVOC would, with a 90% cap, release instead, 0.08 TPD of HRVOC and 0.02 TPD of OVOC.

Figure 2.9 illustrates the change in mass of emissions that would occur under Case 1 conditions for a hypothetical account. This conceptual drawing shows an initial total VOC mass emitted from the site equal to 1.191 tons per day (TPD), of which 0.745 TPD are HRVOCs and 0.446 TPD are OVOCs. With a 90% reduction, such as is expected to occur in Harris County on EPNs in HRVOC service, the total VOC mass is reduced to 0.238 TPD. A 60% reduction, as might occur in the surrounding seven counties, results in total VOC emissions of 0.556 TPD. If HRVOCs alone were reduced, the final VOC mass would be 0.541 TPD and 0.764 TPD respectively.

Case 0 emulates the attainment demonstration using the same methods of direct manipulation of the emissions inventory as do the other case studies in this project. The attainment demonstration assumes that only HRVOCs are reduced at all non-fugitive VOC sources with no ancillary reductions in OVOCs. All VOC fugitive emissions (HRVOCs and OVOCs) are assumed to be reduced at all accounts (capped and uncapped) in all eight counties by 64%. Because of the complex flows described above, the ability to limit the amount of HRVOCs released to the atmosphere without significant ancillary reductions in OVOCs is restricted largely to either (1) preferential control of FINs or EPNs that are associated with flows dominated by

HRVOCs or (2) change in production patterns in order to reduce the amount of HRVOCs used. While the analyses performed in this project assume that neither of these approaches is very likely, the first strategy (preferential control of EPNs) is examined in one case study (Case 2, discussed later in this report) as part of a series of sensitivity analyses. The second scenario is not considered. In all cases presented in this body of work, except Cases 0 and 4, it is assumed that the amount of OVOCs reduced at a specific source as the result of HRVOC reductions will be in proportion to the initial ratio of OVOC to HRVOC (prior to controls). A summary of all case studies used for photochemical modeling sensitivity analyses is given in Appendix C.

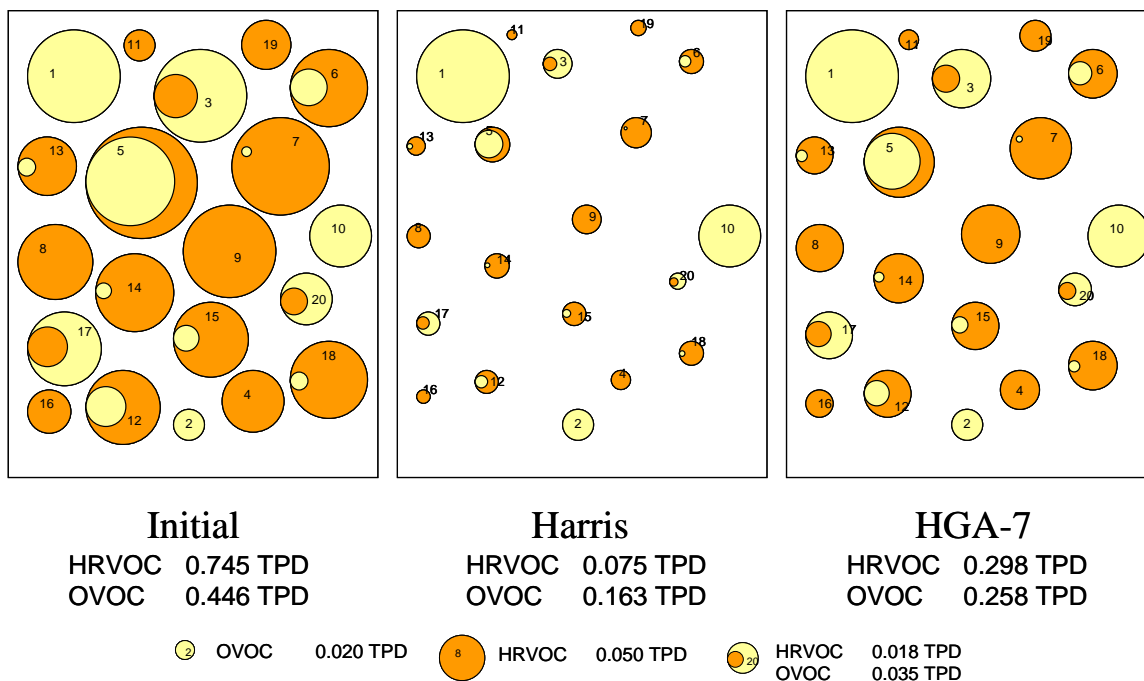


Figure 2.9. A conceptual drawing of Case 1 is shown for a hypothetical account (site) containing a number of EPNs that emit all OVOCs (shown as yellow circles), EPNs that emit all HRVOCs (shown as orange circles), and EPNs that emit a mixture of both (shown as overlapping yellow and orange circles). The circles are drawn to scale such that their area is proportional to the mass emitted. The drawing on the left shows an initial mass emitted of 0.745 tons per day (TPD) of HRVOCs and 0.446 TPD of OVOCs. VOC EPNs that are not in HRVOC service experience no change in mass. VOC emissions (both OVOCs and HRVOCs) from all other EPNs are reduced uniformly by 90% in Harris County. In the surrounding seven counties (HGA7), all VOC emissions from all EPNs in HRVOC service are reduced uniformly by 60%.

Photochemical grid modeling using CAMx (Comprehensive Air Quality Model with Extensions) and the modified net emissions inventories developed as Case 0 and Case 1 suggests that further reduction of OVOCs through the uniform decrease of emissions at HRVOC EPNs can result in the formation of decreased levels of ground-level ozone. However, because there is also a greater reduction of HRVOCs from fugitive sources in Harris County (90% in Case 1 vs. 64% in Case 0) it is not possible to determine by comparison of these two cases alone, which has the greater effect.

Figure 2.10 illustrates the difference in maximum daily ozone for the 1-hour attainment demonstration, with up to 12 ppb more ozone produced in Case 0 than Case 1. Table 2.3 lists four different metrics used to evaluate the two different cases relative to the 1-hour ozone standard. A description of these metrics is given in Appendix E. Tile plots with the distribution and magnitude of ozone produced in Case 0 and Case 1 for two days during the attainment demonstration episode are presented in Figure 2.11.

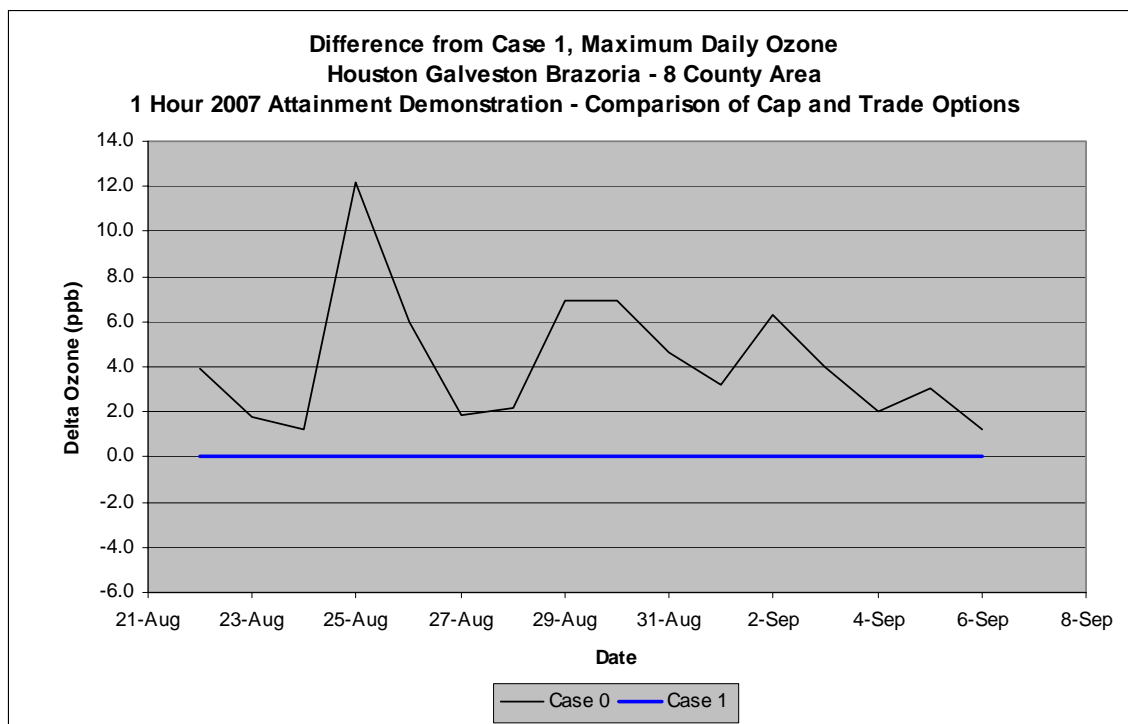


Figure 2.10. Case 0 which has no ancillary reduction of OVOCs from non-fugitive EPNs in HRVOC service and a uniform 64% reduction in fugitive emissions exhibits maximum daily ozone levels of up to 12 ppb higher than Case 1. Case 1 is modeled as uniform reduction of all VOCs from all EPNs (including fugitive EPNs) in HRVOC service at capped accounts.

Table 2.3. Results of photochemical modeling, Case 0 vs. Case 1

Date	Max. Daily Ozone (ppb)		Area of Exceedance (km ²)		Integrated Area of Exceedance (km ²)		Population Exposure (ppm*capita)	
	Case 0	Case 1	Case 0	Case 1	Case 0	Case 1	Case 0	Case 1
22-Aug	87.82	83.88	0	0	0	0	0	0
23-Aug	75.71	73.94	0	0	0	0	0	0
24-Aug	75.32	74.07	0	0	0	0	0	0
25-Aug	122.28	110.09	0	0	0	0	0	0
26-Aug	114.31	108.30	0	0	0	0	0	0
27-Aug	88.52	86.65	0	0	0	0	0	0
28-Aug	103.62	101.46	0	0	0	0	0	0
29-Aug	115.14	108.20	0	0	0	0	0	0
30-Aug	122.88	115.93	0	0	0	0	0	0
31-Aug	148.54	143.87	704	560	1,504	1,072	2,602	1,750
1-Sep	120.10	116.92	0	0	0	0	0	0
2-Sep	130.34	124.05	48	0	64	0	19	0
3-Sep	116.28	112.29	0	0	0	0	0	0
4-Sep	128.31	126.27	64	64	64	64	129	43
5-Sep	188.23	185.18	5296	5136	10,352	9,920	180,089	155,425
6-Sep	128.44	127.24	304	208	432	240	215	40

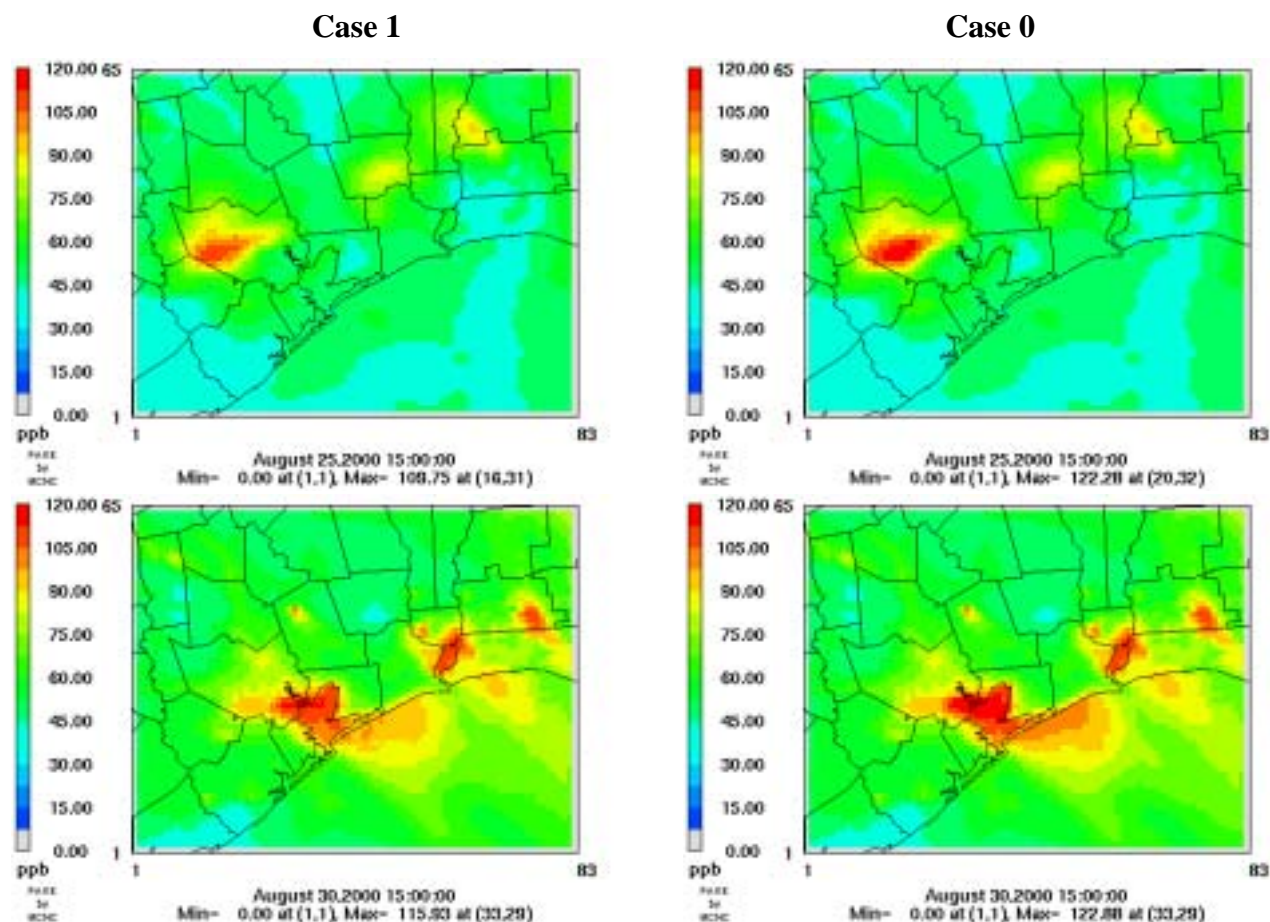


Figure 2.11. Maximum daily ozone plots for 3:00 pm on August 25 and 30 are shown for Case 0 and Case 1. Case 1 is modeled as uniform reduction of all VOCs from all EPNs (including fugitive EPNs) in HRVOC service at capped accounts. Case 0 (equivalent to the attainment demonstration) exhibits a maximum daily ozone level of 122.3 ppb more than 12 ppb higher than Case 1 on August 25 and a maximum daily ozone level of 122.9 ppb nearly 7 ppb higher than Case 1 on August 30. The location of the high shifts approximately 16 kilometers to the east (Case 1 to Case 0) on the 25th but maintains its position on the 30th. Visual inspection suggests that the total area impacted by higher levels of ozone is greater for Case 0.

2.5 Imputation of the OVOC Inventory

The attainment demonstration uses a combination of two negu point source emissions inventories. One is the regular inventory (afs.tx_negu.agg_re.000818-000906.v15b.3pols.lcp) and the other is the imputed terminal olefins inventory (afs.exole.term_v2.2000_v15b.lcp.xls), informally referred to as the “extra ole” inventory. The additional terminal olefins were added based on aircraft data collected during the TexAQS 2000 study. Subsequent data gathered by the TCEQ Technical Analysis Division from a network of Photochemical Air Monitoring Sites (PAMS) using automated gas chromatography (auto GC) suggests that significant other VOCs may also be under-reported in the inventory including pentanes, butanes, hexane, xylene, and toluene (Jolly and Schroeder, 2004a, Jolly and Schroeder, 2004b, Jolly, 2004).

Examination of the net emissions inventory (see section 2.3, above) also suggests that light alkanes and substituted aromatics are expected to be released in significant amounts relative to HRVOCs. In order to determine how critical it is to correctly identify the mass of these OVOCs in terms of photochemical modeling results, an imputed paraffin (alkane) inventory and an imputed aromatics inventory were developed and evaluated in CAMx in conjunction with Case 1. Both imputed inventories increase the mass of these OVOCs, as reported in the VOC speciated inventory by 450% (i.e. 5.5X the original mass). This factor was chosen to match the imputation factor used in creating the extra olefins file. A list of the species imputed is given in Appendix D.

Case 4 combines the extra alkanes (paraffins) inventory and extra aromatics inventory and assumes that no ancillary OVOC reductions occur for these imputed inventories. Case 4.1 imputes only aromatics and Case 4.2 imputes only alkanes. Case 5, 5.1, and 5.2 are parallel to Cases 4, 4.1, and 4.2 but the OVOCs are reduced in accordance to the same guidelines as in Case 1 (90% in Harris County, 60% in the surrounding 7 counties, for all OVOCs co-emitted with HRVOCs at capped accounts (sites)). A summary of these six case studies is given in Table 2.4.

Table 2.4. Summary of Imputed OVOC Case Studies

Case	5.5X Imputation of C7 to C9 Aromatics	5.5X Imputation of C3 to C7 Alkanes	Ancillary Reduction of Imputed OVOCs
4	X	X	–
4.1	X	–	–
4.2	–	X	–
5	X	X	X
5.1	X	–	X
5.2	–	X	X

On August 25, a day conducive to the formation of ozone, imputation of aromatics alone (Case 4.1) with no ancillary reduction has the effect of increasing maximum daily ozone levels by up to 4.5 ppb over Case 1. Imputation of alkanes alone (Case 4.2) with no ancillary reduction has the effect of increasing maximum daily ozone levels by nearly 19 ppb over Case 1. Together the effect is slightly less than additive with an overall increase of 22.73 ppb in the daily maximum ozone. Data for all days in the episode for these 6 cases is presented in Table 2.5. Difference plots for Cases 4, 4.1, and 4.2 and Cases 5, 5.1, and 5.2 are presented in Figures 2.12 and 2.13 respectively. Finally, tile plots of the difference in the daily maximum ozone between Case 4.2 (imputation of alkanes) and Case 1 (control), which occurs at 2 pm (14:00) on both August 25 and 30, are shown in Figure 2.14.

Cases 5, 5.1, and 5.2 can be used to further illustrate the potential co-benefits of ancillary reductions of OVOCs. If it is assumed that the imputation is a closer representation of the actual inventory, then control of alkanes and aromatics in conjunction with HRVOC controls results in a nearly 12 ppb reduction in maximum daily ozone (Case 4 minus Case 5).

Table 2.5. Comparison of Imputed OVOC Case Studies:
Maximum Daily Ozone Based for One-Hour Standard (125 ppbv)

Date	Case 0 ppb O ₃	Case 1 ppb O ₃	Case 4 ppb O ₃	Case 4.1 ppb O ₃	Case 4.2 ppb O ₃	Case 5 ppb O ₃	Case 5.1 ppb O ₃	Case 5.2 ppb O ₃
22-Aug	87.82	83.88	93.02	85.93	90.49	88.35	85.42	87.16
23-Aug	75.71	73.94	77.44	74.96	76.82	75.91	74.74	75.35
24-Aug	75.32	74.07	76.49	74.80	75.85	75.39	74.62	74.91
25-Aug	122.28	110.09	132.82	114.58	128.71	120.74	112.63	116.47
26-Aug	114.31	108.30	118.37	110.59	117.73	113.74	110.02	112.73
27-Aug	88.52	86.65	89.42	87.06	89.52	88.36	87.04	88.30
28-Aug	103.62	101.46	105.75	102.02	105.56	103.70	101.94	103.36
29-Aug	115.14	108.20	118.82	110.69	117.39	113.34	110.06	112.00
30-Aug	122.88	115.93	128.44	119.70	125.84	122.53	118.77	120.37
31-Aug	148.54	143.87	151.51	145.81	150.41	147.90	145.37	146.81
1-Sep	120.10	116.92	122.06	118.43	120.98	119.52	118.01	118.68
2-Sep	130.34	124.05	131.08	126.77	129.03	127.71	125.96	126.23
3-Sep	116.28	112.29	117.47	113.73	116.64	115.03	113.34	114.35
4-Sep	128.31	126.27	128.27	126.53	128.27	127.26	126.52	127.17
5-Sep	188.23	185.18	190.69	185.52	190.92	187.83	185.55	187.79
6-Sep	128.44	127.24	128.94	127.38	129.01	128.05	127.38	128.02

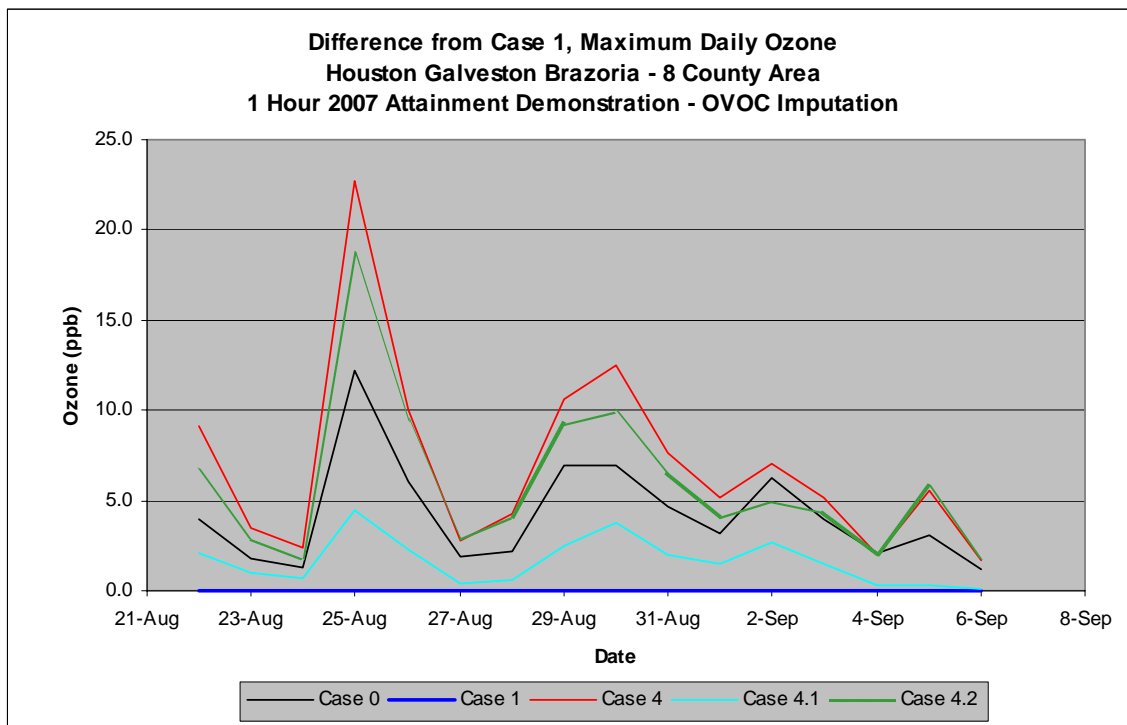


Figure 2.12. Imputation of C3 to C7 alkanes (Case 4.2) has a more significant effect on maximum daily ozone than does imputation of C7 to C9 aromatics (Case 4.1).

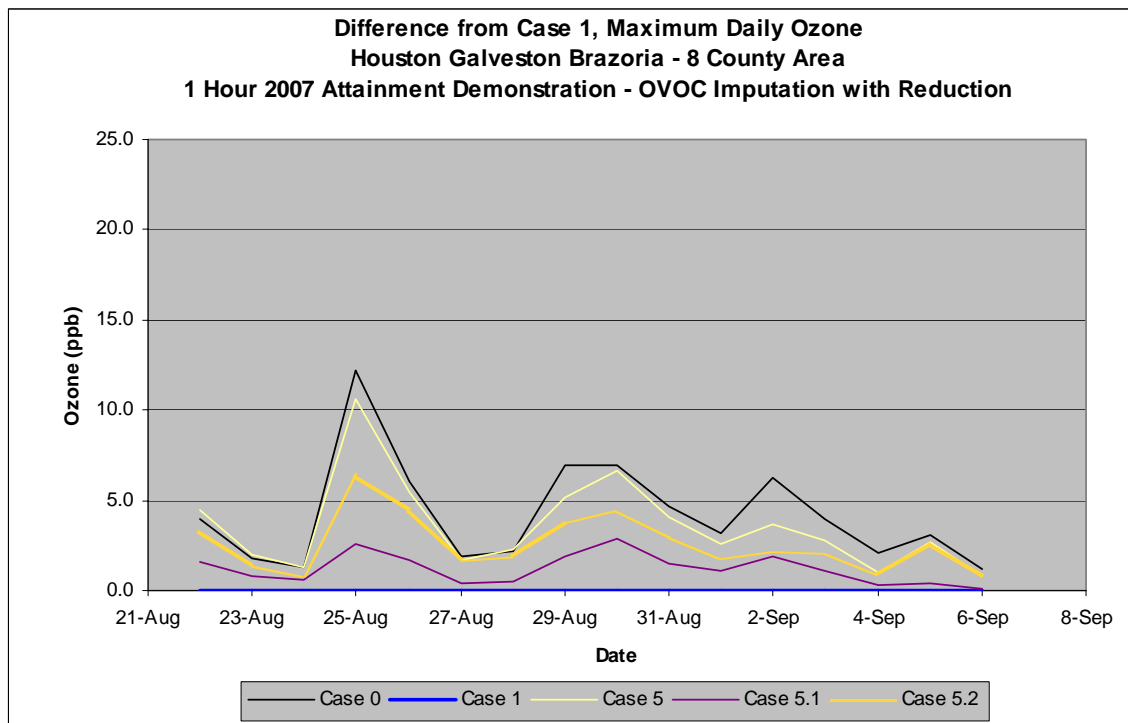


Figure 2.13. Imputed OVOCs, if subjected to ancillary reductions as the result of HRVOC controls, produce a maximum daily ozone level of up to 10 ppb more than Case 1. Most of this increase is due to light alkanes (Case 5.2).

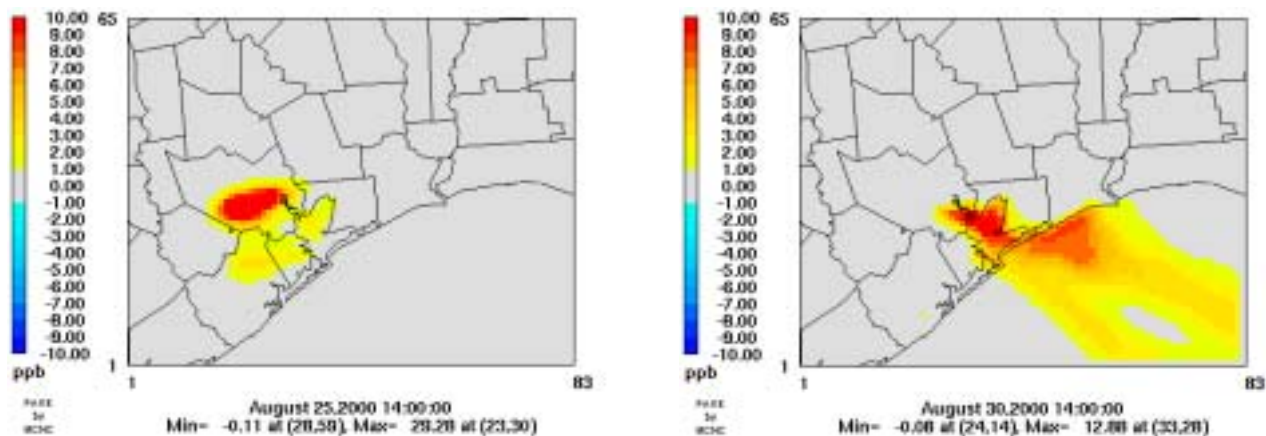


Figure 2.14. The difference in maximum ozone within the 4-kilometer domain is shown for the afternoons of August 25 and August 30 for Case 4.2 minus Case 1. Case 4.2 tests the effects of imputing C3 to C7 alkanes at the same relative amount as for terminal olefins, without any ancillary reductions due to HRVOC controls. The largest daily difference in maximum ozone concentration observed is 29 ppb on the 25th and 13 ppb on the 30th, both at 2:00 pm (14:00).

2.6 Conclusions:

Event emissions account for only about 10% of the total mass of highly-reactive volatile organic compounds (HRVOC) released in the HGB area and only 25% of the mass associated with HRVOC related events consists of other volatile organic compounds (OVOCs) for all events and only 13% for those that have release rates of greater than 1200 pounds of HRVOC per one-hour time block. Therefore, the benefits of controlling OVOCs through control of HRVOC event emissions are likely to be minimal. However, this is not meant to imply that there might not be benefits of controlling event OVOC emissions not co-emitted with HRVOCs.

Most HRVOC emissions are represented by continuous (annual) emissions and nearly 90% of these emissions have other VOC emissions associated with them. The co-benefits of ancillary reduction of OVOCs through HRVOC controls is estimated to be equivalent to an additional 300% of HRVOC based on mass alone or 50% based on relative reactivity (MIR times mass). The most important OVOCs in terms of both mass and reactivity that would be affected by ancillary reductions are light alkanes and substituted aromatics. Furthermore, photochemical modeling demonstrates that reduction of ancillary OVOC emissions has the potential to reduce maximum daily ozone levels by up to 12 ppb.

The cases presented should be considered as sensitivity studies or “what-if” analyses; they are not intended to represent actual changes in the attainment demonstration emissions inventory files. It is hoped that the results will therefore provide guidance as to how best to improve the negu emissions inventories in terms of mass and composition. This could be achieved through the acquisition of additional company specific data and speciation profiles along with continued and improved ambient monitoring of VOC species.

Finally, the analyses completed with regard to co-benefits of reducing HRVOCs, emphasizes the need to promote control strategies and understanding of the results of these strategies with regard to hydrocarbon species other than those four designated as HRVOCs. This becomes even more important if there will be different control strategies applied to different counties or to different types of emission points. In particular, the differences observed between Case 0 (the attainment demonstration) and Case 1 (uniform control) illustrates the need to have better understanding of what EPNs will fall under the fugitive category.

2.7 References

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3. EFFECTS OF CAPS AND TRADING ON OZONE FORMATION

Objective:

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.

Report: Effects of Caps and Trading on Ozone Formation

Through the use of a cap and trade program, a significant amount of autonomy is granted to specific air accounts (sites) as to how reductions in emissions are achieved, as long as overall air-quality goals are met. Therefore, it is important to anticipate how different sites might respond to the program and to understand the effects that various responses might have on ground-level ozone production.

Based on past studies, it is generally accepted that there is substantial temporal and spatial variability of HRVOC emissions within the HGB industrial area, reflecting the types and density of the sources. These temporal and spatial variabilities in emissions can lead to spatial or temporal “spikes” in emissions that are of significance to the ozone attainment strategy. In order to evaluate the likelihood that the cap and trade program might produce spikes in emissions that lead to significant ozone formation, a series of case studies was designed. The primary goal of these sensitivity studies was to determine whether spatial or temporal concentration of emissions associated with trading would lead to ozone formation that was significantly different than ozone formation associated with across-the-board controls. Uniform, across-the-board control was modeled with Case 1, as described in section 2.4. There are two cases that address intra-facility trading (capped accounts with preferential reduction of high mass fraction HRVOC streams, Cases 2 and 2.1) and two that address inter-facility trading of HRVOCs (Cases 3 and 3.1). All four cases were intended to anticipate “worst-case” situations. A summary of the cases is given in Appendix C.

3.1 Caps at the Account-Level with Preferential Reduction of HRVOCs

Cases 2 and 2.1 consider the effects of imposing HRVOC emission caps at the account (site) level. In particular, they examine the preferential reduction of HRVOCs from 100% (or other high percentage) HRVOC EPNs to meet HRVOC emissions target reduction at the account (site) level. By assuming that a facility will meet HRVOC cap by focusing on streams that contain the greatest amounts of HRVOCs, there will be a corresponding minimal reduction in OVOCs.

Case 2 considers the scenario where there is a complete shut down of EPNs with the highest HRVOC content. In addition, all emissions (including OVOC, NO_x, and CO) associated with the EPN are eliminated and there are no fractional reductions, so that in effect the site overcompensates (i.e., more HRVOC is eliminated than specifically required to meet the cap). The net effect of this case on the HGB region is an additional reduction of 10 TPD in HRVOC.

In Case 2.1 only VOCs are eliminated and emissions may be partially reduced from a single EPN in order to obtain the exact decrease as specified by the cap. This case is harder to justify from a “real world sense” but is performed because it most closely emulates the current attainment demonstration and allows for a more effective comparison between the other cases (since total HRVOC is similar).

For both Cases 2 and 2.1, preferential shut-down of high HRVOC content EPNs is also based on the distance (within the site) of the EPN from the NO_x emissions “center of mass” at the site. For the majority of the Harris County sites, where a 90% reduction per site was imposed, most high HRVOC sites were shut down regardless of location, but for the surrounding seven counties

with only a 60% cap, the high HRVOC content EPNs closest to the NO_x center of mass remained. While the intent was to simulate two ‘worst-case’ situations (minimal reduction of OVOCs and concentration of HRVOCs as close as possible to sources of NO_x), the results of Case 3 (discussed below) indicate that the effects of such subtle location changes are not capable of being detected using the 4-kilometer photochemical modeling domain. Thus the results of Cases 2 and 2.1 are interpreted to be primarily due simply to the total mass of HRVOCs and OVOCs emitted under each scenario.

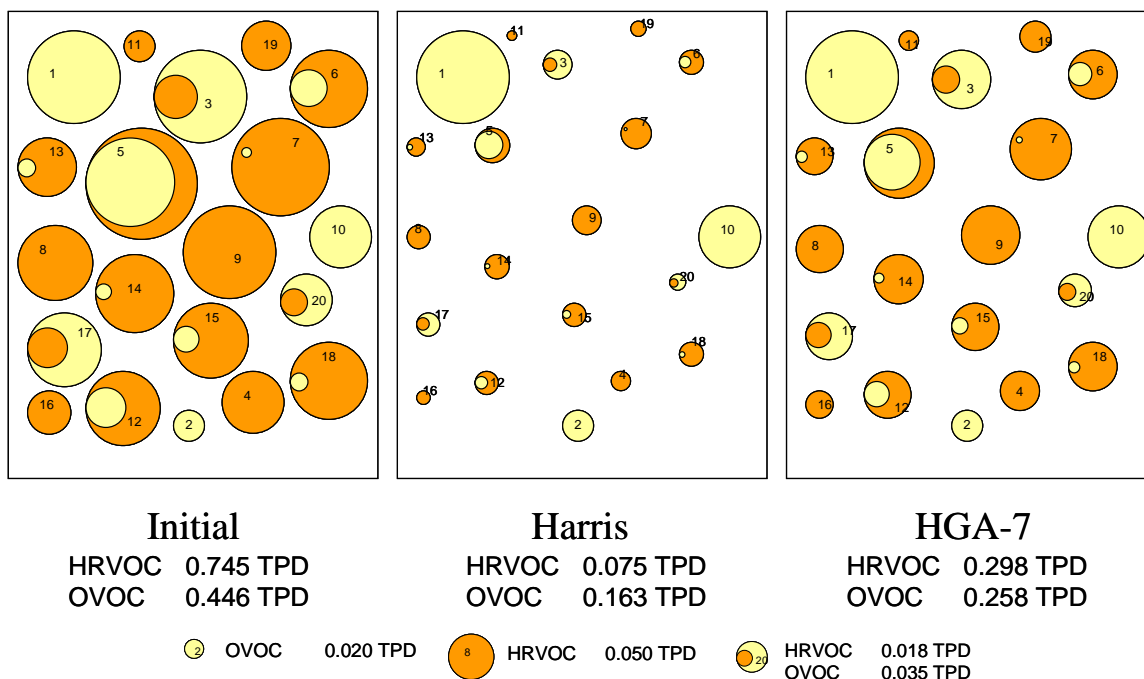


Figure 3.1. A conceptual drawing of Case 2 is shown for a hypothetical account (site) that contains a number of EPNs that emit all OVOCs (shown as yellow circles), EPNs that emit all HRVOCs (shown as orange circles), and EPNs that emit a mixture of both (shown as overlapping yellow and orange circles). The circles are drawn to scale such that their area is proportional to the mass emitted. With a 90% reduction, such as is expected to occur in Harris County, the total VOC mass is reduced to 0.352 TPD vs. 0.656 TPD as would occur assuming a 60% reduction in the surrounding seven counties.

Figure 3.1 illustrates the change in mass of emissions that would occur under Case 2 conditions for a hypothetical account. This conceptual drawing shows an initial total VOC mass emitted from the site equal to 1.191 tons per day (TPD), of which 0.745 TPD are HRVOCs and 0.446 TPD are OVOCs. With a 90% reduction, such as is expected to occur in Harris County on EPNs in HRVOC service, the total VOC mass is reduced to 0.352 TPD. A 60% reduction, as might occur in the surrounding seven counties, results in total VOC emissions of 0.656 TPD. Note that while there is a slightly higher amount of HRVOC reduced than in Case 1 (Figure 2.9), the total OVOC is much less (0.163 vs. 0.278 TPD in Harris County and 0.258 vs. 0.406 TPD in the surrounding seven counties).

In Figure 3.2 the difference in maximum daily ozone for Case 2 and 2.1 relative to uniform reduction (Case 1) is illustrated. Based on one-hour averaged concentrations of ozone,

comparison of the two different capped account scenarios suggests that Case 2.1, where HRVOCs are rigidly controlled to the amount specified by the cap with minimal ancillary reductions, always produces more ozone than uniform controls with ancillary OVOC reductions (Case 1). If, however there is overcompensation, as in Case 2, where there is greater reduction of HRVOCs than is required and a decrease in ancillary NO_x and CO (Case 2), then either more or less ozone is produced than Case 1, depending upon the day. This occurs despite the fact that Case 2 releases 14 more tons per day of OVOC than Case 2.1 because the overcompensation results in 11 tons per day less HRVOC (Appendix C) along with reduced emissions of NO_x.

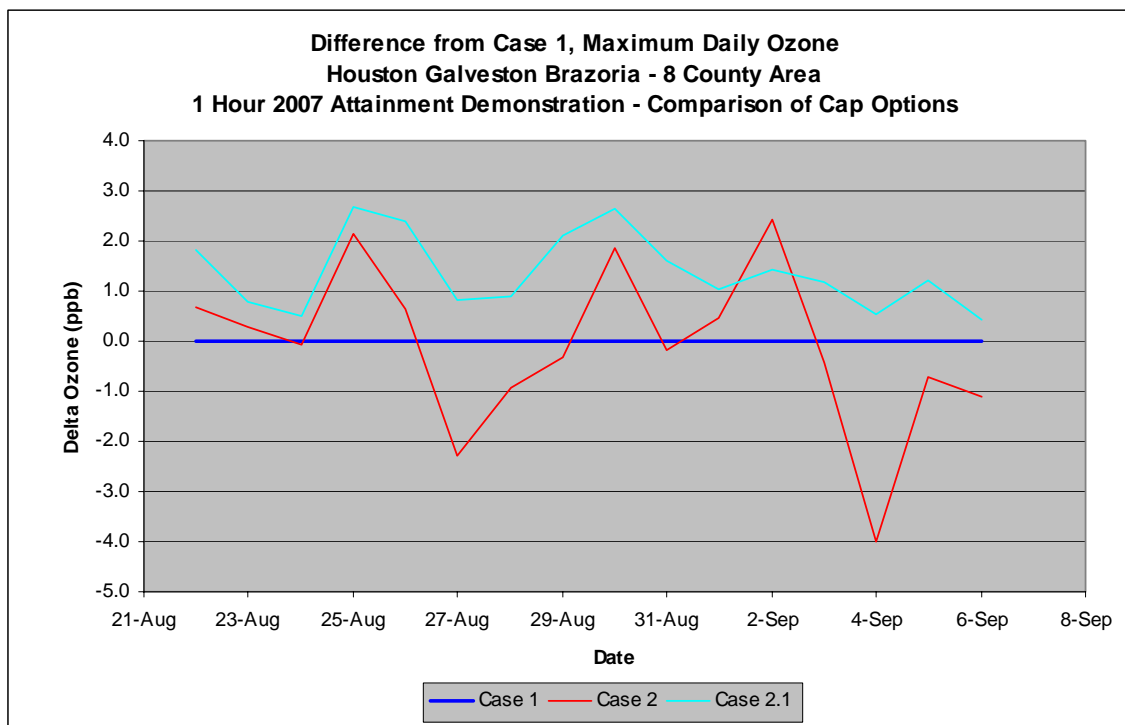


Figure 3.2. Based on the one-hour standard, comparison of two different capped account scenarios illustrates that rigidly controlling HRVOCs to no more than the cap with no ancillary reductions (Case 2.1) always produces more ozone than uniform controls with ancillary OVOC reductions (Case 1). If there is greater reduction of HRVOCs than is required and a decrease in ancillary NO_x and CO (Case 2), then either more or less ozone is produced than Case 1, depending upon the day.

While there are differences between the three cases, they are relatively small despite the fact that these scenarios were intended to look at a worst-case scenario where every account within the region chose to preferentially reduce HRVOC emissions. The conclusion is that however individual sites may chose to cap their HRVOC emissions, there are likely to be minimal effects on regional ozone levels.

3.2 Trading of HRVOC Emissions within Defined Geographic Areas

Cases 3 and 3.1 are similar in concept to Cases 2 and 2.1, but extend the domain over which HRVOC emissions are spatially concentrated from a facility to a region. Cases 3 and 3.1 consider the effects of allowing both capped and uncapped facilities to trade emissions such that the total HRVOC reduction for a geographic region is equivalent to a uniform reduction at capped facilities. Case 3 identifies six geographic regions that represent areas of concentrated annual emissions of both VOC and NO_x and which are characterized by the most significant occurrences of HRVOC event emissions. A description of each of these trading regions including the types of events that occurred during 2003 is presented in Table 3.1. A map showing the location of these boxes in the HGB region is given in Figure 3.3. Each of the boxes includes an area of 100 km².

Both Case 3 and 3.1 consider scenarios for trading of annual HRVOC emissions that are intended to be ‘worst-cases’ such that trades result in spatial concentration of HRVOC emissions in relatively NO_x-rich geographic areas. In Case 3 the center of mass of net NO_x emissions was identified for each of the 6 boxes. To simulate a trading situation, HRVOC EPNs farthest from the NO_x centroid were “turned off” until the reduction target for each box was achieved. In other words, the HRVOC sources closest to the NO_x bought HRVOC trading allowances. In Case 3.1 a similar, but extreme scenario was developed. In this case the “box” was all of Harris County and all sources of NO_x were taken into consideration in locating the most NO_x rich areas.

Table 3.1. Six 100 km² Geographic Trading Regions (“Boxes”)

Sub-region			HRVOC 2003 event emissions				VOC 2003 event emissions				%HRVOC (mass)
Name	LCP range	County	# Event-sources	Mass (lbs)	lbs per event	Events per facility	# Event-sources	Mass (lbs)	Lbs per event	Events per facility	
Houston/Pasadena	455 to 465 and -1105 to -1115	Harris	79	113,095	1,432	13	213	187,288	879	19	60.39%
Channelview/Deer Park	465 to 473 and -1097 to -1110	Harris	168	288,559	1,718	21	595	622,094	1,046	35	46.39%
Baytown/LaPorte	473 to 483 and -1102 to -1112	Harris	271	209,070	771	21	686	449,476	655	46	46.51%
Bayport	473 to 483 and -1117 to -1127	Harris	109	94,891	871	14	322	208,902	649	25	45.42%
Texas City	486 to 496 and -1140 to -1150	Galveston	307	73,060	238	44	1107	467,302	422	101	15.63%
Freeport	446 to 456 and -1184 to -1194	Brazoria	144	492,458	3,420	36	413	579,853	1,404	103	84.93%

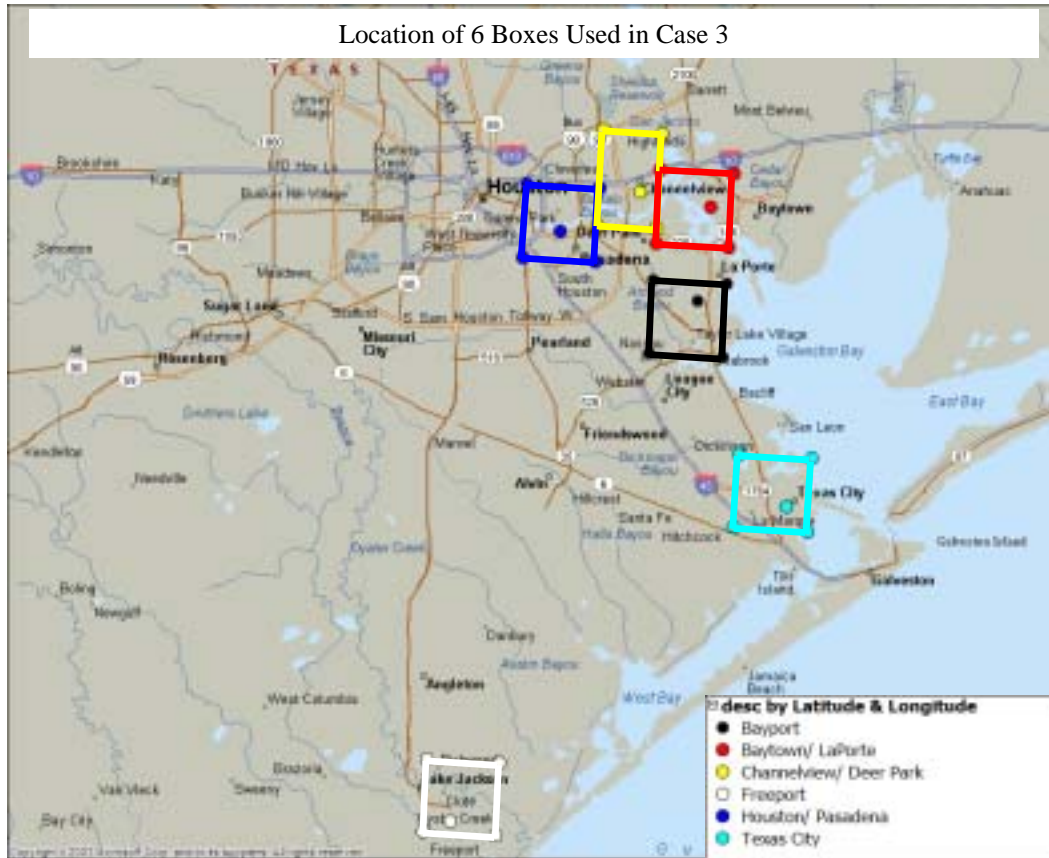


Figure 3.3. Six ‘boxes’ with areas of 100km² were selected as trading regions. These boxes are characterized by high levels of VOC and NO_x, as well as by frequent and large HRVOC emission events.

Figure 3.4 is a conceptual illustration of the change in mass of emissions that would occur under Case 3 conditions for a hypothetical geographic area containing a mixture of capped and uncapped accounts. Depending upon whether the box is in Harris or the surrounding seven counties, the total reduction of HRVOCs within the box is either 90% or 60%. As can be seen most clearly in the center and right-hand drawings, EPNs that are in HRVOC service and located farthest from the center mass are preferentially taken out of service.

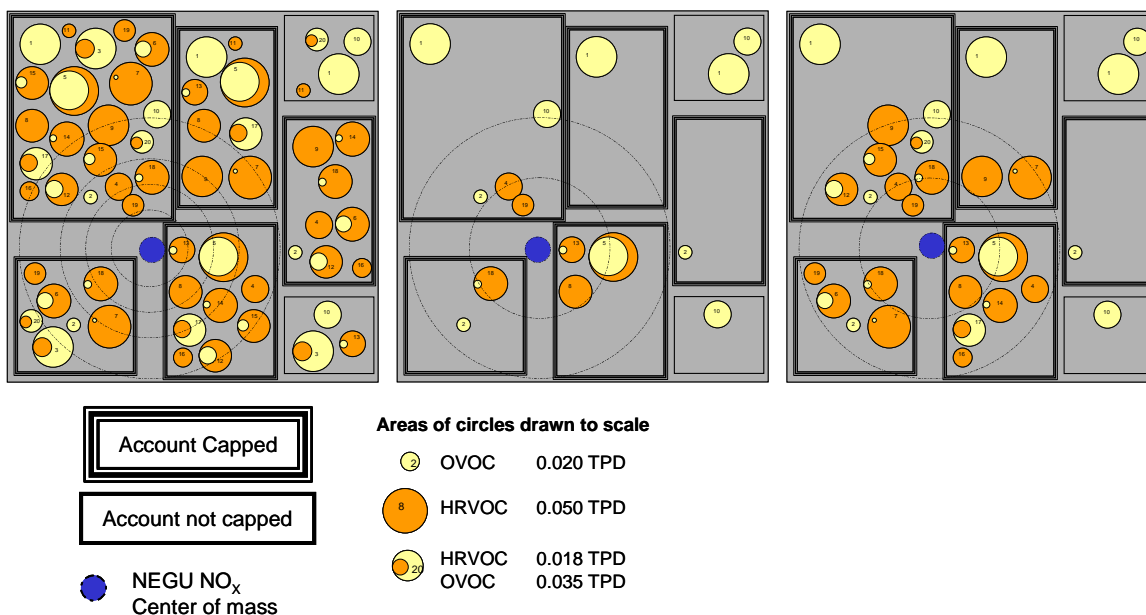


Figure 3.4. A conceptual drawing of Case 3 is shown for a hypothetical box consisting of seven accounts (sites), both capped and uncapped, that each contain a number of EPNs that emit all OVOCs (shown as yellow circles), EPNs that emit all HRVOCs (shown as orange circles), and EPNs that emit a mixture of both (shown as overlapping yellow and orange circles). The circles are drawn to scale such that their area is proportional to the mass emitted. The HRVOC EPNs that are closest to the negu NO_x center of emission mass experience no reduction in HRVOCs or OVOCs because they buy trading allowances from EPNs that are further removed (from both capped and uncapped accounts). EPNs that are not in HRVOC service also remain unchanged. The result is a concentration of HRVOCs in an undesirable area.

Case 3.1 is similar to Case 3, except that the trading area is considered to be all of Harris County. Locations of the maximum areas of NO_x emissions were determined by calculating the amount of NO_x emitted by all sources (including mobile, point, and area) within each 4-km grid cell. The cells were then ranked from highest to lowest in terms of total mass emitted within the cell. All HRVOC sources were preferentially eliminated from the cells that ranked lowest in terms of NO_x emissions until there was a 90% reduction in HRVOCs within Harris County. The result was a concentration of all HRVOC emissions within just 3 cells. One of these cells, while high in NO_x, has very low HRVOC emissions, so in Case 3.1, HRVOC emissions are effectively limited to 2 cells (an area of 32 km²), within the Houston Ship Channel. Figure 3.5 shows the location of the cells as well as the regional NO_x distribution.

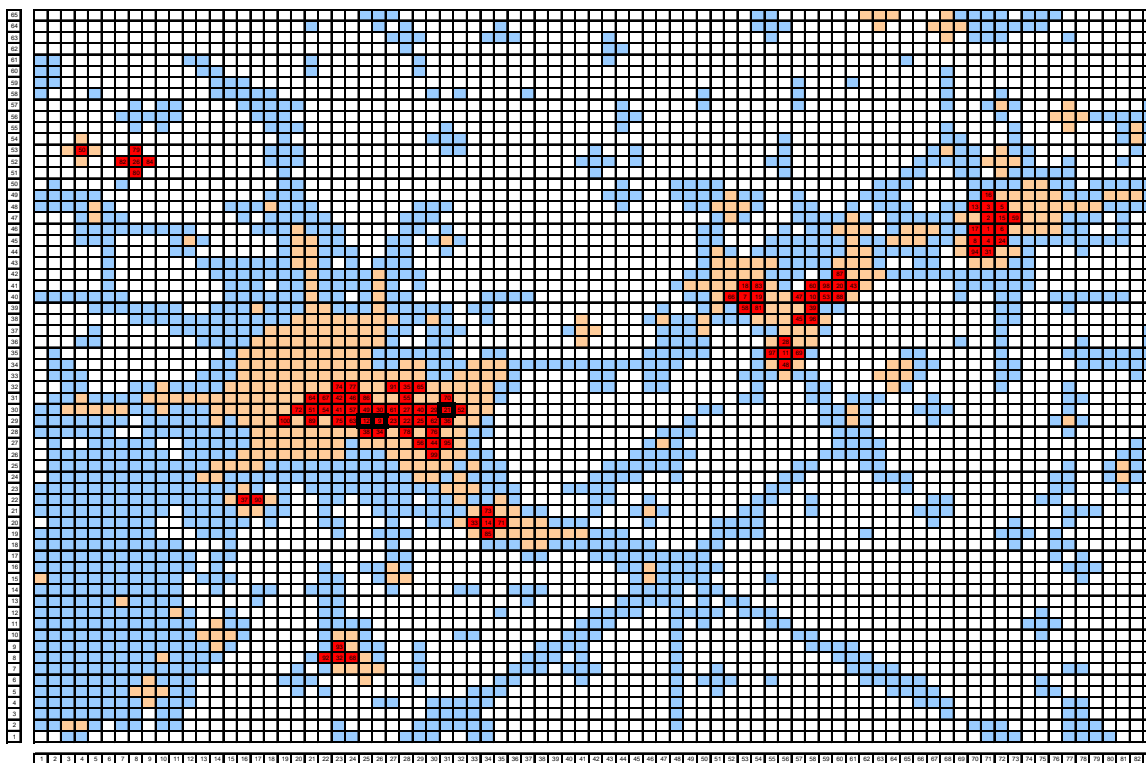


Figure 3.5. The 4-km domain is shown above with relative, 2000 August episode weighted mass of NO_x (from all sources) indicated by color. Red shows the 100 top ranked cells (i.e., those where the most NO_x is emitted), pale orange indicates those that rank 101 to 500, blue illustrates cells that rank between 501 and 2000, white is used for those cells with the lowest NO_x emissions (ranking 2001 to 5395 in the domain). The three cells outlined with a heavier black line are the three cells in Harris County with the highest NO_x emissions and indicate the location of all HRVOC sources within county in Case 3.1.

The effects on ozone for Cases 3 and 3.1 relative to Case 1 (uniform reduction) are shown in Figure 3.6. The plot of the difference in the maximum daily ozone value between Case 3 and Case 1 suggests that there is little to no effect when HRVOCs are concentrated on a scale of roughly 10 km or less. It is also possible that since the photochemical modeling is performed using a 4-km domain, that the model is simply insensitive to such changes. Perhaps more significant, however, are the results of the Case 3.1 simulation. While this case nearly always produces a higher daily ozone maximum, the worst instance is an increase of only 3 ppb and on most days the increase is less than 1 ppb. The largest daily difference in maximum ozone concentration appears to be more significant. On August 25, an increase of 10 ppb for Case 3.1 relative to Case 1 is observed at 12:00 noon in cell 24,28 in the proximity of the HRVOC sources (Figure 3.7). A maximum difference of just under 7 ppb was observed on August 30 at 3:00 pm in cell 26,29 directly above the HRVOC sources. The other concern with trading is the potential to change the location of the maximum ozone. An examination of tile plots (Appendix F) indicates that any shift is minimal. On August 25 the maximum moves by 1 grid cell; on August 30 no change is observed.

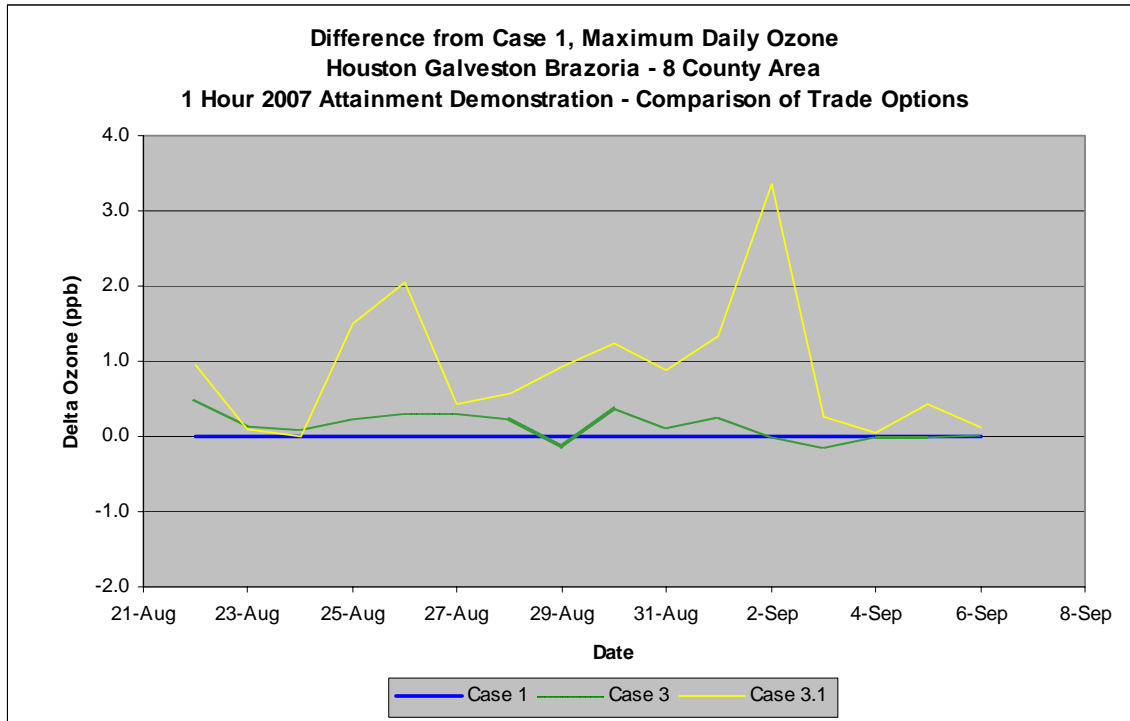


Figure 3.6. Based on the one-hour standard, comparison of two different trading scenarios shows that trading on a geographic scale of 10 kilometers or less (Case 3) produces only marginally higher levels of ozone than a uniformly controlled scenario (Case 1). Trading at the county level, within Harris County (Case 3.1), results in increased ozone over Case 1 on all days, with a maximum of slightly more than 3 ppb on September 2

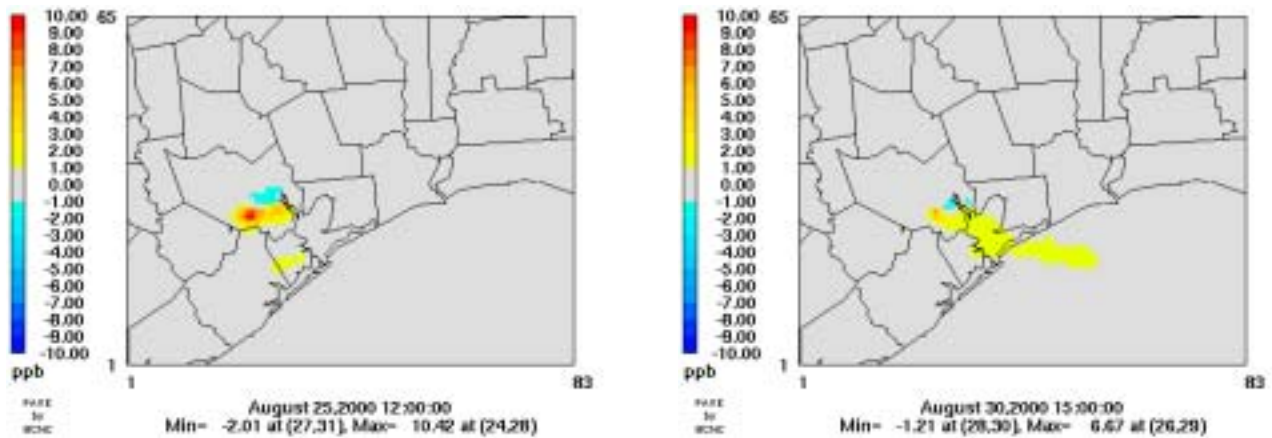


Figure 3.7. Difference plots between Case 3.1 and Case 1 for August 25 and 30 show increased ozone levels of between 7 and 10 ppb in the vicinity of the HRVOC sources.

Based on the results of the preceding scenarios, which consider a change of location but not timing, there are no immediate concerns with the effects of trading HRVOC on even fairly large spatial scales. It should be noted, however, these results do not necessarily provide any guidance as to temporal changes in emissions such as might occur with the trade of short-term event emissions. From the summary of the maximum daily ozone for each of the control, cap, and trade scenarios (Table 3.2) it can be seen that none of the case studies results in higher ozone levels than Case 0 (equivalent to the attainment demonstration).

Table 3.2. Comparison of Control, Cap, and Trade Scenarios:
Maximum Daily Ozone Based for One-Hour Standard (125 ppbv)

Date	Case 0 ppb O ₃	Case 1 ppb O ₃	Case 2 ppb O ₃	Case 2.1 ppb O ₃	Case 3 ppb O ₃	Case 3.1 ppb O ₃
22-Aug	87.82	83.88	84.55	85.68	84.37	84.84
23-Aug	75.71	73.94	74.22	74.73	74.09	74.04
24-Aug	75.32	74.07	73.99	74.57	74.16	74.07
25-Aug	122.28	110.09	112.23	112.76	110.32	111.59
26-Aug	114.31	108.30	108.95	110.69	108.61	110.36
27-Aug	88.52	86.65	84.36	87.46	86.96	87.07
28-Aug	103.62	101.46	100.53	102.36	101.68	102.03
29-Aug	115.14	108.20	107.90	110.29	108.07	109.13
30-Aug	122.88	115.93	117.78	118.58	116.30	117.17
31-Aug	148.54	143.87	143.68	145.47	143.98	144.75
1-Sep	120.10	116.92	117.39	117.95	117.18	118.26
2-Sep	130.34	124.05	126.49	125.46	124.06	127.40
3-Sep	116.28	112.29	111.85	113.48	112.15	112.54
4-Sep	128.31	126.27	122.25	126.79	126.26	126.31
5-Sep	188.23	185.18	184.47	186.40	185.18	185.60
6-Sep	128.44	127.24	126.15	127.65	127.27	127.36

3.3 MIR-Based Trading of HRVOC and OVOC Annual Emissions

Emission trading has the potential to be an effective approach for achieving emission reductions and as such has gained popularity as a flexible and economically efficient alternative to conventional command and control strategies. Conventional cap and trade programs involve trading of only a single pollutant. A notable example is the U.S. Acid Rain Program for sources of sulfur dioxide (SO₂). More recently, the concept of inter-pollutant trading (IPT) applied to ozone precursors, particularly between NO_x and VOCs, has been considered as the underlying concept for the current substitution of the NO_x reduction with HRVOC reductions in HGB area. Trading mass of emissions of one compound for an equivalent mass of emissions of another compound has been done implicitly for VOCs for decades, but trading of VOCs using reactivity-weighted masses is unprecedented.

The latest version of the State Implementation Plan (SIP) allows for up to 5% of the required HRVOC reductions to be replaced or “traded” with an equivalent reactivity-weighted mass of other VOCs (OVOCs), where reactivity is based on the maximum incremental reactivity (MIR) scale. Incremental reactivity is defined as the amount of additional ozone formed as the result of

the addition of a small amount of the compound to the system, divided by the amount of compound added. The MIR value is measured as the incremental reactivity under ozone conducive conditions, including the presence of significant amounts of NO_x

In order to evaluate the effects of such a trade, the controlled extra OVOCs in Cases 5, 5.1, and 5.2 (see section 2.5) were replaced with an MIR equivalent amount of propene. This resulted in an overall increase of 33, 15, and 18 tons per day (TPD) of additional HRVOC for Cases 6, 6.1, and 6.2 respectively, but a respective decrease of 195, 39, and 156 TPD in aromatic species plus paraffins, aromatic species, and paraffins, respectively. A list of the species replaced with propene, along with their MIR values is given in Appendix D.

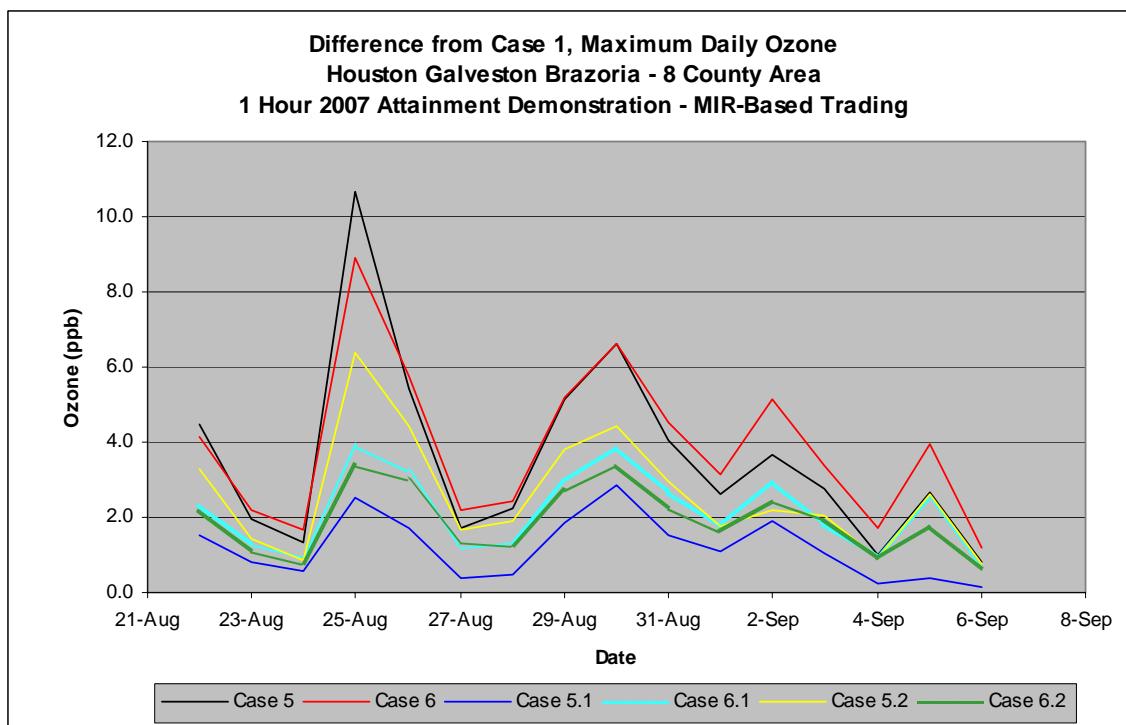


Figure 3.8. Trading of aromatics (C7 to C9) for an MIR equivalent mass of propene (Case 6.1) results in an approximately 1 ppb higher maximum daily ozone. Trading of alkanes (C3 to C7) results in values that are up to 3 ppb lower (Case 6.2).

An evaluation of the maximum daily ozone values that are produced with these scenarios suggests that MIR-based trading of annual emissions in amounts significantly higher than anticipated by the proposed SIP revisions would result in minimal changes in the regional ozone levels (Figure 3.8 and Table 3.3). As indicated in both the table and the graph, trading of C7 to C9 aromatics for an MIR equivalent mass of propene (Case 6.1) results in increased maximum daily ozone levels approximately 1 ppb higher than Case 5.1, with daily variations that range from 0.4 ppb to 2.1 ppb higher levels. Trading of C3 to C7 alkanes for propene, as demonstrated in Case 6.2, results in maximum daily ozone levels that are typically lower by as much as 3 ppb.

Table 3.3. Differences in Maximum Daily Ozone for MIR-based Trading of Substituted Aromatics and Light Alkanes for Propene

Date	Aromatics plus Alkanes			C7 - C9 Aromatics			C3 - C7 Alkanes		
	Case 5 ppb O ₃	Case 6 ppb O ₃	Case 6 – 5 ppb O ₃	Case 5.1 ppb O ₃	Case 6.1 ppb O ₃	Case 6.1 – 5.1 ppb O ₃	Case 5.2 ppb O ₃	Case 6.2 ppb O ₃	Case 6.2 - 5.2 ppb O ₃
22-Aug	88.35	88.03	-0.32	85.42	86.19	0.77	87.16	86.09	-1.07
23-Aug	75.91	76.12	0.21	74.74	75.23	0.49	75.35	75.05	-0.3
24-Aug	75.39	75.74	0.35	74.62	75.02	0.4	74.91	74.86	-0.05
25-Aug	120.74	118.97	-1.77	112.63	113.97	1.34	116.47	113.48	-2.99
26-Aug	113.74	114.06	0.32	110.02	111.53	1.51	112.73	111.31	-1.42
27-Aug	88.36	88.86	0.5	87.04	87.82	0.78	88.3	87.96	-0.34
28-Aug	103.7	103.89	0.19	101.94	102.8	0.86	103.36	102.71	-0.65
29-Aug	113.34	113.4	0.06	110.06	111.17	1.11	112	110.93	-1.07
30-Aug	122.53	122.56	0.03	118.77	119.81	1.04	120.37	119.32	-1.05
31-Aug	147.9	148.4	0.5	145.37	146.51	1.14	146.81	146.12	-0.69
1-Sep	119.52	120.06	0.54	118.01	118.67	0.66	118.68	118.55	-0.13
2-Sep	127.71	129.2	1.49	125.96	127.02	1.06	126.23	126.49	0.26
3-Sep	115.03	115.67	0.64	113.34	114.08	0.74	114.35	114.22	-0.13
4-Sep	127.26	127.98	0.72	126.52	127.2	0.68	127.17	127.19	0.02
5-Sep	187.83	189.12	1.29	185.55	187.66	2.11	187.79	186.92	-0.87
6-Sep	128.05	128.41	0.36	127.38	127.89	0.51	128.02	127.86	-0.16
Max			1.49			2.11			0.26
Min			-1.77			0.40			-2.99
Mean			0.32			0.98			-0.70

3.4 MIR-Based Trading of HRVOC and OVOC Event Emissions

The annual emissions inventory and TCEQ event database were used to identify OVOCs that might (in addition to HRVOCs) be significant contributors to ozone formation in the HGB area (section 2.3). Considering both total mass and reactivity based on the maximum incremental reactivity scale, two categories of OVOCs were determined to be of the greatest interest. Trading of continuous (ozone season daily) emissions of these compounds was considered in section 3.3 and both categories appeared to be reasonable candidates for a trading program. However, there is also interest in understanding what effects trading of short-term emissions of aromatics and alkanes for HRVOCs might have on ozone formation. This is of particular concern as event emissions of HRVOCs have been demonstrated to have significant impact on rapid formation of ozone in the Houston area, while other VOCs have not.

The specific methodology for simulating emission events of different species using photochemical grid modeling is covered in detail in section 1.2. For this study, three model species were chosen to represent each class. Propene was selected as a typical HRVOC. It is extremely reactive and represents the second largest mass observed in event emissions. The model species selected for alkanes was n-pentane. It is a relatively common event emission species and is one the more reactive of the C3 to C5 alkanes. Isomers of xylene were selected to represent substituted aromatics. Xylene is often associated with short-term releases (although not typically in combination with HRVOCs) and is very reactive. The base inventory, location, and time of release were selected in order to match the scenarios simulated in Project H13; this is intended to facilitate comparison of results between the two projects. The 1-km modeling

domain in addition to the 4-km modeling domain was also selected for this reason. The emission rate of propene was set at 5819 lbs/hr for a period of two hours. The MIR equivalent rates of n-pentane and isomers of xylene were 44,004 lbs/hr and 9045 lbs/hr, respectively.

Figures 3.9 and 3.10 illustrate the domain-wide maximum ozone for the three different event emission species on August 25 and August 30. These analyses suggest aromatic event emissions can produce more ozone than HRVOC event emissions, adjusted for equal reactivity. In contrast, it would appear that equivalent reactivity alkane event emissions produce less ozone than either alkenes or aromatics.

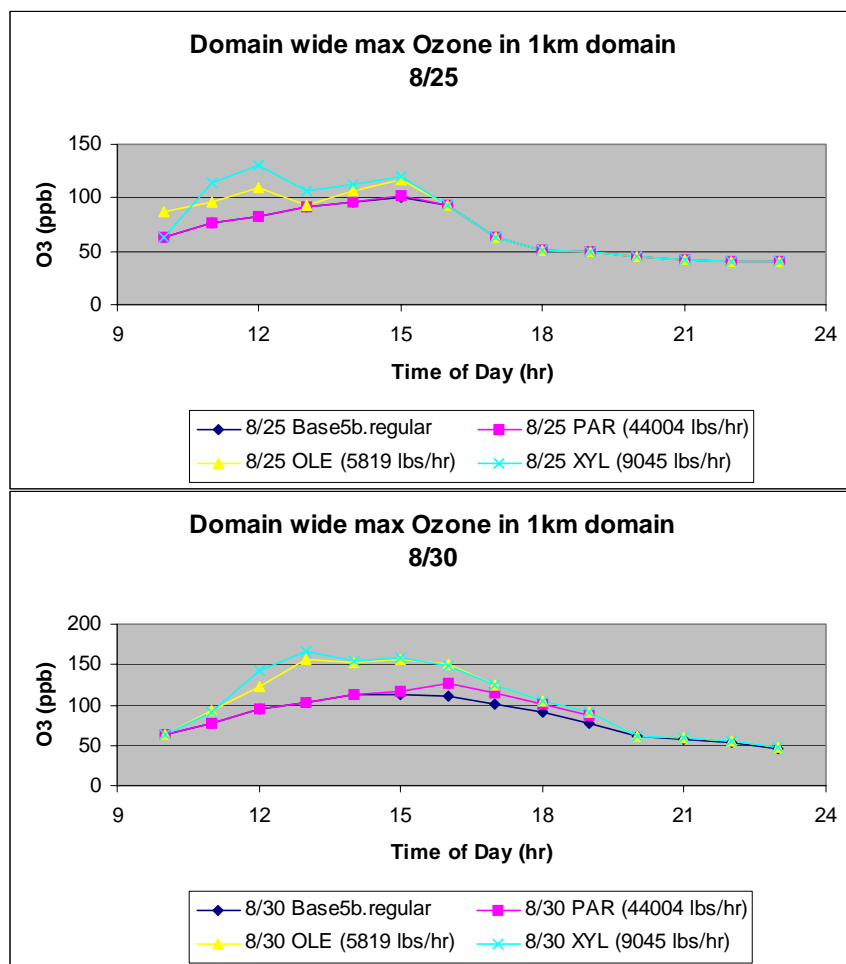


Figure 3.9. The domain-wide ozone maximum produced with the xylene event (XYL) in the 1-km domain is higher than that produced by an MIR equivalent amount of propene (OLE) for both August 25 and August 30. This suggests that making reductions of aromatic emissions in place of (MIR-equivalent) HRVOC emission reductions would be beneficial in terms of ozone production. In contrast, making reductions of alkane (paraffin) emissions instead of (MIR-equivalent) HRVOC emission reductions could result in undesirable increases in ozone production.

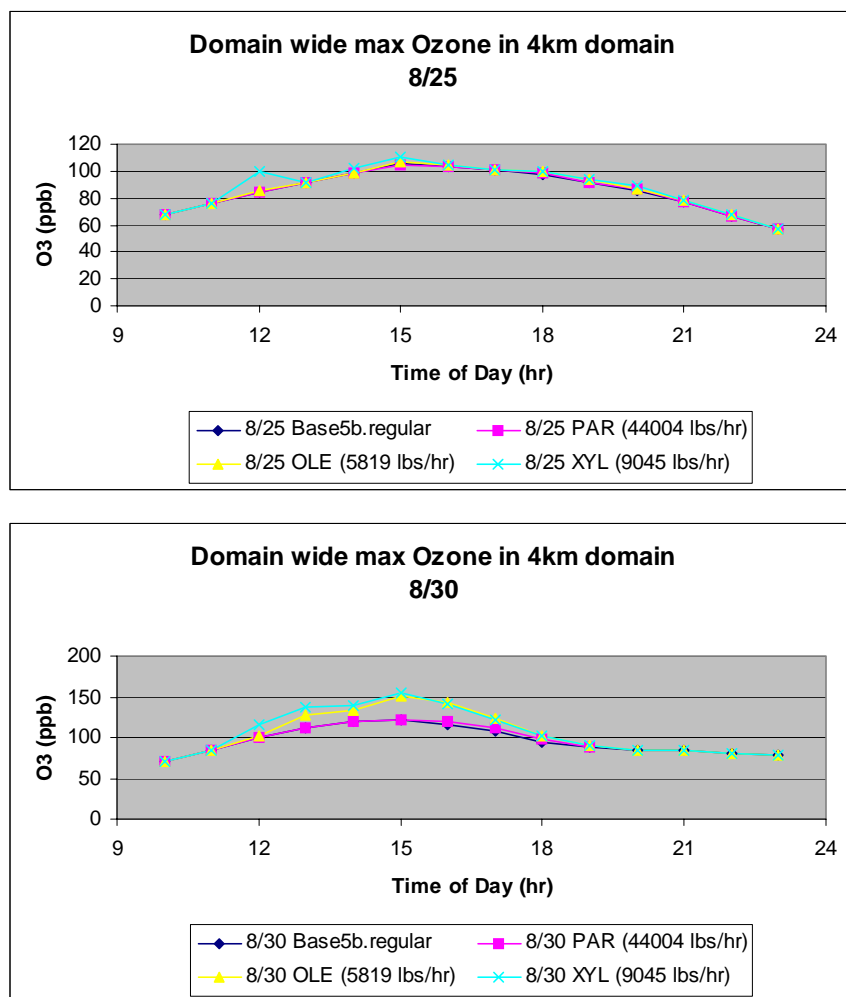


Figure 3.10. There is little sensitivity on August 25 to event emissions of any composition when modeled in the 4-km domain. On August 30, the relationships are similar to, although less pronounced, than those observed in the 1-km domain. The xylene event (XYL) results in a higher domain-wide maximum ozone level than that produced by an MIR equivalent amount of propene (OLE). This suggests that trading of HRVOCs for aromatics would be equal to or better in terms of ozone production. In contrast, the n-pentane (PAR) is significantly lower than the propene, indicating that trading of alkane (paraffin) event emissions for HRVOC could result in undesirable increases in ozone production.

The observation that trading of aromatic event emissions for HRVOC is likely to be more desirable than trading of alkanes is also seen in Figure 3.11 which compares the maximum difference between the base case and the three events on the two different days. The difference in ozone formation is also seen in tile plots (Figure 3.12), where the geographic area covered by high ozone levels is roughly equivalent for the propene (OLE) and xylene (XYL), but smaller for the n-pentane (PAR).

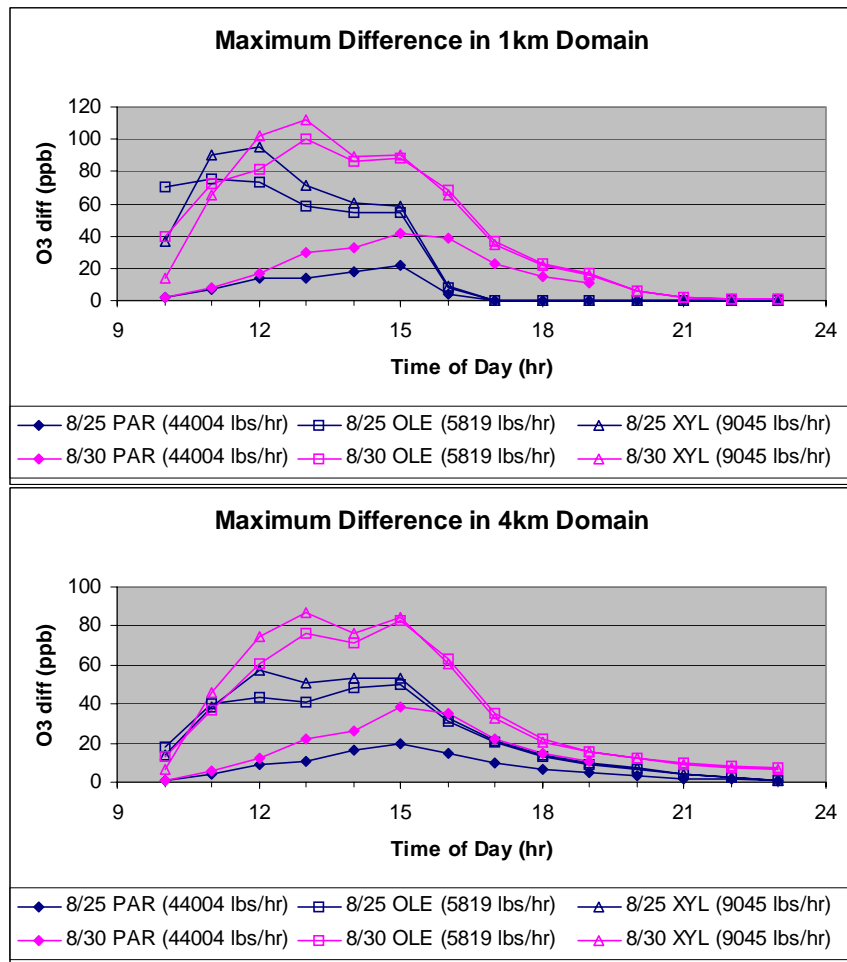


Figure 3.11. Graphs of the maximum difference in ozone production between the base case and three events of different composition but of equivalent MIR mass suggest that HRVOC events are likely to produce less ozone than aromatic emission events but significantly more than alkane events.

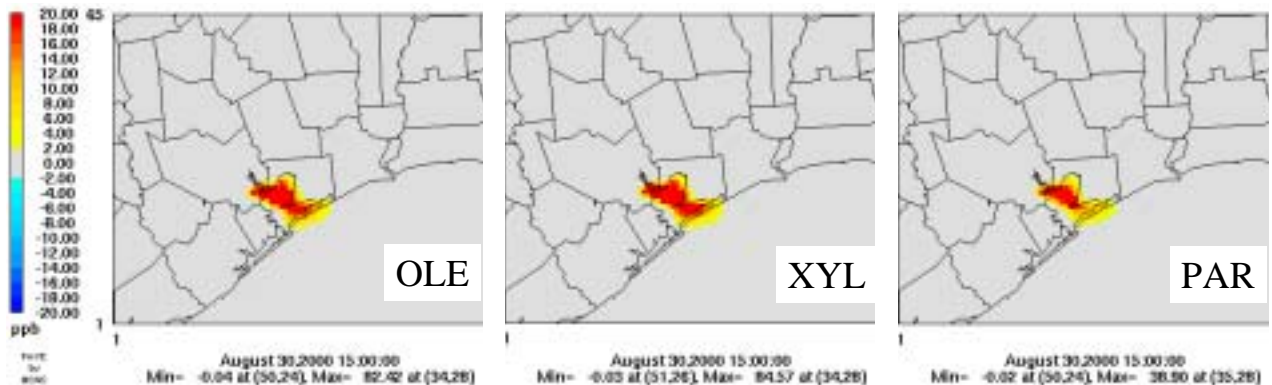


Figure 3.12. The geographic extent of the maximum difference in ozone production show propene (OLE) slightly lower than xylene (XYL) and slightly higher than n-pentane (PAR).

3.5 Conclusions

Photochemical modeling of a number of case studies where annual (ozone season daily) emissions were manipulated in order to simulate presumably worst-case situations that might occur under a cap and trade program resulted in minimal changes in daily maximum ozone concentrations (3 ppb or less). In particular, this study found no evidence that intra-facility capping strategies or inter-facility trading are likely to produce emission spikes that resemble event emissions. This observation extends to trading based on reactivity (MIR) for annual emissions that are distributed in space and time. Photochemical modeling of event emissions where HRVOCs are traded for significantly less reactive species, such as light alkanes indicated that this type of trading might be more problematic. However, it should be noted that the sizes of the events modeled are quite large and that the current SIP places a short-term cap of 1200 pounds per one-hour time block. 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.

4. SURVEY OF REGULATORY STRATEGIES

Objective:

The objective of task 3 is to provide a list of regulatory strategies (regulations and control technologies) used in different parts of the world to reduce VOCs, and to discuss how those items might be used in the Houston/Galveston/Brazoria area to reduce HRVOC's.

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.

Recommendation

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.

Report: Survey of Regulatory Strategies

See attached report submitted by ENVIRON.