

Variable Industrial VOC Emissions and their Impact on Ozone Formation in the Houston Galveston Area

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Abstract

The Houston-Galveston area (HGA) is designated as a severe ozone non-attainment region, and the State of Texas is charged with developing a State Implementation Plan (SIP) for reducing emissions that lead to ozone formation. A first step in developing the SIP is to characterize and quantify the emissions that lead to high ozone concentrations. In the HGA, developing inventories of emissions that lead to high ozone concentrations is more complicated than in many other urban areas because of the extensive industrial operations in the region.

Emissions from industrial facilities (point sources) are generally assumed, for SIP development purposes, to be continuous and at a nearly constant level. Emissions from Electricity Generating Units (EGUs) are the exception, and the State of Texas, and most other regions of the United States, use continuously collected data on emissions to characterize the role of EGUs in ozone formation. For petroleum refineries, chemical manufacturing facilities, and other industrial operations (non-EGUs), however, SIP analyses generally assume emissions are constant and continuous. This assumption is made because many non-EGUs operate 24 hours per day, 7 days per week, and their material throughput is nearly constant.

Recent evidence, from a variety of sources, demonstrates that while some types of emissions of volatile organic compounds from non-EGU point sources are constant, others are not. Daily emissions from a single facility can vary from annual average emissions by a factor of 10-1000. Variations of this magnitude at any single facility typically occur only a few times per year, but because there are so many facilities in the HGA, on many days, there is likely to be a facility experiencing significant emission variability.

Air quality measurements taken in recent field studies have also found evidence of localized regions with elevated concentrations of highly reactive volatile organic compounds (HRVOC). These regions with elevated HRVOC concentrations are frequently associated with very rapid ozone formation, leading to exceedances of the ozone air quality standard.

This paper characterizes the nature of the variability in HRVOC emissions in the Houston-Galveston area and assesses the impact of variability on ozone formation processes in the HGA.

Introduction

The Houston-Galveston area (HGA) is designated as a severe ozone non-attainment region, and the State of Texas, through the Texas Commission on Environmental Quality (TCEQ), is charged with developing a State Implementation Plan (SIP) for reducing emissions that lead to ozone formation in the HGA. A first step in developing the SIP is to characterize and quantify emissions of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) that lead to ozone formation, especially the emissions of ozone precursors that produce the highest ozone concentrations.

Emissions are characterized and quantified in emissions inventories, and emission inventories are used for a variety of purposes. For example, emission inventories are used to establish state-wide and nation-wide trends in air quality. They are used to determine which categories of emission sources are most important in specific geographical areas. They are also used as inputs to models that attempt to predict air quality on specific days. The type of information that is required in an emission inventory depends on the way in which the inventory will be used. Emission inventories that are used to establish air quality trends at regional or national scales need only have information about average emission rates. However, emission inventories that will be used in models that predict air quality on specific days, or that are used to predict the likelihood of extremes in air pollutant concentrations, must consider both average emission rates and the daily variability in emissions.

The concept that daily, even hourly, variability in emissions must be accounted for in air quality modeling of specific days, or analyses used to predict extremes in air pollutant concentrations, is well established for certain categories of emissions. For example, when considering biogenic emissions (compounds released by vegetation) or the vaporization of fuel from vehicles, inventories used to establish national trends report emissions developed for average "ozone season days". Temperatures and the intensity of sunlight, which influence these emissions, are based on average data or data from representative days. In contrast, when an emission inventory is to be used for modeling air quality on a specific day or days, the temperatures and sunlight intensities for those specific days are used. Emission rates on specific days can be significantly different than on average days.

This same concept is also applied to some, but not all, emissions from large industrial facilities (commonly referred to as point sources). For electricity generating units (EGUs) that emit largely NO_x and sulfur oxides (SO_x), emissions inventories are used in defining rules that limit acid precipitation. These inventories are based on annual or seasonal emission rates. In contrast, when emissions from EGUs are needed to evaluate ozone formation on specific days, hourly emission rates on those days are used in models designed to predict air quality.

For petroleum refineries, chemical manufacturing facilities, and other industrial operations (non-EGUs), however, emissions, even those used to predict air quality on specific days, are generally assumed to be continuous and at a nearly constant level. A large body of observational evidence from the Houston-Galveston area indicates that these emissions are not constant and can have variability that has a significant impact on the prevalence of extreme ozone concentrations. This paper characterizes the nature of the variability and assesses the impact of variability on ozone formation processes in the HGA.

Variability in emissions from industrial sources

Emissions from industrial sources can be divided into four major categories:

- Emissions released at a constant rate due to continuous process operation (nearly constant emissions)
- Emissions released at a variable rate due to fluctuations in process operations (routinely variable emissions)
- Episodic emissions that lead to a significant increase in daily emission rate, yet are below the maximum daily permit level (allowable episodic emission events)
- Emergency releases and other event driven emissions that lead to daily emissions greater than permitted levels (large episodic emission events)

Conceptually, these categories of emissions are shown in Figure 1, and the major categories of emission are described in more detail below.

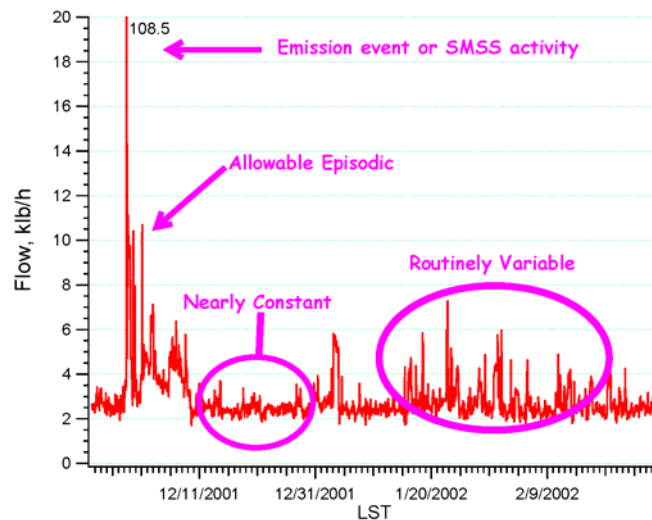


Figure 1. Major types of phenomena that may lead to emission variability

Event Emissions

Prior to late 2002, emission events above permitted levels were not recorded on a regular basis in Texas unless a reportable emission of greater than 5000 pounds in a 24-hour period was released. Effective early 2003, reporting requirements were changed and reportable quantities were reduced from 5000 lbs. to 100 lbs. for most compounds in the Houston/Galveston ozone non-attainment area. These newly available data provide new insight into the magnitude and variability of emission events, especially those of highly reactive volatile organic compounds.

As of December 31, 2003, for the first 11 months of reporting, a total of 1727 emission events occurring in the Houston-Galveston area had been posted on the TCEQ web site (TCEQ, 2003a,b). The mass of VOCs, in emission events was relatively low when considered on an annual time-scale and over a broad geographic region (i.e., at the county level). The mass of VOCs emitted as events, relative to annual VOC emissions, is less than 4%; for a specific group of compounds defined as highly reactive VOCs (HRVOCs, ethylene, propylene, butanes and 1,3-butadiene) event emissions constitute about 12% of the total annual emissions for these compounds. However, events are extremely limited in time and space and thus event emissions

have the potential to be extremely concentrated. This characteristic is critical to development of an accurate HGA emissions inventory and consequently to understanding and modeling the formation of ground-level ozone.

When the data are presented as emission rates for each hour, over the course of a year (an annual time series), the temporal pattern of the emissions becomes clearer. Figure 2 presents a time series of NO_x event emissions facilities in a 4 county region (Brazoria, Harris, Galveston and Chambers counties). To provide a point of comparison for the event emissions, the average annual flow rate in pounds per hour for all facilities in the 4 county region has been calculated from the 2001 TCEQ Point Source Database (TCEQ, 2003c) and is graphed as a horizontal line at 24,083 lbs/hr. As can be seen in the figure, only one event exceeds a NO_x flow rate of 1000 lbs/hr and that event, at 7665 lbs/hr is less than a third of the annual average, routine emissions. In the case of NO_x emissions, it appears that individual events do not significantly add to the magnitude of the inventory. Furthermore the total mass of NO_x contributed by events is only 140 tons (280,954 lbs) per year or 0.1% of the 105,482 tons per year emitted by point sources located within the four counties. Thus the magnitude of NO_x from events appears not to be significant relative to that of routine emissions, either singularly or collectively.

Figure 3 presents a time series of VOC event emissions in the same format as the NO_x event emissions. The average annual flow rate for routine emissions for all of the facilities in the 4 county region, 10,359 lbs/hr based on historical inventories, appears as a horizontal line. In contrast to NO_x, there are 14 times during the eleven-month period in which VOC event emissions exceed the annual average. The time involved is 18 hours. In four instances, the flow rate of event emissions is more than five times the annual average with a maximum of 86,557 lbs/hr. The total mass of greater than 4 millions pounds (2000 tons) contributes 4% to the 45,373 tons of VOC emitted during a single year from point sources in the four counties. Therefore, if event reports are complete and reasonably accurate, individual VOC events may have an impact on the magnitude (total mass) of the inventory when considered locally and over limited amounts of time, but collectively they do not add significantly to the annual, regional inventory.

A time series for HRVOC emissions is shown in Figure 4. The annual average of routine HRVOC emissions is calculated from the 2000 special inventory (TCEQ, 2003d). The flow of HRVOC event emissions exceeds the 1500 lb/hr annual average 29 times during the eleven-month period (almost 3 times per month), impacting a total of 115 hours. There are 7 times (8 hours) when the flow exceeds 5 times that of the annual average, with a maximum of 39,340 lbs/hr. HRVOC event emissions also account for an estimated 12% of the total HRVOC mass emitted over the year based on the 828 tons (1.6 million pounds) emitted in 2003. Therefore, if event reports are complete and reasonably accurate, HRVOC events have a significant impact on the magnitude (total mass) of the inventory when considered both individually and collectively. In addition, the frequency is such that they have a marked effect on the temporal profile.

Four species, or groups of species have been designated as HRVOCs; these are 1,3-butadiene, all isomers of butene, propene (propylene), and ethene (ethylene). For events beginning January 31, 2003 and posted through December 31, 2003, the total 1,3-butadiene event mass is 53,383 pounds, the total butene event mass is 105,089 pounds, the total propene (propylene) mass is 543,783, and the total ethene (ethylene) mass is 954,418 pounds. Time series for event emissions for each of these have been developed and are given in Figures 5-8.

To summarize the available data, if event reports are complete and reasonably accurate, HRVOC events contribute approximately 12% to the total annual HRVOC mass emitted, and large events (those that exceed the annual average) occur on the order of almost three times a

month (29 in an 11 month period). More than half of the mass is attributable to ethene and almost one third is due to propene. The remaining 10% consists of isomers of butene and 1,3-butadiene. In addition to dominating the mass, ethene has the most frequent events, with emissions from events exceeding the annual average flow rate for this compound more than once per week.

The length of the events is relatively short. Of the 711 HRVOC events, 523 (74%) last 24 hours or less, 175 (25%) last one hour or less, and 82 (12%) last 10 minutes or less. Despite their short duration, however, the magnitude of the emissions can still be quite large. 27 of the events lasting one hour or less release more than 1000 pounds of HRVOCs.

Roughly two-thirds of the mass is attributable to reporting entities with a primary SIC code of 2869 (Industrial Organic Chemicals) and 90% of the reported mass in 2003 can be assigned to 15 reporting entities. Although the amount of HRVOC event emissions per event in 2003 ranged from one pound to 203,000 pounds, more than half of the events (375 out of 711) emitted between 100 and 1000 lbs.

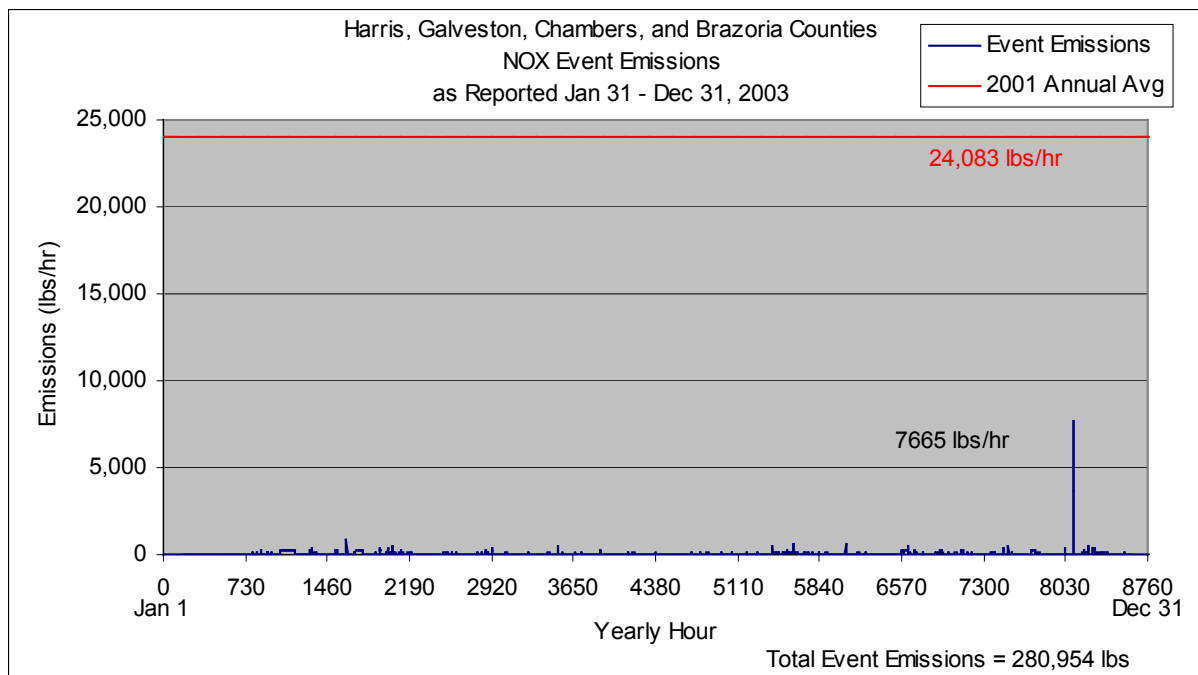


Figure 2. NO_x emissions (lbs/hr) from events and as an annual average (from 2001) are presented in a time series using 8760 one-hour time blocks for a single year. NO_x event emissions exceed 1000 lbs/hr only once and never exceed the total 2001 annual average for all facilities in the 4 county area. Event emission data are from TCEQ (2003b) and point source data are from TCEQ (2003c).

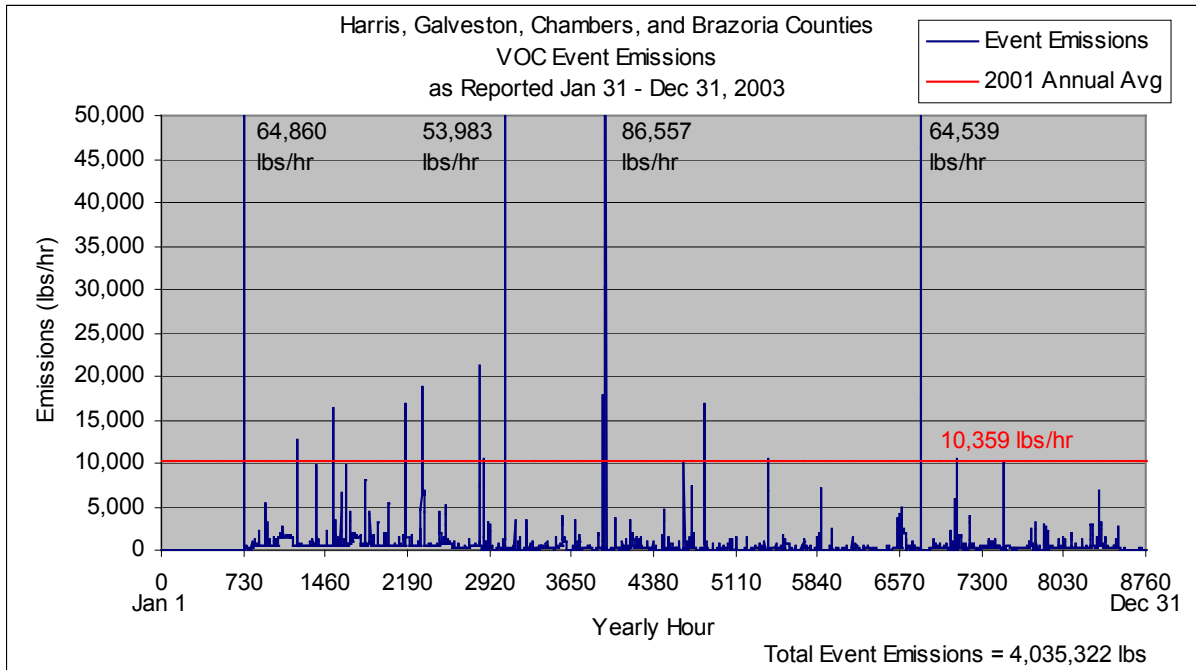


Figure 3. VOC emissions (lbs/hr) from events and as an annual average (from 2001) are presented in a time series using 8760 one-hour time blocks for a single year. There are 14 times during a roughly eleven-month time period when VOC event emissions exceed the total 2001 annual average of 10,359 lbs/hr for all facilities in the 4 county area. Event emission data are from TCEQ (2003b) and point source data are from TCEQ (2003c).

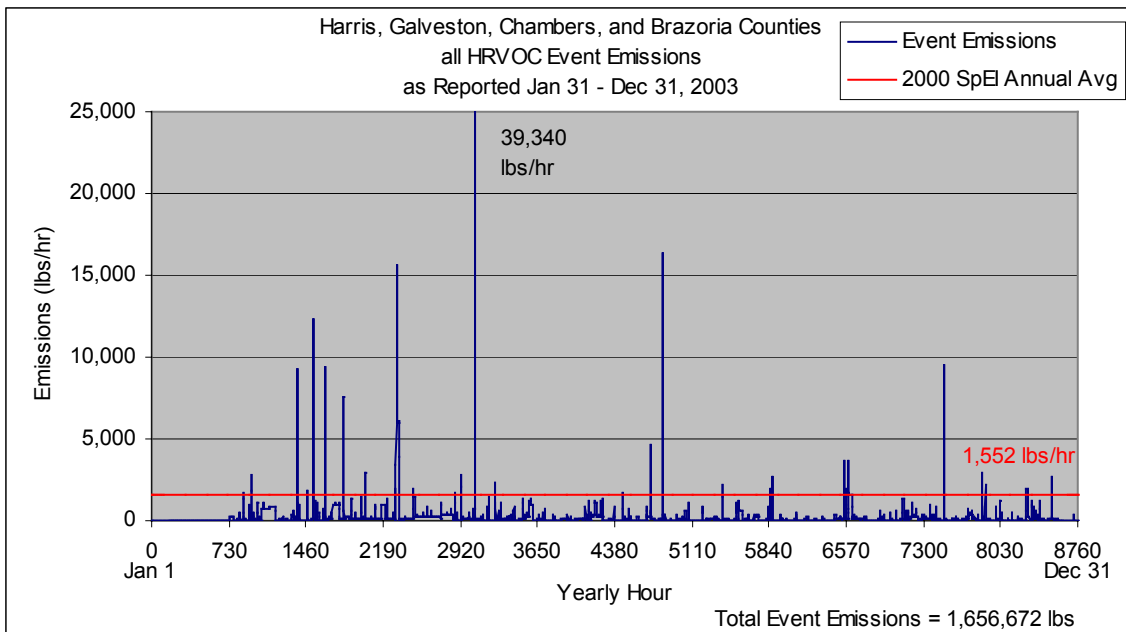


Figure 4. HRVOC emissions (lbs/hr) from events and as an annual average (from 2001) are presented in a time series using 8760 one-hour time blocks for a single year. There are 29 times during a roughly eleven-month time period when HRVOC event emissions exceed the 2000 annual average of 1,552 lbs/hr. Event emission data are from TCEQ (2003b) and point source data are from TCEQ (2003d).

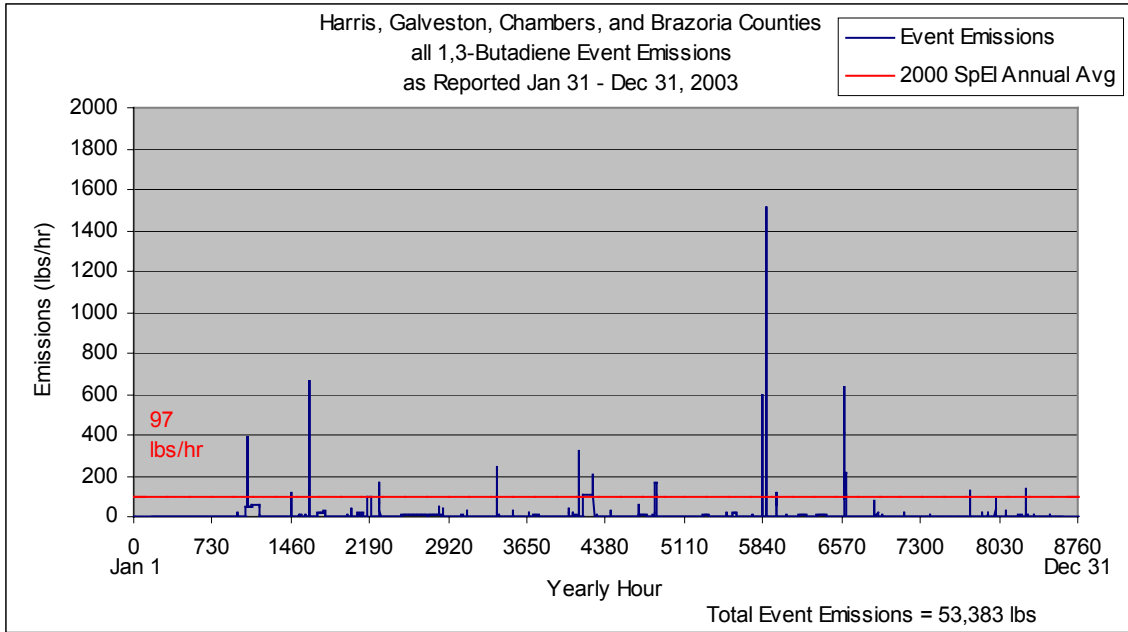


Figure 5. 1,3-butadiene emissions (lbs/hr) from events and as an annual average are presented in a time series using 8760 one-hour time blocks for a single year. Over an 11-month period there are 17 times (affecting 206 hours) when 1,3-butadiene emissions event emissions exceed the 2000 annual average of 97 lbs/hr. Event emission data are from TCEQ (2003b) and point source data are from TCEQ (2003d).

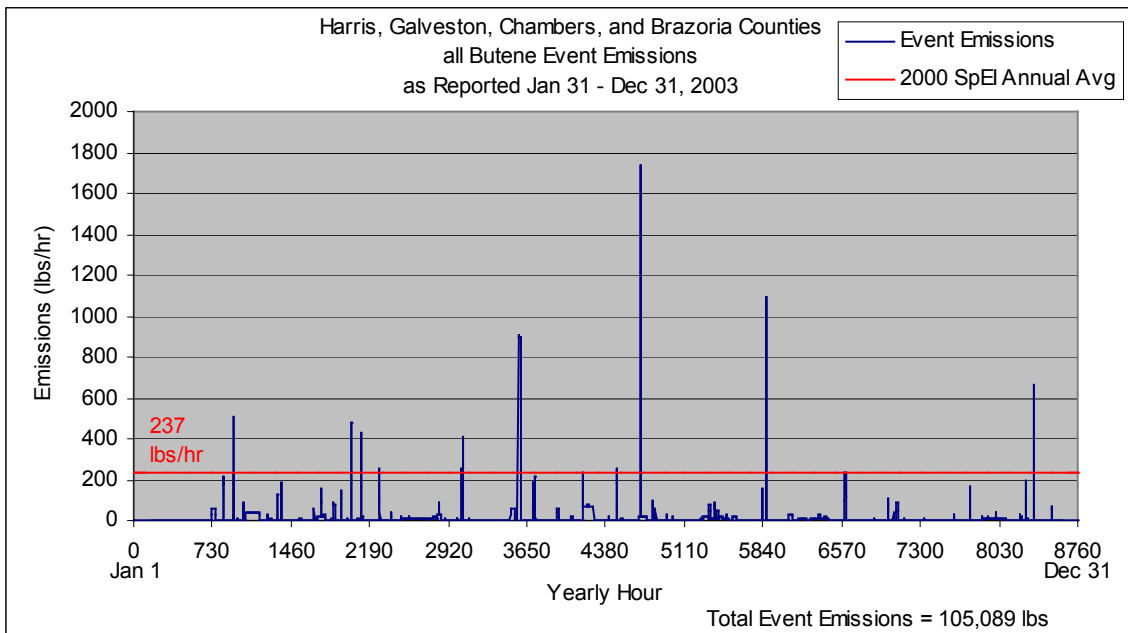


Figure 6. Butene emissions (lbs/hr) from events and as an annual average are presented in a time series using 8760 one-hour time blocks for a single year. Over an 11-month period there are 10 times (affecting 64 hours) when butene emissions event emissions exceed the 2000 annual average of 237 lbs/hr. Event emission data are from TCEQ (2003b) and point source data are from TCEQ (2003d).

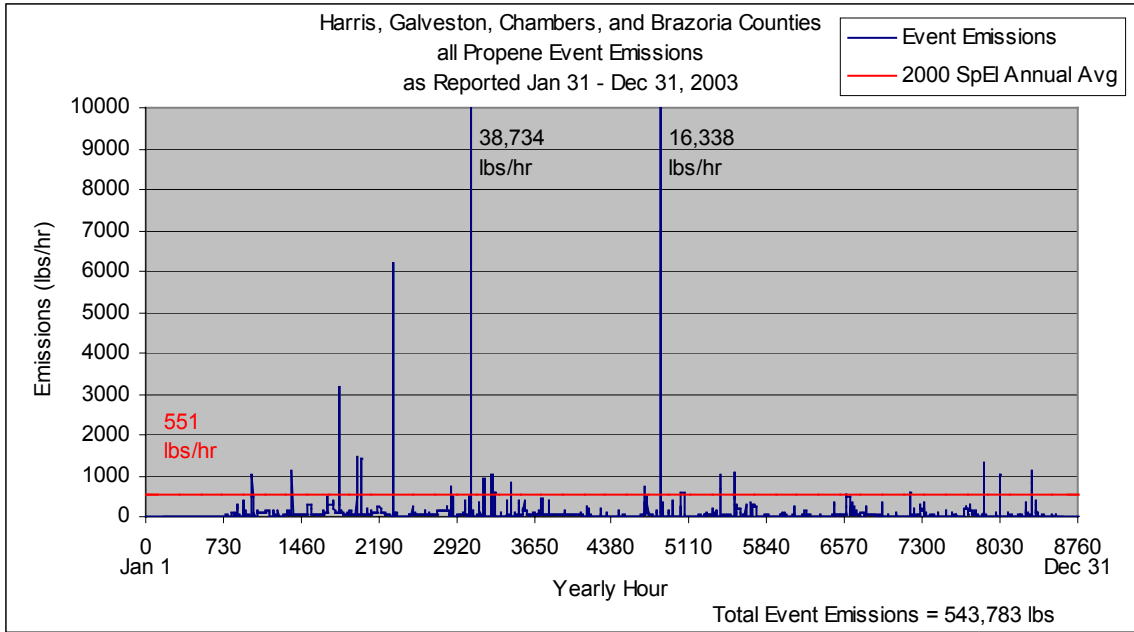


Figure 7. Propene emissions (lbs/hr) from events and as an annual average are presented in a time series using 8760 one-hour time blocks for a single year. Over an 11-month period there are 21 times (affecting 87 hours) when propene emissions event emissions exceed the 2000 annual average of 551 lbs/hr. Event emission data are from TCEQ (2003b) and point source data are from TCEQ (2003d).

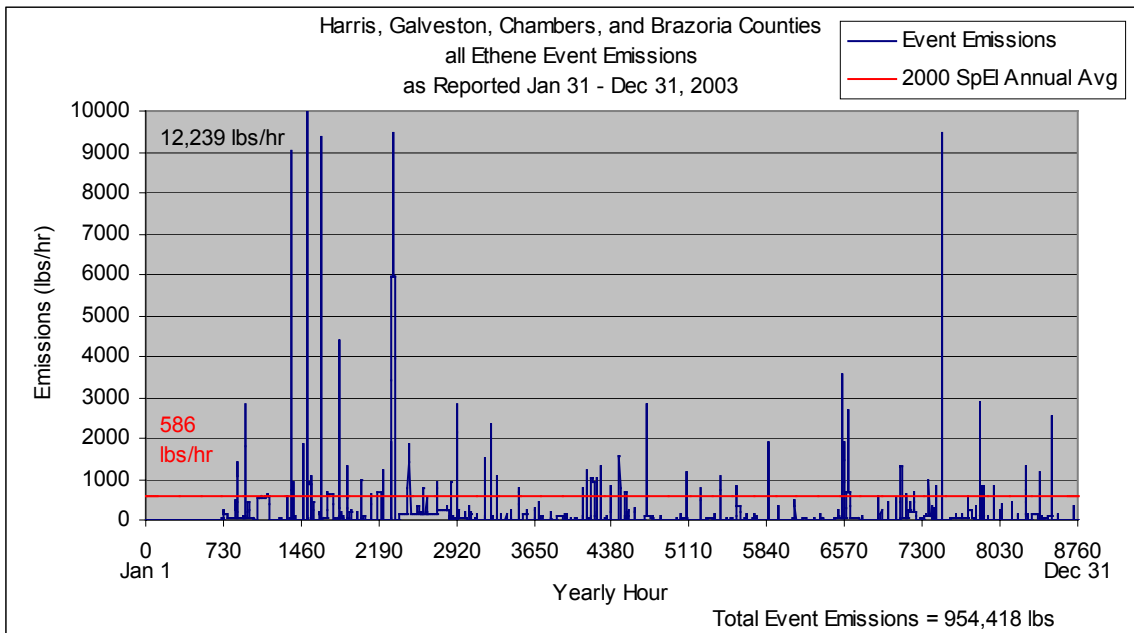


Figure 8. Ethene (ethylene) emissions (lbs/hr) from events and as an annual average are presented in a time series using 8760 one-hour time blocks for a single year. Over an 11-month period there are 58 times (affecting 395 hours) when ethylene event emissions exceed the 2000 annual average of 586 lbs/hr. Event emission data are from TCEQ (2003b) and point source data are from TCEQ (2003d).

Continuous emissions

The data summarized in Figures 2-8 characterize large episodic emission events; the variability in emissions introduced by routinely variable and allowable episodic emissions can also be significant. To more clearly define the characteristics of continuous variability in emissions, Figure 9 reports the mass flow rate to a flare at an olefins facility, over approximately a year of operation. The flare has constant continuous emissions associated with a mass flow rate of approximately 2000 lb-mol/hr. Variable continuous mass flows add approximately 1000 lb-mol/hr, leading to the actual annual average mass flow rate of 2930 lb-mol/hr (blue line). This is below the average annual permitted mass flow rate of 3430 lb-mol/hr (purple line). Approximately weekly, episodic emissions lead to daily mass flows that are double the annual average (6000 lb-mol-hr). This is well below the daily allowable maximum flow to the flare of 34,700 lb-mol/hr. Twice during the year, large episodic emission events led to exceedances of the daily allowable maximum flow.

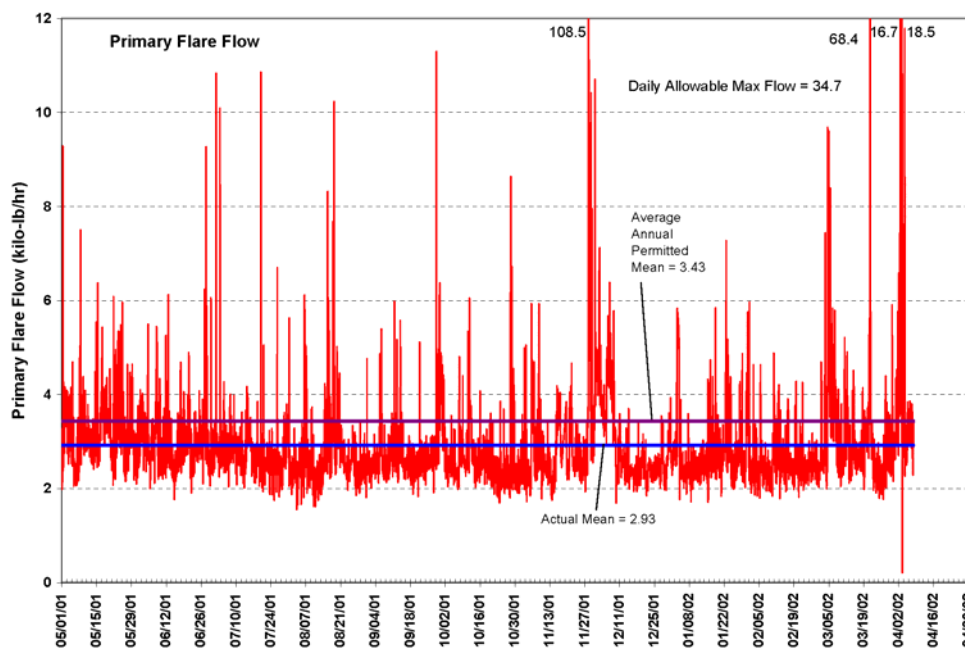


Figure 9. Variability in mass flow rates (a surrogate for emissions) to a flare at an olefins facility

Work is currently underway to link physical causes to these different types of mass flows; for example, an emission event may be caused by the failure of a compressor that feeds hydrocarbons to a reactor. This type of event leads to a very different PDF than the diurnal cycling of tanks (a nearly constant or routinely variable emission). Therefore, it should not be surprising that multiple PDFs might be required to represent an emission source. Figure 10 shows the multiple PDFs used to model a flare, and Figure 11 shows a simulated time series of emissions predicted using the multiple PDF model and an actual time series.

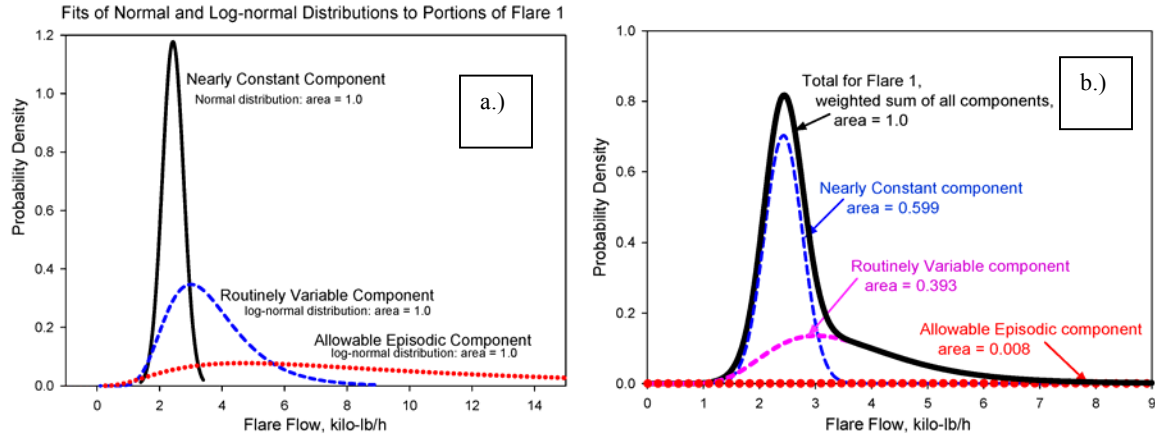
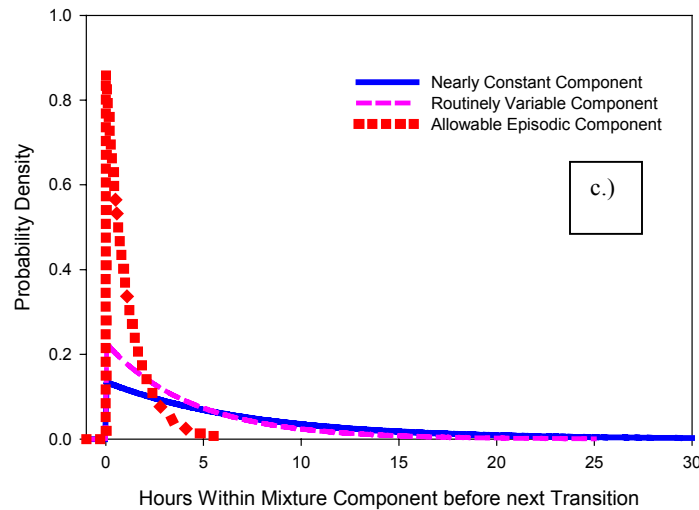


Figure 10. Three PDFs are used to model the emissions from a flare. To simulate an hourly emission, the emission model first randomly selects which flow mode the flare is in, nearly constant, routinely variable or allowable episodic (emission events are handled separately). Then an emission flow rate is selected for that hour, based on the PDF in Figure a. The combination of time in mode and probability of emission rate in each mode can be plotted as a composite PDF, shown in Figure b. For the next hour of emissions, the mode is selected based on the probability that the flare operates in the same mode as the previous hour, or transitions to a new mode – this probability is shown in Figure c.



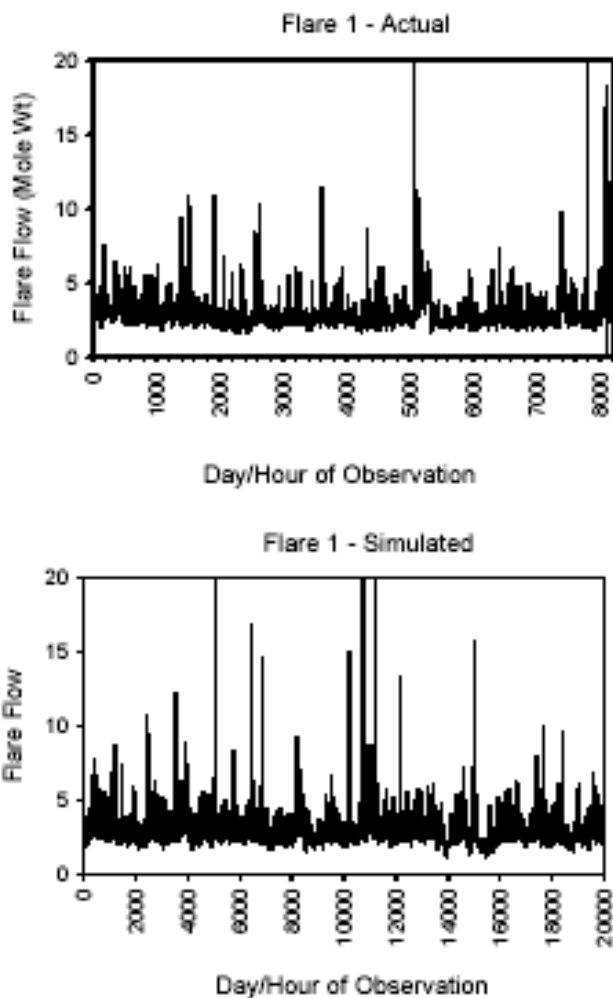


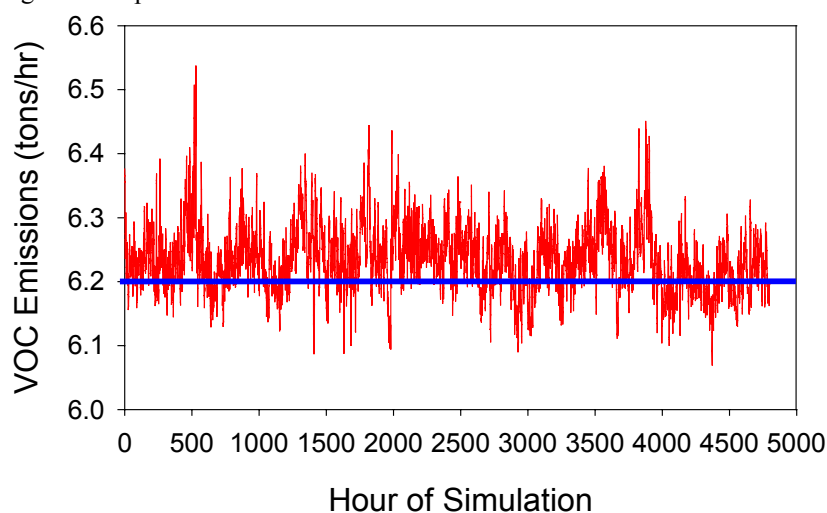
Figure 11. Simulated and actual time series of flare flow simulated using the model of Figure 10. Note that the goal is not to represent the exact time series, but to represent the variability in the time series.

With multiple PDFs, it is possible to provide a reasonable representation of emission variability from emission sources such as flares. The next step is to apply the variable emissions models to the entire Houston-Galveston area, rather than to just a single emission source. This involves some uncertainties, since the available data indicate that individual sources like flares may have very different emission variabilities, and there is not yet a reasonable basis for assigning specific emission types for every source in the region.

Nevertheless, some preliminary results are shown. The point of presenting these preliminary results is to assess how the overall emission variability will be affected by a large number of independently variable sources.

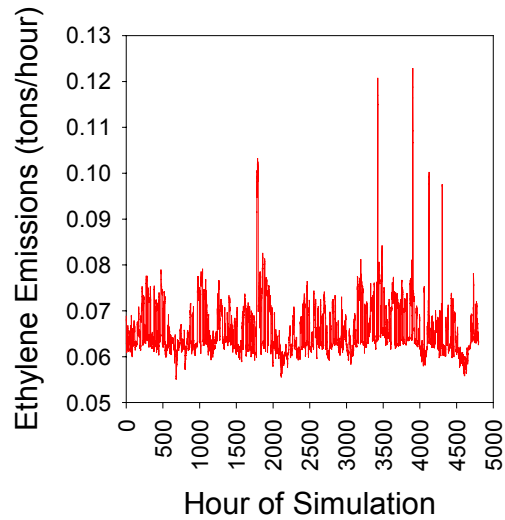
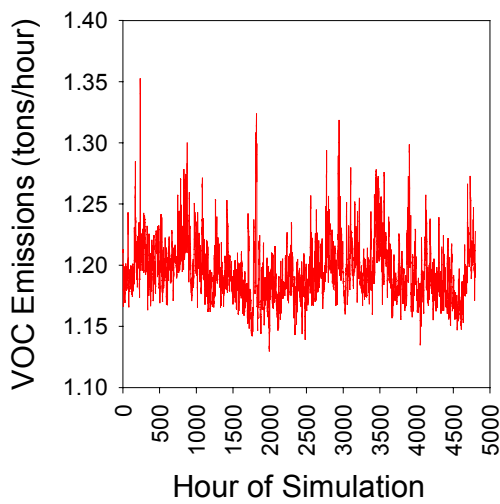
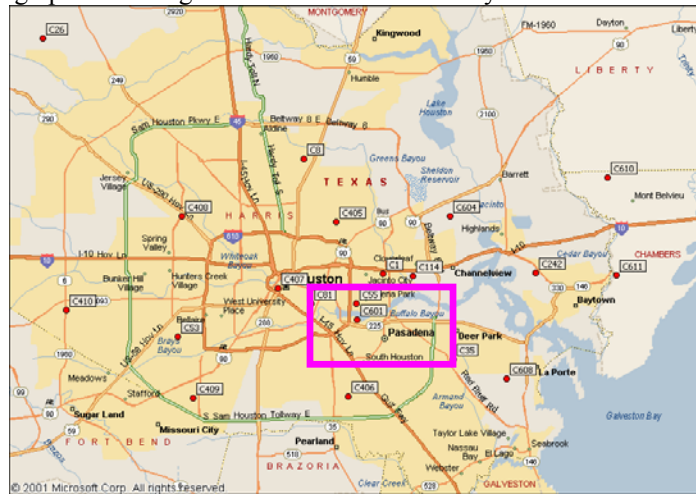
The analysis assumes that total annual emissions remain fixed, but that individual sources exhibit independent variability; so, if one source is in an allowable episodic emission mode, another source might be in a routine variability mode. Using these constraints, and eliminating large episodic events, a time series of the emissions for the entire region can be estimated. Figure 12 shows one possible hourly profile of total VOC emissions for 200 days (not including large emission events). This is an “instance” or random sample for the aggregate of all point source VOC emissions over all of the Houston Galveston area. Many other instances are possible. Note that the total variability in emissions, summed over the entire domain, is much less than the variability in any single source. The estimates suggest that the mass associated with this combined variability is about 5-10% of the inventory, comparable to the mass due to emission events (which are not included in this time series).

Figure 12. One possible hourly profile of total VOC emissions for 200 days. This is an “instance” or random sample for the aggregate of all point source VOC emissions over all of the Houston Galveston area.



To better characterize local impacts of variability in emissions, it is useful to focus on a specific geographic sub-region of interest. As an example, Figure 13 shows an estimated inventory for a region south of the ship channel and including Deer Park. Figure 13 also shows the estimated variability in the emissions in the subregion.

Figure 13. Geographical subregion and estimated variability in the emissions in that subregion



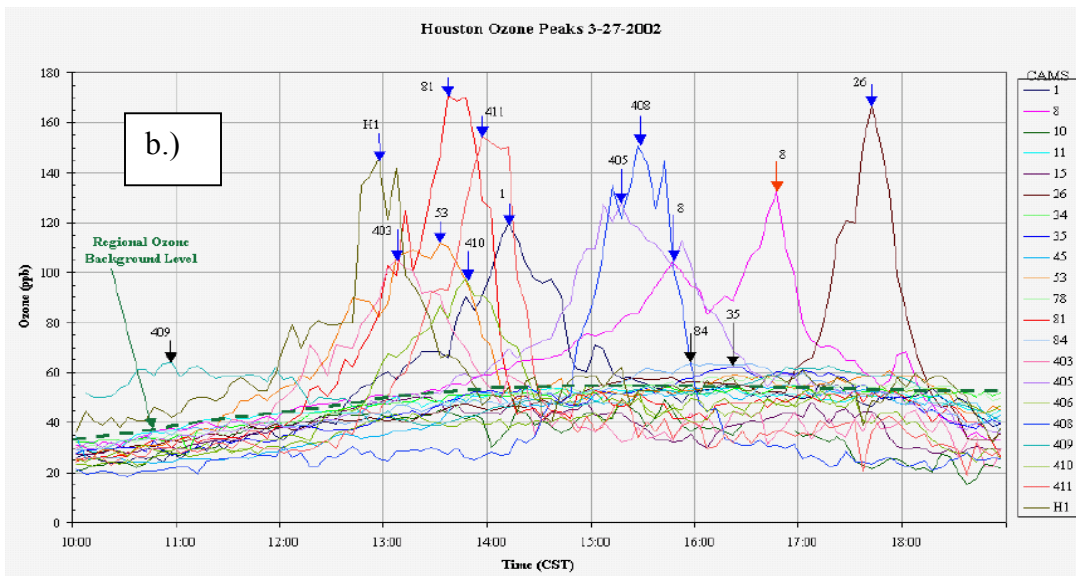
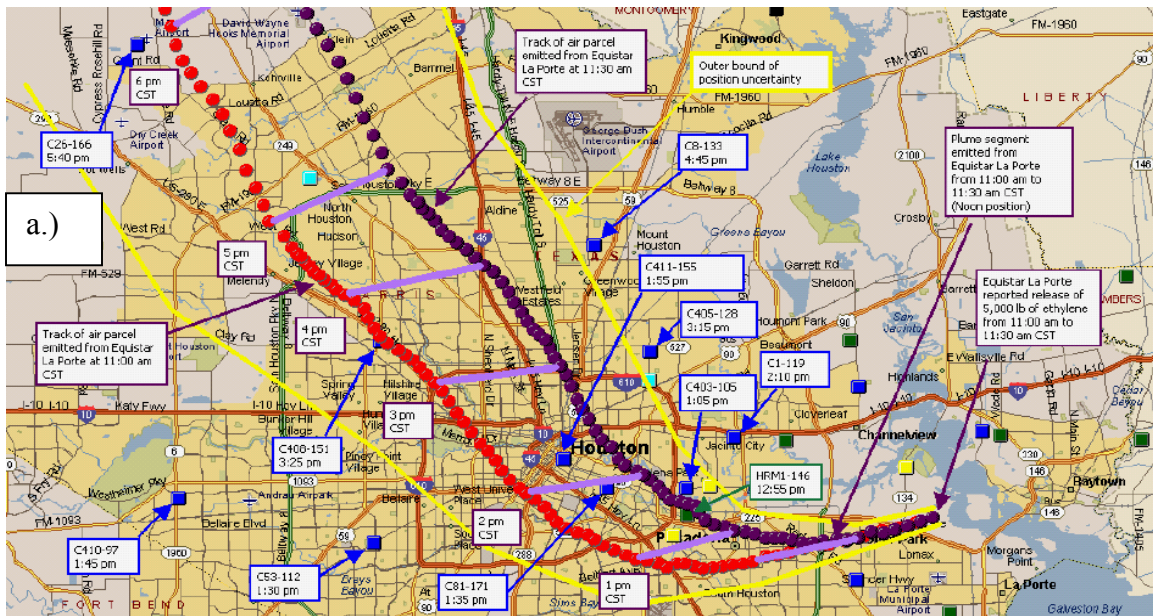
The 5-10% variability of total emissions in the subregion, with an area of approximately 100 km², is comparable to the variability in total emissions for the entire region, but for specific compounds, such as ethylene, the variability increases because a smaller number of sources is being considered. For ethylene, Figure 13 suggests that variability in emissions could cause emission rates in localized sub-regions to double for specific compounds roughly once per month.

Impact of Emission Variability on Ozone Formation

Only a small fraction of instances where emissions increase substantially above annual averages will lead to changes in the peak ozone concentrations in Houston. In order for emission events and other sources of emission variability to influence peak ozone concentrations, they must occur during times that are conducive to ozone formation and at locations that provide sufficient sources of other emissions (principally nitrogen oxides) that will lead to significant reactions of the emissions. Other work is examining the ozone formation consequences of the full range of emission variability, using computationally efficient tools. In this paper, the goal is to document the potential magnitude of changes in peak ozone concentrations, due to emission variability. The air quality episodes selected are, of necessity, extreme examples of the impact of emission variability on ozone concentrations, since these are the instances that are most evident in the observational record and in air quality modeling. While they should be recognized as extreme instances, they are useful to examine since they define the magnitudes of changes in ozone concentrations that emission variability can introduce.

One extreme episode that has been well documented by TCEQ staff occurred on March 27, 2002. In LaPorte, a series of ethylene releases totaling more than 10,000 pounds were released over several hours. One release of approximately 6700 pounds occurred between 11 AM and noon, lasting for approximately 30 minutes. This release was advected initially to the west, then to the northwest, passing over significant highway sources of NO_x . Most of the monitors in the Houston area showed peak concentrations of roughly 60 ppb on this day, however, several of the monitors that were in the path of the plume reached peak ozone concentrations in excess of 160 ppb. The estimated air parcel plume and the data from the ozone monitors are shown in Figure 14.

Figure 14. a.) Estimated trajectory of a 10,000+ lb ethylene release at LaPorte, (6700 lb between 11 and 11:25 AM) on 3/27/2002. b.) Multiple ozone monitors were in the path of the plume; other monitors were outside of the path.



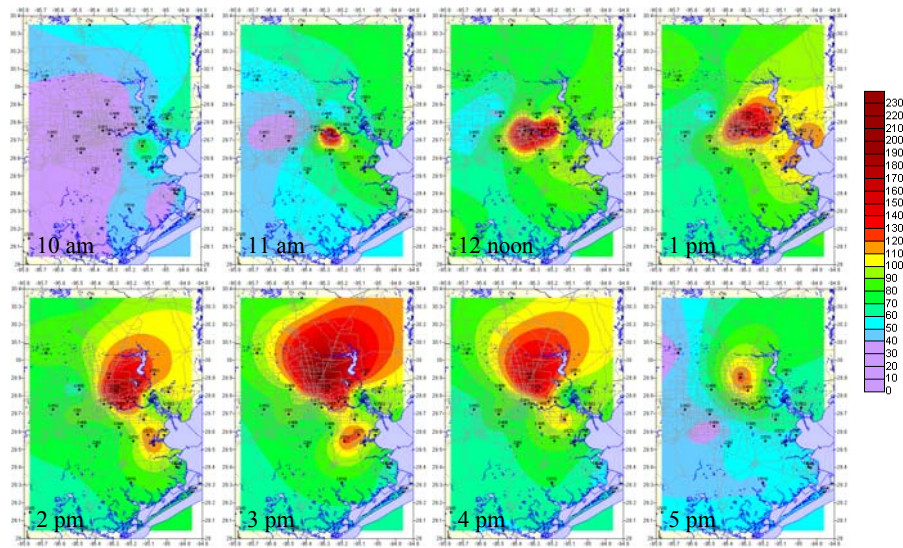
Another ozone episode that appears to be related to a emission variability occurred on October 23, 2003. On this date, ozone monitors detected a large plume of ozone originating in the area near the Clinton Drive monitor, which is located just east of the East 610 Loop where it intersects the 10 Freeway. As shown in Figure 15, peak ozone concentrations eventually reached more than 200 ppb at sites as distant as Aldine (near Bush Intercontinental Airport). Also detected at the Clinton site, were very high concentrations of hydrocarbons. These data are also shown in Figure 15.

Figure 15. Data from an ozone episode that occurred on October 23, 2003.

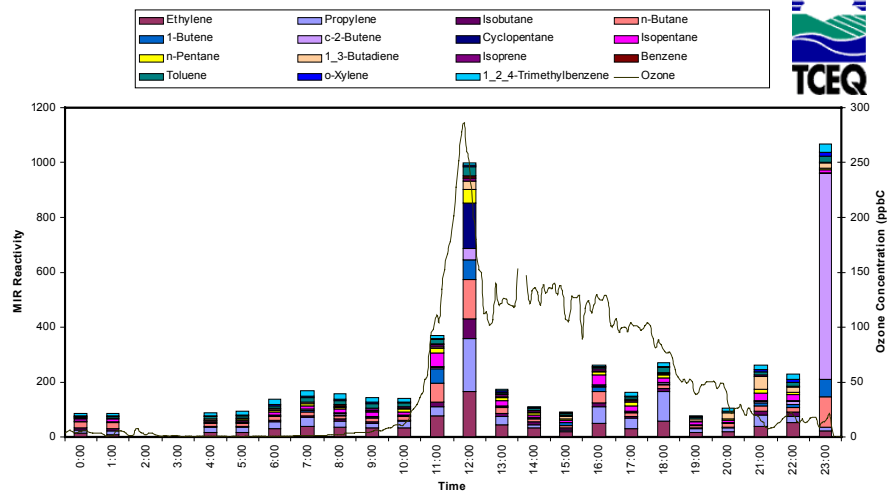
a.) high ozone concentrations, including concentrations in excess of 200 ppb were detected initially near the Clinton monitor at 11AM; high concentrations subsequently spread over a large region

b.) high hydrocarbon concentrations (represented in units of reactivity) were detected at the Clinton site at the start of the event

Contour Maps Showing the Progression of High Ozone on 10-23-03



Ozone Concentration (5 Min. Data) and VOC Reactivity Vs. Time at Clinton C403 for 10-23-03



Air quality models can also be used to assess the effect of instances of emission variability on peak ozone concentrations. One such analysis is shown in Figure 16, which shows the impact of a 10,000 lb/hr, 2 hour release in the region near Deer Park. This modeling was done using a 1-km grid resolution in the region of the release. The difference in peak ozone concentration between the simulation with the release and without the release is more than 50 ppb.

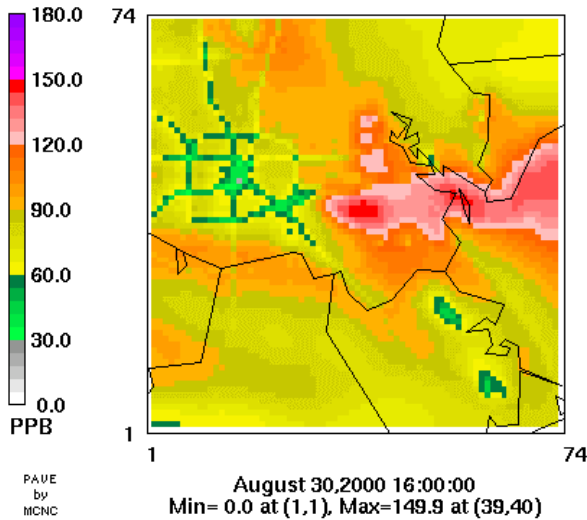
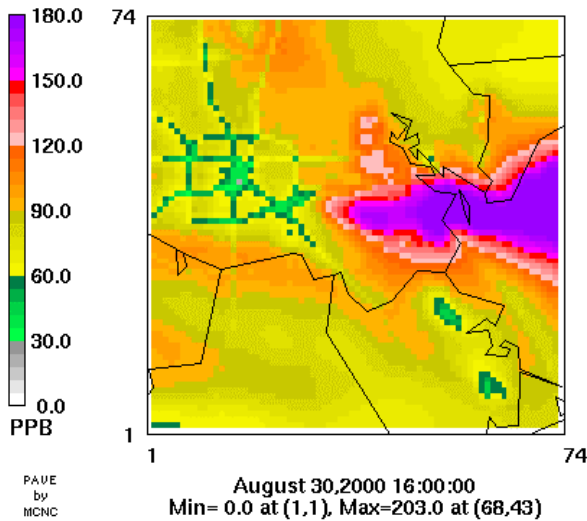


Figure 16. 3-D photochemical grid model simulation of an ozone episode on August 30, 2000, performed using the Comprehensive Air Quality Model with extensions (CAMx) at a 1-km grid resolution; the upper plot shows the base case simulation (peak ozone concentration of 150 ppb) with no emission event; the lower plot shows the ozone concentrations predicted if a 10,000 lb/hr, 2 hour reactive olefin release is added to the base case. The peak ozone concentration in the simulation with the release is in excess of 200 ppb, more than 50 ppb higher than in the base case.



Conclusions

Variability in VOC emissions from point sources is significant and is due to both variability in continuous emissions and discrete emission events. Roughly 3 times per month in 2003 in the Houston-Galveston area, reported emission events caused single facilities to have HRVOC

emissions that were greater than 10,000 lb/hr (the total annual average emissions of HRVOCs, from all industrial point sources in the Houston-Galveston region is approximately 5,000 - 10,000 lb/hr). Roughly 3 times per week in 2003, reported emission events caused single facilities to have HRVOC emissions that were greater than 1,000 lb/hr. Roughly once a day in 2003, reported emission events caused single facilities to have HRVOC emissions that were greater than 100 lb/hr. Variability in continuous emissions is more difficult to quantify than emission variability due to reported emission events, but preliminary modeling indicates that variations in continuous (as opposed to discrete) emissions could cause emissions of total VOCs, averaged over areas larger than 100 km², to vary by 5-10%. This emission variability can have a significant impact on ozone formation.

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