Appendix A

Event emissions in the Houston-Galveston Area

Event Emissions in the Houston Galveston Area (HGA)

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Summary

Characterization of emission events is critical to development of an accurate and representative emissions inventory in the Houston/Galveston Area (HGA). The recent implementation of Texas Commission on Environmental Quality on-line reporting has greatly facilitated access to event emission data, and a reduction in the reportable quantities for highly reactive volatile organic compounds (HRVOCs) has increased the number of events reported significantly. In this work, time series analyses are used to compare average annual flow rates for air pollutant emissions with those released during reported emission events. The results indicate that the magnitude and frequency of HRVOC event emissions are an important element in accurately reflecting HRVOC emission patterns in HGA, particularly in Harris, Brazoria, Galveston, and Chambers counties. More than 50% of the emissions are ethene, and approximately a third are propene; the remainder are isomers of butene and 1,3-butadiene. Most events last less than 24 hours and produce between 100 and 1000 pounds of emissions. Chemical manufacturing sources (SIC 2869) dominate the submitted reports. However, while there appears to be consistency in the type of source that is the greatest contributor, the specific facilities (reporting entities) that dominate appears to vary from year to year. Follow on work will require additional characterization of the nature of the events such that it is clear how best to include them in emission inventories used in photochemical modeling and policy development.

Introduction

Point sources in the Houston Galveston Area (HGA) are significant contributors to emissions associated with the formation of ground-level ozone. Those described as non-electric generating units (negus) are dominated by industrial operations which, for the purposes of photochemical modeling and State Implementation Plan (SIP) development, are generally assumed to produce constant and continuous emissions, as they typically operate 24 hours per day, 7 days per week, with relatively uniform material throughput. However, there are non-routine emissions referred to as "upsets" or "events" where, for short periods of time (typically less than 24 hours), greater than normal quantities of emissions are released. Aircraft data from the HGA gathered in the summer of 2000 suggests that these emissions are large (in terms of mass released), frequent, and highly localized [1] but characterization of these events over extended periods of time, and broad geographical areas, has proven difficult. Prior to late 2002, non-routine events were not recorded on a regular basis unless a reportable emission of greater than 5000 pounds in a 24-hour period was released. If included in photochemical modeling and emissions inventories, event emissions are generally treated as an average over time, effectively resulting in a uniform increase of routine emissions. Both lack of data and the lack of easy access to the data has made it difficult to quantitatively and accurately determine whether the magnitude and or frequency of event emissions appreciably affects ozone concentrations and rates of ozone formation, and if so how they are most effectively addressed in photochemical modeling and policy development.

Effective September 12, 2002, per Texas Administrative Code (TAC) Title 30 Chapter 101 [2], 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. Section 101.1, paragraph (83) defines a reportable emissions event as "Any emissions event which, in any 24-hour period, results in an unauthorized emission equal to or in excess of the reportable quantity…". Alkanes remain at the 5000 lb limit provided they contain less than 0.02% of ethene (ethylene), propene (propylene), butene (butylenes), toluene, acetaldehyde, or oxides of nitrogen, and less than 2.0% of any other reportable compound. In addition, Texas House Bill (HB) 2912 requires that air emission incidents be filed electronically and be posted in a publicly accessible database [3, 4]. This has resulted in the availability of on-line data for events beginning January 31, 2003 [5]. Since only one reportable compound triggers the generation of a report, the amount of data that has been collected and made available beginning in 2003 will allow a much more thorough and accurate characterization of event emissions.

Determining Effect of Upsets on Total Emissions

The purpose of the study described in this report is to determine the magnitude and variability of non-routine emissions relative to average annual emissions with a focus on the highly reactive volatile organic compounds (HRVOC) ethene (ethylene), propene (propylene), all isomers of butene (butylenes), and 1,3-butadiene [1]. In particular there are three key questions that are addressed:

Question 1: *Are the magnitudes of these events, singularly and collectively, significant relative to that of routine emissions*? The effect of individual events is examined by calculating flow rates (pounds per hour) of oxides of nitrogen (NO_X), volatile organic compounds (VOC), and

HRVOC during events and comparing these against annual average flow rates within the region and at specific facilities. Collective magnitudes are described by summing the mass of contaminants emitted at regional, local, and facility levels.

Question 2: *What variability in the emissions inventory is introduced by these events and does the frequency of the events warrant treating their associated emissions as a unique type, rather than simply adding them to routine emissions (as is currently the practice)?* If the frequency is very low, then the events may not be significant contributors to ozone events. If the frequency is very high, it might be just as effective (and simpler) to treat the events as a simple increase to routine emissions.

Question 3. *What are the characteristics of the events in terms of time, space, and composition?* The facilities, types of facilities, and/or facility locations that have the largest (greatest mass), most frequent, and most persistent events are identified. To the extent possible, 2003 event emissions are compared to emissions in prior years.

In order to answer these questions, data are being collected from the Texas Commission on Environmental Quality (TCEQ) Air Emission Event Reports, which can be downloaded from the Internet through an on-line reporting system [5]. The data are imported into a relational Microsoft Access® database developed by the University of Texas at Austin and data for analysis are selected and aggregated by enacting queries within the database. The specifics of the database and results of analyses conducted to date are presented later in this document. Event reports from the TCEQ website are searchable by customer (the owner or operator of a regulated entity), reporting entity (site), county, or TCEQ region. For the purposes of creating the relational database, the data are gathered by TCEQ region. The earliest date available is January 31, 2003. Initially, it was necessary for facilities to fax in reports for TCEQ personnel to enter. This resulted an average lag time of approximately one month between the actual onset of an event and the date it was posted to the web site. Between March 31 and October 22 final reports (but not initial reports) could be either entered electronically or faxed. As of October 22, 2003, all reports can be submitted electronically [3]. This has resulted in nearly “real-time” reporting.

Air Emission Event Reports

The data available at the TCEQ website [5] were downloaded for all of Region 12, which includes the 8-county HGA non-attainment area (Figure 1). All events that have occurred and have been posted since January 31, 2003 are included in the Access database developed by the University of Texas. This report will examine emissions through December 31, 2003. Each event is called up as a single screen, referred to as an air emission incident report, and appears as in Figure 2. All of the elements contained in each report are imported into the Access database; those that are not self-explanatory are described below.

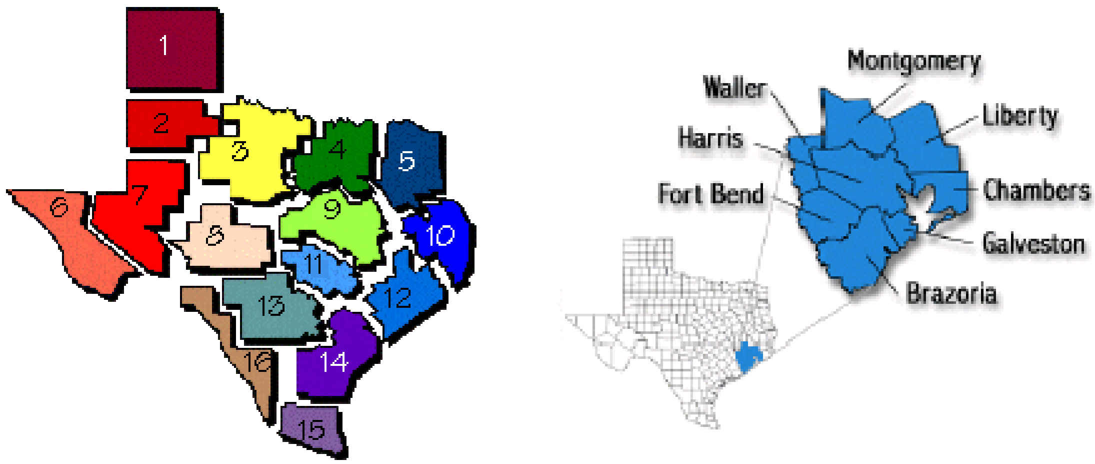


Figure 1. Map of TCEQ Region 12 and the 8-county HGA non-attainment area [6].

<u>Tracking Number</u>

Each event is assigned a tracking number. The tracking number is a unique identifier. Facilities must submit a report within 24 hours of the onset of an emission event [7]. They may first submit an initial report, to be replaced by a final report within 2 weeks. When this occurs the tracking number does not change. The intent is for each tracking number to represent a particular failure or maintenance event. However, instances do occur where lack of immediate understanding of the problem can result in multiple tracking numbers and therefore multiple "events" for a single root cause. Conversely, what may be reported as a single event might actually have a number of releases and possibly multiple root causes. This is particularly likely in the case of maintenance related activities.

Search Results - Air Emission Event Report for Tracking Number 27125

Regulated entity name	EXXON MOBIL BAYTOWN FACILITY	**Physical location**	2800 DECKER DRIVE
Regulated entity RN number	RN102579307	**City, County**	BAYTOWN, HARRIS
Type(s) of air emissions event:	EMISSIONS EVENT	**Event began:**	09/03/2003 10:00AM
This is based on the:	INITIAL REPORT	**Event ended:**	09/04/2003 10:00AM
Cause	Coker handling problems.		
Action taken	Rerouted gas to other equipment.		
Emissions estimation method			

Source 1: Baytown Refinery, FIN number NO FIN

Source 2: Flare Stack 25, EPN number FS25

Contaminant	Authorization	Limit	Amount Released
Carbon Monoxide		0.0	660.0 lbs (est.)
Hydrogen sulfide		0.0	100.0 lbs (est.)
Nitrogen dioxide		0.0	12.0 lbs (est.)
Nitrogen oxide		0.0	110.0 lbs (est.)
OPACITY		0.0	100.0 % op (est.)
Sulfur dioxide		0.0	9250.0 lbs (est.)
VOC		0.0	250.0 lbs (est.)

Source 3: Flare Stack 26, EPN number FS26

Contaminant	Authorization	Limit	Amount Released
Carbon Monoxide		0.0	3195.0 lbs (est.)
Hydrogen sulfide		0.0	270.0 lbs (est.)
Nitrogen dioxide		0.0	59.0 lbs (est.)
Nitrogen oxide		0.0	528.0 lbs (est.)
Sulfur dioxide		0.0	24903.0 lbs (est.)

Source 4: Flexicoker Unit, FIN number

No other sources

Initial Reports replaced with
Final Reports using same Tracking Number
but must open report to determine type

One report may include multiple sources

VOCs may or may not be speciated

Figure 2. Example of an air emission incident report from TCEQ web site [5]. Downloaded October 2003.

Regulated Entity Name and Number

A "regulated entity" is a person, organization, place, or thing that is of environmental interest to the TCEQ. In almost all instances it can be identified by a physical location and may therefore be referred to as a site. The entities are coded by a number starting with RN and followed by nine digits. Note that air operating permit accounts numbers are not included and that reported events are not always associated with permitted facilities.

Type(s) of Air Emissions Event

There are two general and five specific categories of air emissions events [7]. Unscheduled events include Emissions Events (EEs) (formerly Upset Events) and Excess Opacity Events (EOE). Scheduled events are referred to collectively as Scheduled Maintenance, Startup and Shutdown (SMSSA) but are entered specifically as Maintenance, Air Startup, or Air Shutdown in the air emission incident report.

This is Based on the

Facilities must submit an initial report within 24 hours of the onset of an unscheduled emission event (Emissions Event or Excess Opacity Event). An “Initial” report for scheduled events is to be submitted ten days in advance (or as soon after as possible) of the activity using projected, potential emissions. For both scheduled and unscheduled events, a “Final” report is to be submitted within 2 weeks of the end of the event. If all the required information is available at the time of the event, a final report may be submitted in lieu of the initial report. Early in 2003, it was common for the database to contain primarily final reports, but with the implementation of electronic submission of initial reports, the appearance of initial reports has become more common.

It has been observed that replacement of “Initial” with “Final” reports does not always occur within the prescribed time frame. On December 31, there were 270 reports with events ending on or before December 16 that were still labeled as initial; most (241) are unscheduled events. The HRVOC emissions involved in all 270 reports account for a total of 113,804 pounds of emissions (more than 7% of the total HRVOC event emissions reported in 2003). Most are related to maintenance, shut down, and start up activities; only 34,497 pounds are from unscheduled events. This apparent discrepancy between the low number of scheduled events designated as initial and the large amount of emissions associated with them is due to the requirement that initial scheduled events be filed 10 days in advance and provide what is expected to be a worst case scenario in terms of total emissions.

For the purpose of the analyses presented in this work, data contained in “Initial” reports are treated identically to that in “Final” reports. This decision was based on the number of initial reports that had not been replaced with final reports and on an early comparison between the two that suggested that most changes between initial and final tended to be relatively minor. However, this is not always the case. In one instance involving a maintenance event, there was an extremely large drop in reported emissions from 19,528 lbs of 1,3-butadiene to only 1055 lbs. This difference resulted in an apparent 40% increase in the inventory for this species during the time that data from the initial report were being used in the analysis.

The website does not allow for searches based on whether the reports are final or initial; each report must be opened separately to check for updates. In addition, since initial reports are replaced by final reports it can be difficult to analyze historical changes. It is suggested that a specific effort be made to characterize the potential errors that can occur through the use of initial reports.

Event Ended

There are 21 events with start dates prior to December 16,2003 and with an end date of Dec 30, 1899. 12 are emission events. No explanation was found as to the significance of the use of the 1899 date. The reports are a mixture of "Initial" and "Final" reports. In order to include these events in the analysis, a one-hour duration was assumed.

Sources

Typically there is only one source involved in a single event, but as many as six have been noted in the reports filed for 2003. There are four columns of information associated with the "Source" portion of the report (Figure 2) but only the first (Contaminant) and last (Amount Released) are used consistently. The naming convention in the first column (Contaminant) is not uniform so an analysis of the contaminants must include a grouping by CAS number or other uniform identification system. Information included in the second column (Authorization) usually lists the permit number if applicable. The third column (Limit) is intended to include the permitted amount in pounds per hour. Roughly half the events list a permitted value of zero. The value entered in the fourth column under "Amount Released" is almost always in estimated pounds (as in Figure 2). In at least two instances, however, the amount was entered in pounds per hour. In the case of the more significant event, this was found (through communication with the reporting entity) to be an error and should in fact have been reported simply as pounds. This was made into a universal assumption (i.e., any report with pounds per hour is automatically converted to pounds). One event listed the amounts as unknown; it was not included in the time series analysis.

Relational database

Data from each air emission incident report available at the TCEQ web site [5] are imported into a relational Access database. There are five key tables included in the database: tbl_Header, tbl_Source, tbl_Time_Series, tbl_Contaminant_Codes, and tbl_Reporting_Entities.

Header and Sources

The table tbl_Header includes separate fields for each of the elements included at the top of the incident report (the area of the report above "Source 1" in Figure 2). The fields are named in a manner similar to that used in the report. There are two additional fields that allow for comments to be added and for data to be excluded during the query process if desired.

The table tbl_Source is linked to tbl_Header by the tracking number. Each record includes the description of the source and the four columns included under each source (Figure 2). In addition, the source is identified by number as well as description, the event duration is calculated, and a column is added to allow the contaminant to be excluded. Contaminants that are not assigned a mass, such as opacity, are automatically excluded (Table 1) for the purposes of time series analysis.

Table 1. Records for event 27125 (shown in Figure 2) as imported into "tbl_Source" in the Access relational database.

Tracking_ Number	Source_ Number	Source	Event_ Began	Event_ Ended	Duration_ Minutes	Contaminant	Authorization	Limit	Amount_ Released	Rate_Per_ Minute	Exclude
27125	2	Source 2: Flare Stack 25, EPN number FLARE25	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	Carbon Monoxide	Not specifically authorized	0.0	666	0.4625	FALSE
27125	2	Source 2: Flare Stack 25, EPN number FLARE25	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	Hydrogen sulfide	Not specifically authorized	0.0	100	0.0694444	FALSE
27125	2	Source 2: Flare Stack 25, EPN number FLARE25	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	Nitrogen dioxide	Not specifically authorized	0.0	12	0.0083333	FALSE
27125	2	Source 2: Flare Stack 25, EPN number FLARE25	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	Nitrogen oxide	Not specifically authorized	0.0	110	0.0763889	FALSE
27125	2	Source 2: Flare Stack 25, EPN number FLARE25	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	Sulfur dioxide	Not specifically authorized	0.0	9250	6.4236111	FALSE
27125	2	Source 2: Flare Stack 25, EPN number FLARE25	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	VOC	Not specifically authorized	0.0	250	0.1736111	FALSE
27125	2	Source 2: Flare Stack 25, EPN number FLARE25	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	OPACITY	Not specifically authorized	0.0		0	TRUE
27125	3	Source 3: Flare Stack 26, EPN number FLARE26	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	Carbon Monoxide	Not specifically authorized	0.0	3195	2.21875	FALSE
27125	3	Source 3: Flare Stack 26, EPN number FLARE26	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	Hydrogen sulfide	Not specifically authorized	0.0	270	0.1875	FALSE
27125	3	Source 3: Flare Stack 26, EPN number FLARE26	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	Nitrogen dioxide	Not specifically authorized	0.0	59	0.0409722	FALSE
27125	3	Source 3: Flare Stack 26, EPN number FLARE26	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	Nitrogen oxide	Not specifically authorized	0.0	528	0.3666667	FALSE
27125	3	Source 3: Flare Stack 26, EPN number FLARE26	9/3/03 10:00 AM	9/4/03 10:00 AM	1440	Sulfur dioxide	Not specifically authorized	0.0	24903	17.29375	FALSE

Not shown in Table 1 is a field entitled Contaminant_Code. If the contaminant name has been previously used, the identifying number from the table tbl_Contaminant_Codes (described below) is assigned. If the name has not previously been entered into tbl_Source, a new identifying number is assigned. This allows the table tbl_Contaminant_Codes to be updated.

Time Series

The table tbl_Time_Series is used to assign 1-hour blocks of time to yearly hours from 1 to 8760 (1 being January 1 12:00 AM to 12:59 AM and 8760 being December 31 11:00 PM to 11:59 PM). Data are stored in minutes, but one hour is consistent with the photochemical model used for the Houston Galveston area and is a manageable unit for time series analyses. The table is also used to assign categories of interest to the time block. These currently include the date, the month, day of the week, hour of the day, and whether the hour is night (6:00 PM to 6:00 AM) or day. These categories are intended for examination of temporal patterns.

Contaminant Codes

The table tbl_Contaminant_Codes unifies the naming convention of individual species, assigns categories related to criteria pollutant names, distinguishes between HRVOC, VOC, and unspeciated VOCs, places the contaminants in general categories of interest, and assigns a Chemical Abstracts Service Registry Number (CAS #) to each species (where appropriate and available). Uniform species names and CAS # are assigned based on entries in the database available at the Chemfinder.com web site [8]. For compounds not listed at the Chemfinder.com web site, a separate search was completed using the Google Internet search engine [9], with limited success. Some of the compounds are proprietary, while others had common names that could be subsequently used in a Chemfinder.com search. Not all of the contaminants are reported in a manner specific enough to assign a CAS #, such as VOCs, alkanes, and other generalized terms.

The tbl_Contaminant_Codes table will be modified in the near future to include fields that categorize VOC contaminants by Carbon Bond 4 mechanism (CBIV) classification for use in the Comprehensive Air Quality Model with Extensions (CAMx) [10]. Contaminants will also be coded by SAPRC-99 chemical mechanism [11, 12]. Coding will be consistent with that used by Carter at the University of California at Riverside [13].

Table 2 displays a sample of the records contained in tbl_Contaminant_Codes. As of December 31, 2003, a total of 405 different terms, representing 267 different species (240 with CAS #s), had been used in the air emission incident reports downloaded from the TCEQ web site. Not shown in Table 2 is a field entitled Contaminant_Code that is linked to tbl_Source. This is a sequentially assigned, unique identification number based on the exact term (including spelling and punctuation) used in the event report. Table 3, which shows all of the HRVOC species reported to date, includes this field. It can be seen that four different terms for ethene (ethylene) are used and that each has been assigned a unique identification number; however, the remaining three fields (Contaminant_Name, Gen_Category, and CAS#) are identical.

As data are imported into tbl_Source, the term used to name the contaminant in the report is matched to that those contained in tbl_Contaminant_Codes using this sequentially assigned identification number. If the term is not currently in the table, no code is assigned until an update query is run. This must be done manually and is completed after each session of importing data.

Table 2. Fields and sample of records included in tbl_Contaminant_Codes

Contaminant	Contaminant_Name	Critical_Category	Gen_Category	CAS#
2,3 Dimethylbutane	2,3-Dimethylbutane	VOC	>C5 alkane	79-29-8
2-Butene-cis	2-Butene-cis	VOC-HR	Butene (Butylene)	590-18-1
Acetone	Acetone	LROC	Other organic	67-64-1
Acrolein	Acrolein	VOC	Other VOC	107-02-8
Ammonia	Ammonia	NH3	Inorganic	7664-41-7
Argon	Argon	none	Inorganic	7440-37-1
Carbon Monoxide	Carbon Monoxide	CO	Inorganic	630-08-0
Cyclopentadiene	Cyclopentadiene	VOC	>C4 Alkene	542-92-7
Ethylene (gaseous)	Ethylene	VOC-HR	Ethene (Ethylene)	74-85-1
Isobutanol	2-Methyl-1-propanol	VOC	Alcohol	78-83-1
Isopar C	2,2,4-Trimethylpentane	VOC	>C5 alkane	540-84-1
Isopar E	Isopar E	VOC	>C5 alkane	
Isopentane	2-Methylbutane	VOC	C3, 4 or 5 alkane	78-78-4
Nitrogen dioxide	Nitrogen Dioxide	NOX	Inorganic	10102-44-0
polyethylbenzene (PEB)	Naphtha	VOC	Aromatic	8030-30-6
POM	Chloromethyl pivalate	VOC	Other VOC	18997-19-8
Propadiene	propadiene	VOC	Propadiene	463-49-0
Propylene (Propene)	Propylene	VOC-HR	Propene (Propylene)	115-07-1
silica catalyst fines	Silica	PM	Inorganic	7631-86-9
Sulfur dioxide	Sulfur Dioxide	SO2	Inorganic	7446-09-5
1,3-BUTADIENE	Butadiene	VOC-HR	Butadiene	106-99-0
VOC-Sour Light Ends	VOC	VOC	VOC unspeciated	
C6 Parafins	hexane	VOC	>C5 alkane	110-54-3
1,2-Butadiene	1,2-Butadiene	VOC	Butadiene	590-19-2
Cresol-Formaldehyde novalak Resin	Cresol-Formaldehyde novolac Resin	VOC	Polymer	proprietary

Contaminant: Term imported directly from the TCEQ air emission event report
Contaminant Name: Common term assign to compound based on ChemFinder.com database.
Critical Category: Category assigned for current analysis; includes criteria pollutant names plus LROC (low reactivity organic compound) for organic compounds that are excluded from the VOC category from a regulatory standpoint and VOC-HR for compounds that are regulated as highly reactive VOCs.
(General) Gen Category: Coarse grouping of compounds for general analysis (not currently in use except to search for all isomers of butene).
CAS# (Chemical Abstracts Service Registry Number) Based on ChemFinder.com database.

Table 3. HRVOC Records Included in tbl_Contaminant_Codes

Contaminant	Contaminant_Code	Contaminant_Name	Gen_Category	CAS#
Ethene	411	Ethylene	Ethene (Ethylene)	74-85-1
Ethylene (gaseous)	420	Ethylene	Ethene (Ethylene)	74-85-1
Ethylene (liquid)	421	Ethylene	Ethene (Ethylene)	74-85-1
Ethylene, gaseous	423	Ethylene	Ethene (Ethylene)	74-85-1
Propene	546	Propylene	Propene (Propylene)	115-07-1
Propylene (Propene)	549	Propylene	Propene (Propylene)	115-07-1
butene, 1-	357	1-Butene	Butene (Butylene)	106-98-9
1-Butene	885	1-Butene	Butene (Butylene)	106-98-9
2-Butene	311	2-Butene (cis and trans)	Butene (Butylene)	107-01-7
c-2-butene	365	2-Butene (cis and trans)	Butene (Butylene)	107-01-7
Isobutene	455	isobutylene	Butene (Butylene)	115-11-7
Isobutylene	457	isobutylene	Butene (Butylene)	115-11-7
Butene	356	Butene	Butene (Butylene)	25167-67-3
butenes	358	Butene	Butene (Butylene)	25167-67-3
butenes/butanes	359	Butene	Butene (Butylene)	25167-67-3
Butylene	363	Butene	Butene (Butylene)	25167-67-3
2-Butene-cis	312	2-Butene-cis	Butene (Butylene)	590-18-1
Cis-2-butene	382	2-Butene-cis	Butene (Butylene)	590-18-1
2-Butene-trans	313	2-Butene-trans	Butene (Butylene)	624-64-6
t-2-butene	560	2-Butene-trans	Butene (Butylene)	624-64-6
Trans-2-butene	568	2-Butene-trans	Butene (Butylene)	624-64-6
Butadiene	349	Butadiene	Butadiene	106-99-0
butadiene, 1,3-	351	Butadiene	Butadiene	106-99-0
Butadiene, 1-3	352	Butadiene	Butadiene	106-99-0
1,3-BUTADIENE	883	Butadiene	Butadiene	106-99-0

Contaminant: Term imported directly from the TCEQ air emission event report
Contaminant Code: Unique sequential number assigned to terms used in event reports.
Contaminant Name: Common term assign to compound based on ChemFinder.com database.
(General) Gen Category: Coarse grouping of compounds for general analysis (not currently in use except to search for all isomers of butene)
CAS# (Chemical Abstracts Service Registry Number) Based on ChemFinder.com database.

Reporting Entities

The table tbl_Reporting_Entities is linked to tbl_Header by the Regulated Entity RN number, a number starting with RN and followed by nine digits (see Figure 2). Two fields in this table, RN_Number and Company_Name are updated from data in tbl_Header using an append query within the Access database. All other fields are entered manually. Information for the fields County, TCEQ Air Account Number, SIC, and NAICS were acquired from the TCEQ Central Registry web site [14]. Annual NO_X and VOC emissions by TCEQ Air Account Number are from the TCEQ 2000 and 2001 point source databases [15]. The 2000 special inventory, which includes HRVOC emissions from selected accounts in Harris, Galveston, Brazoria, and Chambers Counties has also been included [16]. Total 2001 HRVOC event emissions based on a threshold of 5000 rather than 100 lbs are provided to allow for comparison with 2003 data [17].

In order to locate entities, it is planned that latitude and longitude data will ultimately be entered for all sources for which a location can be determined with some precision. For those reporting entities that represent the larger permitted entities in the Houston Galveston non-attainment area (HGA), Lambert Conformal Projections (LCP) location data are available from the current photochemical model input files. These have been entered into tbl_Reporting_Entities.

Between January 31, 2003 and December 31, 2003, there were 162 different entities reporting event emissions (154 in HGA and 140 in four of the HGA counties - Brazoria, Chambers, Galveston, and Harris). Of the 79 entities reporting HRVOC events only one was outside HGA (Markham Plant Station 24, listed as a natural gas separation and dehydration facility, emitted one pound of ethylene) and only one within HGA was outside the four major counties (Chevron Pipeline in Liberty County emitted 558 pounds of ethylene in a single 30 minute event).

Analysis of Event Magnitude and Frequency

General Characteristics of Events

As of December 31, 2003 a total 1727 events occurring in TCEQ Region 12 and beginning on or after January 31, 2003 had been posted on the TCEQ web site [5]. A summary of these events is presented in Table 4. The release of HRVOCs was involved in approximately 40% (711) of these events. Significant HRVOC event emissions, both in terms of frequency and mass are limited to four counties, Harris, Brazoria, Galveston, and Chambers; 709 out of 711 (99.72%) events and 1,666,540 lbs out of 1,667,009 lbs (99.97%) occur in these four counties.

Table 4. TCEQ Region 12 events posted between January 31, 2003 and December 31, 2003

County	All Events	HRVOC Events	Event HRVOCs		Point Source HRVOCs TPY (2000)**	Point Source VOCs TPY (2001)*
			lbs	tons		
Harris	934	423	816,961	408	4,736	28,992
Brazoria	331	187	759,853	380	1,433	6,251
Galveston	329	86	69,229	35	515	8,342
Chambers	53	13	20,497	10	112	1,788
4 County Total	1,647	709	1,666,540	833	6,796	45,373
Fort Bend	40					798
Montgomery	19					730
Liberty	1	1	558	<1		475
Waller	2					205
HGA Total	1,709	710	1,667,098	833	6,796	47,581
Matagorda	11	1	1	<1		290
Colorado	4					170
Wharton	2					525
Walker	1					16
Austin	0					458
Region 12 Total	1,727	711	1,667,099	833	6,796	49,040

*TCEQ Point Source Database [15]
**TCEQ Special Inventory [16]

It can be seen from Table 4 that the mass of emitted HRVOCs is relatively low when considered on an annual time-scale and over a broad geographic region (i.e., at the county level). The mass of HRVOCs emitted as events, relative to annual VOC emissions, is less than 2%; relative to annual HRVOC emissions HRVOC event emissions constitute about 12% of the total. As will be discussed below, 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.

Time Series

The first step in performing time series analyses is to create time series data sheets for contaminants and groups of contaminants. In order to do this, emissions are first converted to flow rates by dividing the total amount of each contaminant emitted during an event by the duration of the event. Second, blocks of time are selected. For this analysis, each of the 8760 hours in a year is designated as a time-block. Third, the function that describes the flow rate as a function of time is defined. In the work presented below, all are assumed to be uniform flow rates, therefore the function is defined as y = mass/time. Last, the integrated emissions are distributed over each block of time and each block of time is assigned a total mass.

The uniform flow rate used in these analyses is the most conservative estimate of peak emissions flow rate. For example, assume that there is an event that starts on August 13 at 3:15 am and ends at 5:30 pm of the same day. During this 14.5 hour time interval, 1250 pounds of HRVOC are emitted. A graph of the resulting values entered into the time series data sheet are illustrated in Figure 3. Modeled as a uniform flow, the mean (and peak) flow of HRVOC during this episode is 86 pounds per hour between 4:00 am and 5:00 pm. In the first one-hour block, the flow is only three-fourths that (or 64.5 lbs per hour) because the event does not start until 15 minutes into the interval. Similarly, the flow rate in the last block is only 43 pounds per hour.

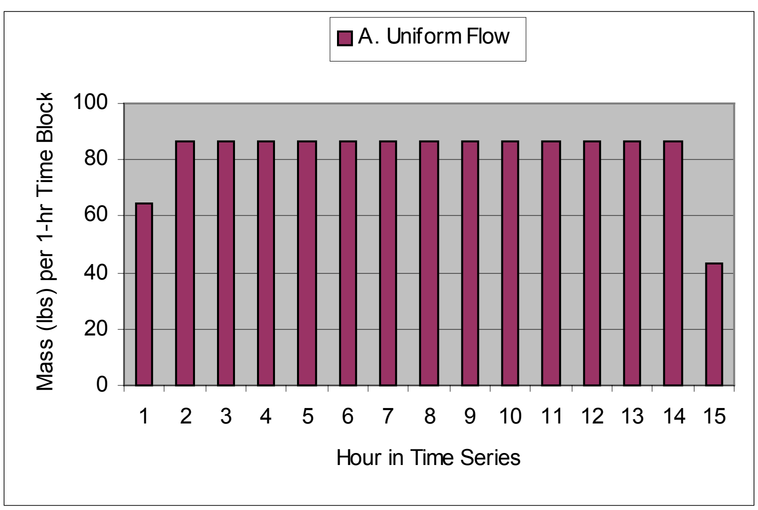


Figure 3. The graph gives the mass per one-hour time block for a 14.5 hour 1250 pound event beginning 15 minutes into a one hour time block and ending 30 minutes into the final one hour time block, modeled as a uniform flow.

If instead this event were modeled as a “burst” of emissions with exponential decay, the peak would be much higher than 86 pounds per hour. In the example shown in Figure 4, the peak occurs at 391 lbs/hr.

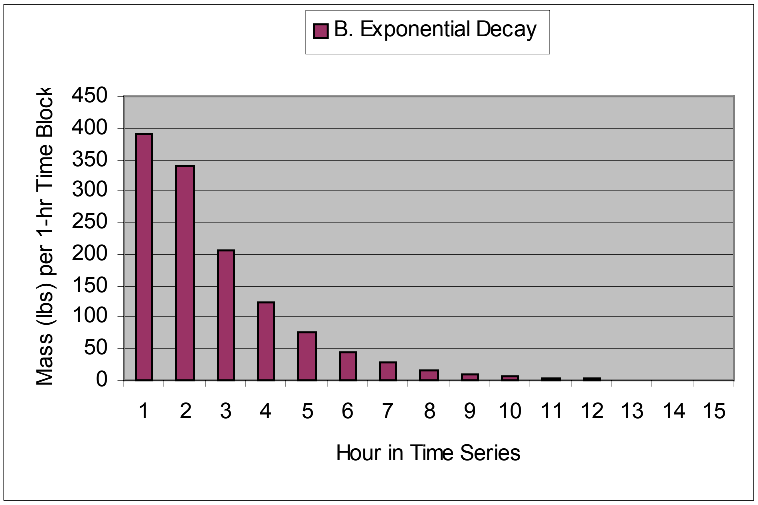


Figure 4. The graph gives the mass per one-hour time block for a 14.5 hour 1250 pound event beginning 15 minutes into a one hour time block and ending 30 minutes into the final one hour time block, modeled as a burst of emissions with exponential decay.

The use of non-uniform flow rates will require more information to determine the most appropriate distributions. One possibility is to use different distributions based on the cause and/or nature of the event

More important than determining the shape of the curve may be selection of an appropriate time unit. The one-hour unit is consistent with the photochemical model used to model ozone formation in the Houston Galveston Area. However, independent of the model, several questions need to be considered if one wishes to optimize for this factor. First to be considered are reaction rates. Based on reaction rate data [10], it is estimated that 60% of propylene emitted during ozone season, daylight hours, in urban areas, will react within 60 minutes. While not conclusive, this suggests that a shorter unit of time might provide more definition in modeling.

Second is the length of actual events. If the typical length of time for an individual event is equal to or less than the time-block, the flow rate can be significantly underestimated. As an illustration of this, consider an event that lasts 30 minutes and emits 1000 pounds. If the event begins and ends within a single 1-hour time block, the flow rate assigned to that block is 1000 lbs/hr. However, during the event, the actual rate is 2000 lbs/hr. If the event begins 15 minutes before and ends 15 minutes after a 1-hour time block, each block is assigned half the mass and the flow rate in each block is determined to be 500 lbs/hr or only 25% of the actual flow rate.

Despite these limitations, current time series analyses can be used to help answer the first two questions posed earlier in this document:

Question 1. *Are the magnitudes of these events, singularly and collectively, significant relative to that of routine emissions?*

Question 2. *What amount of variability in the emissions inventory is introduced by these events and does the frequency of the events warrant treating their associated emissions as a unique type, rather than simply adding them to routine emissions (as is currently the practice)?*

All of the time series assume a uniform flow and a 1-hour time block. Based on the minimal contribution to event emissions from entities located in counties other than Harris, Galveston, Chambers, and Brazoria (Table 4), all of the data are limited to these four counties.

Figure 5 presents a time series graph of NO_X event emissions as reported and retrieved from the TCEQ on-line reporting system between January 31 and December 31, 2003 [5]. In addition, 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 [15] 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. 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 NOx 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. Because the magnitude is low, the frequency was not evaluated.

Figure 6 presents a time series graph of VOC event emissions in the same format as for NO_X. The average annual flow rate for all of the facilities in the 4 county region, 10,359 lbs/hr, appears as a horizontal line. In contrast to NO_X, there are 14 times during the eleven-month period in which 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 (2018 tons) contributes only a little over 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.

The frequency of these events (more than one per month) warrants further investigation. Many of the events involve unspeciated VOCs and it is unknown whether these many involve significant amounts of HRVOCs. In addition, VOCs that have lower reaction rates than the four identified HRVOC species may be of interest because of their large total mass and persistence. However, a larger examination of VOCs is out of the scope of the current effort.

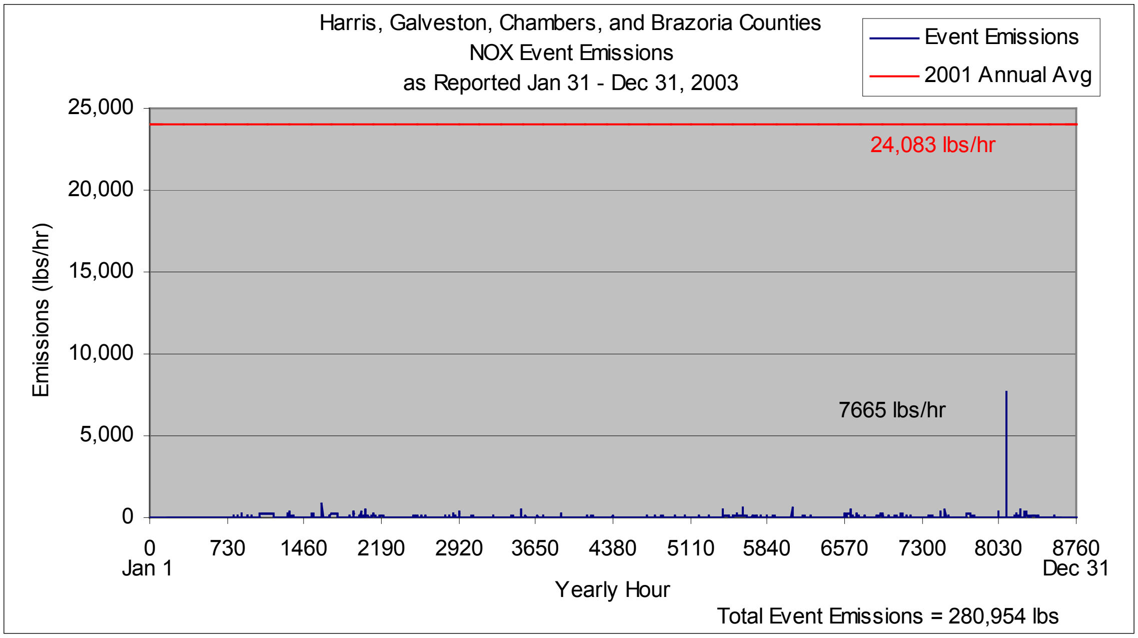


Figure 5. NO_X emissions (lbs/hr) from events and as an annual average (from 2001) are presented in a time series using 8760 one-hour time blocks for a single year. NO_X event emissions exceed 1000 lbs/hr only once and never exceed the total 2001 annual average for all facilities in the 4 county area. Event emission data are from [5] and point source data are from [15].

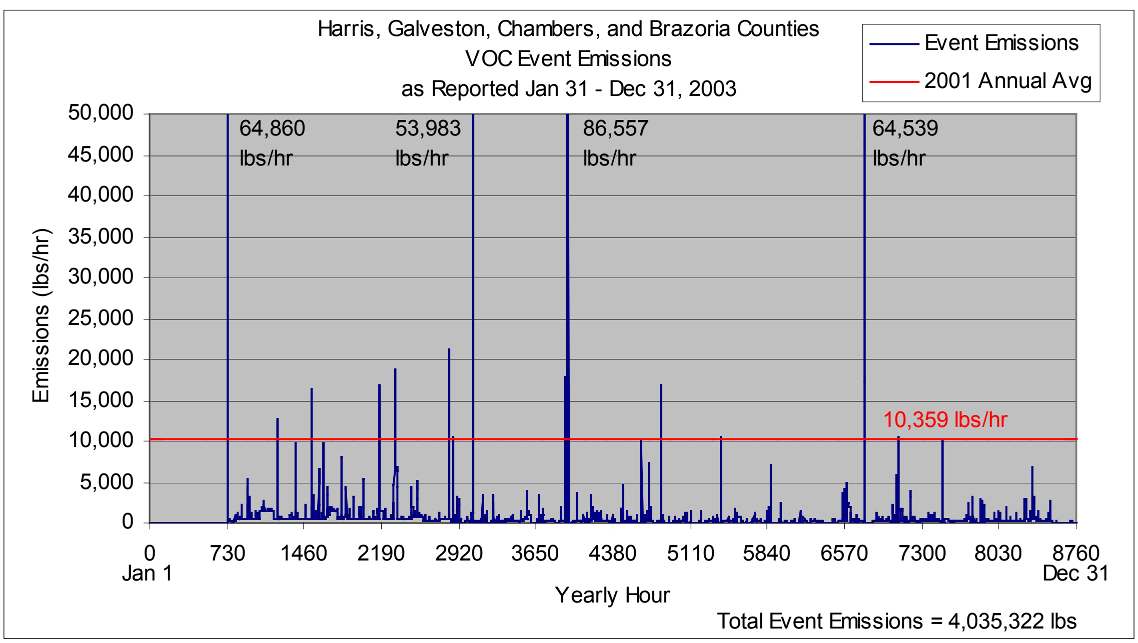


Figure 6. VOC emissions (lbs/hr) from events and as an annual average (from 2001) are presented in a time series using 8760 one-hour time blocks for a single year. There are 14 times during a roughly eleven-month time period when VOC event emissions exceed the total 2001 annual average of 10,359 lbs/hr for all facilities in the 4 county area. Event emission data are from [5] and point source data are from [15].

A time series for HRVOC emissions is shown in Figure 7. The annual average is calculated from the 2000 special inventory [16], which is the only generally available TCEQ inventory that contains speciated HRVOC emissions. The flow of HRVOC event emissions exceeds the 2000 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 more than an estimated 12% of the total mass emitted over the year based on the 828 tons (1.6 million pounds) emitted in 2003 and 6797 total tons emitted 2000. 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.

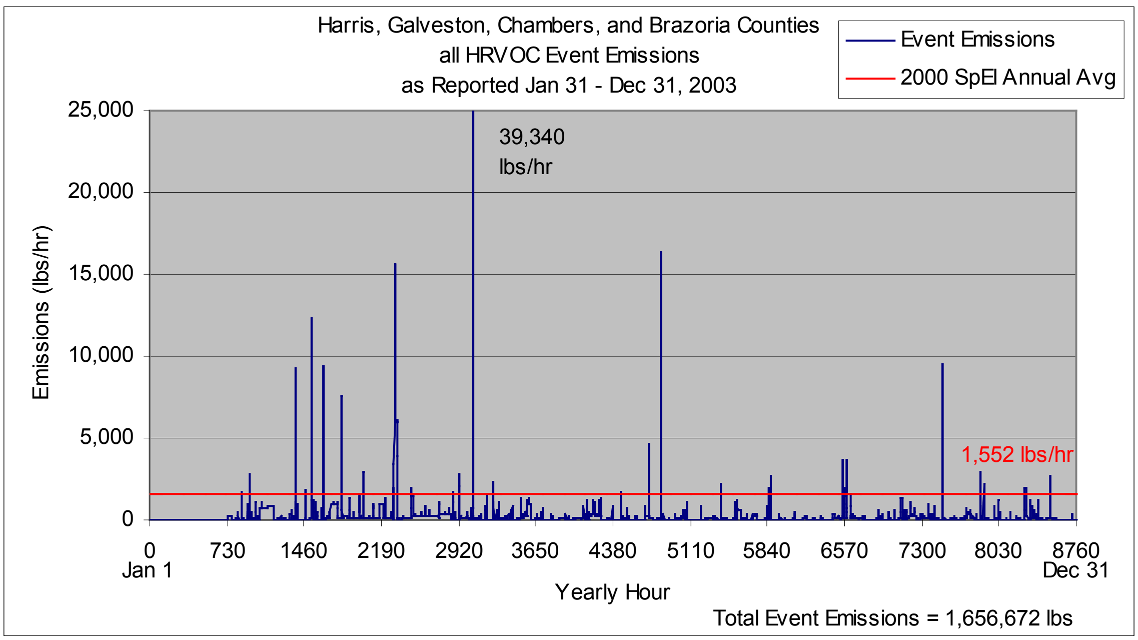


Figure 7. HRVOC emissions (lbs/hr) from events and as an annual average (from 2001) are presented in a time series using 8760 one-hour time blocks for a single year. There are 29 times during a roughly eleven-month time period when HRVOC event emissions exceed the 2000 annual average of 1,552 lbs/hr. Event emission data are from [5] and point source data are from [16].

Four species, or groups of species have been designated as HRVOCs; these are 1,3-butadiene, all isomers of butene (represented by different CAS numbers in Table 3), 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 8, 9, 10, and 11.

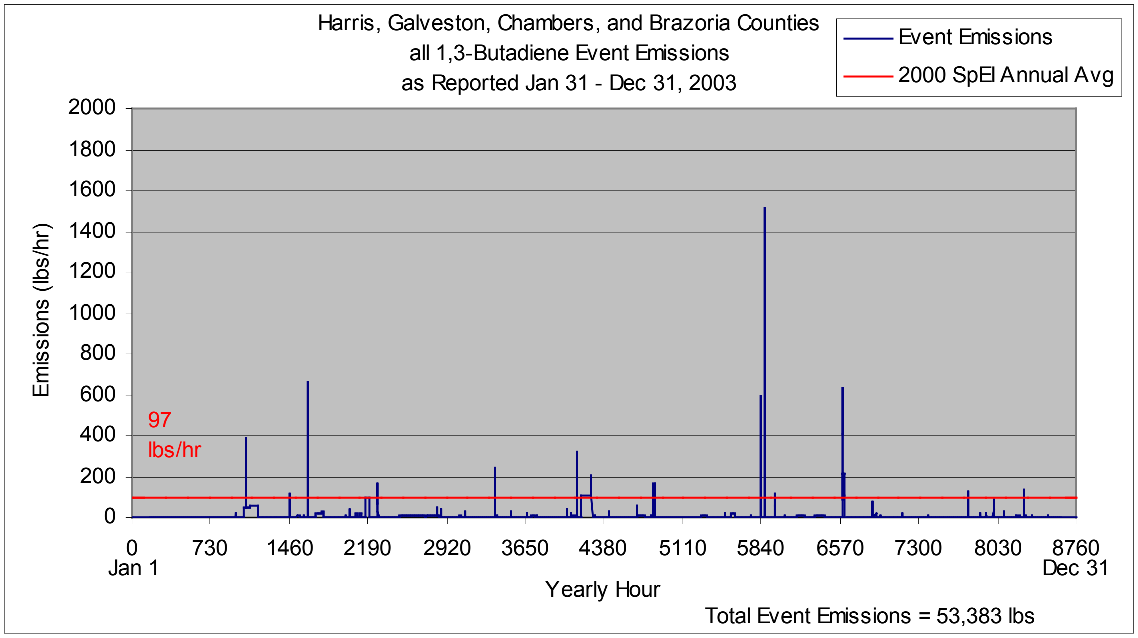


Figure 8. 1,3-butadiene emissions (lbs/hr) from events and as an annual average are presented in a time series using 8760 one-hour time blocks for a single year. Over an 11-month period there are 17 times (affecting 206 hours) when 1,3-butadiene emissions event emissions exceed the 2000 annual average of 97 lbs/hr. Event emission data are from [5] and point source data are from [16].

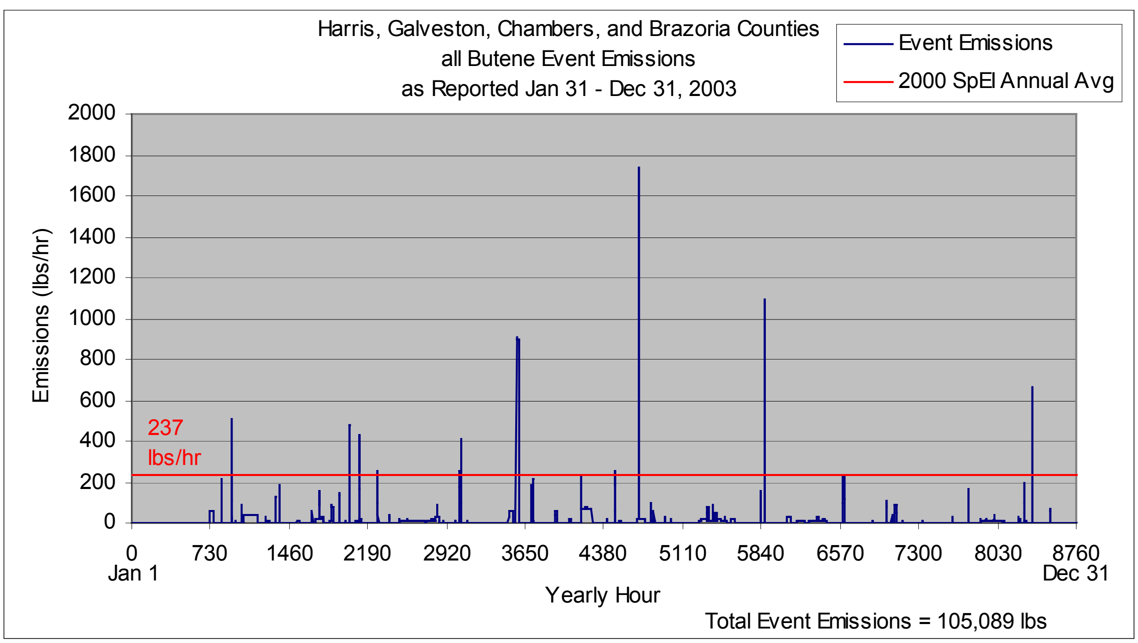


Figure 9. Butene emissions (lbs/hr) from events and as an annual average are presented in a time series using 8760 one-hour time blocks for a single year. Over an 11-month period there are 10 times (affecting 64 hours) when butene emissions event emissions exceed the 2000 annual average of 237 lbs/hr. Event emission data are from [5] and point source data are from [16].

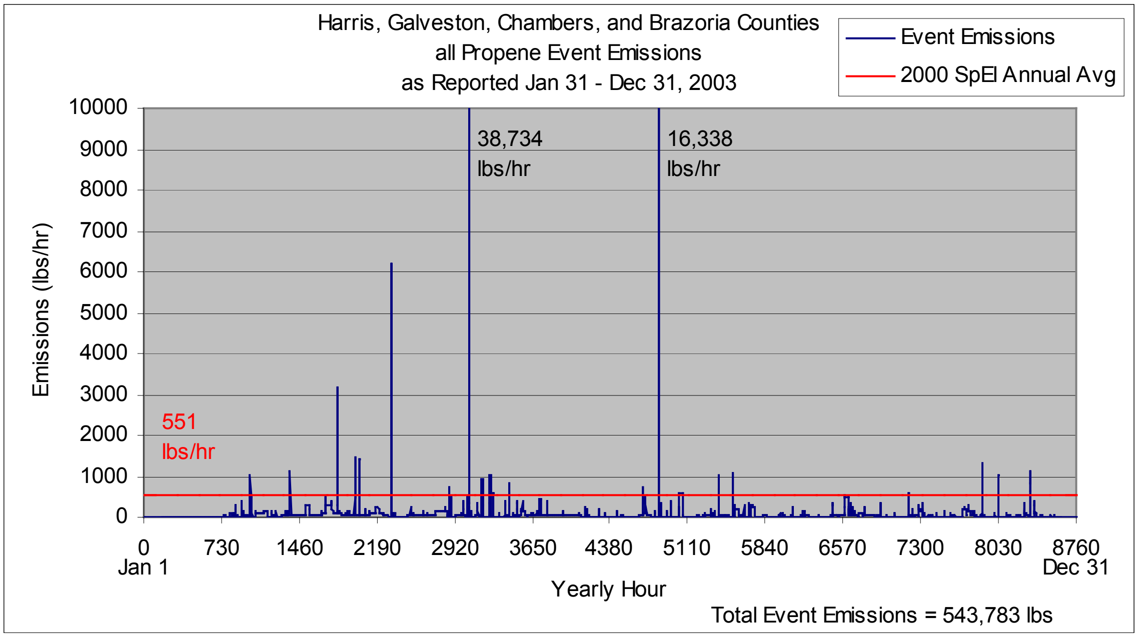


Figure 10. Propene emissions (lbs/hr) from events and as an annual average are presented in a time series using 8760 one-hour time blocks for a single year. Over an 11-month period there are 21 times (affecting 87 hours) when propene emissions event emissions exceed the 2000 annual average of 551 lbs/hr. Event emission data are from [5] and point source data are from [16].

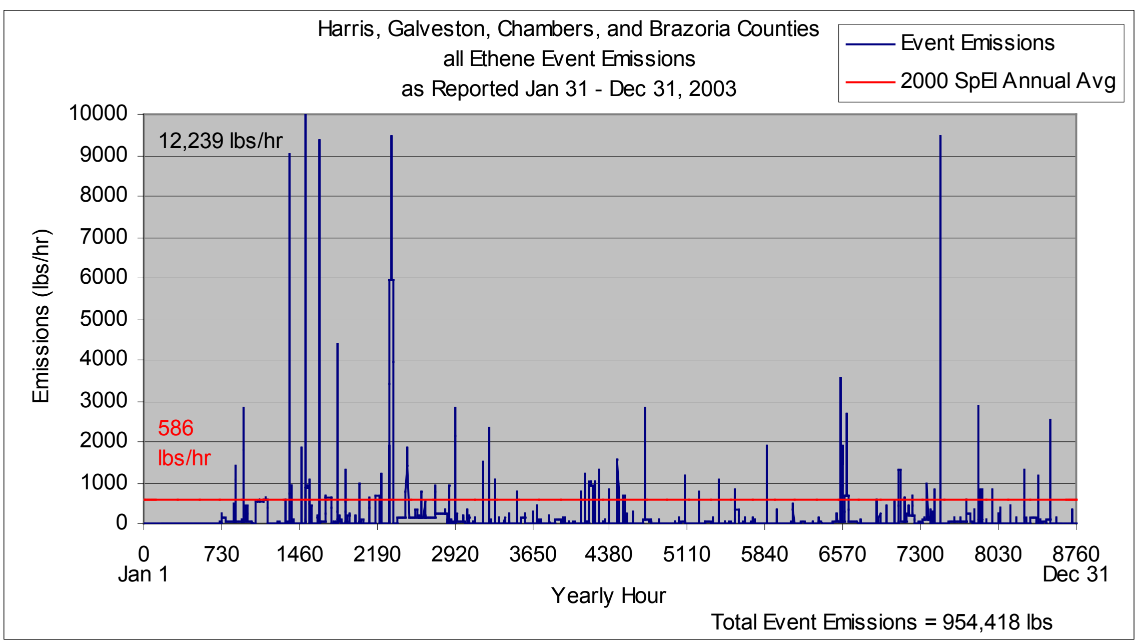


Figure 11. Ethene (ethylene) emissions (lbs/hr) from events and as an annual average are presented in a time series using 8760 one-hour time blocks for a single year. Over an 11-month period there are 58 times (affecting 395 hours) when ethylene event emissions exceed the 2000 annual average of 586 lbs/hr. Event emission data are from [5] and point source data are from [16].

Ethene (ethylene) exhibits the most significant frequency and magnitude of event emissions. 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 and 7 times (affecting 44 hours) when event emissions exceed 5 times the annual average. Next most significant is propene (propylene). Over the same period of time there were 21 instances (affecting 87 hours) where event emissions exceeded the 2000 annual average of 551 lbs/hr. In 4 cases (affecting 8 hours), the amount was 5 times the annual average. 1,3-butadiene contributes only about half the total mass to event emissions when compared to butene, however it has nearly double the number of instances where event emissions exceed the 2000 annual average (17 for 1,3-butadiene vs. 10 for butene) and four times the number of events where the amount is 5 times the annual average (4 for 1,3-butadiene vs. 1 for butene).

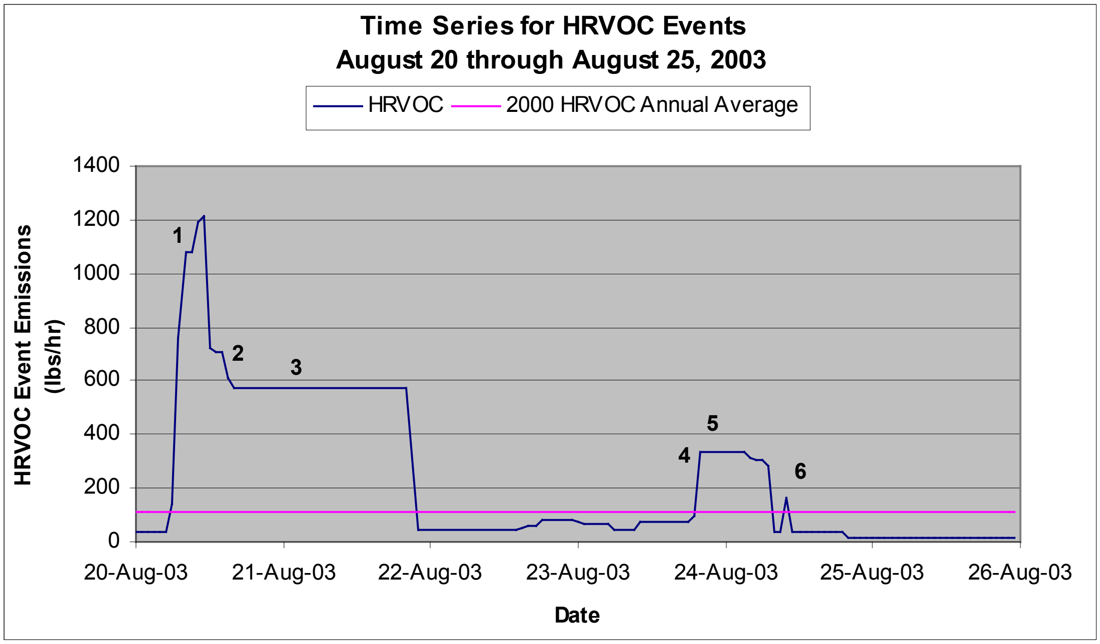
Note that the analyses above include events that are from both final and initial reports. Especially in the case of scheduled events, where initial reports are filed up to 10 days in advance, amounts tend to be overestimates (in order to account for all potential emissions). Consequently, these numbers may change once the final report is submitted. Currently emissions defined only through initial reports account for almost 38 thousand pounds of HRVOC emissions, most of which (37, 216) are propene (propylene). It should be noted, however, that most of this is from events with end dates in August 2003 or earlier, so whether or not these numbers are accurate or not, it appears unlikely that they will be changed. For scheduled events with end dates in December, there are 9296 pounds of propene (propylene) and 3109 pounds of ethene (ethylene) from initial reports. If these were to vary by even 100% they would have a negligible effect on the total annual event mass for these species.

The time series graphs presented above compare emission events, which may be confined to relatively small geographic areas, to the annual flow rates across all four counties. In order to illustrate, in another way, the effect that the event emissions might have on ozone formation processes , a six day period from August 20 through August 25, 2003 was selected for additional time series analysis. During this period there were 16 exceedances of the National Ambient Air Quality Standard for ozone as measured on 15 different monitors with average ozone concentrations of 144 ppb. Also during this period there were 20 HRVOC emission events. Eleven of these were confined to the week of interest, the remaining were reported as lasting between one and nine weeks. Table 5 lists the 15 facilities reporting events during the time period; 5 of the reporting entities report 2 events. Note that three of the events lasting longer than one week have more than 1000 lbs of emissions associated with them. It is unlikely that there were continuous emissions over the entire reporting period, so it is possible that during the week of interest that actual flow rates could be much higher than indicated. Note that 5 of the facilities (6 events) exceed their annual HRVOC flow rate as indicated by the 2000 special inventory [16], one by as much as 37 times. The average event emissions for all 5 facilities are 9 times the annual flow rate.

A time series graph showing the events and the annual flow rates for the 5 facilities is given in Figure 12.

Table 5. HRVOC events occurring August 20 through August 25, 2003.

Reporting Entity	# Events	HRVOC/hr per RN	HRVOC lb/hr in annual inventory	% of Annual Average	Multiplier (if >1)	Events > 1 week	Events > 1000 lbs, > 1 week
Equistar Chemicals La Porte Complex	2	25.0	117.5	21%		2	1
Equistar Chemicals Chocolate Bayou Complex	1	533.3	14.4	3713%	37		
Basell USA Bayport Plant	2	263.9	22.6	1170%	12		
Kaneka Texas Corporation	1	0.2	0.5	46%		1	
Dow Texas Operations Freeport	1	5.6	141.3	4%			
Celanese Clear Lake Plant	1	248.6	18.3	1361%	14		
BP Amoco Chemical Chocolate Bayou Plant	2	21.4	90.3	24%			
Equistar Chemicals Channelview Complex	2	8.3	227.2	4%		2	1
Exxon Mobil Chemical Baytown Olefins Plant	1	3.0	56.1	5%		1	1
BP Products North America Texas City	1	34.1	2.4	1394%	14		
ExxonMobil Chemical Baytown Chemical Plant	2	135.2	58.8	230%	2	1	
Sunoco La Porte Plant	1	20.8					
Shell Proplylene Pipeline Brazoria County	1	0.2	11.1	2%		1	
Shell Proplyene Pipeline Harris County	1	0.2				1	
Chevron Cedar Bayou Chemical Plant	1	507.8	82.5	616%	6		
Average per facility		337.7	39.3				
TOTAL	20	1688.7	196.4	860%	9	9	3



ID	Facility	Event_Began	Event_Ended	Total HRVOC	Ethylene	Propylene	Butenes	1,3-Butadiene
1	Chevron Cedar Bayou Chemical Plant	8/20 6:47 AM	8/20 12:02 PM	2,666	2,664	2		
2	ExxonMobil Chemical Baytown Chemical Plant	8/20 10:11 AM	8/20 3:16 PM	684		684		
3	Equistar Chemicals Chocolate Bayou Complex	8/20 7:35 AM	8/21 9:30 PM	20,220	12,366	6,116	881	857
4	Basell USA Bayport Plant	8/23 6:50 PM	8/24 4:10 AM	263	23	240		
5	Basell USA Bayport Plant	8/23 8:00 PM	8/24 8:00 AM	2,829		2,829		
6	Celanese Clear Lake Plant	8/24 10:00 AM	8/24 10:30 AM	124	124			

Figure 12. A total of 6 events occur between August 20 through August 25 where the flow rate from the facility exceeds its annual average. Total annual flow from all 5 facilities [16] is also shown. The table below the graph provides a key to the event numbers indicated on the time series.

Event Characteristics

An analysis of HRVOC event magnitude and frequency strongly indicates that further characterization of these events is justified. The third question posed early in this report was

Question 3. *What are the characteristics of the events in terms of time, space, and composition?*

These characteristics will be determined by examining event durations, the facilities involved, and the magnitude of these events.

Event Duration

Visual analysis of the time series plots (Figures 7 –11) suggests that the length of the events is relatively short. Quantitative evaluation reveals that of the 711 events involving the release of HRVOCs, 523 events (74%) last 24 hours or less (Figure 13 and Table 6A.). 175 events (25%) last one hour or less and 82 events (12%) last 10 minutes or less (Table 6B). The distribution of event durations for events of up to one hour is shown in Figures 14 and 15 for all HRVOC events and for those emitting greater than 1000 pounds of HRVOC. All 27 of the events lasting less than one hour and emitting more than 1000 pounds of HRVOC are unscheduled. More than half (17) last less than 10 minutes. The average release during these large events (greater than 1000 lbs) lasting 10 minutes or less was 2588 pounds of HRVOC. The average release of large events lasting 60 minutes or less was 3771 pounds of HRVOC.

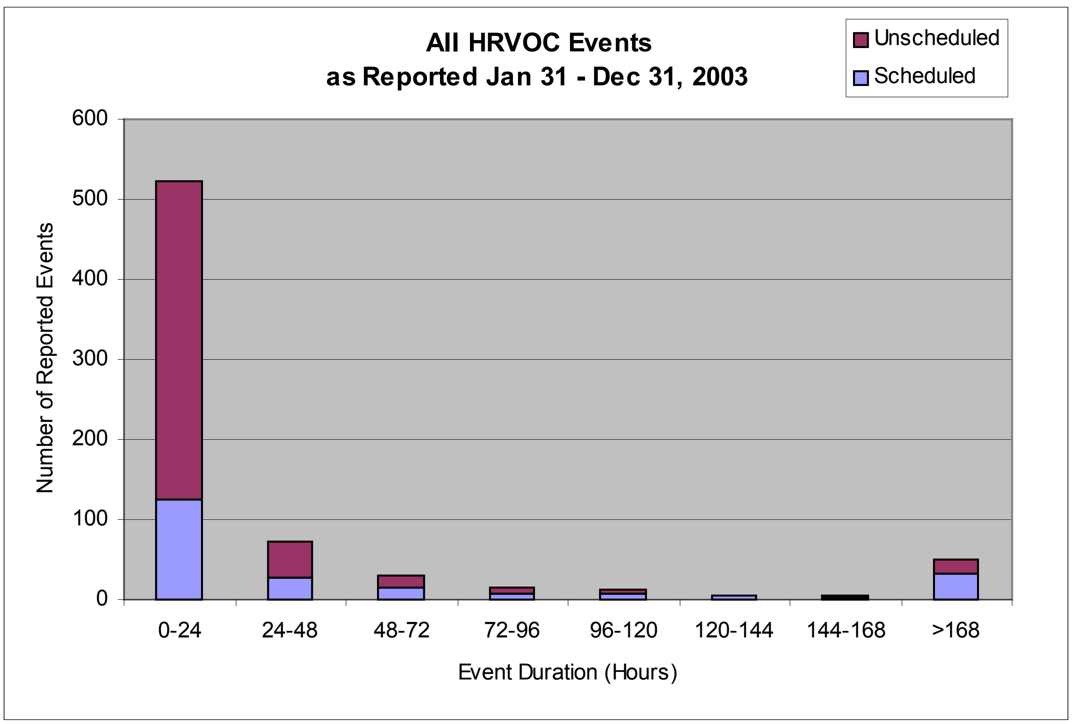


Figure 13. Most events, both scheduled and unscheduled, last less than 24 hours. More than 50% of events that last more than two days (48 hours) are scheduled (see Table 5A.)

Table 6. Distribution of all HRVOC events by duration hours (A) and for HRVOC events lasting one hour or less by duration minutes (B).

A

Event Duration (hrs)	All HRVOC Events	Unscheduled	Scheduled	% Unscheduled
0-24	523	397	126	76%
24-48	72	45	27	63%
48-72	30	14	16	47%
72-96	14	6	8	43%
96-120	13	6	7	46%
120-144	6	1	5	17%
144-168	4	1	3	25%
>168	49	17	32	35%
Total	711	487	224	35%

B

Event Duration (min)	All HRVOC Events	Unscheduled	Scheduled	% Unscheduled
1-5	63	58	5	92%
6-10	19	19	0	100%
11-15	13	13	0	100%
16-20	15	14	1	93%
21-25	7	7	0	100%
26-30	12	11	1	92%
31-35	4	4	0	100%
36-40	6	6	0	100%
41-45	6	5	1	83%
46-50	9	8	1	89%
51-55	3	3	0	100%
56-60	18	15	3	83%
Total	175	163	12	93%

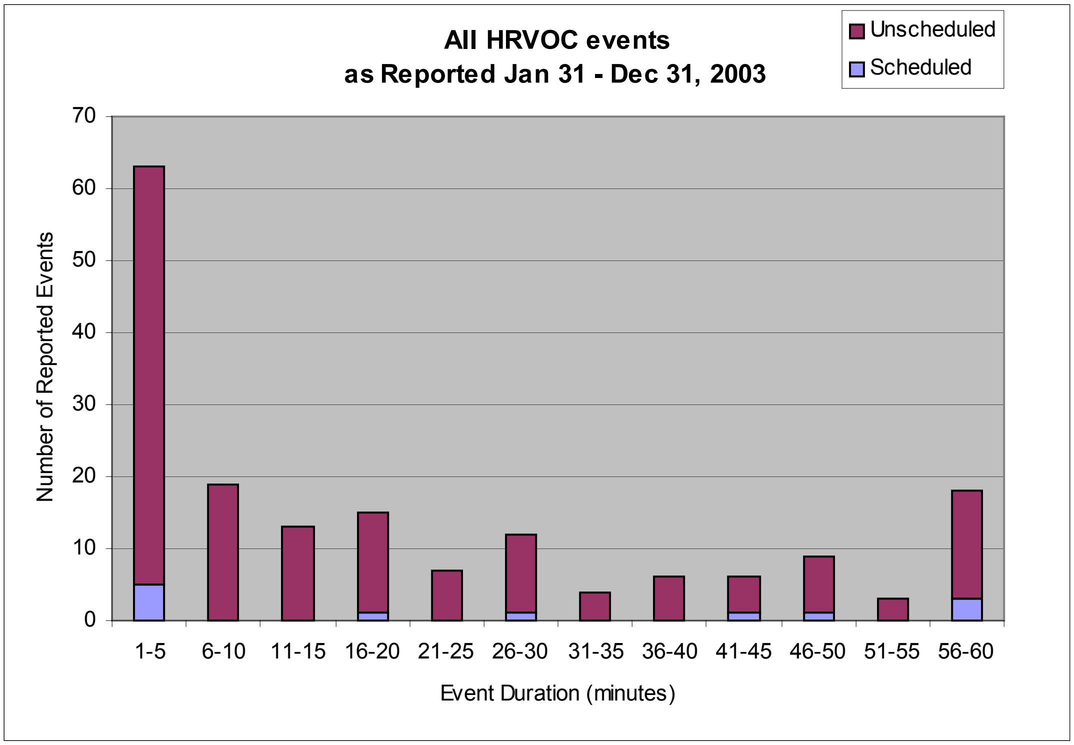


Figure 14. Of the 711 HRVOC events 175 (25%) last one hour or less and 82 (12%) last ten minutes or less. Increased frequency in the 30, 45, and 60-minute bins is probably an artifact of reporting estimates.

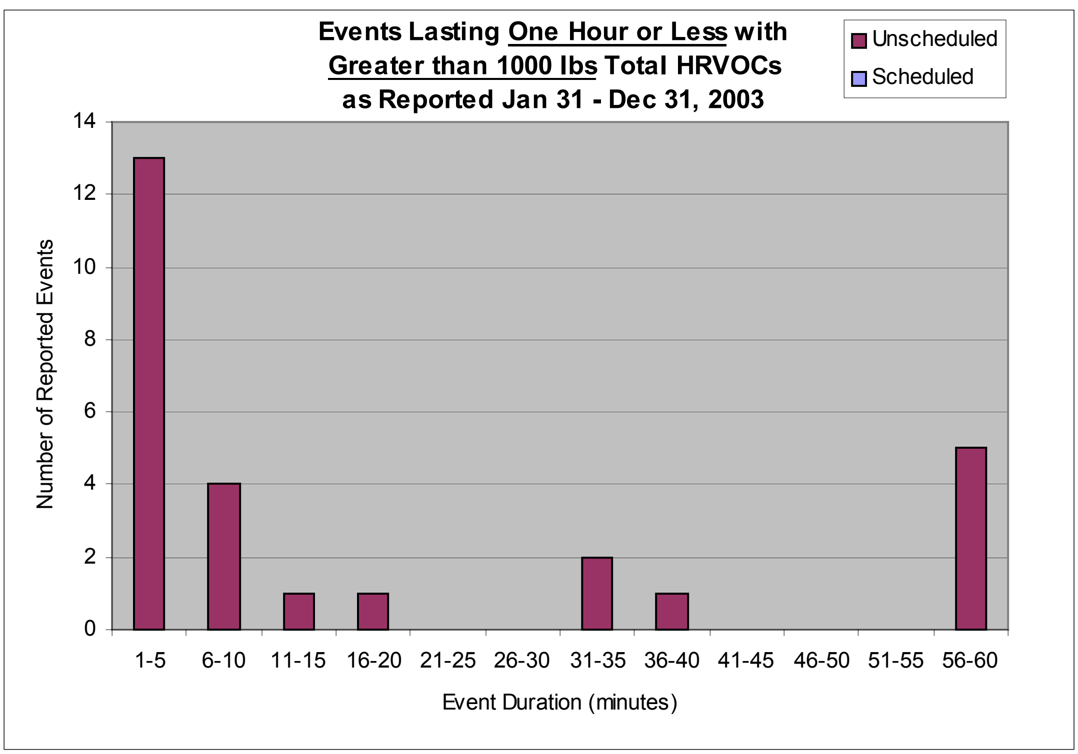


Figure 15. All 27 of the events lasting less than one hour and emitting more than 1000 pounds of HRVOC are unscheduled. More than half (17) last less than 10 minutes.

Comparison with Prior Years

Event emission data are available from 2001 [17] and 2000 [16]. The 2001 data are from a similar reporting system as that used in 2003 except that the threshold for reporting events was 5000 pounds rather than 100 pounds. The 2000 data are from a special inventory focused on HRVOC from data gathered by individual facilities. 2003 event data are compared with each of these prior years using only those reporting entities for which there are data in both years being compared. The data are plotted as scatter plots and linear regression trend lines with corresponding correlation coefficients (R^2) are determined (Figures 16 and 17). While the analyses suggest that there is a significant amount of variability between reporting years, some of the lack of correlation is likely due to the different thresholds. However, the data also suggest that events with very large emissions are unlikely to occur at the same facility year after year, which will prove to be very important in developing a systematic way to predict future year and impute past year inventories.

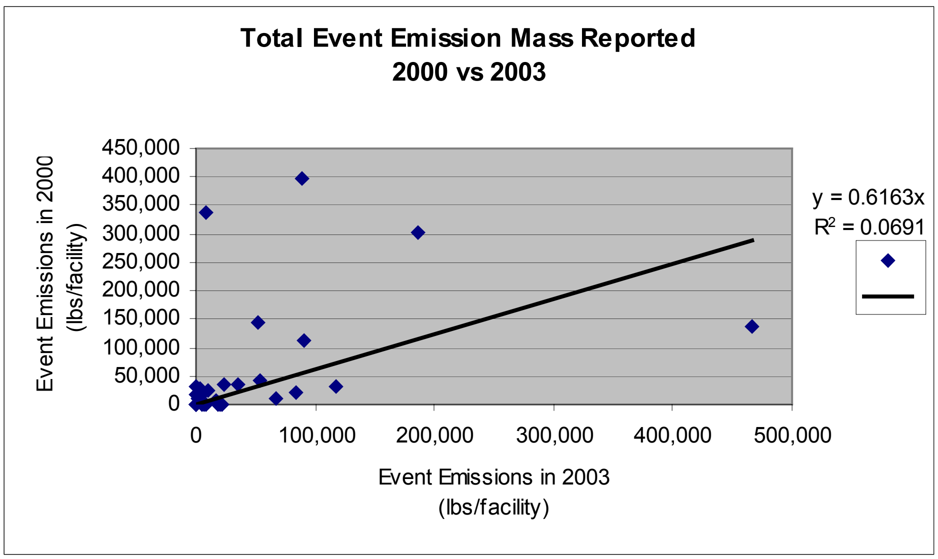


Figure 16. Total event emissions for 2003 (by reporting entity) are compared with total event emissions from 2000. While differences in reportable requirements might influence the lack of correlation for smaller masses, the amount of scatter in the larger quantities suggests that extremely large events occur at different facilities in different years.

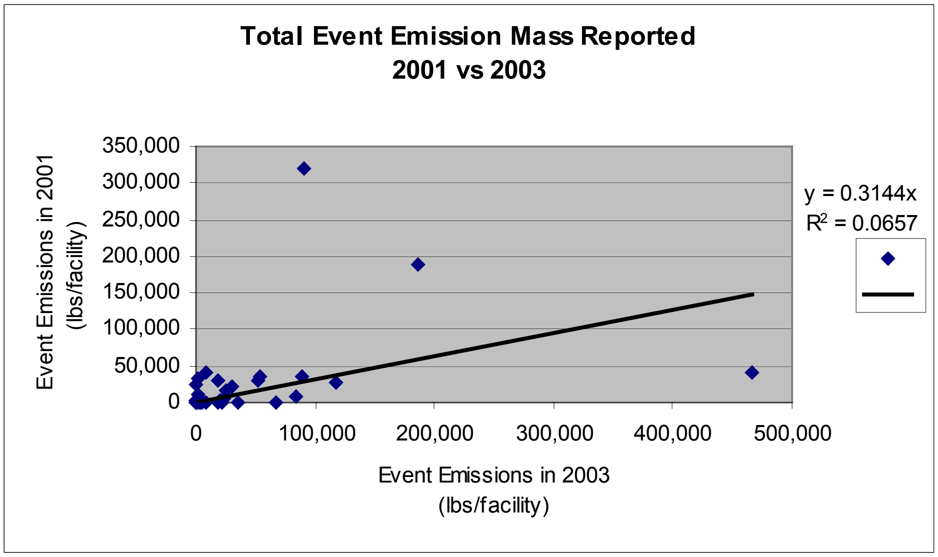
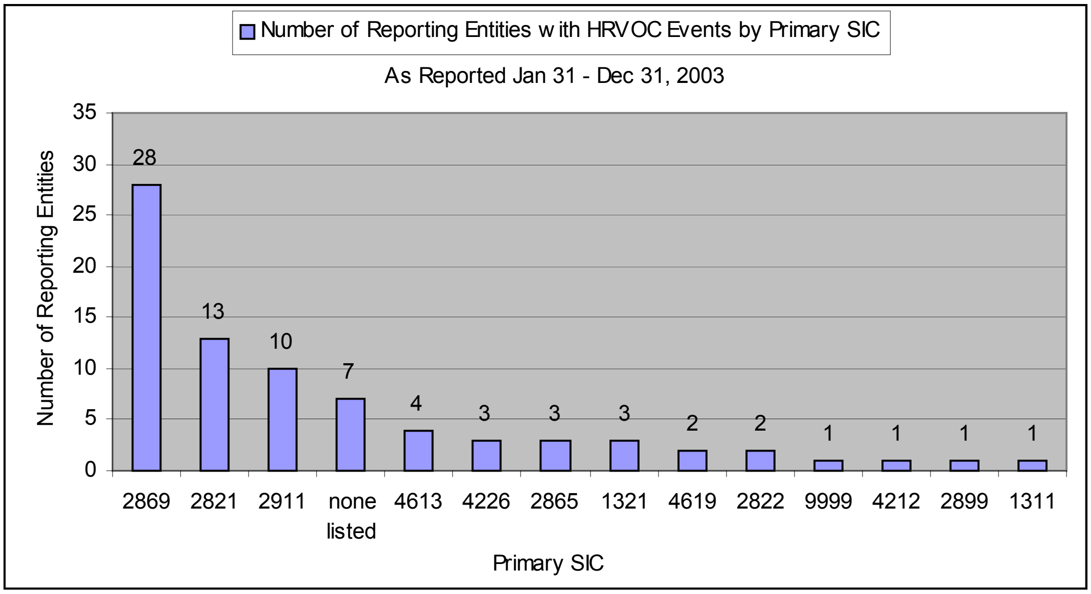


Figure 17. Total event emissions for 2003 (by reporting entity) are compared with total event emissions from 2001. While differences in reportable emissions might influence the lack of correlation for smaller masses, the amount of scatter in the larger quantities suggests that extremely large events occur at different facilities in different years

Event Sources

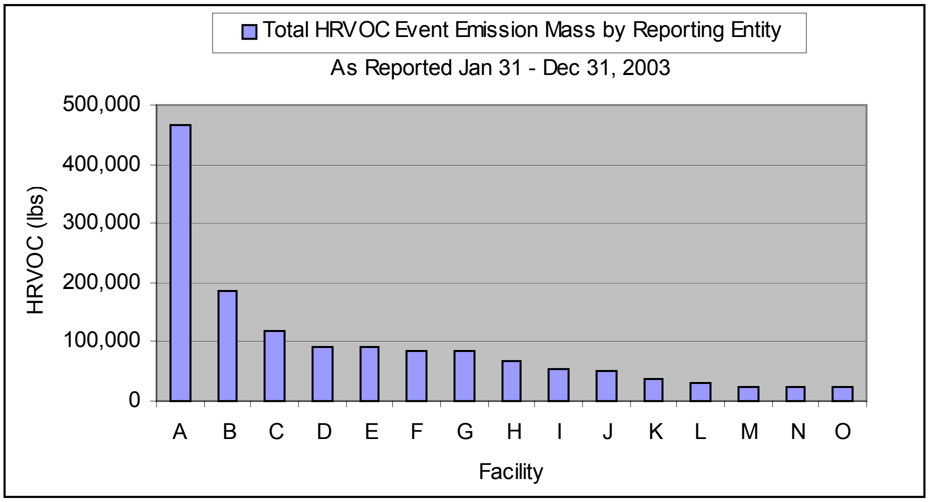
As of December 31, 2003 a total of 79 entities had reported events with HRVOC emissions beginning on or after January 31, 2003. Approximately one third of these entities are identified in the TCEQ Central Registry [14] with a primary standard industrial code (SIC) of 2869, Industrial Organic Chemicals. Just under 20% (13) entities have the primary SIC 2821, Plastics Materials. 10 entities are petroleum refineries (SIC 2911) and at least 8 are pipelines (SICs 4613 and 4619 plus some of the entities for which no SIC is listed). The distribution of HRVOC event emitting entities by primary SIC is shown in Figure 18.

While only 35% of the reporting entities had a primary SIC code of 2869, this industrial sector accounts for more than 1 million of the 1.6 million pounds of HRVOC event emissions reported for the last eleven months of 2003. In addition, the top six facilities in terms of total HRVOC emission mass all fall within this SIC classification (Figure 19). The total mass for these six reporting entities is 951,579 lbs. Figure 18 shows the total mass and corresponding SIC codes for the 15 entities with the largest amounts of HRVOC event emissions. Together these 15 facilities released a total of 1,429,244 lbs or almost 90% of all 79 reporting entities.



SIC	SIC Description	SIC	SIC Description
2869	Industrial Organic Chemicals	1321	Natural Gas Liquids
2821	Plastics Materials	4619	Pipelines
2911	Petroleum Refining	2822	Synthetic Rubber (Vulcanizable Elastomers)
none listed*	*includes some pipelines	9999	Nonclassifiable Establishments
4613	Refined Petroleum Pipelines	4212	Local Trucking Without Storage
4226	Special Warehousing and Storage	2899	Chemicals and Chemical Preparations
2865	Cyclic Organic Crudes and Intermediates	1311	Crude Petroleum and Natural Gas

Figure 18. There were 79 reporting entities representing 14 different primary standard industrial codes (SICs) reporting HRVOC event emissions in the last 11 months of 2003. 28 of the entities (35%) had a primary SIC of 2869, Industrial Organic Chemicals.



	Reporting Entity	Primary SIC	SIC Description	Total HRVOC lbs
A	Dow Texas Operations Freeport	2869	Industrial Organic Chemicals	467,138
B	Equistar Chemicals Channelview Complex	2869	Industrial Organic Chemicals	186,813
C	Equistar Chemicals Chocolate Bayou Complex	2869	Industrial Organic Chemicals	117,498
D	BP Amoco Chemical Chocolate Bayou Plant	2869	Industrial Organic Chemicals	90,366
E	Equistar Chemicals La Porte Complex	2869	Industrial Organic Chemicals	89,763
F	Lyondell Chemical Channelview	2869	Industrial Organic Chemicals	83,596
G	Lyondell-Citgo Refining	2911	Petroleum Refining	83,017
H	Sunoco Inc R & M Bayport Polypropylene	2821	Plastics Materials	67,148
I	Chevron Phillips Chemical Sweeny Complex	2911	Petroleum Refining	54,451
J	Chevron Cedar Bayou Chemical Plant	2869	Industrial Organic Chemicals	51,583
K	Exxon Mobil Baytown Facility	2911	Petroleum Refining	36,045
L	Union Carbide Texas City Operations	2869	Industrial Organic Chemicals	31,034
M	Shell Oil Deer Park	2911	Petroleum Refining	25,059
N	BP Solvay Polyethylene NA	2821	Plastics Materials	23,319
O	BP Products North America Texas City	2911	Petroleum Refining	22,414

Figure 19. The top 15 reporting entities for 2003 in terms of total HRVOC event emissions mass account for nearly 90% of the total HRVOC event emissions mass in Harris, Brazoria, Galveston, and Chambers Counties. The top 6, all with a primary SIC of 2869 (Industrial Organic Chemicals) emitted 951,579 lbs and thus contributed approximately 60% of the four county total.

Event Magnitude

The amount of HRVOCs reported as emitted during any single event ranges from one pound to 203,000 pounds. More than half of the events (375 out of 711) emitted between 100 and 1000 lbs (Figure 20). However, the actual number of events with less than 100 lbs of HRVOC is likely to be higher than the reported 160, since 100 lbs is the reporting threshold. Data on these events are available only because a reportable quantity of one or more compounds other than an HRVOC was emitted during the same event.

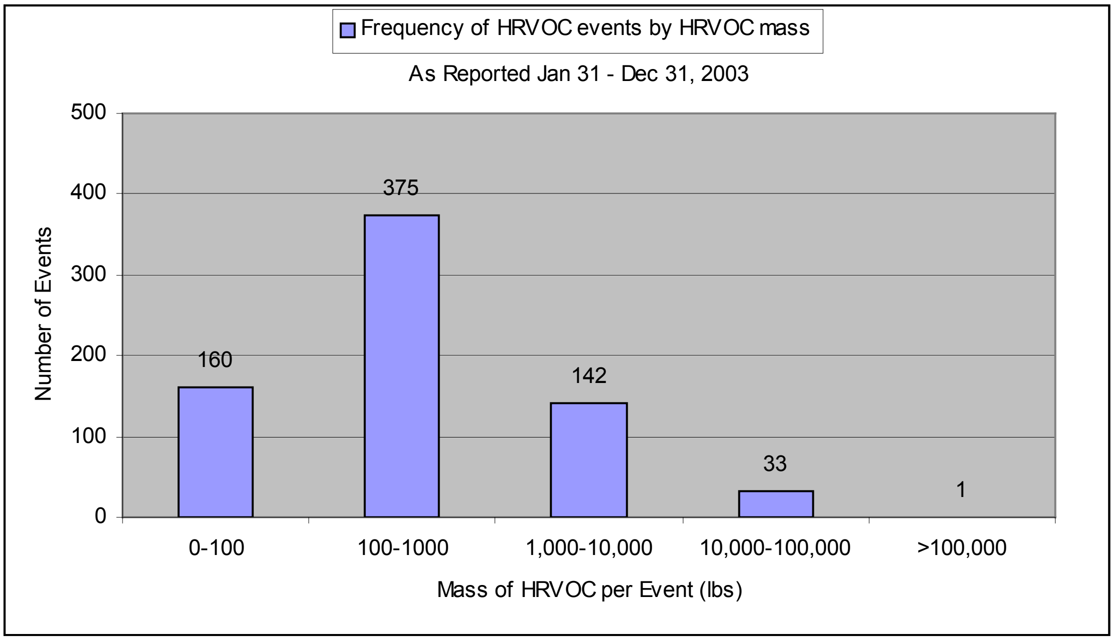


Figure 20. The amount of HRVOCs emitted during any single event, as reported in 2003, ranges from one pound to 203,000 pounds. More than half of the events (375 out of 711) are reported to have emitted between 100 and 1000 lbs.

Summary and Conclusions

The magnitudes and variability of emission events in the Houston-Galveston area between January 31 and December 31, 2003 have been examined using event reports made available through the recently developed TCEQ on-line reporting system. Data in these reports were entered into a relational database in order to facilitate analysis. The magnitude and frequency of emission events were investigated by calculating flow rates (pounds per hour) of NO_X, VOCs, and HRVOC during events and comparing these against annual average flow rates within the region and at specific facilities. Evaluation of the data shows that HRVOC events and possibly VOC emissions events have the potential to contribute significantly to ozone formation in HGA. In contrast, the mass associated with NO_X events, whether considered collectively or singularly, is an extremely small faction of the total NO_X point source emissions. If event reports are complete and reasonably accurate, HRVOC events contribute approximately 12% to the total annual mass, 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.

Identifying the types of facilities that report HRVOC event emissions indicates that 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. However, comparing total event emissions by facility from 2003 to those in 2001 and 2000. suggests that the same facilities may not be the major emitter from one year to the next or that reporting might not be complete. 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.

The data from the TCEQ electronic reporting system will facilitate understanding of event emissions in the Houston Galveston Area. The collection and analysis of this data will continue. It is hoped that feedback from use of this reporting system will result in improved specificity in certain aspects of the data, particularly the cause and time elements. The next critical steps will be to determine how these data can be used effectively in photochemical modeling and policy development.

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