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Final Report

Design Considerations for an Ambient Air Monitoring Network and Related Components of an Environmental Monitoring and Response System in the Houston Ship Channel

HARC Project H31-PhaseIB

Prepared for

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EXECUTIVE SUMMARY

Currently, the Houston-Galveston area (HGA) does not meet EPA's National Ambient Air Quality standard for ozone. Results of air monitoring and emission inventory analyses have shown that emissions of volatile organic compounds (VOCs) in general, and highly reactive volatile organic compounds (HRVOCs) in particular, from industrial petrochemical facilities in the HGA are highly variable on sub-hourly to daily time scales. Modeling analyses have shown that short-term releases of large quantities of HRVOCs (a relatively common occurrence) can, under the right conditions, contribute significantly to exceedances of the ozone standard. These findings prompted new regulations designed to limit HRVOC releases, and the establishment of an Environmental Monitoring and Response System (EMRS) pilot program for HRVOCs. Under the pilot program, HRVOCs are monitored by automated gas chromatographs (auto-GCs) installed at seven locations in the vicinity of the Houston Ship Channel. Hourly data are transmitted to TCEQ and any values exceeding a pre-selected threshold concentration trigger an automated communications alert system which notifies participating facilities located within a 90 degree wedge oriented upwind of the trigger event location. Facilities notified of an event then review their operations for conditions that might be associated with a release of HRVOCs and, if appropriate, take actions to reduce or eliminate the release of excess emissions. One of the principal goals of an EMRS is to foster pollution prevention by providing for the rapid transmittal of environmental changes to decision makers. Given the demonstrated role of HRVOC releases from facilities in the Ship Channel area in the formation of high ozone concentrations, reducing or preventing HROVC releases from these facilities will make an important contribution to achieving attainment of the ozone air quality standard.

In keeping with its mission of enhancing the understanding of, and improving air quality in Texas, the Houston Advanced Research Center contracted with ENVIRON to develop recommendations for the design and operation of an EMRS capable of detecting potential sources of episodic releases of VOCs from sources in the vicinity of the Houston Ship Channel on a near real-time basis. Our investigation of EMRS system design alternatives included an analysis of ambient monitoring network designs, applicability of alternative monitoring technologies to EMRS, and a review of available analytical and procedural options for responding to an event identified by the EMRS monitoring network.

EMRS Monitoring Network Design

Implementation of an effective EMRS targeting HRVOCs requires deployment of an ambient monitoring network that has sufficient spatial coverage, sensitivity, selectivity, and a sufficiently fast response time to provide useful near real-time data on high HRVOC concentration events to participating government agencies and industrial facility operators. Ideally, the EMRS ambient monitoring network would be able to detect a significant fraction of emission events within the size range of concern. For HRVOC releases in the HGA, simplified photochemical modeling results from previous studies have shown that HRVOC releases of 1,000 lb/hour are potentially capable of producing a 2 to 3 ppb increase in ambient ozone levels under the right conditions so releases of at least this size should be given highest priority. Examinations of records of reported emission events show that such events occur on average once per day somewhere in the HGA.

EMRS ambient monitoring network designs were evaluated using an emissions simulator and photochemical dispersion modeling system to simulate a random sample of the types of emission events the EMRS is intended to detect. This system was used to quantitatively analyze the ability of existing or potential future alternative monitoring networks to detect and identify the source of each release event. Results indicate that tens of monitoring sites would be required to adequately detect significant releases from potential HRVOC emissions sources in the Ship Channel area. In particular, the existing 7-site network used in the 2004 EMRS pilot study can be expected to detect only the largest releases (i.e., those exceeding 10,000 lb/hr) with any degree of reliability. For reliable detection of events exceeding 1,000 lb/hr (i.e., a probability of detection of such events of at least 50%), a much larger network with spatial coverage similar to that provided by the expanded, 27 site network analyzed in this study and using event trigger threshold concentrations set near the low end of the range of thresholds used in the pilot study would be needed for reliable detection. Furthermore, analysis of the predicted spatial distribution of impacts from the simulated release events suggests that new monitoring sites in the eastern portion of the area (around Baytown, North Channelview, and Bayport) may be particularly useful for detecting emission events which the current seven site network does not appear to be picking up particularly well. These conclusions, derived from the emission event simulation study described in Section 3, are based on the frequency, size, and locations of *reported* emission events in Harris County during the January 2003 – January 2004 period for which records were available for this study and does not account for the impacts of any unreported events or changes in the spatial distribution of events that might occur in future years.

Auto-GC monitoring equipment used in the EMRS pilot study, while capable of detecting HRVOCs with sufficient sensitivity, suffers from a slow response time (nearly two hours from sample initiation to reporting of results) and limited availability due to high equipment and operating expenses. Currently available alternatives to the auto-GC network for EMRS applications are for the most part limited to FTIR devices such as the dual cell extractive FTIR currently operating at the Seabrook monitoring site. FTIRs offer the requisite response time at detection levels adequate for EMRS applications but the costs of setup and operation are roughly on par with that of the auto-GCs. New technologies based on micro electromechanical systems (MEMS) hold considerable promise for building denser ambient monitoring networks with greater capability (primarily with respect to speed of response) at relatively low cost in the not to distant future. MEMS devices are expected to begin to become available on the market place by the end of this decade and should be given serious consideration in future EMRS network development efforts.

Source Identification

Current procedures for identifying sources potentially responsible for a give trigger event (based on examining a 90 degree upwind wedge) are too imprecise. Several procedures are recommended for improving the precision of source identification, thus reducing the number of trigger alerts any given source would need to respond to and making it more acceptable to increase the detail and scope of the follow-up activities that local officials and source operators would undertake in response to a trigger alert. One approach which has already been considered for implementation in Houston is the automated calculation of near real-time air parcel back trajectories showing the paths most likely to have been taken by air parcels arriving at the time and location of each trigger event. These results could then be used to determine with greater precision the upwind area within which sources potentially contributing to the event should be notified. Another approach involves the use of ground level or airborne mobile monitoring equipment to trace the source of a release. This would, however, be limited to longer releases which could be captured within the total response time of the ambient surveillance network and the mobile monitoring resources. A more sophisticated approach which has been suggested by some participants in the current EMRS program is to compile information on unique chemical identifiers which may be associated with a small subset of (or even individual) potential sources. In theory, a library of source “fingerprints” could be developed by conducting source-oriented multi-species monitoring of routinely emitted chemicals just downwind of the sources of interest. Some of the newer remote sensing monitoring technologies described in Section 4 are well suited to this purpose. Once the key identifier species have been determined, the EMRS ambient network could be modified to include these species among the list of target compounds in addition to the HRVOCs of interest. By including data on correlations between HRVOCs and concentrations of the key indicator compounds during the trigger event, it would be possible to further refine the set of potential upwind sources at which follow-up activities would be needed.

Local Response to Trigger Events

Procedures employed within the EMRS protocol for responding to the occurrence of a trigger event should be refined to include expanded follow-up activities at facilities notified of an event, including examining fence-line or other routine on-site monitoring data. The quantity, quality and usefulness of these data would be greatly enhanced by the use of advanced remote sensing instrumentation that has been developed for fence-line monitoring applications and leak detection programs, including open path optical methods and plume visualization cameras such as those described in Section 4. Automated integrative analyses of process control data such as is used in predictive emission monitoring systems (PEMS) could in theory also be useful for identifying potential HRVOC releases.[1] It must be recognized, however, that the equipment and personnel time needed for these expanded follow-up activities will be expensive. One method for reducing costs would be to limit the number of trigger alerts requiring a full-scale response by giving highest priorities to facilities that are closest to the trigger event and focusing only on the largest events.

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[1] PEMS have been developed, for example, by Pavilion Technologies but have not been used for this particular type of application.

1. INTRODUCTION

Ambient air quality in several metropolitan areas of Texas does not meet health-based standards set by the U.S. Environmental Protection Agency. In particular, the Houston-Galveston area does not meet EPA's National Ambient Air Quality standard for ozone. In August and September of 2000, a major field study known as the Texas Air Quality Study (TexAQS) was conducted to provide a better understanding of conditions associated with poor air quality in the Houston – Galveston area (HGA). Data collected as part of the TexAQS 2000 study showed that ratios of concentrations of certain highly reactive volatile organic compounds (HRVOCs) to concentrations of nitrogen oxides (NO_x) downwind of large industrial source complexes in the HGA exceeded ratios which would have been expected on the basis of available inventories of volatile organic compound (VOC) and NO_x emissions. Since NO_x emission estimates are believed to be reasonably accurate on the basis of independent information, this lead researchers to the conclusion that VOC emissions in general, and HRVOC emissions in particular, are significantly underestimated. The TexAQS 2000 data also revealed periods of rapid ozone formation in the combined VOC and NO_x plumes downwind of the industrial complexes, resulting in episodes of high ozone concentrations (Daum et al., 2002).

Results from the TexAQS 2000 field study prompted a reexamination of the VOC emissions inventory for petrochemical sources in the HGA. Particular attention has been paid to episodic releases of VOCs from these sources associated with changes in source operations such as upsets, startups and turnarounds. These investigations have been aided in part by new rules which require sources to report any releases exceeding 100 lbs of most compounds to the Texas Commission on Environmental Quality (TCEQ). The TCEQ is in turn required to compile the reports and make them publicly available. An analysis of these reports has demonstrated that VOC emissions in the HGA are highly variable on sub-hourly to daily time scales and that the large short-term spikes in emissions, which dominate the total annual emissions from these facilities, are not accounted for in the routine emission inventory estimates which had previously been relied upon for air quality planning (Allen et al., 2004).

Findings from the TexAQS 2000 field study and the analysis of emission event reports described above have prompted the TCEQ and other groups to develop and evaluate new approaches to identifying and controlling sources of VOC emissions from industrial facilities. One such new approach is the establishment of an Environmental Monitoring and Response System (EMRS) for pollution prevention. An EMRS consists of a network of monitoring devices designed to identify changes in the environment on a near real-time basis, a system for integrating and reporting data from the monitoring network, and a set of procedures for identifying the cause of the change and responding appropriately. One of the principal goals of an EMRS is to foster pollution prevention by providing for the rapid transmittal of environmental changes to decision makers.

To date, TCEQ has spearheaded the implementation of two pilot EMRS programs: a water quality EMRS in the Brazos River Basin Leon-Bosque Watershed and an air quality EMRS in Houston (Spaw and Rozacky, 2005). The Houston air pilot EMRS is a joint government – industry effort designed to detect elevated concentrations of HRVOCs in the Houston Ship Channel area and notify participating industrial facilities in the area of such events in near real-time. Facilities notified of an event then review their operations for conditions that might be associated with a release of HRVOCs and, if appropriate, take actions to reduce or eliminate the release of excess emissions. One of the principal goals of the Houston EMRS is foster pollution prevention by providing near real-time data to project participants on HRVOC impacts. Given the important role of HRVOC releases from facilities in the Ship Channel area in the formation of high ozone concentrations as demonstrated by the studies described above, reducing or preventing HRVOC releases from these facilities will make an important contribution to achieving attainment of the ozone air quality standard. Operation of and results from the Houston EMRS air pilot project which was conducted between June and November, 2004 are described in more detail in Section 2.

Implementation of an effective EMRS targeting HRVOCs requires deployment of an ambient monitoring network that has sufficient spatial coverage, sensitivity, selectivity, and a sufficiently fast response time to provide useful near real-time data on high HRVOC concentration events to participating government agencies and industrial facility operators. In addition, procedures for responding to data indicating HRVOC levels exceeding a defined event trigger level must be formulated and the ancillary data (for example, wind measurements and concentration measurements from mobile, fenceline and on-site air monitoring equipment) needed to implement the procedures must also be available. Due to time and resource constraints, existing monitoring and data telemetry resources within the Ship Channel area were used for the 2004 Houston pilot study. However, future versions of the EMRS could be modified to improve system performance by optimizing the deployment of available resources, adding additional monitoring resources to the system, integrating new, advanced monitoring technologies into the system, and expanding the scope and efficiency of activities that are to be conducted in response to a trigger event.

In keeping with its mission of enhancing the understanding of and improving air quality in Texas, the Houston Advanced Research Center contracted with ENVIRON to develop recommendations for the design and operation of an EMRS capable of detecting potential sources of episodic releases of VOCs from sources in the vicinity of the Houston Ship Channel on a near real-time basis. Our investigation of EMRS system design alternatives included the following components:

- A quantitative performance evaluation of alternative EMRS monitoring network designs based on dispersion model simulations of a large number of hypothetical HRVOC emission events.
- A review of available monitoring technologies previously evaluated by ENVIRON under a companion project with respect to their applicability to an air quality EMRS.
- A review of available analytical and procedural options for responding to an event identified by the EMRS monitoring network.

2. EMRS 2004 HOUSTON AIR PILOT PROJECT

During June – November, 2004, the TCEQ conducted a pilot version of an Environmental Monitoring and Response System (EMRS) designed to detect high concentrations of HRVOCs within the vicinity of the Houston Ship Channel (Pendleton and Rozacky, 2005). The pilot project was operated by a joint TCEQ – industry group and included participants from the City of Houston. TCEQ emissions inventory data list approximately 90 companies in the Houston Ship Channel area that operate processes potentially associated with HRVOC emissions (**Figure 2-1**). Sixty of these companies eventually elected to participate in the 2004 EMRS pilot study.

The pilot system was based on a network of seven auto-GC monitors (**Figure 2-2**), which collect data over a 60-minute sampling cycle. Routine wind speed and direction data were also collected at 5-minute intervals over a network of 35 sites. All data were transmitted to TCEQ and processed through the EMRS notification system within one hour of receipt. Automatic “trigger alert” notifications were sent via e-mail to participating facilities whenever a specified threshold concentration of one or more of six target HRVOCs was exceeded.[1] Only those participating facilities located within a 90-degree upwind wedge centered on the hourly average wind direction coincident with the time the threshold concentration was exceeded and extending for a distance of 10 miles upwind from the monitoring site which generated the “trigger event” were notified. This process is illustrated in **Figure 2-3**.

During the pilot study, two sets of threshold levels were set for each HRVOC species:

1. A low-level threshold set to two standard deviations above the historical mean
2. A medium threshold was set based on HROVC species concentrations contributing to the fifth highest OH^- reactivity event during each time of day period at each monitoring site. These levels were intended to result in approximately 40 alerts during the pilot program period based on a statistical analysis of historical measurements.

Specific threshold levels were set by time of day for each site as shown in **Table 2-1**. Exceedances of the low-level threshold were used for information purposes only but no action was taken. The original EMRS design also called for setting a “high” threshold for each monitored species based on short-term health effects levels but this was not used as part of the pilot program. During the pilot study period, notifications of medium threshold exceedance events were sent to all participating facilities located within a 90 deg arc of radius 10 miles centered on the wind direction observed at the time and location of the threshold exceedance.

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[1] Species included in the pilot study were: ethylene, propylene, 1,3-butadiene, and butanes (isobutene, cis-2-butene, trans-2-butene).

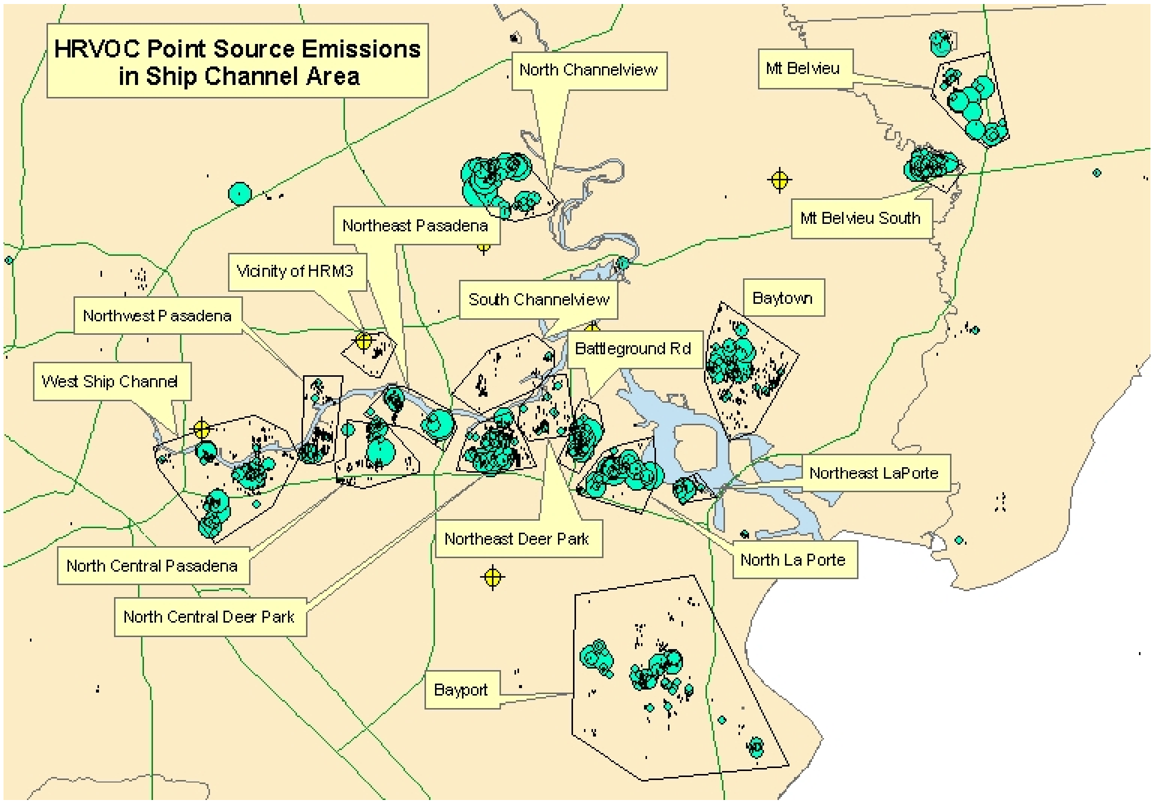

Figure 2-1. HRVOC point sources in the Ship Channel area (source: TCEQ).

Figure 2-2. Seven-site auto-GC ("PAMS") monitoring network used in the 2004 EMRS Houston Ship Channel pilot study (note that HRM sites indicated by black squares are not part of the auto-GC network). Source: TCEQ.

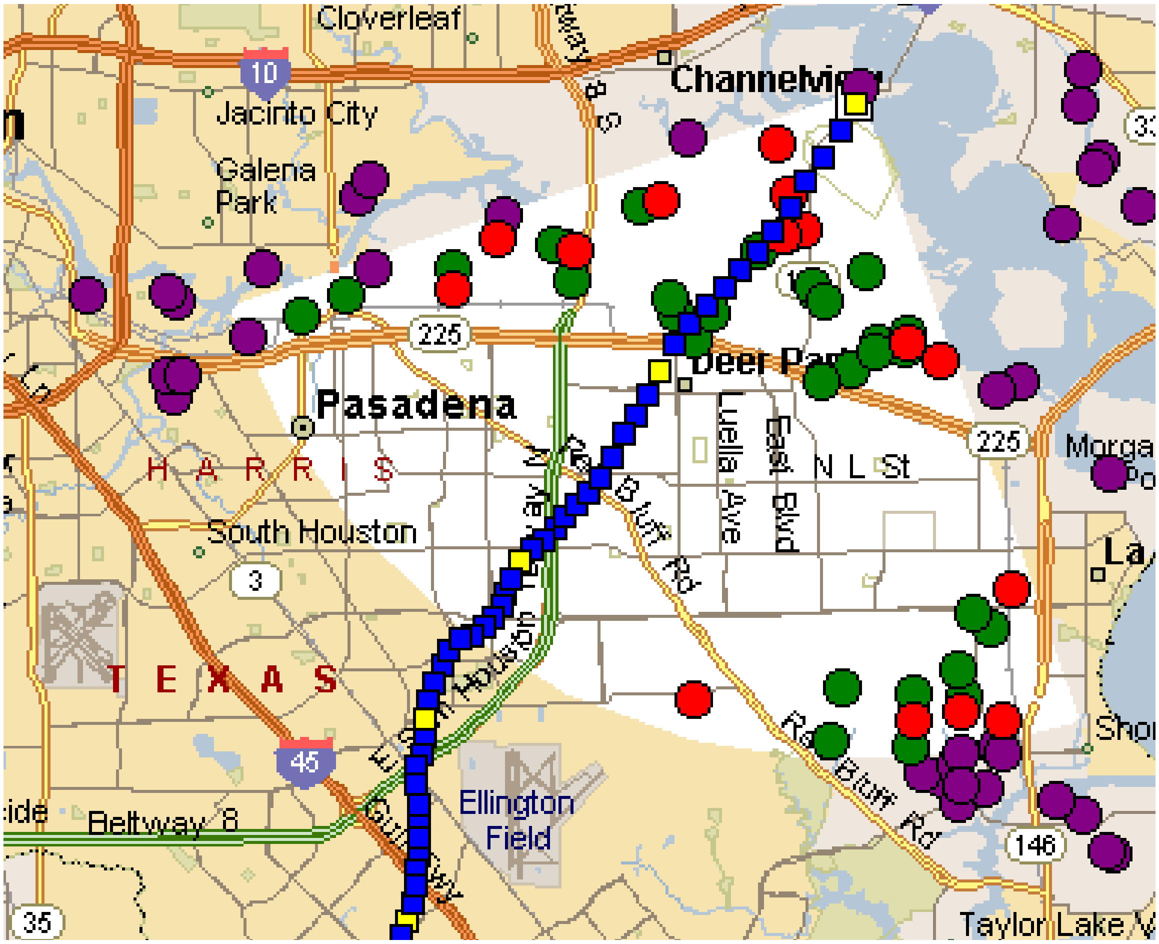

Figure 2-3. Example of upwind trigger alert notification zone (white area). Colored dots show industrial facilities that produce or handle HRVOCs (green = EMRS participating facilities in notification zone; red = EMRS non-participating facilities in notification zone; purple = facilities outside of notification zone). Source: TCEQ (2005).

Table 2-1. Medium notification threshold levels used in the 2004 EMRS pilot study (Pendleton and Rozacky, 2005).

	C617	**C1015**	**C115**	**C055**	**C603**	**C1020**	**C035**
	Wallisville	**Lynchburg Ferry**	**Channelview**	**Clinton Drive**	**HRM 3**	**Cesar Chavez**	**Deer Park**
Parameter	**48-201-617**	**48-201-1015**	**48-201-0026**	**48-201-1035**	**48-201-0803**	**48-201-6000**	**48-201-1039**
	PpbC	**PpbC**	**ppbC**	**ppbC**	**ppbC**	**ppbC**	**ppbC**
0000 - 0700							
Ethylene	742.46	1203.64	318.58	114	382.38	114	1232
Propylene	361.2	585.54	154.98	55.47	186.03	55.47	600
1,3-Butadiene	190.2	308.36	81.6	29.2	97.96	29.2	316
1-Butene	403.4	653.96	173.08	61.96	207.76	61.96	668
t-2-Butene	198.4	321.6	85.12	30.48	102.16	30.48	328
c-2-Butene	224.72	364.28	96.44	34.52	115.72	34.52	372
0800 - 1500							
Ethylene	229.46	536.08	292.88	116.66	220.44	116.66	516
Propylene	111.63	260.79	142.47	56.76	107.25	56.76	252
1,3-Butadiene	58.8	137.32	75.04	29.88	56.48	29.88	132
1-Butene	124.68	291.28	159.12	63.4	119.76	63.4	280
t-2-Butene	61.32	143.24	78.24	31.16	58.92	31.16	136
c-2-Butene	69.44	162.24	88.64	35.32	66.72	35.32	156
1600 - 2300							
Ethylene	420.64	1174.38	563.48	158.48	417.4	158.48	592
Propylene	204.63	571.32	274.11	77.1	203.07	77.1	288
1,3-Butadiene	107.76	300.84	144.36	40.6	106.92	40.6	152
1-Butene	228.56	638.08	306.16	86.12	226.8	86.12	320
t-2-Butene	112.4	313.8	150.56	42.36	111.52	42.36	160
c-2-Butene	127.32	355.44	170.56	47.96	126.32	47.96	180

Analysis of results from the 2004 pilot study period (Pendleton and Rozacky, 2005) showed that a total of 160 exceedances of the medium threshold levels were recorded between June and November. Exceedances were most common at Cesar Chavez and Clinton Drive with most exceedances occurring during the 0:00 – 7:00 time period (see **Table 2-2**). [2]

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[2] Exceedance events shown in Table 2-2 are based on individual hourly measurements and thus may include multiple events during a single 8-hour period.

Table 2-2. Exceedances of medium trigger levels during June – November 2004 pilot program.

Monitor Site	Compound	Midnight to 7 AM	8 AM to 3 PM	4 PM to 11 PM	Number of Alerts
Cesar Chavez	1,3-Butadiene	10	9	3	22
	1- Butene	8	0	0	8
	Ethylene	5	0	0	5
	Propylene	22	5	2	29
	c-2-Butene	1	0	0	1
	t-2-Butene	3	0	0	3
Clinton Drive	1,3-Butadiene	18	5	2	25
	1-Butene	1	2	0	3
	c-2-Butene	1	0	2	3
	t-2-Butene	2	2	2	6
	Ethylene	2	2	0	4
	Propylene	3	1	6	10
Channelview	1-Butene	3	0	0	3
	t-2-Butene	0	0	1	1
	Ethylene	1	0	0	1
	Propylene	8	0	0	8
HRM Site 3	1,3-Butadiene	1	2	0	3
	t-2-Butene	1	0	2	3
	1-Butene	4	1	0	5
	Ethylene	0	0	1	1
	Propylene	1	3	0	4
Deer Park	Propylene	0	0	1	1
Lynchburg	Propylene	4	1	2	7
Wallisville	Propylene	1	3	0	4
Totals		**100**	**36**	**24**	**160**

(source: Spaw and Rozacky, 2005)

At the conclusion of the 2004 pilot study, participants prepared a summary of operations occurring at facilities which fell in the 90-degree pie wedge contact zone associated with each trigger event. This review found that, of the 160 alerts issued, a reportable emissions event occurred upwind 13% of the time. Of the other non-routine activities, loading/unloading was the most frequently reported. However, for 37% of alerts, no non-routine activities were identified by the participating facilities. These alerts may have been triggered by releases from non-participating facilities or otherwise unidentified non-routine releases.

3. EVALUATION OF ALTERNATIVE EMRS NETWORK DESIGNS

For purposes of the 2004 EMRS pilot study described in Section 2, existing ambient monitoring resources in the Ship Channel area were used to identify high HRVOC events. These resources consisted of a network of seven sites equipped with automatic Gas Chromatographs (auto-GCs) as illustrated in Figure 2-2, supplemented by a total of 35 wind monitoring sites in the Houston area. Although the 7-site auto GC network covers a broad extent of the Houston Ship Channel, the spacing between monitors is fairly large (averaging 7 km) and the ability of this network to detect intermittent releases from individual HRVOC sources is not known. It is possible that a more comprehensive or reconfigured monitoring network in the Ship Channel may be needed to increase the probability of identifying releases to an acceptable level.

EMISSIONS EVENT DETECTION SIMULATION SYSTEM

In order to quantitatively evaluate the level of performance to be expected from alternative designs for an ambient monitoring network suitable for use in the EMRS, we designed a dispersion modeling system to simulate a variety of the types of emission events the EMRS is intended to detect and quantitatively analyzing the ability of existing or potential future alternative monitoring networks to detect and identify the source of each release event. The modeling system developed for this study consists of three components:

1. An emission events simulator capable of generating a random sample of realistic release scenarios of the type to be detected and located by the EMRS.
2. An atmospheric dispersion model that accurately characterizes the advection, dispersion, and chemical transformation of simulated releases over the Ship Channel area under a variety of meteorological conditions.
3. An analysis module that provides quantitative performance measures of the ability of alternative monitoring networks to detect and localize contaminant releases.

Each component is described in more detail in the following subsections.

Emissions Events Simulator

VOC releases to be detected and localized by the EMRS may involve one or more VOC species released from any one of the many potential sources in the Ship Channel area over time periods ranging from less than an hour to several hours or longer with a broad range of release rates. Given the wide variety of resulting emission scenarios, we developed an emissions event simulator (EES) that randomly generates emission scenarios of the type the EMRS is designed to detect. A large number of random emission events generated by the EES were then simulated by the atmospheric dispersion model as described below. By modeling many randomly selected but realistic release scenarios, it was possible to prepare statistical evaluations of the performance of alternative EMRS network designs.

The EES was designed to generate emission events that are as realistic as possible, i.e., that are similar to the types of actual events that the EMRS is intended to detect. Information on release parameters from HRVOC emission events reported to TCEQ as required by the revised provisions of Texas Administrative Code (TAC) Title 30 Chapter 101 which became effective on 12 September 2002,was used to create the EES. These revised rules require sources to report any “unauthorized” releases exceeding 100 lb in any 24-hour period. While releases of smaller amounts are not required to be reported, releases below this threshold are most likely too small to be of primary concern within the context of the EMRS. Sources are required to report their releases to TCEQ electronically and TCEQ is required to make the reports publicly available.

Allen et al. (2004) created an integrated database of HRVOC emission events based on releases reported to the TCEQ for a 12 month period (1/31/03 – 1/30/04). This database contains information on event locations, compositions, magnitudes, and durations. These data were made available for use in our study by the authors (Murphy, 2005). Sources in the Houston Ship Channel area with reported HRVOC releases are shown in **Figure 3-1**. To prepare the release event data for use with the EES, the data were processed into set of 1,238 records in which each record consists of information for an individual HRVOC species released from an individual source as part of one of the 764 events reported in Harris Co during this period. Events with reported durations in excess of 24-hours were then excluded, as were events for which valid geographic coordinates were not recorded, leaving a total of 417 events. Releases with reported durations in excess of 24 hours are likely to have actually consisted of one or more releases of much shorter duration (Murphy, 2005). Simulation of these releases as continuous events lasting longer than 24 hours would therefore be inaccurate. In addition, most longer events are characterized by relatively low average release rates which makes it far less likely that the release would be “detected” at a monitoring site.

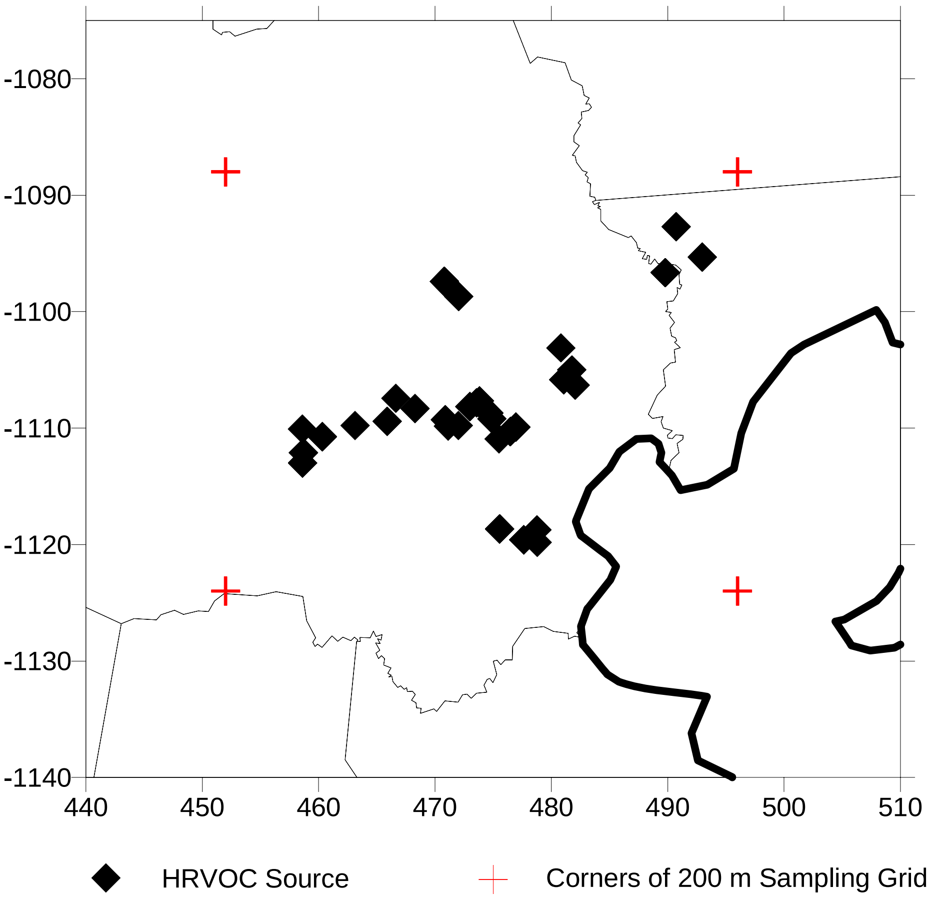

Figure 3-1. Sources in the Houston Ship Channel area reporting HRVOC releases.

The EES generates events based on random sampling with replacement of records from the final set of 417 events described above. Thus, the simulated events represent a random sample from the empirical joint distributions of event magnitudes, durations and locations contained within the HRVOC emissions event database. A set of 100 random events were generated for each of the 11 modeling days corresponding to the 22 August – 1 September 2000 ozone episode for which photochemical dispersion modeling has been performed by TCEQ, thus resulting in a total of 1,100 simulated events. Although actual reported events occur much less frequently than 100 times per day, generating a large number of simulated events for each day of modeling made it possible to build up a large sample of modeled event detections for subsequent statistical analysis. Simulation of more than 100 events per day was deemed impractical since each simulated event must be tracked individually by the dispersion model, thus consuming greater amounts of computing resources. Since a total of 1,100 simulated events were generated by randomly sampling with replacement from the original set of 417 events, each emission event was selected an average of roughly three times. Although the emission parameters are the same for each resampled event, the meteorological conditions at the times of the simulated events are different since each randomly selected event is assigned by the EES to a different date and time as described below.

Magnitudes of the simulated events represent the total mass of an individual HRVOC (ethene, propene, 1,3 butadiene, or total butenes) from the randomly selected event.

Simulated event start times were randomly generated by the EES using the assumption that the start times occur with equal probability during any hour of the day but with the constraint that each randomly selected n-hour event must end on or before midnight. Due to the manner in which emissions are simulated in the dispersion model (described below), simulated event durations must be in whole hours. Thus, the duration of each randomly sampled event was rounded up to the nearest whole hour but the total amount of the release was unaltered. This has the effect of reducing the lb/hour release rates for releases with durations that are not multiples of whole hours but avoids the problem of artificially inflating the total size of a release, especially for very short (sub-hourly) releases.

Statistical summaries of the 1,100 simulated HRVOC release events is provided in **Table 3-1**; the empirical cumulative distribution functions for total amount released, release rate, and event duration are shown in **Figure 3-2.** Distributions of release rates and total amount of release are highly skewed, with a relatively small number of very high values in each case. Event durations are also somewhat skewed: half the events last less than three hours and long duration events are less common. For example, just 25% of events are longer than 8 hours. A total of 330 (30%) of the 1,100 simulated events lasted less than an hour, 261 (24%) lasted less than 30 minutes and 218 (20%) lasted less than 15 minutes. Thus, while over two-thirds of reported events lasted over an hour (excluding events lasting more than 24 hours as noted above), there is a small but significant fraction of short duration events.

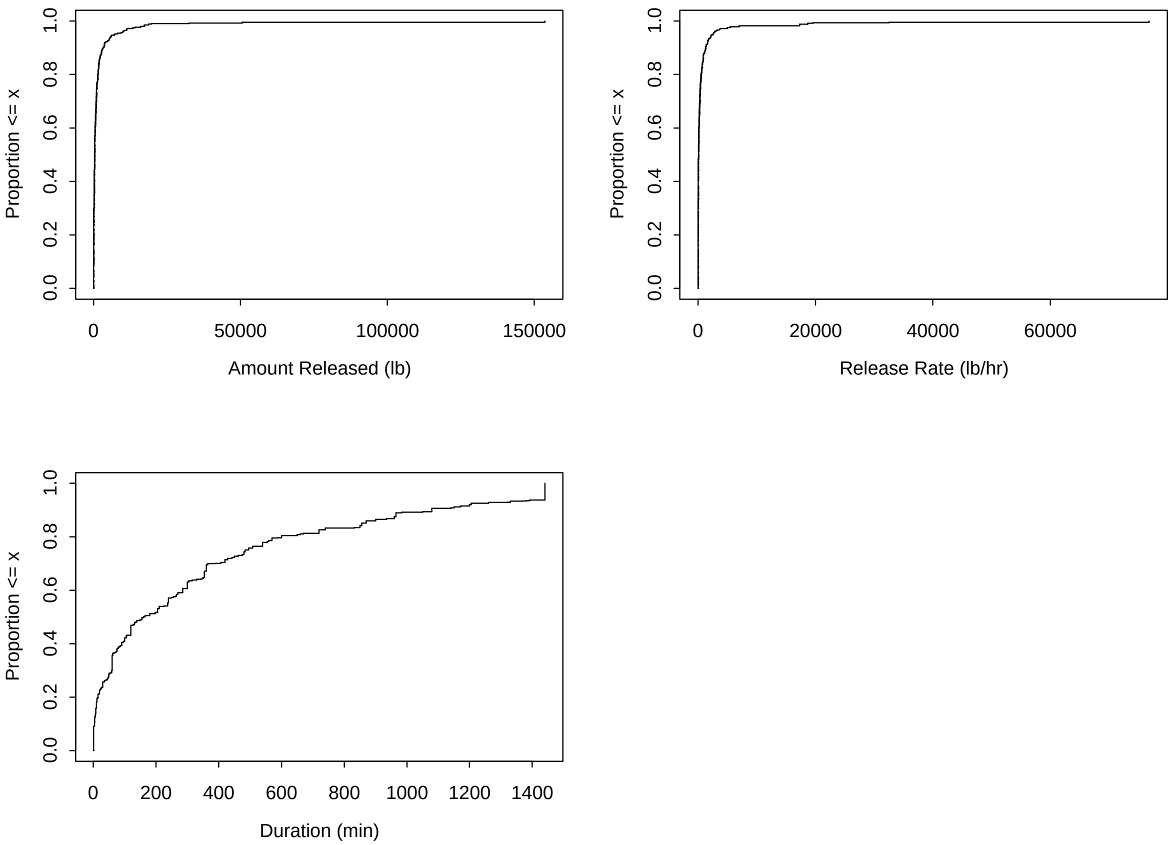

Figure 3-2. Empirical cumulative distributions of amount released (top left), release rate (top right) and release duration (bottom left) from the set of 1,100 randomly generated HRVOC release events.

A summary of simulated events and the actual events data from which they were sampled by release rate is provided in **Table 3-2.** Simulated and actual percentage values are nearly identical since the random events were generated by randomly sampling from the set of 417 actual events. Note that there were 49 actual events with emission rates greater than 1,000 lb/hour within the 12 month events database which translates into roughly one such event every week on average.

Table 3-1. Summary statistics for 1,100 random HRVOC release events.

	Min.	1st Quartile	Median	Mean	3rd Quartile	Max.
Release Rates (lb/hr)[1]	0.04	13.65	78	990.1	390	76,832
Duration (hrs)	1	1	3	6	9	24
Amount Released (lb)	0.2	44.0	339.4	2,137.6	1,064.8	153,664.0

Table 3-2. Summary of simulated and actual reported HRVOC release events by release rate.[2]

	Release Rate (lb/hr)						
	>0	>10	>50	>500	>1,000	>10,000	>20,000
No. Simulated Releases (%)	1100 (100%)	875 (80%)	614 (56%)	231(21%)	135 (12%)	19 (2%)	7 (1%)
No. of Actual Releases (%)	417 (100%)	333 (80%)	228 (55%)	84 (20%)	49 (12%)	5 (1%)	2(0.5%)

A map of the Harris County sources showing the number of actual reported emission events at each facility is provided in **Figure 3-3**; the total amount of HRVOCs from all reported events at each facility is shown in **Figure 3-4.** Facilities with the greatest number of events can be found in most parts of the Ship Channel area. However, the total amount of HRVOC from reported releases is much greater at some locations than at others. Of particular note is the facility with the largest amount of material released located at the east end of the Ship Channel, very close to the Clinton Drive and Cesar Chavez monitoring sites. Although not by any means constituting proof of a cause and effect relationship, this geographic match up is consistent with results from the EMRS pilot study, during which the Clinton and Cesar Chavez sites recorded the greatest number trigger events (see Table 2-2).

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[1] Based on rounding release durations to next highest hour.

[2] Based on all reported releases less than 24 hours duration in Harris Co. during the 12 month period 1/31/03 – 1/30/04 with valid geographic coordinates.

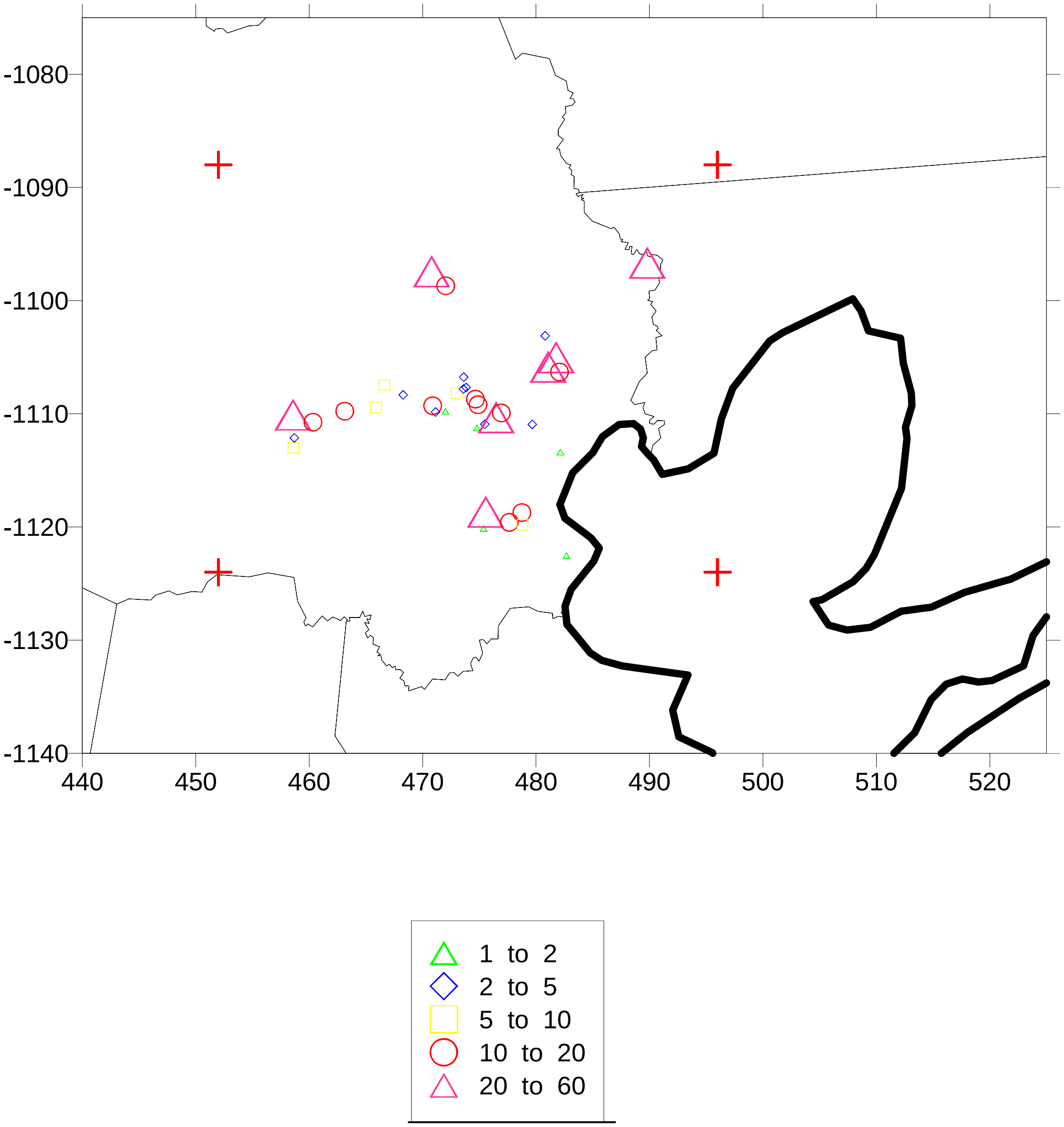

Figure 3-3. Number of reported HRVOC emission events at each Harris County facility (red plus signs indicate corners of the 200 m sampling grid used in the dispersion model).

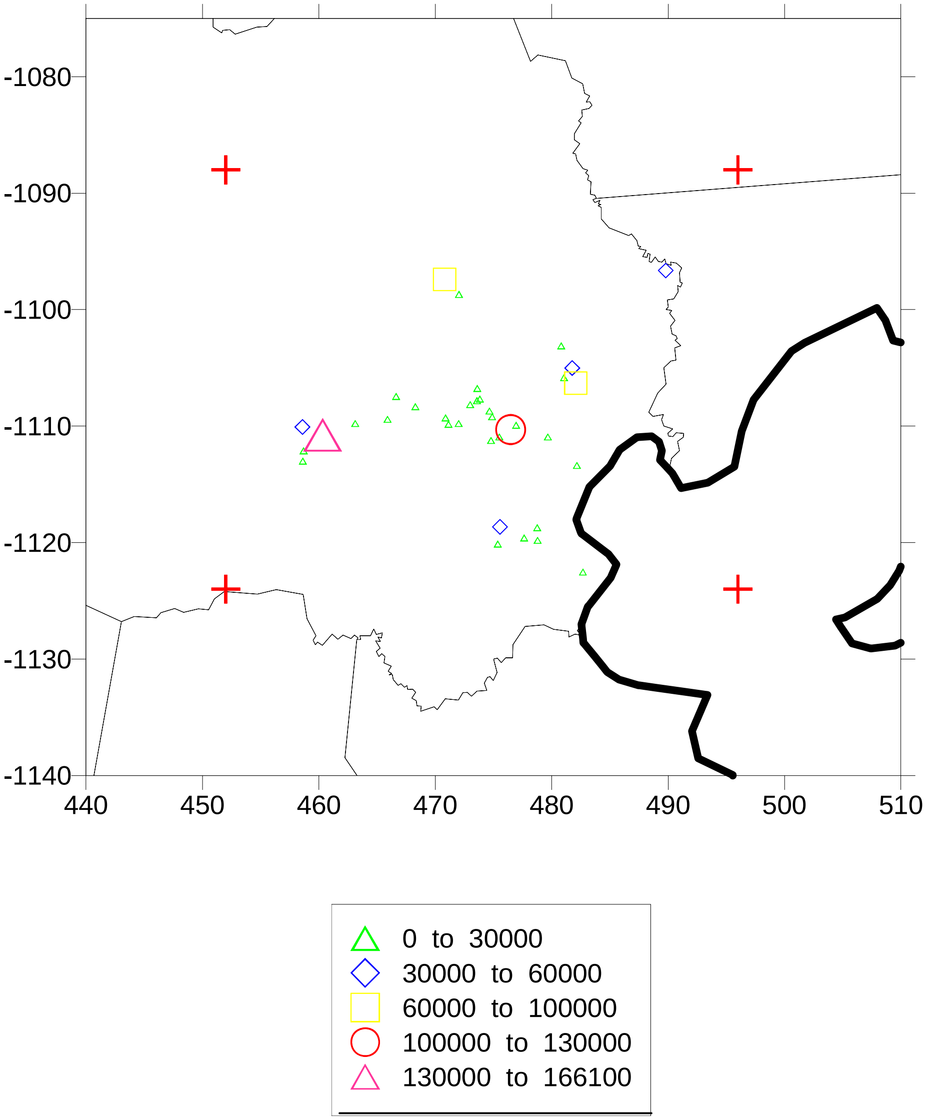

Figure 3-4. Total amount of HRVOCs (lb) from reported emission events at each Harris County facility (red plus signs indicate corners of the 200 m sampling grid used in the dispersion model).

Dispersion Modeling

A dispersion model was needed to predict the advection and diffusion of simulated HRVOC releases, taking into account spatial and temporal variations in meteorological conditions and the sometimes rapid chemical transformations of the released hydrocarbons. These requirements were met using the CAMx 3-D photochemical model with the full-chemistry Plume-in-Grid (PiG) sub-grid scale puff dispersion module. CAMx with PiG was recently applied to the problem of modeling HRVOC releases in the Ship Channel under HARC Project H12 (Kemball-Cook et al., 2004). By using the CAMx RTRAC technology, it was possible to individually track the downwind dispersion of all 1,100 simulated HRVOC release events within a single model run, thus allowing us to develop results for a statistically meaningful sample of emission events within a reasonable amount of computing time.

CAMx version 4.03 was applied to the model input files previously developed for the 25 August – 1 September 2000 episode as described by Kemball-Cooke et al. (2004). This episode is representative of summertime conditions with high ozone formation potential. CAMx was run on the 36 - 12 – 4 km nested grid domain as shown in **Figure 3-5** using the unadjusted ("base5b.regular") Houston area inventory developed by TCEQ. Dispersion of the simulated HRVOC releases from sources in the Ship Channel area was modeled via the CAMx PiG module which uses the Gaussian dispersion equations to model emission "puffs" released from each simulated point source in a Lagrangian framework until each puff is large enough to be resolved by the 4 km modeling grid. To simulate the rapid chemical transformation of HRVOCs as they travel downwind, the Incremental Reactions for Organics and NO_x treatment of the puffs simulated in the PiG module (IRON PiG) was employed (Kemball-Cook et al., 2004). Under the IRON PiG methodology, puffs interact chemically with each other and with the "background" species simulated on the modeling grid, using the full CAMx VOC/NO_x/Ozone chemistry.

Figure 3-5. The CAMx modeling domain showing the nested 36, 12 and 4 km grids.

A sampling grid with 200 m spacing between grid nodes was used over the Ship Channel area to specify the receptor locations at which the CAMx/PiG predicted concentration impacts of each HRVOC release were output. The location of the outer corners of this grid relative to the Ship Channel HRVOC sources is shown in Figure 2-1. CAMx outputs the sum of the simulated puff and grid concentrations of each tracked generic HRVOC release at each grid node. Examples of the resulting hourly concentration fields over the Ship Channel area are presented in Figure 3-6. Concentration plumes from the individual simulated releases as resolved by the CAMx/PiG model on the 200m sampling grid are clearly visible.

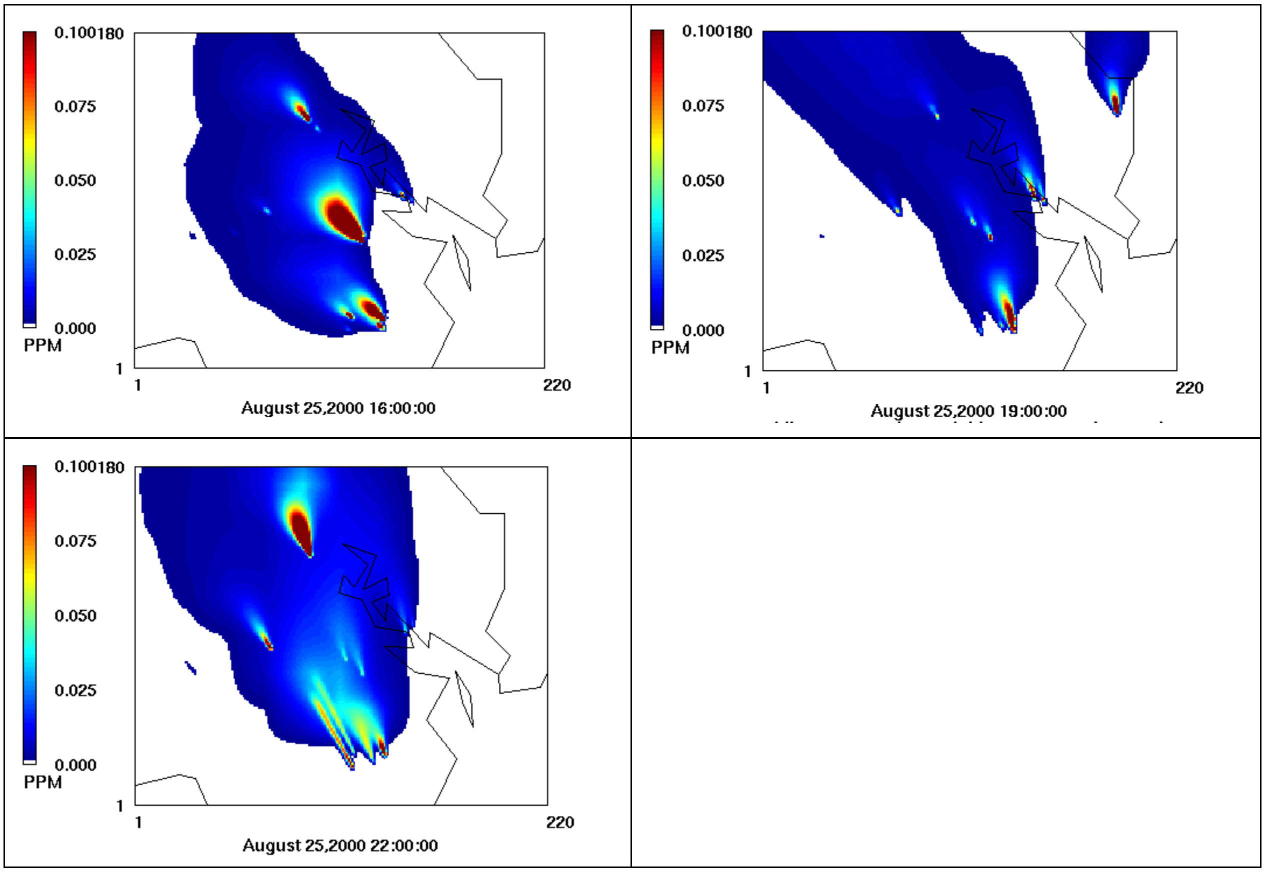

Figure 3-6. Examples of hourly surface layer HRVOC concentrations resulting from all simulated releases for hours 16:00 to 22:00 on 25 August 2000 as predicted by CAMx with the IRON PiG module over the Houston Ship Channel.

Each simulated HRVOC release was modeled as a generic HRVOC species with reactivity parameters set equal to that of OLE in the CB-IV chemical mechanism. OLE reactivity parameters were selected as OLE is the most reactive of the CB-IV species and was thus judged to provide the best overall representation of a generic HRVOC available within the CB-IV framework. Gaussian puff modeling of the simulated HRVOC releases in the PiG module requires data on the physical release parameters (height, temperature, flow rate) in addition to the emission rate. As data on release parameters are not available in the HRVOC event database, each source was modeled at a release height of 10 m, a volumetric flow rate of 5.45 m^3/s (equivalent to a 50 m diameter release area with an exit velocity of 10 m/hr) and with zero thermal buoyancy. This resulted in a near ground level source with almost no plume rise and should lead to the most conservative estimate of near-source ground level impacts.

ANALYSIS OF MODEL RESULTS

Results of the model runs described above were analyzed to determine the theoretical potential for detecting and localizing emission sources with a given monitoring network configuration as defined by subsets of the 200 m sampling grid nodes. Two alternative monitoring network configurations were specified:

1. The existing network of seven auto-GCs used in the 2004 EMRS pilot study (**Figure 3-7**).
2. A hypothetical expanded monitoring network as shown in **Figure 3-8**, consisting of the seven existing sites as in (1) above plus 20 additional monitoring sites selected from other locations in the Ship Channel area where other air monitoring activities are currently underway or which were formerly used as monitoring sites and where, at least in some cases, it may be possible to re-establish monitoring.[3] This network provides reasonably good spatial coverage of the entire area and can be interpreted to represent at least as comprehensive an ambient monitoring network for the EMRS as one could reasonably hope to establish in the Ship Channel area within the foreseeable future.

In each case, modeled concentrations at the actual monitor locations were approximated by the predicted ground-level concentration at the nearest node of the 200 m sampling grid. This results in a maximum location error of $100*2^{1/2}$ = 141 m.

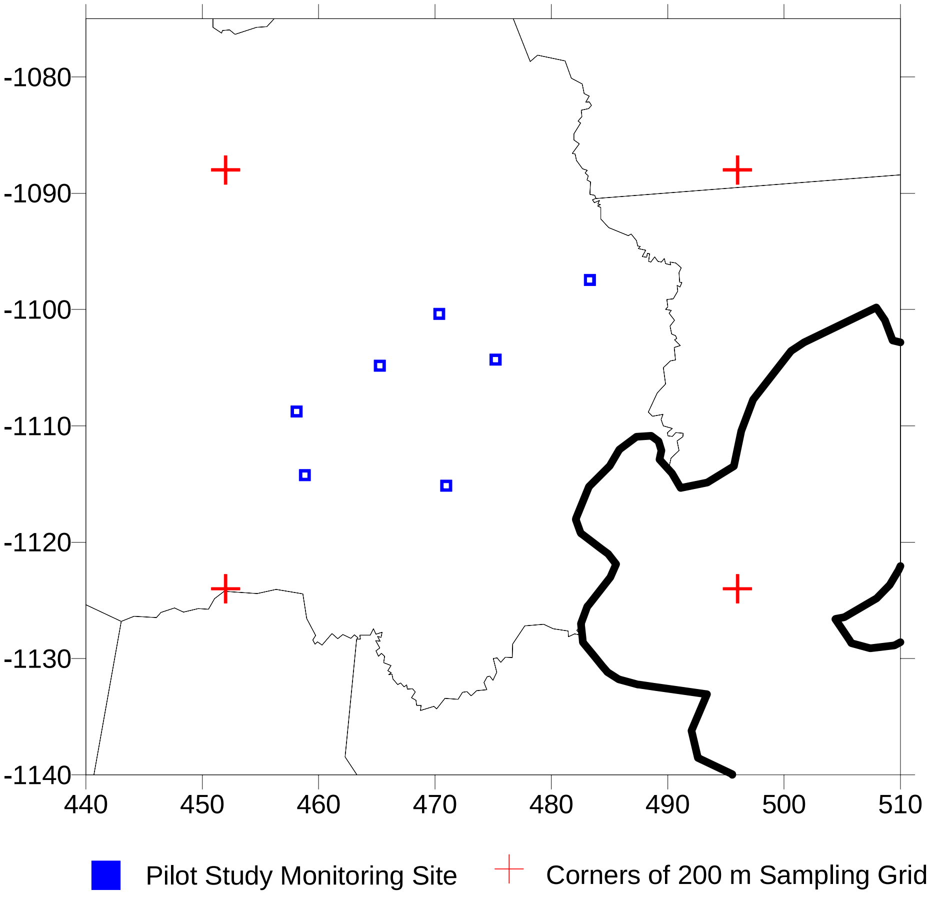

Figure 3-7. Location of seven auto-GC sites in the Houston Ship Channel used in the 2004 EMRS pilot study.

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[3] Hypothetical monitoring locations for the expanded network were derived from locations listed on TCEQ's monitoring operations web site (http://www.tnrcc.state.tx.us/cgi-bin/monops/site_info).

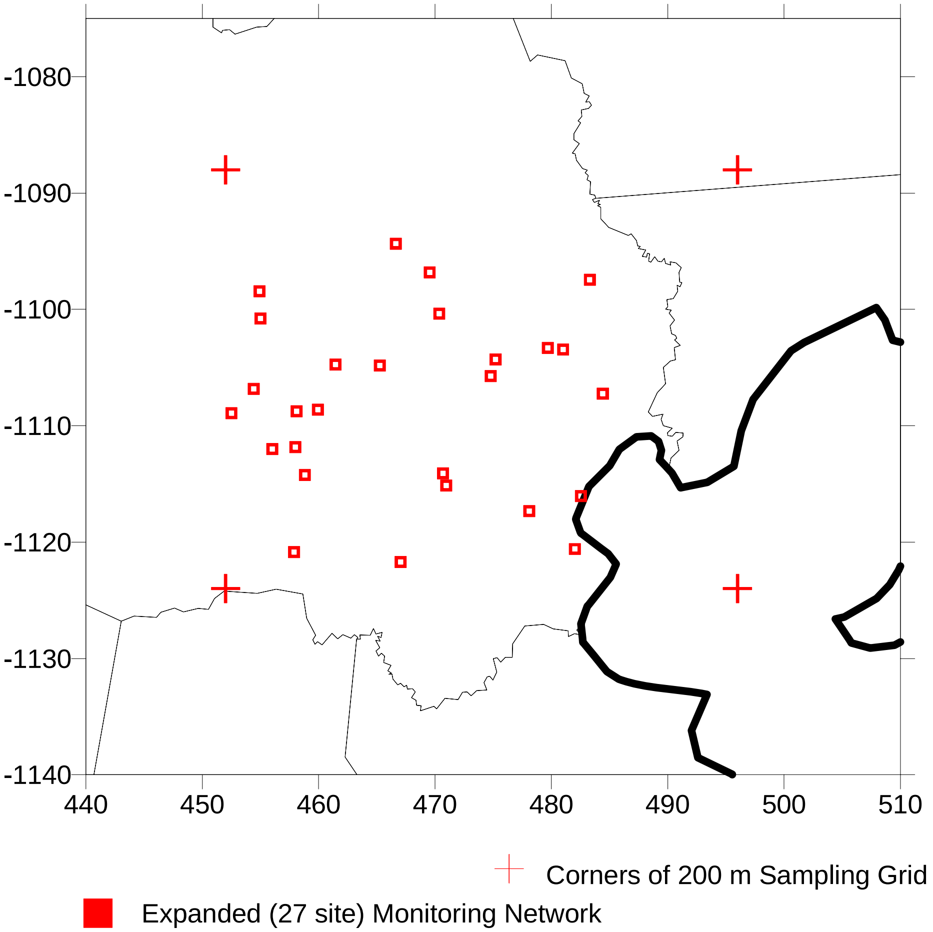

Figure 3-8. Locations of potential monitoring sites in a hypothetical, expanded 27-site EMRS network.

Network Performance

Modeling results were summarized in terms of the frequency with which concentrations were predicted to exceed plume detection thresholds at the selected monitoring locations.[4] Plume detection thresholds were based on the "medium" thresholds by time of day and monitoring site used in the 2004 pilot study as described in Section 1 and shown in Table 2-1. Since the modeled releases represent a generic HRVOC species, the median value of the six species-specific thresholds as shown in **Table 3-3** was used in the initial network performance evaluation.

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[4] Each release was tracked only until midnight on the day of release. Thus a short duration release occurring late in the day may not have time to travel to a potential receptor site before midnight and would thus not be counted as a detected event even if the concentration exceeded the applicable threshold value.

Table 3-3. Concentration threshold values used to evaluate simulation results.

	C617	**C1015**	**C115**	**C055**	**C603**	**C1020**	**C035**
	Wallisville	**Lynchburg Ferry**	**Channelview**	**Clinton Drive**	**HRM 3**	**Cesar Chavez**	**Deer Park**
	48-201-617	**48-201-1015**	**48-201-0026**	**48-201-1035**	**48-201-0803**	**48-201-6000**	**48-201-1039**
	PpbV	**ppbV**	**ppbV**	**ppbV**	**PpbV**	**ppbV**	**ppbV**
0000 - 0700	78.5	127.3	33.7	12.1	40.4	12.1	130.0
0800 - 1500	24.3	56.7	31.0	12.3	23.3	12.3	54.5
1600 - 2300	44.5	124.2	59.6	16.8	44.1	16.8	62.5

Results for 2004 EMRS Pilot Study Network

Detection event frequencies based on the seven site 2004 EMRS pilot study monitoring network are summarized in **Table 3-4**. Of the 1,100 simulated HRVOC releases, just 45 (4%) produced an impact exceeding the applicable concentration threshold at one or more of the seven monitoring locations listed in Table 3-3. As one would expect, the longer, larger releases are more likely to be detected than the smaller releases. These results show that the duration of the release is less important than the size. We note that this may be at least partially due to the requirement that the minimum simulated release event length was 1-hour since (this limitation was imposed for the reasons described above). Results stratified by the release rate (lb/hour) are shown in **Table 3-5**. The probability of detecting an event increases monotonically with release rate. However, even some of the bigger events have a low probability of detection on this network – only the seven biggest events (with release rates ranging from 32,500 to 76,832 lb/hr) were detected 100% of the time. Results from the HARC H13 study (Allen et al., 2004) show that HRVOC releases of 1,000 lb/hour or more are potentially capable of producing a 2 to 3 ppb increase in ambient ozone levels under the right conditions. Our simulation shows that such releases have just over a 20% probability of detection using the pilot study 7-site network (see Table 3-5). The current seven auto-GC site network can only be expected to reliably detect releases exceeding 10,000 or 20,000 lb/hr; the probability of detection for these very large events is above 50%. Releases in this size range only comprise between and 5 and 14% of all releases greater than 1,000 lb/hr, suggesting that the seven site network can be expected to reliably detect just a small fraction of all potentially significant events.

Detections of simulated HRVOC release events were fairly evenly distributed among the seven monitoring sites with the notable exception that detections at the Clinton Drive site at the western end of the Ship Channel were about twice as common as the other sites, including the nearby Cesar Chavez site (**Figure 3-9)**. These two sites used the same sets of threshold concentrations for defining an event detection (Table 3-3) so the differences in the number of detection events at these sites are due to the prevailing wind flow pattern during the eleven day modeling period and the frequency and magnitude of simulated releases at upwind facilities as shown in Figures 3-3 and 3-4.

Table 3-4. Summary of a) number of simulated HRVOC releases, b) number of releases detected on the seven-site EMRS network and c) the associated probability of detection stratified by the total quantity of HRVOC released and duration of release event.

a) No. of Releases	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	257	120	14	0	**391**
2	67	53	0	5	**125**
3 thru 6	145	96	9	0	**250**
7 thru 24	191	128	12	3	**334**
TOTAL	**660**	**397**	**35**	**8**	**1,100**
b) No. Detected	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	3	12	6	0	**21**
2	1	2	0	5	**8**
3 thru 6	4	1	3	0	**8**
7 thru 24	1	4	1	2	**8**
TOTAL	**9**	**19**	**10**	**7**	**45**
c) Prob. Of Detection	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	0.012	0.100	0.429	NA	**0.05**
2	0.015	0.038	NA	1.000	**0.06**
3 thru 6	0.028	0.010	0.333	NA	**0.03**
7 thru 24	0.005	0.031	0.083	0.667	**0.02**
TOTAL	**0.01**	**0.05**	**0.29**	**0.88**	**0.04**

Table 3-5. Summary of simulated EMRS network event detections stratified by event HRVOC release rate.

	Release Rate (lb/hr)						
	>0	**>10**	**>50**	**>500**	**>1,000**	**>10,000**	**>20,000**
No. Releases	1100 (100%)	875 (80%)	614 (56%)	231 (21%)	135 (12%)	19 (2%)	7 (1%)
No. Detected	45	44	40	32	30	11	7
Prob. Of Detection	0.04	0.05	0.07	0.14	0.22	0.58	1.00

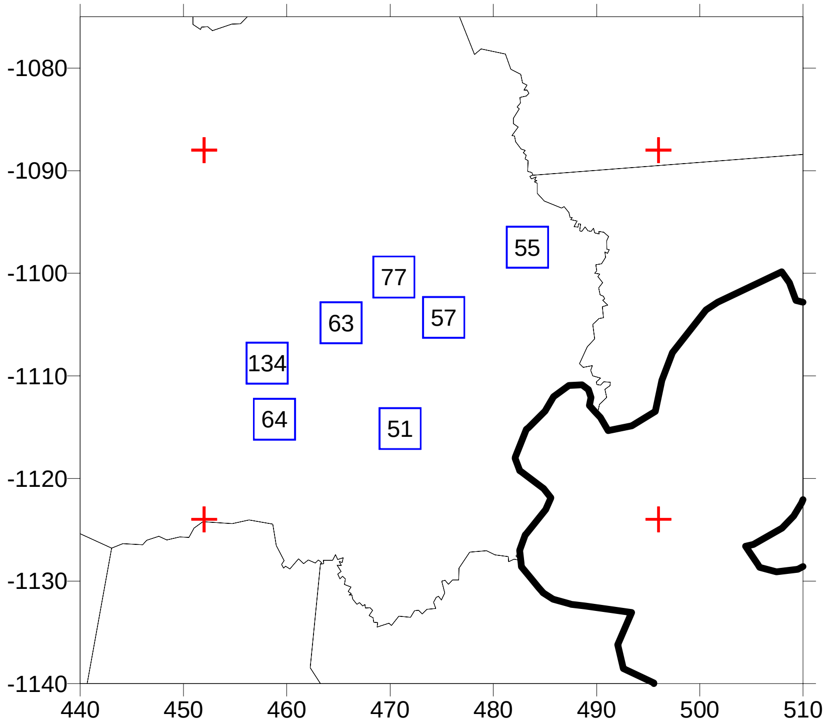

Figure 3-9. Number of simulated event detections at each monitoring site location in the seven site network used in the 2004 Houston EMRS pilot study (see Figure 2-2). Note that a single simulated HRVOC release may be detected multiple times at multiple sites.

Results for Expanded EMRS Network

Simulated network detections over the "expanded EMRS network" consisting of the 27 sites shown in Figure 3-9 were tabulated in the same manner as described for the 7 site EMRS network above. Since site-specific threshold levels have not been set for all 27 locations, the detection thresholds for the Clinton Drive site listed in Table 3-3 were initially used for all of the potential new locations. This results in a fairly optimistic detection rate for the expanded network since the median of the species-specific thresholds shown for Clinton Drive in Table 3-3 are the lowest among the seven 2004 EMRS sites.

A summary of detection events simulated over the expanded EMRS network is shown in **Table 3-6** as a function of release duration and total amount of HRVOC released. Detection probabilities are significantly higher as compared to the existing seven site network (see Table 3-5). While the larger releases are more likely to be detected than the smaller releases, there is no obvious relationship between release duration and probability of detection for a given size release. A similar examination of the probability of detection as a function of release rate and duration (**Table 3-7**) shows that the influence of release duration is largely secondary to that of the release rate (at least for releases of minimum 1-hour duration examined in this analysis). A cumulative summary of the probability of detection as a function of release rate (**Table 3-8**) shows that, for the expanded network, releases greater than about 500 lb/hr have a better than 50% detection rate; releases in this size range comprise 21% of the simulated HRVOC releases.

The spatial distribution of the number trigger events modeled to occur at each hypothetical monitoring location is shown in **Figure 3-10**. An interesting feature of these results is the relatively large number of event detections modeled to occur in the vicinities of Baytown, North Channelview, and Bayport. This suggests that the current seven site auto-GC network may be missing a significant number of release events impacting these areas and that expanding the existing network in the eastern portion of the Ship Channel should be given priority over other locations.

Table 3-6. Summary of a) number of simulated HRVOC releases, b) number of releases detected on the 27-site EMRS network and c) the associated probability of detection (equal to b divided by a) stratified by the total quantity of HRVOC released and duration of release event.

a) No. of Releases	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	257	120	14	0	**391**
2	67	53	0	5	**125**
3 thru 6	145	96	9	0	**250**
7 thru 24	191	128	12	3	**334**
TOTAL	**660**	**397**	**35**	**8**	**1,100**
b) No. Detected	**Total Quantity Released (lbs)**				**TOTAL**
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	
1	19	68	10	0	**97**
2	3	11	0	5	**19**
3 thru 6	6	40	9	0	**55**
7 thru 24	6	41	11	3	**61**
TOTAL	**34**	**160**	**30**	**8**	**232**
c) Prob. Of Detection	**Total Quantity Released (lbs)**				**TOTAL**
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	
1	0.074	0.567	0.714	NA	**0.248**
2	0.045	0.208	NA	1.000	**0.152**
3 thru 6	0.041	0.417	1.000	NA	**0.220**
7 thru 24	0.031	0.320	0.917	1.000	**0.183**
TOTAL	**0.052**	**0.403**	**0.857**	**1.000**	**0.211**

Table 3-7. Summary of: a) number of simulated HRVOC releases, b) number of releases detected on the 27-site EMRS network and c) the associated probability of detection (equal to b divided by a) stratified by the HRVOC release rate (lb/hour) and duration of release event.

a) No. of Releases	**Release Rate (lb/hr)**						
Duration (hrs)	**0 thru 14**	**14 thru 80**	**80 thru 400**	**400 thru 10000**	**10000 thru 20000**	**20000 thru 80000**	**TOTAL**
1	78	78	88	133	12	2	**391**
2	13	18	54	35	0	5	**125**
3 thru 6	65	62	71	52	0	0	**250**
7 thru 24	125	123	66	20	0	0	**334**
TOTAL	**281**	**281**	**279**	**240**	**12**	**7**	**1100**
b) No. Detected	**Release Rate (lb/hr)**						
Duration (hrs)	**0 thru 14**	**14 thru 80**	**80 thru 400**	**400 thru 10000**	**10000 thru 20000**	**20000 thru 80000**	**TOTAL**
1	0	2	14	71	8	2	**97**
2	0	1	2	11	0	5	**19**
3 thru 6	1	4	12	38	0	0	**55**
7 thru 24	2	10	31	18	0	0	**61**
TOTAL	**3**	**17**	**59**	**138**	**8**	**7**	**232**
c) Prob. Of Detection	**Release Rate (lb/hr)**						
Duration (hrs)	**0 thru 14**	**14 thru 80**	**80 thru 400**	**400 thru 10000**	**10000 thru 20000**	**20000 thru 80000**	**TOTAL**
1	0.00	0.03	0.16	0.53	0.67	1.00	**0.25**
2	0.00	0.06	0.04	0.31	NA	1.00	**0.15**
3 thru 6	0.02	0.06	0.17	0.73	NA	NA	**0.22**
7 thru 24	0.02	0.08	0.47	0.90	NA	NA	**0.18**
TOTAL	**0.01**	**0.06**	**0.21**	**0.58**	**0.67**	**1.00**	**0.21**

Table 3-8. Summary of simulated expanded (27 site) EMRS network event detections stratified by event HRVOC release rate: Clinton Drive detection thresholds.

Cumulative	**Release Rate (lb/hr)**						
	>0	**>10**	**>50**	**>500**	**>1,000**	**>10,000**	**>20,000**
No. Releases (%)	1100 (100%)	875 (80%)	614 (56%)	231(21%)	135 (12%)	19 (2%)	7 (1%)
No. Detected	232	230	219	144	105	15	7
Prob. Of Detection	0.21	0.26	0.36	0.62	0.78	0.79	1.00

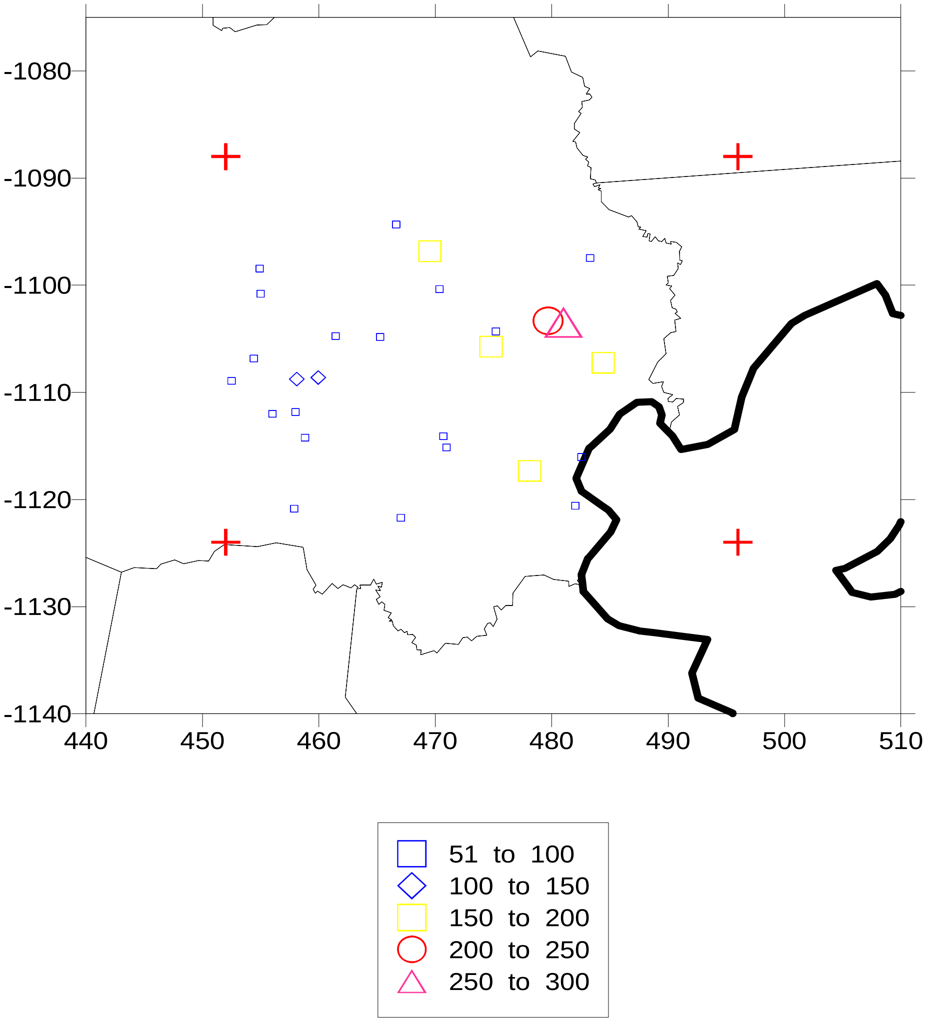

Figure 3-10. Number of simulated event detections at each monitoring site location in the hypothetical 27-site EMRS network. Note that a single simulated HRVOC release may be detected multiple times at multiple sites.

An examination was performed of the sensitivity of the detection probabilities to the use of different detection threshold levels by rerunning the above analysis with the threshold in each time period *for all sites* set to:

1. The maximum over the seven pilot study sites of the maximum species-specific thresholds (“High” thresholds),
2. The maximum over the seven pilot study sites of the median species-specific thresholds (“Medium” thresholds), and
3. The minimum over the seven pilot study sites of the minimum species-specific thresholds (“Low” thresholds).

These thresholds are shown in **Table 3-9**.

Table 3-9. Thresholds (ppbV) used for the expanded network threshold sensitivity analysis.

Threshold Type	0:00 – 7:00	8:00 – 15:00	16:00 – 23:00
1. High	616.00	268.04	587.19
2. Medium	130.00	56.69	124.19
3. Low	7.30	7.47	10.15

Probabilities of detection as a function of release size and duration for the high, medium, and low threshold levels are summarized in **Tables 3-10, 3-11, and 3-12**, respectively. These results can be compared with those shown in Tables 3-4 and 3-6. Cumulative probabilities of detection as a function of release rate for using these threshold sets are presented in **Tables 3-13, 3-14, and 3-15**; these results can be compared with those in Table 3-8. Detection probabilities under the high, medium and low threshold levels are also illustrated in **Figure 3-11**. As both the High and Medium threshold sets are higher than those used to construct the results shown in Table 3-6 and 3-8, the number of detected events using these thresholds is quite small, ranging from just 13 for the High threshold set to 51 for the Medium threshold set out of the total of 1,100 simulated releases. These values are considerably less than both the 232 releases detected using the Clinton Drive median thresholds (Table 3-6 and 3-8) and the 298 releases detected using the Low threshold set (Tables 3-13 and 3-14). Thus, even with a very comprehensive monitoring network, it is necessary to set thresholds at the lower end of the range used in the 2004 pilot study (i.e., near the levels used for the Clinton Drive monitor) in order to capture more than just a small percentage of reported releases.

Table 3-10. Summary of a) number of simulated HRVOC releases, b) number of releases detected on the 27-site EMRS network and c) the associated probability of detection (equal to b divided by a) stratified by the total quantity of HRVOC released and duration of release event: detections based on the “High” threshold set as listed in Table 3-9.

a) No. of Releases	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	257	120	14	0	**391**
2	67	53	0	5	**125**
3 thru 6	145	96	9	0	**250**
7 thru 24	191	128	12	3	**334**
TOTAL	**660**	**397**	**35**	**8**	**1,100**
b) No. Detected	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	1	0	4	0	**5**
2	1	0	0	4	**5**
3 thru 6	2	0	1	0	**3**
7 thru 24	0	0	0	0	**0**
TOTAL	**4**	**0**	**5**	**4**	**13**
c) Prob. Of Detection	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	0.004	0.000	0.286	NA	**0.013**
2	0.015	0.000	NA	0.800	**0.040**
3 thru 6	0.014	0.000	0.111	NA	**0.012**
7 thru 24	0.000	0.000	0.000	0.000	**0.000**
TOTAL	**0.006**	**0.000**	**0.143**	**0.500**	**0.012**

Table 3-11. Summary of a) number of simulated HRVOC releases, b) number of releases detected on the 27-site EMRS network and c) the associated probability of detection (equal to b divided by a) stratified by the total quantity of HRVOC released and duration of release event: detections based on “Medium Max” threshold set as listed in Table 3-9.

a) No. of Releases	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	257	120	14	0	**391**
2	67	53	0	5	**125**
3 thru 6	145	96	9	0	**250**
7 thru 24	191	128	12	3	**334**
TOTAL	**660**	**397**	**35**	**8**	**1,100**
b) No. Detected	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	2	12	7	0	**21**
2	2	4	0	5	**11**
3 thru 6	2	6	4	0	**12**
7 thru 24	1	1	3	2	**7**
TOTAL	**7**	**23**	**14**	**7**	**51**
c) Prob. Of Detection	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	0.008	0.100	0.500	NA	**0.054**
2	0.030	0.075	NA	1.000	**0.088**
3 thru 6	0.014	0.063	0.444	NA	**0.048**
7 thru 24	0.005	0.008	0.250	0.667	**0.021**
TOTAL	**0.011**	**0.058**	**0.400**	**0.875**	**0.046**

Table 3-12. Summary of a) number of simulated HRVOC releases, b) number of releases detected on the 27-site EMRS network and c) the associated probability of detection (equal to b divided by a) stratified by the total quantity of HRVOC released and duration of release event: detections based on the “Minimum” threshold set as listed in Table 3-9.

a) No. of Releases	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	257	120	14	0	**391**
2	67	53	0	5	**125**
3 thru 6	145	96	9	0	**250**
7 thru 24	191	128	12	3	**334**
TOTAL	**660**	**397**	**35**	**8**	**1,100**
b) No. Detected	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	27	72	11	0	**110**
2	5	19	0	5	**29**
3 thru 6	15	50	8	0	**73**
7 thru 24	11	60	12	3	**86**
TOTAL	**58**	**201**	**31**	**8**	**298**
c) Prob. Of Detection	**Total Quantity Released (lbs)**				
Duration (hrs)	**0 thru 500**	**500 thru 10,000**	**10,000 thru 50,000**	**> 50,000**	**TOTAL**
1	0.105	0.600	0.786	NA	**0.281**
2	0.075	0.358	NA	1.000	**0.232**
3 thru 6	0.103	0.521	0.889	NA	**0.292**
7 thru 24	0.058	0.469	1.000	1.000	**0.257**
TOTAL	**0.088**	**0.506**	**0.886**	**1.000**	**0.271**

Table 3-13. Summary of simulated expanded (27 site) EMRS network event detections stratified by event HRVOC release rate: High detection thresholds.

Cumulative	**Release Rate (lb/hr)**						
	>0	**>10**	**>50**	**>500**	**>1,000**	**>10,000**	**>20,000**
No. Releases (%)	1100 (100%)	875 (80%)	614 (56%)	231(21%)	135 (12%)	19 (2%)	7 (1%)
No. Detected	13	13	11	9	9	8	6
Prob. Of Detection	0.01	0.01	0.02	0.04	0.07	0.42	0.86

Table 3-14. Summary of simulated expanded (27 site) EMRS network event detections stratified by event HRVOC release rate: Medium detection thresholds.

Cumulative	**Release Rate (lb/hr)**						
	>0	**>10**	**>50**	**>500**	**>1,000**	**>10,000**	**>20,000**
No. Releases (%)	1100 (100%)	875 (80%)	614 (56%)	231(21%)	135 (12%)	19 (2%)	7 (1%)
No. Detected	51	51	48	43	40	12	7
Prob. Of Detection	0.05	0.06	0.08	0.19	0.30	0.63	1.00

Table 3-15. Summary of simulated expanded (27 site) EMRS network event detections stratified by event HRVOC release rate: Low detection thresholds.

Cumulative	**Release Rate (lb/hr)**						
	>0	**>10**	**>50**	**>500**	**>1,000**	**>10,000**	**>20,000**
No. Releases (%)	1100 (100%)	875 (80%)	614 (56%)	231(21%)	135 (12%)	19 (2%)	7 (1%)
No. Detected	298	294	265	156	103	16	7
Prob. Of Detection	0.27	0.34	0.43	0.68	0.76	0.84	1.00

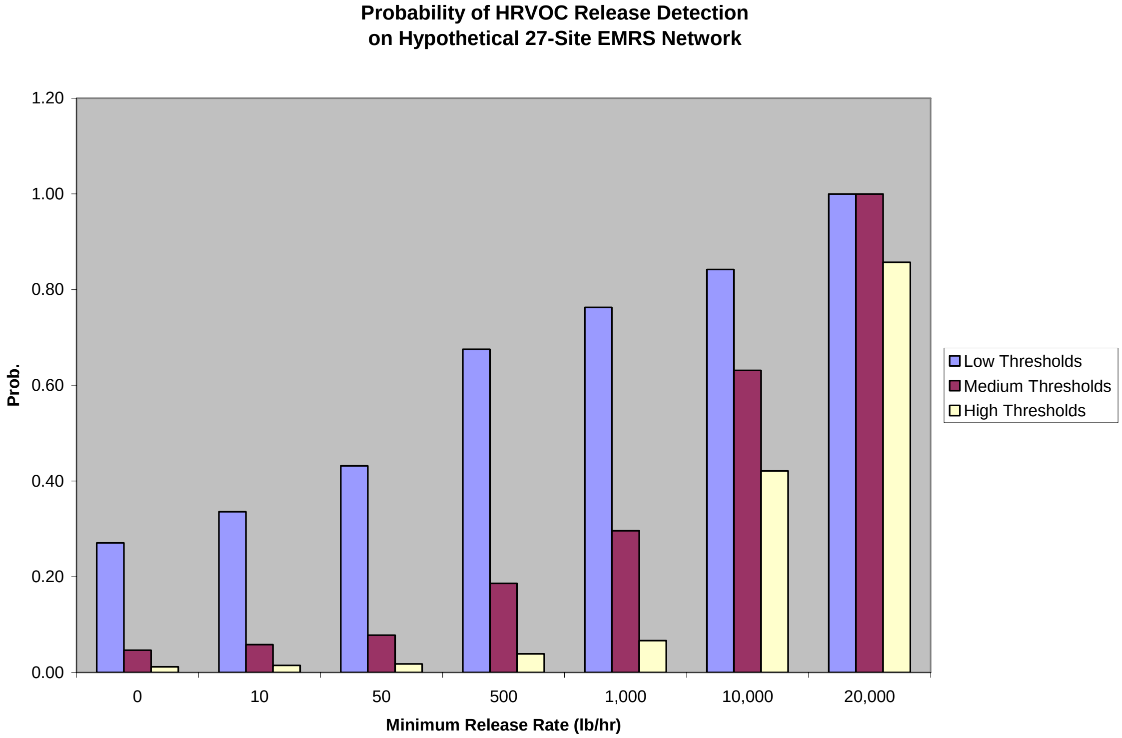

Figure 3-11. Comparison of the probability of detecting a simulated HRVOC event as a function of the minimum event release rate (lb/hr) based on the high, medium, and low detection thresholds listed in Table 3-15.

If the thresholds shown in Table 2-1 for Clinton Drive were to have been applied at all sites for the period June – November, 2004, a review of the monitoring data at six of the auto-GC sites used in the 2004 pilot study (data for HRM3 were not available) indicates trigger alerts would have been quite frequent as summarized in **Tables 3-16, 3-17 and 3-18.** The alert totals shown in Table 3-16 represent the number of days on which one or more species exceeded the applicable threshold during one or more hours of the indicated period (i.e., multiple threshold exceedances during the same 8-hour period of the same day are counted as one event). Overall, a trigger alert would have occurred at one or more of these six sites on nearly 40% of the days (70 of the 183) with monitoring data as shown in Table 3-18. Although such a frequent rate of trigger alerts may be impractical from an EMRS operational standpoint, it is not inconsistent with results of the HARC H13 study of reported emission events, which found that "…variability in the range of 100 to 1000 pounds per hour can be expected daily, at some time and some location in the Houston-Galveston area." (Allen et al., 2004).

Table 3-16. Number of trigger alerts which would have occurred based on monitoring data for the 183 day period 6/1/04 – 11/30/04 if an event were defined as one or more hours exceeding the applicable Clinton Drive threshold level listed in Table 2-1.

Site	Period			
	Morning	Midday	Evening	Any
Channelview	4	0	4	7
Cesar Chavez	15	9	5	25
Clinton Dr.	20	10	15	35
Deer Park	3	0	0	3
Lynchburg Ferry	6	4	6	13
Wallisville Rd.	0	0	0	0
Any Site	42	20	25	70

Table 3-17. No. of days with monitoring data during 6/1/04 – 11/30/04.

Site	Period			
	Morning	Midday	Evening	Any
Channelview	128	129	127	134
Cesar Chavez	180	180	178	181
Clinton Dr.	162	161	161	164
Deer Park	108	110	108	111
Lynchburg Ferry	173	177	175	177
Wallisville Rd.	178	176	177	178
Any Site	183	183	183	183

Table 3-18. Probability of trigger alerts.

Site	Period			
	Morning	Midday	Evening	Any
Channelview	0.031	0.000	0.031	0.052
Cesar Chavez	0.083	0.050	0.028	0.138
Clinton Dr.	0.123	0.062	0.093	0.213
Deer Park	0.028	0.000	0.000	0.027
Lynchburg Ferry	0.035	0.023	0.034	0.073
Wallisville Rd.	0.000	0.000	0.000	0.000
Any Site	0.230	0.109	0.137	0.383
Average Site	0.050	0.022	0.031	0.084

Selection of Sources for Notification

During the 2004 EMRS pilot study, the selection of participating upwind industrial facilities to be notified when a trigger event occurred at one of the seven monitoring sites was based on drawing a 90 deg. upwind wedge with a ten mile radius centered on the wind direction at the time of the trigger event (see Section 2). Using results from the model simulations described above, we evaluated the ability of an EMRS monitoring network to isolate sources of releases based on this simple upwind wedge approach. Hourly resultant wind directions at each monitoring site were extracted from the CAMx simulation for this purpose. These wind directions represent the *simulated* winds in the meteorological input files used in the CAMx run. The hourly resultant wind direction at the time and location of each modeled detection event was then compared with the heading from the location where the event was detected to the source of the detected HRVOC release and the angular deviation between the wind direction and source heading was noted (see **Figure 3-12**). These angular deviations were compiled over all event detections. Examination of the resulting distribution of angular deviations provides an indication of the likelihood that the source of a trigger event will be contained within a given size wedge extending upwind from the location of the event. This analysis was performed for two cases:

- Trigger events recorded by the 7 site network with thresholds used in the 2004 EMRS pilot study (this is the case used to generate the results shown in Table 3-5).
- Trigger events recorded by the expanded 27 site network with the Low threshold values (this is the case used to generate the results shown in Table 3-14).

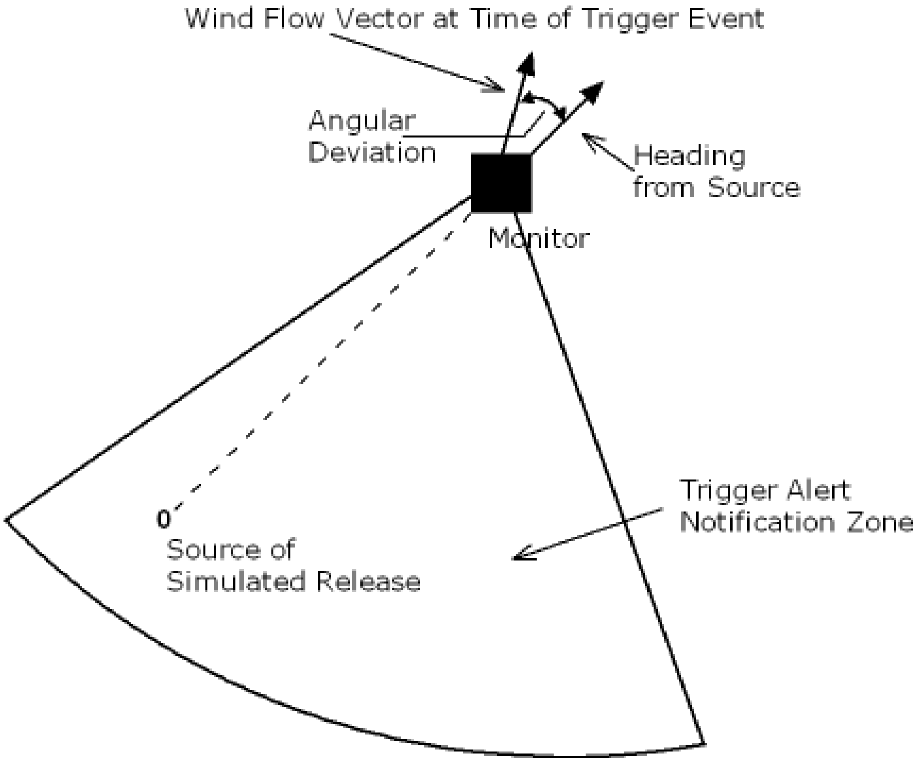

Figure 3-12. Schematic diagram showing derivation of the angular deviation between wind direction at the time an event is detected at the monitoring site (i.e., a “trigger event”) and the upwind direction from the monitoring site to the source of the release. Also shown is the location of the 90 deg. wide upwind wedge centered on the wind direction which was used during the 2004 EMRS pilot study to determine which sources would be notified of the trigger event.

Results are summarized in the cumulative distributions shown in **Figure 3-13**. For roughly half of the trigger events, the deviation from the hourly wind direction of the heading to the source at the time of the trigger event is within +/- 45 deg. Thus, a 90 degree wedge extending upwind from the trigger point would have a roughly 50% chance of covering the source of the release. In contrast, analysis of the 2004 pilot study data showed that the 90 deg upwind wedge used to identify sources to notify of a trigger event spanned the wind trajectory projected back from the monitoring site on 89% of the trigger events for which valid wind speed and wind direction were available for determining the notification wedge (TCEQ, 2005). This apparent discrepancy in the "coverage probability" of the 90 deg wedge judged against back trajectories (via the analysis of the 2004 pilot study data) as compared to the back heading from the monitor to the source (as was done for this study) is most likely due to differences in the temporal and spatial variations of modeled winds vs. the wind observations on which the back trajectories were calculated. However, additional comparisons of back trajectories calculated from observed and modeled winds would be need to confirm this and more clearly diagnose the source of the differences. It would be premature to conclude on the basis of the currently available results that the notification procedure based on a 90 deg. upwind wedge used in the 2004 pilot study should be altered. Additional analyses of the simulation results could also be performed to evaluate the optimal downwind distance (currently set to 10 miles) used to define the notification zone.

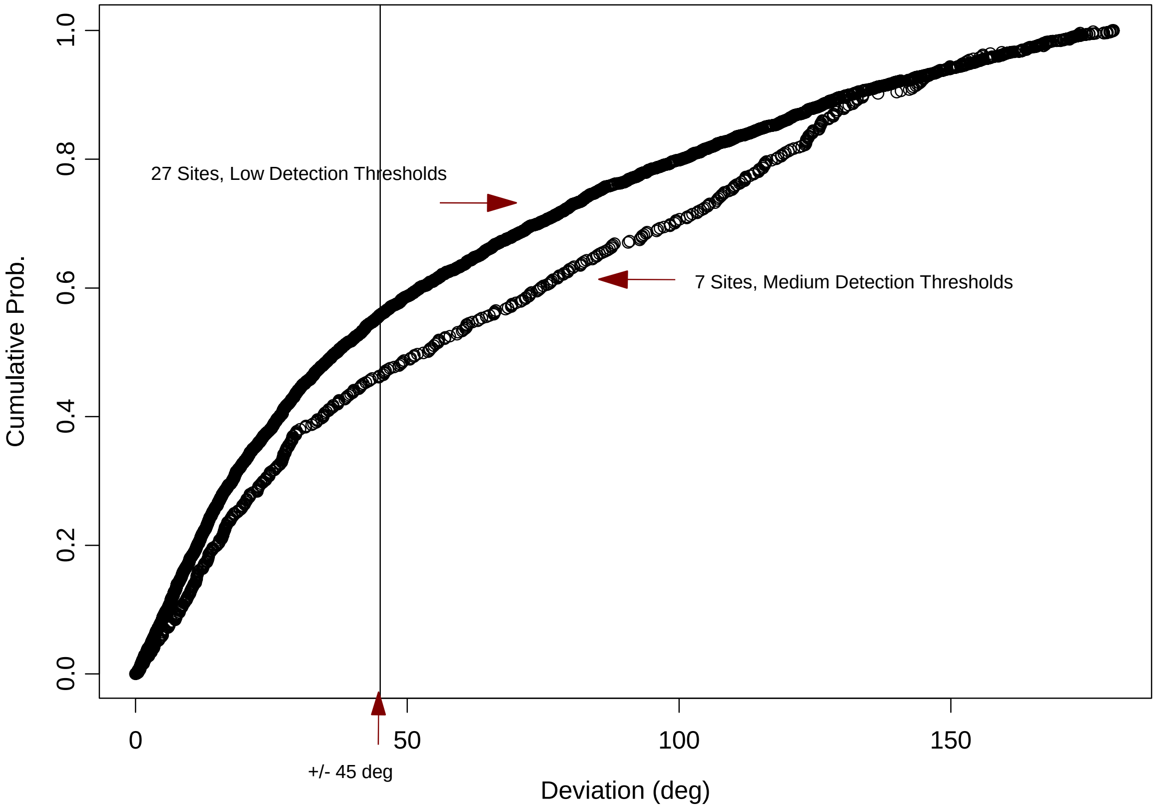

Figure 3-13. Empirical cumulative distributions of the angular deviations between wind direction at the time and location of a trigger event (source detection) and the upwind direction to the source of the release which was detected (see Figure 3-12). Upper line is for detections on the hypothetical 27-site monitoring network, lower line is for detections on the 7-site monitoring network used in the 2004 pilot study (see text).

4. MONITORING TECHNOLOGIES AND PROCEDURES FOR EMRS

An effective EMRS system for HRVOCs requires the ability to continuously monitor for high HRVOC concentration events and to have at hand ancillary data (wind measurements, mobile and/or fenceline monitors, on-site monitoring) needed to identify the sources of releases most likely to be responsible for an event. The EMRS ambient air monitoring network must therefore provide sufficient geographic coverage to detect events originating from different facilities of interest, be able to distinguish between impacts of actual significant episodic emission events from "normal" elevated concentration episodes associated with poor dispersion conditions, and to provide results rapidly enough to be useable for identifying potential sources. As a result of experience gained from the 2004 EMRS pilot study, and in consideration of the event simulation results described in Section 3, several drawbacks of the auto-GC network are apparent:

- As demonstrated via the event simulation results presented in Section 3, the 7-site network is too sparse to reliably detect all but the largest emission events. A less expensive monitoring technology which could be more widely deployed is needed to reliably detect emission events of 1,000 lb/hour or more. A larger network would have the added advantage of increasing confidence in the identification of emission events which are recorded at multiple sites within a narrow time window.
- The auto-GC instruments require over an hour to report results from a 40 minute sample which was collected starting two hours prior to the report. This delay in analysis time makes it more difficult to conduct timely follow-up activities at upwind facilities.

Ideally, ambient monitors used for EMRS will be sufficiently inexpensive and reliable to allow deployment at more locations than the seven auto-GC sites. Strictly for EMRS purposes, precision and accuracy requirements can be less stringent than is normally required for other applications since the network is only used to identify large concentration excursions (for "go, no-go" decisions). In particular, the minimum detection limits for target HRVOCs need not be significantly lower than the selected trigger levels. Using the pilot study trigger levels as a guide, this means MDLs generally as high as 10 – 50 ppb are acceptable for this purpose whereas MDLs below about 5 ppb might otherwise be required. From this perspective, FTIR devices, which can be difficult to configure to achieve < 5 ppb MDLs, are acceptable for EMRS applications.

Another advantage of FTIR and other optical devices is that they produce results in near real-time, which, as discussed above is another important attribute for EMRS applications. Based on the durations of reported HRVOC releases described in Section 3, a response time of no more than a few minutes for sample averages of 15 minutes or less would be ideal for EMRS applications.

In addition to a comprehensive, sensitive, selective, and fast responding ambient monitoring network for detecting trigger events, an effective EMRS requires secondary sources of information that will allow facilities alerted to a trigger event to quickly survey their operations for a possible emission event and, when applicable, to correct the conditions causing the event. To date, this ability has been limited by the lack of secondary detection networks (mobile and fenceline monitors) and the ability to quickly survey potential HRVOC sources for unanticipated emissions.

SURVEY OF HRVOC MONITORING TECHNOLOGIES

In recent years, a number of new extractive and remote sensing technologies for qualitative and quantitative evaluation of hydrocarbon mixtures have been developed. As exemplified by the FTIR monitoring devices discussed above, these technologies have the potential to enhance the effectiveness of the EMRS.

A survey and evaluation of a range of remote sensing and air sampling gas detection technologies suitable for identifying and monitoring hydrocarbon plumes from petroleum refineries and petrochemical plants was recently performed for HARC by an ENVIRON-lead research team (ENVIRON, 2005). This review focused primarily on three types of devices:

1. Plume imaging devices
2. Optical remote sensing devices
3. Micro-electromechanical Systems (MEMS)

Plume imaging technologies are based on the principles of absorption and/or emission of infrared or ultraviolet light by a chemical emissions cloud and the optical detection and video imaging of the cloud against the background scene. Optical remote sensing technologies send and receive an infrared and/or ultraviolet light beam to determine the change in spectra of light due to absorption in the chemical plume, allowing determination of the chemical speciation and integrated concentration along the beam pathway. Micro-electromechanical systems (MEMS) are miniaturized versions of direct sampling and analysis methods that take advantage of recent advances in nanotechnology.

Devices were evaluated with respect to effectiveness, sampling and post-processing time, accuracy, range, safety and utilization, annualized cost and commercial readiness. Two general classes of application were considered with respect to these criteria and appropriate weighting factors were assigned to each criteria (and associated sub-criteria) depending on the application type:

- on-site sampling programs designed to localize the emissions source to a portion of a facility or a specific leaking component, and
- off-site sampling programs designed to locate and map larger-scale plumes.

Remote sensing devices were reviewed by ENVIRON (2005), included:

- Open Path Fourier Transform Infrared (OP-FTIR) instruments which come in a variety of configurations including long path (on the order of 100 - 500 m) systems capable of detecting multiple hydrocarbon species (including selected HRVOCs), at the ppb level. These systems are suitable for routine, continuous, unattended operation
- Differential Optical Absorption Spectrometry (DOAS) systems which operate at IR and UV frequencies over open paths with lengths up to 1 km and could potentially be configured to measure HRVOCs at or near ppb level of detection. Similar to OP-FTIR, these systems are suitable for routine, continuous, unattended operation.
- Light Detection and Ranging (LIDAR) systems which scan hundreds of meters or more depending on conditions and are mounted on a mobile van or large aircraft. LIDAR systems must be tuned to detect a specific single compound or class of compounds and are designed for short-term deployment for surveys or field studies.

- Solar Occultation Flux (SOF) is a remote sensing system which measures absorption bands in the spectrum of sunlight passing through the industrial source plume being measured. The mobile platform SOF system is designed to measure the total mass flux of target compounds within the plume. As with the LIDAR systems, the SOF is designed for short-term deployment for surveys or field studies.
- Plume imaging cameras as described above.

ENVIRON (2005) also surveyed two types of non-remote sensing devices that measure concentrations of hydrocarbons in ambient air:

- Tunable Diode Laser Absorption Spectrometers (TDLAS) are small, lightweight, low power devices that are highly selective (do not suffer from interferences from non-target species) and sensitive (potentially down to the ppt level). Each device is typically built to detect a single target species. Although in principal such devices could be built to detect selected HRVOCs, currently commercially available devices are not designed for HRVOC detection.
- MEMS devices as described above which are essentially miniaturized versions of conventional air monitoring methods. MEMS potentially suitable for HRVOC detection are currently under development by various groups. Devices examined by ENVIRON (2005) include non-dispersive infrared (NDIR) systems and a micromechanical gas chromatograph based on a Phased Heater Array Structure for Enhanced Detection (PHASED) method under development by Honeywell which is designed to be capable of detecting all of the Houston HRVOC species at sub-ppb levels. Availability of the Honeywell system is estimated for 2008 – 2009.

In addition to the TDLAS and MEMS devices, the FTIR devices described above can be configured operate as extractive (closed path) instruments although the shorter path lengths generally result in higher minimum detection limits as discussed below.

Principal characteristics of the systems reviewed by ENVIRON (2005) that are capable of detecting HRVOCs are summarized in **Table 4-1**. Within the context of the EMRS, we are interested in measurement technologies for four purposes:

- Devices suitable for routine, unattended, ambient surveillance at fixed sites that are able to detect HRVOCs at offsite locations which may be on the order of 10 km or more downwind of the source (MEMS, OP-FTIR, DOAS).
- Devices suitable for active mobile (ground vehicle or aircraft) applications and able to detect plumes just beyond the fenceline and for 1 – 5 km kilometers downwind (LIDAR/DIAL and mobile versions of other devices).
- Devices suitable for routine monitoring along the source fenceline (OP-FTIR and DOAS)
- Devices suitable for localizing emission sources such as leaking components within a plant (e.g., plume imaging cameras)

Table 4-1. Air monitoring devices capable of detecting HRVOCs reviewed by ENVIRON (2005).

Company/ System	Type[1]	Applications			Mobile Capability?	Potential EMRS Application	Annualized Cost (5 year amortization)[2]	Comments
		On-Site	Fence-line	Neighbor-hood				
IMACC	OP-FTIR	X	X	X	Yes (passive mode)	Routine monitoring	$17,000/yr[3]	
Unisearch	OP-FTIR	X	X	X	Yes (passive mode)	Routine monitoring	$26,000/yr[4]	
Honeywell	MEMS	X	X	X	Yes	Routine monitoring	est. $2,000 - $15,000 for sensor unit	Under development; est. availability 2008 - 2009
Chalmers Inst.	SOF		X		Yes	Limited to special surveys	$50,000 - $100,000 per survey	Mobile van with trained crew
Spectrasyne	DIAL		X		Yes	Limited to special surveys	$13,000/day	Large bus with trained crew
OPSIS	DOAS	X	X	X	Possible	Routine monitoring	$10,000/yr	Path lengths up to 1 km
GasOptics	IR Plume Imaging	X			Un-proven	Follow-up	Unknown	
LIS/BAGI	Plume Imaging	X			Un-proven	Follow-up	$24,000	
Sandia/BAGI	Plume Imaging	X			Un-proven	Follow-up	Unknown	
PAT/Sherlock	Plume Imaging	X			Un-proven	Follow-up	Unknown	
LSI/Hawk	Plume Imaging	X			Yes (in passive mode)	Follow-up	$30,000/yr	

Of particular interest to the further development of the EMRS are measurement technologies suitable for the first purpose listed above (routine ambient surveillance) but that are faster and cheaper than the auto-GC systems currently being used. While the open path (FTIR and DOAS) units provide near real-time output, their relatively high cost makes it less likely that a sufficient number of units can be deployed to outfit a full-scale EMRS network. On the other hand, the MEMS units currently under development as exemplified by the Honeywell PHASED device hold out the promise of a small, fast, and (assuming full-scale commercial production), cheap device which could be widely deployed when they become available in the next three to five years. If these devices fulfill their promise, they will be ideally suited to EMRS applications.

An extractive FTIR instrument has been operating in the community of Seabrook near Baytown since 2002. This unit is configured to measure a variety of hydrocarbons including three HRVOCs: 1-butene, ethylene, and propylene. Reported minimum detection limits (MDLs) for these three HRVOCs are 12, 10 and 20 ppbV, respectively. Although higher than MDLs typically reported for auto-GCs, the Seabrook FTIR MDLs are lower than the trigger levels used

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[1] OP-FTIR = open path fourier transform infrared; SOF = solar occultation flux, LIDAR = light detection and ranging; DIAL = differential absorption LIDAR; DOAS = differential optical absorption spectrometer; MEMS = micro electromechanical system

[2] These estimates do not include the infrastructure cost for a new monitoring site (trailer with a/c, power, etc.) which is estimated at $53,000 per site (based on TxAQS II planning documents). The cost of preparing an existing site for a new instrument is estimated at $3,600 (www.tceq.state.tx.us/policy/ta/am/TexAQS_II.htm#workshops).

[3] Based on vendor information reported by ENVIRON (2005). Five year amortized cost of the contractor run dual-cell extractive FTIR operating at Seabrook is $140,000 per year.

for the 2004 EMRS pilot study, with the exception of the lowest propylene trigger level (18.5 ppbV). Data from such an FTIR would therefore appear suitable for use in an EMRS network. The Seabrook FTIR is configured to report 14 minute average concentrations. An analysis of the lengths of individual periods during which the ethylene (or propylene) concentrations remained above the MDL showed that nearly all events lasted at least four measurement periods, i.e., 52 minutes or nearly an hour (Allen et al., 2004). As reported by Allen and co-workers, these results are "qualitatively consistent" with the duration of emission events reported to the TCEQ. These events are therefore long enough to be detected by an auto-GC operating with the standard 40 minute sampling cycle. However, the auto-GC requires approximately another 80 minutes before results from the sample are available whereas the FTIR reports results in near real time. Thus, the value of an IR instrument for EMRS applications lies more in its ability to quickly report observed values rather than its ability to perform sub-hourly sampling. While an auto-GC can be configured to operate with a shorter turnaround time, this would require narrowing the list of target compounds, thus making the resulting data less useful for other applications.

The need for a rapid response monitoring network that can provide timely notification of a trigger event is further emphasized by an examination of the joint distribution of event duration and release rate as summarized in **Table4-2** for the 1,100 randomly simulated events generated by the Emission Event Simulator system described in Section 3 above. Taking partial sums of applicable rows and columns of the individual percentages listed in this table shows that, while just 12% of all events exceed 1,000 lb/hr, 67% of these large events have durations of less than one hour. Thus, for events in the size range of most concern (as explained in Section 3), fully two-thirds lasted less than an hour. This suggests that the minimum response time for an effective EMRS should be no more than one hour.

Table 4-2. Joint distribution of event duration and release rate (as a percentage of 1,100 randomly generated HRVOC release events described in Section 3).

	Release Rate (lb/hr)							
Duration (min)	**0+ thru 10**	**10+ thru 50**	**50+ thru 500**	**500+ thru 1,000**	**1,000+ thru 10,000**	**10,000+ thru 20,000**	**20,000+**	**Total**
0+ thru 1	5.64%	7.45%	10.27%	4.09%	6.82%	1.09%	0.18%	35.55%
1+ thru 2	1.00%	1.18%	6.27%	1.55%	0.91%	0.00%	0.45%	11.36%
2+ thru 6	4.73%	3.91%	9.55%	2.82%	1.73%	0.00%	0.00%	22.73%
6+ thru 24	9.09%	11.18%	8.73%	0.27%	1.09%	0.00%	0.00%	30.36%
Total	20.45%	23.73%	34.82%	8.73%	10.55%	1.09%	0.64%	100%

Devices designed primarily for on-site applications (such as the plume imaging devices) are applicable to EMRS in terms of their usefulness in conducting follow up activities at upwind facilities upon notification of an EMRS trigger alert. Similarly, routine fenceline monitoring programs based on open path (FTIR or DOAS) systems could potentially provide information on emissions at upwind facilities and thus help identify the potential source of a trigger alert. This would realistically be limited to a relatively small number of fixed locations, however, and undetected leaks would still be a very real possibility. Direct, continuous observation of emissions via continuous emissions monitoring (CEM) systems is not currently feasible for HRVOCs because the necessary low cost, reliable, fast response sensors have not been developed and, in any event, such systems must be installed at known, fixed release points and are thus not applicable to fugitive emissions sources. In some situations, however, it is possible to use data from existing process monitoring equipment to estimate emissions in real time via a

Predictive Emissions Monitoring System in which advanced software algorithms use process data to continuously predict emissions.[4] In theory, such a system could help a facility identify HRVOC release events.

EMRS Mobile Monitoring

To increase the chances of identifying sources causing or contributing to a trigger alert, the EMRS protocol could be modified to include follow-up mobile monitoring of trigger events. This could include ground level or even airborne monitoring via mobile units. Examples of mobile units include:

- Ground Level Monitoring
  - TCEQ mobile van with loop-injection GC which can process one sample every 15 minutes.
  - EPA's Atmospheric Trace Gas Analyzer (TAGA) van mounted triple quadruple MS/MS for continuous real-time speciated VOC
- Remote Sensing Ground-Based Monitoring
  - Mobile DIAL/LIDAR platforms (ground)
  - Mobile SOF (ground) as described above
- Airborne Remote Sensing
  - Mobile broad-band FTIR (HAWK camera aboard helicopter planned for TxAQS II operation by the Remote Sensing Group)
  - Proton Transfer Reaction Mass Spectrometry and Rapid Alkene Detector instruments on the TVA de Havilland DHC-6 Twin Otter aircraft.
  - Airborne Hyperspectral Imager (AHI) operated by the University of Hawaii
  - Airborne thermal IR and FTIR (e.g., EPA – Los Alamos National Laboratory ASPECT system[5])

All of the above units require highly trained operators. Mobile remote sensing via OP-FTIR, LIDAR/DIAL or SOF has the advantage of providing more complete coverage by measuring conditions within at least the lower portion of the atmospheric boundary layer above the mobile unit. Aircraft mounted units such as the University of Hawaii's Airborne Hyperspectral Imager (AHI), etc. would be able quickly cover larger areas and to fly directly over sources, thus increasing the chances of finding source plumes. While mobile monitoring follow-up to a trigger event may be feasible as part of a special study program, the cost of keeping such a unit on standby for lengthy periods is likely to be prohibitive, especially for airborne units. As much of the potential value of the EMRS system is in compiling a history of the results of responses to a large number of trigger alerts, the value of a follow-up measurement program that can only be occasionally deployed is limited. Hopefully, some valuable experience will be gained with this as a result of ground-based and airborne monitoring planned for August – September 2006 as part of the TxAQS II field study.

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[4] For example, Pavilion Technologies sells a Software CEM™ system, which is designed as a less costly alternative to conventional continuous emissions monitoring (CEM) instrumentation for recording calculated emission rates from certain sources including calculated HRVOC emissions from flares, vents, pressure relief valves, and cooling towers.

[5] See //www.epa.gov/earth1r6/6en/a/taga-ecp.pdf

5. SUMMARY AND RECOMMENDATIONS

An effective EMRS for detecting and responding to HRVOC releases from industrial facilities must consist of:

- An ambient air quality monitoring network that has sufficient spatial coverage, sensitivity, selectivity, and a sufficiently fast response time to provide useful near real-time data to participating government agencies and industrial facility operators on the occurrence of HRVOC concentrations that exceed the pre-set trigger levels.
- A trigger event response plan that specifies the steps each participating agency or group will take upon notification of a trigger event.
- Ancillary data sources (a wind monitoring network and source-oriented air monitoring programs) which provide information needed to identify sources potentially contributing to the high HRVOC concentration event.
- A communications and data processing network that rapidly provides EMRS participants with the analyzed data needed to take actions specified in the response plan.

Ideally, the EMRS ambient monitoring network would be able to capture a significant fraction of emission events within the size range of concern. For HRVOC releases in the Houston – Galveston area, analyses of simplified photochemical modeling results suggest HRVOC releases of 1,000 lb/hour or more are potentially capable of producing a 2 to 3 ppb increase in ambient ozone levels under the right conditions (Allen et al., 2004) so releases of at least this size should be given highest priority. Examination of records of reported emission events shows that such events occur on average once per day somewhere in the HGA.

The ability of an EMRS ambient monitoring network to detect the emission events of interest is limited by the available number of monitoring sites. Results from the analyses described in Section 3 above indicate that tens of sites would be required to adequately localize potential HRVOC emissions sources producing events of this size in the Houston Ship Channel area. In particular, our simulation results show that the 7-site network used in the 2004 EMRS pilot study can be expected to detect only the largest releases (i.e., those exceeding 10,000 lb/hr) with any degree or reliability. For detection of events exceeding 1,000 lb/hr, a network with spatial coverage similar to that provided by the 27 site network analyzed in this study and using event trigger threshold concentrations set near the low end of the range of thresholds used in the pilot study would be needed for reliable detection (i.e., a probability of detection above 50%). Given that events of this magnitude were reported to occur about once per week on average in Harris Co., an EMRS network that achieves 50% probability of detection of events of this magnitude would produce a trigger event associated with a *reported* emission event every other week on average. Additional alerts would be generated by smaller releases from sources close to a monitoring site and, perhaps significantly, by unreported releases. Of course, much can still be learned from smaller, less sensitive networks but the number of events captured will be correspondingly less.

Our analysis of potential additional HRVOC monitoring locations within the Houston Ship Channel suggests that new monitoring sites in the eastern portion of the area (around Baytown, North Channelview, and Bayport) may be particularly useful for detecting emission events which the current seven site network does not appear to be picking up particularly well. This conclusion, derived from the emission event simulation study described in Section 3, is based on the frequency, size, and locations of *reported* emission events in Harris County during the January 2003 – January 2004 period for which records were available for this study and does not account for the impacts of any unreported events or changes in the spatial distribution of events that might occur in future years.

Development of larger-scale ambient monitoring networks needed to detect a higher percentage of emission events would involve considerable expense. Our review of currently available monitoring technologies suitable for application in the ambient monitoring network component of an EMRS indicates that new technologies based on micro electromechanical systems (MEMS) hold considerable promise for building denser networks with greater capability (primarily with respect to speed of response) at relatively low cost in the not to distant future. MEMS devices are expected to begin to become available on the market place by the end of this decade.

Currently, alternatives to the auto-GC network for EMRS applications are for the most part limited to FTIR devices such as the dual cell extractive FTIR currently operating at the Seabrook monitoring site. From the standpoint of application in an EMRS, the primary advantage of the FTIR over the auto-GCs is that measurements are available in near-real time. This is a very important advantage given the significance of short duration emission events as discussed above. At the present time, costs of setup and operation of FTIRs of this type are roughly on par with costs for auto-GCs.

As discussed in Section 3, a number of refinements could be undertaken to procedures employed within the EMRS to respond to the occurrence of a trigger event. One approach which has already been considered for implementation in Houston is the automated calculation of near real-time air parcel back trajectories showing the paths most likely to have been taken by air parcels arriving at the time and location of each trigger event. These data could then be used to determine with greater precision the upwind area within which sources potentially contributing to the event could be notified. This would reduce the number of trigger alerts any given source would need to respond to and thus make it more acceptable to increase the detail and scope of the follow-up activities that a source operator would undertake in response to a trigger alert. A suitable back trajectory analysis tool has already been developed by TCEQ. This tool, which is based on a spatial interpolation of surface (10 m) wind observations, is already routinely applied to provide quick turnaround analyses of notable air pollution events and could be fairly easily adapted to routine, automated use as part of the EMRS. An even more sophisticated approach would be to compute back trajectories using wind fields from a routinely applied prognostic mesoscale meteorological model similar to the one currently under development at the University of Houston.

Another approach to more precisely identifying sources potentially responsible for a trigger event which has been suggested by some participants in the current EMRS program is to compile information on unique chemical identifiers which may be associated with a small subset of (or even individual) potential sources. In theory, a library of source “fingerprints” could be developed by conducting source-oriented multi-species monitoring of routinely emitted chemicals just downwind of the sources of interest. Some of the newer remote sensing monitoring technologies described in Section 4 are well suited to this purpose. Once the key identifier species have been determined, the EMRS ambient network could be modified to include these species among the list of target compounds in addition to the HRVOCs of interest. By including data on correlations between HRVOCs and concentrations of the key indicator compounds during the trigger event, it may be possible to further refine the set of potential upwind sources at which follow-up activities would be needed.

Sources receiving a trigger event alert could expand their follow-up activities by examining fenceline or other routine on-site monitoring data. The quantity, quality and usefulness of these data would be greatly enhanced by the use of advanced remote sensing instrumentation that has been developed for fenceline monitoring applications and leak detection programs. These devices include open path optical methods and plume visualization cameras such as those described in Section 4. It must be recognized, however, the equipment and personnel time needed for these activities will be expensive. One possible method for reducing costs would be to limit the number of trigger alerts requiring a full-scale response by giving highest priorities to facilities that are closest to the trigger event and focusing only on the largest events.

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7. GLOSSARY

AHI	Airborne Hyperspectral Imager
CAMx	Comprehensive Air Quality Model with Extensions
DIAL	Differential Adsorption Light Detection and Ranging
EES	Emissions Event Simulator
EMRS	Environmental Monitoring and Response System
FTIR	Fourier Transform Infrared
HGA	Houston – Galveston area
HRVOC	Highly Reactive Volatile Organic Compound
IRON	Incremental Reactions for Organics and NO_x
LIDAR	Light Detection and Ranging
MDL	Minimum Detection Level
NO_x	Nitrogen oxides
OP-FTIR	Open Path – Fourier Transform Infrared
PiG	Plume-in-Grid
SOF	Solar Occultation Flus
TCEQ	Texas Commission on Environmental Quality
TexAQS	Texas Air Quality Study
VOC	Volatile Organic Compound