URS

Measurement of VOC Emissions from Pressurized Railcar Loading Arm Fittings

FINAL REPORT

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Executive Summary

Factors and correlation equations for estimating fugitive emissions during loading and unloading of pressurized railcars (pressure cars) are presented. The factors and correlation equations were derived from measurements made using the U.S. Environmental Protection Agency (EPA) method for screening and bagging fugitive leak sources, as described in the EPA document titled, *"Protocol for Equipment Leak Emission Estimates"* (EPA-453/R-95-017). The measurements were made at railcar loading and unloading terminals in the Houston-Galveston-Brazoria (HGB) area during February-March and July 2006.

Pressure cars are loaded and unloaded from the top. The top of each car is equipped with a pressure head assembly and protective housing that contains valves for loading and unloading liquid product. The pressure head assembly also contains a vapor line that is used during loading to vent the railcar back to a storage tank or flare and during unloading to pressure the product out of the railcar with compressed product vapors or an inert gas (e.g., nitrogen). Other items contained within the pressure head assembly include a sampling valve that is used for sampling liquid from the bottom of the railcar, a safety valve, a thermometer well, and a gauging device.

To load and unload a railcar, a pipe extension is usually inserted into the liquid valve so that the connection to the loading arm can be made outside of the pressure head assembly protective housing. The valve and pipe extension are joined by a threaded connection designed to American National Pipe Tapered Thread (NPT) specifications. The connection from pipe extension to loading arm is usually made with a quick connect dry break coupler that is designed to prevent liquid leaks and spills. Several variations are commercially available. Opposite ends of the quick connect are joined to the pipe extension and loading arm, respectively, using NPT connections.

The average emission factors for threaded pipe connections and quick connect couplers measured during this study were 0.0097 kg/hr/source and 0.0025 kg/hr/source, respectively. These estimates are higher than the SOCMI and refinery average emission factors for connectors reported by EPA[1], which are 0.00183 kg/hr/source and 0.00025 kg/hr/source, respectively.

The measured emission factors were used with previously reported estimates of railcar loading and unloading activity in the HGB to estimate the regional VOC emissions from pressure

[1] EPA, 1995. *Protocol for Equipment Leak Emission Estimates* (EPA-453/R-95-017).

car loading and unloading. For chemicals having boiling points less than 75 ºF at one atmosphere pressure, the total fugitive emissions estimate from pressure car loading and unloading is 2.69 tons per year. This estimate is less than one percent of the total railcar loading emissions in the HGB (392 tons per year) that was estimated by ERG (2004)[2].

Options for reducing fugitive VOC emissions from pressure car loading arm connections were investigated. The substitution of bolted flanged connections in place of the typical threaded connections to liquid and vapor valve assemblies resulted in zero detectable emissions at the four valves where the flanged connections were tested. Hot-welding of threaded connections on the inlet and outlet side of quick connect (dry break) couplers would eliminate other potential emissions sources. Other means for reducing fugitive VOC emissions during pressure car loading and unloading include implementation of leak detection and repair protocols and good piping practices (e.g., routine inspection, care, and maintenance of pipe threads).

[2] ERG, 2004, *Development of Emission estimates for Railroad Tank Cars for the Houston-Galveston Nonattainment Area*, Draft Report.

1.0 Introduction

This document reports factors and correlation equations for estimating fugitive emissions during loading and unloading of pressurized railcars (pressure cars). Additionally, this report presents regional emission estimates for the Houston-Galveston-Brazoria (HGB) area based on the reported emission factors and recommendations for reducing fugitive emissions from pressure car loading and unloading. Pressure cars, which are most commonly classified as DOT-105, -109, -112, -114, or -120, are used to transport a variety of inorganic and organic commodities to and from petroleum refineries and chemical manufacturing facilities in the HGB. This study focuses on the fugitive emissions from handling liquefied light hydrocarbons that are gases at standard temperature and pressure. Examples include 1,3-butadiene and isobutylene.

1.1 Background

Measurements conducted in the HGB by the National Oceanic and Atmospheric Administration (NOAA) and other research organizations during the 2000 Texas Air Quality Study (TexAQS 2000) suggested that the levels of volatile organic compounds (VOC) found in the ambient air, particularly several of the most highly reactive VOC (HRVOC), could not all be accounted for based on reported emissions estimates. Following this finding, the Texas Commission on Environmental Quality (TCEQ) began an intensive effort to identify, quantify, and reduce VOC emissions that previously had been underestimated. In 2005, using its HAWK gas imaging camera[3] on behalf of TCEQ, Leak Surveys, Inc. (LSI) found vapors escaping from pressure car loading arm connections during several repeated tests, thereby identifying pressure car loading arm connections as a potential source category of underestimated emissions.

Unlike non-pressurized railcars, where loading emissions are driven mostly by vapor displacement, no factors specifically intended for estimating fugitive emissions from pressure car loading or unloading are reported in the U.S. Environmental Protection Agency's AP-42 compilations. Indeed, fugitive emissions associated with valves, pipe connections, quick connect couplers, etc. from loading and unloading were previously widely assumed to be controlled 100% through the use of vapor-tight, leak-proof equipment. However, the recent images from the HAWK camera of vapors leaking from pressure car loading arm connections have shown this assumption, at least in some cases, to be not true.

[3] http://leaksurveysinc.com/hawks_work.htm

2.0 Objectives and Approach

The objective of this Texas Environmental Research Commission (TERC) study is to support the Texas Commission on Environmental Quality (TCEQ) in its efforts to evaluate ozone control strategies for the HGB by conducting three specific tasks:

1) Develop factors and correlation equations for estimating fugitive emissions from pressure car loading arm connections;
2) Apply the new emission factors to estimate regional emissions from pressure car loading and unloading in the HGB; and
3) Identify options for reducing fugitive emissions from pressure car loading and unloading.

Although pressure cars may be used to transport a wide variety of materials, this study addresses only hydrocarbons that are gases at standard temperature.

2.1 Experimental Approach

Emission factors and correlation equations for loading arm fugitive leak sources were developed using the methodology described by the EPA document *"Protocol for Equipment Leak Emission Estimates"* (EPA-453/R-95-017). This involved leak detection and screening using a portable total hydrocarbon analyzer and mass emissions measurements by bagging fugitive components. The measurements were made at railcar loading and unloading facilities in the HGB over a period of eleven days during February-March and July 2006.

Pressure cars are loaded and unloaded from the top (Figure 2-1). The top of each car is equipped with a pressure head assembly and protective housing as shown in Figure 2-2. The pressure head assembly contains two liquid eduction valves connected to separate liquid eduction pipes that extend to the bottom of the tank. Either valve may be used to load or unload product. The pressure head assembly also contains a vapor line that is primarily used during loading to vent the railcar back to a storage tank or a flare. The vapor line is also used during unloading to pressure the product out of the railcar with compressed product vapors or an inert gas (e.g., nitrogen). Other items contained within the pressure head assembly include a sampling valve that is used for sampling liquid from the bottom of the railcar, a safety valve, a thermometer well, and a gauging device.

Figure 2-1. Typical Pressure Car Loading with Articulated Loading Arm (American Chemistry Council, 2002).

To load and unload a railcar pipe extensions are typically inserted into the valves so that connections to loading arms can be made outside the dome of the car (Figure 2-3). The connection from pipe extension to loading arm is usually made with a dry break coupler that is specially designed to prevent liquid leaks and spills. Several types of dry break couplers are commercially available that use a built in valves and spring-loaded poppets in both halves to automatically form tight seals when disconnected before the main fluid seal releases to the atmosphere.

For this study, fugitive emissions during pressure car loading and unloading were measured at liquid eduction valves, threaded pipe connections, and dry break (quick connect) couplers (Figure 2-4). Note that threaded pipe connections were typically made at three locations. These were on both sides of the dry break couplers and at the eduction valves.

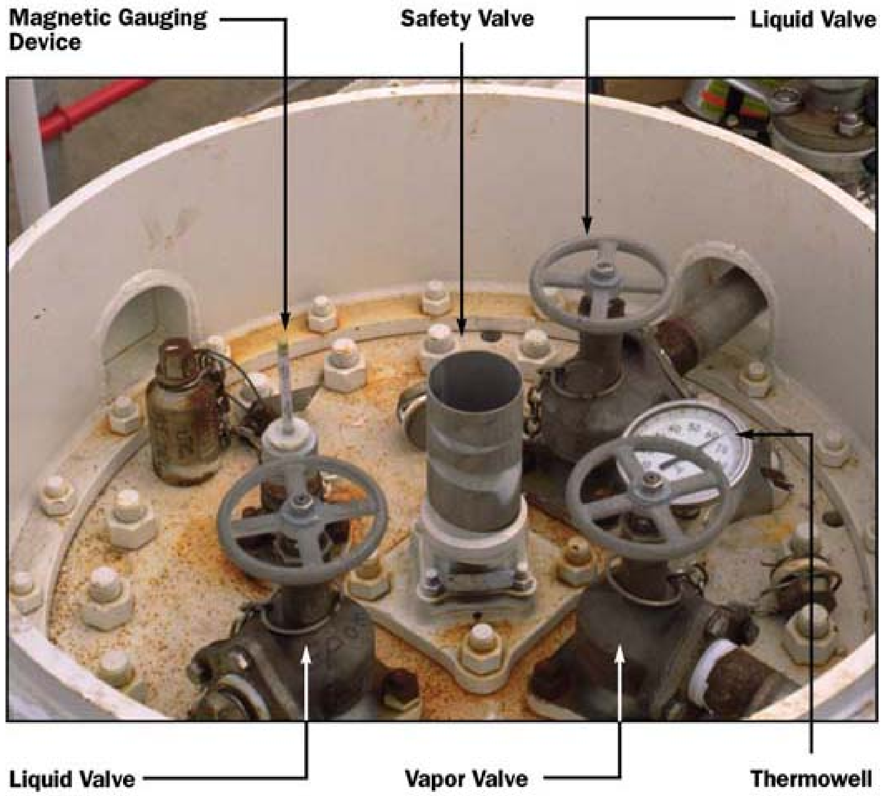

Figure 2-2. View of Railcar Pressure Head Assembly (http://www.ethyleneoxide.com/html/body_transportation.html)

Figure 2-3. Pipe Extension Being Inserted into Liquid Eduction Valve (http://www.ethyleneoxide.com/html/body_transportation.html)

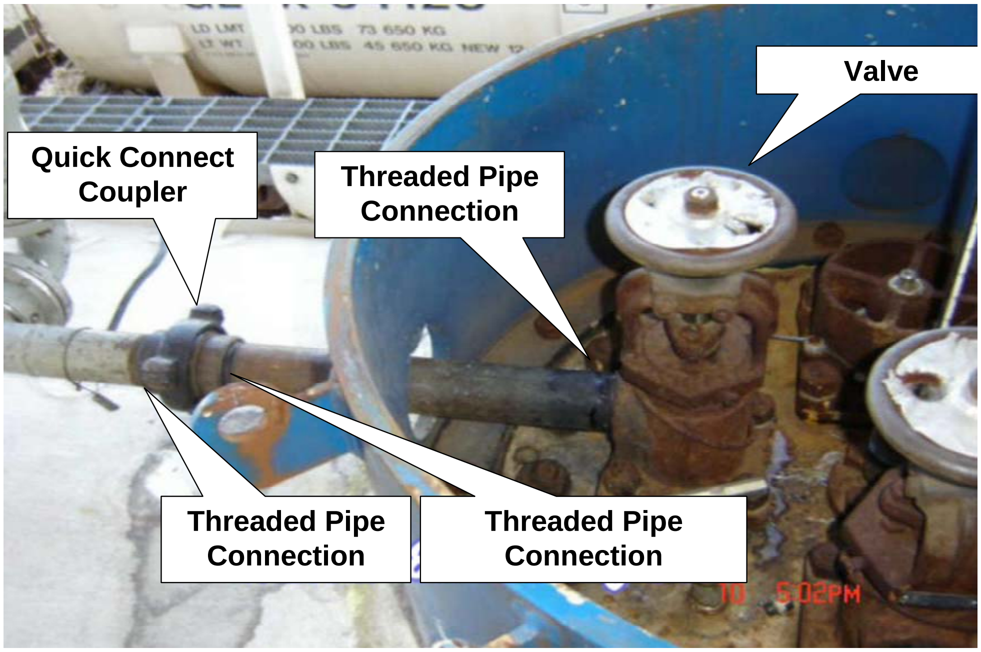

Figure 2-4. Photograph of Railcar Loading Arm Connection Showing Measured Fugitive Emission Sources (Photograph Taken by Leak Surveys, Inc.)

A Foxboro TVA-1000 analyzer was used for leak detection and screening. This analyzer meets or exceeds all the performance criteria for EPA Method 21, "*Determination of Volatile Organic Compound Leaks*". Sources of fugitive emissions were enclosed (bagged) using mylar and duct tape and sampled using the "blow though" method with nitrogen carrier gas as described in the EPA protocol. Vapors drawn from bagged emissions sources were captured in tedlar bags and analyzed by gas chromatography using flame ionization detection. The gas chromatograph (GC) was housed in a mobile laboratory that was parked next to the loading/unloading terminal. The Method 21 analyzer and GC were each calibrated at least once per day. Additional details of the measurement approach are given in the Quality Assurance Project Plan (Appendix C).

Screening values were obtained and recorded twice at each emissions source: once before and once after the source was bagged for an emission rate determination. Additionally, replicate emission rate determinations were made for each bagged source.

To identify candidate facilities for conducting the emissions measurements URS contacted the Houston Regional Monitoring (HRM) Technical Advisory Committee in person and distributed a project description and request for participation via email to all members of the East Harris County Manufacturers Association (ECHMA) Environmental Committee. Follow up discussions with seven companies led to the selection of three host facilities for conducting the emissions measurements. The three facilities were selected based on comparatively high throughputs of the hydrocarbons of interest for this study (i.e., they all offered opportunities for sampling several active loading arms per day over consecutive days). Emissions measurements were made during the loading or unloading of the following hydrocarbons: 1,3-butadiene, crude butadiene (i.e., a mixture of butadiene, butene, and butane), and isobutylene.

2.2 Development of Regional Emission Estimates

Regional estimates of pressure car loading and unloading emissions for the HGB were developed using the measurement results from this study and estimates of railcar loading and unloading activity reported compiled by ERG (2004). The ERG report lists the annual tonnage shipped and received by railcar for 115 different VOC. The information was compiled from a survey of 274 petroleum refineries, chemical manufacturing facilities, warehousing and storage facilities, and gasoline distribution terminals in the HGB. The ERG database did not differentiate between commodities shipped in pressurized versus non-pressurized railcars. Therefore, it was assumed that shipments of all VOC having normal boiling points of less than 75 °F at one atmosphere pressure were transported in pressure cars.

3.0 Measurement Results

Emission measurements were made at multiple sampling points including valves, threaded pipe connections, and dry break couplers during the loading or unloading of more than 20 pressurized railcars. Four flanged seals connecting liquid and vapor valves to loading arms were also tested during a return visit to one of the test facilities after the flanged connections had been recently installed. A total of 106 valid leak rate determinations were made (four leak rate measurements were invalidated because of poor agreement between replicate measurements). Table 3-1 gives the number of components of each type that were sampled and the minimum, maximum, and average valid leak rates. Average leak rates are expressed as both arithmetic and geometric means. The leak rates are reported for total VOC. SOCMI and refinery average emission factors reported by EPA (1995) are given in Table 3-2 for comparison. The equations used to estimate leak rates and example calculations are given in Appendix B.

Table 3-1. Number of Leak Rate Determinations for Valves, Threaded Pipe Connections, and Couplers

Equipment Type	Number Sampled	Minimum (kg/hr)	Maximum (kg/hr)	Arithmetic Mean (kg/hr)	Geometric Mean (kg/hr)
All	**106**	**3.4E-08**	**1.3E-01**	**4.4E-03**	**4.4E-06**
Valves	29	3.4E-08	4.4E-05	4.0E-06	5.8E-07
Threaded Pipe Connections	42	5.5E-08	1.3E-01	9.7E-03	2.2E-05
Liquid Line Couplers	22	1.0E-07	3.3E-02	2.5E-03	1.6E-05
Vapor Line Couplers	9	3.4E-08	1.8E-05	2.4E-06	4.0E-07
Flanged Connections	4	1.0E-07	1.0E-07	1.0E-7	1.0E-7

Table 3-2. SOCMI, Refinery, and Marketing Terminal Average Emission Factors for Valves and Connectors (EPA, 1995)

Equipment Type	Service	Emission Factor (kg/hr/source)		
		SOCMI Average	Refinery Average	Marketing Terminal Average
Valves	Gas	5.97E-03	2.68E-02	1.3E-05
	Light Liquid	4.03E-03	1.09E-02	4.3E-05
	Heavy Liquid	2.3E-04	2.3E-04	
Connectors	All	1.83E-03	2.5E-04	
	Gas			4.2E-05 [a]
	Light Liquid			8.0E-06 [a]

[a] Includes flanged and non-flanged connectors.

Threaded pipe connections and liquid line dry break couplers were the greatest sources of fugitive VOC emissions. On average, these sources emitted greater than two orders of magnitude more VOC per source than valves and vapor line couplers. The greatest variability of mass emission rates was measured for threaded pipe connections. For forty-two sources, the range of mass emission estimates was greater than six orders of magnitude. For each source type, the arithmetic mean was at least one order of magnitude greater than the geometric mean.

3.1 Correlation Equations

Correlation equations for emission estimation were developed using the method described in the EPA document titled *"Protocol for Equipment Leak Emission Estimates"* (EPA-453/R-95-017). This method expresses a leak rate (kg/hr) in terms of a concentration screening measurement (ppmv) by regressing the log of the leak rate on the log of the screening concentration. For these calculations, the leak rate for each sampled component was taken as the average of replicate leak rate determinations for the particular component. Initial and final screening measurements were not averaged together; they were treated as separate values and paired up with the average leak rate measurement for the component. The regression equation has the form:

$$\text{Log}_{10}\ (\text{leak rate [in kg/hr]}) = \beta_0 + \beta_1 \times \text{Log}_{10}\ (\text{SV})$$

Where:

β_0, β_1 = Regression constants; and

SV = Screening Value (ppmv)

The transformed equation is expressed as:

$$\text{Leak Rate} = \text{SBCF} \times 10^{\wedge}\beta_0 \times \text{SV}^{\wedge}\beta_1$$

Where:

Leak Rate = Emission rate of VOCs from the individual equipment piece (kg/hr)

SBCF = Scale Bias Correction Factor

The SCBF is a function of the mean square error of the correlation in log space and is obtained by summing a sufficient number (usually 10-15) of the terms from the infinite series given below:

$$SBCF = 1 + \frac{(m-1)\times T}{m} + \frac{(m-1)^3 \times T^2}{m^2 \times 2! \times (m+1)} + \frac{(m-1)^5 \times T^3}{m^3 \times 3! \times (m+1) \times (m+3)} + \dots,$$

Where:

T = (MSE/2) × ((ln10)^2);

MSE = mean square error from the regression; and

M = number of data pairs

The EPA protocol generally requires a minimum of 30 leak rate measurement and screening value pairs to establish a new correlation equation. Additionally, the protocol recommends a minimum of six sampled components having screening values in each of the following ranges:

Screening Value Range (ppmv)
1 – 100
101 – 1,000
1,001 – 10,000
10,001 – 100,000
> 100,000

If six sources are not available in a particular screening value range, additional sources from the nearest range should be tested.

Table 3-3 summarizes the screening values that were observed. The minimum data capture requirements are met for the aggregate dataset (all equipment types) but not for specific equipment types. The resulting scatter plot and regression line for all equipment types are shown in Figure 3-1. The r-square of the regression line is 0.65, which exceeds the r-square values reported by EPA for petroleum industry correlations (EPA, 1995). Table 3-4 gives the correlation equation, default zero emission rate, and pegged emission rate for entire dataset.

A scatter plot and regression line for threaded pipe connections is shown in Figure 3-2. The r-square for this subset of the data is 0.80, indicating that the regression equation is capable of predicting about 80% of the variability of the mass emission rate; however, a minimum of six screening values were only found for two of the five recommended concentration ranges. Scatter plots and regression lines for couplers and valves are presented in Figures 3-3 and Figures 3-4, respectively.

Table 3-3. Numbers of Measured Screening Values in Various Concentration Ranges

Equipment Type	Screening Value Range (ppmv)						
	<1	1-100	101-1,000	1,001-10,000	10,001-100,000	>100,000	Total
All	**10**	**62**	**4**	**9**	**9**	**12**	**106**
Valves	5	23	0	1	0	0	29
Threaded Pipe Connections	3	20	1	5	4	9	42
Liquid Line Couplers	0	9	2	3	5	3	22
Vapor Line Couplers	0	8	1	0	0	0	9
Flanged Connections	2	2	0	0	0	0	4

Table 3-4. Correlation Equation, Default Zero Emission Rate, and Pegged Emission Rate for Pressure Car Loading/Unloading Fugitive Emissions

Correlation Equation (kg/hr/source)	$LEAK = 7.1E\text{-}07 \times (SV)^{0.805}$
Default Zero Emission Rate (kg/hr/source)	2.0E-07
Pegged Emission Rate (kg/hr/source)	0.034

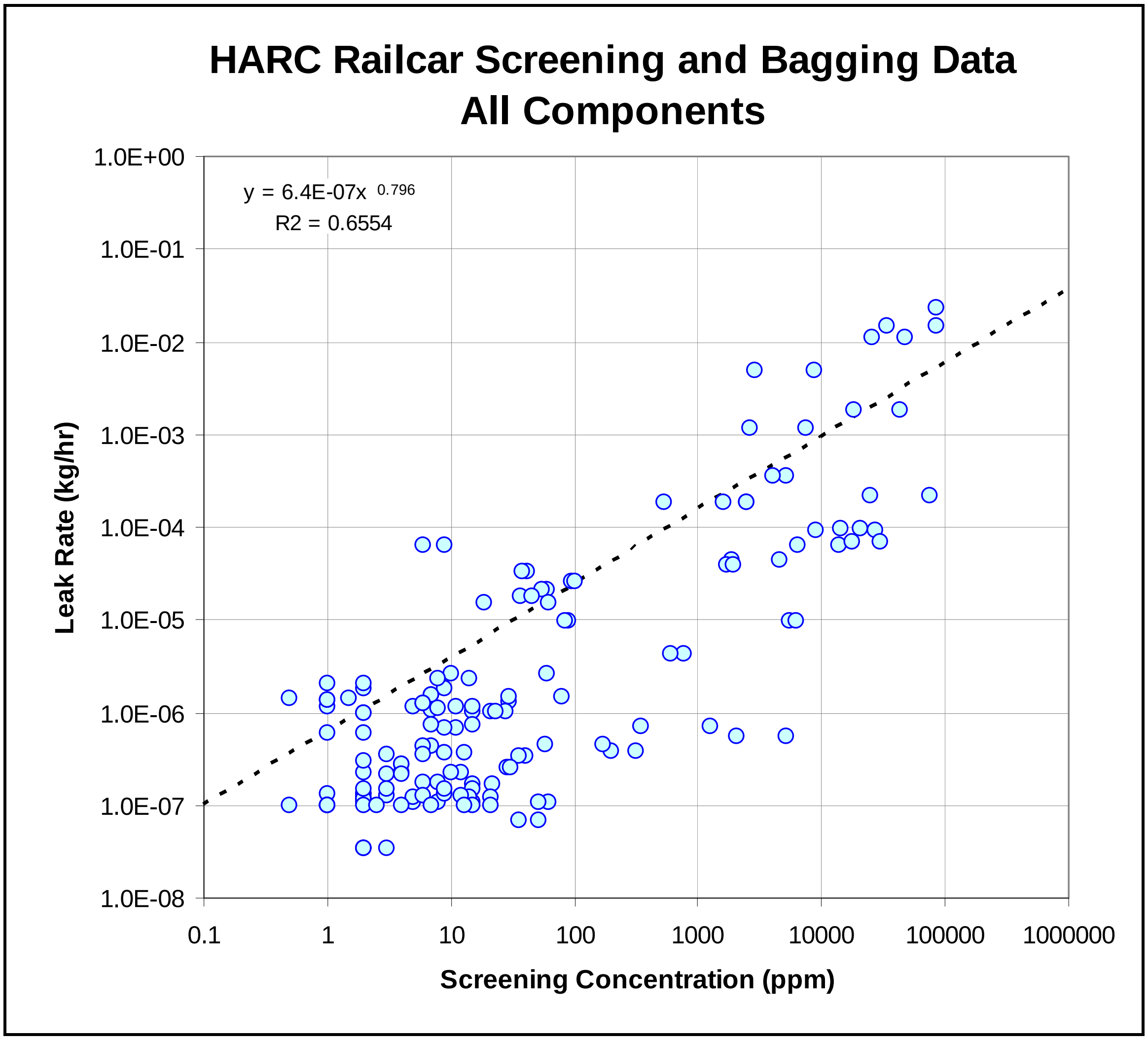

Figure 3-1. Scatter Plot and Regression Line for All Sources

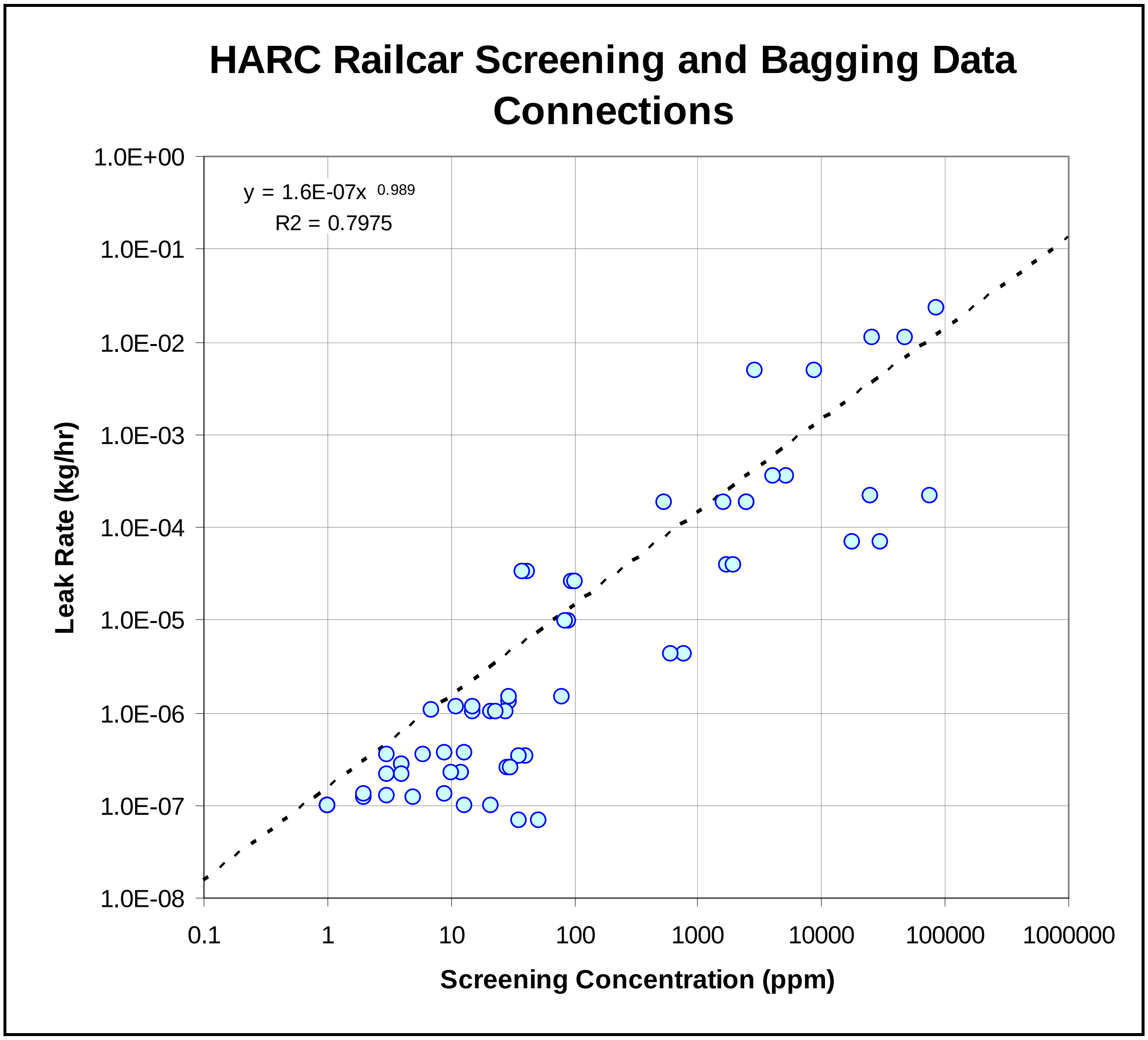

Figure 3-2. Scatter Plot and Regression Line for Threaded Pipe Connections

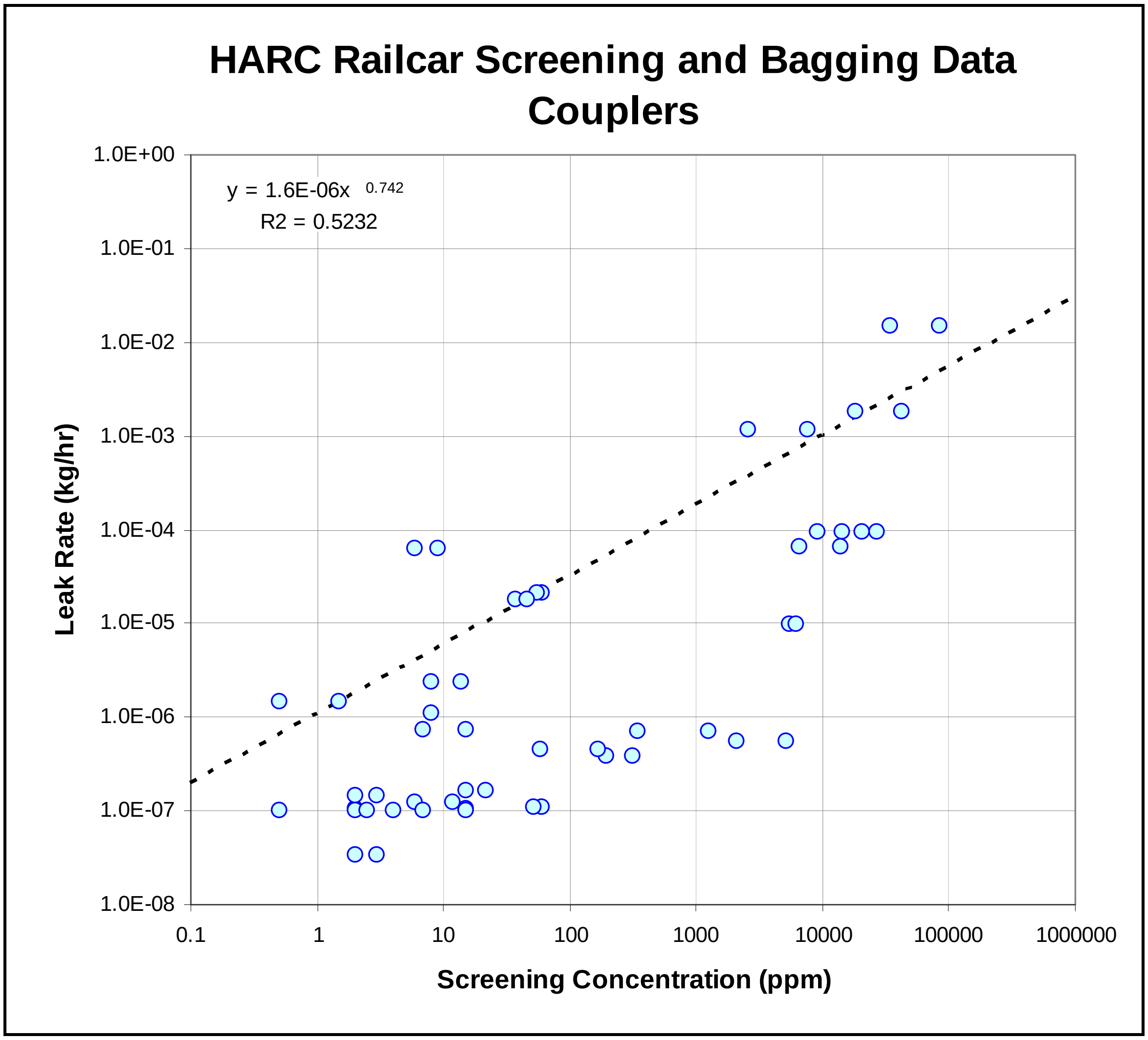

Figure 3-3. Scatter Plot and Regression Line for Line Couplers

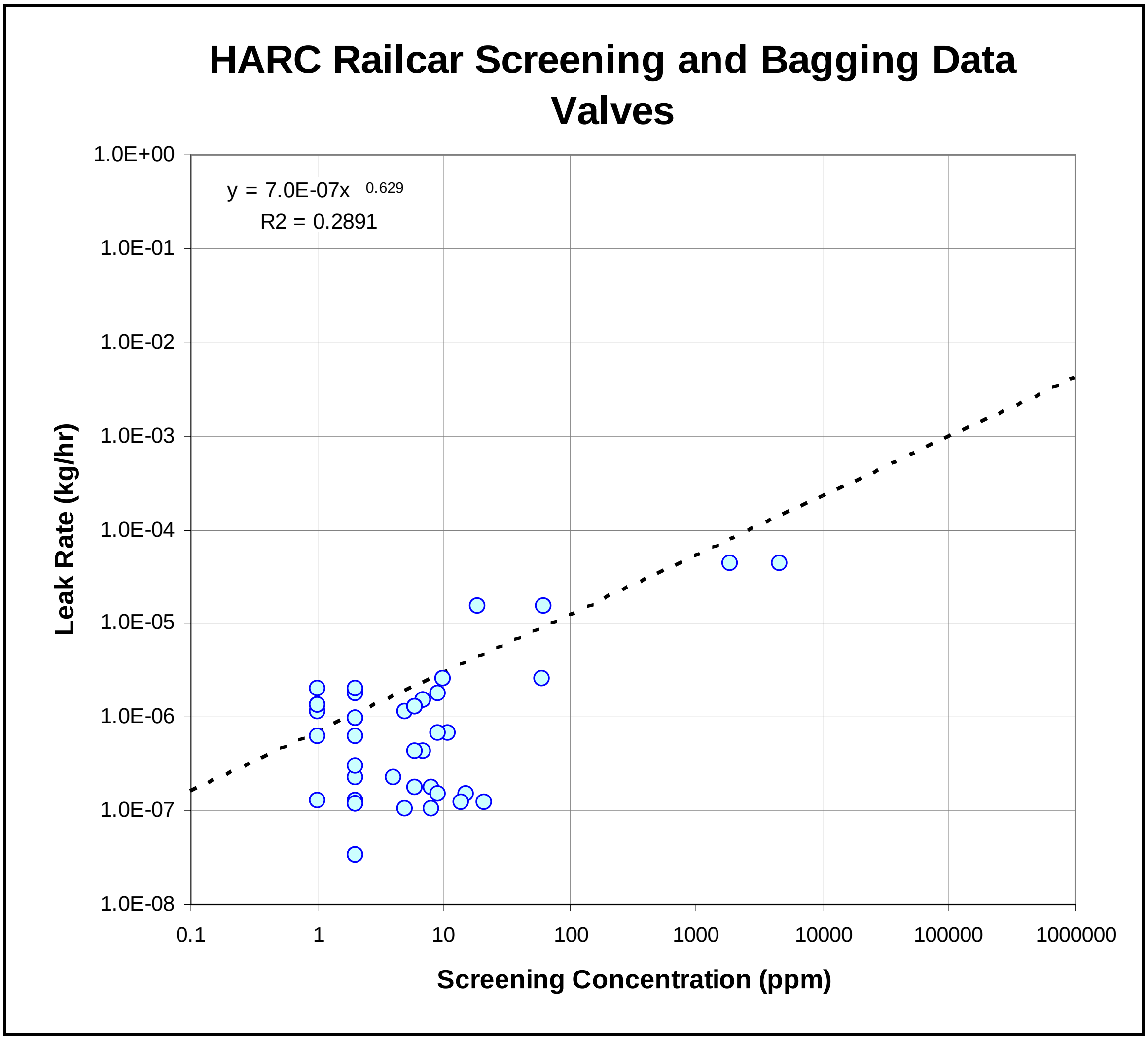

Figure 3-4. Scatter Plot and Regression Line for Valves

3.2 Regional Emissions Estimates

Regional emissions estimates for pressure car loading and unloading were developed using average leak rates reported in Table 3-1 and estimates of railcar loading and unloading activity reported by ERG (2004). The ERG report lists the annual tonnage shipped and received by railcar for 115 different VOCs. The information was compiled from a survey of 274 petroleum refineries, chemical manufacturing facilities, warehousing and storage facilities, and gasoline distribution terminals in the HGB. To account for a large number of facilities that did not respond to the survey, ERG adjusted the total amount shipped and received upward by a factor related to the number of facilities located near rail lines that did not respond. The ERG database did not differentiate between commodities shipped in pressurized versus non-pressurized railcars. Therefore, it was assumed that shipments of all VOC having normal boiling points of less than 75 °F at one atmosphere pressure were transported in pressure cars.

Table 3-5 gives the regional emission estimates based on the ERG activity data and the emission factors reported here. Note that the arithmetic mean leak rates reported in Table 3-1 were used as the average emission factors. Annual emissions for the HGB were estimated by multiplying the estimated number of 30,000 gallon railcars by the time it takes to load or unload each rail car. The product was then multiplied by emission factors for threaded pipe connections and dry break couplers, assuming three threaded pipe connections for each loading arm. Emissions from valves and vapor line couplers were assumed negligible since these averaged two orders of magnitude less than the other source types. Estimates reported for the facilities where sampling was conducted of the time required for completely loading and unloading a 30,000 gallon railcar ranged from 2-4 hours and 6-8 hours for loading and unloading, respectively. Therefore, and average duration of five hours was assumed. A summary of the calculations used in deriving these estimates is given in Figure 3-5.

Table 3-5. Regional Emission Estimates for Pressure Car Loading and Unloading in the HGB

Chemical	Total Shipped and Received (tons/yr)[a]	Density (lb/gal)	Total Shipped and Received (gallons/yr)	Number of 30,000 Gallon Railcars	Emissions (tons/yr)[b]
1,3-Butadiene	16,706	5.13	6,510,856	217	0.04
Butenes	118,106	4.91	48,136,520	1,605	0.28
Ethylene Oxide	362,642	7.36	98,523,894	3,284	0.57
Isobutylene	152,122	4.92	61,895,497	2,063	0.36
Liquid Petroleum Gas	37,583	4.52	16,629,794	554	0.10
Olefins	185,708	4.56	81,437,215	2,715	0.47
Propane	54,386	4.24	25,653,826	855	0.15
Propylene	263,636	4.21	125,110,917	4,170	0.73
Total					**2.69**

[a] From ERG (2004), adjusted using the methodology described in the ERG report.

[b] Derived using the arithmetic average leak rates reported in Table 3-1 for threaded pipe connections and liquid line couplers.

Step 1: Determine the Volume of Liquid Being Transferred

Chemical	Total Shipped and Received (tons/yr) [a]	Density (lb/gal)	Density Reference	Total Shipped and Received (gallons/yr)
1,3-Butadiene	16,706	5.13	3	6,510,856
Butenes	118,106	4.91	3,4	48,136,520
Ethylene Oxide	362,642	7.36	3	98,523,894
Isobutylene	152,122	4.92	3	61,895,497
Liquid Petroleum Gas	37,583	4.52	1	16,629,794
Olefins	185,708	4.56	6	81,437,215
Propane	54,386	4.24	2	25,653,826
Propylene	263,636	4.21	3,5	125,110,917

[a] From ERG (2004) Report

References

1. North American Combustion Handbook, Volume 1: Combustion, Fuels, Stoichiometry, Heat Transfer, Fluid Flow, Third Edition, 1986.
2. EPA AP-42, Appendix A, Miscellaneous Data Conversion Factors, 1995.
3. CRC Handbook of Chemistry and Physics, 81st Edition (2000-2001), 2000.
4. Used the density of 1-Butene for "Butenes".
5. Used the density of 1-Propene for "Propylene".
6. The olefins density is based on the average density for butenes and propylene.

Step 2: Determine the Number of 30,000 Gallon Railcars

No. Railcars = Total Gallons Shipped ÷ 30,000

Step 3: Determine the Number of Hours of Loading/Unloading Activity

The average times for loading and unloading 30,000 gallon railcars was reported to range from 2-4 and 6-8 hours, respectively. The average loading/unloading duration was assumed to be 5 hours.

Hours = No. Railcars × 5

Step 4: Estimate Emissions

Assumed threaded connections and dry break (quick connect) couplers are the only significant sources. Also assumed there are 3 threaded connections and one dry break coupler per loading arm.

Emissions (kg/yr) = Hours × (3 × 0.0097 +0.0025) where 0.0097 and 0.0025 are the

Figure 3-5. Summary Calculations of the Regional Emissions Estimates

4.0 Control Options

Pressurized railcars are loaded and unloaded from the top through an angle valve housed in a protective enclosure. To load or unload a railcar, two types of connections from the loading arm to the railcar are usually made. First, a pipe extension is inserted into the valve assembly so that connections to the loading arm can be made outside the protective housing. The loading arm is then connected to the pipe extension using one of many types of quick connect or dry break couplers. Both types of connections may be a source of fugitive emissions.

The threaded connection, which is designed to American National Pipe Tapered Thread (NPT) specifications, is inherently very sensitive to installation and maintenance practices. Any degradation of the thread at the female (valve) or male (pipe) end may cause a leak, even with the use of thread sealants like Teflon tape. Under or over torque of the connection and improper thread sealants may also promote leak paths.

Implementing leak detection and repair and good piping practices may reduce fugitive emissions from threaded pipe connections. For example, the leak rate at one source was reduced from 0.038 kg/hr to 0.00035 kg/hr when a site operator, after being alerted of the high initial measurement, retightened the connection. The screening level at this source went from pegged to 5167 ppmv after the operator retightened the connection.

Periodically inspecting threaded connections with an appropriate thread gauge may also help to reduce fugitive emissions. Connections should be inspected to verify that the threads are in good condition and do not exhibit flattening, upset threads, foreign material contamination, or other conditions that might prevent a leak-tight seal. Careful handling and storage of pipe extensions may also help to preserve thread condition. Threaded connections that join opposite ends of quick connects to pipe extensions and loading arms can be welded to eliminate those potential leak pathways.

The greatest reductions in fugitive emissions are likely to be achieved by eliminating threaded pipe connections. Several alternative connection types are commercially available to reduce or eliminate leak paths from threaded connections including flanged and o-ring boss fittings. Figure 4-1 shows an example of a type of flanged connection that was tested during a return visit to one facility after the connection had been recently installed. Zero fugitive emissions were detected from any of the four flanged connections that were tested.

Replacement of threaded connections with additional quick connects would not be recommended as the quick connect threaded mounts might, themselves, be a leak source.

Figure 4-1. OPW Flanged Elbow Connection to Valve

5.0 Summary, Conclusions, and Recommendations

Factors and correlation equations for estimating fugitive emissions during loading and unloading of pressurized railcars (pressure cars) are presented. The factors and correlation equations were derived from measurements made using the U.S. Environmental Protection Agency (EPA) method for screening and bagging fugitive leak sources, as described in the EPA document titled, *"Protocol for Equipment Leak Emission Estimates"* (EPA-453/R-95-017). The measurements were made at railcar loading and unloading terminals in the Houston-Galveston-Brazoria (HGB) area during February-March 2006.

The average emission factors for threaded pipe connections and quick connect couplers were 0.0097 kg/hr/source and 0.0029 kg/hr/source, respectively. These estimates are slightly higher than the SOCMI and refinery average emission factors for connectors reported by EPA (1995), which are 0.00183 kg/hr/source and 0.00025 kg/hr/source, respectively. The measured emission factors were used with previously reported estimates of railcar loading and unloading activity in the HGB to estimate the regional VOC emissions from pressure car loading and unloading. For chemicals having boiling points less than 75 °F at one atmosphere pressure, the total fugitive emissions estimate from pressure car loading and unloading is 2.69 tons per year. This estimate is less than one percent of a previously reported estimate of total railcar loading emissions in the HGB, which was 392 tons per year (ERG, 2004). Uncertainties in the number of pressure cars loaded and unloaded per year in the HGB could account for part of this difference.

Options for reducing fugitive VOC emissions from pressure car loading arm connections were investigated. Implementation of leak detection and repair protocols and good piping practices may be the best and most practical means for reducing fugitive VOC emissions during pressure car loading and unloading. Alternatives to NPT pipe thread connections used at loading/unloading valves, such as bolted flanged or o-ring seal connections might also be effective but would require testing, coordination between shipper and receiver, and possibly review by the U.S. Department of Transportation.

6.0 References

EPA, 1995. *Protocol for Equipment Leak Emission Estimates*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. November 1995.

ERG, 2004. *Development of Emission Estimates for Railroad Tank Cars for the Houston-Galveston Nonattainment Area, Draft Report*. Eastern Research Group, Morrisville, NC. August 2004.

American Chemistry Council, 2002. *Butadiene Product Stewardship Guidance Manual*. March 2002.

APPENDIX A

Screening Concentrations and Leak Rate Measurements

Screening and Bagging Data Used to Develop Average Emission Rates and Correlation Equations

Component ID	Component Category	Initial Screening Value (ppmv)	Final Screening Value (ppmv)	Measured Emission Rate #1 (kg/hr)	Measured Emission Rate #2 (kg/hr)	Average Emission Rate (kg/hr)
LIQDRYLOCK2	Liquid Line Coupler	0.5	2.5	1.0E-07	1.0E-07	1.0E-07
LIQDRYLOCK1	Liquid Line Coupler	15	4	1.0E-07	1.0E-07	1.0E-07
IQCA11	Liquid Line Coupler	15	2	1.6E-07	5.7E-08	1.1E-07
LIQDRYLOCK3	Liquid Line Coupler	3	2	1.3E-07	1.6E-07	1.5E-07
IQCA06	Liquid Line Coupler	22	15	1.5E-07	1.8E-07	1.7E-07
IQCA07	Liquid Line Coupler	197	321	2.2E-07	5.3E-07	3.7E-07
OQCA10	Liquid Line Coupler	2086	5218	5.5E-07		5.5E-07
IQCA10	Liquid Line Coupler	0	8	1.4E-06	7.9E-07	1.1E-06
IHLB04	Liquid Line Coupler	8	14	3.3E-06	1.5E-06	2.4E-06
ODLA02	Liquid Line Coupler	130	568	1.6E-06	8.0E-06	4.8E-06
OQCA12	Liquid Line Coupler	5480	6183	1.1E-05	9.1E-06	9.8E-06
IDLA03	Liquid Line Coupler	60	55	2.2E-05	2.0E-05	2.1E-05
IHLB06	Liquid Line Coupler	9	6	8.1E-05	4.7E-05	6.4E-05
OQCA13	Liquid Line Coupler	14088	6516	6.0E-05	6.9E-05	6.4E-05
ODLA04	Liquid Line Coupler	27297	9130	6.8E-05	1.2E-04	9.4E-05
OQCA08	Liquid Line Coupler	20497	14297	9.2E-05	9.8E-05	9.5E-05
OQCA07	Liquid Line Coupler	pegged	pegged	1.8E-04	6.7E-05	1.3E-04
OQCA11	Liquid Line Coupler	7598	2628	1.1E-03	1.2E-03	1.1E-03
OQCA09	Liquid Line Coupler	42797	18297	1.9E-03	1.7E-03	1.8E-03
IHLB05	Liquid Line Coupler	pegged	pegged	3.5E-03	4.1E-03	3.8E-03
ODLA05	Liquid Line Coupler	34097	84097	1.4E-02	1.5E-02	1.5E-02
IHLB02	Liquid Line Coupler	pegged	pegged	3.1E-02	3.4E-02	3.3E-02
OVLVCA13	Pipe Connection	0	0	5.5E-08	5.5E-08	5.5E-08
OQCCA08	Pipe Connection	36	51	9.4E-08	4.0E-08	6.7E-08
OVLVCA12	Pipe Connection	0	0	1.2E-07	7.7E-08	9.8E-08
VAPVLVCONN1	Pipe Connection	21	13	1.0E-07	1.0E-07	1.0E-07
VAPFLG1	Flanged Connection	1	1	1.0E-07	1.0E-07	1.0E-07
LIQFLG1	Flanged Connection	1	1	1.0E-07	1.0E-07	1.0E-07
LIQVLVFLG3	Flanged Connection	0	0	1.0E-07	1.0E-07	1.0E-07
VAPVLVFLG3	Flanged Connection	0	0	1.0E-07	1.0E-07	1.0E-07
OVLVCA10	Pipe Connection	2	5	9.5E-08	1.5E-07	1.2E-07
IVLVCA11	Pipe Connection	0	3	1.2E-07		1.2E-07
OQCCA12	Pipe Connection	2	9	2.0E-07	6.5E-08	1.3E-07
IHLCB03	Pipe Connection	4	3	9.1E-08	3.4E-07	2.2E-07
OVLVCA09	Pipe Connection	12	10	2.3E-07	2.2E-07	2.2E-07
IVLVCA10	Pipe Connection	0	0	2.4E-07	2.4E-07	2.4E-07
OVCCB02	Pipe Connection	29	31	3.0E-07	2.1E-07	2.5E-07
OVCCB03	Pipe Connection	4	4	4.7E-07	7.7E-08	2.7E-07
OQCCA09	Pipe Connection	40	36	4.7E-07	1.9E-07	3.3E-07
IVLVCB02	Pipe Connection	6	3	2.5E-07	4.4E-07	3.5E-07
OVCCB07	Pipe Connection	9	13	3.0E-07	4.2E-07	3.6E-07
IVLVCA06	Pipe Connection	28	21	2.8E-06		1.0E-06
IQCA06	Pipe Connection	23	15	9.8E-07	3.4E-07	1.0E-06
OQCCA07	Pipe Connection	7		1.0E-06		1.0E-06

Component ID	Component Category	Initial Screening Value (ppmv)	Final Screening Value (ppmv)	Measured Emission Rate #1 (kg/hr)	Measured Emission Rate #2 (kg/hr)	Average Emission Rate (kg/hr)
OVCCB06	Pipe Connection	15	11	1.9E-06	4.8E-07	1.2E-06
ODLCA02	Pipe Connection	30		1.1E-06	1.5E-06	1.3E-06
LIQVLVCONN1	Pipe Connection	80	30	1.5E-06	1.5E-06	1.5E-06
OVLVCB05	Pipe Connection	780	612	1.2E-06	7.3E-06	4.3E-06
IHLCB02	Pipe Connection	89	85	1.0E-05	9.5E-06	9.8E-06
IQCCA11	Pipe Connection	94	100	2.8E-05	2.4E-05	2.6E-05
IVLVCA03	Pipe Connection	42	38	4.3E-05	2.3E-05	3.3E-05
IVLVCA07	Pipe Connection	1697	1932	2.1E-05	5.5E-05	3.8E-05
OVCCB05	Pipe Connection	17998	29998	6.9E-05	6.9E-05	6.9E-05
IQCCA10	Pipe Connection	529	2508	1.7E-04	1.9E-04	1.8E-04
IQCCA07	Pipe Connection	1622	2457	2.0E-04	1.8E-04	1.9E-04
OQCCA13	Pipe Connection	25288	76386	1.2E-04	3.2E-04	2.2E-04
OVLVCA04b	Pipe Connection	5167	4087	3.7E-04	3.3E-04	3.5E-04
OVLVCA05	Pipe Connection	pegged	pegged	1.5E-03	1.6E-03	1.6E-03
OVLVCA02	Pipe Connection	pegged	pegged	1.9E-03	1.7E-03	1.8E-03
OVLVCB04	Pipe Connection	pegged	pegged	3.6E-03	3.7E-03	3.7E-03
OVLVCA08	Pipe Connection	2923	8897	5.1E-03	4.9E-03	5.0E-03
IVLVCB01	Pipe Connection	pegged	pegged	1.1E-02	4.7E-03	7.9E-03
IDLCA03*	Pipe Connection	46997	25997	1.3E-02	1.0E-02	1.1E-02
ODLCA04	Pipe Connection	pegged	pegged	1.5E-02	1.9E-02	1.7E-02
ODLCA05	Pipe Connection	84297	pegged	2.4E-02	2.3E-02	2.3E-02
OVLVCA04a	Pipe Connection	pegged	pegged	4.1E-02	3.5E-02	3.8E-02
IVLVCB04	Pipe Connection	pegged	pegged	4.5E-02	4.7E-02	4.6E-02
ODLCDSA04	Pipe Connection	pegged	pegged	1.4E-01	1.1E-01	1.3E-01
IVLVCB07	Pipe Connection	pegged	pegged	1.3E-01	1.2E-01	1.3E-01
OVLVB06	Valve	2	2	3.4E-08	3.4E-08	3.4E-08
OVLVA12	Valve	0	0	4.1E-08	8.0E-08	6.1E-08
OVLVA13	Valve	0	0	1.2E-07	5.5E-08	9.0E-08
OVLVA09	Valve	0	-1	1.2E-07	8.2E-08	1.0E-07
OVLVA10	Valve	8	5	1.0E-07	1.1E-07	1.1E-07
IVLVB06	Valve	2	2	1.2E-07	1.1E-07	1.2E-07
VAPVLV3	Valve	0	0	1.3E-07	1.0E-07	1.2E-07
OVLVB03	Valve	21	14	1.1E-07	1.3E-07	1.2E-07
IVLVA11	Valve	2	1	7.7E-08	1.8E-07	1.3E-07
IVLVB03	Valve	15	9	2.1E-07	9.0E-08	1.5E-07
OVLVB02	Valve	8	6	1.8E-07	1.8E-07	1.8E-07
IVLVA10	Valve	4	2	3.8E-07	7.1E-08	2.2E-07
OVLVA11	Valve	0	2	2.4E-07	3.7E-07	3.0E-07
IVLVA07	Valve	7	6	6.3E-07	2.4E-07	4.4E-07
IVLVA03	Valve	0	0	6.3E-07	4.1E-07	5.2E-07
IVLVB04	Valve	1	2	5.8E-07	6.4E-07	6.1E-07
OVLVA05	Valve	11	9	7.7E-07	5.8E-07	6.8E-07
OVLVB04	Valve	2	2	5.1E-07	1.4E-06	9.6E-07
OVLVA06	Valve	1	5	1.6E-06	6.9E-07	1.1E-06
IVLVB02	Valve	6	6	1.5E-06	1.0E-06	1.3E-06
OVLVB07	Valve	1	1	1.9E-06	7.8E-07	1.3E-06
OVLVA07	Valve	7	7	1.6E-06	1.4E-06	1.5E-06
OVLVA04	Valve	2	9	1.5E-06	2.1E-06	1.8E-06

Component ID	Component Category	Initial Screening Value (ppmv)	Final Screening Value (ppmv)	Measured Emission Rate #1 (kg/hr)	Measured Emission Rate #2 (kg/hr)	Average Emission Rate (kg/hr)
IVLVB07	Valve	2	1	2.0E-06	2.1E-06	2.0E-06
OVLVA08	Valve	10	60	3.7E-06	1.4E-06	2.6E-06
IVLVA01	Valve	3		2.4E-06	5.2E-06	3.8E-06
LIQVLV2	Valve	18.5	62.5	1.4E-05	1.7E-05	1.5E-05
OVLVA02	Valve	68	82	3.2E-05	3.8E-05	3.5E-05
OVLVA03	Valve	4597	1862	5.6E-05	3.2E-05	4.4E-05
OVCB03	Vapor Coupler	2	3	3.3E-08	3.4E-08	3.4E-08
VAPDRYLOCK1	Vapor Coupler	7	2	1.0E-07	1.0E-07	1.0E-07
OVCB02	Vapor Coupler	61	52	1.2E-07	1.0E-07	1.1E-07
OVCB06	Vapor Coupler	12	6	1.3E-07	1.2E-07	1.2E-07
VAPDRYLOCK3	Vapor Coupler	170	58	4.7E-07	4.4E-07	4.6E-07
OVCB04	Vapor Coupler	1255	345	8.9E-07	4.9E-07	6.9E-07
OVCB07	Vapor Coupler	7	15	7.8E-07	6.7E-07	7.2E-07
VAPDRYLOCK2	Vapor Coupler	0.5	1.5	1.5E-06	1.3E-06	1.4E-06
OVCB05	Vapor Coupler	37	46	1.8E-05	1.8E-05	1.8E-05

* Measured Emission Rate #3 = 9.9 E-03
Component ID IVLVCA06 was measured twice and is listed twice in the table

APPENDIX B

Leak Rate Equations and Example Calculations

Leak Rates were calculated using the following equation (EPA, 1995):

$$\underset{(kg/hr)}{\text{Leak Rate}} = \left(\frac{1.219 \times 10^{-5}\ (Q)\ (MW)\ (GC)}{T + 273.15} + \frac{(\rho)\ (V_L)}{16.67\ (t)} \right) \times \left(\frac{10^6 ppmv}{10^6 ppmv - GC} \right)$$

where:

1.219×10^{-5} = A conversion factor taking into account the gas constant and assuming a pressure in the tent of 1 atmosphere:

$$\frac{{}^{\circ}K \times 10^6 \times kg\text{-}mol}{m^3};$$

Q = flow rate out of tent (m^3/hr);

$$= \frac{N_2 \text{ Flow Rate } (\ell/min)}{1 - [\text{Tent Oxygen Conc. (volume \%)}/21]} \times \frac{[0.06\ (m^3/min)]}{(\ell/hr)}$$

MW[a] = Molecular weight of organic compounds in the sample bag or alternatively in the process stream contained within the equipment piece being bagged (kg/kg-mol);

GC[b] = Sample bag organic compound concentration (ppmv), corrected for background bag organic compound concentration (ppmv);[c]

T = Temperature in tent (°C);

ρ = Density of organic liquid collected (g/mℓ);

V_L = Volume of liquid collected (mℓ);

16.67 = A conversion factor to adjust term to units of Kilograms per hour (g × hr)/(kg × min); and

t = Time in which liquid is collected (min).

With a N_2 flow rate of 10 l/min, a butadiene molecular weight (MW) of 54.09 g/mole, a GC concentration (GC) of 9343 ppm, a temperature (T) of 17 degrees Celsius and a Tent (bag) Oxygen Conc. of 0%, the leak rate would be calculated as follows:

Leak Rate = $1.219 * 10^{-5} \times 10/(1 - 0/21) \times 0.06 \times 54.09 * 9343 / (17 + 273.15)$
Leak Rate = 0.0127 kg/hr

Tent oxygen was not accurately measured on February 9 and 10. All oxygen concentrations for this two day period were assumed to be zero. No organic liquid was collected during the bagging process so the second term in the above equation wasn't necessary when calculating leak rates.

Butadiene, 1-butene, n-butane, and isobutylene were all measured separately by the GC. The leak rate for each compound was determined and these leak rates were summed together to determine the total leak rate.

APPENDIX C

Quality Assurance Project Plan

Quality Assurance Project Plan

Measurement of VOC Emissions from Pressurized Railcar Loading Arm Fittings

Prepared for:

Houston Advanced Research Center
4800 Research Forest Drive
The Woodlands, TX 77381

February 6, 2006

Approved by:

Alex Cuclis, HARC Project Manager	(Date)
Brian Cochran, URS QAPP Author	(Date)
Albert Hendler, URS Project Manager	(Date)
Don Burrows, URS QA Officer	(Date)

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A. PROJECT MANAGEMENT

A4 Project/Task Organization

This project, Measurement of VOC Emissions from Pressurized Railcar Loading Arm Fittings, is divided into five tasks, the first of which is the development of this Quality Assurance Project Plan (QAPP). The second task is Data Collection, the third task is Data Analysis, the fourth task is Control Strategy Evaluation and the last task is Reporting.

The URS Corporation (URS) project team is organized using task leaders who are responsible for execution of the primary tasks of the project. Each task leader is responsible for schedule, budget, and coordination of work with other team members. The task leaders report to the Project Manager, who is responsible for the project team's progress toward meeting schedule, quality, and budget goals specified for the project. Albert Hendler will serve as project manager and will be responsible for maintaining the official, approved QAPP. Mr. Hendler will also serve as task leader on the Control Strategy Evaluation Task and the Reporting Task. Brian Cochran will serve as task leader for the QAPP Preparation Task and the Data Analysis Task. Carl Galloway will serve as task leader for the Data Collection Task and will be assisted by Darrin Barton.

Don Burrows is a quality assurance specialist who has no other duties within this project team. Mr. Burrows will be responsible for reviewing all project deliverables prior to submittal to ensure that project specifications and corporate quality requirements established by URS are being met.

An organizational chart that depicts the project team is presented in Figure 1.

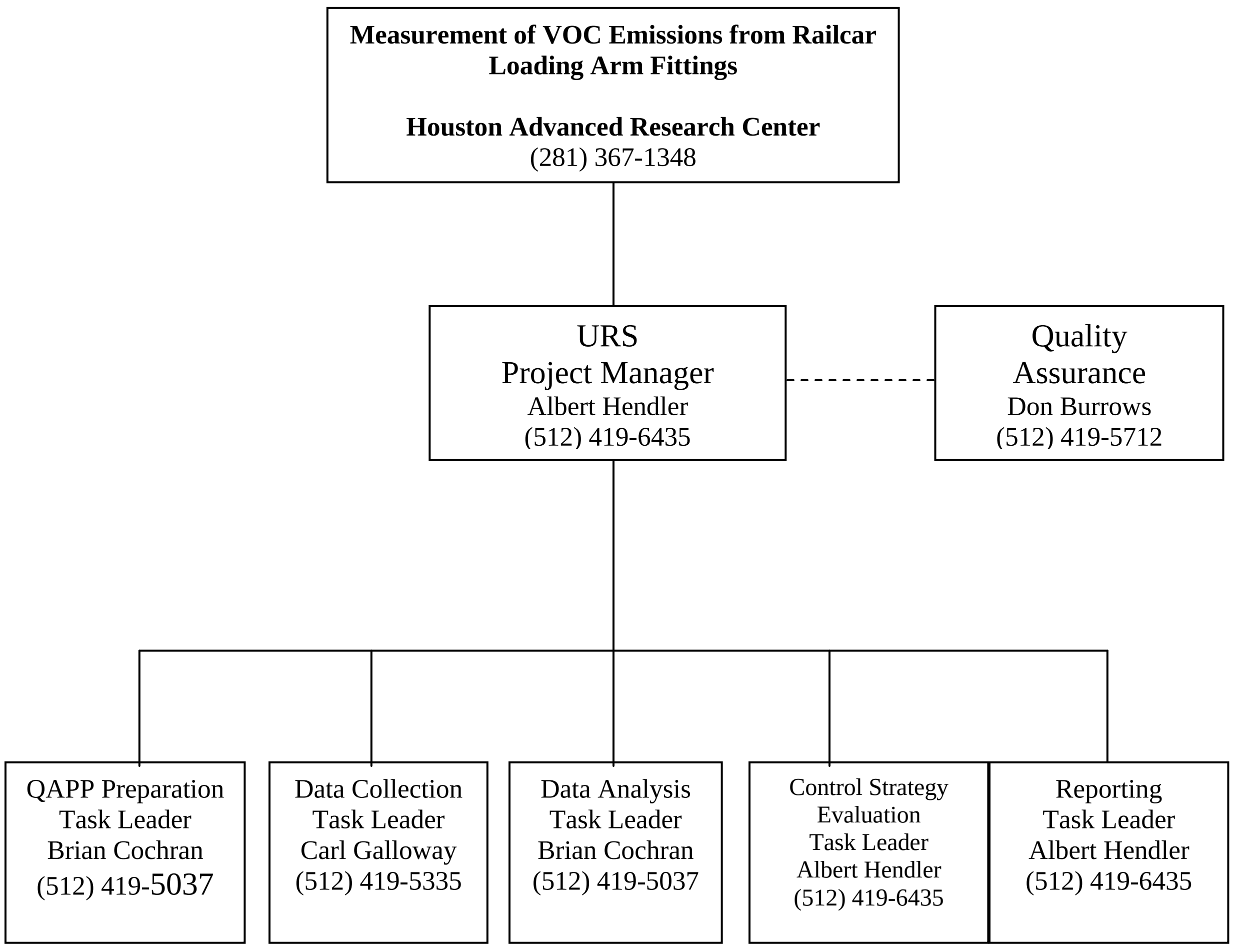

Figure 1. Organization Chart

A5 Problem Definition/Background

Previous research has identified leaking pressurized railcar loading arm fittings as potentially under-reported sources of VOC emissions. Data from this project will be used to develop new pressurized railcar loading arm emission factors and correlation equations, which will improve estimates of VOC emissions associated with pressurized railcar loading activity in the Houston-Galveston-Brazoria (HGB) Ozone Nonattainment Area.

A6 Project/Task Description and Schedule

This project is divided into five tasks, the first of which is the development of this QAPP. This QAPP describes the methods that will be used to acquire and analyze data as well as the procedures that will be used to assure the quality of the collected data and the accuracy of all calculations. This QAPP conforms, in content and format, to guidelines offered in the US EPA document titled, *EPA Requirements for Quality Assurance Project Plans QA/R-5*. A draft QAPP will be submitted by January 20, 2006. The QAPP should obtain final approval by January 27, 2006.

The second task is the Data Collection Task. The Data Collection Task will begin February 6, 2006 and should be finished by February 17, 2006. During this task, field measurements will be collected at pressurized railcar loading terminals in the HGB area, shown in Figure 2. Pressurized railcar loading arm fittings will be screened during loading and unloading activities according to EPA Method 21, and mass emission rates will be determined using EPA guideline procedures for bagging fugitive leak components.

The next task is the Data Analysis Task, where data collected during the Data Collection Task will be used to develop new emission factors and correlation equations for pressurized railcar loading arm fittings during the loading of pressurized tank cars. Once emissions factors and correlation equations have been developed, annual VOC emissions from pressurized railcar loading in the HGB will be estimated using railcar activity data available from earlier research. For the last task, Control Strategy Evaluation, control strategy options will be identified and evaluated; and potential emission reductions associated with each option will be discussed. Additionally, the feasibility of additional quick connections on pressurized railcars will be explored.

A complete draft report will be completed and submitted by April 30, 2006. The draft report will include the sampling approach used, sampling results, and data analysis methods and results. These results will include average emissions factors, correlation equations, and HGB annual emission estimates. An analysis of control strategy options, including potential emission reductions, will also be included in this report. This draft report will be submitted along with all raw measurement data, calculations, and spreadsheets. The final report will be submitted by May 15, 2006. Throughout this project, URS will provide HARC with monthly progress reports.

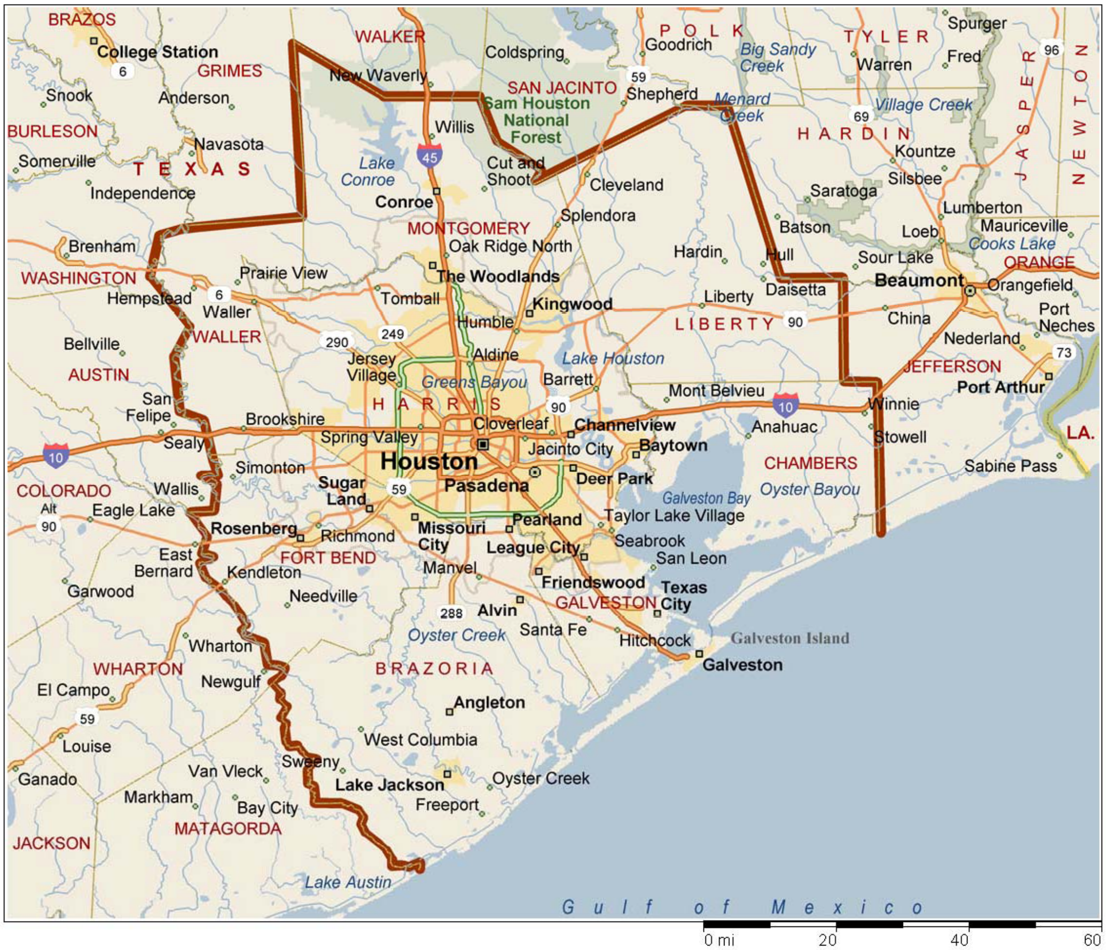

Figure 2. The HGB Study Area

A7 Quality Objectives and Criteria

Data collected from this project will be used to develop new emission factors and correlation equations for loading arm fittings during loading and unloading of pressurized tank cars. These emissions factors and correlation equations will be used in the future to estimate VOC emissions from pressurized railcar loadings in the HGB. As such, data collected during this project needs to be of the highest quality.

Measurement data collected for this project must meet the Measurement Quality Objectives listed in Table 1. Section B1 discusses requirements for data completeness.

6.0 Table 1. Measurement Quality Objectives

Parameter	Precision [1]	Accuracy [1]	Detection Limit [2]
VOC (measured as methane)	<10%	±20%	<1 ppmv

1 Precision and accuracy objectives are demonstrated through the procedures described in Section B5

2 To be demonstrated through specifications provided by instrument manufacturer

A8 Special Training/Certification

Experienced field staff will perform all measurement activities, and the Project Manager will ensure that field personnel firmly understand the project objectives and measurement requirements. URS personnel involved in the Data Collection Task will complete all applicable Health and Safety requirements prior to the commencement of sampling.

A9 Documents and Records

This QAPP and any future revisions will be provided by the Project Manager to each project team member via hardcopy or email according to the distribution list given in Section A3 of this QAPP. Version control will be maintained using the document control format prescribed by the EPA QA/R-5 guidance document, an example of which is shown in the page header.

For all documentation in written form, black indelible ink must be used, and any hand corrections must be made by a single line through the incorrect entry with the author's initials immediately following the correction. All work performed during the data collection, review, and validation process must be traceable to the author, and all data products must be able to be reversed to their original result at all times.

A list of documents and records that will be developed and maintained by the project team follows. Each item will be submitted to HARC as a draft for review before being submitted in final form. Note that information identifying the facilities from where data were collected will be deleted from all hardcopy and electronic files delivered to HARC or its designees. The following items will be delivered:

- Field sampling logs (hardcopy);
- Raw measurement data used for emission factor calculation (electronic spreadsheet); and
- Report of methods, activities, and results (hardcopy and electronic document).

URS will store all records and documents developed for this project in a centralized filing system maintained by its Austin office for at least ten years following the completion of the project.

B. DATA GENERATION AND ACQUISITION

B1 Sampling Process Design

During the Data Collection Task, field measurements will be collected at loading terminals in the HGB during transfer of liquefied gases into and out of pressurized railcars. The project manager will be responsible for the selection of specific railcar loading terminals. The Data Collection Task is scheduled to begin on February 6 and should take ten working days to complete. During this task, pressurized railcar loading arm fittings will be screened according to EPA Method 21, and mass emission rates will be determined using EPA guideline procedures for bagging fugitive leak components. Highly reactive VOCs (1,3-butadiene, butene, ethylene, and propylene) are of particular interest due to their role in ozone formation. Sampling will therefore be limited to HRVOCs or other light VOCs.

For the development of new correlation equations, at least 60 loading arm connections will be screened and bagged. Ideally, half of these loading arm connections should be involved with loading activities and the other 30 loading arms should be involved with unloading activities. Subsequent analysis will then be able to reveal if there is any statistically significant difference between loading arm fugitive emissions from loading vs. unloading activities.

For both unloading and loading, a random sample of a minimum of six loading arms should be chosen for bagging from each of the following five screening value ranges:

Screening Value Ranges (ppmv)
1 – 100
101 – 1,000
1,001 – 10,000
10,001 – 100,000
> 100,000

In accordance with EPA Method 21, if six sources are not available in a particular screening range, additional sources from the nearest range should be tested so that a minimum of 30 emission rate/screening value pairs are obtained.

Those sources that have a screening value of “zero” (when the emissions of a source cannot be detected over general background levels of VOCs) should be bagged in order to develop a default zero emission factor. Up to five “zero” screening sources should be bagged in order to develop new default zero values. Any emissions source that goes beyond the upper range (or pegs) the screening instrument should also be bagged in order that a pegged source emission factor can be developed. Up to five “pegged” screening sources should be bagged. These bagging quotas are data-quality based goals that may not reflect the reality that there may be very few loading arms whose fugitive emissions result in zero or pegged screening results.

B2 Sampling Methods

During the Data Collection Task screening and bagging will take place. Pressurized railcar loading arm fittings will be screened according to EPA Method 21. A Thermo Environmental Instruments HVM 680 Analyzer and a Foxboro TVA-1000 analyzer will be used. These analyzers are functionally equivalent and meet all performance criteria specified in EPA Method 21 (see Table 2 below). These analyzers have an approximate dynamic measurement range of 1 to 50,000 ppmv, and with the incorporation of a dilution probe the upper limit of this range becomes 500,000 ppmv.

When performing source screening, the portable analyzer probe opening will be placed at the leak interface of the loading arm fitting to obtain a "screening value." The probe will be held perpendicular, not tangential, to this interface. The probe will then be moved along the interface periphery while observing the instrument readout. If an increased meter reading is observed, the probe will be moved slowly along the interface where concentrations register until the maximum meter reading is obtained. The probe inlet will be left at this maximum reading location for approximately two times the instrument response time. The maximum reading will be recorded as the screening value on a prepared data collection form.

The instrument measurement may exceed the scale of the instrument. This is referred to as a pegged readout. When a pegged readout is encountered a dilution probe can be employed in order to measure concentrations greater than the instrument's normal range.

Care will be taken to avoid fouling the probe with grease, dust, or liquids. A short piece of Teflon® tubing will be used as a probe tip extender. This extender will be snipped off as the tip fouls.

Table 2. Summary of EPA Method 21 Requirements

1. Analyzer Response Factor < 10
2. Analyzer Response Time ≤ 30 seconds
3. Calibration Precision ≤ 10% of Calibration Gas
4. Internal Pump Capable of Pulling 0.1 to 3 L/min
5. Intrinsically Safe
6. Single Hole Probe with Maximum ¼" Outer Diameter
7. Linear and Measuring Ranges Must Include Leak Definition Value (may include dilution probe)
8. Instrument Readable to ± 2.5% of Leak Definition

Although there is not an official reference method for bagging, the techniques are well established and documented in the EPA document, "Protocol for Equipment Leak Emission Estimates – Section 4.0 Mass Emission Sampling (1995)." Bagging is a technique which involves enclosing a leaking source in a "bag" made of a type of plastic that is impermeable to the components of the leak. A known rate of carrier gas is then induced through the bag and a sample of the gas from the bag is collected and analyzed to determine the concentration of leaking material.

Once the leaking loading arm fitting has been bagged, a sample for analysis will be collected using the "blow-through" method with nitrogen carrier gas, as described in the EPA Protocol document. The carrier gas will forced through the bag at a known flow rate less than 60 liters per minute. An example of this sampling train is depicted in Figure 3. For analysis it is important to ensure that steady-state conditions exist within the bag. To make sure of this, sample analysis will not take place until at least five time constants (volume of bag/gas flow rate) have passed.

Samples will be drawn from each bag and into tedlar bag using a syringe filler. The tedlar bags will then be transported a short distance to an on-site mobile laboratory where they will be analyzing using a gas chromatograph equipped with a flame ionization detector.

Since only light VOCs are going to be sampled in this project, it is not expected that any VOC condensate will be collected during the bagging process. Therefore, no steps need to be taken for condensate collection.

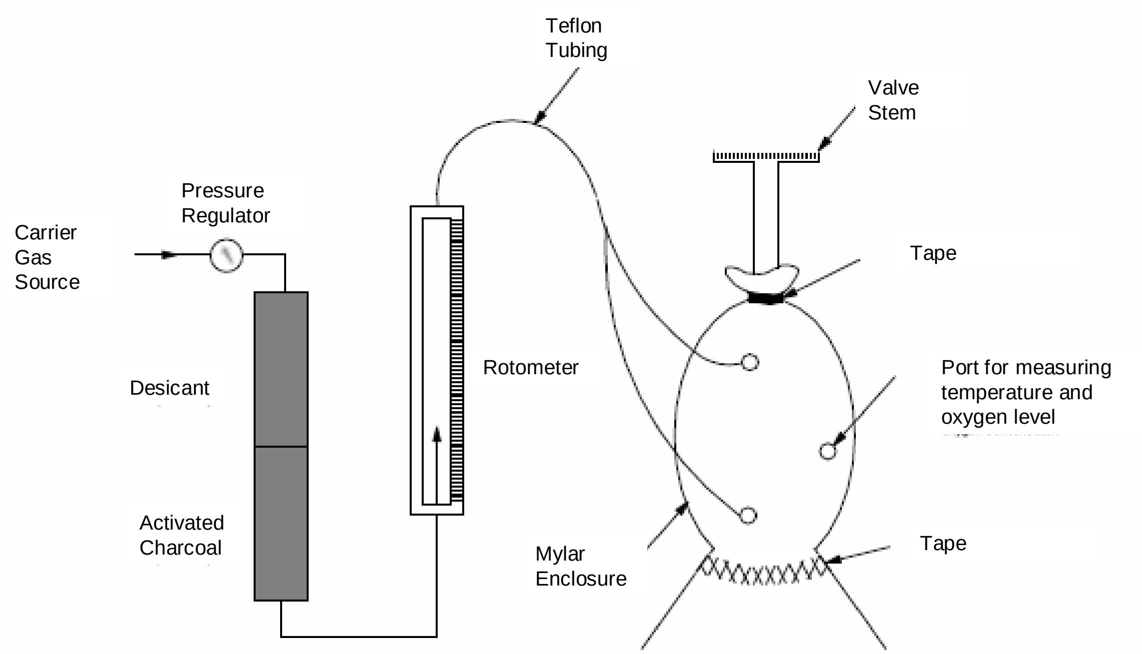

Figure 3. Example Sampling Train for Bagging a Source Using the Vacuum Method.

B3 Sample Handling and Custody

All analyses will take place in the field, so transport and shipment of samples is not necessary. All bagging samples will be analyzed concurrent with sample collection, so there are no special requirements for sample preservation.

B4 Analytical Methods

All measurements will be made in the field concurrent with sampling activities. All measurement activities are discussed in Section B2.

B5 Quality Control

Drift checks will be performed to assess analyzer accuracy. All field analyzers will undergo a drift check before and after each loading arm is bagged and analyzed. Drift checks will also be performed if a flameout of the portable analyzer occurs. These checks will be performed by analyzing one of the calibration gases used to calibrate the portable monitoring instrument. The choice of calibration gas should reflect the screening value. For example, if the screening value is 1000 ppmv, then the calibration standard closest to 1000 ppmv will be used.

If the drift check measurement is within 10% of the actual concentration the instrument is considered to have passed the drift check and no adjustment need be made to the instrument. If the drift check reading is off by 10% to 20% the analyzer is considered to have passed the drift check, but it will be recalibrated according to the procedure outlined in Section B7. If the drift reading is off by more by than 20% then the instrument is considered to have failed the drift test, in which case the instrument must be recalibrated, and the measurements since the last calibration or passed drift test must be repeated. All drift check data will be recorded on prepared data sheets.

Calibration precision is the degree of agreement between measurements of the same known value. To ensure that readings obtained are repeatable, a calibration precision test will be performed following the initial calibration of the instrument on the first day of sampling. Following calibration, three measurements of each non-zero standard will be made. Measurements will be made by first introducing the zero gas and adjusting the analyzer to zero. The specified calibration gas will then be introduced and the meter reading will be recorded. This procedure will be performed three times. The average of the three reading will then be calculated along with the standard deviation. The standard deviation will then be divided by the average to obtain the coefficient of variation for the three readings. If the coefficient of variation if less than 10% for each of the three non-zero standards then the precision check passes. If it does not pass the analyzer will be inspected to look for potential problems (e.g., sampler flow variability, etc.) and repaired. All calibration precision data will be recorded on prepared data sheets.

The validity of the bagging data is established by performing an accuracy check, which involves bagging a “dummy” source with a known, artificially induced leak rate. The accuracy test will be done at the beginning of the testing, ideally in the field and copying the standard bagging procedures as closely as possible. Two concentrations will be tested: a low level standard, and a high level standard.

The bagging accuracy test will be repeated each time the bagging equipment or analytical procedures are significantly modified. If the result is not within 20% of the expected value the problem must be investigated and corrected before sampling continues. The problems and associated solutions will be noted in the test report. All bagging accuracy test data will be recorded on prepared data sheets.

B6 Instrument/Equipment Testing, Inspection, and Maintenance

All instruments and equipment to be used during the Data Collection Task will be tested in the laboratory prior to deployment in the field to ensure proper working condition. During this testing, all analyzers will be calibrated according to the procedure in Section B7 to ensure proper instrument response. This testing will be conducted by the field personnel assigned to the Data Collection Task and should only take several hours to complete.

In the event of instrument or equipment failure in the field during the Data Collection Task, replacement equipment from URS laboratories will be shipped to the job site via next day delivery.

B7 Instrument/Equipment Calibration and Frequency

When bagging data are collected, it is critical that the screening value associated with mass emission rates is accurate. For this reason, a more rigorous calibration of the portable monitoring instrument is required than if only screening data were being collected.

Calibrations will be performed using a methane-in-air standard gas and will take place at the start of each working day. A total of five calibration gas standards will be used including a zero gas standard, a standard approaching the maximum readout of the screening instrument, and three standards between these values. If the analyzer does not permit five points to be used in the calibration then the maximum number of points the analyzer does permit will be used.

Following calibration of the instrument, all four non-zero standards will be reanalyzed to verify that the response at each standard is within 10% of the actual concentration. This is done to verify the degree of fit of the calibration. The response at each of these points will be recorded on prepared data sheets. If any responses are off by more than ten percent then the analyzer will be recalibrated.

All reference gases will be analyzed and certified by the manufacturer to be within ± 2% accuracy.

B8 Inspection/Acceptance of Supplies and Consumables

Acceptance criteria for calibration gases are discussed in Section B7.

B9 Non-direct Measurements

The Data Analysis Task requires that annual VOC emissions from pressurized railcar loading in the HGB be calculated using loading activity compiled during previous research. These loading activity figures will be provided by the TCEQ document, "Development of Emission Estimates for Railroad Tank Card for the Houston-Galveston Nonattainment Area."

B10 Data Management

The Project Manager is responsible for all data management. Wherever possible, data collected in the field will be recorded on prepared data collection sheets (see Figures 4-6 for examples). All other data will be recorded in field logs. Once field work has been completed, all field documentation will be electronically scanned and backed-up on one of the URS-Austin network servers.

Applicable data from the field will eventually be transferred to an electronic spreadsheet. At the completion of the project the spreadsheet will be copied to a compact disc and stored by URS along with all other hardcopy documentation for at least 10 years. All data (spreadsheets and scanned documents) will be saved electronically for ten years as well.

EXAMPLE FIELD SHEETS FOR EQUIPMENT SCREENING DATA

Detector model no. ____________

Operator name ____________

Date ____________

Component ID	Component Type	Location/ Stream	Service	Operating hrs/yr	Screening value (ppmv)	Background (ppmv)	Comments

Figure 4. Example Field Data Sheet for Screening Data

EXAMPLE DATA COLLECTION FORM FOR FUGITIVE EMISSIONS
BAGGING TEST (VACUUM METHOD)

Equipment Type ____________________ Component ID _____________

Equipment Category ________________ Plant ID _________________

Line Size _________________________ Date _____________________

Stream Phase (G/V, LL, HL) ________ Analysis Team ____________

Barometric Pressure _______________ __________________________

Ambient Temperature _______________ Instrument ID ____________

Stream Temperature ________________ Stream Pressure __________

Stream Composition (Wt %) ___________________, ______________________

______________________, ______________________, ______________________

Time — Bagging Test Measurement Data

_______ Initial Screening (ppmv) Equipment Piece[a] ______ Bkgd.______

_______ Background Bag Organic Compound Conc. (ppmv)[b] _____________

_______ Dry Gas Meter Reading (ℓ/min) _____________

_______ Sample Bag 1 Organic Compound Conc. (ppmv) _______________

_______ Vacuum Check in Bag (Y/N) (Must be YES to collect sample.)

_______ Dry Gas Meter Temperature[c] (°C) _________

_______ Dry Gas Meter Pressure[c] (mmHg) _________

_______ Dry Gas Meter Reading (ℓ/min) _________

_______ Sample Bag 2 Organic Compound Conc. (ppmv) _______________

_______ Vacuum Check in Bag (Y/N) (Must be YES to collect sample.)

_______ Dry Gas Meter Temperature[c] (°C) _________

_______ Dry Gas Meter Pressure[c] (mmHg) _________

Condensate Accumulation: Starting Time ______ Final Time ______

Organic Condensate Collected (mℓ) _____________

Density of Organic Condensate (g/mℓ) _____________

_______ Final Screening (ppmv) Equip. Piece[a] ________ Bkgd. ______

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[a]The vacuum method is not recommended if the screening value is approximately 10 ppmv or less.

[b]Collection of a background bag is optional.

[c]Pressure and temperature are measured at the dry gas meter.

Figure 5. Example Data Collection Form for Fugitive Emissions Bagging Test

EXAMPLE DRIFT TEST REPORT FORM

Plant ID_______________________

Instrument ID ________________

Analyst Name ________________

Date	Standard Gas Conc. (ppmv)	Time	Measured Conc. (ppmv)	% Error[a]	ID Number of Component Bagged Since Last Test

[a]% Error = $\frac{\text{Certified Conc.} - \text{Measured Conc.}}{\text{Certified Conc.}} * 100$

Figure 6. Example Drift Test Report Form

C. ASSESSMENT/OVERSIGHT

C1 Assessment and Response Actions

No performance or systems audits are planned for this project. The project QA officer is responsible for reviewing data reports associated with each task as well as final deliverables. The QA officer or any project staff may initiate a Corrective Action Report to identify, resolve and track any problems using the URS Ambient Air Monitoring Corrective Action Reporting System.

C2 Reports to Management

Field sampling personnel will communicate with the URS Project Manager via telephone or email at least once per day during the sampling effort to report on progress and any problems encountered.

D. DATA VALIDATION AND USABILITY

D1 Data Review, Validation, and Verification Requirements

Data review, validation, and verification procedures are presented in this section. Data will be declared invalid whenever documented evidence exists demonstrating that an analyzer was not collecting data under representative conditions or was malfunctioning.

The activities involved in validation of the data in general include the following:

- reviewing the field logs, calibration data, and project memoranda for indications of malfunctioning equipment;
- examining the analyzer data for unusual persistence, unusually high concentrations, or measurement values that seem incongruous with normal measurement ranges.

Data validation is the responsibility of the Data Collection Task Leader. Any issues raised during the data validation process will be communicated to the Project Manager for resolution. Any limitations in data usability will be discussed in the project data reports.

D2 Verification and Validation Methods

The URS Project Manager will conduct the final review of the data and emission factor calculations prior to their being considered valid. Data from all monitored sources, and emission factor calculation results, will be combined into a single spreadsheet to facilitate this review. Graphical displays of each parameter will be made and any outlying data points will be investigated.

The uncertainty of the validated data will be evaluated through analysis of precision and accuracy data collected during the Data Collection Task. After careful analysis of all collected data, any identified limitations on data use will be reported and thoroughly explained.

D3 Reconciliation with User Requirements

Emission factors and correlation equations developed from this project are intended for use by the TCEQ to evaluate ozone control strategies for the HGB areas. To meet the user requirements, the data resulting from this project must be of known and defensible quality. The quality control procedures to be implemented during this project are intended to help achieve this objective.