Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals

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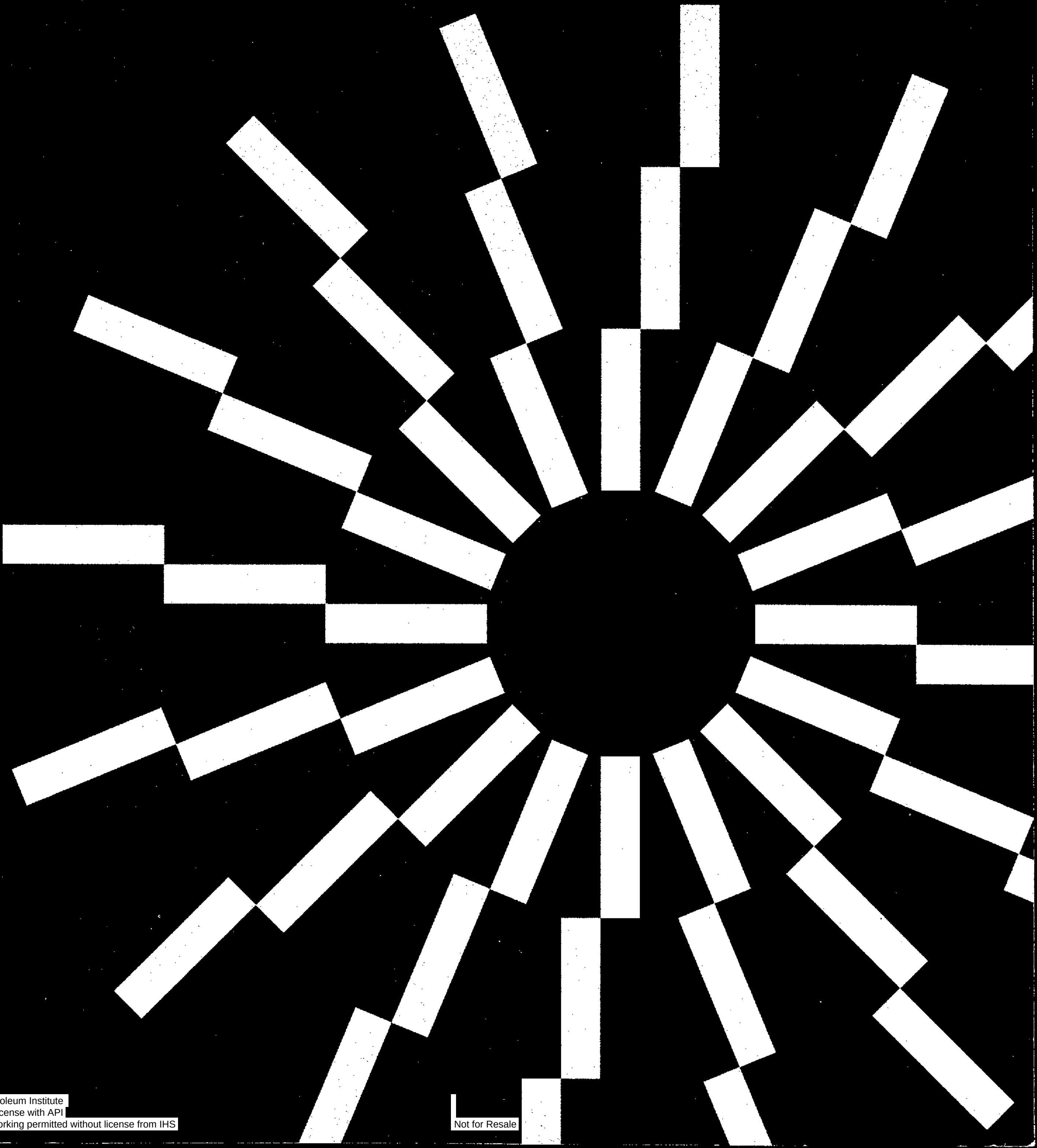

Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals

Volume I: Text

Health and Environmental Sciences Department

PUBLICATION NUMBER 4588

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**American
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ABSTRACT

The American Petroleum Institute (API) commissioned this study to "Develop Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals" by screening and/or bagging components at three marketing terminals. The United States Environmental Protection Agency (U.S. EPA) separately funded the same test contractor (Radian) to test an additional terminal. The results for all four marketing terminals are presented in this report.

New average emission factors, new default zero emission factors, and new emission correlation equations were developed for the majority of the component types found in petroleum marketing terminals. In almost all cases the new average emission factors, new default zero emission factors and new emission correlation equations predict substantially lower emissions than those factors and equations determined in previous studies of the chemical and petroleum refinery industries. These emission factors are lower because of lower leak distributions and lower correlations between mass emissions and screening values.

In addition to screening and bagging, a test was performed to determine the quantities of liquid gasoline that leaked out of loading arms after filling the gasoline tank trucks. These drips occur immediately after the trucks have been loaded and the liquid loading arms released from the trucks. In almost all cases the measured drip volumes per loading arm were below the detection limit of the measuring instrument (0.1 mL per truck loading event), indicating that these drips result in minimal emissions.

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EXECUTIVE SUMMARY

The American Petroleum Institute (API) commissioned this study to "Develop Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals" by screening and/or bagging components at three marketing terminals. The United States Environmental Protection Agency (U.S. EPA) separately funded the same test contractor (Radian) to test an additional terminal. The results for all four marketing terminals are presented in this report. The study's main objective was to:

- Determine emission factors and fugitive emission correlation equations for components (e.g., valves, pumps, etc.) in light liquid and gas services[1] specifically related to the petroleum marketing terminals.[2]

The secondary objectives were to:

- Develop correlations between chemical composition of the liquids in the lines and the chemical composition of the fugitive emissions.
- Compare the physical characteristics of the petroleum marketing terminals and the effect of these characteristics on the levels of fugitive emissions.

In this study, components analyzed for fugitive emissions were:

- Valves (ball, plug, butterfly, gate, check, diaphragm, globe, etc.).
- Connectors (flanges, screwed connectors, tubing connectors, union connectors, etc.).
- Pumps (centrifugal).
- Open-ended lines.

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[1] Gas service in this study is defined as the vapor phase of the liquid product.

[2] The U.S. EPA's primary objective was the development of emission correlation equations and stratified emission factors (but not average emission factors) specific to marketing terminals.

- Pressure relief valves.
- Tank truck loading arm valves (check valves on lines that connect to trucks including liquid loading arms and gas/vapor return arms).

Components at four marketing terminals were studied. The locations of the marketing terminals are:

- Los Angeles, California.
- Bridgeport, Connecticut.
- Providence, Rhode Island.
- Irving, Texas.

Leak rate data were gathered from components at all four marketing terminals with an organic vapor analyzer (OVA). Bagging data were gathered from three of the four terminals. Liquid stream composition and fugitive emission composition data were obtained at the three locations bagged.

New average emission factors, new default zero emission factors, and new emission correlation equations were developed for the majority of the components found in petroleum marketing terminals. In almost all cases the new average emission factors, new default zero emission factors, and new emission correlation equations predict substantially lower emissions than the factors and equations developed in previous studies of the chemical and petroleum refinery industries. Table 1 shows the new default zero emission factors. Table 2 shows the new emission correlation equations. Table 3 shows the new average and stratified (<1,000 parts per million [ppm] and ≥1,000 ppm) emission factors.

The distribution of leaking components from the petroleum marketing terminals showed significantly fewer components with high screening values than the distribution observed in the 1980 Refinery Assessment Study. Marketing terminals were not included in the refinery study; however, that study was used as a comparison because refinery component character-

Table 1

Default Zero Emission Factors (Total Hydrocarbons)

Component Type	Service	Number of Tests	Default Zero Emission Rate (lbs/hr)	Lower 95% Confidence Limit (lbs/hr)	Upper 95% Confidence Limit (lbs/hr)
Connectors[a]	Light Liquid	12	6.5×10^{-6}	3.9×10^{-6}	1.1×10^{-5}
Valves	Gas	8	5.9×10^{-6}	3.8×10^{-6}	9.3×10^{-6}
Valves	Light Liquid	11	3.5×10^{-6}	2.4×10^{-6}	5.2×10^{-6}
Open-Ended Lines[b]	Light Liquid and Gas Combined	8	4.5×10^{-6}	2.6×10^{-6}	7.7×10^{-6}
Pumps	Light Liquid	8	3.9×10^{-5}	2.1×10^{-5}	7.4×10^{-5}

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[a] Also recommended for Gas Connectors and "Other" (gas, LL) component types such as hatches, covers, manholes, thermal wells, and pressure relief valves.

[b] Also recommended for Loading Arm Valves (gas, LL).

Table 2

Predictive Emission Correlation Equations for Total Hydrocarbon Mass Emission Rates

Component Type	Service	Number of Data Pairs	Emission Correlation Equation [a,b]	Correlation Coefficient	Standard Deviation of Regression	Default Zero Screening Value (ppm)
Connectors [c]	Light Liquid and Gas Combined	36	$ER = (4.65 \times 10^{-5}) \times (SV)^{0.426}$	0.412	0.604	0.01[d]
Valves	Light Liquid	46	$ER = (6.34 \times 10^{-6}) \times (SV)^{0.708}$	0.845	0.460	0.44
Loading Arms Valves/ Open-Ended Lines [e]	Light Liquid and Gas Combined	40	$ER = (7.66 \times 10^{-6}) \times (SV)^{0.959}$	0.838	0.632	0.57
Pumps	Light Liquid	12	$ER = (6.57 \times 10^{-5}) \times (SV)^{0.534}$	0.757	0.667	0.38

[a] ER = Emission Rate (lbs/hr).

[b] SV = Screening value (ppm) using the OVA calibrated with methane.

[c] Also use for "other" component types (Gas, LL).

[d] The default zero screening value for this category is based only on connectors in light liquid service.

[e] Used the default zero emission factor for open-ended lines (light liquid and gas services combined) to estimate the default zero screening value.

Table 3

Petroleum Marketing Terminal Average and Stratified Total Hydrocarbon Emission Factors

Component Type	Service	Average Emission Factor (lbs/hr)	Stratified Emission Factor (lbs/hr)	
			0 – 999 ppm	≥1000 ppm
Connectors	Gas	0.000067	0.000030	0.0020
	Light Liquid	0.000023	0.000020	0.0010
Valves	Gas[a]	0.00016	0.000084	0.0090[b]
	Light Liquid	0.00015	0.000026	0.0046
Loading Arm Valves	Gas	0.045	0.00066	0.15
	Light Liquid	0.00087	0.00047	0.015
Open-Ended Lines	Gas	0.0067	0.00022	0.037
	Light Liquid	0.0065	0.00017	0.097
Pump Seals	Light Liquid	0.00093	0.00015	0.011
"Other"[c]	Gas	0.0014	0.00062	0.0025
	Light Liquid	0.00025	0.000073	0.0021

[a] Based on refinery correlation equation (Radian, 1989).
[b] Emission factor based on only one screening value.
[c] "Other" includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

istics were believed to be similar to marketing terminals in many respects. Figure 1 shows the distribution of the screening values of all component types and service types combined for the 1980 Refinery Assessment Study and the current petroleum marketing terminals study.

The physical characteristics of the petroleum marketing terminals, such as size, age, and throughput, did not show conclusive ties to screening value distributions.

- Traditionally, it has been assumed that the composition in the vapor leak was the same as in the liquid stream. The mechanism for this assumption is that the liquid in the line leaks through the component seal as a liquid and then vaporizes after reaching ambient air.
- As an alternative, Raoult's Law could be applied to determine the speciated vapor fraction based on liquid stream composition if the mechanism is identified as liquid vaporizing in the line with a pocket of gas trapped below a seal area.
- In this study, an attempt was made to determine the relationship between the composition of air toxics in the vapor (fugitive emissions) and the composition in associated liquid. However, the results were inconclusive.

No satisfactory physical explanation of the results has yet been determined. The results do not follow pre-study or traditional expectations. The limited data set may not have been sufficient to overcome random data scatter. It should be noted that the stringent QA/QC objectives defined at the start of this study were not fully met for the speciation of the liquids and vapors at two of the marketing terminals. However, the data indicate that even with improved precision and accuracy, the results would still be inconclusive. Without an explanation of the results that fits the physical principles, we do not recommend that these results be used to estimate individual species fractions of the total hydrocarbon emissions from marketing terminals.

In addition to screening and bagging, Radian performed a test at two marketing terminals to determine the quantities of liquid gasoline that leaked out of loading arms after filling the gasoline tank trucks. These drips occur immediately after the trucks have been loaded and the liquid loading arms are disconnected from the tank trucks. In almost all cases the measured volume of the drips per loading arm release were below the detection limit of the measuring instrument (0.1 mL per truck loading event), indicating that these drips result in minimal emissions.

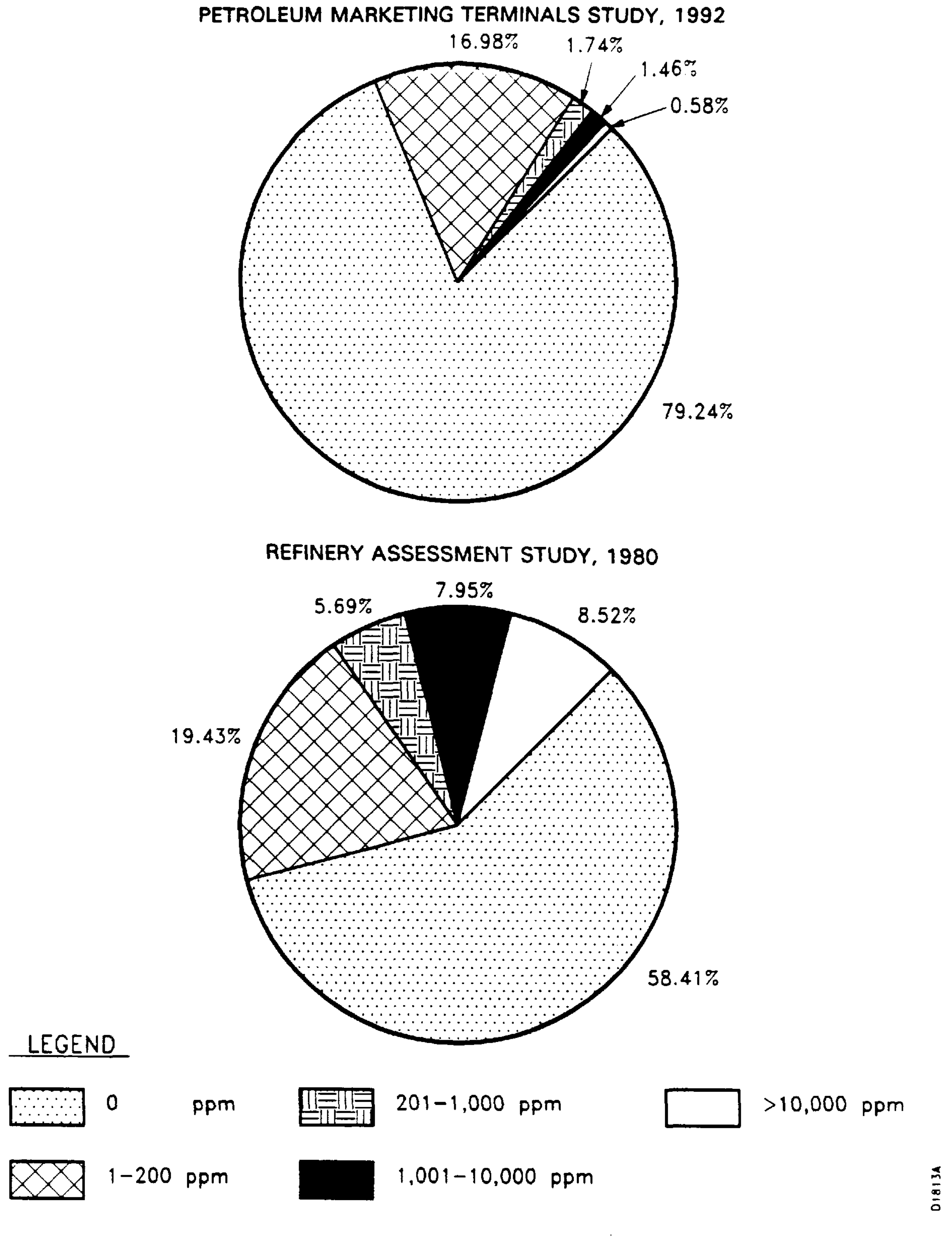

Figure 1. Comparison of Screening Value Distributions (LL, HL, and Gas) Between Petroleum Marketing Terminals Study (1992) and Refinery Assessment Study (1980).

1.0 INTRODUCTION

Fugitive emission factors that are specific to petroleum marketing terminals have not existed to date. Therefore, fugitive emission estimates for petroleum marketing terminals have typically been based on average emission factors derived from petroleum refining or chemical industries. Furthermore, the average emission factors for these industries were primarily developed more than 10 years ago and may no longer reflect current technology or operating procedures. To improve the accuracy of fugitive emission estimates for petroleum marketing terminals, the American Petroleum Institute (API) commissioned this study to "Develop Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals." The United States Environmental Protection Agency (U.S. EPA) separately funded the same contractor (Radian) to test at one terminal.

1.1 STUDY OBJECTIVES

This study's main objective was to:

- Determine average emission factors and fugitive emission correlation equations for components in light liquid and gas services specifically related to the petroleum marketing terminals.[3]

The secondary objectives were to:

- Develop correlations between chemical composition of the liquids in the lines and tanks and the chemical composition of the fugitive emissions.
- Compare the physical characteristics of the petroleum marketing terminals and the effect of these characteristics on the levels of fugitive emissions.

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[3] The U.S. EPA's primary objective was the development of emission correlation equations and stratified emission factors (but not average emission factors) specific to marketing terminals.

1.2 HISTORICAL PERSPECTIVE

In the past, those attempting to estimate fugitive emissions from petroleum marketing terminals used information prepared for the petroleum refining or chemical industries. Information for these industries was primarily gathered during the late 1970s and early 1980s. In this report, comparisons are made to some of these study results. Other studies, that discuss fugitive emission protocols, are also referred to in this report. This section discusses earlier studies.

The *Assessment of Atmospheric Emissions from Petroleum Refining* (Radian, 1980), also called the 1980 Refinery Assessment Study, was one of the first programs to rigorously examine fugitive emissions from petroleum refineries. Components were screened with a portable hydrocarbon analyzer and mass emission rates for components were measured (bagged) in 13 refineries throughout the United States (U.S.). The assessment developed screening value distributions, average emission factors, and correlations between screening values and mass emission rates (emission correlation equations).

The 1980 Refinery Assessment Study results were significant, but not always easily implemented. The screening values were obtained using a Threshold Limit Value (TLV®) Sniffer, calibrated with hexane. Therefore, the correlation equations developed could only be used when the screening value measurements were done using a TLV® Sniffer. Many refineries, however, obtain screening values with an organic vapor analyzer (OVA), calibrated with methane. In a screening study conducted in 1979, a correlation analysis was performed between screening values obtained with a TLV® Sniffer, calibrated with hexane, and an OVA, calibrated with methane (Radian, 1979). One of the results of this analysis was an equation that related these two types of screening values.

In 1982, the U.S. Environmental Protection Agency (U.S. EPA) published a document entitled *Fugitive Emission Sources of Organic Compounds -- Additional Information on Emissions, Emissions Reductions, and Costs (AID)* (U.S. EPA, 1982a). This document presented average emission factors for Synthetic Organic Chemical Manufacturing Industry (SOCMI) plants, developed using SOCMI screening value distributions and supplemented with refinery screening value to mass-emission rate correlation data from the 1980 Refinery Assessment Study.

In January 1986, the U.S. EPA published a document entitled *Emission Factors for Equipment Leaks of VOC and VHAP* (U.S. EPA, 1986). In this document, U.S. EPA explained the development of the average emission factors presented in AID, and the procedures for developing leak/no-leak emission factors. With the exception of gas/vapor service valves, these emission factors are based largely on the data collected in the 1980 Refinery Assessment Study.

In October 1988, U.S. EPA published a document entitled *Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP* (U.S. EPA, 1988). In this document, the emission factors were extended from two categories (leak/no-leak) to three categories (stratified emission factors). The basis for these emission factors continued to be the same as the previous studies. Therefore, with the exception of gas/vapor service valves, the stratified emission factors were based largely on the data collected in the 1980 Refinery Assessment Study.

In 1989, API contracted with Radian Corporation to complete the development of leak/no-leak and stratified emission factors for all component and service types that existed in the 1980 Refinery Assessment Study. This included the development of emission factors for gas/vapor service valves, as well as emission factors for components in hydrogen service. The emission factors, and corresponding emission correlation equations, developed during the study (API, 1989 Draft Report) are the most accurate and appropriate for refineries currently available. As a result, they are used as comparisons to the emission factors, and emission correlation equations determined in the current study of petroleum marketing terminals.

1.3 REPORT ORGANIZATION

Section 2.0 identifies characteristics of the four marketing terminals tested. Section 3.0 outlines the testing methodology. Section 4.0 presents the quality control results. Section 5.0 describes the data analysis procedures and results. Section 6.0 summarizes the conclusions and recommendations. References are shown in Section 7.0.

2.0 CHARACTERISTICS OF MARKETING TERMINALS TESTED AND HOW THESE CHARACTERISTICS AFFECT EMISSIONS

Fugitive emission screening value data were collected at four petroleum marketing terminals. At three of these marketing terminals, bagging and speciation of liquid streams and fugitive emissions were conducted. At two terminals, a test of the amount of liquid leaking from liquid loading arms (after tank truck loading) was conducted. A general description of each terminal and testing condition is provided in Table 2-1.

It was not possible within the scope of this study to determine the exact impact of the variables identified on Table 2-1. However, several of the variables are believed to have some impact on the distribution of screening values obtained while testing. The distribution of screening values by facility for all components combined is provided on Table 2-2. The variables identified on Table 2-1 and, in some cases, their relationship to the screening value distribution shown in Table 2-2 are discussed briefly in this section.

The age of the facility, or at least the age of the components, may have some relationship to the screening value distribution. In general, newer facilities had slightly lower percentages of components with screening values over 100 ppm. However, the age of each component, or the age of the packing or seal of each component was not determined. It seems reasonable to believe that increased component age increases the chance that seals no longer hold as well as they did when new. If so, and if older facilities have, in general, older components, then the relationship of slightly higher screening values for older facilities can be readily understood. The volume throughput, number of loading racks, and number of tank trucks per day tends to impact the overall emissions from each facility. Higher throughput increases the number of tank trucks loaded per day and the potential for drip leaks after loading a tank truck. In general, higher volume throughput also means increased numbers of components, which means higher fugitive emissions. However, no information gathered would indicate that the higher throughput means a change of screening value distribution. The marketing terminal

Table 2-1

Comparison of Selected Petroleum Marketing Terminal Characteristics

Terminal Description	Terminal A	Terminal B	Terminal C	Terminal D
Age of Facility (yrs.)	>40. Major modifications in late 1970s on loading racks.	>50. Major modifications in late 1970s on loading racks.	>80. Major modifications in late 1970s on loading racks.	>45. Major modifications in early 1970s on loading racks.
Average Throughput (All Products) (Gal./Day)	>900,000 (100,000 gallons of which is piped to airport).	>2,500,000	>1,300,000	>650,000
Number of Loading Racks	7 (bottom load)	8 (bottom load)	10 (7 bottom load, 3 top load)	4 (bottom load)
Number of Trucks per Day (Avg.)	90	>300	>180	12[c]
Type of Vapor Recovery System	Carbon adsorption	Refrigeration	Carbon adsorption	Carbon adsorption
Product Types	Motor gasolines; Jet A; Distillates; Solvent	Motor gasolines; Distillates	Motor gasolines; Aviation gas; Distillates	Motor gasolines; Environmental gasoline; Distillates
Approximate Ambient Temperature While Testing (°F)[a]	66	78	70	74
Approximate Wind Speed While Testing (mph)[b]	7	2	2	4
Approximate Number of Light Liquid and Gas Fugitive Components	3,600	6,800	5,800	4,300
Have Marine Terminal?	No	No	Yes	Yes
Routine I/M Program?	No	Yes	No	No
Type of Vapor Return Line Controls	Check valves (single and dual)	Posts and check valves (single)	Posts and check valves (single)	Posts and check valves (single)

[a] Temperature estimates based on the averaged measured data while bagging at three terminals, and on a rough estimate at the terminal not bagged.

[b] Wind speed estimates based on estimated and recorded data while bagging of three terminals, and on a rough estimate at the terminal not bagged.

[c] Terminal D also loads 150 barges per year.

mph = miles per hour

I/M = inspection/maintenance

Table 2-2

Distribution of Screened Values Per Facility For Components in Light Liquid and Gas Services

Screening Value Range (ppm)	Terminal A		Terminal B		Terminal C		Terminal D	
	Number of Components	Percent of Total (%)	Number of Components	Percent of Total (%)	Number of Components	Percent of Total (%)	Number of Components	Percent of Total (%)
X < 1	1,148	85.8	1,201	78.8	898	71.6	1,114	77.3
1 ≤ X < 100	168	12.6	237	15.6	230	18.3	262	18.2
100 ≤ X < 500	10	0.7	50	3.3	56	4.5	24	1.7
500 ≤ X < 1,000	4	0.3	9	0.6	14	1.1	8	0.6
1,000 ≤ X < 10,000	5	0.4	17	1.1	40	3.2	26	1.8
10,000 ≤ X < 100,000	3	0.2	8	0.5	13	1.0	5	0.3
X ≥ 100,000	0	0.0	2	0.1	3	0.2	2	0.1
Total Components Screened[a]	1,338	100.00	1,524	100.00	1,254	100.00	1,441	100.00

[a] In most cases only every tenth connector was screened; therefore, total components screened will not equal the total components of each terminal.

with the highest number of components with screening values >1000 parts per million (ppm) was not the marketing terminal with the highest volume throughput.

The type of vapor recovery system may impact the emission rates from the facility. The number of leaking components from each type of vapor recovery system was analyzed. The number of higher leaking components from the vapor recovery system in the marketing terminal with the refrigeration system was greater than in the three marketing terminals with carbon adsorption systems. Some of the leaking areas of the refrigeration system did not fall easily within the traditional categories of components and have been included in the "other" category. For example, some hatch covers to boxes associated with the refrigeration unit, which is in the "other" category, had hydrocarbon emissions that exceeded 100,000 ppm.

The product type (within the light liquid and gas service categories) at each marketing terminal influenced the screening value distribution at each terminal. The definition of "heavy liquid" used for this analysis is a liquid or gas/liquid stream with a vapor pressure equal to or less than that of kerosene (≤0.1 psia at 100°F or 689 Pa at 38°C), based on the most volatile class present at >20% by volume. Heavy liquids include diesel, fuel oil, and jet fuels. Components carrying heavy liquids had fewer higher leaking components than components carrying light liquids or gases. Because not all components in heavy liquid service were screened, they are not included in the screening distributions shown in Table 2-2. Gasoline additives are not a heavy liquid by the definition used in this study, but have a relatively low vapor pressures compared with gasolines. Components carrying gasoline additives at each loading rack also showed lower screening values than those carrying liquids with higher vapor pressures. In contrast, components carrying aviation gasoline, a particularly light liquid, had a high number of components leaking over 1,000 ppm. The numbers of components carrying gasoline additives or aviation gasoline will influence the screening value distribution at each terminal.

The effects of ambient temperature and wind speed on measured emission rates are inconclusive. There are too many competing variables to isolate the effects of ambient temperature and wind speed data. Ambient temperature and windspeed were based on measured data and estimated data gathered while on site. These data are based on temperatures and wind speeds while bagging or screening, and not the average daily temperatures or wind speed.

One of the marketing terminals had marine loading and unloading facilities. Marine loading and unloading of petroleum products could impact the total emissions from such a terminal. The marine environment has the potential to affect fugitive components differently than in nonmarine environments; however, too few components were available to be measured at the marketing terminal with marine loading and unloading facilities to reach any conclusions on screening value distribution.

Available literature strongly supports that inspection/maintenance (I/M) programs are effective in reducing fugitive emissions (U.S. EPA, 1982b). Interestingly, Terminal B was the only terminal with an I/M program (quarterly inspections, 1,000 ppm leak definition), but it was not the terminal with the lowest percentage of leaking components. This result may be anomalous, with other factors outweighing the contributions of the I/M program. Some of the other factors that may outweigh the contribution of the I/M program are the age of the facility, age of the component or seal, temperature while testing, temperature changes during the year, type of products handled, or specific types of components within a component category (i.e., more gate valves than butterfly valves, etc.). None of these potential factors was studied in enough detail to reach conclusions on their impact.

One of the highest sources of emissions, on a mass emitted per component basis, at the marketing terminals was from the gas loading arm valves (vapor return valves). The vapor return valves are check valves in the vapor return lines that connect to the trucks during loading. A schematic drawing of the vapor return line system is shown as Figure 2-1. The vapor return arms allow the hydrocarbon vapors in the tank trucks to be displaced to a collection and recovery system while the tank truck is loaded with the product. The check valves in these vapor return arms have as a primary purpose the prevention of liquids that can

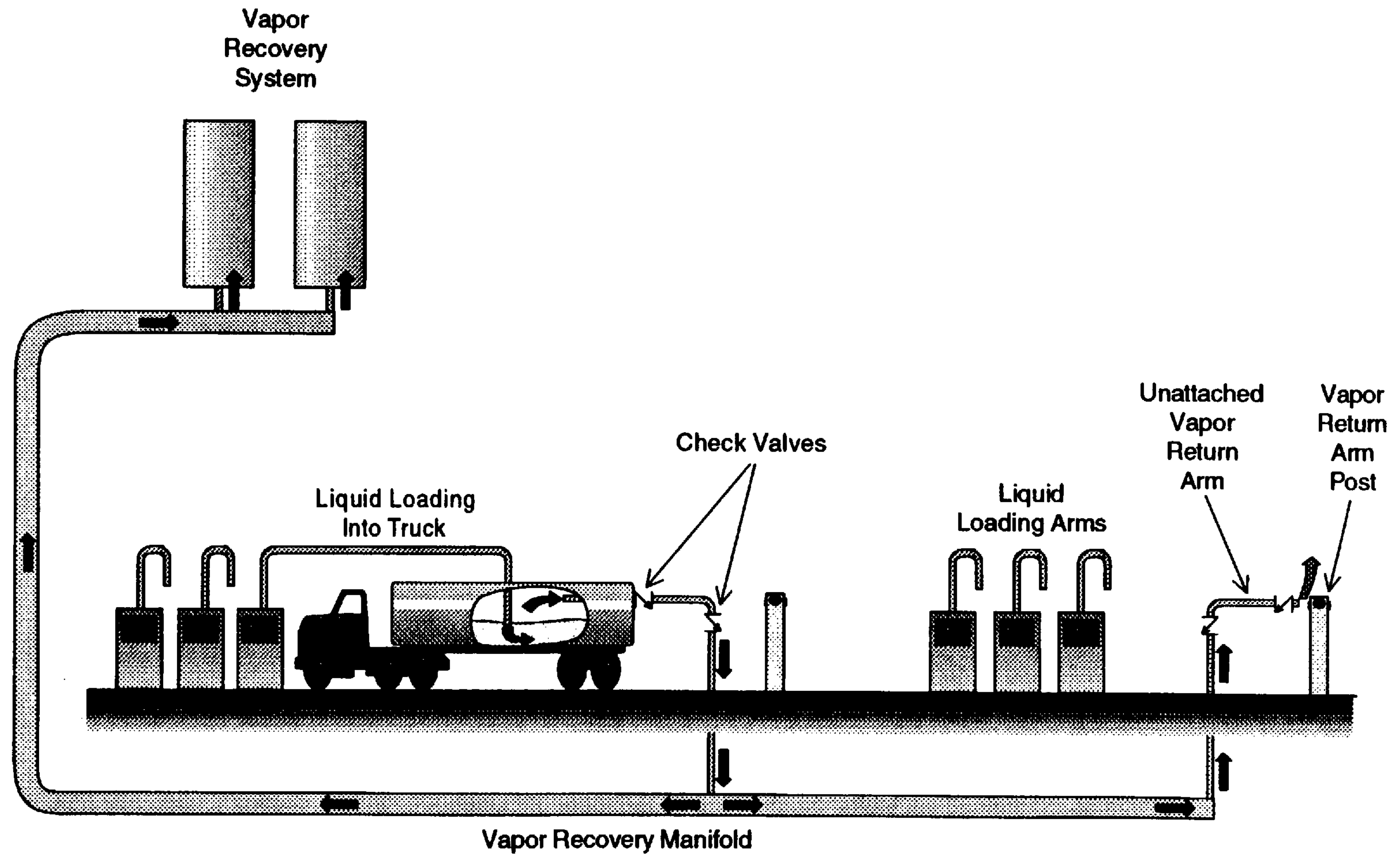

Figure 2-1. Vapor Recovery from Trucks at Petroleum Marketing Terminals

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accumulate in the lines and in the vapor recovery unit from coming back up the vapor return lines. One reason for the high leak rates from these vapor return arms is that all of the loading rack vapor return lines are connected to a common underground header. Vapors recovered from one truck are often emitted from vapor return valves several rows away. For instance, while a truck was loading at one loading rack, emissions from an idle vapor return valve exceeded 100,000 ppm. In summary, the check valves frequently do not stop vapors from being released through idle vapor return arms.

Some terminals solved the problem of backflowing vapors by installing blinds on posts to attach idle vapor return arms. The blinds, when latched or fastened to the idle vapor return arm, prevent vapors from backflowing. When blinds were properly attached, the emissions from these vapor return arms were very small. The vapor return arms were frequently not correctly fastened in place, with either one latch or two not secured. In at least one observed case the vapor return arm was not attached to the blind at all. Emissions from unsecured vapor return arms were very high. From earlier studies the U.S. EPA estimated that 10 to 30% of the displaced vapors from tank truck loading do not reach the vapor control device. Emissions from unsecured vapor return arms may account for part of these losses.

Terminal C did not use vapor return arms while top loading trucks with fuel oil. Vapors from the trucks were emitted to the atmosphere while top loading. Screening values at the open hatch cover for these trucks while loading were approximately 2,500 ppm.

3.0 TECHNICAL APPROACH

This section discusses the screening, soap-scoring, bagging, and liquid sampling procedures that were followed at the four petroleum marketing terminals. Also discussed are the quality control procedures and the data analysis techniques.

3.1 SCREENING PROCEDURES

Screening measurements were made on safely accessible components carrying gasoline, gas, gasoline additives, diesel, Jet A and fuel oil. The focus of this study was on the gas/vapor and light liquid components. Components in heavy liquid service (Jet A, fuel oil, diesel) were occasionally screened, but results were not included in the development of emission correlation equations or emission factors. Over 1,400 components (heavy liquid, light liquid, and gas services) at each marketing terminal were screened. The screening measurements were made with the Foxboro Organic Vapor Analyzer (OVA) Model 108, in accordance with the latest version of U.S. Environmental Protection Agency (U.S. EPA) Reference Method 21. Method 21 instrument specifications are summarized in Table 3-1.

The OVA 108 is a portable, flame ionization detector (FID). The Model 108 has a logarithmic readout which ranges between 1 part per million (ppm) to 10,000 ppm. Through the use of a dilution probe, the range of the OVA 108 can be extended to 100,000 ppm. Because of its broad range, the OVA 108 was selected for this testing.

Table 3-2 outlines the general screening procedures that were followed using the OVA 108. These procedures closely follow the guidelines discussed in U.S. EPA Method 21. The following component categories were screened at each facility:

- Valves (ball, plug, butterfly, gate, check, diaphragm, globe, etc.).
- Connectors (flanges, screwed connectors, tubing connectors, union connectors, etc.).
- Pumps (centrifugal).

Table 3-1

Summary of EPA Method 21 Requirements

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS LEAKS
(Including Proposed Revisions Published May 30, 1989)

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-Inch OD
7. Linear and Measuring Ranges Must Include Leak Definition Value (May Include Dilution Probe)
8. Instrument Readable to ±2.5% of Leak Definition
9. No Detectable Emissions (NDE) Value Defined as ±2.5% of Leak Definition (i.e., ±500 ppm)

Table 3-2

Summary of Screening Procedures

GENERAL SCREENING PROCEDURES

1. Prepare analyzer for sampling.
2. Calibrate analyzer.
3. Complete top portion of screening data sheet.
4. Place analyzer probe as close as possible and approximately perpendicular to the component surface or seam where leakage could occur.
5. Move the probe slowly along the line of potential leakage to obtain the maximum reading.
6. Leave the probe tip at the maximum reading location for approximately two times the instrument response time.
7. If the reading exceeds full scale use the dilution probe.

- Open-ended lines.
- Pressure relief valves.
- Tank truck loading arm valves (check valves on lines that connect to trucks including liquid loading arms and gas/vapor return arms).

Components were screened while moving liquid products through the lines (load) and while the lines were full of liquid but the liquid was not moving (no-load).

During the screening process, the following data were recorded:

- Component identification number.
- Component type.
- Service (i.e., light liquid, heavy liquid, gas/vapor) of material flowing through the component.
- Screening value of the component in ppm.
- Additional supportive data (temperature, background volatile organic compound [VOC] concentration, etc.).

3.2 SOAP SCORING PROCEDURES

Soap scoring procedures were applied to nearly all of the components at the first terminal tested. Soap testing of components is a relatively simple and inexpensive strategy that may be used on potential leak sources that:

- Have no continuously moving parts.
- Have a surface temperature less than the boiling point and greater than the freezing point of the soap solution.
- Do not have open areas to the atmosphere the soap cannot bridge (the solution must cover all holes).
- Are not leaking liquid.

Table 3-3 summarizes general soap scoring procedures.

Table 3-3

Summary of Soap Scoring Procedures

GENERAL SOAP SCORING PROCEDURES

1. Obtain a commercial soap solution or prepare one.
2. Spray a soap solution over the selected component. The solution may be applied with either a squeeze bottle or pressure sprayer.
3. Observe the component and record whether or not bubbles are formed.
4. If no bubbles are formed, the component is assumed to have no detectable emissions or leaks.
5. If any bubbles are formed, measure the rate of bubble formation and apply existing correlations to determine emission rate or measure the VOC concentration directly with the OVA.

Because only two components out of over 1,500 measured showed any response to soap scoring at the first terminal tested, soap scoring was not conducted at the remaining sites. Please note that all components of Marketing Terminal A were also screened with the OVA. It is hypothesized that the lack of effectiveness of soap scoring at marketing terminals is due to the lower volatility of the products tested. Soap scoring has been used successfully in gas production and gas plants, even in very volatile liquid services. The apparent mechanism at the terminals is that a small leak of liquid gasoline would appear at the surface of the seal and below a layer of soap film. Instead of vaporizing and bubbling up through the soap film, however, the gasoline liquid would float to the top of the soap film, since gasoline is less dense than water. The gasoline would then evaporate slowly from the surface of the soap without causing any bubbling. This would explain the apparent lack of sensitivity of the soap scoring on components that showed elevated OVA readings.

3.3 BAGGING PROCEDURES

In this section both the sampling techniques for bagging and the analytical techniques for bagging are discussed.

3.3.1 Bagging Sampling Techniques

The "bagging technique" was used at three of the four sites to determine quantitative mass emissions from gasoline components. Bagging refers to a sampling method in which the component is completely enclosed in an impermeable plastic "bag." The internal atmosphere of the bag is allowed to equilibrate and then a sample of the gas within the enclosure is collected for analysis. Although there is not an official reference method for bagging, the technique is well established and documented in both the U.S. EPA *Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP* (U.S. EPA, 1988) and the Chemical Manufacturers Association (CMA) *Guidance for Estimating Fugitive Emissions* (CMA, 1989).

The "Blow-Through" bagging technique, referring to the method of flowing nitrogen gas (N_2) through the bag, was used for all bagging measurements. After the bag was assembled around the component, it was flushed with N_2 until the oxygen concentration inside the bag equilibrated to below 5%. A sample of the exit gas was then collected for expeditious analysis by a laboratory gas chromatograph (GC) brought to the site. During the bagging process, the diluent gas (N_2) flow rate was noted, along with the internal bag temperature. A summary of general bagging procedures is provided in Table 3-4.

To collect samples for GC analysis from a bagged component, a small air sampling pump was temporarily connected to the sample port of the bag. The pump flow rate was set well below the flow of the diluent gas to ensure that ambient air was not drawn into the bag. The output of the pump was used to fill a 2-liter Tedlar® bag. The Tedlar® bag was delivered to the on-site analyst who injected the sample into a Byron 301 (Byron) and Tracor Model 540 GC (Tracor GC) for analysis.

Bagging data recorded include:

- Component identification number.
- Component type.
- Initial screening value.
- Dilution gas flow rate.
- Bag temperature.
- Bag concentration.
- Final screening value.
- Additional supportive data (temperature, background VOC concentration, etc.).

A thermocouple with a digital readout was used to measure ambient and bag temperatures. The thermocouple and readout were calibrated before and after each site visit using icepoint and boiling water temperatures as well as NIST-traceable thermometers.

Table 3-4

Summary of Fugitive Emissions Bagging Test Protocol

GENERAL BAGGING PROCEDURES

1. Perform accuracy test (once per site).
2. Record component data.
3. Perform initial screening tests.
4. Install tent enclosure.
5. Measure diluent gas flow (N_2).
6. Initiate tent diluent gas flow and measure tent temperature.
7. Ensure tent concentration equilibrium (O_2 <5%, THC reading steady on OVA).
8. Collect bag sample (THC, VOC).
9. Check to ensure O_2 still <5%.
10. Check THC reading on OVA.
11. Measure tent temperature.
12. Measure diluent gas flow.
13. Remove tent.
14. Perform final screening tests.
15. Record ambient conditions.
16. Record stream parameters.

Barometric pressure was obtained from the local National Weather Service office or from on-site equipment.

Diluent gas flowrate was measured prior to and after each bagging run with a Mini-Buck® flow calibrator. The Mini-Buck® is a primary flow calibrator with a rated accuracy of ±1 percent.

Additional procedures had been planned if any bagged component had a liquid leak or emitted a liquid aerosol. However, no liquid leaking or liquid aerosol leaking components were found. Therefore, these planned additional bagging procedures are not discussed in this text.

3.3.2 Analysis of Bag Samples

The bagging samples were analyzed on-site by a Byron 301 and a Tracor Model 540 GC. Total hydrocarbon concentration (THC), as methane and nonmethane were provided by the Byron 301. The Tracor GC was used for sample compound speciation. Table 3-5 identifies the compounds for speciation from bag samples.

Samples were introduced to both the Byron 301 and the Tracor GC by connecting the Tedlar® sample bag to the instrument inlet and pressurizing the bag (by squeezing the bag) for 20 to 30 seconds to fill the GC injection loop. The bag was then removed and the sample injected into the chromatographic column. All samples and calibration standards were introduced to the analyzers from bags in a consistent fashion in order to account for surface effects or other errors and interferences.

Table 3-5

Bagging Sample Analyte Target List

LIST OF COMPOUNDS
Total Hydrocarbons (Methane & Non-Methane)
Benzene
Cumene
Ethyl Benzene
Hexane
Methyl Tertiary Butyl Ether (MTBE)
Toluene
2,2,4 Trimethyl Pentane (isooctane)
Xylenes (p, m, o)

3.4 LIQUID STREAM SAMPLES

One of the objectives of this program was to compare measured fugitive emissions with the concentrations of gasoline compounds in the associated bulk streams. To achieve this objective, liquid samples were collected and analyzed from process lines that bagging measurements were made on. Ten types of analyses were performed on each liquid sample. Table 3-6 summarizes general liquid sampling procedures. Liquid samples were taken by petroleum marketing terminal operations staff.

Analysis of the liquid samples was performed on-site using the Byron 301 and Tracor GC. Liquid stream sampling data were recorded in a Master Logbook.

After sampling had been concluded, a revised procedure for the liquid sampling was developed and is recommended for future liquid stream sampling projects. The revised procedure is to chill the sample bottles prior to collecting the sample. Chilling will reduce the potential for the most volatile components to be lost during sample collection. Of course, the samples should be kept refrigerated until laboratory analysis is performed.

3.5 INTERNAL QUALITY CONTROL CHECKS

This section discusses the quality control (QC) procedures that were followed in this project to assess and control sampling and analytical data quality. The specific QC checks, required frequency, acceptance criteria, and corrective action requirements are listed in Table 3-7. The QC data results are presented in Section 4.0 and Appendix D. Much of the quality assurance (QA) and QC was conducted in the field. If instruments failed QA/QC tests, repeat testing was typically performed.

Review of these quality control checks at the conclusion of this study suggests that some of these QA/QC objectives were probably overly stringent and unrealistic. In particular, there was difficulty in meeting the precision and accuracy objectives for the Tracor GC.

Table 3-6

Summary of Liquid Sampling Protocol

GENERAL LIQUID SAMPLING PROCEDURES	
1.	Fill two sample bottles completely with sample liquid.
2.	Cap bottles and turn upside down to check for bubbles. If bubbles appear in either bottle, empty that bottle and refill.
3.	Complete a sample ID label. Wipe dry the outside of the sample bottles and attach the labels to them.
4.	Package samples in double Zip-Lock bags and store on ice or in a cooler.
5.	Record sample information in Master Logbook.
6.	Complete sample chain-of-custody form.

Table 3-7

QC Checks

Parameter/ Instrument	QC Check	Frequency	Calibration Standards	Criteria	Corrective Action
OVA 108	Drift Test	Daily	Mid-Span std.	±20%	- Repeat Test - Recalibrate - Repair Instrument
	Blank	Daily	Zero Air	≤5 ppm	
	Precision	Daily	Mid-Span std.	±20%	
	Accuracy	Daily	Multi-Point Calibration	—	
Byron 301	Drift Test	Daily	Mid-Span std.	±20%	- Repeat Test - Recalibrate - Repair Instrument
	Blank	Daily	Zero Air	≤1 ppm	
	Precision	Every 10-20 Samples	Dup. Analyses	±30%	
	Accuracy	Daily	QC Check std.	±25%	
Tracor 540	Drift Test	Daily	Mid-Span std.	±20%	- Repeat Test - Recalibrate - Repair Instrument
	Blank	Daily	Zero Air	≤1 ppm	
	Precision	Every 10-20 Samples	Dup. Analyses	±50%	
	Accuracy	Daily	QC Check std.	±35%	
Bagging	Accuracy	Twice	Mid-Span std.	±50%	

3.5.1 OVA 108

Routine QC procedures for the OVA 108 analyzer consisted of several daily performance checks. These included blank analyses, precision checks, and drift check analyses. The results of each test were recorded in a bound laboratory notebook. The QC checks for the OVA 108 consisted of:

- Drift Check - Three or more times each day, before, during, and after testing, a mid-level calibration gas standard was analyzed. The response had to be within ±20% of the morning calibration response to the same standard. If the response was >20%, corrective maintenance was performed and sampling performed since last verified check was repeated.

- Blank Check - At least once daily, zero air (or ambient air which was used for two days) was analyzed by the analyzer to test for possible contamination. The response had to be ≤5 ppm.

- Precision Check - Instrument precision was evaluated on an on-going basis each testing day by means of the drift check described above. If any of the replicate analyses differed from the pre-test response by more than ±20%, then corrective action was taken.

- Accuracy Check - Multipoint calibration was performed at least daily, in place of a separate standard, to ensure response linearity. In addition, a high level multipoint standard was used daily to calculate the dilution ratio of the dilution probe.

3.5.2 Byron 301 and Tracor GC

The routine QC checks of the Byron 301 and Tracor GC were as follows:

- Drift Check - Drift checks were performed several times daily using one of the mid-level span gas standards. The response factor obtained from the drift checks had to be within ±20% of the most recent multipoint average response factor.

- Blank Check - With few exceptions, hydrocarbon-free air was analyzed once per day to assess the zero response of both instruments. Blank checks were conducted daily for the Tracor GC, excluding five days at the first bagging site. Blank checks were conducted daily on the Byron 301, excluding two days at the first bagging site and two days at the second site. A zero response of ≤1 ppm was required.

- Precision Check - Instrument precision was assessed by duplicate analyses of a calibration standard. This was done at regular intervals throughout the testing period (typically once every ten samples). For the Byron 301, the objective was to achieve a 30% RPD for the duplicate analyses. For the Tracor GC, the objective was a 50% RPD. However, these criteria were not always met. Results of these QA/QC checks are discussed in Section 4.0 and Appendix D.

- Accuracy Check - Once daily, following the morning multipoint calibration, a separate QC gas standard was analyzed. The Byron 301's response objective was to be within ±25% of the actual concentration; the Tracor GC's response objective was to be within ±35% of the actual concentration. These criteria were not always met (as discussed in Section 4.0 and Appendix D).

3.5.3 Bagging Accuracy

An accuracy check was conducted on the entire bagging measurement system. The accuracy check involved performing a test on a component with a known emission rate to check the accuracy of the method. This was performed once at each of the three marketing terminals where bagging was conducted.

The accuracy check consisted of bagging a component with zero emissions (such as a valve serving a water line) and introducing a methane standard gas at a known flowrate. All other aspects of the bagging test were conducted normally, such as establishing the diluent flowrate, monitoring of the outlet O_2 concentration, and extracting a sample for analysis on the Byron 301 and/or Tracor GC. An objective of ±50% accuracy was defined at the start of the study.

3.5.4 Performance and Systems Audits

A system audit is an on-site inspection and review of the quality assurance system used for the total measurement system (sample collection, sample analysis, data processing, etc.). Performance audits refer to independent checks made by an auditor to evaluate the quality of data produced by the total sampling and analysis system. Limited system audits were conducted by a contractor from the U.S. EPA at two of the marketing terminals. Minor changes were made to the testing procedures based on one of these system audits. Both audit reports, less the marketing terminals' location, can be found in Appendix E. Because of the short duration of this project and the limited scope of testing, no performance audit activities were scheduled.

3.6 DATA ANALYSIS TECHNIQUES

Most of the techniques used in this study to analyze data were taken from the U.S. EPA document entitled *Protocols for Generating Unit-Specific Emission Estimates for Equipment Leak of VOC and VHAP* (U.S. EPA, 1988). This document outlines procedures for developing new emission correlation equations and default zero emission factors. This section contains a brief summary of the techniques used. Appendix A contains the detailed statistical methodology.

3.6.1 Development of Mass Emission Estimates From Bagging Data

The bagging data from each petroleum marketing terminal were entered into a spreadsheet that computed the mass emission rate from each bagged component. Calculation of the mass emission rate involves combining the measured hydrocarbon concentration with the diluent gas flow rate through the tent. Data were entered into the spreadsheet by one technician and checked for accuracy by another technician.

For hydrocarbon streams composed primarily of aliphatics and aromatics, the methodology used to estimate the mass of hydrocarbons in the diluent stream is straightforward. Table 3-8 presents the calculation methodology.

The methodology presented in Table 3-8 is based on the fact that, for aliphatics and aromatics, the response of a flame ionization detector (FID) is linear with the mass concentration of hydrocarbon present. In other words, the same weight of any hydrocarbon will result in the same peak area (response) from the FID. This relationship holds for all aliphatics and aromatics with only a few percent variation among compounds. Therefore, the molar concentration of mixed hydrocarbons measured by the FID (measured as ppmv of some calibration gas) can be converted to parts per million by weight (ppmw) using the molecular

Table 3-8

Mass Emission Calculation Procedure for Tented Leak Rate

$$\text{Emission Rate (kg/hr)} = \frac{1.218\text{x}10^{-5}\ (Q)\ (MW)\ (GC)\ (RF)}{T+273}$$

where:

$$Q = \frac{\text{tent } N_2 \text{ flow rate in liters/minute}}{1 - \dfrac{\text{tent } O_2\%}{21}} \left[0.06\ \frac{m^3/\text{hr}}{\ell/\text{min}}\right]$$

and

Q = flow rate into tent in cubic meters per hour

MW = molecular weight of the diluent stream + HCs (≈ 28)

T = temperature in tent in °Celsius

GC = instrument reading in ppmw

RF^a = response factor for leaking gas relative to calibration gas

1.218×10^{-5} = a constant that includes the gas constant and assumes a tent pressure of one atmosphere

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[a] For mixed hydrocarbon streams composed primarily of aliphatics and aromatics, RF = 1.0 (± 5%). For other hydrocarbons, a mass-weighted response factor should be computed for the hydrocarbon stream.

weight of the calibration gas. A similar mass concentration of mixed hydrocarbons will produce a similar response in the FID.

Response factors were not used for the gasoline samples from the petroleum marketing terminals. The bulk of gasoline is made up of aliphatics and aromatics. The only significant exception to this was the MTBE present in many of the gasoline samples. The results of this analysis combine the aliphatics (n-hexane, isooctane, and MTBE) into a single data point because of the difficulty in separating these compounds in the gas chromatograph column used. Thus, the exact MTBE fraction of the gasolines tested is uncertain. The MTBE fraction appears to vary from zero to approximately 20 percent. The relative response of a FID to MTBE (a C_5 ether) will be approximately 0.8. Therefore, the maximum error introduced by the presence of 20% MTBE in the sample would be: (1 - .8) (0.2) = .04 or 4%.

The bag concentration data gathered from Marketing Terminals A, B, and D required an additional adjustment. This was the result of a series of propane calibration gas cylinders that apparently were incorrectly labeled by the vendor. The four propane cylinders used to calibrate the FID for all the marketing terminals were labeled 10, 100, 1,000, and 10,000 ppm. The cylinders came from the same vendor and were apparently generated by controlled dilution of gas from the same source, as the four samples produced linear responses from the FID.

During the Marketing Terminal D study, checks with 100 and 1,000 ppmv hexane calibration gases from two separate vendors suggested that concentrations of the propane calibration gases were all approximately 35% higher than the label values. Subsequent testing against another propane calibration gas in the Radian lab in Austin confirmed that the propane calibration gases used at the petroleum Marketing Terminals (A, B, and D) were incorrectly labeled. The Radian lab test confirmed the magnitude of the error in propane calibration gas within 4% of the value indicated by the hexane calibration gases. Therefore, all FID total hydrocarbon measurements from the marketing terminals were scaled upward by a factor of 1.35 in the mass emission calculations.

The following example illustrates the computation of the mass emission rate from a valve at Marketing Terminal D:

Data:

Sample No.	DO11
Service	Unleaded Gasoline
OVA Background VOC Concentration	6 ppmv
OVA Screening Concentration	3,850 ppmv
FID Bag Concentration	4,505 ppmv (as propane)
Bag Temperature	34.4°C
N_2 Flow	3.31 l/min
O_2 Concentration in Bag	2.5% (by volume)

Bag Flow Rate:

$$\frac{3.31\ \text{l/min}\ N_2}{1 - \dfrac{2.5\%O_2}{21\%}} \left[0.06\ \frac{\text{m}^3/\text{hr}}{\text{l/min}}\right] = 0.225\text{m}^3/\text{hr}$$

The total hydrocarbon concentration in the bag was corrected for background hydrocarbons leaking into the bag. The steady-state oxygen content of the bag was used as an indicator of the amount of leakage into the bag. This correction is not significant to this example, but is significant to default zero (OVA screen conc. ≈ 0) emission factor development.

$$(4{,}505\ \text{ppmv measured}) - (6\ \text{ppmv background}) \left[\frac{2.5\%\ O_2}{21\%}\right] = 4{,}504\ \text{ppmv}$$

The measured ppmv was converted to ppmw and scaled upward using the 1.35 correction for the faulty calibration gases.

$$(4{,}504\ \text{ppmv}) \left[\frac{44.1\ \text{g/mol propane}}{28.4\ \text{g/mol diluent}}\right] * 1.35 = 9{,}442\ \text{ppmw}$$

The mass emission rate is therefore:

$$\frac{(1.218\times\ 10^{-5})(0.225\,\text{m}^3\,\text{diluent/hr})(28.4\,\text{kg diluent/kmol})(9{,}442\ \text{ppmw})}{34°\text{C}+273} = 0.0024\,\frac{\text{kg}}{\text{hr}}$$

3.6.2 Default Zero Emission Factors

The average emission rates (assuming a lognormal distribution) associated with components whose screening values are zero ppm is referred to as the default zero emission factor for that type of component and service. The default zero concept was developed by the U.S. EPA to account for the fact that bagging measurements are more sensitive than screening measurements at detecting low-level leakage. As described in the U.S. EPA protocols document, the default zero emission factors in the Synthetic Organic Chemical Manufacturing Industry (SOCMI) study were developed from twelve valves in gas service with screening values of "zero" (i.e., no difference between the maximum screening value and the ambient background concentrations). These valves were bagged and found to have nonzero leak rates. The average leak rate for these components was calculated and used to determine the total non-methane hydrocarbon (TNMHC) default zero emission factor for gas valves. This default zero emission factor was used to determine a "default zero screening value" by back calculating using the gas vapor valve emission correlation equation. The results of this analysis was a "default zero" screening value of 8 ppm that the U.S. EPA recommended be used for all component categories.

The data from this present study corresponding to components with zero screening values were averaged (assuming a lognormal distribution) to determine an emission rate for components with screening values of zero. For this study, because no methane was in any liquid or gas, TNMHC was equivalent to total hydrocarbon (THC). The new default zero emission factors were statistically compared to the existing default zero emission factors to determine if a real difference exists and, if so, if the new factor is appropriate. In order to determine whether a difference was statistically significant, the existing default zero emission factors were evaluated to determine if they fall within the 95% confidence limits of the new default zero emission factors. If the upper 95% confidence limits of the new default zero emission factors were less than the existing default zero emission factors, then the new default zero emission factors were significantly lower than the existing factors and were judged to be appropriate for use.

New default zero screening values were calculated and were determined to be less than 1 ppm for every component type evaluated.

The U.S. EPA does not provide any recommendations concerning the amount of data necessary for developing new default zero emission factors. Radian believes that because the entire previously existing SOCMI default zero data set currently consists of 12 measurement pairs (for valves), anything near that number of measurements is probably sufficient if the confidence intervals for the new default zero emission factors are sufficiently accurate. There were sufficient data to determine default zero values for THC emissions for the following component types and services:

- Connectors in light liquid service (12 tests).
- Valves in gas service (8 tests).
- Valves in light liquid service (11 tests).
- Open-ended lines in light liquid and gas service combined (8 tests).
- Pumps in light liquid service (8 tests).

All of the new default zero emission factors developed were shown to be significantly lower ($\alpha = 0.05$) than the existing SOCMI default zero emission factors. For this study, any component that screened at less than 1.0 ppm was indistinguishable from the ambient background and considered to be "zero."

3.6.3 Emission Correlation Equations

For components with screening values above zero, the mass emission rates are compared graphically as well as mathematically to determine if they are statistically different from the existing emission correlation equations. In general, the procedures involve comparing the logarithms of the bagged emission rates to the logarithms of their corresponding screening values. A linear least square comparison is then made on the logarithms of the data. Graphical and statistical comparisons can then be made which compare the new emission correlation equations to the existing SOCMI and refinery emission correlation equations to determine if and how they differ. If the new equations are found to be statistically different from the existing equations, then appropriate factors are developed to transform the emission correlation equation back into linear space to be used for predictive purposes.

In developing new emission correlation equations, the U.S. EPA protocols recommend that 30 mass emission rate and screening value measurement pairs be obtained, or that fewer data pairs can be obtained if the estimates are within 50% of the mean values with 95% confidence. That is, the mean predicted values plus or minus their 95% confidence intervals should be accurate to within plus or minus 50% in log space. There were sufficient total hydrocarbon emission data to develop emission correlation equations for the following component and service types:

- Connectors in light liquid and gas services combined.
- Valves in light liquid service.
- Loading arm valves in light liquid and gas services combined.
- Open-ended lines in light liquid and gas services combined.
- Pumps in light liquid service.

Each of the above emission correlation equations met the U.S. EPA statistical goal of being accurate to within ± 50% with 95% confidence in log space. In addition, the emission correlation equations for connectors in light liquid service and for valves in light liquid service were shown to be significantly lower than the existing SOCMI and refinery emission correlation equations. The emission correlation equation for pumps in light liquid service was not significantly different from the SOCMI emission correlation equation, but was significantly lower than the refinery emission correlation equation. No emission correlation equations were developed for open-ended lines or loading arm valves during the SOCMI and refinery studies. Thus, there was no basis for comparison for these two component types.

After developing each of the individual emission correlation equations listed above, an analysis was done to determine if any of the above emission correlation equations were statistically equivalent. The results of this analysis showed that the emission correlation equation for connectors (in light liquid and gas services combined) and valves in light liquid service could be combined; and that the emission correlation equation for loading arm valves and open-ended lines (in light liquid and gas services combined) could be combined. It is recommended, however, that the equations for valves and connectors be kept separate; and that the one combined equation be used for loading arm valves and open-ended lines (in light liquid and gas services combined). Historically, separate equations have been developed for valves and connectors, and thus it is reasonable to maintain separate emission correlation equations for these components to accommodate the industry's needs.

There were not sufficient data to develop new emission correlation equations for valves in gas service and "other" component types. The "other" category includes components such as hatches, hoses, covers, manholes, thermal wells and pressure relief valves. For these component types Radian recommends using the established refinery correlation equation for valves in gas service and the new connector equation for the "other" category, respectively. Analysis of the component types included in the "other" category shows that these components are most similar to connectors in terms of physical characteristics and emission rates.

Additional theoretical considerations concerning the U.S. EPA methodology for developing and evaluating both default zero emission factors and emission correlation equations are given in Appendix A of this report.

3.6.4 Average Emission Factors

When possible, the new default zero emission factors and emission correlation equations were used to develop the average emission factors. For some component types there were insufficient data to develop new default zero emission factors and emission correlation equations. For these component types the refinery default zero emission factors and emission correlation equations were used.

The following procedures were used to develop new average emission factors:

- If the screening value was less than the default zero screening value, then the default zero emission factor for that component was used to estimate the emission rate for that component.
- If the screening value of the component was greater than or equal to the default zero screening value, then the emission correlation equation for that component type was used to estimate the emission rate for that component.
- If the screening value pegged the instrument (i.e., the screening value was greater than 100,000 ppm), then the upper quantitation limit (i.e., 100,000 ppm) was used in the extrapolated emission correlation equation for that component type to estimate the emission rate for that component.

Screening values for "pegged" readings (>100,000 ppm on the OVA) are not as accurate as those screening values that screened within the instrument screening value range. Hydrocarbon concentrations with these pegged readings could be anywhere above 100,000 ppmv. Emission rates were determined for the few components with pegged screening values that were bagged. However, there were insufficient components with pegged readings to develop separate "pegged" emission factors. Emission rates determined from the few bagged components with pegged screening values were compared with the emission rates obtained from the emission correlation equations. This comparison showed that the new emission correlation equations resulted in higher estimated emission rates for all of the cases for all components for which an emission correlation equation was developed. Thus, the approach resulting in higher estimated emission rates for determining pegged component emission factors for these components was to use the upper quantitation limit value (i.e., 100,000 ppm) in the emission correlation equation. The results of this approach are discussed in Section 5.3.

After obtaining the emission rates for all of the components, the average emission factor was obtained by taking the arithmetic average of all of the emission rates. It should be noted that the average emission factors are not intended to provide an accurate estimate of the emission rate from a single component type or piece of equipment. Because leak rates from individual components vary by several orders of magnitude, the average emission factor will not provide an accurate estimate of the mass emission rate from an individual piece of equipment. Rather, the average emission factors are more appropriately applied to the estimation of emissions from populations of components or equipment.

It should also be noted that the average emission factors were developed from bagging results from only three marketing terminals and screening results from only four marketing terminals. Attempts were made to obtain data from different regions of the country to improve the national representativeness of the data. However, various regions have differing control requirements. Use of these average emission factors and the stratified emission factors discussed in the next section should be done with the realization that these factors may not give precise emission estimates for any particular marketing terminal. Use of the emission correlation equations applied to actual screening values measured at a particular marketing terminal is likely to give a more accurate emission estimate regardless of location.

3.6.5 Stratified Emission Factors

Stratified emission factors were obtained for the following screening value ranges:

- 0 - 999 ppm.
- ≥1,000 ppm.

Stratified emission factors could not be obtained for the ≥10,000 ppm screening value range due to the lack of components that screened in this range. Those components that screened at ≥10,000 are included in the range ≥1,000 ppm. The strata could not be broken into smaller categories (e.g., 0–499 ppm, 500–1,000 ppm, etc.) also due to the lack of screening values that were obtained within these smaller ranges.

To develop the stratified emission factors, emission rates were obtained for each of the screening value ranges as described in Section 3.6.4. Next, the average emission factor was obtained for each of the screening value ranges for each component type by taking the arithmetic average of the emission rates.

3.7 Comparison of Fugitive Emission Composition with Liquid Stream Composition

Traditionally, it has been assumed that the composition of fugitive hydrocarbon emissions was the same as the compositions in the lines. This assumption was based on limited testing of mixtures. Additional fugitive emission and liquid stream samples were gathered at three terminals for the purpose of investigating this assumption. Testing was conducted to determine concentrations of n-hexane, isooctane, MTBE, benzene, toluene, ethylbenzene, xylenes (p, m, o) and cumene. These chemicals were selected because of their known presence in motor gasolines, to study chemicals with various characteristics, and to obtain information on specific air toxics.

A sample calculation of the determination of the ratio of mass fraction of a chemical in the fugitive emission (gas) to the ratio of the same chemical in the liquid is given in Appendix C.

The Tracor GC reports the mass of each hydrocarbon species as it leaves the column. This reported mass is combined with the known volume of the liquid or gas sample injected into the column to give hydrocarbon concentrations in units of g/liter sample.

The mass fraction of each constituent in the liquid stream was approximated by assuming a specific gravity of 0.75 (750,000 mg/l) for all gasoline samples. The concentration of each constituent in mg/l was obtained from the Tracor GC and divided by 750,000 mg/l to give the mass fraction.

$$X_{liq}: = \frac{(\mathrm{mg/l})}{750{,}000\ \mathrm{mg/l}}$$

The mass fraction of each constituent in the gas sample was approximated by comparing the ppmw of each constituent in the diluent (nitrogen plus hydrocarbon plus air) sample by the ppmw of total hydrocarbons (THC) in the sample. The concentration of each constituent in the gas was determined by the Tracor GC. The concentration of THC was determined by the Byron 301 FID.

$$X_{i\ gas} = \frac{\mathrm{mg/l}_i}{\mathrm{mg/l\ THC\ in\ diluent}}$$

The mass relationships was calculated as follows:

$$\frac{X_{i\ gas}}{X_{i\ liq}}$$

Data points for which the analyte was not detected in the gas sample were not included in this analysis. The substitution of detection limit values for non-detects could theoretically skew the analysis heavily if an analyte were present in only trace amounts in the gas sample, as was typically the case with cumene. It should be noted, however, that sample anomalies such as erratic emission rates that caused data points to be unusable for mass calculations did not necessarily render the data points unusable for gas/liquid composition comparisons.

4.0 QUALITY CONTROL RESULTS

This section briefly discusses the quality control (QC) results obtained from samples taken at each of three marketing terminals (A, B, and D). Section 4.1 discusses accuracy. Section 4.2 discusses precision. Specific details on the QC results and a discussion of the bag samples that were not used in the results are included in Appendix D.

4.1 ACCURACY

4.1.1 Analytical Accuracy of Byron Total Hydrocarbon Analysis

Daily calibrations of the Byron 301 using up to three different concentration levels of methane and propane were performed at Marketing Terminals A, B and D. The accuracy of the instrument response is measured by evaluating the linearity of these calibrations and by comparing the individual responses to the given standard values.

The QC information indicates that the accuracy of the instrument response to methane and propane is acceptable. The calibration curves were linear and no indication of systematic bias was exhibited by the instrument.

Please note that the measures used in this process to gauge accuracy are entirely dependent upon the integrity of the standard gases. As explained in Section 3.6.1, the propane standard gases used for the majority of the analyses were found to be inaccurately labeled. The propane standards were determined to be biased high by a factor of 35%. The acceptable accuracy of the instrument response indicates that when the noted bias (caused by the inaccurately labeled standards) is corrected for, the adjusted results should be accurate. For a detailed presentation of Byron analytical accuracy results, please refer to Appendix D2.0.

4.1.2 Method Accuracy of Byron Total Hydrocarbon Analysis

One method accuracy check was performed at each marketing terminal where bagging was performed. This method accuracy check is performed on a component with zero emissions (i.e., water valve). A known concentration and flow rate of methane is injected into the tent. The bagging and analysis procedures then follow routine protocols.

The Byron accuracy results again support the fact that the emission correlation equations and emission factors in this study were based on data within accepted accuracy ranges. The method accuracy checks were within the RPD acceptance criteria of <50% between the theoretical and obtained concentrations. The method accuracy was as follows:

- Marketing Terminal A = +37% (Byron).
- Marketing Terminal B = +13% (Byron).
- Marketing Terminal D = +13% (Byron).

4.1.3 Analytical Accuracy of Specific Hydrocarbon GC/FID (Tracor GC) Analysis

Several different types of QC samples and checks, including calibrations using multiple concentration levels and daily analyses of QC standards were performed and evaluated to measure the accuracy of the Tracor GC data produced. QC information was available for assessment from Marketing Terminals A, B, and D for both liquid and vapor analysis.

The QC information suggests that the analytical accuracy of the liquid data is quite good for Marketing Terminal D. The calibration curve was linear, the instrument response was stable, and the agreement between the QC checks from one day to the next was acceptable. The liquid results for Marketing Terminals A and B were not, for the most part, nearly as good as those obtained for Marketing Terminal D. The results of the liquid analysis from Marketing Terminals A and B need to be used with caution or used primarily for qualitative, not quantitative, purposes.

The QC checks for vapor analyses also show that, of the three marketing terminals, Marketing Terminal D accuracy results again were the best. Marketing Terminal A accuracy results were reasonably good at first and became progressively worse while testing (apparently due to progressive detector fouling). Marketing Terminal B accuracy results indicate that the specific hydrocarbon analysis of the vapor data may not be quantitatively accurate. As with the liquid results, the vapor results from Marketing Terminals A and B need to be used with caution or used primarily for qualitative, not quantitative, purposes.

Please note that the lack of quantitative liquid and vapor results at Marketing Terminals A and B does not in any way impact the accuracy of the emission correlation equations, default zero emission factors, average emission factors, or stratified emission factors developed in this study. All of these equations and emission factors are based on the Byron total hydrocarbon emission results (a different instrument) which, as previously discussed, demonstrated acceptable accuracy. For a detailed description of Tracor GC analytical accuracy results, please refer to Appendix D3.0.

4.2 PRECISION

4.2.1 Analytical Precision

Duplicate samples are used to evaluate the precision of the sampling and analytical procedures. Precision is calculated as the relative percent difference (RPD) between duplicate samples and is an indication of the variability, or reproducibility, of the process used to obtain the results. RPDs are calculated only if both members of the duplicate pair had detectable concentrations of target compounds. Hence, when either one or both results from a duplicate pair have a value of zero, or not detected, an RPD is not calculated.

A laboratory duplicate is when one field sample is analyzed in duplicate in the laboratory. Laboratory duplicates were used to determine precision of the Tracor GC. Excellent overall laboratory duplicate agreement was achieved for both liquid and vapor GC/FID (Tracor GC) analyses. Data collected from Marketing Terminal D, in particular, are quite precise. The assessment of laboratory duplicate results, presented by method and marketing terminal, can be found in Appendix D3.0.

4.2.2 Method and Sample Precision

Method and sample duplicates were collected to evaluate total hydrocarbon bagging precision. The sampling tent is dismantled and rebuilt between tests for method duplicates. For sample duplicates, a second bag is pulled from the same tent arrangement. Method and sample duplicates were analyzed by the OVA and Byron. Four method duplicate pairs were collected and analyzed at Marketing Terminal A, and seven at Marketing Terminal D. Seven sample duplicate pairs were collected at both Marketing Terminals B and D.

Method and sampling duplicates can have sampling variability, analytical variability, and component leak variability. Component variability occurs when emissions from the component leak vary between sampling events as a function of time. A comparison of the method and sampling duplicate data indicates approximately the same degree of precision was obtained for method duplicates as for sample duplicates. This precision was generally good: most RPDs were less than 50%. Considering the analytical instrumentation and the component leak rate variability with time, the agreement between these duplicates is acceptable. Please refer to Appendix D4.0 for a detailed presentation of method and sampling results.

5.0 DATA ANALYSIS PROCEDURES AND RESULTS

The procedures used to analyze the data and data results are explained in this section. Data treatment of default zero emission factors, emission correlation equations, and pegged components are reviewed in Sections 5.1, 5.2, and 5.3, respectively. Section 5.2 also contains the results of additional analyses performed on the new emission correlation equations. This includes an evaluation of the effects of connector size and type on the connector emission correlation equation, and the results of a multivariate test to determine emission correlation equations that are statistically equivalent. Sections 5.4 and 5.5 explain the new average emission factors and stratified emission factors, respectively, and explain the development of these factors. Section 5.6 contains an evaluation of the screening value data. Section 5.7 presents the results of the comparison of fugitive emission compositions with the liquid stream compositions. Section 5.8 discusses the results of the vapor leak and liquid stream composition analysis. Finally, Section 5.9 presents the results of the loading arm drip measurements.

5.1 DEFAULT ZERO EMISSION FACTORS

The average of actual emission rates (assuming a lognormal distribution) associated with components whose screening values are zero parts per million (ppm) is referred to as the default zero emission factor for that type of component and service. The method for developing default zero emission factors is given in detail by the U.S. Environmental Protection Agency (U.S. EPA, 1988). Verification of the applicability of the new factors is also described in the document.

5.1.1 Default Zero Emission Factor Development

For this study usable default zero measurements were obtained for the following component types and services:

- Connectors in light liquid services.
- Valves in gas service.
- Valves in light liquid service.

- Open-ended lines in light liquid and gas services combined.
- Pumps in light liquid service.

The complete data set used to develop these default zero emission factors is given in Appendix B. Any component that had a net screening value at less than 1.0 ppm (screening value minus background) was considered to be a zero, given the instrument sensitivity and variable background readings.

For each component type and service, total hydrocarbon (THC) measured emission rates for the zero-screening components were averaged assuming a lognormal distribution as described by the U.S. EPA (U.S. EPA, 1988). The default zero emission factors are given in Table 5-1. The 95% confidence intervals for the mean default zero emission factors were calculated and are also shown in Table 5-1. The new default zero emission factors range from 3.5×10^{-6} lbs/hr for light liquid valves to 3.9×10^{-5} lbs/hr for light liquid pumps. Default zero emission factors for light liquid connectors and light liquid valves were based on at least ten bagged emission rates. The default zero values for gas valves, open-ended lines in all service, and light liquid pumps were each based on eight data pairs.

5.1.2 Comparison of New Default Zero Emission Factors With Established U.S. EPA and Refinery Default Zero Emission Factors

As suggested by the U.S. EPA, each new default zero emission factor was compared to the corresponding established Synthetic Organic Chemical Manufacturers Industry (SOCMI) default zero emission factors (U.S. EPA, 1988). New default zero emission factors were also compared to the petroleum refinery default zero emission factors. The refinery default zero emission factors were determined by inserting the 8 ppm default screening values into the refinery emission correlation equations given in Appendix A. The refinery emission correlation equations that relate emission rates to screening values (using a Bacharach TLV® sniffer) were developed in a 1980 study done by Radian for the U.S. EPA (Radian, 1980). These emission correlation equations were modified to relate emission rates to screening values using a Foxboro OVA in a 1989 study performed by Radian (API, 1989).

Table 5-1

Marketing Terminal Default Zero Emission Factors (THC) and 95% Confidence Intervals

Component Type	Service	Number of Tests	Default Zero Emission Factor (lbs/hr)	Lower 95% Confidence Limit (lbs/hr)	Upper 95% Confidence Limit (lbs/hr)
Connectors[a]	Light Liquid	12	6.5×10^{-6}	3.9×10^{-6}	1.1×10^{-5}
Valves	Gas	8	5.9×10^{-6}	3.8×10^{-6}	9.3×10^{-6}
Valves	Light Liquid	11	3.5×10^{-6}	2.4×10^{-6}	5.2×10^{-6}
Open-Ended Lines[b]	Light Liquid and Gas Combined	8	4.5×10^{-6}	2.6×10^{-6}	7.7×10^{-6}
Pumps	Light Liquid	8	3.9×10^{-5}	2.1×10^{-5}	7.4×10^{-5}

THC = total hydrocarbons

[a] Also recommended for Gas Connectors and "Other" (gas,LL) component types such as hatches, covers, manholes, thermal wells, and pressure relief valves.

[b] Also recommended for Loading Arm Valves (gas, LL).

Comparisons of the new and established default zero emission factors are shown in Table 5-2. According to U.S. EPA guidelines, if the new default zero emission factor is less than the existing value and if the upper confidence limit for the new value is less than the established default zero emission factor (i.e., the confidence interval does not overlap with the established default zero emission factor), then the new default zero emission factor is valid and can be used. If the upper confidence limit overlaps with the established default zero emission factor, the established default zero emission factor should continue to be used for the component category involved. Every default zero emission factor developed for this study had upper 95% confidence limits that were less than the established default zero emission factors, and are therefore considered valid for future use.

The extent of reduction of the new default zero emission factors from established default zero emission factors are shown in Table 5-3. Percent reduction was calculated from the equation:

$$\textbf{\% Reduction} = 100 \times \left(\frac{\textbf{Established Value - New Value}}{\textbf{Established Value}}\right)$$

For the refinery default zero emission factor comparisons, the percent reductions varied from 74.3% for valves in gas service to 98.4% for pumps in light liquid service. The ratio of refinery default zero emission factors to the new default zero emission factors varied from 3.9 to 63.2 for the same component categories. For the SOCMI default zero emission factor comparison, the percent reductions varied from 54.2% for pumps in light liquid service to 99.6% for valves in light liquid service. The ratio of SOCMI default zero emission factors to the new default zero emission factors varied from 2.2 to 283.5 for the same component categories. Each of the new default zero emission factors represent a substantial reduction from the established default zero emission factors.

Table 5-2

Comparison of New Marketing Terminal Default Zero Emission Factors (THC) With Established Default Zero Emission Factors (THC)

Component Type	Service	Default Zero Emission Factor (lbs/hr)	Lower 95% Confidence Limit (lbs/hr)	Upper 95% Confidence Limit (lbs/hr)	SOCMI Default Zero Emission Factor (lbs/hr)[a]	Overlap With New Default Zero Confidence Intervals?	Refinery Default Zero Emission Factor (lbs/hr)[b]	Overlap With New Default Zero Confidence Intervals?
Connectors	LL	6.5×10^{-6}	3.9×10^{-6}	1.1×10^{-5}	2.051×10^{-4}	No	2.1×10^{-4}	No
Valves	Gas	5.9×10^{-6}	3.8×10^{-6}	9.3×10^{-6}	7.060×10^{-5}	No	2.3×10^{-5}	No
Valves	LL	3.5×10^{-6}	2.4×10^{-6}	5.2×10^{-6}	9.967×10^{-4}	No	3.9×10^{-4}	No
Pumps	LL	3.9×10^{-5}	2.1×10^{-5}	7.4×10^{-5}	8.600×10^{-5}	No	2.5×10^{-3}	No

THC = Total hydrocarbons
LL = Light liquid
[a] U.S. EPA, 1988.
[b] Petroleum refinery default zero emission factors obtained by substituting a default zero screening value of 8 ppm into the refinery correlation equations (Radian, 1989)

Table 5-3

Percent Reduction of New Default Zero Emission Factors (THC) When Compared to the Established Default Zero Emission Factors (THC)

Component Type	Service	Marketing Terminals Default Zero Emission Factor (lbs/hr)	SOCMI Default Zeros[a]		Refinery Default Zeros[b]	
			Emission Factor (lbs/hr)	Percent Reduction (%)	Emission Factor (lbs/hr)	Percent Reduction (%)
Connectors	LL	6.5×10^{-6}	2.051×10^{-4}	96.8%	2.1×10^{-4}	96.8%
Valves	Gas	5.9×10^{-6}	7.060×10^{-5}	91.6%	2.3×10^{-5}	74.3%
Valves	LL	3.5×10^{-6}	9.967×10^{-4}	99.6%	3.9×10^{-4}	99.1%
Pumps	LL	3.9×10^{-5}	8.600×10^{-5}	54.2%	2.5×10^{-3}	98.4%

THC = Total hydrocarbons
LL = Light liquid

[a] U.S. EPA, 1988.

[b] Refinery default zero emission factors developed by substituting a default zero screening value of 8 ppm into the refinery correlation equations (Radian, 1989).

There are no established default zero emission factors for total hydrocarbon emissions from open-ended lines (OELs) from either the SOCMI or the refinery studies. Thus, there was no basis for comparison for this component category.

There were not sufficient default zero bag tests to develop new default zero emission factors for connectors in gas service, "other" components in gas or light liquid service, or loading arm valves in gas or light liquid service. The results of the few bag tests that were made for these categories were compared to the other marketing terminal default zero emission factors and assigned to the category that fit them best. The footnotes to Table 5-1 present those default zero emission factor category assignments.

5.2 EMISSION CORRELATION EQUATIONS

Emission correlation equations that relate total hydrocarbon screening values (in ppm) to their mass emission rates (in lbs/hr) were developed for five component categories and service types. The results of the emission correlation equation development are presented in Section 5.2.1. Section 5.2.2 contains a comparison of the new emission correlation equations to the established SOCMI and refinery emission correlation equations. Lastly, Section 5.2.3 details the results of additional analyses performed on the correlation screening and bagging data pairs. The additional analysis included an evaluation of the effects of component size and type on the connector emission correlation equation. This evaluation suggested that the component size and type appear to have an effect on the emission rate versus screening value relationship. Additional statistical analyses of the emission correlation equations were also performed to determine if any of the newly developed emission correlation equations were statistically equivalent and could therefore be combined.

The new emission correlation equations recommended for future use are given in Table 6-2 in the Conclusions Section and in Table 2 of the Executive Summary. These new emission correlation equations are for the following component types and service:

- Connectors in light liquid and gas services combined.
- Valves in light liquid service.

- Open-ended lines in light liquid and gas services and loading arm valves in light liquid and gas services, combined.
- Pumps in light liquid service.

This study focused on development of emission correlation equations for gas service and light liquid service only. Light liquids were various types of gasoline. Measured emissions from heavy liquid streams such as jet fuel and diesel fuel were not included in these emission correlation equations.

5.2.1 Emission Correlation Equation Development

Emission correlation equations were developed for emitting components where an emitter is defined as a component with a screening value between 1 ppm and 100,000 ppm. Components with screening values between 0 and 1 ppm were considered to be default zeros. Pegged components (i.e., those that screened at greater than 100,000 ppm) were also not included in the emission correlation equations development. Therefore, the emission correlation equations are based only on components for which a finite screening value between the upper and lower limits of detection could be obtained. For several component types no data in the range >10,000 ppm and <100,000 ppm were found at any studied marketing terminal. Use of the emission correlation equations developed in this study in this screening value range (>10,000 ppm, <100,000 ppm) is still recommended for lack of a better alternative. However, evaluation of the pegged component data (discussed in Section 5.3) suggests that extrapolating this emission correlation equation to these higher screening value ranges could overstate emissions. At least this appears to be the case for components screening >100,000 ppm.

In developing new emission correlation equations, the following separate component categories were initially examined for relationships between measured total hydrocarbon mass flow versus corrected OVA screening values (corrected OVA screening value = measured OVA screening value minus background OVA screening value):

- Connectors in light liquid and gas services combined.
- Valves in light liquid service.
- Open-ended lines in light liquid and gas services combined.

- Loading arm valves in light liquid and gas services combined.
- Pumps in light liquid service.

Statistical analysis was performed to determine if any of the above emission correlation equations were statistically equivalent. The results of this analysis are discussed in detail in Section 5.2.3. The results of this analysis showed that connectors (in light liquid and gas services combined) and valves in light liquid service could be combined to form one emission correlation equation; and that open-ended lines (in light liquid and gas services combined) and loading arm valves (in light liquid and gas services combined) could be combined to form one equation. However, Radian recommends that separate equations be used for valves in light liquid service and connectors (in light liquid and gas services combined); and that the combined equation be used for open-ended lines and loading arm valves.

This section presents the individual emission correlation equations that were initially developed for each component type. The complete data sets used for developing all of the emission correlation equations are shown in Appendix B.

Least squares regression analyses were conducted for each component type and service, regressing the logarithm of the emission rate on the logarithm of the screening concentration according to the following equation:

$$\text{Log (Emission Rate)} = \beta_o + \beta_1 \text{ Log (Screening Concentration)}$$

where: β_o = the intercept; and
β_1 = the slope.

All analyses were run in log-log space (i.e., using the logarithms of both the emission rate values and the screening values). Historically, emission rate and screening data have been shown to be lognormally distributed. The natural logarithms of the data will thus be normally distributed, and a normal, linear least-squares analysis can be performed. After performing the least-squares regression in log-log space, the emission correlation equation must be transformed back to linear-linear space by exponentiating and multiplying by a scale-bias correction factor (SBCF). The SBCF is needed to account for the fact that the mean from a lognormal distribution is being estimated, not the mean from a normal distribution. Thus, predicting the mean emission rate for a given screening value is similar to predicting the mean from a lognormal distribution. The SBCF is discussed in more detail in Appendix A. The mean emission rate for a given screening value was computed as follows:

$$\text{Mean Emission Rate} = \text{SBCF} \times (10)^{\beta_0} \times (\text{Screening Value})^{\beta_1}$$

$$= K \times (\text{Screening Value})^{\beta_1}$$

where: K = the constant of the emission correlation equation

$$= \text{SBCF} \times (10)^{\beta_0}$$

A summary of the predictive emission correlation equations for mean emission rates is given in Table 5-4. Comprehensive results of the calculations are shown in Appendix A.

Data with OVA screening values of 0 ppm and those OVA screening values that were less than 1 ppm that were indistinguishable from background concentrations were not included in the regression analyses. However, the screening values required to obtain the "default zero" emission factors for each of the new emission correlation equations were determined. These are given in the last column of Table 5-4. The default zero screening value is calculated using the following equation:

$$\textbf{Default Zero Screening Value (ppm)} = \left(\frac{\textbf{Default Zero Emission Factor}}{\textbf{K}}\right)^{\frac{1}{\beta_1}},$$

where: Default Zero Emission Factor = the default zero mass emission factor in lbs/hr (Table 5-1);

K = the constant from the emission correlation equation; and

β_1 = the slope from the emission correlation equation.

Table 5-4

Predictive Emission Correlation Equations for THC Mass Emission Rates

Component Type	Service	Number of Data Pairs	Emission Correlation Equation [a,b]	Correlation Coefficient	Standard Deviation of Regression	Default Zero Screening Value (ppm)
Connectors	Light Liquid and Gas	36	$ER = (4.65 \times 10^{-5}) \times (SV)^{0.426}$	0.412	0.604	0.01[c]
Valves	Light Liquid	46	$ER = (6.34 \times 10^{-6}) \times (SV)^{0.708}$	0.845	0.460	0.44
Loading Arm Valves	Light Liquid and Gas	24	$ER = (8.24 \times 10^{-6}) \times (SV)^{0.955}$	0.825	0.601	0.57[d]
Open-Ended Lines	Light Liquid and Gas	16	$ER = (5.69 \times 10^{-6}) \times (SV)^{0.995}$	0.859	0.701	0.78
Pumps	Light Liquid	12	$ER = (6.57 \times 10^{-5}) \times (SV)^{0.534}$	0.757	0.667	0.38

THC = Total hydrocarbons

[a] ER = Emission Rate (lbs/hr).

[b] SV = Screening value (ppm) using the OVA calibrated with methane.

[c] Used the default zero emission factor for connectors (light liquid service) to estimate the default zero screening value for connectors (all services).

[d] Used the default zero emission factor for open-ended lines (all services) to estimate the default zero screening value for loading arm valves (all services).

The emission correlation equation developed for connectors consisted of three data pairs in gas service and 33 data pairs in light liquid service. The emission correlation equation developed for loading arm valves consisted of five data pairs in gas service and eighteen data pairs in light liquid service. Lastly, the emission correlation equation developed for open-ended lines (OELs) consisted of one data pair in gas service and fifteen data pairs in light liquid service. For each of these component types, initially emission correlation equations were developed for light liquid service only. The data pairs from gas service were then compared to these emission correlation equations to determine if they differed appreciably from the light liquid service emission correlation equations. The one data pair from gas service for OELS and the three data pairs from gas service for connectors were insufficient to perform a statistical test. However, each of these data pairs fell within the 95% confidence intervals for individual values in the light liquid OEL and the light liquid connector emission correlation equations, respectively. This indicates that these gas service data pairs do not differ significantly from their respective light liquid service emission correlation equations.

For loading arm valves (LAVs), separate emission correlation equations were first developed for LAVs in gas service (vapor return valves) and LAVs in light liquid service. These two emission correlation equations were evaluated to determine if they were statistically different. The statistical tests performed included a test of the slopes and intercepts of the regression. Table 5-5 shows the results of this statistical comparison. As is shown in Table 5-5 the confidence intervals for the parameters (i.e., the slopes and intercepts) overlap appreciably. This large overlap in the confidence intervals indicates that there is no statistical difference between the parameters that define the emission correlation equations for LAVs in gas service and LAVs in light liquid service. Combining the gas LAV data with the light liquid LAV data resulted in a regression with a substantially larger correlation coefficient and smaller variability. In fact, adding the gas service data pairs to the light liquid service emission correlation equation increased the regression correlation coefficient from 0.45 to 0.83. Thus, it was decided to combine the service types for loading arm valves in the emission correlation equation development.

Table 5-5

Comparison of Regression Parameters for Loading Arm Valves in Gas Service and Loading Arm Valves in Light Liquid Service

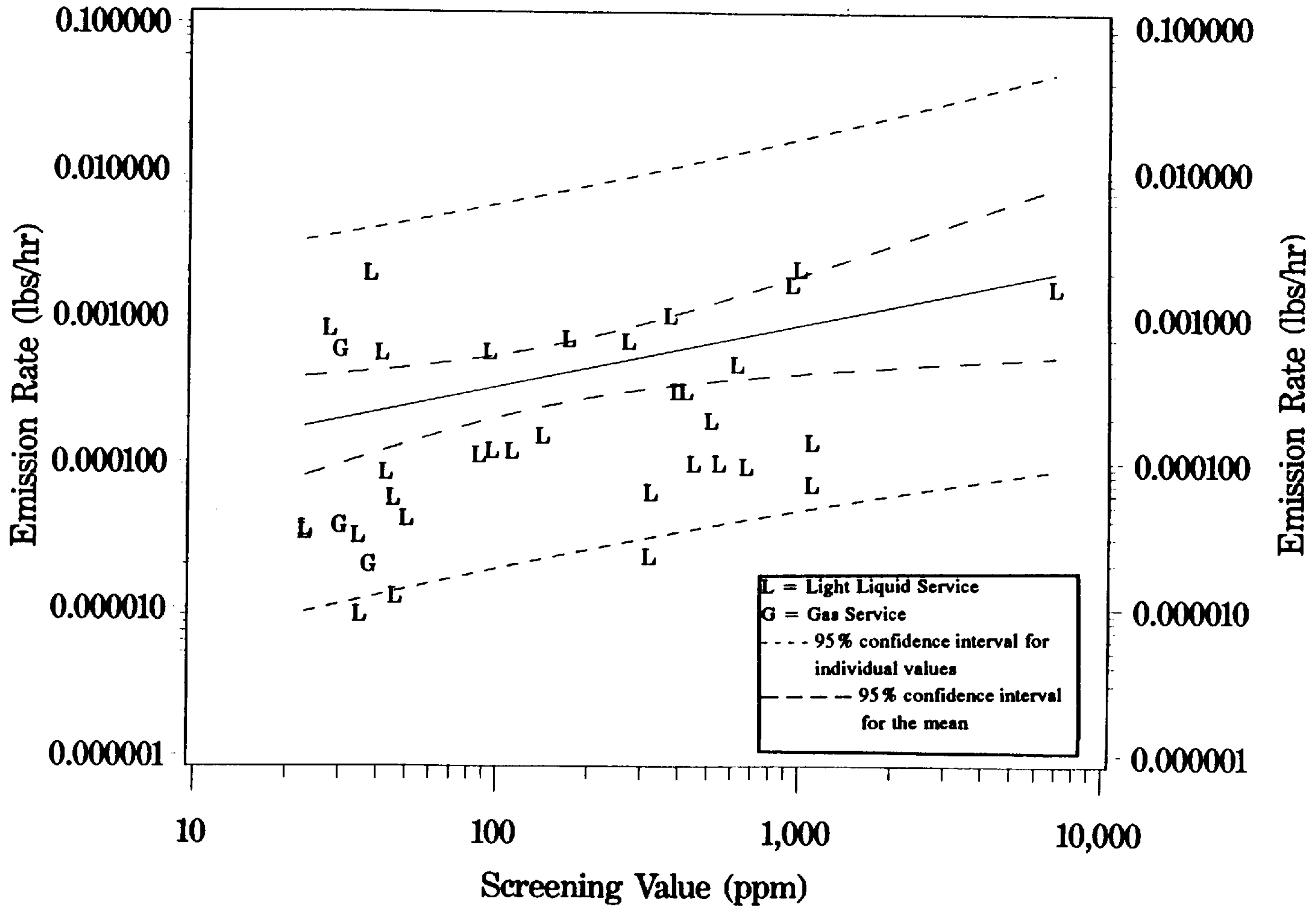
Parameter	LAVs in Gas Service Regression Estimates[a]		LAVs in Light Liquid Service Regression Estimates[a]	
	Parameter Estimate	95% Confidence Interval	Parameter Estimate	95% Confidence Interval
Slope	0.772	(0.109, 1.435)	0.446	(-0.025, 0.917)
Intercept	-4.54	(-6.46, -2.63)	-4.91	(-5.60, -4.22)

[a] LAVs = Loading Arm Valves

Figures 5-1 through 5-5 show the new emission correlation equations for each of the component and service types with the 95% confidence intervals for the mean predicted values and the 95% confidence intervals for individual predicted values. The raw data are overlaid on these regression lines. In Figures 5-1, 5-3 and 5-4 for connectors, loading arm valves and open-ended lines, respectively, the service type is also indicated (G=gas, L=liquid) by symbols. The 95% confidence intervals for the mean should be interpreted as meaning that we can expect to be correct at least 95% of the time when we state that the true mean emission rate falls within the limits computed. The 95% confidence intervals for individual values should be interpreted as meaning that we can expect to be correct at least 95% of the time when we state that individual emission rates fall within the limits computed.

The data shown in the figures throughout this section cover only the screening value ranges where bagging data could be obtained. No bagging samples, other than a few pegged component bagging samples, were obtained for screening values over 10,000 ppm for light liquid connectors, loading arm valves, open-ended lines, and light liquid pumps. Care should be exercised in extrapolating these emission correlation equation lines to the higher screening value ranges.

The predicted mean values shown in Figures 5-1 through 5-5 represent the mean assuming a lognormal distribution. Lognormal models have been found to have a better correlation between mass emissions and screening values than normal models. However, because lognormal distributions are often skewed to the right the mean can be substantially larger than the median (i.e., the 50th percentile). Thus, it is not unusual for more data points to fall below the line of the predicted emission correlation equation than above this line. This is different than normal (not lognormal) least squares regression. In normal least squares regression the predicted mean regression line represents the mean of a normal distribution, which is typically close to the median. Thus, one would expect roughly half of the raw data points to fall above the regression line and half of the data points to fall below the regression lines in normal least squares regression.



Connectors
Light Liquid and Gas Services Combined

Figure 5-1. THC Mass Emission Rate Versus Actual OVA Screening Value and the 95% Confidence Intervals for the Mean Emission Rate and for Individual Values - Connectors in Light Liquid and Gas Services Combined.

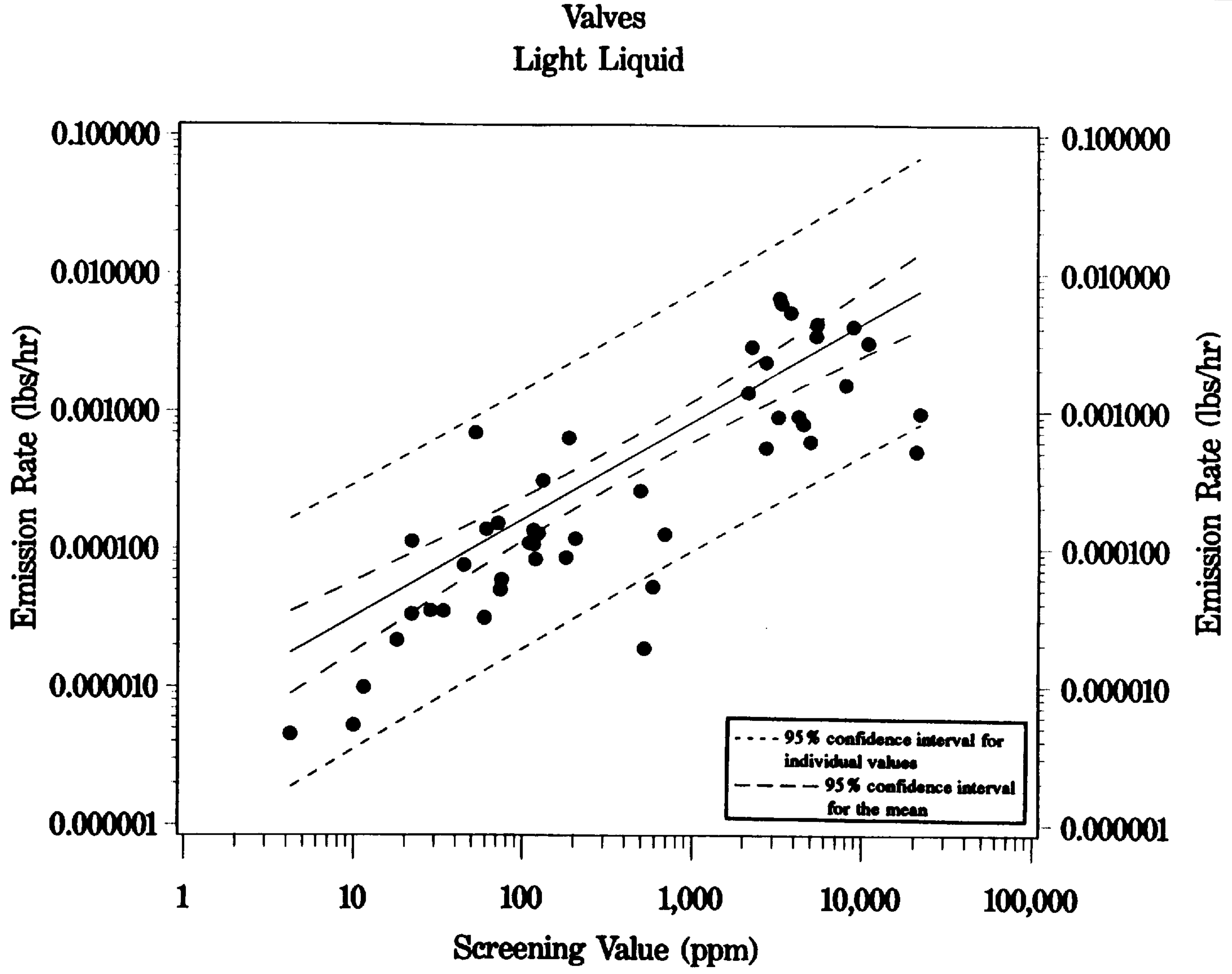


Figure 5-2. THC Mass Emission Rate Versus Actual OVA Screening Value and the 95% Confidence Intervals for the Mean Emission Rate and for Individual Values - Valves in Light Liquid Service.

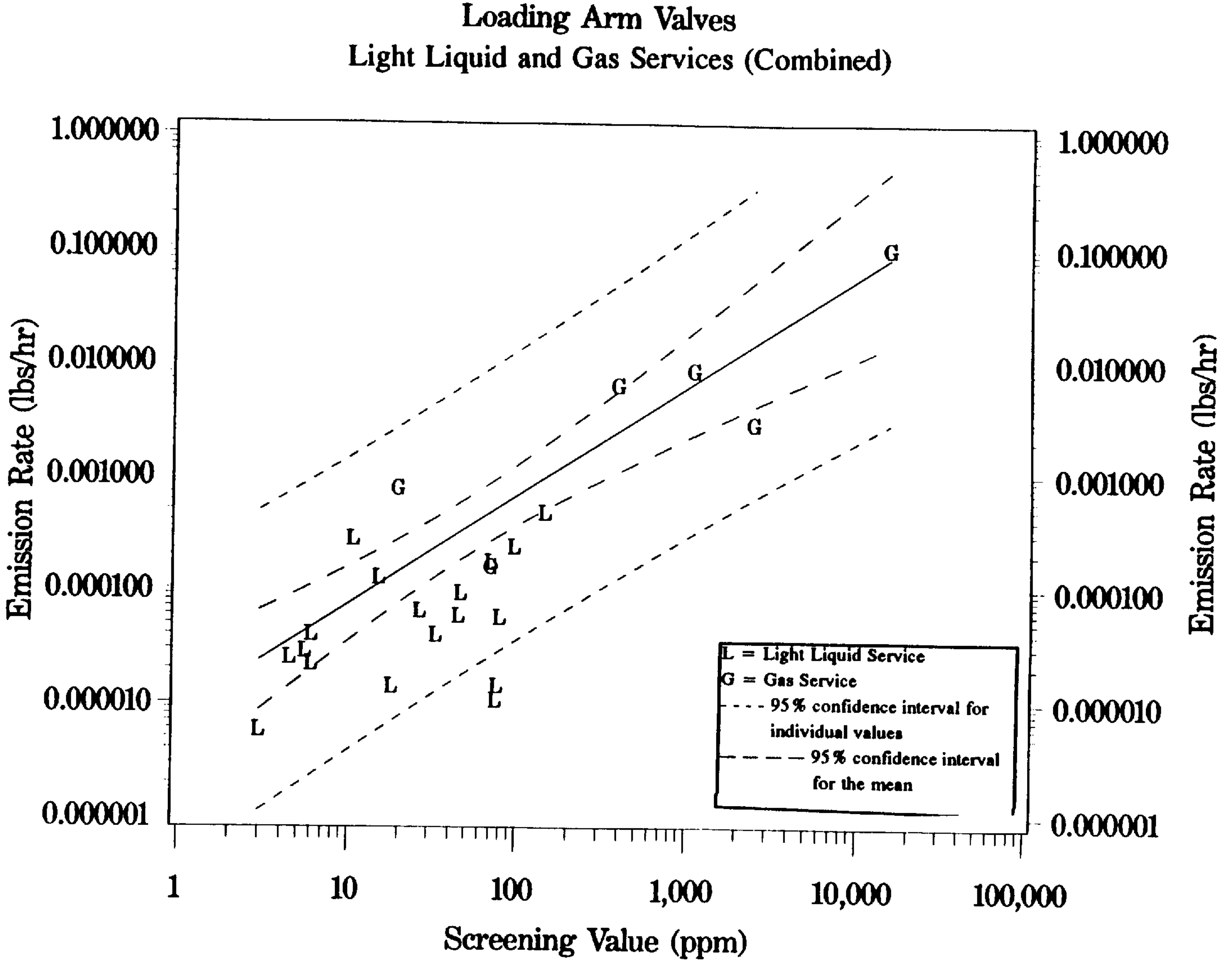


Figure 5-3. THC Mass Emission Rate Versus Actual OVA Screening Value and the 95% Confidence Intervals for the Mean Emission Rate and for Individual Values - Loading Arm Valves in Light Liquid and Gas Service (Combined).

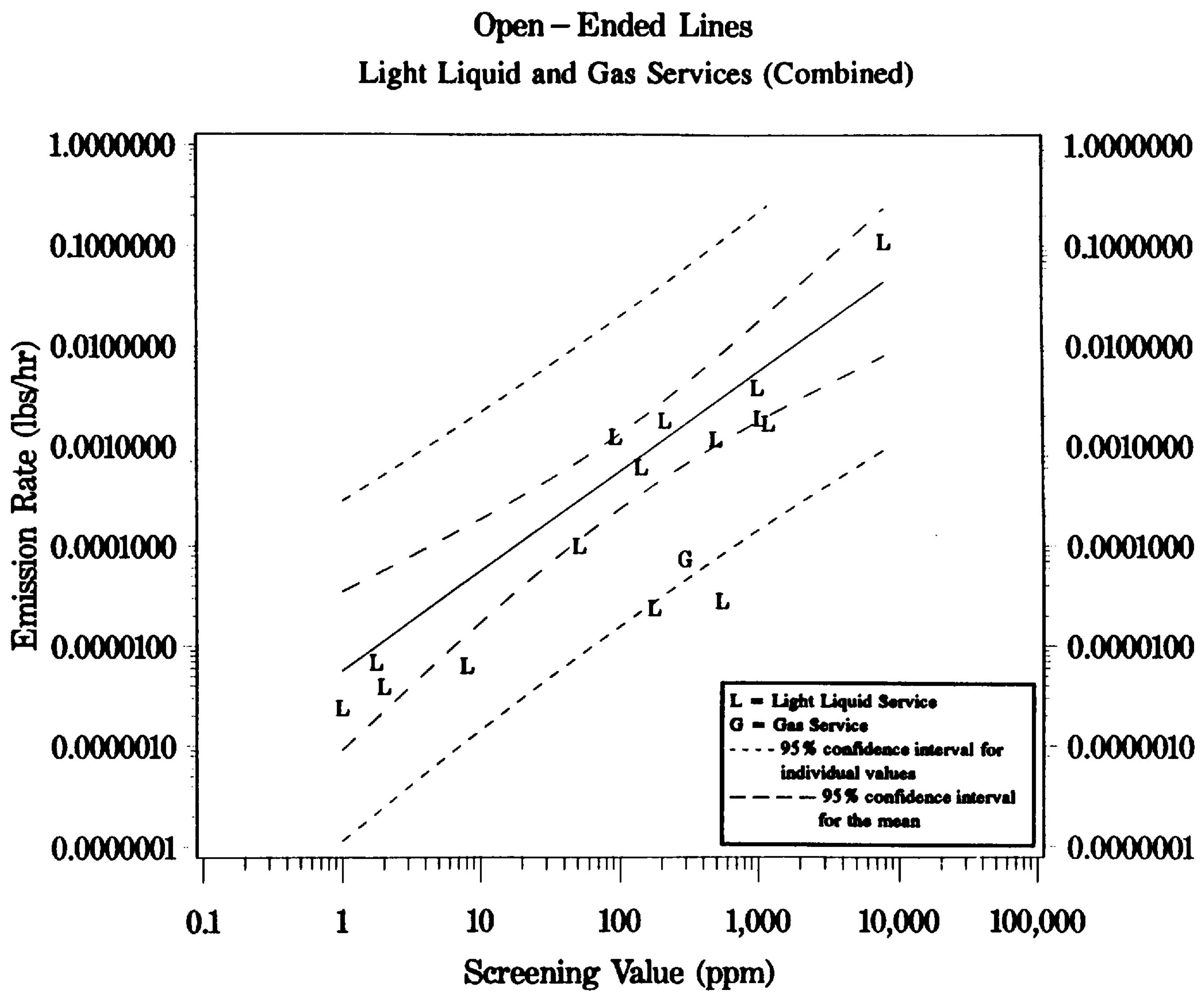


Figure 5-4. THC Mass Emission Rate Versus Actual OVA Screening Value and the 95% Confidence Intervals for the Mean Emission Rate and for Individual Values - Open-Ended Lines in Light Liquid and Gas Services Combined.

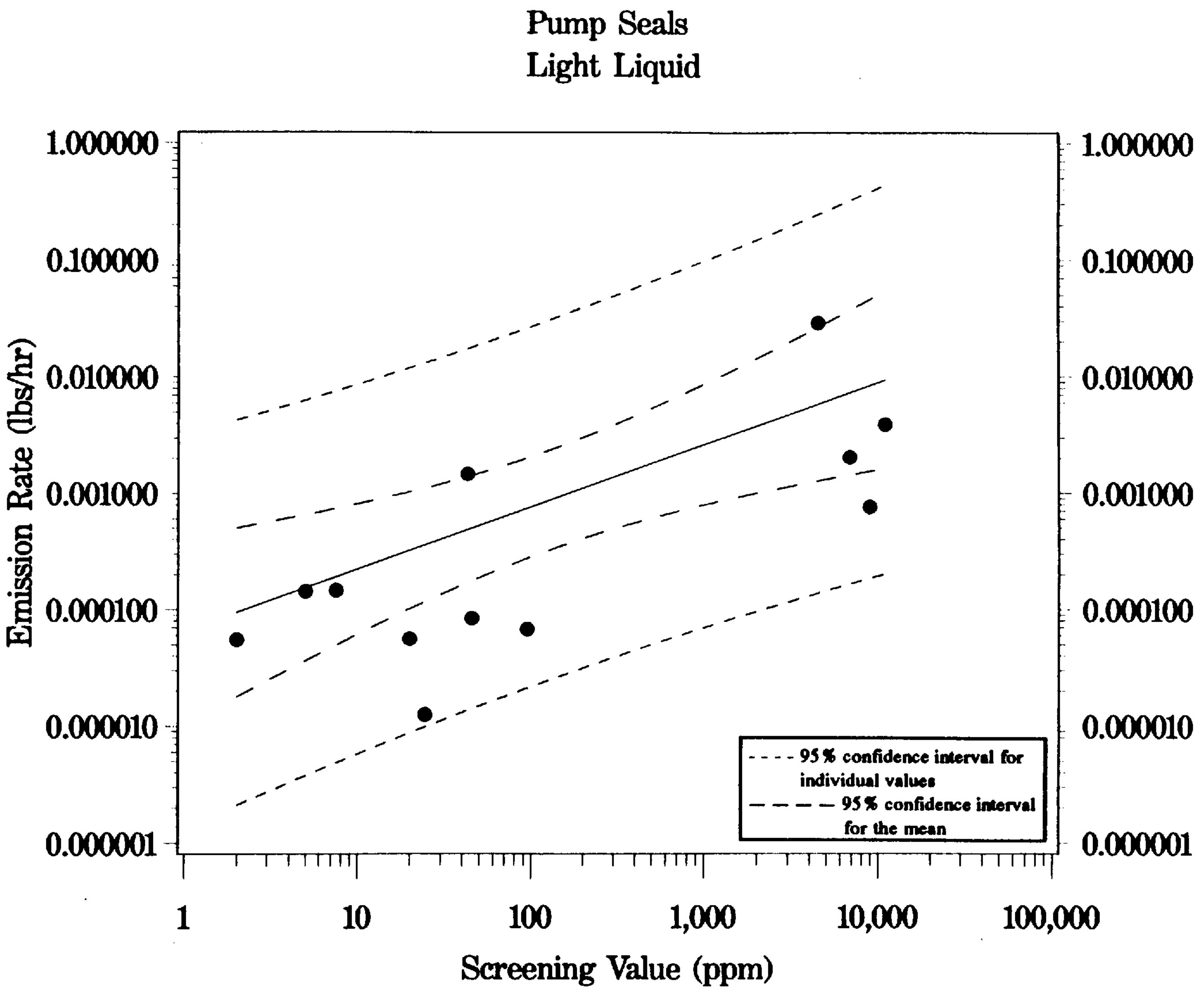


Figure 5-5. THC Mass Emission Rate Versus Actual OVA Screening Value and the 95% Confidence Intervals for the Mean Emission Rate and for Individual Values - Pumps in Light Liquid Service.

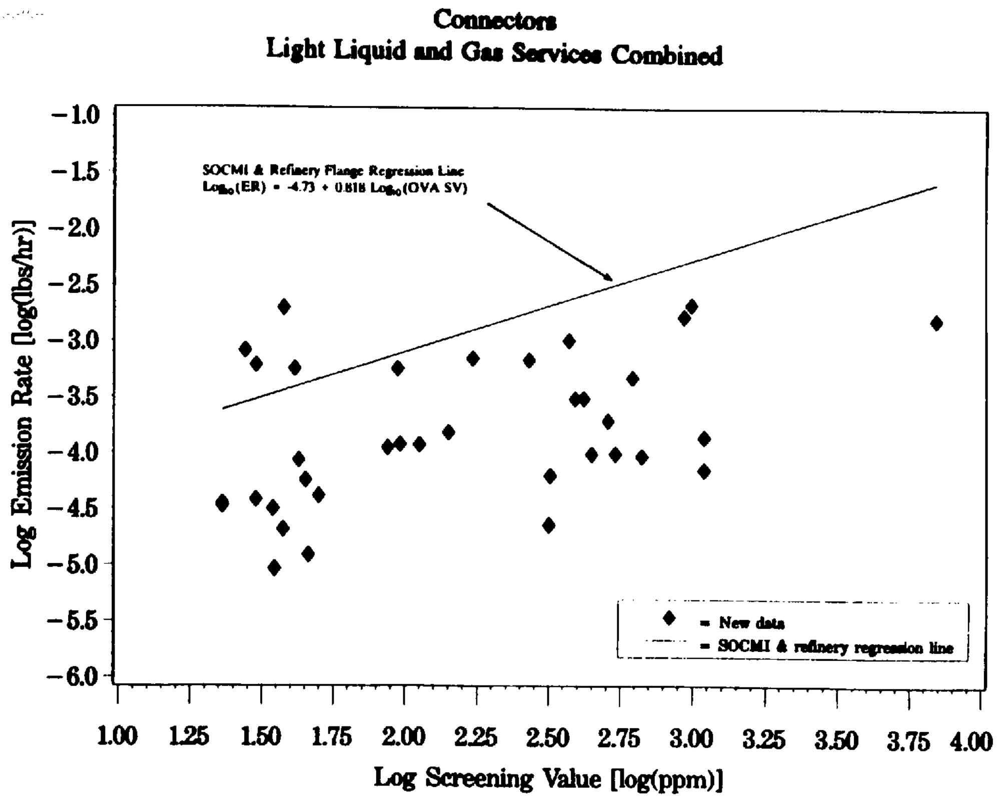
In developing new emission correlation equations, the U.S. EPA recommends that 30 emission rate measurements and screening values be obtained. If this is not possible, the EPA protocols document states that the "statistical goal is to generate estimates that are within 50% of the mean values with 95% confidence." Thus, the mean predicted values plus or minus their 95% confidence intervals should be accurate to within plus or minus 50% (when evaluated at the average screening value). As stated previously, all evaluations of the new emission correlation equations were done in log-log space. Analysis of the new emission correlation equations in log space showed that all of the five emission correlation equations met the statistical criteria of being accurate to within ± 50% with 95% confidence. These valid total hydrocarbon emission correlation equations are expected to give better estimates of total hydrocarbon emission rates in petroleum marketing terminals than the SOCMI and refinery emission correlation equations. As shown in the next section, the SOCMI and the refinery equations result in overestimates of the current marketing terminal predicted total hydrocarbon emission rates.

5.2.2 Comparison of New Emission Correlation Equations to the SOCMI and Refinery Emission Correlation Equations

The newly developed total hydrocarbon emission correlation equations resulting from the least-squares regression analysis were compared to the emission correlation equations developed during the SOCMI and refinery studies. The results of this analysis showed that the new emission correlation equations developed for connectors in light liquid and gas services (combined) and valves in liquid service were significantly different from the corresponding SOCMI and refinery emission correlation equations. The new emission correlation equation developed for pumps in liquid service was not significantly different from the corresponding SOCMI emission correlation equation, but was significantly different from the corresponding refinery emission correlation equation. Emission correlation equations were not developed for open-ended lines and loading arm valves during the SOCMI and refinery studies. Therefore, the new emission correlation equations for open-ended lines and loading arm valves were not compared to any other previously developed emission correlation equation. Both graphical and statistical comparisons were made to compare the new emission correlation equations to the SOCMI and refinery correlation equations.

In comparing the new emission correlation equations to the SOCMI and refinery emission correlation equations it should be noted that the emission correlation equations developed during the SOCMI and refinery studies cover the 1 to 100,000 ppm screening value range. For the current study less than 1% (i.e., 0.58%) of the total components screened were greater than 10,000 ppm. Thus, there were only a limited number of measured or "bagged" values that could be obtained for components that screen at greater than 10,000 ppm. Several of the newly developed emission correlation equations, therefore, only predict emission rates in the 1 to 10,000 ppm screening value range and were only compared to the existing emission correlation equations for this range. Pegged component data (discussed in Section 5.3) suggest that extrapolating the emission correlation equations into screening value ranges >10,000 could overstate emissions. At least this appears to be the case for components screening >100,000 ppm.

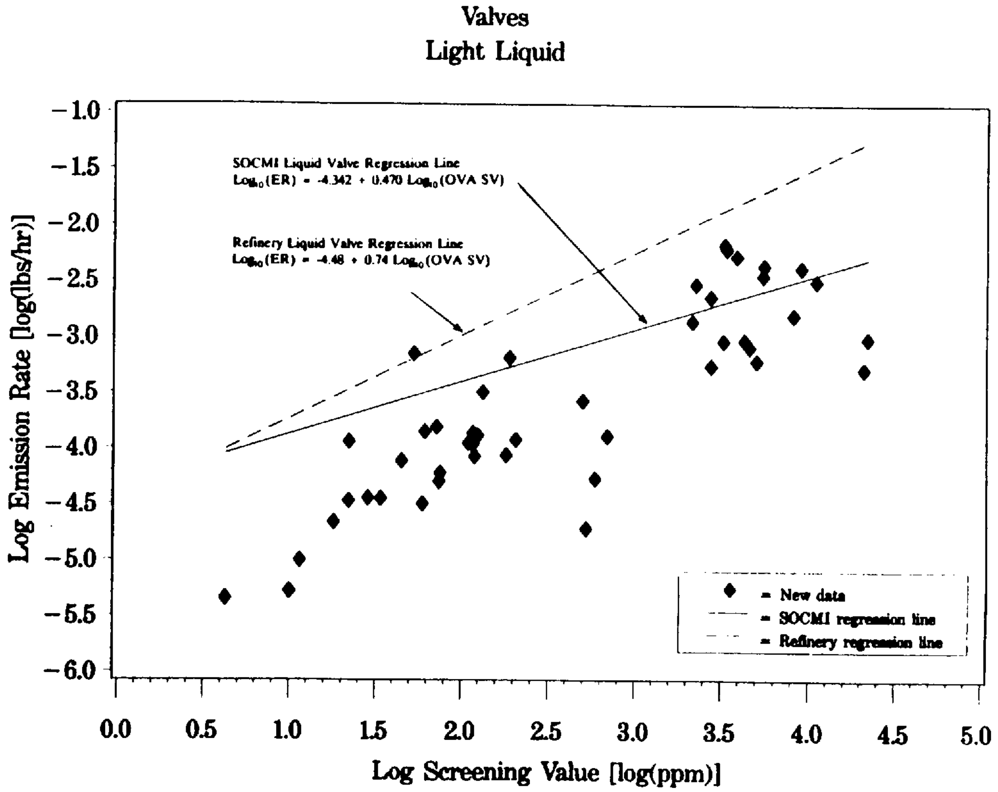
Graphical Comparison of the Petroleum Marketing Terminal Emission Correlation Equations to the SOCMI and Refinery Emission Correlation Equations. The SOCMI and refinery regression lines (representing emission correlation equations) were compared graphically to the new data by plotting the emission rate and screening value data collected from each component over a plot of the SOCMI and refinery regression lines. These graphs were prepared in the log scale so that a linear comparison could be made. Figures 5-6 through 5-8 show graphs of these data and equations. Because the data are lognormally distributed, taking the logarithms transforms the data into a normal distribution. The regression lines shown in Figures 5-6 through 5-8 show the predicted mean concentrations, assuming a normal distribution. For normally distributed data, the mean is approximately equal to the median. Thus, half the data points should fall below the regression line and half the data points should fall above the regression line. It should be noted that the SOCMI screening values were primarily obtained using an OVA screening instrument similar to the one used in the current study, whereas the refinery emission correlation equations were originally developed using a



Wilcoxon Test SOCMI & Refinery:	N For Test	Wilcoxon Statistic	Normal Approximation	P-Value
	36	879.0	-4.89	0.0001

Conclusion: Data suggest SOCMI & refinery models are inappropriate.

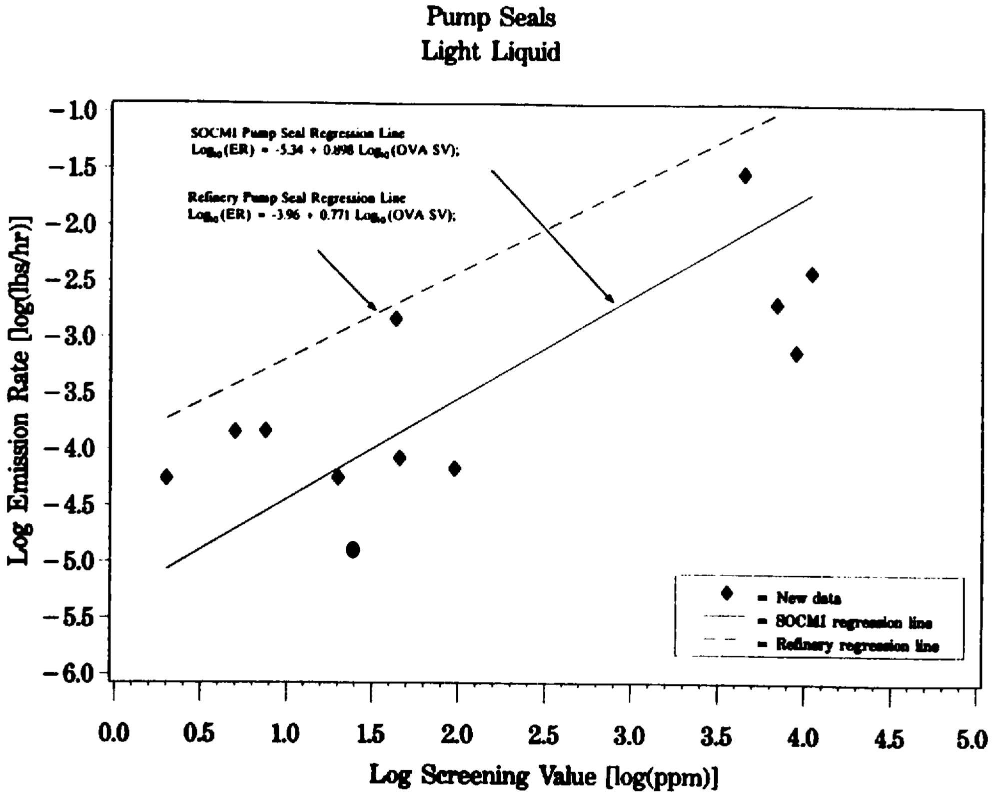
Figure 5-6. SOCMI and Refinery Emission Correlation Equations for Connectors in Light Liquid and Gas Services Combined Overlaid with Marketing Terminals Data - Log-Log Scale.



Wilcoxon Test	N For Test	Wilcoxon Statistic	Normal Approximation	P-Value
SOCMI	46	1779.0	-2.81	0.0050
Refinery	46	1480.0	-5.14	0.0001

Conclusion: Data suggest SOCMI and refinery models are inappropriate.

Figure 5-7. SOCMI and Refinery Emission Correlation Equations for Valves in Light Liquid Service Overlaid with Marketing Terminals Data - Log-Log Scale.



Wilcoxon Test	N For Test	Wilcoxon Statistic	Normal Approximation	P-Value
SOCMI	12	152.0	0.09	0.9310
Refinery	12	108.0	-2.40	0.0166

Conclusion: Data do not provide enough evidence to reject SOCMI model.
Data suggest refinery model is inappropriate.

Figure 5-8. SOCMI and Refinery Emission Correlation Equations for Pump Seals in Light Liquid Service Overlaid with Marketing Terminals Data - Log-Log Scale.

Bacharach TLV® screening instrument and subsequently revised to be used with OVA screening results.

If an approximately equal number of points fall on both sides of the SOCMI or refinery regression line in a log-log plot (log of emission rates vs. log screening values) of the data, it can be inferred that the new data adequately fit the published equations. Thus, the existing emission correlation equations could be used to estimate emissions for that component type. In the connectors plot (Figure 5-6), only 4 of the 36 data points lie above the SOCMI and refinery regression line. Figure 5-7 for light liquid valves shows that 10 of the 46 data points lie above the SOCMI regression line and only one data point lies above the refinery regression line. Lastly, Figure 5-8 for light liquid pumps shows that 4 of the 12 data points lie above the SOCMI regression line and none of the data points lies above the refinery regression line.

Figures 5-9 through 5-11 show the SOCMI and refinery emission correlation equations overlaid with the new marketing terminals emission correlation equations and their 95% confidence intervals for the mean after being transformed back to a linear scale. These graphs possess the same units as the emission rate and screening value variables (e.g., lbs/hr and ppm, respectively) and are useful for numerical comparisons.

Statistical Comparison of the Petroleum Marketing Terminal Emission Correlation Equations to the SOCMI and Refinery Emission Correlation Equations. The Wilcoxon test (Gilbert, 1987) was performed to statistically compare the differences between the SOCMI and refinery curves and the new measured data. The Wilcoxon test is a rank sum test for comparing two populations. Here the populations being compared are predicted emission rates from the SOCMI curves and the new measured bagged results; or the predicted emission rates from the refinery curves and the new measured bagged results. A more detailed description of this test is given in *Statistical Methods for Environmental Pollution Monitoring* (Gilbert, 1987). The results of these tests are shown in Figures 5-6 through 5-8. In performing this test, a significance level of 0.05 was used (i.e., $\alpha = 0.05$). The null

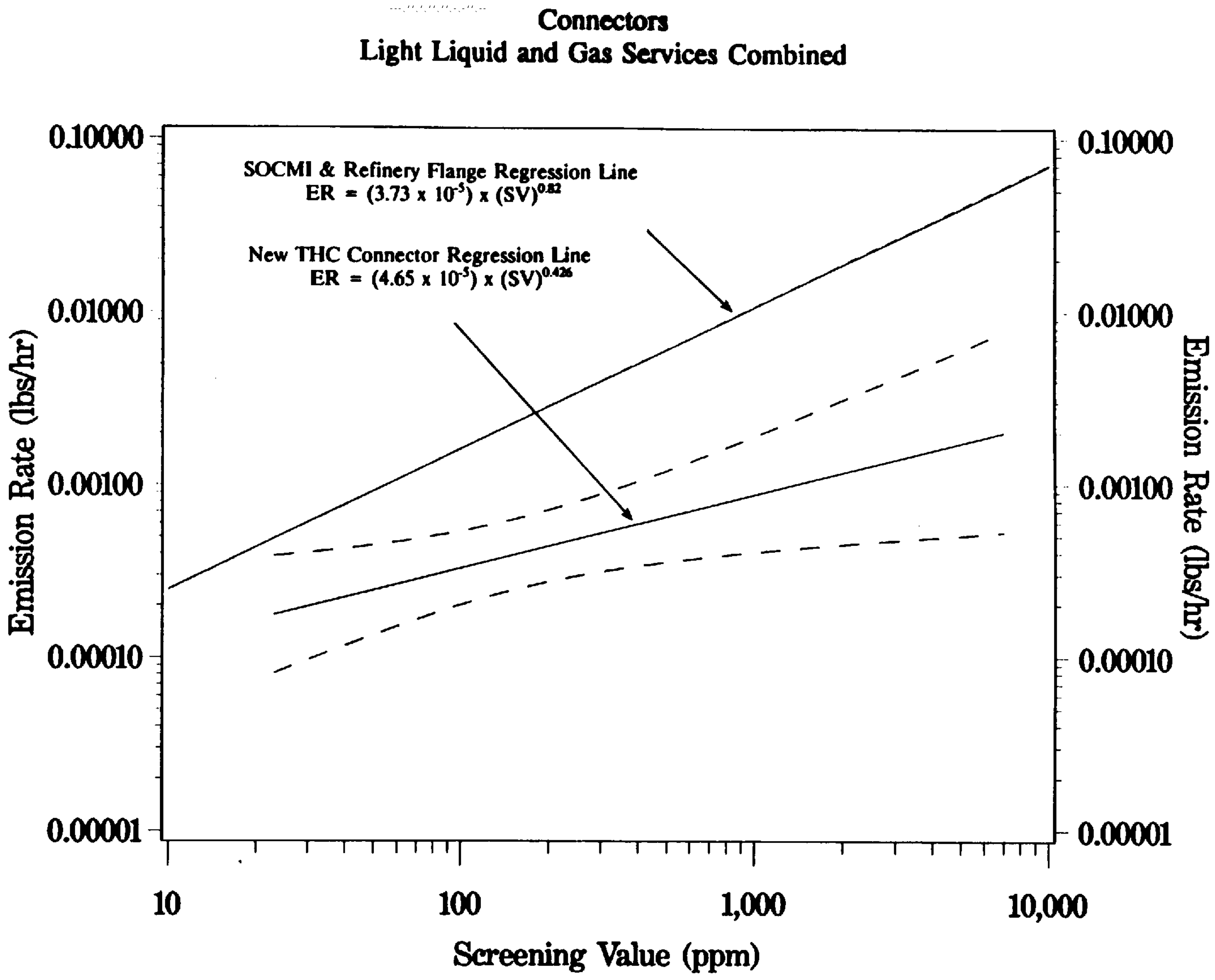


Figure 5-9. New THC Emission Equation and 95% Confidence Intervals Overlaid on SOCMI and Refinery Emission Correlation Equations -- Connectors in Light Liquid and Gas Services Combined.

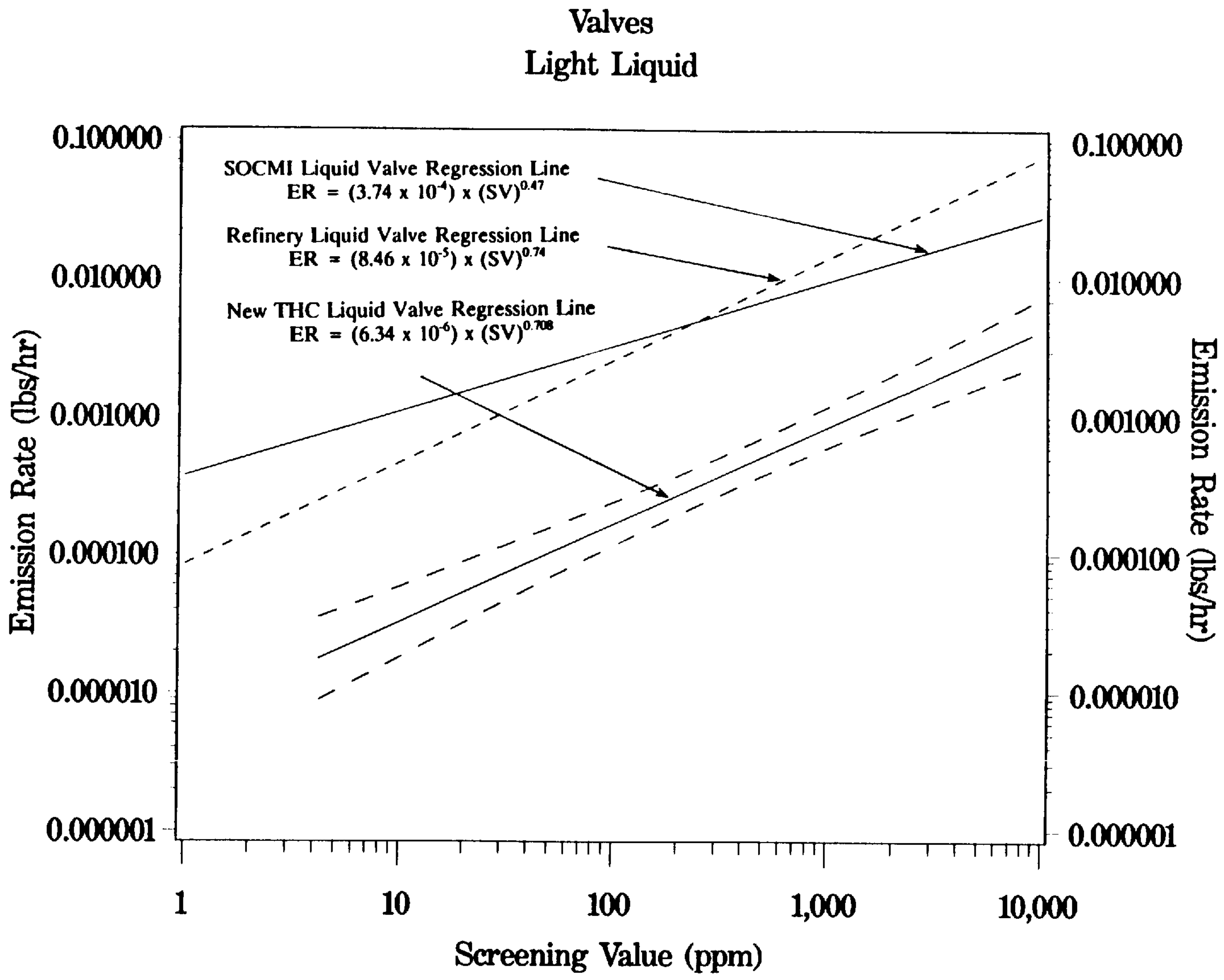


Figure 5-10. New THC Emission Equation and 95% Confidence Intervals Overlaid on SOCMI and Refinery Emission Correlation Equations -- Valves in Light Liquid Service

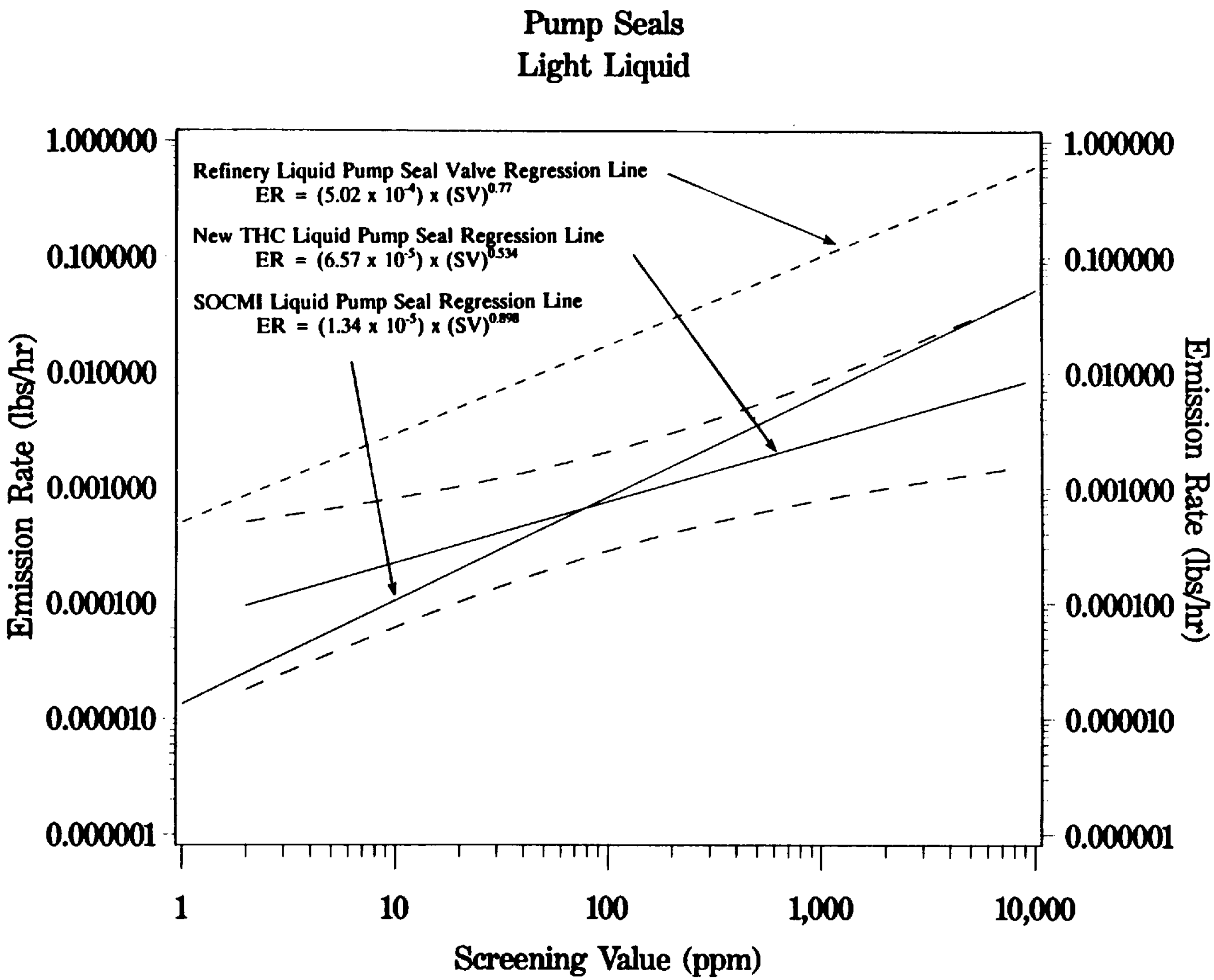


Figure 5-11. New THC Emission Equation and 95% Confidence Intervals Overlaid on SOCMI and Refinery Emission Correlation Equations -- Pump Seals in Light Liquid Service

hypothesis for this test is that the bagged emission rate data are from the same population as the concentrations predicted from the SOCMI or refinery models. This test was performed in log-log space so that the data would be approximately normally distributed. If a p-value shown in Figures 5-6 through 5-8 is less than 0.05, then this is an indication that the null hypothesis can be rejected. A p-value greater than 0.05 indicates that there is not enough evidence to reject the null hypothesis that the new data are from the same population as the values predicted from the historical equations.

The Wilcoxon test shows that the distributions of new emission rate data for connectors and light liquid valves are statistically different from the distributions of the values predicted by the SOCMI and refinery equations. For pump seals, the new emission rate data are statistically different from the refinery equation. However, the assumption that the pump seal data differ significantly from the SOCMI emission correlation equation could not be rejected (i.e., there is not a clear statistical difference between the new pump seal measurements and the SOCMI emission correlation equation for pump seals).

Statistical tests were also used to compare the estimated parameters of the equations. The parameters that determine the emission rate and screening value emission correlation equations are the following:

- The intercept (β_o).
- The slope (β_1).
- The standard error of the regression (S_e).

These parameter estimates are developed in the Log_{10} scale. Table 5-6 shows the parameter estimates for the slopes and intercepts for the new equations and the existing equations. The linear correlation coefficients obtained for the new equations and for the existing equations are also shown in Table 5-6.

The first column of Table 5-6 lists the component type (i.e., connector, valve, or pump) and parameter estimate (i.e., slope, intercept, or correlation coefficient) being compared. The last four columns show the parameter estimates for the slope and intercept for the refinery and SOCMI emission correlation equations and the 95% confidence intervals for these parameter estimates, and the correlation coefficients. Confidence intervals were not developed for the correlation coefficients. If the new marketing terminal estimates for the slope or intercept are contained within the 95% confidence intervals for the existing parameter estimates, then the new parameter estimates do not differ from the existing parameter estimates. For example, the parameter estimate for the slope of the marketing terminal light liquid valve emission correlation equation was determined to be 0.71 which is contained within the 95% confidence intervals for the slope of the refinery liquid valve emission correlation equation, but is not contained within the 95% confidence intervals for the slope of the SOCMI emission correlation equation. Thus, the slope for the new light liquid valve emission correlation equation is not significantly different from the slope of the refinery emission correlation equation but it is significantly different from the slope of the SOCMI emission correlation equation. Similarly, the intercept for the marketing terminal light liquid valve emission correlation equation was determined to be -5.43. This value is not contained within the 95% confidence intervals for the refinery nor the SOCMI intercepts. Thus, the intercept for the marketing terminal light liquid valve emission correlation equation is significantly different from the intercept for both the refinery and SOCMI light liquid valve emission correlation equations.

Equations for the 95% confidence intervals for the slope and intercept of an emission correlation equation are given in Appendix A.

5.2.3 Additional Analyses of the Marketing Terminals Emission Correlation Equations

Additional analyses were performed on the newly developed marketing terminal emission correlation equations. These analyses included an evaluation of the effects of component size and type on the connector emission correlation equation and an evaluation to determine if any of the newly developed emission correlation equations were statistically equivalent and could therefore be combined. The results of these additional analyses performed are discussed briefly in this section.

Table 5-6

Comparison of New Regression Parameters to Established Regression Parameters

Component Type	Petroleum Marketing Terminal Regression Estimates		EPA-SOCMI Regression Estimates[a]		Petroleum Refinery Regression Estimates[b]	
	Parameter Estimate	95% Confidence Intervals	Parameter Estimate	95% Confidence Intervals	Parameter Estimate	95% Confidence Intervals
Connectors, All Services						
R_{XY}:	0.41	– c	0.77	– c	0.77	– c
Slope:	0.43	(0.097, 0.754)	0.82	(0.68, 1.08)	0.82	(0.63, 1.00)
Intercept:	-4.73	(-5.48, -3.98)	-4.73	(-5.9, -4.5)	-4.73	(-5.4, -4.0)
Valves, Light Liquid						
R_{XY}:	0.85	– c	0.47	– c	0.79	– c
Slope:	0.71	(0.57, 0.84)	0.47	(0.31, 0.63)	0.74	(0.64, 0.85)
Intercept:	-5.43	(-5.81, -5.05)	-4.34	(-5.0, -3.7)	-4.48	(-4.9, -4.1)
Pump Seals, Light Liquid						
R_{XY}:	0.76	– c	0.81	– c	0.68	– c
Slope:	0.53	(0.21, 0.86)	0.90	(0.71, 1.1)	0.77	(0.67, 0.87)
Intercept:	-4.62	(-5.43, -3.81)	-5.34	(-6.1, -4.6)	-3.96	(-4.5, -3.5)

R_{XY} = Correlation coefficient.

[a] U.S. EPA, 1988.

[b] Radian, 1989 (parameter estimates corrected to an OVA screening value).

[c] Confidence intervals not calculated for the correlation coefficients.

Evaluation of Effects of Component Size and Type on the Light Liquid Connectors Emission Correlation Equation. Evaluation of the connector emission correlation equation showed that the correlation data pairs were considerably more variable than the data pairs used in the development of the other emission correlation equations. This larger variability is also revealed by the smaller correlation coefficient and the large standard error of the regression obtained for the connector emission correlation equation. The component sizes and types were further evaluated for connectors in an attempt to better understand the source of this large variability and to determine whether there were differences in the emission rate versus screening value relationship for different connector sizes and types.

The types of connectors used in the emission correlation equation development included flanges, plugs, tubing, union connectors, and threaded connectors. The sizes of connectors used in the emission correlation equation development included sizes of 0.5, 0.75, 1.0, 1.5, 2, 3, 6, 8, 18, and 24 inches. It was hypothesized that component size would affect emissions for flanges more than for the other connector types because of the wider range of flange sizes compared to the other types of connectors. Thus, component size was evaluated for flanges only. Component sizes less than or equal to 6 inches were considered "small", between 6 inches and less than or equal to 10 inches were considered "medium", and greater than 10 inches were considered "large."

Figure 5-12 shows a plot of the connector emission correlation equation with the connector types and sizes identified for each data point. The symbols in the figure indicates the connector type and for flanges the connector size is also indicated as follows:

- F-S = Small flange (≤ 6" in diameter).
- F-M = Medium flange (> 6" and ≤ 10" in diameter).
- F-L = Large flange (> 10" in diameter).
- P = Plug.
- Tu = Tubing.
- Th = Threaded connector.
- U = Union connector.

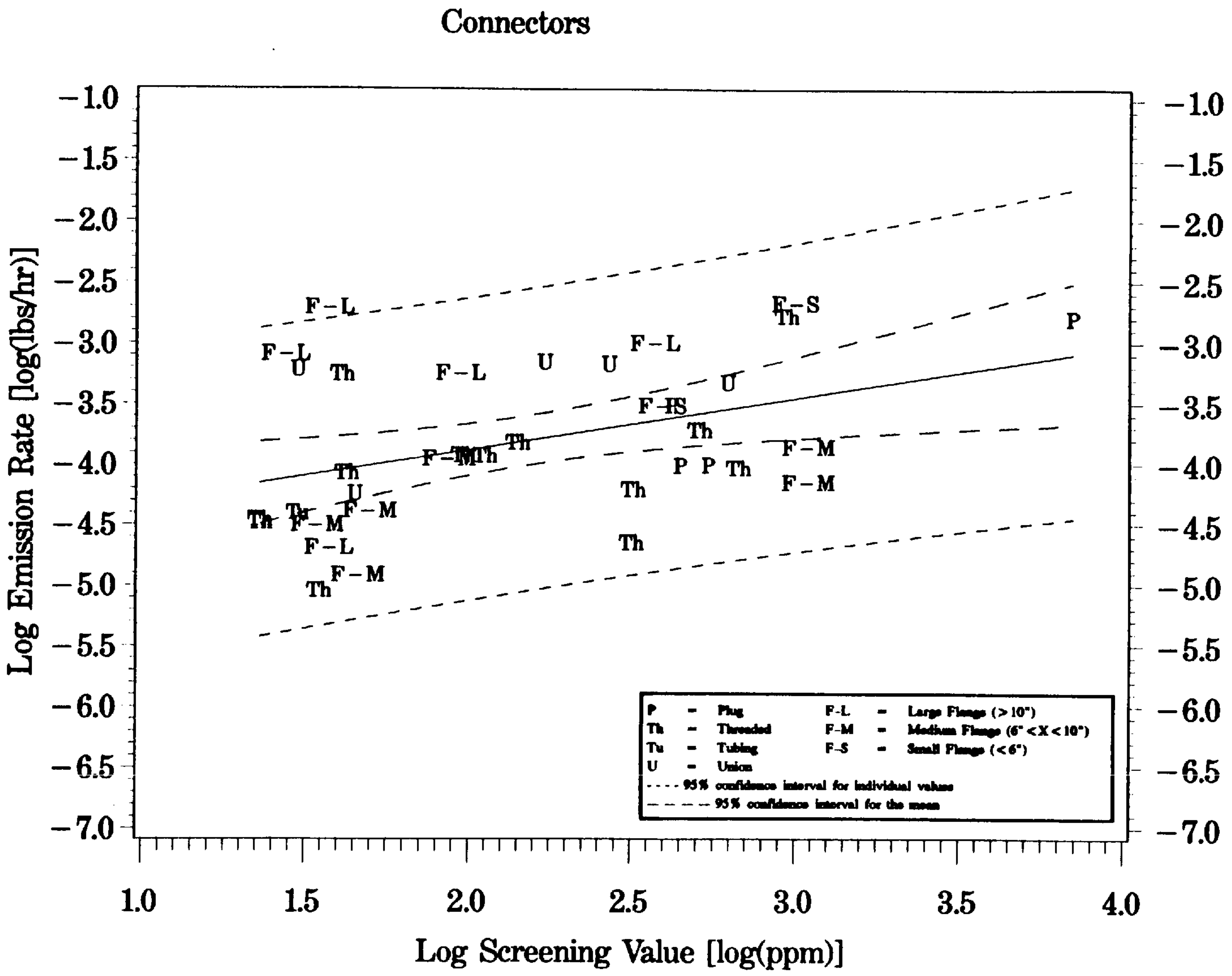


Figure 5-12. THC Mass Emission Rate Versus Actual OVA Screening Value and the 95% Confidence Intervals for the Mean Emission Rate and for Individual Values Illustrating Connector Type and Size.

As shown in Figure 5-12 the components with larger emission rates appeared to be large flanges or union connectors. The higher emission rate from large flanges (up to 24" in diameter) compared with the smaller flanges or the much smaller connectors (most threaded connectors were ≤1") makes physical sense. The screening value taken was from the highest leaking point on the flange. The large diameter flanges could be leaking from several other locations at lower rates. The smaller flanges and other connectors have less area for non-screened emissions to contribute to the mass emission rate. Union connectors have threads on two sides. Again, non-screened emissions from smaller leaks are more likely to be found on union connectors than other connectors that connect on one side only. This trend is interesting, but the amount of data in connector subtype/size categories prevents meaningful statistical analysis. The only conclusion that can be drawn is that the connectors category is only marginally homogeneous, and further testing might yield a set of subcategory correlations with better correlation coefficients.

<u>Evaluation to Combine the Emission Correlation Equations</u>. A statistical evaluation was performed to determine if any of the five individual emission correlation equations developed could be combined. A multivariate regression was performed on all of the categories combined to determine which component categories had similar slopes and intercepts. This analysis was only performed on the data used to develop the five emission correlation equations presented in Section 5.2.1. In order to perform this type of regression, an indicator variable was created for each of the component types for which an emission correlation equation had previously been developed. Thus, the following variables were created:

conct = 1, if the component is a connector 0, otherwise;
vlv = 1, if the component is a light liquid valve 0, otherwise;
la = 1, if the component is a loading arm valve 0, otherwise;
oel = 1, if the component is an open-ended line 0, otherwise;
pmp = 1, if the component is a light liquid pump, 0 otherwise.

The above variables were used in the regression model to determine whether the intercepts for different component types were statistically significant. Each of the above variables was also multiplied by the logarithm of the screening value concentration. These multiplicative variables were used in the regression model to determine whether the slopes for different component types were statistically significant. The model for this regression was as follows:

$$\text{log\_er} = \beta_o + \beta_1(\text{log\_sv}) + \beta_2(\text{conct}) + \beta_3(\text{conct*log\_sv}) + \beta_4(\text{vlv}) + \beta_5(\text{vlv*log\_sv}) + \beta_6(\text{la}) + \beta_7(\text{la*log\_sv}) + \beta_8(\text{oel}) + \beta_9(\text{oel*log\_sv}) + \beta_{10}(\text{pmp}) + \beta_{11}(\text{pmp*log\_sv})$$

where: log_er = the logarithm of the mass emission rate; and
log_sv = the logarithm of the screening value concentration.

The significance of the above parameters was used to determine which emission correlation equations could be combined. For example, suppose β_o and β_1 (the overall intercept and slope) were determined to be the only significant parameters, then β_2 through β_{11} could be eliminated from the above equation. This would suggest that one equation would be sufficient for all component types. The type of component would therefore not be significant in estimating emissions, and the only significant variable would be the screening value concentration.

On the other hand, suppose the only significant parameters were β_o, β_1, β_{10}, and β_{11}. This would imply that the equation for pumps was statistically different from the other equations; and that connectors, light liquid valves, loading arm valves, and open-ended lines were all statistically equivalent. Further, the equation for connectors, valves, OELs, and loading arm valves would be:

$$\text{log\_er} = \beta_o + \beta_1\ (\text{log\_sv})$$

where: β_o = the intercept of the emission correlation equation
β_1 = the slope of the emission correlation equation

and the equation for pump seals would be:

$$\log\_er = (\beta_o + \beta_{10}) + (\beta_1 + \beta_{11})\ (\log\_sv)$$

$$= \beta_o' + \beta_1'(\log\_sv)$$

where: $\beta_0' = \beta_o + \beta_{10}$

= the intercept for the pump emission correlation equation; and

$\beta_1' = \beta_1 + \beta_{11}$

= the slope for the pump emission correlation equation.

The results of this multivariate analysis showed the following:

- The equations for connectors in light liquid and gas services combined and valves in light liquid service were statistically equivalent.
- The equations for open-ended lines in light liquid and gas services combined and loading arm valves in light liquid and gas services combined were statistically equivalent.
- The equation for pumps in light liquid service was different from the other emission correlation equations.

The combined emission correlation equations for valves and connectors, and for OELs and LAVs are shown in Table 5-7. These new equations are shown graphically in Figures 5-13 and 5-14, respectively. Symbols are used in these figures to illustrate the component type (C = connector, V = valve, O = open-ended line, and L = loading arm valve).

Although is was possible, statistically, to develop a single emission correlation equation for valves and connectors, it is recommended that the equations for valves and connectors be kept separate. Historically, separate equations have been developed for valves and connectors, and thus it is reasonable to maintain separate equations for these components to accommodate the industry's needs. Also, the combined valve and connector emission correlation had a lower correlation coefficient than the equation for valves in light liquid service alone. Because the valve component type has a higher leak frequency and is more likely to be subject to regulation, it is important to maintain a better correlation for this component type.

Table 5-7

Predictive Emission Correlation Equations for THC Mass Emission Rates for Combined Component Types

Component Type and Service	Number of Data Pairs	Emission Correlation Equation [a,b]	Correlation Coefficient	Standard Deviation of Regression
Connectors (LL and Gas) & Valves (LL)	82	$ER = (1.26 \times 10^{-5}) \times (SV)^{0.635}$	0.729	0.532
Loading Arm Valves (LL and Gas) and Open-Ended Lines (LL and Gas)	40	$ER = (7.66 \times 10^{-6}) \times (SV)^{0.959}$	0.838	0.632

THC = Total hydrocarbons
LL = Light liquids
[a] ER = Emission Rate (lbs/hr).
[b] SV = Screening value (ppm) using the OVA calibrated with methane.

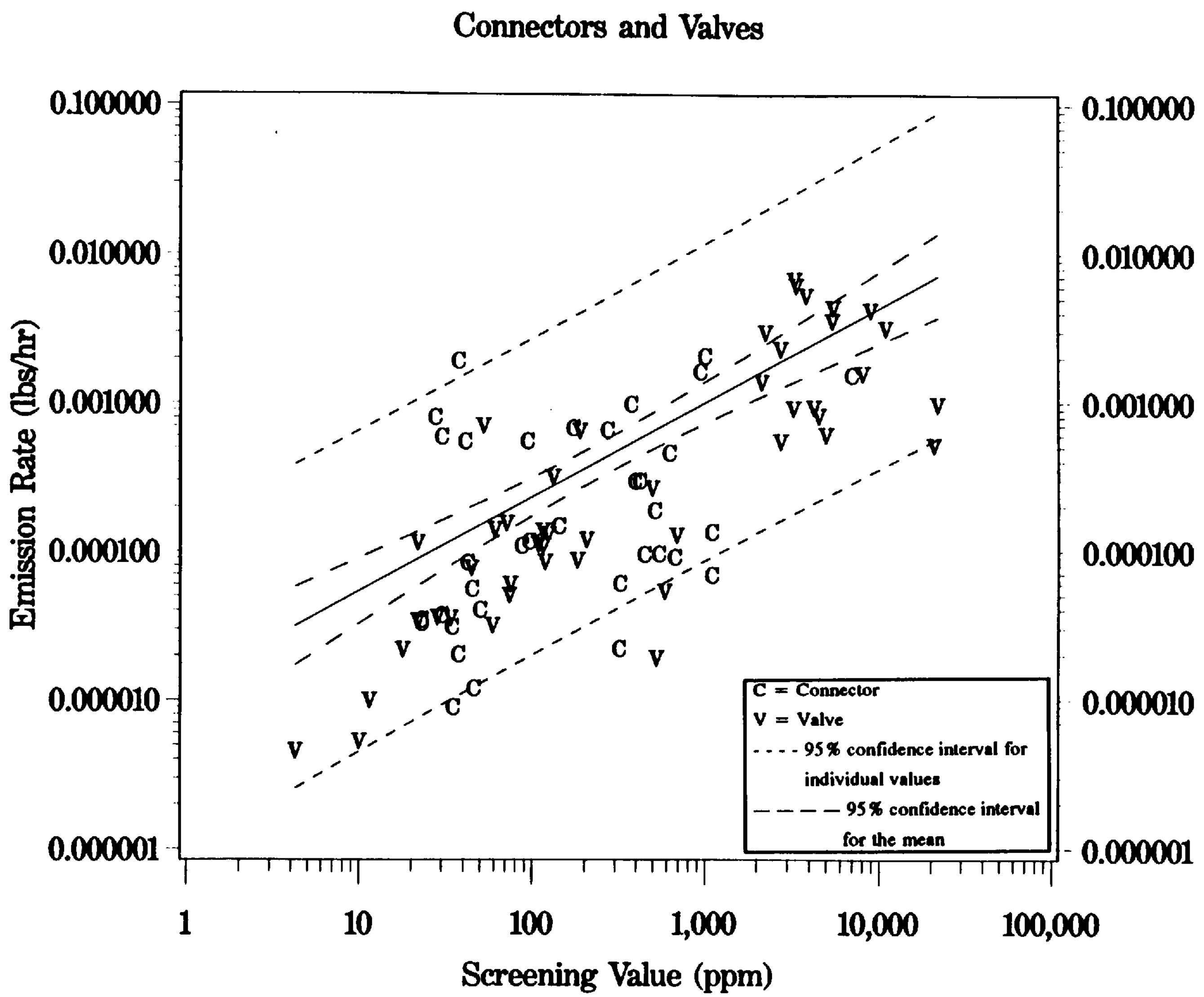


Figure 5-13. THC Mass Emission Rate Versus Actual OVA Screening Value and the 95% Confidence Intervals for the Mean Emission Rate and for Individual Values - Connectors in Light Liquid and Gas Services and Valves in Light Liquid Service, Combined.

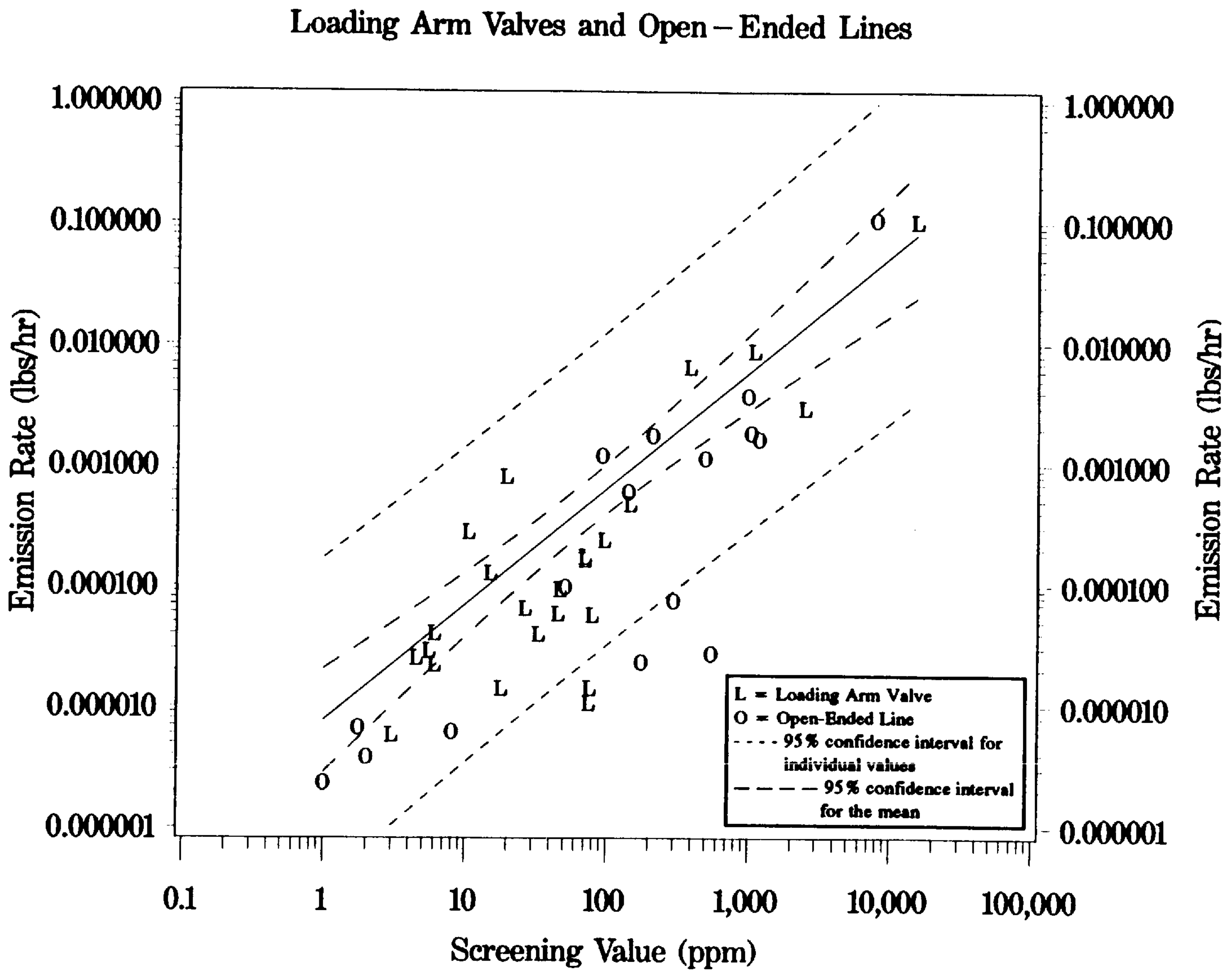


Figure 5-14. THC Mass Emission Rate Versus Actual OVA Screening Value and the 95% Confidence Intervals for the Mean Emission Rate and for Individual Values - Loading Arm Valves (in Light Liquid and Gas Services) and Open-Ended Lines (in Light Liquid and Gas Services) Combined.

5.3 EVALUATION OF PEGGED COMPONENTS

A pegged component is a component whose screening value is above the upper quantitation limit of the analyzer (i.e., > 100,000 ppm for the OVA analyzer with a dilution probe) used in this study. Under these circumstances, the actual screening value is unknown. Following the protocol presented by the U.S. EPA, the estimated emission rate for such pegged components would be the average value for several components subjected to the bagging test.

Of the 6,161 components that were screened and the 200 components that were screened and bagged, there were only 15 (i.e., 0.24%) pegged components. The component types and services for these 15 components are shown below:

Component Type	Number of Pegged Components
Connectors, Gas Service	2
Valves, Light Liquid Service	2
Valves, Gas Service	1
Loading Arm Valves, Gas Service	5
Open-Ended Lines, Light Liquid Service	1
Pump Seals, Light Liquid Service	1
Other, Gas Service	3
Total	15

Nine of these fifteen components were bagged and two were bagged twice, for a total of eleven bagged measurements from pegged components. The average measured emission rates for these eleven components are shown in Table 5-8. Emission rates for the eleven bagged components were also calculated using the newly developed marketing terminals emission correlation equations. Average errors were calculated to compare the average measured (i.e., "bagged") values to the average calculated values (i.e., from the emission correlation equations) as follows:

$$\%\ \text{Average Error} = 100 \times \left(\frac{\text{Measured Value} - \text{Calculated Value}}{\text{Measured Value}} \right)$$

Table 5-8

Summary of Pegged Component Data

Component Type	Service	Number of Bagged Pegged Components	Average Measured Mass Flow Rate (lbs/hr)	Calculated Mass Flow Rate Using the Emission Correlation Equation[a,b] (lbs/hr)	Average Error[c] (%)
Connectors	Gas	2	0.00345	0.00628	-82
Valves	Gas	2	0.06981	1.08256	-1,450
Loading Arm Valves	Gas	3	0.06422	0.4778	-644
Open-Ended Lines	LL	2	0.00561	0.4778	-8,409
"Other"[d]	LL	2	0.03878	0.00628	+84

LL = Light liquids

[a] Calculated from the correlation equations using 100,000 ppm as the screening value.

[b] The combined marketing terminal correlation equation was used for loading arm valves and open-ended lines, the marketing terminal emission correlation equation for connectors was used for "other" components, and the refinery (Radian, 1989) emission correlation equation was used for gas valves.

[c] Error = (measured value - calculated value) x 100/measured value

[d] "Other" includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

The average error values are negative for each of these components, except for the "other" category, indicating that using 100,000 ppm in the new emission correlation equations provides an emission estimate that is higher than the measured value. No emission correlation equation was developed for the "other" category. Thus, the approach resulting in higher estimated emission rates for determining pegged component emission factors was to use the upper quantitation limit value (i.e., 100,000 ppm) in the emission correlation equation, for all components for which an emission correlation equation was developed. More bagging data from pegged components are needed to provide a more suitable choice. The pegged component emission factors using this approach are shown in Table 5-8.

The fact that the measured mass emissions from these pegged components are lower than using the value calculated with the emission correlation equations suggests that the emission correlation equations overstate emissions in the higher screening value ranges (at least those >100,000 ppmv).

5.4 AVERAGE EMISSION FACTORS

Average emission factors were developed for each component type. Average emission factors were developed for the gas and light liquid service types only. Average emission factors were not developed for heavy liquid services, because the scope of work for this study did not call for complete testing of heavy liquid service components. The emphasis for this study was placed on testing gasoline service components, and to a lesser degree heavy liquids (i.e., diesel, fuel oil).

Unlike the default zero emission factors and the emission correlation equations, the average emission factors were always segregated into different component types and services. This was to reflect the differences in the screening value concentrations. Analysis of the screening value data showed that for a number of the components, screening value concentrations differed on the average, depending on the service of the component. Thus, emission factors were segregated to reflect potential differences in average screening value concentrations obtained for different component types and services, and to obtain more accurate average emission factors.

When possible, the new default zero emission factors and emission correlation equations were used to develop the average emission factors. For some component types there were insufficient data to develop new default zero emission factors and emission correlation equations. For these component types the refinery default zero emission factors and emission correlation equations were used. Table 5-9 shows the default zero emission factors and the emission correlation equations that were used to develop the average emission factors for each component type. The "other" category includes components such as hatches, hoses, covers, manholes, thermal wells, and pressure relief valves. Only five bagged emission rate measurements were obtained for the "other" category. Comparison of these screening and emission rate measurements to the other emission correlation equations showed that all of these emission rate measurements fell below the new emission correlation equations. However, because the types of components in the "other" category are most similar to connectors, it was decided to use the new connector equation and default zero emission factor to estimate emissions for the "other" category.

The following procedures were used to estimate emission rates from each screened component in the average emission factor development:

- If the screening value was less than the default zero screening value for that component type, then the default zero emission rate for that component type was used as the emission rate.
- If the screening value was greater than or equal to the default zero screening value for that component type, then the emission correlation equation for that component type was used to estimate the emission rate.
- If the screening value pegged the instrument (i.e., the screening value was greater than 100,000 ppm), then the upper quantitation limit value (i.e., 100,000 ppm) was used in the extrapolated emission correlation equation for that component type to estimate the emission rate.

Table 5-9

Emission Correlation Equations and Default Zero Emission Factors Used to Calculate Average THC Mass Emission Rates

Component Type	Service	Emission Correlation Equation[a]	Default Zero Emission Factor
Connectors[b]	Light Liquid and Gas Combined	$(4.65 \times 10^{-5}) \times (SV)^{0.426}$	6.5×10^{-6}
Valves[c]	Gas	$(2.16 \times 10^{-6}) \times (SV)^{1.14}$	5.9×10^{-6}
Valves	Light Liquid	$(6.34 \times 10^{-6}) \times (SV)^{0.708}$	3.5×10^{-6}
Loading Arm Valves & Open-Ended Lines[d]	Light Liquid and Gas Combined	$(7.66 \times 10^{-6}) \times (SV)^{0.959}$	4.5×10^{-6}
Pumps	Light Liquid	$(6.57 \times 10^{-5}) \times (SV)^{0.534}$	3.9×10^{-5}
"Other"[e,f]	Light Liquid and Gas Combined	$(4.65 \times 10^{-5}) \times (SV)^{0.426}$	6.5×10^{-6}

THC = Total hydrocarbons

[a] SV = Screening value (ppm) using the OVA calibrated with methane.

[b] Used the default zero emission factor for light liquid connectors to estimate emissions for connectors in all service.

[c] Used the refinery correlation equation for gas valves (Radian, 1989).

[d] Used the new default zero emisson factor for open-ended lines to estimate emissions for loading arm valves.

[e] Used the new emission correlation equation for connectors and the new default zero emission factor for connectors to estimate emissions for "other" component types.

[f] "Other" component types includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

Screening values for "pegged" readings are (>100,000 ppm on the OVA) not as accurate as those screening values that screened within the instrument screening value range. Hydrocarbon concentrations could be anywhere from 100,000 ppmv to 1,000,000 ppmv. There were insufficient leaking components, however, to develop separate "pegged" emission factors, as discussed in Section 5.3. Comparison of measured emission rates obtained from pegged components (i.e., those that were "bagged") to the emission rates obtained from the emission correlation equations, showed that the emission correlation equations resulted in higher estimated emission rates for every case for which an emission correlation equation was developed. As previously stated, the approach resulting in higher estimated emission rates for pegged component emission factors was to use the upper quantitation limit value (i.e., 100,000 ppm) in the emission correlation equation.

After obtaining emission rates for all of the screened components, the average emission factor was obtained by taking the arithmetic average of all of the emission rates. These average emission factors and the 95% confidence intervals are given in Table 5-10 for each component type.

It should be noted that the average emission factors are not intended to provide an accurate estimate of the emission rate from a single component type or piece of equipment. Because leak rates from individual components often vary by several orders of magnitude, the average emission factor may not provide an accurate estimate of the mass emission rate from an individual piece of equipment. Rather, the average emission factors are more appropriately applied to the estimation of emissions from larger populations of components or equipment.

Table 5-11 shows a comparison of the new average emission factors to the SOCMI and refinery average emission factors. This comparison was performed for connectors, valves, open-ended lines, and pump seals. No average emission factors were developed for loading arm valves and the "other" category during the SOCMI and refinery studies, thus there was no basis for comparison. The SOCMI and refinery average emission factors were evaluated

Table 5-10

Petroleum Marketing Terminal Average THC Emission Factors in lbs/hr/component

Component Type	Service	Number of Observations	Average Emission Factor (lbs/hr)	Lower 95% Confidence Limit (lbs/hr)	Upper 95% Confidence Limit (lbs/hr)
Connectors	Gas	157	0.000067	0.000022	0.00011
	LL	2,561	0.000023	0.000020	0.000027
Valves	Gas*	114	0.00016	0.00000	0.00034
	LL	2,245	0.00015	0.00010	0.00021
Loading Arm Valves	Gas	43	0.045	0.0097	0.080
	LL	108	0.00087	0.00037	0.0014
Open-Ended Lines	Gas	17	0.0067	0.0000	0.017
	LL	92	0.0065	0.0000	0.017
Pump Seals	LL	88	0.00093	0.00013	0.0017
"Other"	Gas	19	0.0014	0.00064	0.0022
	LL	113	0.00025	0.00013	0.00037

THC = Total hydrocarbons
LL = Light liquids
* Used refinery correlation equation (Radian, 1989) to determine the average emission factor.

Table 5-11

Comparison of New Marketing Terminal Average THC Emission Factors To Established Average Emission Factors

Component Type	Phase	Marketing Terminal Average Emission Factor (lbs/hr)	Lower 95% Confidence Limit (lbs/hr)	Upper 95% Confidence Limit (lbs/hr)	SOCMI Average Emission Factor (lbs/hr)[a]	Overlap With Confidence Intervals of New Average?	Refinery Average Emission Factor (lbs/hr)[b]	Overlap With Confidence Intervals of New Average?
Connectors	Gas	0.000067	0.000022	0.00011	0.00183	No	0.00056	No
	LL	0.000023	0.000020	0.000027	0.00183	No	0.00056	No
Valves	Gas	0.00016	0.00000	0.00034	0.01235	No	0.05900	No
	LL	0.00015	0.00010	0.00021	0.01566	No	0.02400	No
Open-Ended Lines	Gas	0.0067	0.0000	0.017	0.00375	Yes	0.00500	Yes
	LL	0.0065	0.0000	0.017	0.00375	Yes	0.00500	Yes
Pump Seals	LL	0.00093	0.00013	0.0017	0.10917	No	0.2500	No

THC = Total hydrocarbons
LL = Light Liquid
[a] U.S. EPA, 1988
[b] Radian, 1989 and Refinery, 1980

to determine if they fall within the 95% confidence intervals for the new average emission factors. If the established average emission factors are not contained within these 95% confidence intervals and are higher than the new emission factors, then we can conclude that the new average emission factors are significantly lower than the established SOCMI and refinery emission factors.

As shown in Table 5-11 the confidence intervals do not overlap with the established average emission factors for any of the component types except for open-ended lines. Thus, with the exception of open-ended lines, all of the average emission factors in Table 5-11 are significantly lower than the established SOCMI and refinery average emission factors.

5.5 STRATIFIED EMISSION FACTORS

Stratified emission factors were obtained for the following screening value ranges:

- 0–999 ppm; and
- ≥1,000 ppm.

Stratified emission factors could not be obtained for the ≥10,000 ppm screening value range due to the lack of components that screened in this range. Components that were pegged and that screened at ≥10,000 ppm are included in the ≥1,000 ppm range. The strata could not be broken into smaller categories (e.g., 0–499 ppm, 500–1,000 ppm, etc.) also due to the lack of screening values that were obtained within these smaller ranges.

To develop stratified emission factors, emission rates were obtained for each of the screened components, as described in Section 5.4. The average emission factor was then calculated for each of the above screening value ranges for each component type. Table 5-12 gives the stratified emission factors, the number of screening values used to develop each stratified emission factor, and the 95% confidence interval for each stratified emission factor. Emission factors obtained for the ≥1,000 were based on a total of 124 light liquid and gas service screening values that were screened in this range. The small sample sizes used to develop the

Table 5-12

Petroleum Marketing Terminal Stratified Total Hydrocarbon Emission Factors in Lbs/Hr/Component

Component Type	Phase	Stratified Emission Factors					
		0-999 ppm			≥ 1000 ppm		
		N	Emission Factor	95% Confidence Limits	N	Emission Factor	95% Confidence Limits
Connectors	Gas	154	0.000030	(0.000017,0.000043)	3	0.0020	(0.00049,0.0034)
	LL	2553	0.000020	(0.000018,0.000023)	8	0.0010	(0.00095,0.0011)
Valves	Gas[a]	113	0.000084	(0.0000054,0.00016)	1	0.0090[b]	NC
	LL	2182	0.000026	(0.000022,0.000029)	63	0.0046	(0.0031,0.0061)
Loading Arm Valves	Gas	30	0.00066	(0.00020,0.0011)	13	0.15	(0.043,0.25)
	LL	105	0.00047	(0.00026,0.00068)	3	0.015	(0.0071,0.022)
Open-Ended Lines	Gas	14	0.00022	(0.00000,0.00054)	3	0.037	(0.000,0.13)
	LL	86	0.00017	(0.000018,0.00033)	6	0.097	(0.000,0.29)
Pump Seals	LL	82	0.00015	(0.000073,0.00024)	6	0.011	(0.00093,0.022)
Other[c]	Gas	11	0.00062	(0.00050,0.00073)	8	0.0025	(0.00080,0.0043)
	LL	103	0.000073	(0.000043,0.00010)	10	0.0021	(0.0014,0.0027)

THC = Total hydrocarbons.
LL = Light liquid service.
N = Number of components screened in this screening value range.
NC = Confidence interval could not be calculated due to insufficient data.

[a] Used refinery correlation equation (Radian, 1989) to determine stratified emission factors.

[b] Emission factor only based on one screening value.

[c] "Other" includes component types such as hatches, covers, manholes, thermal wells, and pressure relief valves.

emission factors for this upper strata are reflected in the broad confidence intervals obtained for these emission factors. The upper stratum emission factor for valves in gas service was based on only one screening value.

5.6 EVALUATION OF SCREENING VALUE DATA

The screening values represent the maximum hydrocarbon concentrations detected at baggable components using the Foxboro OVA calibrated to methane. Screening values are expressed as ppmv of total hydrocarbons and were measured in accordance with the latest version of EPA Reference Method 21 (U.S. EPA, 1988). This section contains an evaluation of all of the screening data collected from the four marketing terminals tested. Section 5.6.1 gives a summary of the components studied, Section 5.6.2 contains an evaluation of the distribution of screening values and leaking components, where a leaker is defined as a component that screens at greater than 10,000 ppm. Lastly, Section 5.6.3 gives the results of a statistical evaluation of the effects of phase and load on the screening value concentrations.

5.6.1 Summary of Components Studied

A total of 21,981 individual components were counted from four petroleum marketing terminals. Table 5-13 summarizes the total number of components counted for each of the six component types (connectors, valves, loading arm valves, open-ended lines, pump seals and "other") and three service types (gas, heavy liquid, and light liquid). Connectors included components such as clamps, flanges, hoses, plugs, screwed connectors, threaded connectors, tubing and union connectors. These varied in size from 0.5 inches to 30 inches in diameter. Types of valves included ball valves, butterfly valves, check valves, control valves, diaphragms, gate valves, globes, meters, motors, needle valves, plugs, schraeder valves, and solenoid valves. Valves varied in size from 0.5 inches to 18 inches in diameter. Loading arm valves were check valves on lines used to connect to trucks while loading product and receiving residual vapors remaining in the truck tanks. Open-ended lines are drainage or vent lines from process vessels, tanks, or product lines. Open-ended lines usually included a block valve or another type of valve farther up the line designed to prevent fluid flow when not in use. Open-ended lines that were capped or plugged were included in the connectors category.

Table 5-13

Summary of Components Studied

Component Type and Service	Number of Components Screened	Number of Components Skipped[a]	Number of Inaccessible Components	Total Components[b]	Percent of Total[c]
Connectors:					
Gas Vapor	157	891	84	1,132	5.15
Heavy Liquids	284	846	17	1,147	5.22
Light Liquids	2,561	13,644	250	16,455	74.86
Valves:					
Gas Vapor	114	0	12	126	0.57
Heavy Liquids	277	0	9	286	1.30
Light Liquids	2,245	0	59	2,304	10.48
Loading Arm Valves:					
Gas Vapor	43	0	0	43	0.20
Heavy Liquids	8	0	0	8	0.04
Light Liquids	108	0	0	108	0.49
Open-Ended Lines:					
Gas Vapor	17	0	0	17	0.08
Heavy Liquids	16	0	1	17	0.08
Light Liquids	92	0	4	96	0.44
Pump Seals:					
Gas Vapor	NA	NA	NA	NA	NA
Heavy Liquids	12	0	0	12	0.05
Light Liquids	88	0	3	91	0.41
"Other"[d]:					
Gas Vapor	19	0	0	19	0.09
Heavy Liquids	7	0	0	7	0.03
Light Liquids	113	0	0	113	0.51
Totals	6,161	15,381	439	21,981	100.00

NA = not applicable (there were no gas pump seals)

[a] Only 16% of all accessible connectors screened.

[b] Total component count = number of components screened + number of components skipped + number of inaccessible components.

[c] Percent of total components = (100 x total components) / overall total.

[d] "Other" includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

Pumps were all centrifugal pumps with mechanical seals. Lastly, the "other" category included components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

As shown in Table 5-13, approximately 2.0% (i.e., 439 out of 21,981) of the components were inaccessible. Inaccessible components were generally located out of sampling reach, but occasionally included components in unsafe areas or components covered with ice. The inaccessible components were not included in any emission factor development or development of the emission correlation equations. Of the 21,542 accessible components, 6,161 (28.6%) were screened using the OVA analyzer. Virtually all valves, loading arm valves, open-ended lines, pump seals, and "other" component types in the light liquid and gas streams were screened. Table 5-13 does not represent an exact count of all heavy liquid components, however, because the scope of work for this study did not call for complete testing of heavy liquid service components. Approximately 16% of the connectors (i.e., 3,002 out of 18,383) were screened. The third column of Table 5-13 shows the number of accessible components not screened.

Table 5-14 shows a breakdown of the number of components counted at each marketing terminal. Terminal A contained the smallest number of components (4,176) and Terminal B contained the largest number of components (6,754). As shown in Table 5-14 the distribution of component types is about the same for each terminal, with connectors comprising the bulk of all component types (approximately 85% connectors). The next largest component category at each terminal is valves, which comprise about 12% of all components. The other component categories each comprised less than 1% of all components counted. Pump seals is the least numerous component type, accounting for only 0.47% of all components.

It is interesting to note that the majority of the components counted were in light liquid service, which comprised 87.2% of all the components counted. The heavy liquid phase and the gas phase were comparable, accounting for 6.7% and 6.1%, respectively, of all components counted. As stated previously, however, this does not represent an exact breakdown of

Table 5-14

Total Component Counts Per Facility

Component Type	Terminal A[a]	Terminal B[b]	Terminal C[c]	Terminal D[d]	All Sites	
					Total Components	Percent of Total (%)
Connectors	3,659	5,793	5,639	3,643	18,734	85.23
Valves	434	779	905	598	2,716	12.36
Loading Arm Valves	30	60	48	21	159	0.72
Open-Ended Lines	24	32	36	38	130	0.59
Pumps	26	20	30	27	103	0.47
"Other"[e]	3	70	23	43	139	0.63
Total Components	4,176	6,754	6,681	4,370	21,981	100.00

[a] 5 connectors and 8 valves inaccessible

[b] 96 connectors and 13 valves inaccessible

[c] 239 connectors, 49 valves, and 3 open-ended lines inaccessible

[d] 11 connectors, 10 valves, 2 open-ended lines, and 3 pump seals inaccessible

[e] "Other" includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves

components by service, because the scope of this study did not call for complete testing of heavy liquid service components. The emphasis was placed on testing gasoline service components, and only a relative few components in heavy liquid service (i.e., diesel, fuel oil).

5.6.2 Analysis of Distribution of Leaking Screening Values

The distribution of the screening values are presented in Tables 5-15a and 5-15b. They are given as a function of component types and service categories. Table 5-15a gives the counts of components screened in each screening value range and Table 5-15b gives the percent of components screened in each screening value range. As shown in Table 5-15b, the concentrations are not evenly distributed. The distribution of screening values for all of the components is skewed, with the majority of the components having screening values of 500 ppm or less and only a relative few screening in the highest ranges (i.e., greater than 10,000 ppm).

For comparison, the distribution of screening values for all component types obtained during the petroleum refinery fugitive emissions studies was also evaluated. This comparison is shown in Tables 5-16a and 5-16b, for the marketing terminals study and the Refinery Assessment Study, respectively. The ranges of screening values shown in these tables are the ranges of screening values given in the Refinery Assessment Study (Radian, 1980). In these tables the screening value counts are summarized for all component types combined.

As shown in the Tables 5-16a and 5-16b, a total of 6,161 components were screened during the marketing terminals study and 5,610 components were screened during the Refinery Assessment Study. Please note that Table 5-16 includes gas, light liquid, and heavy liquid screening values. Approximately 79% of the components screened during the marketing terminals study were less than 1 ppm, whereas only 58% of the components screened during the Refinery Assessment Study were less than 1 ppm. In addition, less than 1% of the marketing terminal components screened at greater than 10,000 ppm, whereas more than 8% of the refinery components screened at greater than 10,000 ppm. As shown in Tables 5-16a and 5-16b the marketing terminals show an overall reduction in screening value concentrations when compared to the refinery components.

Table 5-15a

Distribution of Number of Components By Screening Value: All Plants and All Components

Component Type	Number of Components in Screening Value Range						
	0-0.9 ppm	1-499 ppm	500-999 ppm	1,000-9,999 ppm	10,000-99,999 ppm	≥ 100,000 ppm	Total
Connectors:							
Gas Vapor	135	19	0	2	1	0	157
Heavy Liquids	258	26	0	0	0	0	284
Light Liquids	2,275	275	3	8	0	0	2561
Valves:							
Gas Vapor	93	19	1	1	0	0	114
Heavy Liquids	239	38	0	0	0	0	277
Light Liquids	1,603	562	17	48	13	2	2245
Loading Arm Valves:							
Gas Vapor	7	21	2	4	7	2	43
Heavy Liquids	0	7	0	1	0	0	8
Light Liquids	35	65	5	3	0	0	108
Open-Ended Lines:							
Gas Vapor	11	3	0	2	1	0	17
Heavy Liquids	9	7	0	0	0	0	16
Light Liquids	66	18	2	4	1	1	92
Pump Seals:							
Gas Vapor	NA	NA	NA	NA	NA	NA	NA
Heavy Liquids	9	3	0	0	0	0	12
Light Liquids	58	23	1	4	1	1	88
"Other"*:							
Gas Vapor	0	8	3	5	2	1	19
Heavy Liquids	6	0	0	1	0	0	7
Light Liquids	78	24	1	7	3	0	113

* "Other" includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

Table 5-15b

Distribution of Percent of Components By Screening Value: All Plants and All Components

Component Type	Percent of Components in Screening Value Range					
	0-0.9 ppm	1-499 ppm	500-999 ppm	1,000-9,999 ppm	10,000-99,999 ppm	≥100,000 ppm
Connectors:						
Gas Vapor	86.0	12.1	0.0	1.3	0.6	0.0
Heavy Liquids	90.8	9.2	0.0	0.0	0.0	0.0
Light Liquids	88.8	10.7	0.1	0.3	0.0	0.0
Valves:						
Gas Vapor	81.6	16.7	0.9	0.9	0.0	0.0
Heavy Liquids	86.3	13.7	0.0	0.0	0.0	0.0
Light Liquids	71.4	25.0	0.8	2.1	0.6	0.1
Loading Arm Valves:						
Gas Vapor	16.3	48.8	4.7	9.3	16.3	4.7
Heavy Liquids	0.0	87.5	0.0	12.5	0.0	0.0
Light Liquids	32.4	60.2	4.6	2.8	0.0	0.0
Open-Ended Lines:						
Gas Vapor	64.7	17.6	0.0	11.8	5.9	0.0
Heavy Liquids	56.3	43.8	0.0	0.0	0.0	0.0
Light Liquids	71.7	19.6	2.2	4.3	1.1	1.1
Pump Seals:						
Gas Vapor	NA	NA	NA	NA	NA	NA
Heavy Liquids	75.0	25.0	0.0	0.0	0.0	0.0
Light Liquids	66.0	26.1	1.1	4.5	1.1	1.1
"Other"*:						
Gas Vapor	0.0	42.1	15.8	26.3	10.5	5.3
Heavy Liquids	85.7	0.0	0.0	14.3	0.0	0.0
Light Liquids	69.0	21.2	0.9	6.2	2.7	0.0

* "Other" includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

Table 5-16a

Petroleum Marketing Terminals Study, 1992

OVA Screening Value Range	Number of Components	Percent of Components
0-0.99 ppm	4,882	79.24%
1-200 ppm	1,046	16.98%
201-1,000 ppm	107	1.74%
1,001-10,000 ppm	90	1.46%
>10,000 ppm	36	0.58%
TOTAL	**6,161**	**100.00%**

Table 5-16b

Refinery Assessment Study, 1980

TLV Screening Value Range	Number of Components	Percent of Components
0-0.99 ppm	3,277	58.41%
1-200 ppm	1,090	19.43%
201-1,000 ppm	319	5.69%
1,001-10,000 ppm	446	7.95%
>10,000	478	8.52%
TOTAL	**5,610**	**100.00%**

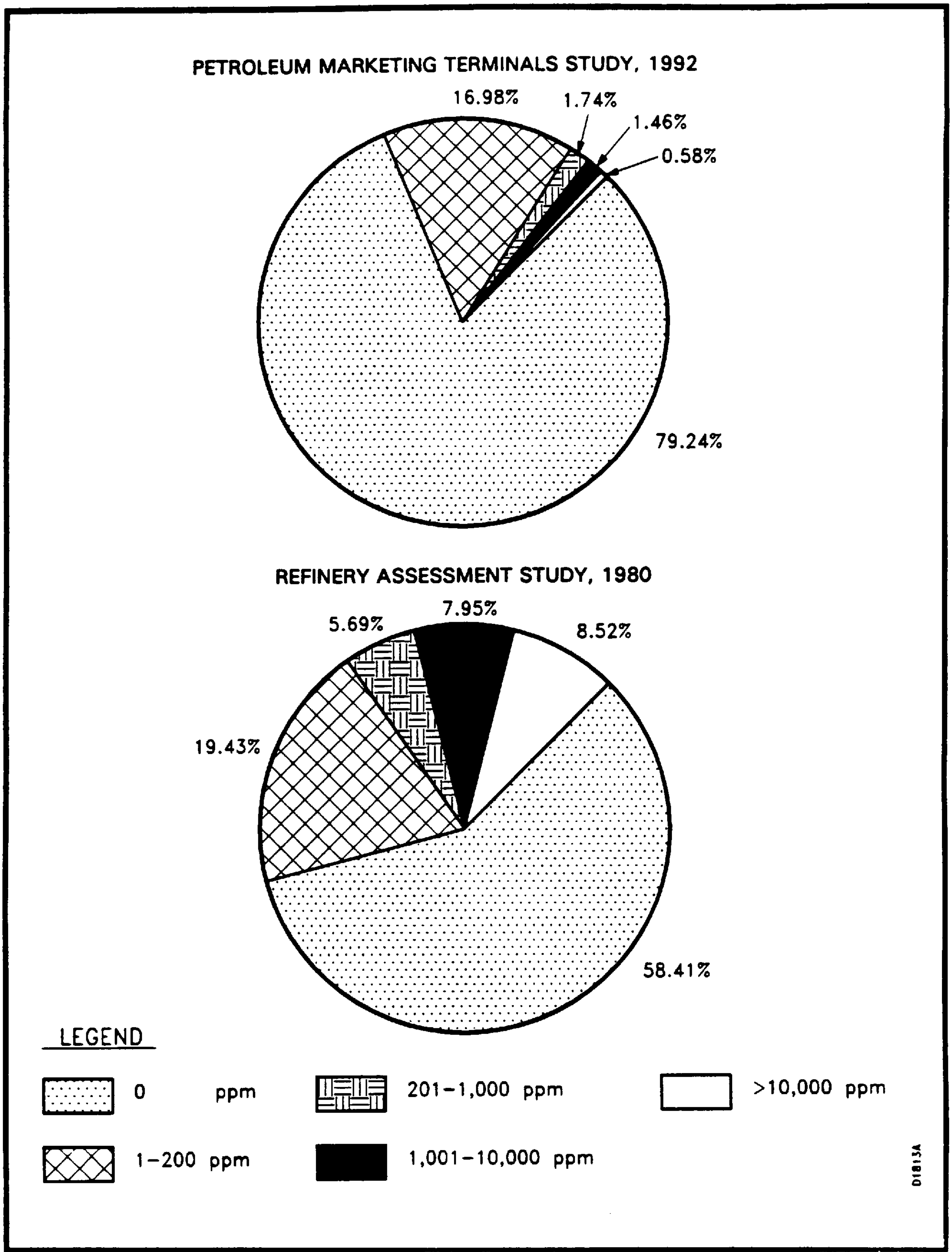


Figure 5-15. Comparison of Screening Value Distributions (LL, HL, and Gas) Between Petroleum Marketing Terminals Study (1992) and Refinery Assessment Study (1980).

The screening value ranges shown in Tables 5-16a and 5-16b are depicted graphically in the pie charts shown in Figure 5-15. In reviewing the screening value concentrations from the marketing terminal study and the Refinery Assessment Study several differences between the two studies should be noted:

- The refinery screening measurements were collected using a Bacharach Instrument TLV® Sniffer calibrated with hexane; marketing terminal screening measurements were collected using an OVA instrument calibrated with methane. However, even if screening values in the 1980 refinery Assessment Study were revised to an OVA calibrated to methane basis, the percent of higher leaking components in the marketing terminal study would still be far lower than the adjusted refinery results. It should also be noted that the OVA will read approximately the same when measuring hexane or methane.

- The refinery screening measurements were collected in 1979 from 13 different refineries, none of which regularly screened their components for leaks; the marketing terminals measurements were collected in 1992 from 4 different marketing terminals, one of which screened components for leaks.

- The total number of components screened at the marketing terminals actually exceeded the number of components screened in the 1980 Refinery Assessment Study.

The distribution of leaking components by component type was also evaluated for the marketing terminals screening data. Here a leaker in defined as a component that has a screening value greater than or equal to 10,000 ppm. Table 5-17 summarizes the number of leaking components for each component type and service category. The fourth column in Table 5-17 shows the percent of components within a particular component category that were leaking. Thus, for example, 1 out of 17, or 5.9% of gas vapor open-ended lines were "leakers." The totals on the bottom of Table 5-17 show the total number of components screened and the total number of leakers. The total number of leakers was 36 out of 6,161 components screened or 0.58%. The last column of Table 5-17 shows the distribution of leakers for the 36 leaking components. Thus, for example, gas vapor open-ended lines accounted for 1 out of 35, or 2.8% of the leaking components.

Table 5-17

Distribution of Leaking Components By Screening Value: All Plants and All Components

Component Type	Total Number of Components Screened	Number of Components Leaking (≥ 10,000 ppm)	Percent of Components Leaking	Percent of Total Leakers
Connectors:				
Gas Vapor	157	1	0.64	2.78
Heavy Liquids	284	0	0.00	0.00
Light Liquids	2,561	0	0.00	0.00
Valves:				
Gas Vapor	114	0	0.00	0.00
Heavy Liquids	277	0	0.00	0.00
Light Liquids	2,245	15	0.65	41.67
Loading Arm Valves:				
Gas Vapor	43	9	20.93	25.00
Heavy Liquids	8	0	0.00	0.00
Light Liquids	108	0	0.00	0.00
Open-Ended Lines:				
Gas Vapor	17	1	5.89	2.78
Heavy Liquids	16	0	0.00	0.00
Light Liquids	92	2	2.17	5.56
Pump Seals:				
Gas Vapor	NA	NA	NA	NA
Heavy Liquids	12	0	0.00	0.00
Light Liquids	88	2	2.33	5.56
"Other"[a]:				
Gas Vapor	19	3	15.79	8.33
Heavy Liquids	7	0	0.00	0.00
Light Liquids	113	3	8.11	8.33
Totals	6,161	36	0.58	100.00

[a] "Other" includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

Evaluation of Table 5-17 reveals the following:

- A large percent of loading arm valves in gas service (vapor return valves) leak (20.9%) and they account for 25.0% of all leakers.
- Although only a small percent of valves leak (0.65%), they account for 41.7% of all leakers.
- 0.6% of connectors leaked and they accounted for 2.8% of all leakers.
- All of the leakers for connectors and loading arm valves were in gas service.
- All of the leakers for valves and pump seals were in light liquid service; and
- There were no leakers in heavy liquid service for any of the component types.

5.6.3 Effects of Load and Service on Screening Value Concentrations

It was considered desirable to determine whether the service or load conditions had an effect on the screening value concentrations. Table 5-18 presents statistics for the mean screening value concentrations by service (gas vapor, heavy liquid, or light liquid) and load (load or no load). "Load" is defined as process fluid flowing through the component and "no load" is defined as a liquid-filled component but with no flow. Analysis of variances (ANOVAs) were performed to determine if the average screening value concentrations presented in Table 5-18 differed significantly depending on the service and load conditions. These ANOVAs were performed for each component type.

To test the effects of service and load for each component type, the number of screened values within each service and load must be sufficiently large. As shown in Table 5-18, most of the screened components were connectors and valves. In addition, there were sufficient numbers of connector and valves representing each of the service types and load conditions. For the remaining four component types (i.e., loading arm valves, open-ended lines, pump seals, and "other"), there was not a large number of screened values representing each of the service types and load conditions. Therefore, reliable statistical conclusions about the effects of service and load could only be drawn for connectors and valves.

Table 5-18

Summary Statistics for Phase and Load Screening Concentrations by Component

Component Type and Phase	Load					
	No			Yes		
	Number Screened	Mean (ppm)	Std. Dev. (ppm)	Number Screened	Mean (ppm)	Std. Dev. (ppm)
Connectors:						
Gas Vapor	100	199.4	1352.9	57	46.8	331.2
Heavy Liquid	281	0.8	5.0	3	15.7	27.1
Light Liquid	2,302	7.8	88.7	259	8.0	78.1
Valves:						
Gas Vapor	67	8.1	50.4	47	59.1	241.6
Heavy Liquid	269	1.1	4.9	8	2.3	4.2
Light Liquid	1874	363.3	4435.0	371	842.0	7768.6
Loading Arm Valves:						
Gas Vapor	32	15194.7	40026.1	11	423.2	1194.7
Heavy Liquid	7	10.4	6.9	1	2700.0	--[a]
Light Liquid	93	147.0	494.8	15	166.5	296.0
Open-Ended Lines:						
Gas Vapor	16	1343.2	3804.7	1	0.0	--[a]
Heavy Liquid	16	20.2	36.3	0	--[b]	--[b]
Light Liquid	73	4952.7	39783.1	19	4.5	14.0
Pump Seals:						
Gas Vapor	NA	NA	NA	NA	NA	NA
Heavy Liquid	11	6.6	12.2	1	0.0	--[a]
Light Liquid	65	2165.2	12661.2	23	185.5	831.9
"Other"[c]:						
Gas Vapor	8	10021.6	24271.5	11	10655.5	29766.7
Heavy Liquid	5	0.0	0.0	2	1050.0	1484.9
Light Liquid	102	918.4	4053.3	11	409.1	1356.8

[a] Not sufficient data to calculate standard deviation.

[b] No screening value data obtained for given load and phase.

[c] "Other" includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

The results of this analysis showed that, for connectors, there was no significant service or load effect. For valves, service had a significant effect on the average screening value concentrations. An additional ANOVA was performed for valves to determine the effects of service and valve size. In this analysis the following size categories were used: 0-2", 2-4", 4-6", 6-8", and >8". The results of this analysis showed that size and the size service interaction had significant effects on the screening value concentrations. Detailed results of this analysis are given in Appendix A.

5.7 RESULTS OF COMPARISON OF VAPOR LEAK COMPOSITIONS WITH LIQUID STREAM COMPOSITIONS

This section presents a comparison of the relative concentrations of selected chemical species in the vapor leaking from various components (i.e. the fugitive emissions) to the concentrations of those species in the liquid flowing through the line on which the component is located. The selected chemical species are:

- n-Hexane.
- Isooctane.
- MTBE.
- Benzene.
- Toluene.
- Ethylbenzene.
- p-Xylene.
- m-Xylene.
- o-Xylene.
- Cumene.

The results of this comparison are shown in Tables 5-19, 5-20, and 5-21, for Marketing Terminals A, B, and D, respectively. This testing was not conducted at Marketing Terminal C. These tables present the ratio of the mass fraction of each species in the vapor leak divided by the mass fraction of each species in the comparable liquid stream. Also shown are the mean, the standard deviation, the confidence intervals, and the "T" statistic

Table 5-19

Results of Non-parametric Tests to Determine Significance of Effects of Service and Load on Screening Value Concentrations

Component Type	Service	Load	Service x Load
Connectors	NS*	NS	NS*
Valves	0.0343	NS	NS
Loading Arm Valves	0.0409	NS	0.0231
Open-Ended Lines	NS	NS	NS
Pump Seals	NS	NS	NS
"Other"	0.0001	NS	NS

Note: The values in the table are p-values at which the indicated effect is statistically significant. Where NS appears, the effect is not statistically significant at the 0.05 level.

* Significant at the 0.05 level on the basis of a parametric test.

• "Other" includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

Table 5-20

Results of Nonparametric ANOVA to Determine Significance of Effects of Phase and Size on Screening Value Concentrations for Valves

Component	Phase	Size	Phase*Size
Valves	0.0001	0.0001	0.0004

Table 5-21

Terminal "D" Fugitive vs. Stream Composition Ratios - Mass Fraction Basis

Gas Sample	Liquid Sample	Component	Product	OVA Screen Value	n-Hexane	Isooctane MTBE	Total Speciated Aliphatics	Benzene	Toluene	Ethyl Benzene	p-Xylene	m-Xylene	Cumene	o-Xylene
D012	D015B	Valve	Spr UnPb	3400	0.41	0.80	0.48	0.36	0.89	1.28		2.06		1.08
D013	D015B	Valve	Spr UnPb	3400	0.35	0.68	0.40	0.32	0.80	1.18		1.84		1.10
D014	D015B	Valve	Spr UnPb	3300	0.29	0.75	0.36	0.38	0.75	1.01		1.60		0.81
D018	D019B	Valve	Spr Reg	46	4.27		1.64							
D025	D026B	Valve	Spr Reg	11000	0.44	1.59	0.71	0.30	0.61	0.82		0.16		1.31
D027	D028B	Valve	Reg UnPb	8100	0.81	0.37	0.52		2.24			3.91		
D029	D028B	Valve	Reg UnPb	12000	0.50	1.05	0.72	0.36	0.71			1.84		
D030	D028B	Valve	Reg UnPb	12000	0.66	1.12	0.85							
D032	D028B	Valve	Reg UnPb	21000	0.45	0.96	0.65	0.27	0.72			2.35		1.41
D047	D048B	Connector	Spr Reg	1100	1.34	0.37	0.68							
D049	D048B	Connector	Spr Reg	1100	1.32	0.79	0.96							
D050	D048B	Connector	Spr Reg	1100	2.52	0.49	1.13							
D052	D048B	Connector	Reg UnPb	96	1.17	0.71	0.86							
D057	D048B	Connector	Reg UnPb	79	1.38		0.48							
D061	D048B	Connector	Spr UnPb	27		0.44	0.23							
D071	D048B	Connector	Spr UnPb	NA		1.60	0.31							
D073	D048B	Connector	Spr UnPb	520		0.79	0.15							
D085	D086B	Valve	Spr Env	4200	0.87	0.69	0.84	0.25	0.48	0.56		1.17		
D088	D089B	Connector	Spr Env	320	0.83	0.92	0.84		0.89					
MEANS					1.10	0.83	0.67	0.32	0.90	0.97		1.87		1.14
SAMPLE STANDARD DEVIATION					1.02	0.36	0.35	0.05	0.52	0.29		1.06		0.23
LOWER 95% CONFID. FOR POP. MEAN					**0.55**	**0.65**	**0.51**	**0.28**	**0.50**	**0.61**		**0.98**		**0.86**
UPPER 95% CONFID. FOR POP. MEAN					**1.65**	**1.02**	**0.84**	**0.37**	**1.30**	**1.33**		**2.76**		**1.43**
DATA POINTS					16	17	19	7	9	5		8		5
'T' STATISTIC USED					2.145	2.12	2.101	2.447	2.306	2.776		2.365		2.776

NOTES:

1) Mass fraction ratios are computed as:

$$\frac{\text{(fugitive compound ug/l)/(total fugitive HC ug/l)}}{\text{(liquid stream compound mg/l)/(total liquid stream mg/l)}}$$

2) Upper and lower confidence intervals computed from the formula : INTERVAL = MEAN +/- [@STDS(data)*('T' STATISTIC)/@SQRT(n)]
Where the 'T' statistic for 19 data points and 2 sided 95% confidence is 2.101.
Ref: Table V, Page 514, "Probability and Statistics for Engineers and Scientists", Ronald Walpole 2nd Ed. 1978.

3) **Because of the inability to explain these results in terms that fit the physical principles, we do not recommend that these results be used to estimate individual species emissions.**

used for the data evaluated. It should be noted that the QA/QC data discussed in Section 4.0 and Appendix D indicate that these results should be used with caution, especially for Marketing Terminals A and B. Accuracy checks for the Tracor GC often did not meet QA/QC objectives for these marketing terminals.

The QA/QC objectives were very stringent for this program. Multipoint, multi-species calibration, primarily at Marketing Terminals A and B, often did not meet these stringent objectives for particular chemical species. However, results from all three sites should give at least some idea of trends for mass fraction of vapor to mass fraction of liquid. Furthermore, results from Marketing Terminal D generally did meet the stringent objectives. The trends for Marketing Terminal D were similar to those in Marketing Terminals A and B, although individual mass fraction ratios differed widely.

Some of the data collected on site were not used in the results shown on Tables 5-19 through 5-21; however, all of the data are presented in Appendix C. The rationale for deleting data points from the statistical analyses included sampling/analytical problems, lack of sensitivity of analyses near the detection limits, and liquid sample points that were not representative of the vapor leak.

For example, liquid samples from the vapor recovery units often could not be taken from locations close to the corresponding vapor leak samples. Liquid samples taken from the vapor recovery units were often taken from a hatch or separator, frequently far downstream of the leaking component. The liquids in the vapor recovery unit can vary significantly in concentration from one location to another. The locations where liquid samples were taken were typically reservoirs containing condensate that could have collected for several days or even weeks. Not surprisingly, there is a high variability in the results from these vapor recovery area samples. These samples are not included in the three tables of results.

Several of the vapor samples were taken from components that screened at approximately background levels. Total hydrocarbons from these components were typically extremely low, but above the detection limit. Individual chemical species, however, were often not detectable or at the margins of detectability. The ratios of mass fractions of chemicals in the vapors compared with the mass fractions of the chemicals in the liquid streams showed high variability. These samples with screening values approximately equal to background levels were also not included in Tables 5-19 and 5-21.

A Tracor GC was used to speciate the vapor samples and the liquid streams. The Tracor GC was set-up primarily to determine the aromatic compounds. Because the Tracor GC was set up primarily for the aromatics, the aliphatics (n-hexane, isooctane, and MTBE) had coelution problems and the results were not as reliable as the aromatic data. All three aliphatics co-eluted with one of the other aliphatics at one point or another during testing. Because of these problems, we recommend that the aliphatic species results be combined, as they are presented in the tables.

The results shown on Tables 5-19 through 5-21 are different from what had been expected. Traditionally, it has been assumed that the composition in the vapor leak was the same as in the liquid stream. The mechanism for this assumption was that the liquid in the line leaks through the component seal as a liquid and then vaporizes after reaching the ambient air. If this is the controlling leak mechanism, then the mass fraction of the chemical species in the vapor leak and the mass fraction of the chemical species in the liquid stream would be equal, and the ratios for all species should be approximately equal to one.

Another proposed leak mechanism is that the liquids might vaporize within the line in a pocket of gas trapped below the seal area. If that were the controlling mechanism, then the fraction in the vapor leak should be predictable by applying Raoult's Law to the liquid stream composition. Raoult's Law would predict that the more volatile species should be present at higher fractions in the vapor leak than in the liquid stream (e.g. ratios greater than one), and the less volatile species should be present at lower fractions in the vapor leak than in the liquid stream (e.g. ratios less than one).

There is also the possibility of partial vaporization of some of the more volatile components at intermediate points along the leak pathway as the pressure drops from line pressure to ambient pressure. This mechanism would also result in an enrichment of the more volatile species in the vapor leak as compared to the liquid stream, but perhaps not to exactly the same degree as predicted by Raoult's Law.

None of these mechanisms are evident from an analysis of the data shown in Tables 5-19 through 5-21. The experimental data tend to indicate a result for the aromatics that is the inverse of Raoult's law, that is that the more volatile species are present at <u>lower</u> fractions in the vapor leak than in the liquid stream. The reason for this trend, which is repeated at all three marketing terminals, is not known at this time. There are several possibilities for explaining these results:

- We do not understand the controlling physical principles (i.e. it is not volatility, but viscosity or something else that controls species leak rates, or different types of leaks, such as pinhole vs. annular, that is complicating our analysis).
- The inverse relationship is an artifact of analytical response to the higher molecular weight species.
- We are not as effective at capturing the more volatile species in the bag as we are the less volatile species (i.e. they leak out of the component at or near a ratio of 1:1, but the more volatile species are preferentially lost through leaks in the bag enclosure as compared to the less volatile species).
- The inverse relationship is a random artifact due to scatter among a limited size data set.
- The accuracy and precision of the data analysis were insufficient to allow conclusions to be drawn.

Some combination of the above possibilities, or other unknown factors, could be causing the unexpected results. Without an explanation for the results that fits the physical principles, we do not recommend that these results be used to estimate individual species fractions of the total hydrocarbon emissions from marketing terminals. Additional study in other industries or in a laboratory environment may provide insight into this problem.

It is important to note that the inability to explain the results of the relationship between the vapor leak compositions with liquid stream compositions does not in any way affect the ability to develop meaningful emission correlation equations, default zero emission factors, stratified emission factors, or pegged component emission factors as discussed in this report.

5.8 RESULTS OF VAPOR LEAK COMPOSITION ANALYSIS AND LIQUID STREAM COMPOSITION ANALYSIS

The vapor leak composition was analyzed for Marketing Terminals A, B, and D. However, because of the large degree of scatter in the data (see Appendix C-1), we recommend that these compositions not be used for future stream or emission characterizations.

The liquid composition analysis (shown in Appendix C-1) shows less scatter than the vapor stream composition analysis. Table 5-22 shows the liquid stream analysis for Marketing Terminal D. This table is only for gasoline streams. The oil/water separator data are not included because of the wide differences in composition in this stream compared with the gasoline streams.

The QA/QC results indicated that the data for Marketing Terminal D were far more precise and accurate based on calibration data, stability of the instrument, and QC check agreement from day to day than results from Marketing Terminals A and B. We recommend that only Marketing Terminal D liquid data be used for quantitative purposes.

Please note again that the scatter of data and QA/QC results for the composition analysis for vapor and liquid streams does not in any way affect the ability to develop meaningful emission correlation equations, default zero emission factors, stratified emission factors, or pegged component emission factors as discussed in this report.

Table 5-22

Gasoline Liquid Stream Composition Analysis for Marketing Terminal D

Sample	Product	n-Hexane (mg/L)	Isooctane/MTBE (mg/L)	Total Speciated Aliphatics	Benzene (mg/L)	Toluene (mg/L)	Ethyl Benzene (mg/L)	p-Xylene (mg/L)	m-Xylene (mg/L)	Cumene (mg/L)	o-Xylene (mg/L)	Total (mg/L)	Percent Speciated
D015B	HOUn	278,366	55,089	333,455	13,226	106,885	17,165	14,739	29,743	1,005	17,530	533,748	71%
D019B	HOL	151,457	242,761	394,218	18,600	54,900	12,900	11,600	25,700	839	16,400	535,157	71%
D026B	HOL	240,500	74,500	315,000	17,040	50,840	12,200	11,000	24,600	802	15,700	447,182	60%
D028B	LOUn	130,000	248,000	378,000	20,100	35,170	8,770	8,090	19,700	98	12,400	482,328	64%
D031B	LOUn	196,000	132,000	328,000	21,700	35,400	8,570	8,250	18,500	116	11,700	432,236	58%
D048B	HOL	101,103	220,627	321,730	19,221	52,743	12,645	11,162	25,868	789	18,174	462,332	62%
D053B	LOUn	121,738	239,270	361,008	24,632	34,940	8,736	9,180	18,095	670	12,950	470,211	63%
D058B	LOUn	116,885	220,914	337,799	17,938	32,195	7,599	8,069	15,188	663	11,876	431,327	58%
D063B	HOUn	110,404	123,097	233,501	15,019	100,821	15,143	14,492	24,495	844	15,351	419,666	56%
D072B	HOUn	283,128	67,315	350,443	15,564	115,348	18,019	17,476	29,058	1,203	18,586	565,697	75%
D075B	HOUn	336,726	78,463	415,189	16,517	127,029	19,898	19,269	32,167	1,257	20,362	651,688	87%
D086B	HOUn	277,255	62,439	339,694	15,481	112,995	17,858	17,397	29,383	902	18,537	552,247	74%
D089B	HOUn	278,168	65,281	343,449	16,579	119,626	19,350	17,222	28,753	1,142	18,145	564,266	75%
@AVG		201,672	140,750	342,422	17,817	75,299	13,758	12,919	24,712	795	15,978	503,699	67%
@STDS		83,437	80,435	43,795	3,063	38,218	4,442	4,047	5,311	358	2,919	69,253	—

HOUn = high octane unleaded
LOUn = low octane unleaded

HOL = high octane leaded
LOL = low octane leaded

5.9 LOADING ARM DRIP MEASUREMENT RESULTS

A measurement of drips from the gasoline loading arms was conducted at Marketing Terminals B and D. These drips occur immediately after the trucks have been loaded and the liquid loading arms are disconnected from the tank trucks. The results of the tests are shown on Tables 5-23 and 5-24. In effect, very little dripped out of the lines after loading the gasoline into the trucks. The amount that dripped out was limited to only a few drops for each truck loading event. The measurement device used did not have a scale below 0.1 milliliters (mL). Almost all of the liquid drips from the loading arms at both terminals tested measured below the minimum reading on the measurement device. Liquid volumes measured at Marketing Terminal B may have been slightly undermeasured because of some evaporation or clingage from the collection pan. A different collection device was used at Marketing Terminal D. However, drip amounts from Marketing Terminal D were actually lower than those at Marketing Terminal B, even with reduced clingage and evaporation.

It is clear that most liquid drip losses from the gasoline loading arms are less than 0.1 mL. If it is assumed that the drips below the measurement limit are one-half of the measurement limit (0.05 mL), then the average of the 32 drip measurements is 0.17 mL.

Table 5-23

Terminal B Gasoline
Loading Arm Liquid Drip Measurements

Load Arm No.	LR1	LR2	LR3	LR4	LR5	LR6
1	1.5 mL	<0.1 mL		<0.1 mL		<0.1 mL
2	<0.1 mL					<0.1 mL
3				<0.1 mL		<0.1 mL
4	<0.1 mL	<0.1 mL	<0.1 mL		<0.1 mL	
5		<0.1 mL	<0.1 mL		2.3 mL	
6	<0.1 mL					

LR = Loading Rack
mL = milliliters

Table 5-24

Terminal D Gasoline Loading Arm Liquid Drip Measurements

Load Arm No.	LR1		LR2		LR3		LR4
	A	B	A	B	A	B	A
1	<0.1 mL	<0.1 mL	<0.1 mL	<0.1 mL	<0.1 mL	<0.1 mL	<0.1 mL
2	<0.1 mL	—	<0.1 mL	—	<0.1 mL	—	<0.1 mL
3	<0.1 mL	0.1 mL	0.1 mL	—	<0.1 mL	—	<0.1 mL

LR = Loading Rack
mL = milliliters

6.0 CONCLUSIONS AND RECOMMENDATIONS

In general, the data analysis techniques used for this study were consistent with the approach outlined by the U.S. Environmental Protection Agency (U.S. EPA) in the published document *Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP* (U.S. EPA, 1988). Standard data analysis techniques were followed to ensure the results would be comparable with U.S. EPA published results and those from similar studies. Conclusions and recommendations are made for default zero emission factors and mass emission rate-to-screening value correlation equations and also for the comparison of fugitive emission compositions with liquid stream compositions.

6.1 MASS EMISSION CALCULATIONS

The primary objective to determine emission factors and new fugitive emission correlation equations for components in light liquid and gas services specifically related to the petroleum marketing terminals was achieved.

Default zero emission factors were obtained for connectors, pumps, and valves in light liquid service, for valves in gas service, and for open-ended lines in light liquid and gas services (combined). The new default zero emission factors and their 95% confidence intervals are shown in Table 6-1. Statistical analyses of the data following U.S. EPA procedures indicated that each default zero emission factor was statistically different from the established EPA-SOCMI and the refinery default zero emission factors. The reduction in these default zero emission factors relative to the SOCMI and refinery default zero emission factors ranged from 54 to 99^+ percent.

New emission rate to screening value correlation equations were developed for valves and pump seals in light liquid service, connectors in light liquid and gas services (combined), and a combined equation for loading arm valves and open-ended lines in light liquid and gas services (combined). There were insufficient data to develop a new emission correlation

Table 6-1

Default Zero Emission Factors (Total Hydrocarbons)

Component Type	Service	Number of Tests	Default Zero Emission Rate (lbs/hr)	Lower 95% Confidence Limit (lbs/hr)	Upper 95% Confidence Limit (lbs/hr)
Connectors[a]	Light Liquid	12	6.5×10^{-6}	3.9×10^{-6}	1.1×10^{-5}
Valves	Gas	8	5.9×10^{-6}	3.8×10^{-6}	9.3×10^{-6}
Valves	Light Liquid	11	3.5×10^{-6}	2.4×10^{-6}	5.2×10^{-6}
Open-Ended Lines[b]	Light Liquid and Gas Combined	8	4.5×10^{-6}	2.6×10^{-6}	7.7×10^{-6}
Pumps	Light Liquid	8	3.9×10^{-5}	2.1×10^{-5}	7.4×10^{-5}

[a] Also use for the gas connectors and "other" component types (gas, LL).

[b] Also use for loading arm valves (gas, LL).

equation for valves in gas service. Without sufficient data to determine new emission correlation equations, the recommended equation to use for valves in gas service is the equation developed during the 1980 Refinery Assessment Study. The new equations and the equation for valves in gas service are shown in Table 6-2. Evaluation procedures developed by the U.S. EPA were applied to the new emission correlation equations. All of the newly developed emission correlation equations met U.S. EPA requirements for statistical validity.

Using the U.S. EPA procedures the equations for connectors, light liquid valves, and light liquid pump seals were compared to established SOCMI and refinery equations. No equations were developed for loading arm valves and open-ended lines during the SOCMI and refinery studies. Thus, there was no basis for comparison for the loading arm valve and open-ended line emission correlation equation. The three equations that were compared to the established equations were shown to estimate emissions that were significantly lower than the refinery equations. In addition, the equations for connectors and light liquid valves were shown to estimate emissions that were significantly lower than the SOCMI equations. The new equation for pump seals did not differ significantly from the SOCMI pump seal equation, however.

Analysis of the screening value data also shows that the distribution of screening value concentrations obtained for petroleum marketing terminals are significantly lower than the distribution of screening value concentrations obtained during the SOCMI and refinery studies of the late 1970s and early 1980s. Figure 6-1 shows the distribution of the screening values for the 1980 Refinery Assessment Study and the current petroleum marketing terminals study. Please note that even though an attempt was made to obtain data from several regions of the country to improve data representativeness, data were obtained from only four marketing terminals that may not be representative of the industry as a whole. In an attempt to achieve a representative data set, the owners and/or operators of the marketing terminals were advised at the beginning of the study not to perform any type of unusual maintenance activities prior to testing, and no unusual maintenance activities are believed to have taken place.

Table 6-2

Predictive Emission Correlation Equations for Total Hydrocarbon Mass Emission Rates

Component Type	Service	Number of Data Pairs	Emission Correlation Equation [a,b]	Correlation Coefficient	Standard Deviation of Regression	Default Zero Screening Value (ppm)
Connectors [c,d]	Light Liquid and Gas Combined	36	$ER = (4.65 \times 10^{-5}) \times (SV)^{0.426}$	0.412	0.604	0.01
Valves [e]	Gas	79	$ER = (2.16 \times 10^{-6}) \times (SV)^{1.14}$	0.76	0.78	2.43
Valves	Light Liquid	46	$ER = (6.34 \times 10^{-6}) \times (SV)^{0.708}$	0.845	0.460	0.44
Loading Arms Valves/ Open-Ended Lines [f]	Light Liquid and Gas Combined	40	$ER = (7.66 \times 10^{-6}) \times (SV)^{0.959}$	0.838	0.632	0.57
Pumps	Light Liquid	12	$ER = (6.57 \times 10^{-5}) \times (SV)^{0.534}$	0.757	0.667	0.38

[a] ER = Emission Rate (lbs/hr).

[b] SV = Screening value (ppm) using the OVA calibrated with methane.

[c] Also use for "other" component types (Gas, LL).

[d] Used the default zero emission factor for light liquid connector to estimate the default zero screening value.

[e] Correlation equation developed in the 1980 Refinery Assessment Study (Radian, 1980).

[f] Used the default zero emission factor for open-ended lines (light liquid and gas services combined) to estimate the default zero screening value.

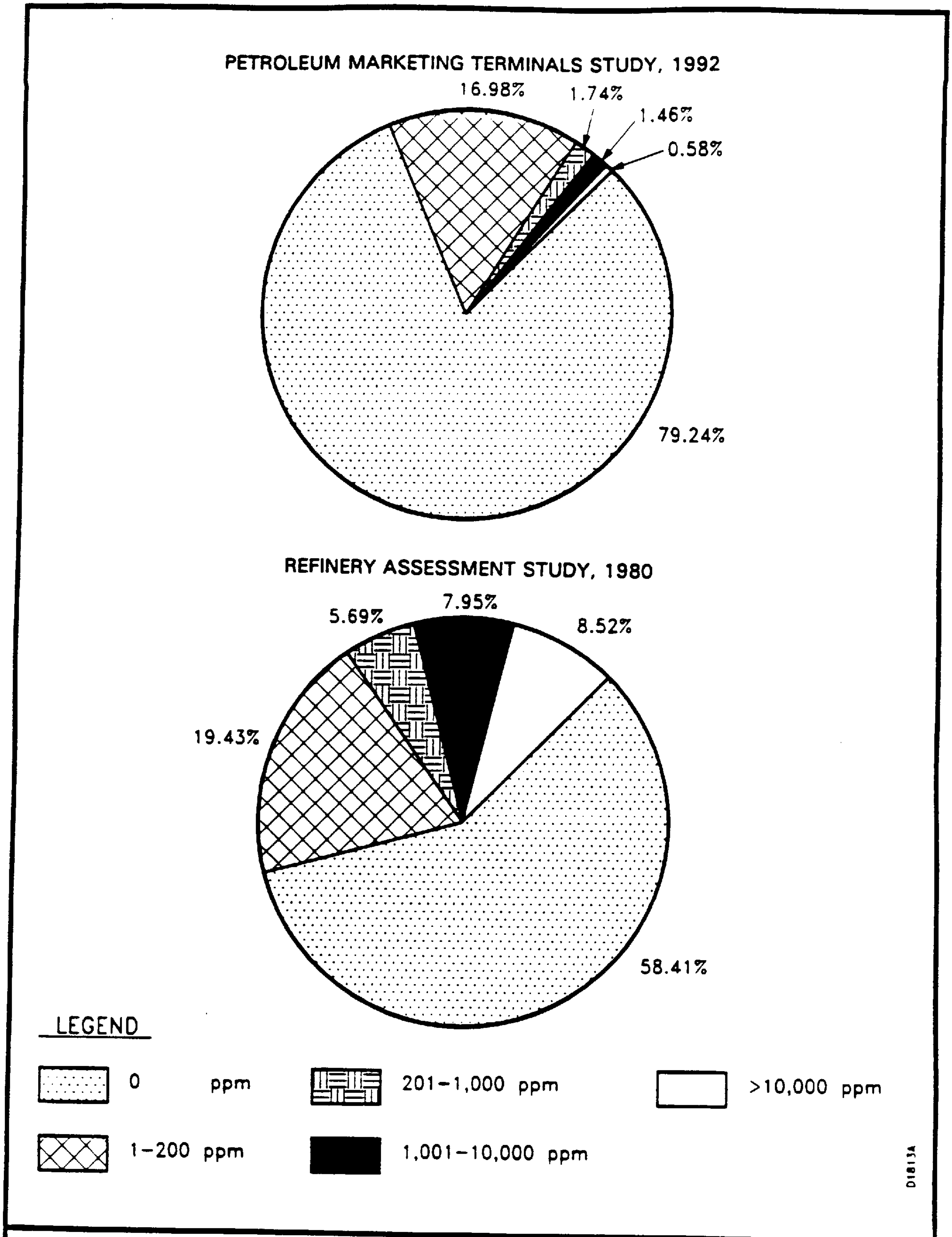


Figure 6-1. **Comparison of Screening Value Distributions (LL, HL, and Gas) Between Petroleum Marketing Terminals Study (1992) and Refinery Assessment Study (1980).**

Average emission factors and stratified emission factors were also developed using the screening value data gathered from the four marketing terminals and the newly developed emission correlation equations. Table 6-3 shows the new average emission factors and stratified emission factors for petroleum marketing terminals. Emission factors were developed for each component type and service category. Although analysis of the new emission correlation equations showed that some component types and services had the same emission rate versus screening value relationship (e.g., gas and liquid connectors, open-ended lines and loading arm valves), average emission factors for these components were found to differ appreciably because the screening distributions for these components differed significantly. Additional analysis performed on the screening value data showed that for some of the components, average screening value concentrations differed, depending on the service of the component. Thus, average and stratified emission factors were always segregated into different component types and services to reflect the differences in the screening value concentrations in order to obtain more accurate emission estimates. Analysis of the average emission factors showed that the new emission factors were significantly lower than the established emission factors for all comparable component types except for open-ended lines. The stratified emission factors given in Table 6-3 represent two screening value ranges:

- 0 – 999 ppm.
- ≥1,000 ppm.

Due to the very small number of components that screened at greater than 10,000 ppm, leak/no leak emission factors could not be developed. Of the 6,161 components screened, only 0.58% were >10,000 ppm, which was insufficient to develop adequate "leaking emission factors" for each component type. The strata could not be broken into smaller categories (0–499, 500–1,000 ppm, etc.) also due to the lack of screening values that were obtained within these smaller ranges.

Based on the analysis performed, it is clear that for petroleum marketing terminals the new emission correlation equations, default zero emission factors, and stratified emission factors will provide more accurate estimates of fugitive emissions from equipment leaks than the

Table 6-3

Petroleum Marketing Terminal Average and Stratified Total Hydrocarbon Emission Factors

Component Type	Service	Average Emission Factor (lbs/hr)	Stratified Emission Factor (lbs/hr)	
			0 – 999 ppm	≥1000 ppm
Connectors	Gas	0.000067	0.000030	0.0020
	Light Liquid	0.000023	0.000020	0.0010
Valves	Gas[a]	0.00016	0.000084	0.0090[b]
	Light Liquid	0.00015	0.000026	0.0046
Loading Arm Valves	Gas	0.045	0.00066	0.15
	Light Liquid	0.00087	0.00047	0.015
Open-Ended Lines	Gas	0.0067	0.00022	0.037
	Light Liquid	0.0065	0.00017	0.097
Pump Seals	Light Liquid	0.00093	0.00015	0.011
"Other"[c]	Gas	0.0014	0.00062	0.0025
	Light Liquid	0.00025	0.000073	0.0021

[a] Based on refinery correlation equation (Radian, 1989).

[b] Emission factor based on only one screening value.

[c] "Other" includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

current SOCMI or refinery emission correlation equations and emission factors. Use of the average emission factors is somewhat more uncertain because they inherently assume that the leak distribution for the four terminals studied is valid for any other terminal which has obtained their own screening values.

6.2 FUGITIVE EMISSION COMPOSITION AND LIQUID STREAM COMPOSITION COMPARISON

Traditionally, it has been assumed the composition in the vapor leak is the same as in the liquid stream. The assumed mechanism is that the liquid in the line leaks through the component seal as a liquid and then vaporizes after reaching ambient air. As an alternative, Raoult's Law could be applied to determine the speciated vapor fraction based on liquid stream composition if the mechanism is identified as liquid vaporizing in the line with a pocket of gas trapped below a seal area. In this study, an attempt was made to determine the relationship between the composition of air toxics in the vapor (fugitive emissions) and the composition in associated liquid. However, the results were inconclusive. No satisfactory physical explanation of the results has yet been determined. The results do not follow pre-study expectations. The limited data set may not have been sufficient for this comparison to overcome random data scatter. It should be noted that the stringent QA/QC objectives defined at the start of this study were not fully met for the liquid and fugitive emission composition analysis at Marketing Terminals A and B. However, even with improved precision and accuracy, the data indicate that the results would still be inconclusive. Without an explanation of the results that fits the physical principles, we do not recommend that these results be used to estimate individual species fractions of the total hydrocarbon emissions from marketing terminals. Additional study in other industries or in a laboratory environmental may provide insight into this problem.

7.0 REFERENCES

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