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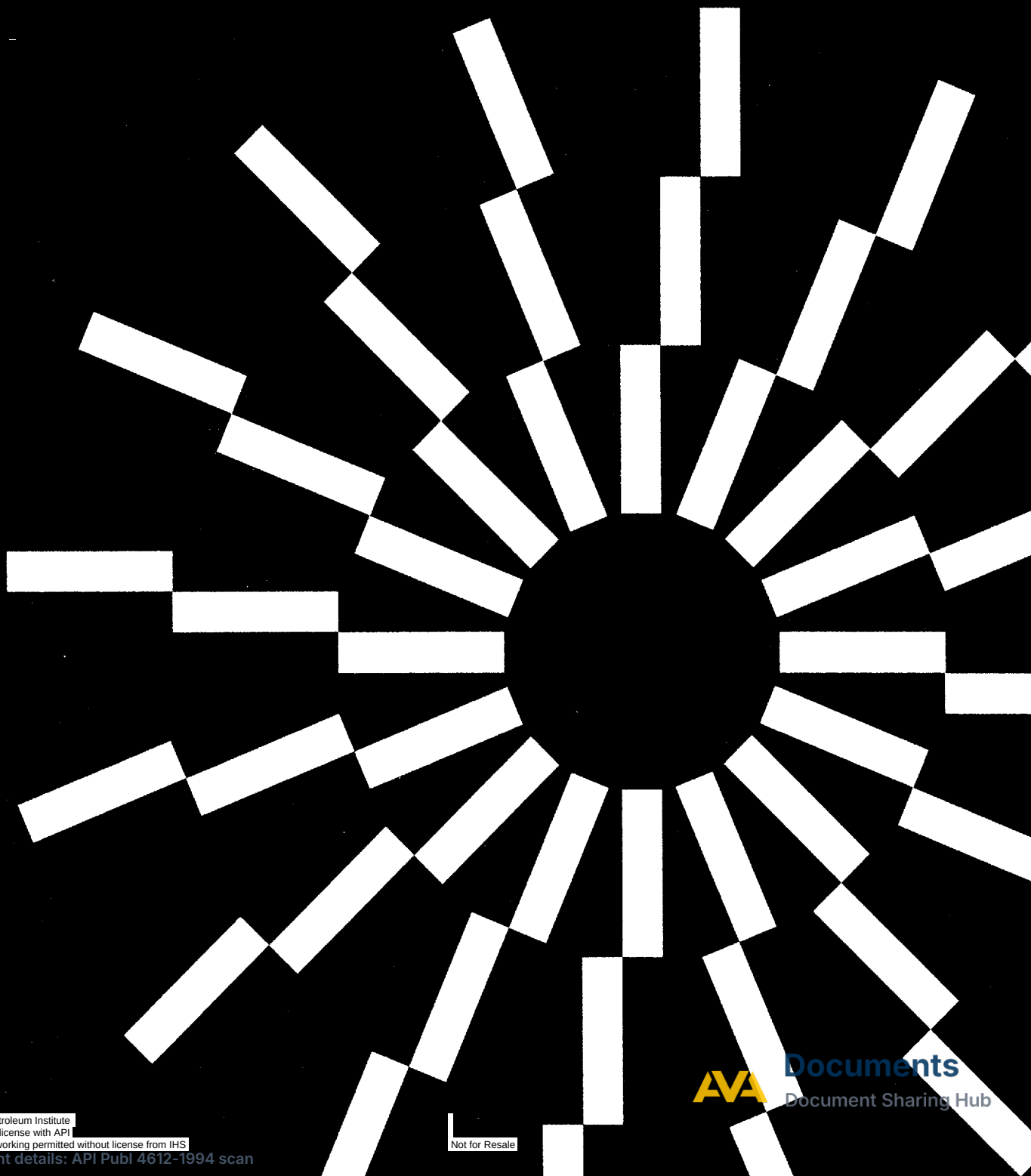
Study of Refinery Fugitive Emissions from Equipment Leaks



Air Toxics Multi-Year Study

April 1994

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1993 Study of Refinery Fugitive Emissions from Equipment Leaks

Volume I: Data Analysis, Conclusions and Recommendations

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NOTE: This is to advise the reader that these studies are now under review by the U.S. Environmental Protection Agency. The Agency's review may be complete by summer 1994.

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API STAFF CONTACTS:

Karin Ritter, Health and Environmental Affairs Department

Paul Wakim, Statistics Department

MEMBERS OF THE AIR TOXICS MULTIYEAR STUDY WORKGROUP:

Julian Blomley, UNOCAL

Miriam Lev-On, ARCO Products Company

Richard Russell, API Consultant

Hal Taback, API Consultant

Daniel VanDerZanden, Chevron Research and Technology Company

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ABSTRACT

The Western States Petroleum Association (WSPA) and the American Petroleum Institute (API) commissioned this "1993 Study of Refinery Fugitive Emissions from Equipment Leaks," called the "1993 Refinery Study" in this document. The results of this study are new emission correlation equations that relate the mass of hydrocarbon emissions to specific emission rates measured by screening components with an Organic Vapor Analyzer (OVA). Emission correlation equations were developed for valves, pumps, connectors, and open-ended lines, based on established statistical methodologies recommended by the United States Environmental Protection Agency (U.S. EPA). An alternative statistical methodology called the measurement error method (MEM) was also examined. The emission correlation equations from the MEM technique account for variabilities in screening values and in the measured mass emissions. Additional evaluation of this methodology is still in progress.

The emission correlation equations from the 1993 Refinery Study result in emission calculations that are significantly lower than emission calculations based on published emission correlation equations developed from data in Radian's *Assessment of Atmospheric Emissions from Petroleum Refining*, called the 1980 Refinery Study in this document. However, much of the difference in emission correlation equations is based on different data collection and data analysis techniques in the two studies. Changes in equipment and operating procedures may also have contributed to the differences in emission correlation equations.

New "zero component emission factors" were developed for components that screen at background hydrocarbon levels and were compared to the zero component emission factors published in the U.S. EPA Protocols Document. Depending on the component category, the factors developed in this study were similar, higher, or lower than those in the EPA document. New emission factors were also developed for components that have screening values above the range of the screening instrument (pegged components). These factors are significantly lower than those published in the EPA document.

Several special studies were also conducted as part of the 1993 Refinery Study as a quality assurance measure and to investigate the variability of factors used to develop the emission correlation equations, zero component emission factors, and pegged component emission factors. The special studies discussed in this report include:

- Effects of potentially leaking OVA probes;
- Screening variability;
- Nitrogen flow rate variability;
- Benefits of additional bagging;
- Effects of dilution probe data; and
- Effects of high screening variability data.

The results of these special studies increase the understanding of the emission correlation equations, zero component emission factors, and pegged component emission factors, but do not indicate that any changes to these equations or emission factors are required.

11/11/11

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EXECUTIVE SUMMARY

Fugitive emissions from equipment leaks are a source of hydrocarbon emissions from refineries. To estimate these emissions, regulatory and industry groups have developed numerous emission factors and emission correlation equations. The primary source of emission factors and emission correlation equations for fugitive emissions from refineries has been a study that was directed by the United States Environmental Protection Agency (U.S. EPA) and conducted in the late 1970s. Therefore, the Western States Petroleum Association (WSPA) and the American Petroleum Institute (API) commissioned this study of refinery fugitive emissions to determine how emission correlation equations have changed since the 1970s.

The primary objective of this 1993 Refinery Study was to develop new emission correlation equations for refineries and to compare these equations to those obtained in the 1980 Refinery Study. Secondary objectives were to obtain new zero component emission factors and pegged component emission factors and to assess the relationship between the vapor leak composition and the corresponding liquid stream composition.

Emission correlation equations allow conversion of hydrocarbon concentration values obtained by a portable hydrocarbon analyzer, or screening values, to a mass emission rate. The hydrocarbon analyzer used in this study was an Organic Vapor Analyzer (OVA), Model 108. The OVA 108 can measure hydrocarbon concentration values from 1 ppm to 100,000 ppm (with a dilution probe). Screening values that measure below 1 ppm or below background hydrocarbon levels often still have some mass emissions. Special emission factors, called zero component emission factors, need to be developed for this category of low-emitting components. Another set of emission factors, called pegged component emission factors, need to be developed for components with screening values >100,000 ppm.

For the 1993 Refinery Study, samples were collected from five refineries: two located in southern California, two in northern California, and one in Pennsylvania. All five refineries had inspection/maintenance (I/M) programs to reduce the number of leaking components.

ES-1

Sampling was conducted over approximately a six-month period by two separate sampling teams. Approximately 100 components were sampled at each of the five refineries.

Approximately 82% of the bag samples were used in the data analysis. The remaining 18% failed to meet the quality control objectives. At each of the five refineries the following component types were sampled:

- Valves;
- Pumps;
- Connectors; and
- Open-ended lines.

Table ES-1 shows the number of valid samples collected for each component type used in the development of the emission correlation equations (248 total), pegged component emission factors (71 total), zero component emission factors (102 total), and those used to ensure data quality (audit sample duplicates, nitrogen flow test duplicates, and accuracy checks; 119 total).

Only a few leaking compressors and pressure relief valves were found at the five refineries, therefore emission correlation equations and pegged component emission factors were not developed for these component types.

A number of special studies were also conducted as a part of the 1993 Refinery Study. These special studies were all conducted as quality assurance measures or to examine the variability of data used to develop the emission correlation equations.

EMISSION CORRELATION EQUATIONS

The 1993 Refinery Study developed two separate sets of new emission correlation equations. The first set of emission correlation equations is based on the methodology established in the U.S. EPA document entitled *Protocol for Equipment Leak Emission Estimates* (U.S. EPA,

Table ES-1 Number of Valid Bagged Samples and High Screening Variability Bagged Samples in 1993 Refinery Study

	Number of Samples Used for Equations	Pegged Components	Zero Components	QA/QC Components ^a
Connectors-Flanges	19	3	9	9
Connectors-Other	29	14	12	14
OEL	22	11	9	4
Pumps-Heavy liquid	10	0	5	5
Pumps-Light liquid	27	5	7	6
Valves	141	38	60 ^b	81
TOTALS	248	71	102	119

OEL = open-ended lines

QA/QC = quality assurance/quality control

^a Includes test duplicates (20), nitrogen flow sample duplicates (60), audit samples (34), and accuracy checks (5).

^b Includes two pressure relief valves.

1993) and is shown in Table ES-2. This set of emission correlation equations follows the established, widely accepted, ordinary least-squares (OLS) statistical methodology.

The second set of 1993 emission correlation equations, developed as part of this study, is based on an alternative statistical analysis technique. This alternative technique, the measurement error method (MEM), is an established statistical method, although it has not been used previously in the development of emission correlation equations. The MEM technique accounts for the variability in screening measurements as well as variability in mass emission rates, while the OLS method does not account for the variability in the screening measurements. If the screening value variability were negligible compared to the mass emission rate variability, the MEM technique would provide equations equivalent to those produced by the OLS method. Because the MEM technique accounts for emission rate and screening value variability, and the screening value variability is not negligible, the MEM technique has the potential to be superior to previously used statistical methods for use in developing emission correlation equations. Additional work is in progress to further evaluate the MEM technique. However, the general impact of using the MEM technique is noteworthy; work performed to

Table ES-2 1993 Refinery Study Emission Correlation Equations

Component Type	Service	Number of Data Points	Emission Rate Using OLS Method
Connectors (flanges)	All	19	$ER=(1.3)(10^{-6})(SV)^{0.93}$
Connectors (non-flanges)	All	29	$ER=(2.8)(10^{-7})(SV)^{1.0}$
Open-Ended Lines	All	22	$ER=(5.3)(10^{-7})(SV)^{0.84}$
Pump Seals	HL	10	$ER=(5.6)(10^{-6})(SV)^{1.1}$
Pump Seals	LL	27	$ER=(2.3)(10^{-4})(SV)^{0.44}$
Valves	All	141	$ER=(3.7)(10^{-6})(SV)^{0.78}$

ER = Emission Rate in lbs/hr/component
 SV = OVA Screening Value (in ppm) obtained at the surface of the component except for pumps. Pump seals screened at ≤ 1 cm.
 ALL = Light liquid, heavy liquid and gas service types
 HL = Heavy Liquid
 LL = Light Liquid
 OLS = Ordinary Least-Squares

date indicates that the established OLS method results in an overestimate of emissions when the variability in the screening values is not negligible.

The 1993 Refinery Study emission correlation equations, which were based on measurements made with an OVA calibrated with methane, were compared with the 1980 Refinery Study emission correlation equations, which were based on measurements made with a Threshold Limit Value Sniffer (TLV Sniffer®) calibrated with hexane. Screening with both instruments was done as close as possible to the surface of the component at the point of maximum leak. Comparisons were made based on the component type and service type categories developed for the 1980 Refinery Study. All of the 1993 Refinery Study emission correlation equations give substantially lower estimates of emissions for screening values than the 1980 Refinery Study emission correlation equations. Table ES-3 compares emission correlation equations from the 1980 and 1993 refinery studies.

A detailed analysis of the emission correlation equations for light liquid valves revealed that the majority of the differences between 1980 and 1993 can be attributed to the difference in screening instruments and calibration gases used, and also to the treatment of pegged compo-

Table ES-3 Comparison of 1993 Refinery Study Emission Correlation Equations with Established Emission Correlation Equations

Component Type	Service	1993 Refinery Fugitive Emissions Study OLS Method ^{a,b} (screened at surface)	Marketing Terminals Study ^{a,b} (screened at surface)	1980 Refinery Study ^{a,c} (screened at surface)
Connectors (Flanges)	All ^d	ER=(1.3)(10 ⁻⁶)(OVA) ^{0.93}	ER=(4.7)(10 ⁻⁵)(OVA) ^{0.43}	ER=(1.3)(10 ⁻⁵)(TLV) ^{0.88}
Connectors (Non-Flanges)	All ^e	ER=(2.8)(10 ⁻⁷)(OVA) ^{1.0}		
Open-Ended Lines	All ^d	ER=(5.3)(10 ⁻⁷)(OVA) ^{0.84}	ER=(5.7)(10 ⁻⁶)(OVA) ^{1.0}	— ^c
Pump Seals	HL	ER=(5.6)(10 ⁻⁶)(OVA) ^{1.1}	— ^e	ER=(1.9)(10 ⁻⁵)(TLV) ^{1.0}
Pump Seals	LL	ER=(2.3)(10 ⁻⁴)(OVA) ^{0.44}	ER=(6.6)(10 ⁻⁵)(OVA) ^{0.53}	ER=(1.8)(10 ⁻⁴)(TLV) ^{0.83}
Valves	Gas	ER=(3.7)(10 ⁻⁶)(OVA) ^{0.78}	— ^e	ER=(4.8)(10 ⁻⁷)(TLV) ^{1.2}
Valves	HL		— ^e	— ^e
Valves	LL		ER=(6.3)(10 ⁻⁶)(OVA) ^{0.71}	ER=(3.2)(10 ⁻⁵)(TLV) ^{0.80}

OLS = Ordinary Least-Squares

LL = Light liquid

HL = Heavy liquid

ER = Predicted emission rate in lbs/hr/component

OVA = OVA screening value (in ppm)

TLV = TLV Sniffer® screening value (in ppm)

^a Emission correlation equation developed using the ordinary least-squares (OLS) method documented in the U.S. EPA Protocols Document (1993).

^b Emission correlation equations developed using OVA screening values obtained at the surface of component except for pumps. Pump seal emission correlation equations based on screening measurements at a distance of ≤ 1 cm. Equations give results for total hydrocarbon.

^c 1980 Refinery Study emission correlation equations for TLV sniffer® screening values obtained at the surface of a component except for pumps. Pump seal emission correlation equations based on screening measurements at a distance of ≤ 1 cm. Equations give results for non-methane organic compounds.

^d "All" services includes HL, LL, and gas services for refinery studies, and LL and Gas services only for the Marketing Terminals Study.

^e No emission correlation equation developed.

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nents. The 1980 Refinery Study included pegged components in the development of the emission correlation equations (pegged instrument readings were counted as if at the pegged value, [i.e., 10,000 ppm or 100,000 ppm]), whereas the 1993 Refinery Study did not include the pegged components in the development of the emission correlation equations. Figure ES-1 illustrates the result of comparing the 1980 and 1993 data sets on the same screening instrument basis and with pegged components removed. Two low screening measurement values from the 1980 Refinery Study, which would be statistical outliers if the data sets were combined, were deleted from this plot for comparison purposes. From this plot, it is apparent that much of the difference in emission correlation equations is based on different data collection and data analysis techniques rather than differences in component behavior.

The emission correlation equations in the API Study entitled *Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals* (API, 1993), referred to here as the Marketing Terminals Study, are included in Table ES-3 and were also compared with the 1993 Refinery Study emission correlation equations. Comparisons were made based on the component type and service type categories developed for the Marketing Terminals Study. The emission correlation equations from the two studies are nearly identical for light liquid valves and are statistically comparable for light liquid pumps. Differences are noted for connectors and open-ended lines; however, these differences may well be a function of component sub-type (i.e. type of connector) and size (particularly for open-ended lines).

ZERO COMPONENT EMISSION FACTORS AND PEGGED COMPONENT EMISSION FACTORS

Zero components are those components that screen at background (also called "default zeros" in previous studies). The 1993 Refinery Study factors are shown in Table ES-4.

The Marketing Terminals Study zero component emission factors are higher than those in the 1993 Refinery Study for connectors, pumps, seals, and open-ended lines. No statistically significant differences exist between the Marketing Terminals Study zero component emission factors and the 1993 Refinery Study zero component emission factors for valves.

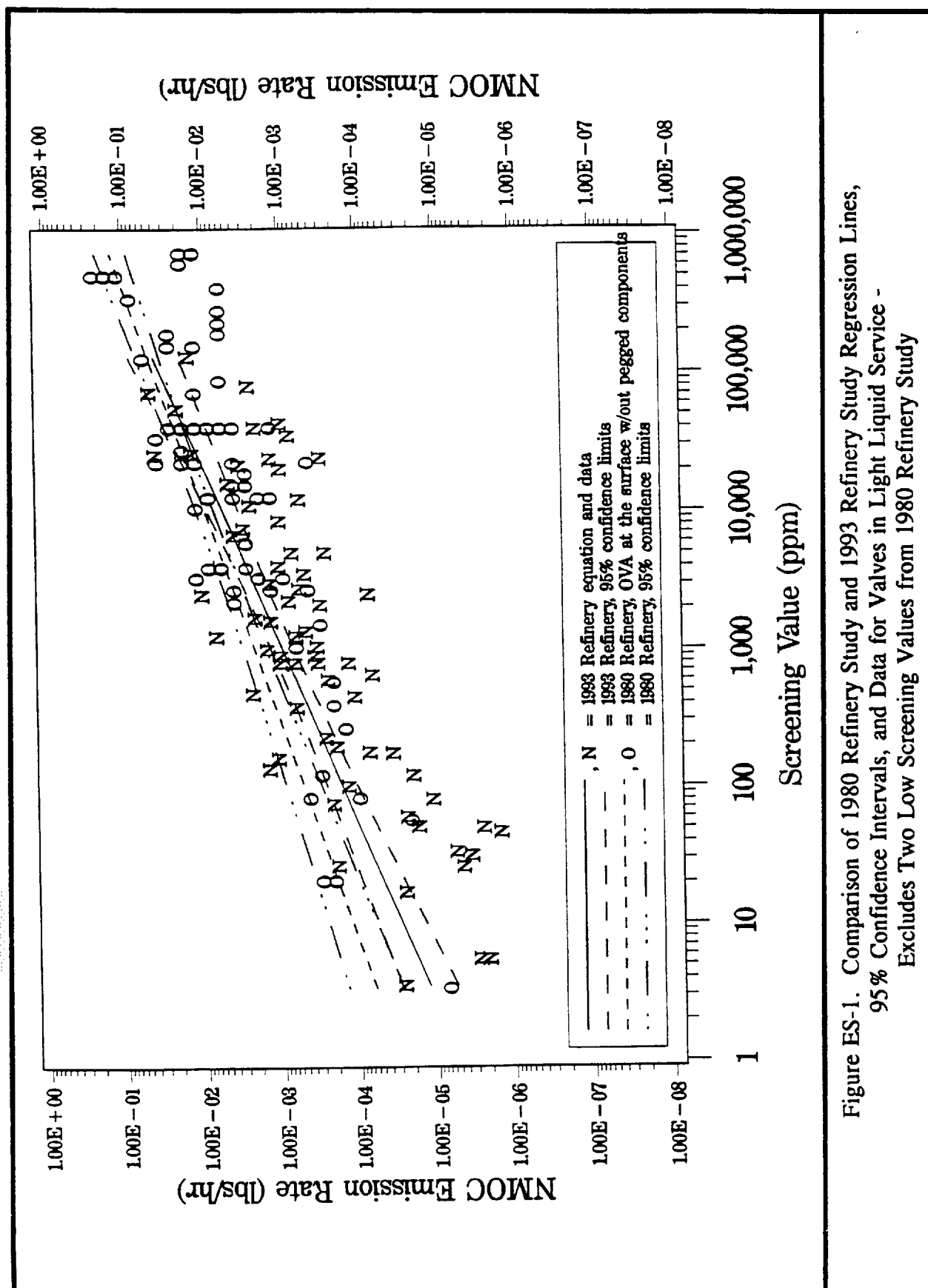


Figure ES-1. Comparison of 1980 Refinery Study and 1993 Refinery Study Regression Lines, 95% Confidence Intervals, and Data for Valves in Light Liquid Service - Excludes Two Low Screening Values from 1980 Refinery Study

Table ES-4 1993 Refinery Study Zero Component and Pegged Component Emission Factors

Component Type	Service	Zero Component Emission Factor ^a (lbs/hr/component)	Pegged Component Emission Factor ^a (lbs/hr/component)
Connectors (Flanges)	All	4.9×10^{-7}	2.1×10^{-2}
Connectors (Non-flanges)	All	1.7×10^{-6}	3.0×10^{-2}
Open-Ended Lines	All	5.7×10^{-7}	2.5×10^{-2}
Pressure Relief Valves	Gas	1.9×10^{-8}	— ^b
Pump Seals	Heavy Liquid	4.3×10^{-7}	— ^b
Pump Seals	Light Liquid	7.3×10^{-6}	6.4×10^{-1}
Valves	All	6.6×10^{-6}	3.6×10^{-2}

^a Components were screened at the surface, except for pumps. Pump seal factors based on screening measurements at a distance of ≤ 1 cm.

^b No pegged component emission factor developed for this component category.

The zero component emission factors in the 1993 Refinery Study are comparable to those presented in the U.S. EPA Protocols Document for connectors (flange and non-flange) and light liquid pumps, are significantly lower for pressure relief valves and heavy liquid pumps, and are significantly higher for valves. The zero components in the U.S. EPA Protocols Document are based on results in the chemical industry, rather than in petroleum refining.

Table ES-4 also lists the pegged component emission factors from the 1993 Refinery Study. A pegged component is a component that has a screening value above the range of the screening instrument. For the 1993 Refinery Study, a pegged component was generally a component that screened above 100,000 ppm. Pegged component emission factors could not be developed for heavy liquid pumps in the 1993 Refinery Study because no heavy liquid pumps were screened above 100,000 ppm. Pegged component emission factors are lower by more than an order of magnitude than those presented in the U.S. EPA Protocols Document.

An alternative technique to determine the mass emissions from pegged components is being considered at this time. The equation for the determination of mass emissions that is currently presented in the U.S. EPA Protocols Document and repeated in this report is based on the assumption that the volume flow of the leaking hydrocarbons into the sample bag is insignificant compared with the flow of nitrogen (and air) through the bag. For components that are not pegged, this assumption is reasonable. However, for pegged components, the volume flow of the hydrocarbon leak can be significant if the leak rate is comparable to the nitrogen flow rate. Alternative pegged component emission factors, that account for the additional contribution of the hydrocarbon flow into the bag, have been calculated and are discussed in more detail in Volume I, Section 2 of this report. Depending on the component type, these alternative factors are 12 to 115 percent greater than those computed using the standard EPA methodology.

VAPOR LEAK COMPOSITION COMPARED WITH LIQUID STREAM COMPOSITION

One of the secondary objectives of this study was to assess the relationship of the vapor leak composition to the liquid stream composition. Fugitive emission samples (vapor leaks) were

collected from refinery components, then analyzed by and compared with corresponding analyses of the liquid in the associated stream or line. The comparison of the vapor data to the associated liquid data was inconclusive. The scatter of the data was random and very large. Because of the scatter of the data, the collection of vapor and liquid samples and use of more involved analysis methods for this comparison were discontinued. It is currently appropriate that refiners continue to estimate emissions of individual volatile organic compound (VOC) species by assuming that the mass fractions in emitted VOCs are the same as the mass fractions in the process streams.

SPECIAL STUDIES

The following special studies were conducted to establish the quality and variability of the data used to develop the emission correlation equations, the zero component emission factors, and the pegged component emission factors:

- Effects of potentially leaking OVA probes;
- Screening variability;
- Nitrogen flow rate variability;
- Benefits of additional bagging;
- Effects of dilution probe data; and
- Effects of high screening variability data.

Potentially leaking OVA probes were discovered during a U.S. EPA-contracted audit of the field testing process. The OVA probes were tested by blocking the end of the probe tip. In this blocked condition, air was found to be entering the OVA from an area away from the probe tip. The OVAs were calibrated with any leak already in place, thereby reducing or eliminating the potential for a leak to affect the results. Side-by-side screening measurements with inspectors from the Bay Area Air Quality Management District (BAAQMD) showed that screening measurements both before and after the potential leaks were discovered had screening variability within the anticipated range of inspector and instrument variability. All data collected before discovering that the OVA probes were potentially leaking were compared statistically to data collected after discovery. No consistent bias in screening measure-

ments before and after discovery was found. Thus, it is believed that the impact of the potentially leaking probes was not significant.

Screening variability tests were designed to quantify the variation due to different specific OVAs and different inspectors. The combined OVA and inspector relative percent difference (RPD) was 89.4%. The variability that screening values have over time was also quantified. The average RPD within one day was 138.8%. The variability of the screening measurements taken by the refinery I/M teams and Radian was also determined. No statistically significant difference between the I/M teams and Radian paired screening value results was found at three of the four refineries tested. One refinery was found to have screening values that were higher than the Radian screening value measurements. Comparisons of the BAAQMD and South Coast Air Quality Management screening values to Radian screening values also showed no statistically significant differences between the paired screening value results.

The effect of different nitrogen flow rates on mass emissions measurements obtained by the blow-through bagging test was also investigated. Components were repeatedly bagged at different nitrogen flow rates. Nitrogen flow rate during component bagging was shown to have an insignificant effect on mass emission calculations.

Bagging of additional components would assist in developing emission correlation equations with tighter confidence intervals. However, the benefits of additional bagging depend on the number of bags already obtained for this study. The benefits are much greater for heavy liquid pumps, where only 10 bags were collected, than for valves, where 141 bags were collected. Although additional bagging would result in tighter confidence intervals, sufficient bagging was performed to meet the U.S. EPA guideline of $\pm 50\%$ of the mean value with 95% confidence when in log space.

The impact of the dilution probe was also investigated. The dilution probe increases the range of the OVA from 10,000 ppm to 100,000 ppm. Including screening value measurements obtained with the dilution probe adds variability into the determination of emission

correlation equations. However, plots of the data and analyses of the slopes, intercepts, and the confidence intervals of the emission correlation equations with and without the dilution probe data indicated that the impact of the dilution probe was not statistically significant in the development of the emission correlation equations.

The effects of high screening variability data were also addressed. The components that had initial screening values that varied by more than a factor of two from the final screening values were not included in the emission correlation equation development for either the OLS method or the MEM technique. These data were removed in an effort to reduce one aspect of variability from the study. Including these data, however, would improve the precision of the emission correlation equations. However, analysis of the emission correlation equations with and without using these highly variable screening value tests indicated that deletion of these tests had no significant effect on the emission correlation equations. This analysis likewise indicated that the results were not biased by eliminating these high screening variability tests.

DATA QUALITY

A high level of attention was directed toward quality assurance and quality control (QA/QC) during this project. These QA/QC efforts extended from project planning stages, through field testing activities, and into the data analysis and reporting activities. Volume II presents the 1993 Refinery Study's test plans and QA/QC results. Protocol documents, screening guidance documents, Quality Assurance Project Plans (QAPPs) and a data analysis plan were all prepared prior to or during this project to ensure a high level of attention to quality control throughout this study.

A Regulatory Advisory Committee (originally organized in early 1992 for the 1993 Refinery Study), was included in project and test planning, test auditing, and intermediate results review. The Regulatory Advisory Committee included the following agencies:

- United States Environmental Protection Agency (U.S. EPA);
- California Air Resources Board (CARB);
- Bay Area Air Quality Management District (BAAQMD); and
- South Coast Air Quality Management District (SCAQMD).

Representatives from each of these regulatory agencies performed audits at test sites. Research Triangle Institute (RTI) was the representative for the U.S. EPA. The other regulatory agencies sent staff members to audit test activities. The audit results indicated that the quality of data produced by the testing was sufficient to meet quality objectives. The BAAQMD and the SCAQMD also performed side-by-side screening tests with Radian; those measurements are well within the anticipated range of screening variability for different inspectors with different screening instruments. The U.S. EPA auditor, RTI, performed duplicate analysis of bagging samples and conducted audit gas testing at four of the five refineries. Results from these duplicate analyses and the audit gas testing help substantiate the quality of data produced during this study.

During auditing, recommendations were made to enhance the data quality. These enhancements were made during the project. Some of the additional analyses performed as part of this study evaluated whether data collected prior to the recommended changes were acceptable. The results of those special investigations support the inclusion of all the data collected for the development of the emission correlation equations.

Radian and its analytical laboratory subcontractor, Air Toxics Limited (ATL), also performed several QA/QC activities to validate data collection and analysis activities. These additional QA/QC tests included:

- Laboratory (method) blanks;
- Field blanks;
- Method spikes;
- Surrogate spikes;
- Laboratory duplicates;
- Field duplicates;
- Field accuracy checks;
- Multi-point calibrations; and
- Canister stability tests.

The QA/QC results for these tests are included in Volume II, Section 4. These tests also indicated that data used for the development of emission correlation equations and pegged component emission factors were valid and within the acceptance criteria for analytical methods used. The zero component emission factors derived for this study might be over-estimated because of detection limits and the potential for a slight amount of contamination from field sampling equipment.

DATA APPLICABILITY

Data were collected from five refineries with widely differing characteristics. One of these refineries was in Pennsylvania, two in southern California, and two in northern California. The refineries ranged in size, based on barrels of crude throughput, from approximately 50,000 barrels per day (BPD) to over 250,000 BPD. The five refineries represented five different oil companies. Sampling took place at several process units at each refinery. Components tested at some refineries had been in use for decades, while those at other refineries had been installed within the previous two years. Because of the diversity of refineries and components tested, and the validity of the data obtained, results from the 1993 Refinery Study can be used by refineries nationwide.

Section 1

INTRODUCTION

Fugitive emissions are emissions from leaking equipment such as valves, pumps, connectors, open-ended lines, and compressors. To estimate these fugitive emissions, regulatory and industry groups have developed numerous emission factors and emission correlation equations. The primary source of emission factors and emission correlation equations for fugitive emissions from refineries has been a study funded by the United States Environmental Protection Agency (U.S. EPA) conducted in the late 1970s and published in 1980 as the *Assessment of Atmospheric Emissions from Petroleum Refining* (referred to here as the "1980 Refinery Study") (Radian, 1980). The Western States Petroleum Association (WSPA) and the American Petroleum Institute (API) commissioned this study of refinery fugitive emissions to determine how the emission correlation equations have changed since the 1970s. WSPA and API believed that technology changes in equipment and changes in operating procedures could necessitate revisions to the past emission correlation equations. In the "1993 Study of Refinery Fugitive Emissions from Equipment Leaks," referred to as the "1993 Refinery Study" in this document, fugitive emissions from equipment leaks were examined and current emission correlation equations were developed. In addition, fugitive emissions were examined that were not thoroughly evaluated in the past.

STUDY OBJECTIVES

This study's main objective was to:

- Develop quantitative correlations between screening values and mass emission rates by component type and service type, and compare the results with the 1980 Refinery Study.

The secondary objectives were to:

- Develop zero component emission factors and pegged component emission factors for different component types and service categories.
- Assess the relationship between the toxics content of the vapor leak and the corresponding toxics content of the liquid stream.

PROJECT DESCRIPTION

For this study, sampling data were collected from five refineries, two located in southern California, two in northern California, and one in Pennsylvania. Three of the refineries were large (> 150,000 barrels crude per day [BPD]). The other two were considerably smaller (< 100,000 BPD). All five refineries had inspection/maintenance (I/M) programs to reduce the number of leaking components. Approximately 100 components were sampled/bagged at each of the five refineries. Approximately 82% of these bag results were used in the emission correlation equation, pegged emission factor, and default zero emission factor development. The remaining 18% did not meet quality assurance objectives and were not used. At each of the five refineries, the following component types were sampled:

- Valves;
- Pumps;
- Connectors; and
- Open-ended lines.

Only a few leaking compressors and pressure relief valves were found at the five refineries, therefore emission correlation equations and pegged component emission factors were not developed for these component types.

HISTORICAL PERSPECTIVE

Information for determining fugitive emissions from refineries 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. These earlier studies are discussed below.

The 1980 Refinery Study (Radian, 1980) in this report, was one of the first programs to rigorously examine fugitive emissions from petroleum refineries. Radian screened components with a portable hydrocarbon analyzer and measured (bagged) mass emission rates for components in 13 refineries throughout the United States. In this assessment, screening value distributions, average emission factors, and correlations between screening values and mass emission rates (emission correlation equations) were developed.

The 1980 Refinery Study results were significant, but not always easily implemented. The screening values were obtained using a Threshold Limit Value Sniffer (TLV Sniffer®) calibrated with hexane. Therefore, the emission 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 (TLV Sniffer® at the surface, OVA at 1 cm).

In 1982, the 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, 1982). This document presented average emission factors for Synthetic Organic Chemical Manufacturing Industry (SOCMI) plants. These average emission factors were developed using SOCMI screening value distributions and the refinery screening value to mass-emission rate correlation data from the 1980 Refinery 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 developed leak/no-leak emission factors. With the exception of gas/vapor service valves, the emission factors presented in this 1986 document are based largely on the data collected in the 1980 Refinery Study.

In October 1988, the 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 that used in 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 Study.

In May 1993, API published a study, prepared by Radian, entitled *Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals* (API, 1993), called the Marketing Terminals Study in this report. This document presented emission correlation equations for component types found in petroleum marketing terminals. Default zero emission factors, average emission factors, and stratified emission factors were developed for these component types.

In June 1993, Radian completed a revision to the 1988 *Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP* (U.S. EPA, 1988) entitled *Protocol for Equipment Leak Emission Estimates* (U.S. EPA, 1993) (U.S. EPA Protocols Document). This revision incorporates currently recommended data collection and analysis procedures. Included in this document are emission factors based on historical and recently collected data from chemical industry facilities.

REPORT ORGANIZATION

This study is presented in three volumes. Volume I contains the summaries and the key data analysis results. Volume II contains the testing approach, special studies to enhance the data analysis, and documentation of quality control results. Volume III contains the appendices with raw data, in-depth discussions of calculations and statistics, and more complete independent audit results. Volumes I and II are presented in this report. Volume III is published separately as API Publication No. 4613.

Volume I is organized as follows:

- Section 2 documents the key data analysis results including the emission correlation equations, the zero component emission factors, the pegged

component emission factors, and the comparison of vapor leak compositions with liquid stream compositions;

- Section 3 discusses the conclusions and recommendations; and
- Section 4 includes the references related to Volume I.

Volume II, meant as a supplement to the data analysis, conclusions and recommendations presented in Volume I, is organized as follows:

- Section 2 explains the testing approach, including sampling procedures, analytical and calibration procedures, and quality assurance objectives and checks;
- Section 3 examines special additional studies to enhance the data analysis;
- Section 4 presents the quality assurance/quality control results; and
- Section 5 shows the references for Volume II.

Additionally, the List of Appendices from Volume III (API Publication No. 4613), which contains the appendices related to the data calculations and independent audit results, is located at the back of this report.

Section 2

DATA ANALYSIS

The procedures used to analyze the data and the data results are explained in this section. The emission rate calculation, the development of the emission correlation equations, zero component emission factors, pegged component emission factors, and the comparison of vapor leak composition to liquid stream composition data are presented.

EMISSION RATE CALCULATION

The methodology used to estimate the mass of hydrocarbons in hydrocarbon stream samples composed primarily of aliphatics and aromatics is illustrated in Figure 2-1. This methodology is based on the fact that, for aliphatics and aromatics, the response of a laboratory flame ionization detector (FID) is linear with respect to the mass concentration of hydrocarbons present. The same weight of any hydrocarbon will result in the same peak area (response) from the FID. This relationship holds for nearly all aliphatics and aromatics with only a minor variation among compounds. Therefore, the molar concentration of mixed hydrocarbons measured by the FID as parts per million by volume (ppmv) of a calibration gas can be converted to parts per million by weight (ppmw) using the molecular weight of the calibration gas. The result will be a relatively accurate ppmw estimate of the mixed hydrocarbon sample.

If the hydrocarbon sample were to contain significant amounts of alcohols, acids, esters, ethers, or nitrogenated or chlorinated compounds, the correlation of the response of the FID would not be linear with respect to hydrocarbon mass. However, none of the hydrocarbon samples in this study are believed to contain significant amounts of the components that would cause a non-linear response on the FID. Therefore, no response factor corrections were made to any of the data in this study.

$$\text{Emission Rate (kg/hr)} = \frac{1.218 \times 10^{-5} (Q) (MW) (GC) (RF)}{T+273} + \frac{(\rho)(V_L)}{16.67(t)}$$

where

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

and

Q	=	flow rate into tent (m ³ /hr)
MW	=	molecular weight of the diluent stream (≈ 28 kg/kg-mol)
T	=	temperature in tent (°Celsius)
GC	=	instrument reading minus background ^a reading (ppmw)
ppmw	=	instrument ppmv (MW of calibration gas)/(MW of diluent stream)
RF ^b	=	response factor for leaking gas relative to calibration gas
1.218 x 10 ⁻⁵	=	a constant that includes the gas constant and assumes a tent pressure of one atmosphere (°K 10 ⁶ kg-mol/m ³)
ρ	=	density of organic liquid collected (g/mL)
V _L	=	volume of liquid collected (mL)
t	=	time in which liquid is collected (min)
16.67	=	a conversion factor to adjust term to units of kilograms per hour (g * hr)/(kg * min)

- ^a Background reading is from the OVA and is applied only to remaining fraction of air based on the oxygen analyzer reading.
- ^b 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.

Figure 2-1. Mass Emission Calculation Procedure for Tented Leak Rate

EMISSION CORRELATION EQUATIONS

The data analysis procedures used to evaluate the relationship between emission rate measurements (in lbs/hr) and screening values (in ppm) are given in this subsection. First, the results of multivariate analyses to determine which factors influence the relationship between measured mass emission rates and screening values are discussed. Emission correlation equations were grouped based on the results of the multivariate analyses. Second, the emission correlation equations that were developed using the statistical procedures documented in the U.S. EPA document entitled *Protocol for Equipment Leak Emission Estimates* (U.S. EPA, 1993) (U.S. EPA Protocols Document) are presented. An alternative statistical procedure for developing the emission correlation equations was also developed and applied to the emission rate and screening value data. The equations generated using this alternative method, a measurement error method (MEM), are presented in the third part of this subsection. Finally, a comparison of the new emission correlation equations to equations developed in previous studies is given.

Multivariate Analysis

Emission correlation equations were grouped based on the results of the multivariate analyses into the following six categories:

- Flange connectors in all services;
- Non-flanged connectors (i.e., plugs, screwed or threaded connectors, union connectors) in all services;
- Open-ended lines in all services;
- Pump seals in heavy liquid service;
- Pump seals in light liquid service; and
- Valves in all services.

Zero component emission factors and pegged component emission factors were developed for these same groupings.

No emission correlation equations or pegged component emission factors were developed for the component types of compressors or pressure relief valves because insufficient numbers of leaking compressors and pressure relief valves were found at the five refineries. A zero component emission factor, however, was developed for pressure relief valves.

Data on the following parameters collected by Radian during the field effort were evaluated in this task to determine the effects they may have on the emission correlation equations:

- Component category (connectors, open-ended lines, pump seals, valves);
- Component service (light liquid, heavy liquid, and gas/vapor);
- Component size;
- Component subcategory (gate valve, flange connector, etc.);
- Site (Refinery V, Refinery W, Refinery X, Refinery Y, Refinery Z);
- Geographic region (Pennsylvania, Bay Area Air Quality Management District [BAAQMD], and South Coast Air Quality Management District [SCAQMD]);
- Process unit (catalytic cracker, hydrocracker, alkylation, etc.);
- Ambient temperature;
- Barometric pressure;
- Windspeed;
- Organic Vapor Analyzer (OVA) screening instrument identification (ID) (Instrument 1, 2, or 3);
- Valve actuation (manual or control); and
- Pump load (on or off).

A number of different statistical procedures are available to evaluate the relationships between multiple variables. These include analysis of variance, analysis of covariance, stepwise regression, principal component analysis, and cluster analysis. These multivariate procedures were used to determine how many different emission correlation equations should be developed, whether additional factors should be incorporated into the emission correlation equations, and whether there were interdependencies (e.g, correlations) between the explana-

tory variables. In evaluating whether additional factors should be incorporated into the emission correlation equations, the key questions were:

- Does the factor affect the relationship between emission rates and screening value measurements?
- Is adding the factor meaningful (that is, can it be physically interpreted)?
- How much more precise will the emission correlation equation be by adding the factor?

Variables that were statistically significant were evaluated for possible confounding relationships that may exist between them and other explanatory variables. In developing an emission correlation equation, it is important to know which explanatory variables may be correlated and are not independent.

One of the assumptions in performing many statistical procedures is that the errors are independent and normally distributed, and that the variances are constant for different factors or ranges. These assumptions were met by taking the natural logarithms (logs) of the emission rate and screening value measurements before performing the statistical analysis.

Screening measurements were obtained by guiding the OVA probe around the periphery of the component. The OVA probe was held as close as possible to the surface without touching the surface (referred to as "at the surface" in this report). Generally, this screening distance was very close to being on the surface, much closer than 1 cm away. The maximum reading obtained for a component was recorded. Additional measurements were taken at 90°, 180°, and 270° from the maximum reading. For the data analysis task, the relationship between emission rates and screening values was first evaluated to determine which screening value measure (i.e., the maximum screening value, the sum of the screening values, the average screening value) provided the best estimator of mass emission rates. All of these screening value measures provided good predictors of mass emissions. The correlation coefficients obtained for these three different screening value measures were all within 2% of each other for a given component type. Although the maximum screening value, the average

screening values, and the sum of the screening values all provided comparable estimators of mass emissions, the maximum screening value was chosen as the most appropriate measure to be consistent with previous studies, all of which used the maximum screening values.

Throughout this report, "screening value" will refer to the average of the maximum screening value before and after bagging.

Analyses of variance (ANOVAs) were first performed to determine which of the factors given above had significant effects on $\log(\text{emission rate})$ after accounting for and controlling the effects of $\log(\text{screening value})$. These "ANOVAs" are the ANOVA tables given in generalized linear model procedures. The interaction between $\log(\text{screening value})$ and each factor was also evaluated. Testing the significance of the main effects (or factors) and the factor multiplied by $\log(\text{screening value})$ interaction in an ANOVA is analogous to testing whether separate regression equations developed for those factors will have statistically significant intercepts and slopes, respectively. These ANOVAs were performed separately for the following four component types:

- Connectors;
- Open-ended lines;
- Pump seals; and
- Valves.

Historically, separate emission correlation equations have been developed for these four component types. In addition, statistical analyses of the current data support developing different equations for these four component types.

Factors found to be statistically significant for each component type based on the ANOVA tests were further evaluated to determine whether they were correlated with other measured parameters. The r^2 (i.e., the correlation coefficient squared) was also evaluated for those factors that were statistically significant to determine which factors produced emission correlation equations with the strongest correlation. The value of r^2 indicates the approximate per-

centage of the total variation in the response variable (i.e., $\log[\text{emission rate}]$) that can be explained by the correlating variable(s). For example, if the r (the correlation coefficient) = 0.50, then $r^2=0.25$ and about 25% of the variation in $\log(\text{emission rates})$ can be explained by the given factor(s). The remaining 75% of the variation is due to other variables and random variation.

The results of these ANOVAs are given in Table 2-1. Table 2-1 also shows the number of observations included in the analysis. For those factors that were not statistically significant at the 0.10 level, "NS" (not significant) is given in the table. For those factors that were statistically significant at the 0.10 level, the p-value, and the multiple correlation coefficient are given (i.e., the correlation coefficient for the model). Cases where both the intercepts and slopes (i.e., the main effect and the interaction with $\log[\text{screening value}]$) were significant are noted in the table.

The p-value provides an indication of how significant a given factor is for a particular test. For example, in the ANOVAs performed, the null hypothesis is that a given factor does not have a significant effect on the emission correlation equation (i.e., the slopes and intercepts for the different levels of the factors being tested are not significantly different). At the outset of a hypothesis test, it is always presumed that the null hypothesis is correct. This position will change only if the sample data show that this is not true. A significance level, or alpha level, of 0.10 was used for the ANOVAs (the alpha level and the significance level are the same). Thus, the test was performed such that there is only a 10% chance of incorrectly concluding that an effect is significant when, in fact, it is not. The p-value is used to determine when the decision can be made to reject the null hypothesis that a given factor has no effect. Thus, a p-value that is greater than 0.10 (the significance level) indicates that there is not enough evidence to reject the null hypothesis. A p-value that is less than 0.10 would result in rejecting the null hypothesis that the effect is not significant (and therefore accepting the alternative hypothesis that the effect is significant). If an effect is judged to be statistically significant (i.e., the p-value is less than alpha or the significance level), the magnitude of the p-value can be used to indicate "how significant" an effect is. For example,

**Table 2-1 Results of Tests to Determine Variables that Affect
Log(Emission Rates) After Accounting for the Variability
Explained by Log(Screening Values)**

	Connectors	Open-Ended Lines	Pump Seals	Valves
<i>Log(Screening Value): N</i> <i>p-value</i> <i>(Correlation Coefficient)^a</i>	N=48 0.0001 (0.82)	N=22 0.0001 (0.83)	N=37 0.0001 (0.74)	N=141 0.0001 (0.81)
Variables Added After Accounting for Log(Screening Value):				
Service ^b	N=48 NS	N=22 NS	N=37 0.01 ^c (0.80)	N=141 NS
Size ^d	N=48 0.03 ^f (0.84)	N=21 NS	NA*	N=141 0.0004 (0.83)
Type ^e	N=48 0.002 ^f (0.86)	NA	NA	N=141 NS
Site	N=48 NS	N=22 NS	N=37 NS	N=141 0.001 (0.83)
Region ^g	N=48 NS	N=22 0.05 (0.89)	N=37 NS	N=141 0.0004 (0.83)
Process Unit ^h	N=48 NS	N=22 0.07 (0.89)	N=37 NS	N=140 NS
Ambient Temperature	N=48 NS	N=22 NS	N=37 NS	N=141 NS
Barometric Pressure	N=23 NS	N=22 NS	N=15 0.02 (0.69)	N=70 NS
Windspeed	N=48 NS	N=22 NS	N=37 NS	N=141 0.04 (0.82)
Instrument ID	N=48 NS	N=21 0.04 (0.90)	N=37 0.02 ^c (0.81)	N=141 0.005 (0.83)
Valve Actuation	NA	NA	NA	N=112 0.004 (0.83)
Pump Load	NA	NA	N=32 0.0003 (0.83)	NA

Table 2-1 (Continued)

NS = Not statistically significant at the 0.10 significance level. The p-value is given for statistically significant effects.
 NA = Not applicable (e.g., types of pumps seals and types of open-ended lines not evaluated).

- a The correlation coefficient (R_{xy}) is given for those factors that are statistically significant. R_{xy}^2 is the variation in $\log(\text{emission rate})$ that can be explained by the given factor and $\log(\text{screening value})$.
- b Service types evaluated are light liquid, heavy liquid, and gas services, with the exception of pump seals which are in light liquid and heavy liquid services only.
- c Both the main effect and the interaction between the factor and $\log(\text{screening value})$ have statistically significant effects on $\log(\text{emission rate})$ [i.e., both the slopes and intercepts are statistically significant].
- d Size treated as a continuous variable.
- e Component types evaluated for connectors are flanges and non-flanges. Component types evaluated for valves are gate valves and non-gate valves.
- f Size and type (flange or non-flange) are confounded for connectors (i.e., the flanges tend to be larger and non-flanges tend to be smaller). Connector emission correlation equations should therefore be separated by either connector size or connector type, but not both.
- g Regions are Pennsylvania, the Bay Area Air Quality Management District (northern California), and the South Coast Air Quality Management District (southern California).
- h Process unit codes are given in Table 2-2.
- * Size not tested for pump seals because of inconsistent recordings of the size variable.

a p-value that is less than 0.10, but very close to 0.10, say 0.09, could be regarded as an effect that is statistically significant at the 0.10 level, but "borderline." Furthermore, a p-value of 0.09 would be statistically significant at the 0.10 significance level but not at the 0.05 significance level. A p-value that is a lot smaller than the significance level indicates that the data strongly support the conclusion that a particular effect is significant. For example, a p-value of 0.0001 would provide strong indication that a particular effect is significant.

The focus of this analysis is to reduce the chance of including an insignificant effect. However, there is a chance some of these effects are significant, but insufficient data were available to establish significance. Therefore, we can be assured that there is less than a 10% chance of incorrectly concluding that an effect is significant when, in fact, it is not, but we cannot conclude that the effect is insignificant based on this analysis.

The first line in Table 2-1 shows the p-value and the correlation coefficient of the ANOVAs performed on $\log(\text{emission rate})$ versus $\log(\text{screening value})$ only. As indicated in the table, these ANOVAs had a p-value of 0.0001 for each of the component types. The correlation

coefficients obtained for these initial analyses varied from 0.74 for pump seals to 0.83 for open-ended lines. All subsequent lines in the table are results of the ANOVAs for the given factors, after explaining the variation due to *log(screening value)*. Results presented in Table 2-1 are for the significance of each of the given variables, separately, after accounting for *log(screening value)* only. Additional tests were performed in which multiple factors and interactions were evaluated in one model. These results are not presented in Table 2-1, but significant findings are discussed in the text.

Step-wise regressions were also performed for each component type. In this type of procedure, variables are added one by one to the regression equation and each variable's contribution to the equation is determined. Variables that do not explain a significant amount of variability (at a pre-set confidence level) at a given step, are not included in the equations. In general, the results of the step-wise regression were consistent with the ANOVA results.

Analyzing the ANOVA results was only the first step in determining statistical significance. If the ANOVA tests indicated statistical significance, further analysis was performed. Frequently, the further analysis indicated that the results were inconclusive, confounded with multiple variables, of minimal significance, or based on inconsistent data recordings. Results obtained for each of the component types are explained below.

Connectors. The ANOVA tests indicated that connector size and connector type were both found to have statistically significant effects ($\alpha = 0.10$) on the emission correlation equations. Connector sizes ranged from 0.5 inches to 8 inches. Connector types evaluated were flange connectors and non-flange connectors. Non-flange connectors were plugs, screwed or threaded connectors, and union connectors. Analysis of the data indicated that connector size and type were correlated (the larger connectors tended to be flanges). Thus, adding either connector size or connector type will improve the emission correlation equation, but including both factors is redundant. Table 2-1 shows that the correlation coefficient obtained by including connector type as a factor is larger than the correlation coefficient

obtained by including size as a factor. Therefore, including type as a factor for connectors provides a better model than including size as a factor.

Figure 2-2 shows a scatter plot of mass emission rates versus screening measurements for connectors. Flanged connectors are denoted with an "F" and connectors other than flanges are denoted with an "O." In examining Figure 2-2 it is apparent that the equation that would be obtained for flanges is different than the equation that would be obtained for non-flanges.

Open-Ended Lines. Process unit, region, and screening instrument ID (specific OVA) were initially found to have statistically significant effects on the emission correlation equations for open-ended lines (OELs) based on the ANOVA tests. Further analysis indicated that the initial results are inconclusive, of minimal significance, or based on limited data. A discussion of the effects of these factors on the emission correlation equations is given below.

As shown in Table 2-1, 22 emission rate and screening value pairs were obtained for OELs. These measurements were obtained from eight different process units (C, E, F, H, K, N, P, and Q). Process unit codes are given in Table 2-2. Only one measurement was obtained from three of the process units (H, P, and Q), two measurements were obtained from three of the other process units (F, K, and N), and four and nine measurements, respectively, were obtained from the remaining two process units (E and C). Due to the fact that only a limited number of observations were obtained from different process units, statistically significant results regarding the effects of process units should be viewed with caution. Thus, although statistically significant effects were found between process units, it would be desirable to collect additional data before making firm conclusions about the effects of process units on the emission correlation equations for OELs.

Geographic region was also initially found to have a statistically significant effect on measured mass emission rates for OELs. Three geographic regions were evaluated: BAAQMD, Pennsylvania, and SCAQMD. Further analysis of the data and plots revealed that the slopes of the regression equations for the three different regions were not statistically different from

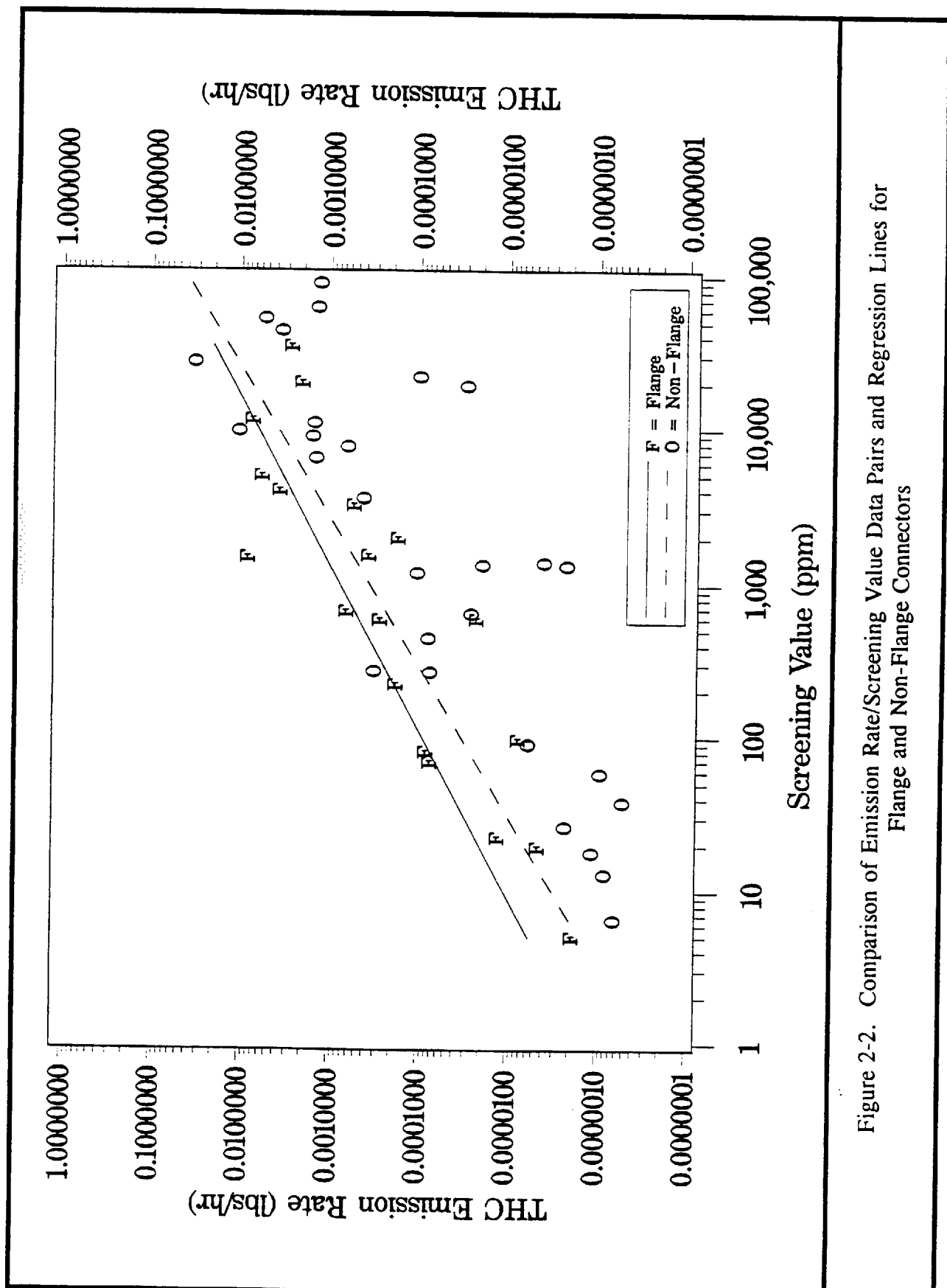


Figure 2-2. Comparison of Emission Rate/Screening Value Data Pairs and Regression Lines for Flange and Non-Flange Connectors

Table 2-2 Process Unit Codes

Code	Process Unit
A	Crude distillation unit
B	Alkylation (HF, sulfuric acid) unit
C	Catalytic reforming unit
D	Hydrocracking unit
E	Hydrotreating/hydrorefining units
F	Catalytic cracking (fluid and other) and CO boiler
G	Thermal cracking (visbreaking and other)
H	Thermal cracking (coking)
I	Hydrogen plant
J	Asphalt plant
K	Product (liquid and gas) blending and treating units
L	Sulfur plant
M	Vacuum distillation towers
N	Full-range distillation units (light ends, naphtha, solvent, etc.)
O	Isomerization unit
P	Polymerization unit
Q	Methylethylketone dewaxing unit
R	Other lube oil and specialties processing
S	Interunit pipeline system
T	Sour and other water strippers
U	Methyltertiarybutyl ether unit
V	Catalytic Separation Plant
W	Product Storage and Loading

one another. Thus, for a given change in screening value measurements, the measured rate of change in emission rates would be the same for the three different regions. Although the intercepts of the regression equations obtained for the three different regions were statistically different, they varied by less than 10% from one another (i.e., *the largest intercept - the smallest intercept*)/the largest intercept < 0.10). In summary, although there is statistical

evidence that the intercepts of the equations obtained for different regions is significant, the magnitude of these differences is probably not of practical significance and does not warrant including region as a factor.

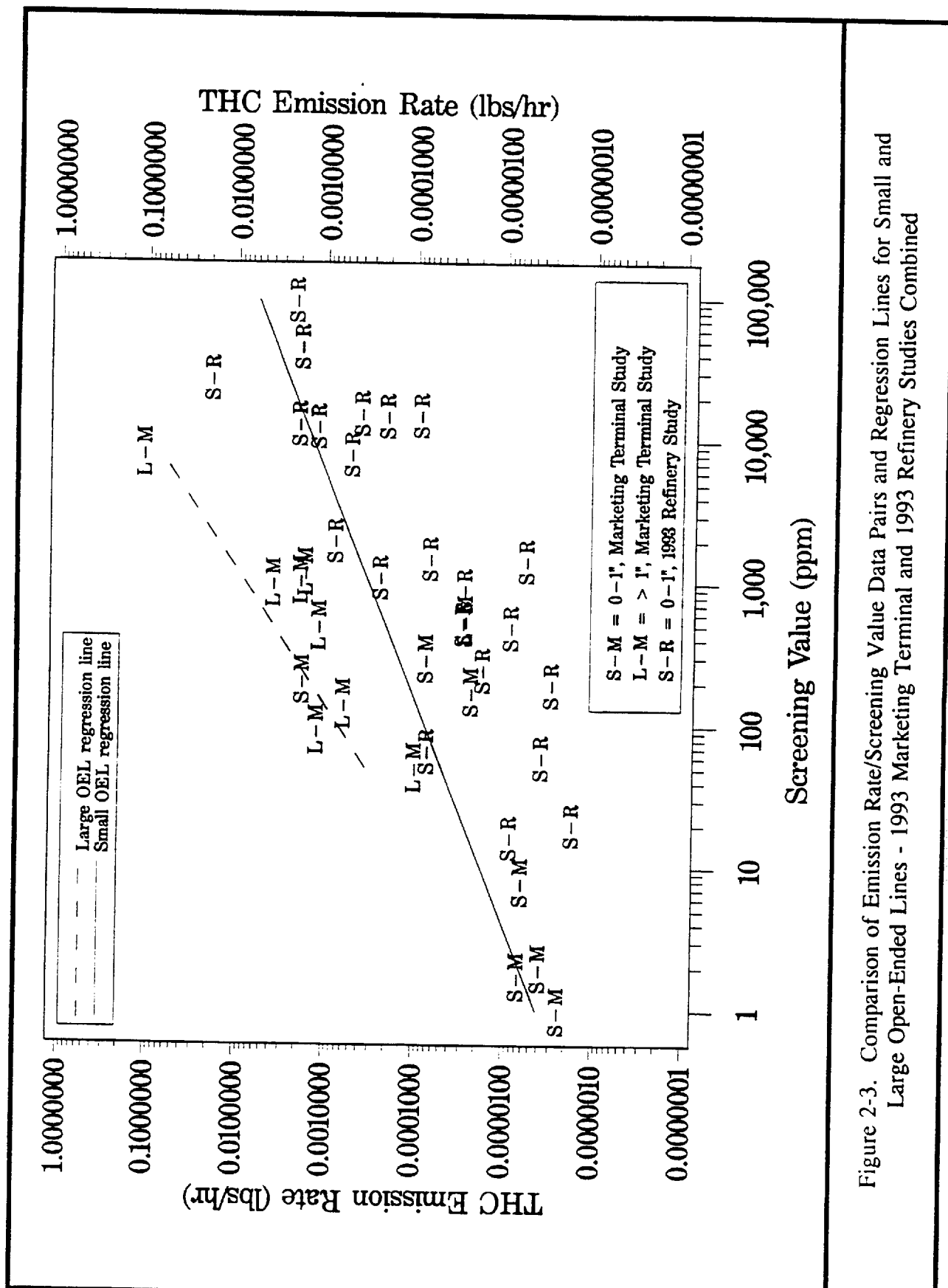
ANOVA results also indicated that the OVA screening instrument caused a statistically significant effect. However, screening instrument differences were confounded with region. Three different screening instruments (specific OVAs) were used in the field. The same OVA was always used in the SCAQMD region and a different OVA was always used in the Pennsylvania region. Roughly half of the screening value measurements collected in the BAAQMD region were obtained using the same OVA that was used in the Pennsylvania region and the remaining BAAQMD region measurements were obtained using a third OVA. Therefore, it is not known whether regional differences found for OELs can be attributed to actual differences in regions, differences between OVA used, some combination of the two, or even other factors. Therefore, statistically significant results regarding the effects of instrument screening device on the OEL mass emission correlation equation are inconclusive.

The lack of significance of component size on the current emission correlation equation for OELs deserves further discussion. In comparing the emission correlation equations developed during this 1993 Refinery Study with those presented in API's *Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals* (API, 1993) (referred to here as the Marketing Terminals Study), it was found that the OEL emission correlation equation developed for the Marketing Terminals Study was roughly an order of magnitude higher than the emission correlation equation developed for the 1993 Refinery Study. It was found that the OEL sizes measured at the marketing terminals were typically > 1 inch, whereas all of the OEL sizes measured during the 1993 Refinery Study were ≤ 1 inch. The OELs in refineries tend to be smaller than those at marketing terminals. No leaking OELs > 1 inch were found at the refineries. Figure 2-3 shows a plot of the 1993 Refinery Study and the Marketing Terminals Study data combined. In the figure, the 1993 Refinery Study data pairs end with "-R" and the Marketing Terminals Study data pairs end with "-M." OEL sizes are denoted as "S" for ≤ 1 inch and "L" for > 1 inch. As shown in the figure,

virtually all of the large OELs have higher emission rates than the small OELs for comparable screening values, with the exception of one of the nine large OELs. Furthermore, the data points for the small OELs for both studies were intermixed. An analysis of variance was performed on the combined data to test whether OEL size was a statistically significant factor after accounting for the variation in $\log(\text{screening value})$. In this ANOVA, size was found to be a statistically significant factor ($p\text{-value} = 0.0008$).

In conclusion, although OEL size was not a statistically significant factor when evaluating only the 1993 Refinery Study OELs, this may be due to the fact that only small OELs were measured at the refineries. After combining the 1993 Refinery Study data with the Marketing Terminals Study data (which consisted of both large and small OELs), size was found to have a statistically significant effect on the combined emission correlation equation. Because the equations being presented are based on the data collected for the 1993 Refinery Study only, and because only small OELs were measured, OEL size has not been included as a factor in the emission correlation equations.

Pump Seals. The only factor for pump seals found to be statistically significant that did not appear to be due to any confounding factors was service type (heavy liquid or light liquid). The definition of "heavy liquid" used for this analysis is a liquid or a 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). As noted in Table 2-1, both the intercept and the slope were found to be statistically significant. Figure 2-4 shows a plot of the emission rate and screening value data for pump seals. The service type is indicated by symbols (H = heavy liquid, L = light liquid). Although there is overlap between the two types of service, there tends to be more heavy liquid service types in the lower left corner (i.e., with lower emission rates for the low screening values). The regression analysis resulted in a heavy liquid emission correlation equation with a steeper slope and lower intercept than the light liquid emission correlation equation.



The initial ANOVA tests of the data indicated several other factors also appeared to be statistically significant for pump seals. However, further analysis indicated that the preliminary results were inconclusive, or the data were based on inconsistent recordings. The factors initially found to be statistically significant for pump seals based on the ANOVA tests that were not included in the final emission correlation equation were:

- Component size;
- Barometric pressure;
- Pump load; and
- Instrument ID.

Pump size was not included in the final analysis because investigation revealed that field collection team members were not consistent in recording pump size, with the pump inlet size being used as a measure of pump size in some instances, pump outlet size being used as a measure of pump size in other instances, and pump shaft size recorded in other instances. Therefore, it would not be meaningful to perform statistical analyses on pump size.

Barometric pressure was initially found to be statistically significant for pump seals, however, inconclusive results were obtained. Note in Table 2-1 that only 15 data pairs were used in this analysis (barometric pressure was only recorded for these 15 measurements). Although barometric pressure was found to have a statistically significant effect in the ANOVAs, its effect on the correlation coefficient could not be directly determined because of the smaller sample size. The correlation coefficient for the regression performed on the 15 data pairs only was 0.39 without barometric pressure and 0.69 with barometric pressure. It is not known, however, whether the data points for which barometric pressure was recorded are representative of all 37 pump seal measurements. Due to inconclusive results, barometric pressure was not included in the emission correlation equations.

Another factor initially found to have statistically significant effects on the pump seal emission correlation equation was pump load (i.e., in service or out of service). Plots of the data showed that pump seals in service had higher emission rates than pump seals not in service.

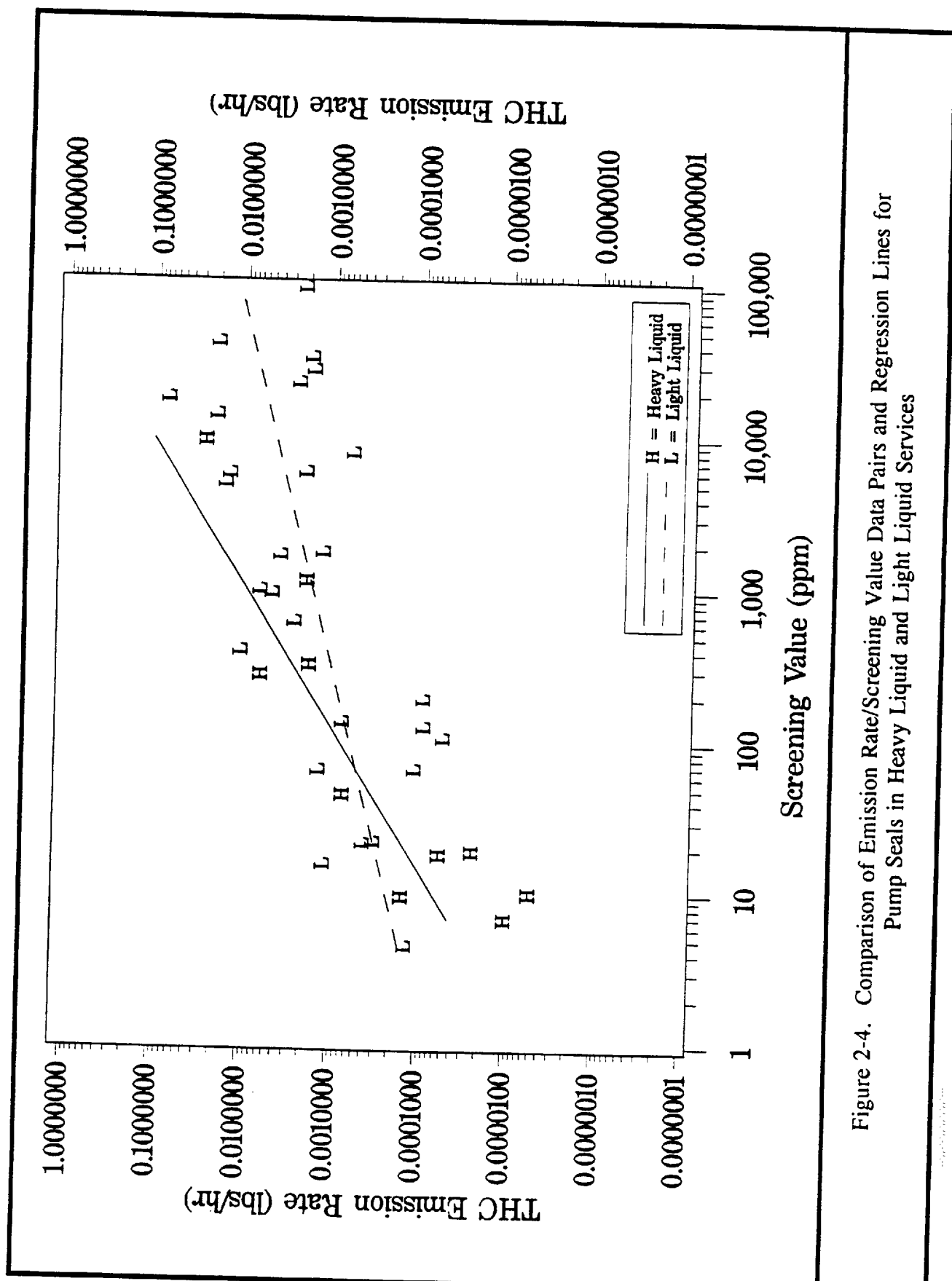


Figure 2-4. Comparison of Emission Rate/Screening Value Data Pairs and Regression Lines for Pump Seals in Heavy Liquid and Light Liquid Services