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Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

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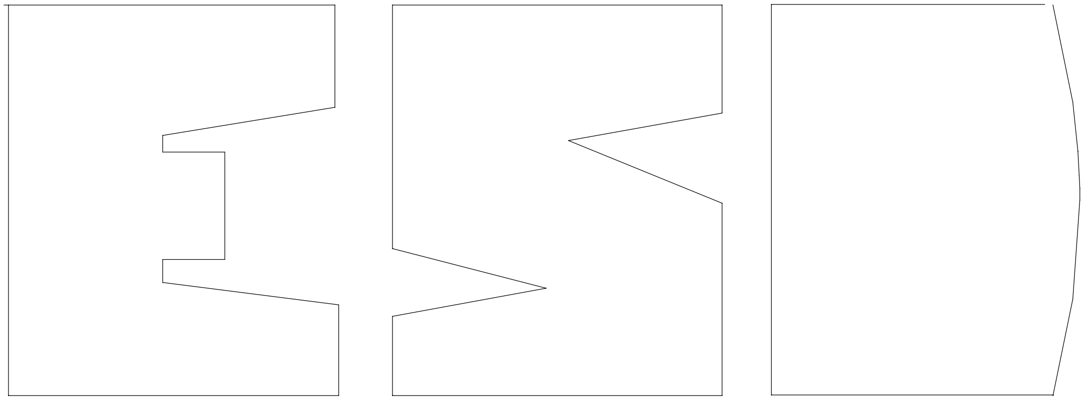
Protocol for Equipment Leak Emission Estimates



EPA-453/R-95-017

1995 Protocol for Equipment Leak Emission Estimates

Emission Standards Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

November 1995

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FOREWORD

The EPA's protocol for estimating equipment leak emissions is the result of detailed information gathering and data analysis. The protocol was written to provide a thorough understanding of acceptable approaches to generating process unit-specific emission estimates. In preparing this document, the EPA has encouraged knowledgeable individuals in industry and the regulatory community to provide comments.

The EPA has put forth considerable effort to make this document as comprehensive as possible. However, it should be understood that not all details and topics pertaining to equipment leaks could feasibly be included in this document. Additionally, it should be understood that the procedures presented in this document are not necessarily suitable for all applications. There will be cases where it will be necessary for the user of the document to make a professional judgement as to the appropriate technical approach for collecting and analyzing data used to estimate equipment leak emissions.

Additional data on equipment leak emissions continues to be collected. It is the intent of the EPA to periodically update this document after analysis of the data warrants such an update. For example, data recently collected in the petroleum industry has been used to revise the existing refinery correlations, which are based on data collected in the late 1970s. Furthermore, as new techniques for collecting and analyzing data are developed, they will be included in updated versions of this document.

Mention of any manufacturer or company name within this document does not represent endorsement by the EPA.

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1.0 INTRODUCTION

This document is an update to the EPA equipment leaks protocol document ("Protocol for Equipment Leak Emission Estimates," EPA-453/R-93-026, June 1993). The purpose of this document is the same as the original protocol document and subsequent revisions- to present standard procedures for estimating mass emissions from equipment leaks. However, this document publishes the results of additional data collection and analysis that has occurred since the original protocol and subsequent revisions were published, and also expands on some of the topics that were covered in the original protocol.

Some of the new features of the updated protocol are:

(1) New correlation equations, default zero emission rates, and pegged emission rates for the petroleum industry that replace the refinery correlations previously published are presented. The correlations relate screening values obtained using a portable monitoring instrument to mass emissions.

(2) The document has been expanded to include emission factors for marketing terminals and for oil and gas production operations. The refinery emission factors were not revised due to an unavailability of new data.

(3) Pegged emission rates for pegged readings at 10,000 ppmv have been added for SOCMI process units.

(4) Several of the equations in this version of the protocol have been revised by simplifying the symbols to more clearly communicate the concept being conveyed.

(5) An adjustment has been added to the blow-through method of calculating mass emissions. This adjustment more accurately accounts for the total flow through the bag.

As with the original protocol document, this document presents standard procedures for general use in generating unit-specific emission estimates for permitting and inventories. The document describes methodologies the EPA considers appropriate for development of equipment leak emission estimates. These methodologies are intended to assist States and industry in their efforts to estimate equipment leak emissions.

The updated protocol is divided into five chapters and several appendices. Chapter 2.0 describes how to estimate equipment leak emissions. Chapter 3.0 describes collecting screening data that can be used in the emission estimates. Chapter 4.0 describes collecting unit-specific equipment leak mass emissions data. Chapter 5.0 describes how to estimate the control efficiencies of equipment leak control techniques. The appendices support information contained in the chapters. Each of these chapters and the appendices are briefly described below.

Chapter 2.0 presents the four approaches for estimating total organic emissions from equipment leaks. These approaches are:

- Average Emission Factor Approach;
- Screening Ranges Approach;
- EPA Correlation Approach; and
- Unit-Specific Correlation Approach.

Additionally, several topics that are relevant to estimating equipment leak emissions are addressed. These topics include speciating equipment leak emissions of individual compounds from an equipment piece containing a mixture, using response factors, estimating emissions of volatile organic compounds, estimating emissions of inorganic compounds, and other topics not specifically related to any one of the four approaches.

Chapter 3.0 explains how to perform a screening survey at a process unit. Requirements for the use of a portable monitoring instrument are described. These requirements are based on the EPA Reference Method 21. Additionally, in chapter 3.0, guidance is provided on how to set up a screening program and how to screen different types of equipment.

Chapter 4.0, explains how to collect equipment leak rate data (bagging data) by enclosing individual equipment in a "bag" and measuring mass emissions. These data can be used to develop unit-specific leak rate/screening value correlations. Chapter 4.0 details the rigorous steps that need to be followed when collecting the bagging data to generate unit-specific correlations. These steps are intended to ensure that the data are of high quality.

Chapter 5.0, explains how to estimate the control efficiency of equipment leak emission control techniques. The two primary control techniques for reducing equipment leak emissions are (1) equipment modifications (such as replacing a standard valve with a sealless type) and (2) implementing a leak detection and repair (LDAR) program. Control efficiencies for different equipment leak modifications are summarized, and an approach for estimating the control efficiency of any LDAR program is provided.

Appendices A through G provide additional information supporting the material in the chapters. Appendix A contains detailed example calculations using the approaches described in chapter 2.0. Appendix B documents how the SOCMI correlations and emission factors were revised. Appendix B also serves as a demonstration of how data can be analyzed to develop unit-specific correlations. Appendix C presents the rationale for the development of the petroleum industry correlations, as well as the background for the development of marketing terminal and oil and gas production operations emission factors. Appendix D summarizes available data on response factors. Appendix E provides guidance on how to collect representative screening data for connectors. Appendix F contains a copy of the EPA Reference Method 21. Finally, appendix G demonstrates how LDAR control efficiencies presented in chapter 5.0 were calculated.

2.0. DEVELOPMENT OF EQUIPMENT LEAK EMISSION ESTIMATES

2.1 INTRODUCTION

The purpose of this chapter is to describe the methods for estimating mass emissions from equipment leaks in a chemical processing unit. Four approaches for estimating equipment leak emissions are presented:

Approach 1: Average Emission Factor Approach;
Approach 2: Screening Ranges Approach;
Approach 3: EPA Correlation Approach; and
Approach 4: Unit-Specific Correlation Approach.

General information on these approaches is presented in section 2.2, and detailed information on applying each of the approaches is presented in section 2.3. Included in section 2.3 are emission factors and leak rate/screening value correlations for use in estimating emissions from equipment leaks in the petroleum industry and the synthetic organic chemical manufacturing industry (SOCMI). The SOCMI emission factors and correlations were revised and introduced in the 1993 update of this document. The refinery correlations that have been revised and expanded to include the entire petroleum industry are introduced in this document. Additionally, emission factors for marketing terminals are introduced in this document. Emission factors for gas plants that have been updated and expanded to included oil and gas production operations are also introduced in this document. The procedures in this document estimate emissions of total organic compounds (TOC’s). However, special procedures are also described for the purpose of estimating volatile organic compounds (VOC’s). As defined by the EPA, VOC’s include all organic compounds except those specifically excluded by the EPA due to negligible photochemical activity.

After the four approaches have been discussed, topics that are not specifically related to any particular approach, but are relevant to how equipment leak emissions are estimated, are addressed in section 2.4. These topics include:

- Estimating emissions of individual compounds within a mixture;
- Using response factors when estimating emissions;
- Considerations regarding the monitoring instrument used;
- Estimating emissions of equipment not screened when other equipment have been screened;
- Using screening data collected at different times;
- Estimating VOC emissions from equipment containing organic compounds excluded from the EPA's classification of TOC's; and
- Estimating emissions from equipment containing inorganic compounds.

Appendices A through E contain supporting documentation for the material presented in this chapter. Appendix A contains detailed example calculations that demonstrate the four approaches for estimating equipment leak emissions, as well as the topics discussed in section 2.4. Appendix B presents details on how unit-specific correlations can be developed, and also presents background information on the revision of the SOCMI correlations and emission factors. Appendix C presents background information on the development of average emission factors and correlation equations for the petroleum industry. Appendix D offers a detailed listing of available response factors. Appendix E contains information on the minimum number of connectors in a process unit that must be screened in order to obtain a representative sample.

2.2 GENERAL INFORMATION ON THE APPROACHES FOR ESTIMATING EQUIPMENT LEAK EMISSIONS

This section presents general information on the four approaches for estimating equipment leak emissions. Each approach is briefly described, and data requirements for each are summarized. Additionally, background information is presented to provide an historical overview of data collection and analysis on emissions of VOC's from equipment leaks.

2.2.1 Equipment Leak Emission Estimation Approaches

The four approaches described here can be used by any chemical-handling facility to develop an inventory of TOC or VOC emissions from equipment leaks. The approaches, in order of increasing refinement, are: Average Emission Factor Approach, Screening Ranges Approach, EPA Correlation Approach, and Unit-Specific Correlation Approach.

In general, the more refined approaches require more data and provide more accurate emission estimates for a process unit. In the Average Emission Factor Approach and the Screening Ranges Approach, emission factors are combined with equipment counts to estimate emissions. To estimate emissions with the EPA Correlation Approach, measured concentrations (screening values) for all equipment are individually entered into general correlations developed by the EPA. In the Unit-Specific Correlation Approach, screening and leak rate data are measured for a select set of individual equipment components and then used to develop unit-specific correlations. Screening values for all components are then entered into these unit-specific correlations to estimate emissions.

Figure 2-1 is an overview of the data collection and analysis required to apply each of the approaches. As can be seen from this figure, all of the approaches require an accurate count of equipment components by type of equipment (i.e., valves, pumps, connectors, etc.). Additionally, for some of the equipment types, the count must be further described by service (i.e., heavy liquid, light liquid, and gas).

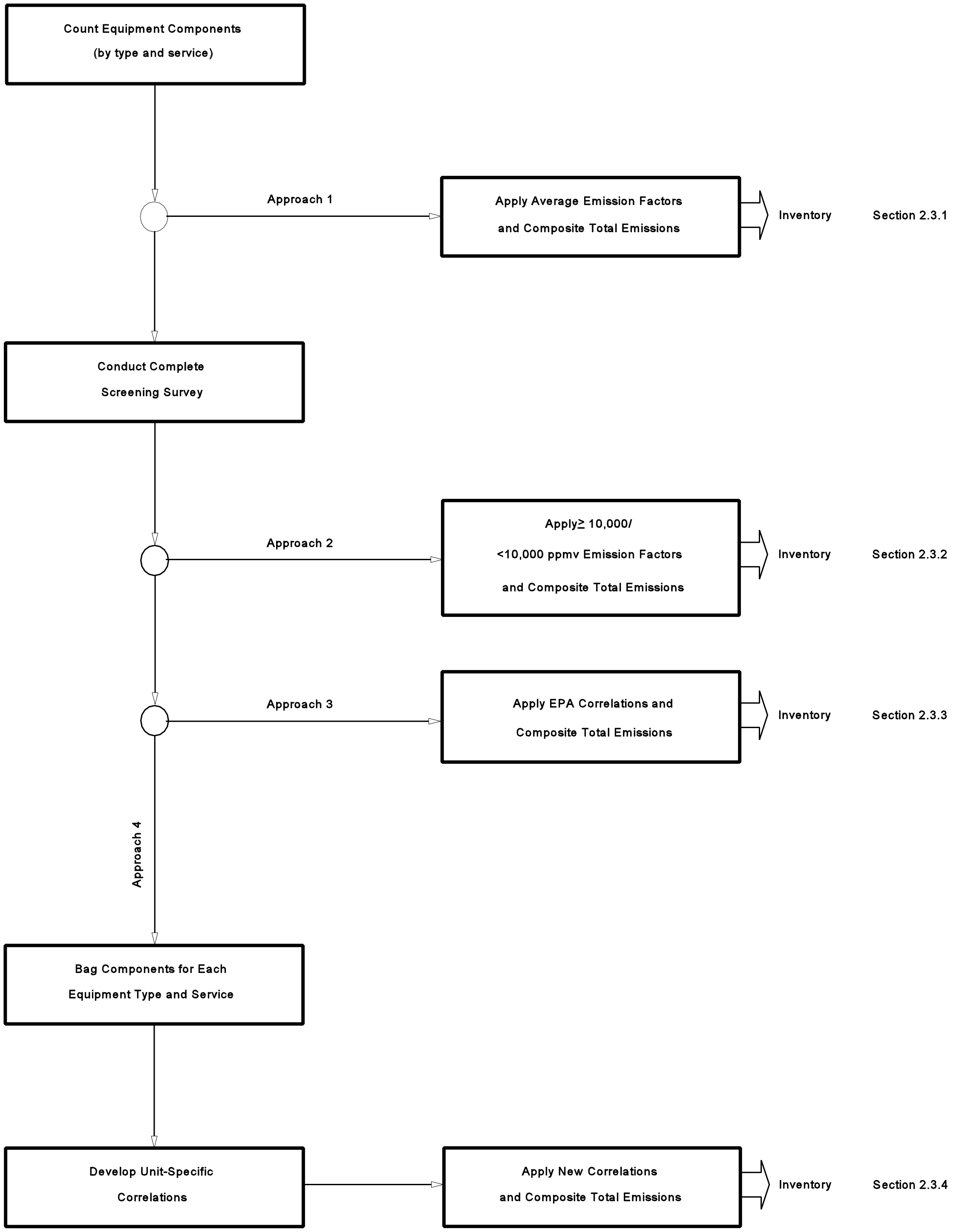

Figure 2-1. Overview of Data Collection and Analysis Approaches for Developing Equipment Leak Emissions Inventory

Except for the Average Emission Factor Approach, all of the approaches require screening data. Screening data are collected by using a portable monitoring instrument to sample air from potential leak interfaces on individual pieces of equipment. A screening value is a measure of the concentration of leaking compounds in the ambient air that provides an indication of the leak rate from an equipment piece, and is measured in units of parts per million by volume (ppmv). The procedures for collecting screening data are presented in chapter 3.0.

In addition to equipment counts and screening data, the Unit-Specific Correlation Approach requires bagging data. Bagging data consist of screening values and their associated measured leak rates. A leak rate is measured by enclosing an equipment piece in a bag to determine the actual mass emission rate of the leak. The screening values and measured leak rates from several pieces of equipment are used to develop a unit-specific correlation. The resulting leak rate/screening value correlation predicts the mass emission rate as a function of the screening value. Procedures for collecting bagging data are described in detail in chapter 4.0.

Each of the approaches are applicable to any chemical-handling facility. However, the EPA has developed more than one set of emission factors and correlations, and the type of process unit being considered governs which set must be used to estimate emissions. Historical data collection on emissions from equipment leaks in SOCMI, refineries, marketing terminals and oils and gas production operations have yielded emission factors and correlations for these source categories. Emission factors and correlations for other source categories have not been developed.

For process units in source categories for which emission factors and/or correlations have not been developed, the factors and/or correlations already developed can be utilized. However, appropriate evidence should indicate that the existing emission factors and correlations are applicable to the source category in question. Criteria for determining the appropriateness of applying existing emission factors and correlations to another source category may include one or more of the following: (1) process design, (2) process operation parameters (i.e., pressure and temperature), (3) types of equipment used, and (4) types of material handled. For example, in most cases, SOCMI emission factors and correlations are applicable for estimating equipment leak emissions from the polymer and resin manufacturing industry. This is because, in general, these two industries have comparable process design and comparable process operation, they use the same types of equipment, and they tend to use similar feedstock.

2.2.2 Overview of Equipment Leak Data Collection

Data on equipment leak emissions of organic compounds have been collected from refineries, marketing terminals, oil and gas production operations, and SOCMI process units. Emission factors and correlations have been developed for the following equipment types: valves, pumps, compressors, pressure relief valves, connectors, flanges, and open-ended lines. An "others" category has also been developed for the petroleum industry. For sampling connections, an average emission factor has been developed that estimates the typical amount of material purged when a sample is collected. A brief history of the development of these factors and correlations is presented below.

2.2.2.1 Refinery Assessment Study.[1,2] In the late 1970s, the EPA initiated the Petroleum Refinery Assessment Study, and equipment leak data from 13 refineries were collected. In this study, equipment was screened and the majority of sources that had screening values over 200 ppmv were bagged. Bagged equipment emission rates were reported as non-methane organic compound emission rates. Average emission factors and correlations for each equipment type were developed based on the screening and bagging data collected in this study.

The Refinery Assessment Study included an investigation of possible correlations between equipment leaks and process variables. The only process variables found to correlate with mass emission rates in a statistically significant manner were

(1) the phase of the process stream (service), and (2) the relative volatility of liquid streams. This finding led to the separation of data for valves, pumps, and pressure relief valves by type of service. Three service categories were defined:

- Gas/vapor - material in a gaseous state at operating conditions;
- Light liquid - material in a liquid state in which the sum of the concentration of individual constituents with a vapor pressure over 0.3 kilopascals (kPa) at 20 ^{o}C is greater than or equal to 20 weight percent; and
- Heavy liquid - not in gas/vapor service or light liquid service.

2.2.2.2 Gas Plant Studies.[3] A total of six gas plants were screened in two studies: Four were screened by the EPA and two by the American Petroleum Institute. Average emission factors were developed, and information on the percentage of equipment with screening values equal to or greater than 10,000 ppmv was presented. The average factors include emissions of ethane and methane, which are hydrocarbons but are not classified as VOC's.

2.2.2.3 Revised Petroleum Industry Correlations and Emission Factors. During the early-1990's, new petroleum industry equipment leak bagging data were collected and analyzed. The Western States Petroleum Association (WSPA) and the American Petroleum Institute (API) jointly commissioned the 1994 refinery equipment leak report[4] to evaluate fugitive emissions collected from five petroleum refineries. The API also commissioned the 1993 marketing terminal equipment leak report,[5] which included bagging data from three marketing terminals, and, along with the Gas Research Institute (GRI), jointly commissioned the 1993 and 1995 oil and gas production operations reports, which included bagging data from 24 facilities.[6,7] In addition to the bagging data, screening data were also collected from 17 marketing terminals[8] and 24 oil and gas production facilities.[6,7] Data from gas/vapor, light liquid, and/or heavy liquid streams were collected for these studies from non-flanged connectors, flanges, open-ended lines, pumps, values, instruments, loading arms, pressure relief valves, stuffing boxes, vents, compressors, dump lever arms, diaphrams, drains, hatches, meters, and polished rods.

A specific goal of the above studies was to collect high quality data to enhance or replace the previously published refinery correlations. As a result of the analyses discussed in appendix C, the bagging data collected from refineries, marketing terminals, and oil and gas production facilities during the early-1990’s were combined to replace the previously published refinery correlations with correlations applicable to the entire petroleum industry. In addition, the new correlations apply across all services for a given equipment type. The previously published refinery correlations were specific to service and equipment.

The screening data were used to develop average emission factors for marketing terminals and for oil and gas production operations. The average emission factors for oil and gas production operations replace the gas plant factors published in previous versions of this document and apply to light crude, heavy crude, gas plant, gas production and off shore facilities. No new screening data were available for refineries, therefore the previously published refinery average emission factors remain unchanged in this version of the protocol. Appendix C contains more detailed information on how the new petroleum industry correlations, marketing terminal emission factors, and oil and gas production operations emission factors were developed.

2.2.2.4 Original SOCMI Average Emission Factors and Correlations. In 1980, two studies were coordinated by the EPA to collect data from SOCMI process units. These studies were the 24-Unit Study,[9] and the Six-Unit Maintenance Study.[10] In the 24-Unit Study, screening data were obtained from equipment containing organic compounds at 24 individual chemical process units representing a cross-section of the SOCMI. In the Six-Unit Maintenance Study, bagging data were collected from six of the process units within the 24-Unit Study to determine the effect of maintenance on equipment leak emissions. Most of the bagging data were collected from equipment with screening values above 1,000 ppmv. As part of the Six-Unit Maintenance Study, correlations were developed for light liquid pumps, gas valves, and light liquid valves.

The original SOCMI average emission factors were first presented in the document "Fugitive Emission Sources of Organic Compounds--Additional Information on Emissions, Emission Reductions, and Costs."[6] This document is referred to as the Fugitive Emissions Additional Information Document (AID). In the Fugitive Emissions AID, the data from the Refinery Assessment Study were further analyzed to develop "leak/no leak" emission factors. (A "leak" was defined as a screening value greater than or equal to 10,000 ppmv.) With the exception of the factor for gas valves, the original SOCMI average emission factors were developed using (1) the leak/no-leak emission factors developed from the Refinery Assessment Study data, and (2) the leak frequencies from the SOCMI 24-Unit Study screening value data set. This approach was based on statistical comparisons that indicated that the most significant characteristic that distinguished equipment in SOCMI facilities from that in refineries was not the leak rate for a given screening value, but rather the fraction of equipment that had screening values greater than or equal to 10,000 ppmv.

Thus, the following equation was used to calculate the original SOCMI average emission factors:

$$\text{SOCMI Average Factor} = (F \times RLF) + (1 - F) \times RNLF$$

where:

F = Fraction of sources from the 24-Unit Study that screened greater than or equal to 10,000 ppmv;

RLF = Refinery leaking emission factor; and

RNLF = Refinery non-leaking emission factor.

For gas valves, the previously collected data suggested that for a given screening value the leak rate at a SOCMI facility was not statistically equivalent to the leak rate at a refinery. Therefore, data from the Six-Unit Maintenance Study were used to develop the gas valve average emission factor.

2.2.2.5 Revised SOCMI Emission Factors and Correlations. In 1987 and 1988, screening data were obtained from 19 ethylene oxide and butadiene producers, and, in 1990, bagging data were collected from 16 of these process units. Screening and bagging data were collected from light liquid pumps, gas valves, light liquid valves, and connectors. A specific goal of the program was to bag equipment that had screening values less than 1,000 ppmv. The bagging data were combined with bagging data previously collected in the Six-Unit Maintenance Study, and this combined bagging data set was used to revise the SOCMI correlations. Likewise, the new screening data were combined with screening data previously collected in the 24-Unit Study, and this combined screening data set was used with the revised correlations to generate new SOCMI emission factors. Appendix B.2 contains more detailed information on how the revised SOCMI correlations and emission factors were developed.

2.3 APPROACHES FOR ESTIMATING EQUIPMENT LEAK EMISSIONS

In this section, each of the approaches for estimating equipment leak emissions are discussed. The description of each approach focuses on the basic method for estimating TOC emissions. Each of the approaches are demonstrated in example calculations contained in appendix A. Special topics at the end of the chapter have been included to address how to estimate VOC emissions when some of the organic compounds in the stream are not classified as VOC’s and also how to speciate emissions for individual chemicals from equipment containing a mixture.

2.3.1 Average Emission Factor Approach

One accepted approach for estimating emissions allows use of average emission factors developed by the EPA in combination with unit-specific data that are relatively simple to obtain. These data include: (1) the number of each type of component in a unit (valve, connector, etc.), (2) the service each component is in (gas, light liquid, or heavy liquid), (3) the TOC concentration of the stream (and VOC or HAP concentrations if speciation is to be performed), and (4) the time period each component was in that service. The average emission factors for SOCMI process units, refineries, marketing terminals, and oil and gas production operations are presented in tables 2-1, 2-2, 2-3, and 2-4 respectively. The SOCMI, marketing terminal, and oil and gas production operations average emission factors predict total organic compound emission rates, whereas the refinery average factors predict non-methane organic compound emission rates. Note that limited data has been collected on the leak rate of agitators, and, until additional data are collected for emissions from agitator seals, the average factor for light liquid pump seals can be used to estimate emissions from agitators.

Although the average emission factors are in units of kilogram per hour per individual source, it is important to note that these factors are most valid for estimating emissions from a population of equipment. The average factors are not intended to be used for estimating emissions from an individual piece of equipment over a short time period (i.e., 1 hour).

To estimate emissions using the Average Emission Factor Approach, the concentration of TOC in weight fraction within the equipment is needed because equipment with higher TOC concentrations tend to have higher TOC leak rates. When using the Average Emission Factor Approach, equipment should be grouped into "streams" where all the equipment within the stream have approximately the same TOC weight fraction.

To apply the average emission factors, use the following equation to estimate TOC mass emissions from all of the equipment in a stream of a given equipment type:

$$E_{TOC} = F_A \times WF_{TOC} \times N$$

where:

E_{TOC} = Emission rate of TOC from all equipment in the stream of a given equipment type (kg/hr);

TABLE 2-1. SOCMI AVERAGE EMISSION FACTORS

Equipment type	Service	Emission factor[a] (kg/hr/source)
Valves	Gas	0.00597
	Light liquid	0.00403
	Heavy liquid	0.00023
Pump seals[b]	Light liquid	0.0199
	Heavy liquid	0.00862
Compressor seals	Gas	0.228
Pressure relief valves	Gas	0.104
Connectors	All	0.00183
Open-ended lines	All	0.0017
Sampling connections	All	0.0150

[a] These factors are for total organic compound emission rates.

[b] The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

TABLE 2-2. REFINERY AVERAGE EMISSION FACTORS[a]

Equipment type	Service	Emission factor (kg/hr/source)[b]
Valves	Gas	0.0268
	Light liquid	0.0109
	Heavy liquid	0.00023
Pump seals[c]	Light liquid	0.114
	Heavy liquid	0.021
Compressor seals	Gas	0.636
Pressure relief valves	Gas	0.16
Connectors	All	0.00025
Open-ended lines	All	0.0023
Sampling connections	All	0.0150

[a] Source: Reference 2.

[b] These factors are for non-methane organic compound emission rates.

[c] The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

TABLE 2-3. MARKETING TERMINAL AVERAGE EMISSION FACTORS

Equipment type	Service	Emission factor (kg/hr/source)[a]
Valves	Gas	1.3E-05
	Light Liquid	4.3E-05
Pump seals	Gas	6.5E-05
	Light Liquid	5.4E-04
Others (compressors and others)[b]	Gas	1.2E-04
	Light Liquid	1.3E-04
Fittings (connectors and flanges)[c]	Gas	4.2E-05
	Light Liquid	8.0E-06

[a] These factors are for total organic compound emission rates (including non-VOC’s such as methane and ethane).

[b] The "other" equipment type should be applied for any equipment type other than fittings, pumps, or valves.

[c] "Fittings" were not identified as flanges or non-flanged connectors; therefore, the fitting emissions were estimated by averaging the estimates from the connector and the flange correlation equations.

TABLE 2-4. OIL AND GAS PRODUCTION OPERATIONS AVERAGE EMISSION FACTORS (kg/hr/source)

Equipment Type	Service[a]	Emission Factor (kg/hr/source)[b]
Valves	Gas	4.5E-03
	Heavy Oil	8.4E-06
	Light Oil	2.5E-03
	Water/Oil	9.8E-05
Pump seals	Gas	2.4E-03
	Heavy Oil	NA
	Light Oil	1.3E-02
	Water/Oil	2.4E-05
Others[c]	Gas	8.8E-03
	Heavy Oil	3.2E-05
	Light Oil	7.5E-03
	Water/Oil	1.4E-02
Connectors	Gas	2.0E-04
	Heavy Oil	7.5E-06
	Light Oil	2.1E-04
	Water/Oil	1.1E-04
Flanges	Gas	3.9E-04
	Heavy Oil	3.9E-07
	Light Oil	1.1E-04
	Water/Oil	2.9E-06
Open-ended lines	Gas	2.0E-03
	Heavy Oil	1.4E-04
	Light Oil	1.4E-03
	Water/Oil	2.5E-04

[a] Water/Oil emission factors apply to water streams in oil service with a water content greater than 50%, from the point of origin to the point where the water content reaches 99%. For water streams with a water content greater than 99%, the emission rate is considered negligible.

[b] These factors are for total organic compound emission rates (including non-VOC’s such as methane and ethane) and apply to light crude, heavy crude, gas plant, gas production, and off shore facilities. "NA" indicates that not enough data were available to develop the indicated emission factor.

[c] The "other" equipment type was derived from compressors, diaphrams, drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, relief valves, and vents. This "other" equipment type should be applied for any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

F_A = Applicable average emission factor for the equipment type (kg/hr/source);

FOR REFINERIES ONLY: The emission factor "F_A" must be adjusted to account for all organic compounds in the stream because the refinery factors are only valid for non-methane organic compounds (percents up to a maximum of 10 percent by weight methane are permitted):

$$F_A = F_A \times \frac{WF_{TOC}}{WF_{TOC} - WF_{methane}} ;$$

WF_{TOC} = Average weight fraction of TOC in the stream;

$WF_{methane}$ = Average weight fraction of methane in the stream; and

N = Number of pieces of equipment of the applicable equipment type in the stream.

Note that the emission factor "F_A" is defined differently for refineries than for SOCMI, marketing terminals, or oil and gas production operations when calculating TOC mass emissions. It is necessary to adjust the "F_A" term when applied to refineries, because when the refinery factors were developed, the methane was subtracted out of the organic total. Adjusting the "F_A" term for refineries is a way to correct for this. Two guidelines when correcting the "F_A" term when applied to refineries are as follows:

- The correction should only be applied to equipment containing a mixture of organics and methane; and
- The maximum correction for the methane weight fraction should not exceed 0.10, even if the equipment contains greater than 10 weight percent methane. (This reflects that equipment in the Refinery Assessment Study[1,2] typically contained 10 weight percent or less methane).

Thus, at a SOCMI process unit, if there were 100 gas valves in a stream containing, on average, 90 weight percent TOC and 10 weight percent water vapor, emissions would be calculated as follows:

$$
\begin{aligned}
E_{TOC} &= F_A \times WF_{TOC} \times N \\
&= 0.00597 \text{ kg/hr/gas valve} \times 0.9 \times 100 \text{ gas valves} \\
&= 0.54 \text{ kg/hr of VOC from gas valves in the stream}
\end{aligned}
$$

At a refinery, if there were 100 gas valves in a stream that, on average, contained 80 weight percent non-methane TOC, 10 weight percent water vapor, and 10 weight percent methane (thus, the TOC weight percent would be 90), emissions would be calculated using the above equation as follows:

$$
\begin{aligned}
E_{TOC} &= F_A \times \frac{WF_{TOC}}{WF_{TOC} - WF_{methane}} \times WF_{TOC} \times N \\
&= 0.0268 \text{ kg/hr/gas valve} \times (0.9/0.9-0.1) \times 0.9 \times \\
&\quad 100 \text{ gas valves} \\
&= 2.71 \text{ kg/hr of VOC from gas valves in the stream}
\end{aligned}
$$

If there are several streams at a process unit, the total TOC emission rate for an equipment type is the sum of emissions from each of the streams. The total emission rates for all of the equipment types are summed to generate the process unit total TOC emission rate from leaking equipment.

Assuming all of the organic compounds in the stream are classified as VOC’s, the total VOC emission for each stream is calculated as the sum of TOC emissions associated with each specific equipment type in the stream. Section 2.4.6 discusses an adjustment that can be made to predict the VOC emission rate if some of the organic compounds in the stream are not classified as VOC’s (such as methane and ethane).

As mentioned earlier, the average emission factors are not intended to provide an accurate estimate of the emission rate from a single piece of equipment. Rather, the average factors are more appropriately applied to the estimation of emissions from populations of equipment. Data indicate that the range of possible leak rates from individual pieces of equipment spans several orders of magnitude. As a result, the majority of total emissions from a population of equipment at any given time will normally occur from a small percentage of the total equipment. The average emission factors account for the span of possible leak rates, but, as a result, they are not necessarily an accurate indication of the mass emission rate from an individual piece of equipment.

Furthermore, the average emission factors do not reflect different site-specific conditions among process units within a source category. Site-specific factors can have considerable influence on leak rates from equipment. Nevertheless, in the absence of screening data, the average emission factors do provide an indication of equipment leak emission rates from equipment in a process unit.

2.3.2 Screening Ranges Approach

The Screening Ranges Approach (formerly known as the leak/no-leak approach) offers some refinement over the Average Emission Factor Approach, thereby allowing some adjustment for individual unit conditions and operation. This approach is included in this section primarily to aid in the analysis of old datasets which were collected for older regulations that used 10,000 ppmv as the leak definition. This approach and the other two remaining approaches require that screening data be collected for the equipment in the process unit. The screening data are an indication of leak rates. When applying this approach, it is assumed that components having screening values greater than 10,000 ppmv have a different average emission rate than components with screening values less than 10,000 ppmv.

This approach may be applied when screening data are available as either "greater than or equal to 10,000 ppmv" or as "less than 10,000 ppmv." Emission factors for SOCMI, refineries, marketing terminals, and oil and gas production operations for these two ranges of screening values are presented in tables 2-5, 2-6, and 2-7, and 2-8, respectively. As with the average factors, the SOCMI, marketing terminal, and oil and gas production operations screening range factors predict total

TABLE 2-5. SOCMI SCREENING RANGES EMISSION FACTORS

Equipment type	Service	≥10,000 ppmv Emission factor (kg/hr/source)[a]	<10,000 ppmv Emission factor (kg/hr/source)[a]
Valves	Gas	0.0782	0.000131
	Light liquid	0.0892	0.000165
	Heavy liquid	0.00023	0.00023
Pump seals[b]	Light liquid	0.243	0.00187
	Heavy liquid	0.216	0.00210
Compressor seals	Gas	1.608	0.0894
Pressure relief valves	Gas	1.691	0.0447
Connectors	All	0.113	0.0000810
Open-ended lines	All	0.01195	0.00150

[a] These factors are for total organic compound emission rates.

[b] The light liquid pump seal factors can be applied to estimate the leak rate from agitator seals.

TABLE 2-6. REFINERY SCREENING RANGES EMISSION FACTORS[a]

Equipment type	Service	≥10,000 ppmv Emission factor (kg/hr/source)[b]	<10,000 ppmv Emission factor (kg/hr/source)[b]
Valves	Gas	0.2626	0.0006
	Light liquid	0.0852	0.0017
	Heavy liquid	0.00023	0.00023
Pump seals[c]	Light liquid	0.437	0.0120
	Heavy liquid	0.3885	0.0135
Compressor seals	Gas	1.608	0.0894
Pressure relief valves	Gas	1.691	0.0447
Connectors	All	0.0375	0.00006
Open-ended lines	All	0.01195	0.00150

[a] Source: Reference 6.

[b] These factors are for non-methane organic compound emission rates.

[c] The light liquid pump seal factors can be applied to estimate the leak rate from agitator seals.

TABLE 2-7. MARKETING TERMINAL SCREENING RANGES EMISSION FACTORS

Equipment type	Service	≥10,000 ppmv Emission factor (kg/hr/source)[a]	<10,000 ppmv Emission factor (kg/hr/source)[a]
Valves	Gas	NA	1.3E-05
	Light Liquid	2.3E-02	1.5E-05
Pump seals	Light liquid	7.7E-02	2.4E-04
Other (compressors and others)[b]	Gas	NA	1.2E-04
	Light liquid	3.4E-02	2.4E-05
Fittings (connectors and flanges)[c]	Gas	3.4E-02	5.9E-06
	Light liquid	6.5E-03	7.2E-06

[a] These factors are for total organic compound emission rates (including non-VOC’s such as methane and ethane). "NA" indicates that not enough data were available to develop the indicated emission factor.

[b] The "other" equipment type should be applied for any equipment type other than fittings, pumps, or valves.

[c] "Fittings" were not identified as flanges or connectors; therefore, the fitting emissions were estimated by averaging the estimates from the connector and the flange correlation equations.

TABLE 2-8. OIL AND GAS PRODUCTION OPERATIONS SCREENING RANGES EMISSION FACTORS

Equipment type	Service[b]	≥10,000 ppmv Emission factor (kg/hr/source)[a]	<10,000 ppmv Emission factor (kg/hr/source)[a]
Valves	Gas	9.8E-02	2.5E-05
	Heavy Oil	NA	8.4E-06
	Light Oil	8.7E-02	1.9E-05
	Water/Oil	6.4E-02	9.7E-06
Pump seals	Gas	7.4E-02	3.5E-04
	Heavy Oil	NA	NA
	Light Oil	1.0E-01	5.1E-04
	Water/Oil	NA	2.4E-05
Others[c]	Gas	8.9E-02	1.2E-04
	Heavy Oil	NA	3.2E-05
	Light Oil	8.3E-02	1.1E-04
	Water/Oil	6.9E-02	5.9E-05
Connectors	Gas	2.6E-02	1.0E-05
	Heavy Oil	NA	7.5E-06
	Light Oil	2.6E-02	9.7E-06
	Water/Oil	2.8E-02	1.0E-05
Flanges	Gas	8.2E-02	5.7E-06
	Heavy Oil	NA	3.9E-07
	Light Oil	7.3E-02	2.4E-06
	Water/Oil	NA	2.9E-06
Open-ended lines	Gas	5.5E-02	1.5E-05
	Heavy Oil	3.0E-02	7.2E-06
	Light Oil	4.4E-02	1.4E-05
	Water/Oil	3.0E-02	3.5E-06

[a] These factors are for total organic compound emission rates (including non-VOC’s such as methane and ethane) and apply to light crude, heavy crude, gas plant, gas production, and offshore facilities. "NA" indicates that not enough data were available to develop the indicated emission factor.

[b] Water/Oil emission factors apply to water streams in oil service with a water content greater than 50%, from the point of origin to the point where the water content reaches 99%. For water streams with a water content greater than 99%, the emission rate is considered negligible.

[c] The "other" equipment type was derived from compressors, diaphrams, drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, relief valves, and vents. This "other" equipment type should be applied for any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

organic compound emissions, whereas the refinery screening range factors predict non-methane organic compound emissions. Note that there are not screening range factors for sampling connections because emissions from sampling connections occur when the line is purged, and, thus, are independent of any screening value. Also, as with the average factors, the screening range factors for light liquid pumps can be applied to agitators.

The Screening Ranges Approach is applied in a similar manner as the Average Emission Factor Approach in that equipment counts are multiplied by the applicable emission factor. Also, for refineries, the screening range emission factors must be adjusted for methane in the equipment because when the refinery factors were developed, the methane was subtracted out of the organic total.

To calculate TOC emissions using the Screening Ranges Approach, the following equation is used:

$$E_{TOC} = (F_G \times N_G) + (F_L \times N_L)$$

where:

E_{TOC} = TOC emission rate for an equipment type (kg/hr);

F_G = Applicable emission factor for sources with screening values greater than or equal to 10,000 ppmv (kg/hr/source);

FOR REFINERIES ONLY: The emission factor "F_G" must be adjusted to account for all organic compounds in the stream because the refinery factors are only valid for non-methane organic compounds (percents up to a maximum of 10 percent by weight methane are permitted):

$$F_G = F_G \times \frac{WP_{TOC}}{WP_{TOC} - WP_{methane}};$$

WP_{TOC} = Average weight percent of TOC in the stream;

$WP_{methane}$ = Average weight percent of methane in the stream;

N_G = Equipment count (specific equipment type) for sources with screening values greater than or equal to 10,000 ppmv;

F_L = Applicable emission factor for sources with screening values less than 10,000 ppmv (kg/hr/source)

FOR REFINERIES ONLY: The emission factor "F_L" must be adjusted to account for all organic compounds in the stream because the refinery factors are only valid for non-methane organic compounds (percents up to a maximum of 10 percent by weight methane are permitted):

$$F_L = F_L \times \frac{WP_{TOC}}{WP_{TOC} - WP_{methane}} \text{ ; and}$$

N_L = Equipment count (specific equipment type) for sources with screening values less than 10,000 ppmv.

Assuming all of the organic compounds in the stream are classified as VOC’s, the total VOC emission for each stream is calculated as the sum of TOC emissions associated with each specific equipment type in the stream. Section 2.4.6 discusses an adjustment that can be made to predict the VOC emission rate if some of the organic compounds in the stream are not classified as VOC’s (such as methane and ethane).

The screening range emission factors are a better indication of the actual leak rate from individual equipment than the average emission factors. Nevertheless, available data indicate that measured mass emission rates can vary considerably from the rates predicted by use of these factors.

2.3.3 EPA Correlation Approach

This approach offers an additional refinement to estimating emissions from equipment leaks by providing an equation to predict mass emission rate as a function of screening value for a particular equipment type. Correlations developed by the EPA relating screening values to mass emission rates for SOCMI process units and for petroleum industry process units are presented in tables 2-9 and 2-10, respectively. Correlations for the petroleum industry apply to refineries, marketing terminals and oil and gas production operations. Figures 2-2 through 2-5 plot the correlations. Both the SOCMI and petroleum industry correlations predict total organic compound emission rates. Appendix B.1 contains additional information on the general development of correlation equations. Additionally, appendix B.2 contains information about the development of the SOCMI correlations and appendix C contains information about the development of the petroleum industry correlations.

The EPA Correlation Approach is preferred when actual screening values are available. Correlations can be used to estimate emissions for the entire range of non-zero screening values, from the highest potential screening value to the screening value that represents the minimum detection limit of the monitoring device. This approach involves entering the non-zero, non-pegged screening value into the correlation equation, which predicts the TOC mass emission rate based on the screening value. Default zero emission rates are used for screening values of zero ppmv and pegged emission rates are used for "pegged" screening values (the screening value is beyond the upper limit measured by the portable screening device).

Correlations for SOCMI are available for (1) gas valves; (2) light liquid valves; (3) connectors; and (4) light liquid pump seals. Correlations for the petroleum industry are available for (1) valves; (2) connectors; (3) pumps; (4) flanges; (5) open-ended lines; and (6) "others" (derived from instruments, loading arms, pressure relief valves, stuffing boxes, and vents).

Limited bagging data for compressors and pressure relief devices have been obtained at SOCMI plants. However, because statistical tests performed as part of the Refinery Assessment Study[2] indicated that emissions from light liquid pumps, compressors, and pressure relief valves could be expressed with a single correlation, until additional data are collected, the SOCMI equation for light liquid pump seals can be applied to

TABLE 2-9. SOCMI LEAK RATE/SCREENING VALUE CORRELATIONS

Equipment type	Correlation[a,b]
Gas valves	Leak rate (kg/hr) = 1.87E-06 × $(SV)^{0.873}$
Light liquid valves	Leak rate (kg/hr) = 6.41E-06 × $(SV)^{0.797}$
Light liquid pumps[c]	Leak rate (kg/hr) = 1.90E-05 × $(SV)^{0.824}$
Connectors	Leak rate (kg/hr) = 3.05E-06 × $(SV)^{0.885}$

[a] SV = Screening value in ppmv.

[b] These correlations predict total organic compound emission rates.

[c] The correlation for light liquid pumps can be applied to compressor seals, pressure relief valves, agitator seals, and heavy liquid pumps.

TABLE 2-10. PETROLEUM INDUSTRY LEAK RATE/SCREENING VALUE CORRELATIONS[a]

Equipment type/service	Correlation[b,c]
Valves/all	Leak rate (kg/hr) = 2.29E-06 × $(SV)^{0.746}$
Pump seals/all	Leak rate (kg/hr) = 5.03E-05 × $(SV)^{0.610}$
Others[d]	Leak rate (kg/hr) = 1.36E-05 × $(SV)^{0.589}$
Connectors/all	Leak rate (kg/hr) = 1.53E-06 × $(SV)^{0.735}$
Flanges/all	Leak rate (kg/hr) = 4.61E-06 × $(SV)^{0.703}$
Open-ended lines/all	Leak rate (kg/hr) = 2.20E-06 × $(SV)^{0.704}$

[a] The correlations presented in this table are revised petroleum industry correlations.

[b] SV = Screening value in ppmv.

[c] These correlations predict total organic compound emission rates (including non-VOC’s such as methane and ethane).

[d] The "other" equipment type was derived from instruments, loading arms, pressure relief valves, stuffing boxes, and vents. This "other" equipment type should be applied to any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

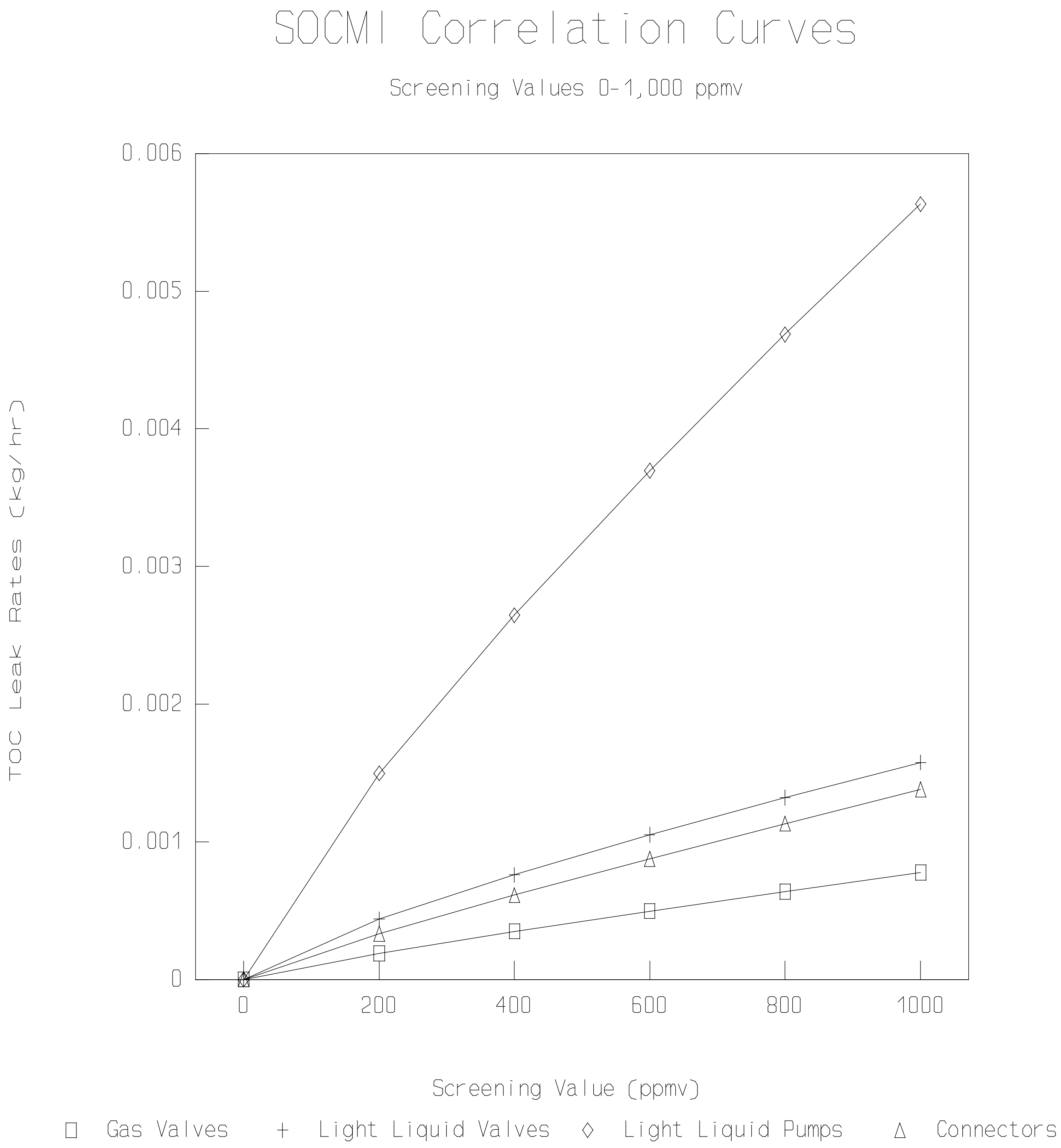

Figure 2-2. SOCMI Correlations relating total organic compound (TOC) leak rate to screening value: 0 - 1,000 ppmv

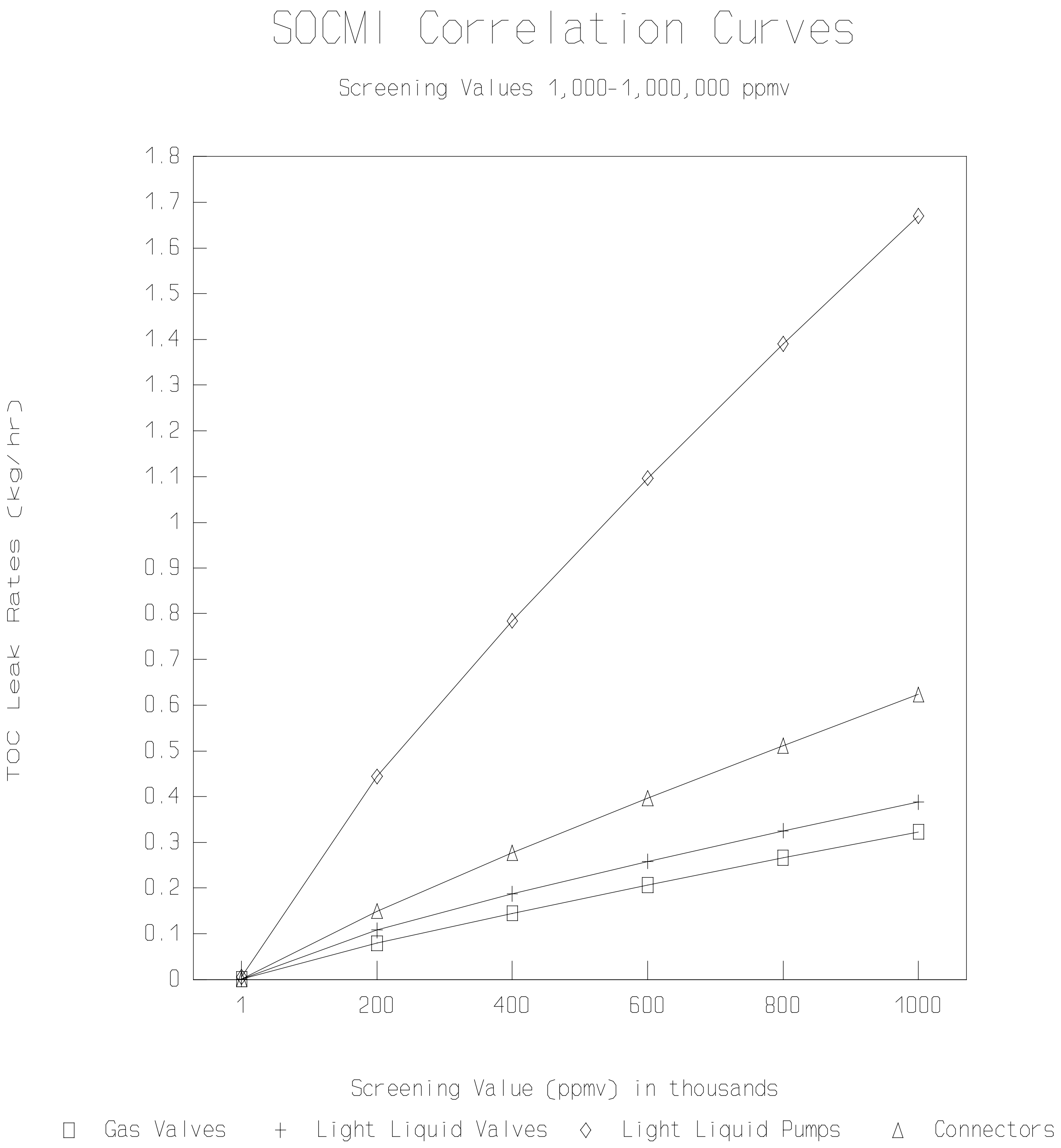

Figure 2-3. SOCMI Correlations relating total organic compound (TOC) leak rate to screening value: 1,000 - 1,000,000 ppmv

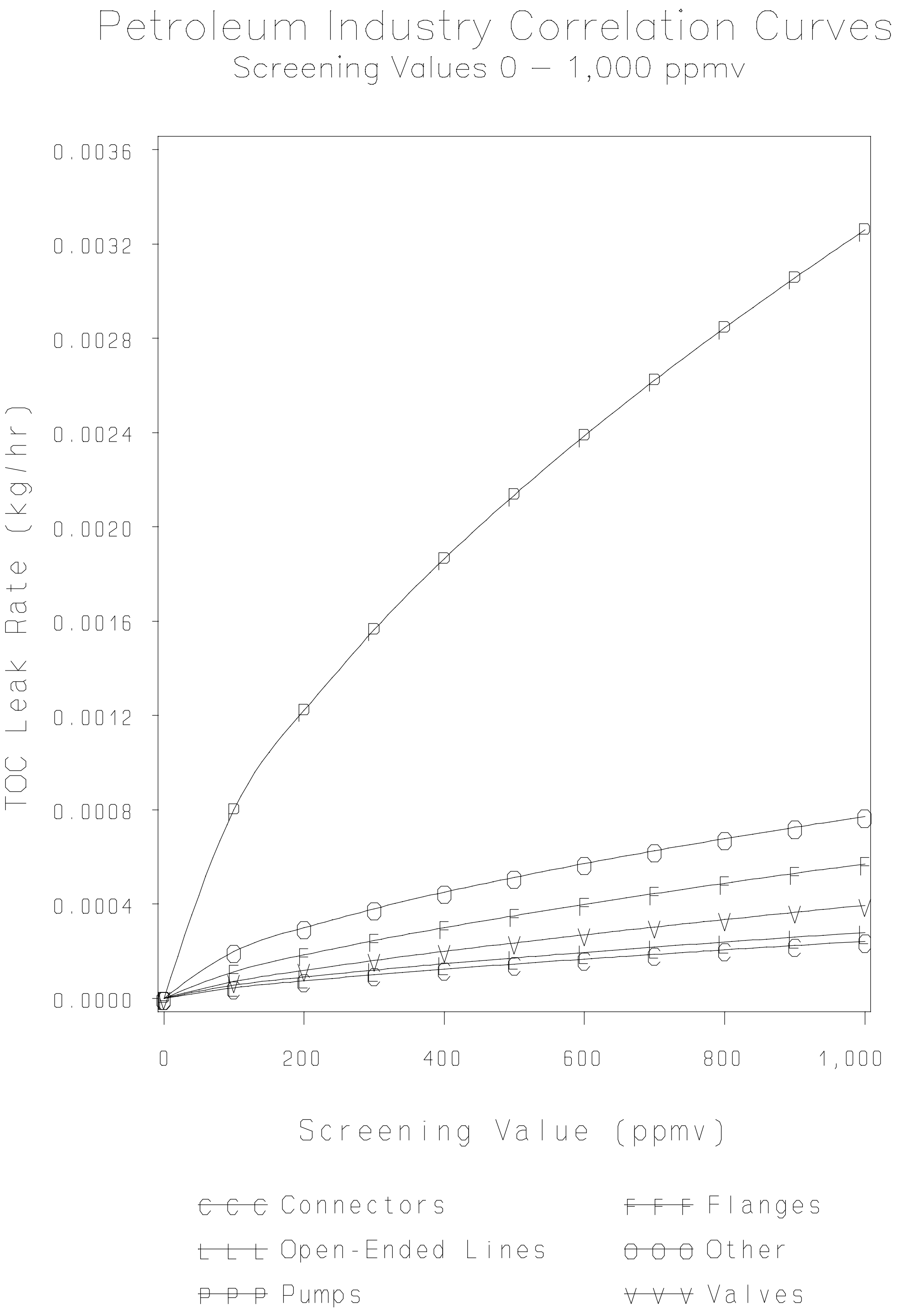

Figure 2-4. Petroleum Industry Correlations relating total organic compound (TOC) leak rate to screening value: 1,000 - 1,000,000 ppmv

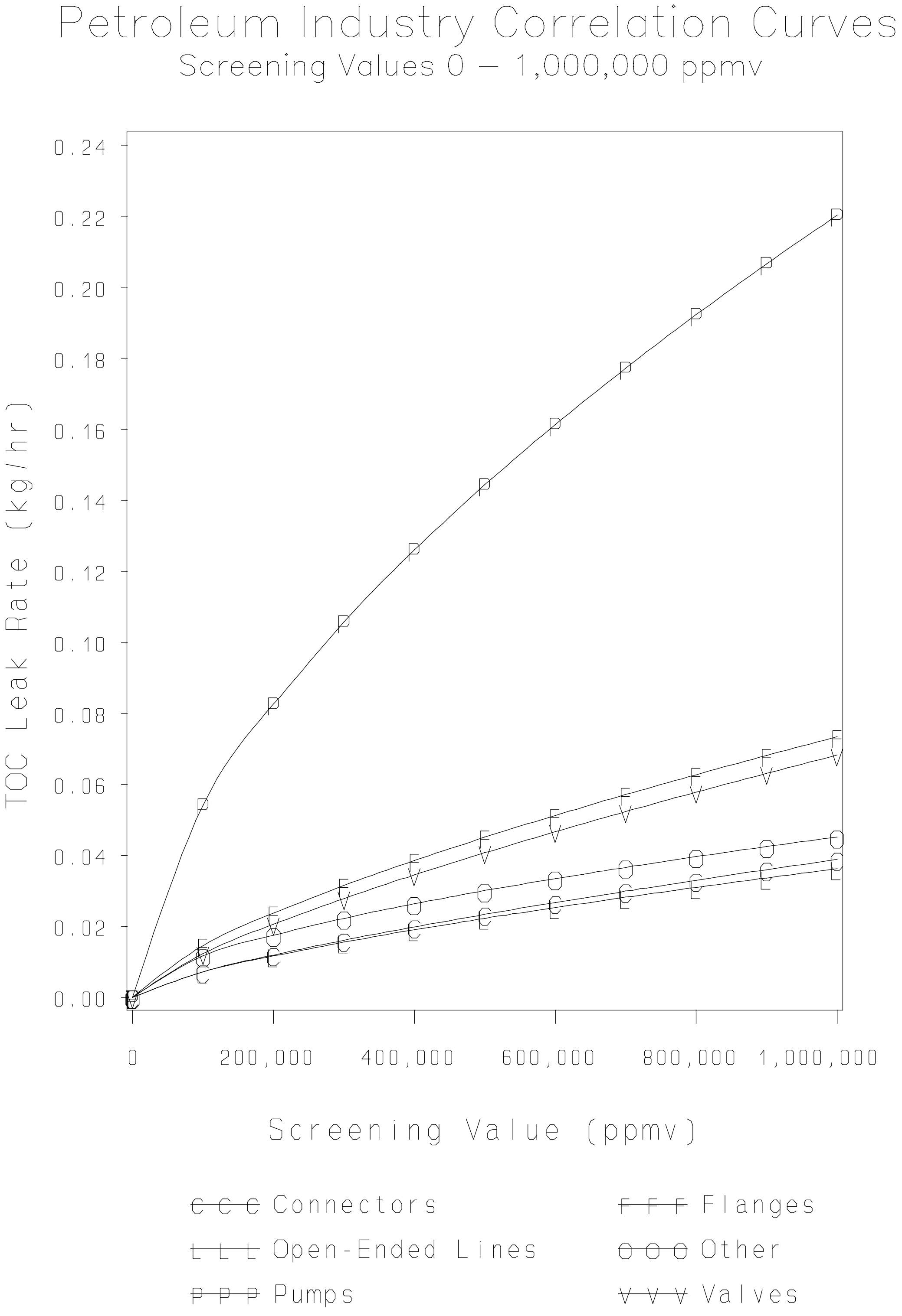

Figure 2-5. Petroleum Industry Correlations relating total organic compound (TOC)leak rate to screening value: 1,000 - 1,000,000 ppmv

estimate emissions for compressor seals and pressure relief valves in SOCMI process units. Because bagging data were limited and the frequency of occurrence of some equipment types was small, a correlation for an "other" equipment type was developed for the petroleum industry correlations to apply to any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

Bagging data for agitator seals at petroleum industry and SOCMI process units are unavailable at this time. Compared to those equipment types that have correlations, agitators most closely resemble light liquid pumps, and, for this reason, the applicable light liquid pump correlation can be used to estimate agitator emissions. Similarly, the SOCMI light liquid pump correlation can be used to estimate emissions from SOCMI heavy liquid pumps.

The "default-zero" leak rate is the mass emission rate associated with a screening value of zero. (Note that any screening value that is less than or equal to ambient [background] concentration is considered a screening value of zero.) The correlations mathematically predict zero emissions for zero screening values. However, data collected by the EPA show this prediction to be incorrect. Mass emissions have been measured from equipment having a screening value of zero.
A specific goal when revising the SOCMI and petroleum industry correlations was to collect mass emissions data from equipment that had a screening value of zero. These data were used to determine a default-zero leak rate associated with equipment with zero screening values.

Table 2-11 lists the SOCMI default-zero leak rates and table 2-12 presents the petroleum industry default-zero leak rates for each of the equipment types with correlation equations. These default-zero leak rates are applicable only when the minimum detection limit of the portable monitoring instrument is 1 ppmv or less above background.

The portable monitoring device used to collect the default-zero data was sufficiently sensitive to indicate a

TABLE 2-11. DEFAULT-ZERO VALUES: SOCMI PROCESS UNITS

Equipment type	Default-zero emission rate (kg/hr/source)[a]
Gas valve	6.6E-07
Light liquid valve	4.9E-07
Light liquid pump[b]	7.5E-06
Connectors	6.1E-07

[a] The default zero emission rates are for total organic compounds (including non-VOC's such as methane and ethane).

[b] The light liquid pump default zero value can be applied to compressors, pressure relief valves, agitators, and heavy liquid pumps.

TABLE 2-12. DEFAULT-ZERO VALUES: PETROLEUM INDUSTRY

Equipment type/service	Default-zero emission rates[a,b] (kg/hr/source)
Valves/all	7.8E-06
Pump seals/all	2.4E-05
Others[c]/all	4.0E-06
Connectors/all	7.5E-06
Flanges/all	3.1E-07
Open-ended lines/all	2.0E-06

[a] Default zero emission rates were based on the combined 1993 refinery and marketing terminal data only (default zero data were not collected from oil and gas production facilities).

[b] These default zero emission rates are for total organic compounds (including non-VOC’s such as methane and ethane).

[c] The "other" equipment type was developed from instruments, loading arms, pressure relief valves, stuffing boxes, vents, compressors, and dump lever arms. This "other" equipment type should be applied to any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

screening value of 1 ppmv or less. In cases where a monitoring instrument has a minimum detection limit greater than 1 ppmv, the default-zero leak rates presented in tables 2-11 and 2-12 are not applicable. For these cases, an alternative approach for determining a default-zero leak rate is to (1) determine one-half the minimum screening value of the monitoring instrument, and (2) enter this screening value into the applicable correlation to determine the associated default-zero leak rate.

The "pegged" emission rate is the mass emission rate associated with a screening value that has "pegged" the meter on the portable screening device (i.e. the screening value is beyond the upper limit measured by the portable screening device). In the case of a screening value pegged at 10,000 ppmv, a dilution probe should be used to extend the upper limit of the portable screening device to 100,000 ppmv. Thus, screening values can be reported up to 100,000 ppmv before pegging the instrument and the correlation equation can be used to estimate the mass emissions. However, in the case of previously-collected data or in the absence of a dilution probe, pegged readings of 10,000 ppmv are sometimes reported. In such cases, the 10,000 ppmv pegged emission rates can be used to estimate the mass emissions.

Table 2-13 presents the 10,000 ppmv and 100,000 ppmv pegged emission rates for SOCMI process units and table 2-14 presents the 10,000 ppmv and 100,000 ppmv pegged emission rates for petroleum industry process units. These pegged emission rates are to be used to estimate emissions when instrument readings are pegged and a dilution probe is not used.

Assuming all of the organic compounds in the equipment are classified as VOC’s, total VOC emissions for each equipment type are calculated as the sum of emissions associated with each of the screening values. Section 2.4.6 discusses a correction that can be made to the predicted VOC emissions rate if some of the organic compounds in the equipment are not classified as VOC’s (such as methane and ethane).

To summarize the correlation approach, each equipment piece with a screening value of zero is assigned the default-zero leak

TABLE 2-13. 10,000 PPMV AND 100,000 PPMV SCREENING VALUE PEGGED EMISSION RATES FOR SOCMI PROCESS UNITS

Equipment type	10,000 ppmv pegged emission rate (kg/hr/source)[a,b]	100,000 ppmv pegged emission rate (kg/hr/source)[a]
Gas valves	0.024	0.11
Light liquid valves	0.036	0.15
Light liquid pump seals[b]	0.14	0.62
Connectors	0.044	0.22

[a] The SOCMI pegged emission rates are for total organic compounds.

[b] The 10,000 ppmv pegged emission rate applies only when a dilution probe cannot be used or in the case of previously-collected data that contained screening values reported pegged at 10,000 ppmv.

[c] The light liquid pump seal pegged emission rates can be applied to compressors, pressure relief valves, and agitators.

TABLE 2-14. 10,000 ppmv and 100,000 PPMV SCREENING VALUE PEGGED EMISSION RATES FOR THE PETROLEUM INDUSTRY

Equipment type/service	10,000 ppmv pegged emission rate (kg/hr/source)[a,b]	100,000 ppmv pegged emission rate (kg/hr/source)[a]
Valves/all	0.064	0.140
Pump seals/all	0.074	0.160[c]
Others[d]/all	0.073	0.110
Connectors/all	0.028	0.030
Flanges/all	0.085	0.084
Open-ended lines/all	0.030	0.079

[a] The petroleum industry pegged emission rates are for total organic compounds (including non-VOC's such as methane and ethane).

[b] The 10,000 ppmv pegged emission rate applies only when a dilution probe cannot be used or in the case of previously-collected data that contained screening values reported pegged at 10,000 ppmv. The 10,000 ppmv pegged emission rate was based on components screened at greater than or equal to 10,000 ppmv; however, in some cases, most of the data could have come from components screened at greater than 100,000 ppmv, thereby resulting in similar pegged emission rates for both the 10,000 and 100,000 pegged levels (e.g., connector and flanges).

[c] Only 2 data points were available for the pump seal 100,000 pegged emission rate; therefore the ratio of the pump seal 10,000 pegged emission rate to the overall 10,000 ppmv pegged emission rate was multiplied by the overall 10,000 ppmv pegged emission rate to approximate the pump 100,000 ppmv pegged emission rate.

[d] The "other" equipment type was developed from instruments, loading arms, pressure relief valves, stuffing boxes, vents, compressors, dump lever arms, diaphrams, drains, hatches, meters, and polished rods. This "other" equipment type should be applied to any equipment type other than connectors, flanges, open-ended lines, pumps, and valves.

rate. For all equipment with a non-zero screening value, the screening value associated with each individual equipment piece is entered into the applicable correlation to predict emissions. *It should be noted that each individual screening value must be entered into the correlation to predict emissions for an equipment piece. Do not average screening values and then enter the average value into the correlation to estimate emissions.* Finally, each equipment piece with a screening value reported as pegged is assigned the appropriate pegged emission rate.

2.3.4 Unit-Specific Correlation Approach

To develop unit-specific correlations screening value and corresponding mass emissions data (i.e., bagging data) must be collected from process unit equipment. (See chapter 4.0 for a detailed discussion on the procedures for bagging equipment.) The equipment selected for bagging should be screened at the time of bagging. The mass emissions rate determined by bagging, and the associated screening value, can then be used to develop a leak rate/screening value relationship (i.e., correlation) for that specific equipment type in that process unit. The correlations must be developed on a process unit basis to minimize the error associated with differing leak rate characteristics between units.

If a unit-specific correlation is developed, as long as the procedures for bagging discussed in chapter 4.0 are followed, it is not necessary to demonstrate that the correlation is statistically different from the EPA correlation for it to be applied. However, before developing unit-specific correlations, it may be desirable to evaluate the validity of the EPA correlations to a particular process unit. As few as four leak rate measurements of a particular equipment type in a particular service can be adequate for this purpose. The measured emission rates can be compared with the rates that would be predicted by the EPA correlations to evaluate whether or not the EPA correlations provide reasonable mass emission estimates. A simple method of comparison is to determine if measured emission rates are consistently less than or greater than what would be predicted by the EPA correlation. If there is a consistent trend, such as all of the measured leak rates being lower than the rate predicted by the EPA correlation, the EPA correlation may not provide reasonable emission estimates for the process unit.

A more formal comparison is the Wilcoxon signed-rank test. This test can be performed by comparing the logarithm of the measured mass emission rates to the logarithm of the corresponding rates predicted by the EPA correlation. The absolute magnitude of the differences are then ranked (e.g., the pair with the smallest difference is assigned a rank of 1, the pair with the next smallest difference a rank of 2, etc.), and the sum of the ranks associated with positive differences is computed. For example, if four bags were measured and they each predicted higher mass emission rates than the EPA correlation, the value of the sum of the ranks associated with those pairs with positive differences would equal:

$$1 + 2 + 3 + 4 = 10$$

On the other hand, if four bags were measured and three predicted higher mass emission rates than the EPA correlation, but the one with the greatest absolute difference predicted a lower rate than the EPA correlation, then the sum of the positive ranks would equal:

$1 + 2 + 3 = 6$. *(Note: The sum of the negative ranks would equal 4).*

The value of the sum of the positive ranks can be compared to given values on statistical tables to evaluate if there are statistically significant differences between the measured rates and the rates predicted by the EPA correlation.

However the comparison is performed, in cases where the EPA correlations provide an adequate estimate of emissions, then the potential increase in accuracy obtained by developing unit-specific correlations may not be worth the effort. Consideration should also be given to the typical screening value measured at a process unit. If a process unit normally has very low screening values, then the difference between the sum of unit equipment leak emissions predicted by a unit-specific correlation and the EPA correlation will likely be relatively small.

In developing new correlations, a minimum number of leak rate measurements and screening value pairs must be obtained according to the following methodology. First, equipment at the process unit is screened so that the distribution of screening values at the unit is known. Then, mass emissions data must be collected from individual sources that have screening values distributed over the entire range. The criteria for choosing these sources is as follows. For each equipment type (i.e., valves, pumps, etc.) and service (i.e., gas, light liquid, etc.), a random sample of a minimum of six components should be chosen for bagging from each of the following screening value ranges:

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

The requirement of six bags per screening value range is based on the EPA experience with bagging components. There are two primary reasons for the above requirement: (1) to be confident in the representativeness of the data, and (2) to accurately reflect the range of possible mass emission rates associated with a given screening value. The importance of the first reason is self-evident: The more data collected the better the representativeness. The importance of the second reason is that a given screening value does not necessarily have a "true" emissions rate. For a single screening value, the mass emissions may range over several orders of magnitude depending upon several factors, including the equipment type (i.e., gate valve versus ball valve versus plug valve, etc.) and operating parameters (i.e., chemical handled, temperature, pressure, etc.). This range of possible mass emission rates is accounted for when the correlation is developed (see discussion on the scale bias correction factor), and it is important to obtain enough data to accurately reflect the range. If six sources are not available in a particular screening value range, additional sources from the nearest range should be tested so that a minimum of 30 emission rate/screening value pairs are obtained for each source type. If 30 or more bags are collected, the process unit-specific correlation can be used to estimate emissions across the entire range of screening values (1 to 1,000,000 ppmv).

In some cases, it may be desirable to develop a correlation with fewer than 30 bags. This can be accomplished by developing a correlation that is not valid across the entire range of screening values. Two alternatives are available: (1) to develop a correlation valid for screening values ranging from 1 to 100,000 ppmv, or (2) to develop a correlation valid for screening values ranging from 1 to 10,000 ppmv. These alternatives may be preferable for process units with equipment that do not normally have high screening values. An example of this type of process unit is one that already has a leak detection and repair program in place to prevent the release of odor-causing chemicals. At this type of process unit, leaks may be quickly detected and repaired.

For the first alternative, a minimum of 24 bags are required, rather than 30, because sources with screening values greater than 100,000 ppmv do not need to be bagged. Thus, a minimum of six sources each should be chosen for bagging from each of the screening ranges presented above except for the greater than 100,000 ppmv range. In the event that a source screens at 100,000 ppmv or greater, emissions can be estimated using "pegged" emission rates shown in table 2-13 for SOCMI process units, and in table 2-14 for petroleum industry process units.

For the second alternative, a minimum of 18 bags are required, because sources screening greater than 10,000 ppmv do not need to be bagged. Thus, a minimum of six sources should be chosen for bagging from the 1 to 100 ppmv range, the 100 to 1000 ppmv range, and the 1,000 to 10,000 ppmv range. In the event that a source screens at 10,000 ppmv or greater, emissions can be estimated using the applicable greater than or equal to 10,000 ppmv pegged emission rate presented in table 2-13 for SOCMI process units, or table 2-14 for petroleum industry process units. An advantage of using the greater than or equal to 10,000 ppmv pegged emission rates is that several of the available portable monitoring instruments have a maximum readout of 10,000 ppmv, and to obtain a screening value from a source screening at 10,000 ppmv, it is necessary to install a dilution probe. However, if the greater than or equal to 10,000 ppmv factor is used, installing a dilution probe is not necessary for this alternative.

The above groupings and recommended number of sources are given as guidelines. They are based on experience in measuring leak rates and developing leak rate/screening value correlations. Other source selection strategies can be used if an appropriate rationale is given.

With mass emissions data and screening values, leak rate/screening value correlations can be generated using the following methodology. Least-squares regression analyses are completed for each equipment type/service, regressing the log of the leak rate on the log of the screening concentration, according to:

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

where:

β_0, β_1 = Regression constants; and

SV = Screening value.

Note that the results are the same whether the base 10 or natural logarithm are used (see appendix B). The equations presented here are written assuming the base 10 logarithm is used. All analyses should be conducted using logarithms of both the leak rate and screening value because this type of data has been shown to be log-normally distributed. A scale bias correction factor (SBCF) is required in transforming the equation in the log-scale back to the original units. The transformed equation is the unit-specific correlation, and is expressed as:

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

where:

Leak rate = Emission rate of TOC’s from the individual equipment piece (kg/hr);

SBCF = Scale bias correction factor;

β_0, β_1 = Regression constants; and

SV = Screening value.

The SBCF is a function of the mean square error of the correlation in log space. The greater the range of possible emission rates for a given screening value, the greater the SBCF will be. The purpose of the SBCF is to reflect this range when transforming the correlation out of log space. When regressed in log space, in general, approximately half of the data points will lie above the correlation line and half will lie below it, and, for a given screening value, the correlation will pass through the mean log leak rate (i.e., the geometric mean). Thus, one way of thinking of the correlation in log space is that it predicts the geometric mean emissions rate across the range of screening values. However, the geometric mean always underestimates the arithmetic mean.

A simplified hypothetical example will help demonstrate this point: For a screening value of 500,000 ppmv, three bagging data points were obtained with mass emission rates of 0.1 kg/hr, 1 kg/hr, and 10 kg/hr. In log space, these emission rates correspond to $\log_{10}(0.1) = -1$, $\log_{10}(1) = 0$, and $\log_{10}(10) = 1$, respectively. Thus, the geometric mean of these three points is $(-1 + 0 + 1)/3 = 0$. Directly transforming this geometric mean to normal space predicts an emission rate for a screening value of 500,000 ppmv of $10^0 = 1$ kg/hr, whereas the arithmetic mean of the emission rates is $(0.1 + 1 + 10)/3 = 3.7$ kg/hr. From this example, it can be seen that the geometric mean underestimates the arithmetic mean.

Thus, if the correlation was directly transformed, it would underestimate the true average emission rate associated with a given screening value, and, for this reason, the SBCF is necessary to transform the correlation out of log space.

In appendix B, additional details on developing a process-unit specific correlation are presented. Appendix B also contains information on development of the revised SOCMI correlations.

2.4 SPECIAL TOPICS

There are several special topics relevant to estimating equipment leak emissions that are not specific to any one of the four approaches that have been described. These special topics are discussed in this section:

- Speciating emissions;
- Using response factors;
- Monitoring instrument type and calibration gas;
- Estimating emissions for equipment not screened (when other screening data are available);
- Using screening data collected at several different times;
- Estimating VOC emission rates from equipment containing organic compounds not classified as VOC’s (such as methane and ethane); and
- Estimating equipment leak emissions of inorganic compounds.

Each of these topics above are addressed in the following sections.

2.4.1 Speciating Emissions

For each of the four approaches for estimating equipment leak emissions, the equations presented are used to estimate TOC emissions for estimating equipment leak emissions. Often, in a chemical-handling facility, material in equipment is a mixture of several chemicals, and, in some cases, it may be necessary to estimate emissions of a specific VOC in the mixture. The following equation is used to speciate emissions from a single equipment piece:

$$E_X = E_{TOC} \times (WP_X/WP_{TOC})$$

where:

E_X = The mass emissions of organic chemical "x" from the equipment (kg/hr);

E_{TOC} = The TOC mass emissions from the equipment (kg/hr) calculated from either the Average Emission Factor, Screening Ranges, Correlation, or Unit-Specific Correlation approaches;

WP_X = The concentration of organic chemical "x" in the equipment in weight percent; and

WP_{TOC} = The TOC concentration in the equipment in weight percent.

An assumption in the above equation is that the weight percent of the chemicals in the mixture contained in the equipment will equal the weight percent of the chemicals in the leaking material. In general, this assumption should be accurate for single-phase streams containing (1) any gas/vapor material, or (2) liquid mixtures containing constituents of similar volatilities.

If the material in the equipment piece is a liquid mixture of constituents with varying volatilities, in certain cases this assumption may not be correct. Whether or not the assumption is valid for a liquid mixture of varying volatilities depends on the physical mechanism of how the leakage occurs from the equipment.

If the physical mechanism is one in which the liquid "flashes" before it leaks from the equipment, the leaking vapor may contain a higher concentration of the more volatile constituents than is contained in the liquid mixture. On the other hand, if the mechanism is one in which the liquid material leaks from the equipment and then evaporates, the assumption that the weight percent of each constituent in the liquid will equal the weight percent of each constituent in the vapor is valid. There are no clear guidelines to determine what mechanism is taking place for any given piece of equipment; for this reason, unless there is information to suggest otherwise, it should be assumed that the leaking vapor has the same concentrations as the liquid.

For those cases where it is suspected the leaking vapor will have different concentrations than the liquid, engineering judgement should be used to estimate emissions of individual chemical species. An example might be equipment containing material in two phases. Another hypothetical example is a case where equipment contain a liquid mixture of two constituents with one of the constituents having a very low vapor pressure and the other a much higher vapor pressure. Leaks may occur from the equipment such that the constituent with higher vapor pressure volatilizes to the atmosphere, but the constituent with lower vapor pressure is washed to the waste water treatment system prior to volatilization.

2.4.2 Using Response Factors

A correction factor that can be applied to a screening value is a response factor (RF) that relates the actual concentration to the measured concentration of a given compound, using a specific reference gas. As stated earlier, screening values are obtained by using a portable monitoring instrument to detect VOC's at an equipment piece leak interface. An "ideal" screening RF value is one that is equal to the actual concentration of VOC's at the leak interface. However, portable monitoring instruments used to detect TOC concentration do not respond to different TOC's equally. (This is discussed in more detail in chapter 3.0). To demonstrate this point, consider a monitoring instrument calibrated using a reference gas. If the instrument is calibrated correctly and is used to measure the concentration of the gas with which it has been calibrated, it will indicate the actual concentration. However, when used to measure other gases for which the monitoring instrument is more or less sensitive than the calibration gas, it will not indicate the actual concentration. To correct for this, RF's have been developed. The RF is calculated using the equation:

$$RF = AC/SV$$

where:

RF = Response factor;

AC = Actual concentration of the organic compound (ppmv); and

SV = Screening value (ppmv).

The value of the RF is a function of several parameters. These parameters include the monitoring instrument, the calibration gas used to calibrate the instrument, the compound(s) being screened, and the screening value.

The correlations presented in this chapter have been developed primarily from screening value/mass emission data pairs collected from equipment containing compounds that had RF's less than three. Thus, for cases in which a calibrated instrument is used to measure concentrations of a compound for which that instrument has an RF of three or less, reasonably accurate emission estimates can be obtained directly without adjusting the screening value. However, for a case in which a compound has an RF greater than three for the calibrated instrument, the emissions estimated using the unadjusted screening value will generally underestimate the actual emissions. The EPA recommends that if a compound (or mixture) has an RF greater than three, then the RF should be used to adjust the screening value before it is used in estimating emissions.

A detailed listing of published RF’s is contained in appendix D. These RF’s were developed by injecting a known concentration of a pure compound into a monitoring instrument and comparing that actual concentration to the instrument readout (i.e., screening value).

As an example of applying a RF, consider chloroform. From table D-2 in appendix D, it can be seen that the RF for chloroform at an actual concentration of 10,000 ppmv is equal to 4.48 for a Foxboro OVA-108 monitoring instrument calibrated with methane. Thus, when the actual concentration of chloroform is 10,000 ppmv, the instrument will read 10,000 ppmv divided by 4.48, which equals 2,230 ppmv. If the measured value for chloroform was directly entered into the correlation, it would tend to underestimate emissions. (Note that when the RF is less than 1 the unadjusted screening value will tend to overestimate actual emissions.)

The RF’s in appendix D are for pure compounds. Those RF’s can be used to estimate the RF for a mixture using the equation:

$$RF_m = \frac{1}{\sum_{i=1}^{n} (x_i/RF_i)}$$

where:

RF_m = Response factor of the mixture;
n = Number of components in the mixture;
x_i = Mole fraction of constituent i in the mixture; and
RF_i = Response factor of constituent i in the mixture.

This equation is derived in appendix A.

An alternative approach for determining the RF of a pure compound or a mixture is to perform analysis in a laboratory to generate the data used to calculate a RF. The approach for generating these data in the laboratory is described in chapter 3.0. The approach involves injecting samples of a known concentration of the material of interest into the actual portable monitoring instrument used to obtain the screening values and calculating the RF based on the instrument readout.

In general, calculating the RF by performing analysis on site will give the most accurate RF information, since, among other factors, RF's have been shown to be a function of the individual monitoring instrument.

Ideally, when using screening values to estimate equipment leak emissions, the RF would be equal to 1, and, in this way, the screening value would be the actual concentration. However, because RF's are a function of several parameters, this cannot normally be achieved. Response factors can be used to correct all screening values, if so desired. To evaluate whether a RF correction to a screening value should be made, the following three steps can be carried out.

(1) For the combination of monitoring instrument and calibration gas used, determine the RF's of a given material at an actual concentration of 500 ppmv and 10,000 ppmv. (See appendix D; in some cases, it may not be possible to achieve an actual concentration of 10,000 ppmv for a given material. In these cases, the RF at the highest concentration that can be safely achieved should be determined.)

(2) If the RF's at both actual concentrations are below 3, it is not necessary to adjust the screening values.

(3) If either of the RF's are greater than 3, then the EPA recommends an RF be applied for those screening values for which the RF exceeds 3.

One of the following two approaches can be applied to correct screening values:

(1) Use the higher of either the 500 ppmv RF or the 10,000 ppmv RF to adjust all screening values.

(2) Generate a response factor curve to adjust the screening values.

A RF curve can be generated in one of two ways. The simplest way is to assume that the RF value is a linear function of the screening value. The first step to generate a line relating screening value to RF is to convert the RF at the actual concentration to the RF at the associated screening value. This is done by dividing the RF by the actual concentration to get the associated screening value. Thus, if, at an actual concentration of 10,000 ppmv, an instrument has a RF of 5, this corresponds to a screening value of 2,000 ppmv (i.e., 10,000 ppmv divided by 5). This procedure is implemented at both actual concentrations of 10,000 ppmv and 500 ppmv, and a line is drawn between the RF’s at each associated screening value. This line can then be used to estimate the RF at any given screening value. (See appendix A for a demonstration of this procedure.) The line should not be extrapolated for screening values beyond the endpoints. For these screening values, the endpoint RF should be applied.

For some materials, the RF is nonlinear as the screening value increases. For these materials, RF’s at several screening values can be estimated by collecting data in a laboratory, as mentioned earlier. The RF/screening value relationship can then be generated by fitting a curve through the data pairs.

When an RF is used, the screening value is multiplied by the RF before mass emissions are estimated. Thus, if a screening value is 3,000 ppmv and the associated RF is 4, then the screening value must be adjusted to 12,000 ppmv (i.e., 3,000 multiplied by 4) before mass emissions are predicted.

It should be noted that if it is possible to calibrate the monitoring instrument with the material contained in the equipment that is being screened, the RF should equal 1. Thus, theoretically, the screening values will equal the actual concentration, and no RF adjustment will be necessary. If it is necessary to apply RF’s, site personnel should use engineering judgement to group process equipment into streams containing similar compounds. All components associated with a given stream can then be assigned the same RF, as opposed to calculating an RF for each individual equipment piece.

2.4.3 Monitoring Instrument Type and Calibration Gas

When the correlations presented in section 2.3 were developed, in general, for each of the source categories, the data were collected using a specific type of monitoring instrument calibrated with a specific calibration gas. The correlations are intended to relate actual concentration to mass emissions. For this reason, screening values obtained from any combination of monitoring instrument and calibration gas can be entered directly into the correlations as long as the screening values are an indication of actual concentration. If the screening values are not an indication of the actual concentration, the guidelines set forth in the previous section on RF’s can be applied to correct the screening values (i.e., screening values should be adjusted if the RF is greater than 3). Otherwise, it is not necessary to correct screening values to account for the instrument type and calibration gas that were used to develop the correlation curves developed by the EPA.

2.4.4 Estimating Emissions for Equipment Not Screened

Often, screening data cannot be collected for all of the equipment pieces in a process unit. In some cases, equipment are difficult or unsafe to screen. Difficult or unsafe to screen equipment must be included in the equipment counts. For these equipment pieces, the average emission factors must be used to estimate emissions.

In other cases, it is not possible to screen every equipment piece due to cost considerations. This is particularly true for connectors. Appendix E provides criteria for determining how many connectors must be screened to constitute a large enough sample size to identify the screening value distribution for connectors. If the criteria in appendix E are met, the average emission rate for connectors that were screened can be applied to connectors that were not screened. It should be noted that if connectors must be included in a leak detection and repair program as part of an equipment leaks standard, then all connectors must be screened. For equipment types other than connectors, if they are not monitored, the Average Emission Factor approach should be used to estimate emissions.

2.4.5 Using Screening Data Collected at Several Different Times

When screening data is collected and used to estimate emissions, the emissions estimate represents a "snapshot" of emissions at the time the screening data were obtained. Over time, it is possible that more screening data will be collected, and that for individual equipment pieces, several screening values will have been obtained at different time periods. For example, if quarterly monitoring is performed on a valve, in an annual period four screening values will be obtained from the valve. The annual emissions from the valve should be calculated by determining the emissions for each quarter based on the operational hours for the quarter, and summing the quarterly emissions together to arrive at emissions for the entire year. See appendix A for an example of estimating emissions from an equipment piece for which more than one screening value has been obtained.

2.4.6 Estimating VOC Emission Rates from Equipment Containing Non-VOC’s

Some organic compounds not classified as VOC’s can be detected by the screening instrument. Because the compounds are detected, the emissions associated with the screening value will include emissions of the "non-VOC’s." The two key organic compounds not classified as VOC’s are methane and ethane, but other organic compounds not classified as VOC’s include methylene chloride, 1,1,1-trichloroethane, and several chlorofluorocarbons. An approach very similar to that outlined in section 2.4.1 (Speciating Emissions) is used to estimate VOC emissions from equipment containing these non-VOC’s mixed with VOC’s.

Once TOC emissions have been estimated by using either the Average Emission Factor, the Screening Ranges, the Correlation, or the Unit-Specific Correlation approaches, the VOC emissions from a group of equipment containing similar composition can be calculated using the equation:

$$E_{VOC} = E_{TOC} \times (WP_{VOC}/WP_{TOC})$$

where:

E_{VOC} = The VOC mass emissions from the equipment (kg/hr);

E_{TOC} = The TOC mass emissions from the equipment (kg/hr) calculated form either the Average

Emission Factor, Screening Ranges, Correlation, or Unit-Specific Correlation approaches;

WP_{VOC} = The concentration of VOC in the equipment in weight percent;

WP_{TOC} = The TOC concentration in the equipment in weight percent.

2.4.7 Estimating Equipment Leak Emissions of Inorganic Compounds

The majority of data collected for estimating equipment leak emissions has been for TOC's or VOC's and not for inorganic compounds. Accordingly, the emission factors and correlations presented in section 2.3 are not intended to be applied for the used of estimating emissions of inorganic compounds. However, in some cases, there may be a need to estimate equipment leak emissions of inorganic compounds--particularly for those that exist as a gas/vapor or for those that are volatile. Some examples of inorganic compounds include sulfur dioxide, ammonia, and hydrochloric acid.

The best way to estimate equipment leak emissions of inorganic compounds would be to develop unit-specific correlations as described in section 2.3.4. To do this, it would be necessary to obtain a portable monitoring instrument that could detect the inorganic compounds. If it is not possible to develop a unit-specific correlation, but a portable monitoring instrument (or some other approach) can be used to indicate the actual concentration of the inorganic compound at the equipment leak interface, then the "screening values" obtained with this instrument can be entered into the applicable correlations presented in section 2.3.3 to estimate emissions. Alternatively, the equal to or greater than 10,000 ppmv, or the less than 10,000 ppmv emission factors could be applied. In the event that there is no approach that can be used to estimate the concentration of the inorganic compound at the leak interface, then in the absence of any other data, the average emission factors can be used.

2.5 REFERENCES

1. Radian Corporation. Assessment of Atmospheric Emissions from Petroleum Refining: Volume 4. Appendices C, D, E. Prepared for U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/2-80-075d. July 1980.

2. Wetherhold, R.G., L.P. Provost, and C.D. Smith (Radian Corporation). Assessment of Atmospheric Emissions from Petroleum Refining: Volume 3. Appendix B. Prepared for U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/2-80-075c. April 1980.

3. DuBose, D.A., J.I. Steinmetz, and G.E. Harris (Radian Corporation). Frequency of Leak Occurrence and Emission Factors for Natural Gas Liquid Plants. Final Report. Prepared for U.S. Environmental Protection Agency. Research Triangle Park, NC. EMB Report No. 80-FOL-1. July 1982.

4. 1993 Study of Refinery Fugitive Emissions from Equipment Leaks, Volumes I, II, and III, Radian DCN No. 93-209-081-02, Radian Corporation, Prepared for Western States Petroleum Association, Glendale, CA, and American Petroleum Institute, Washington, D.C., 1994.

5. Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals, Volumes I and II, API 4588, Radian Corporation, Prepared for American Petroleum Institute, 1993.

6. Fugitive Hydrocarbon Emissions from Oil and Gas Production Operations, API 4589, Star Environmental, Prepared for American Petroleum Institute, 1993.

7. Emission Factors for Oil and Gas Production Operations, API 4615, Star Environmental, Prepared for American Petroleum Institute, 1995.

8. Letter from Robert Strieter, API, to David Markwordt, U.S. EPA, regarding the submittal of gasoline distribution facility fugitive equipment screening data. April 26, 1994.

9. Blacksmith, J.R., et al. (Radian Corporation.) Problem-Oriented Report: Frequency of Leak Occurrence for Fittings in Synthetic Organic Chemical Plant Process Units. Prepared for U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/2-81-003. September 1980.

10. Langley, G.J. and R.G. Wetherhold. (Radian Corporation.) Evaluation of Maintenance for Fugitive VOC Emissions Control.

Prepared for U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/S2-81-080. May 1981.

11. U.S. Environmental Protection Agency. Fugitive Emission Sources of Organic Compounds - Additional Information of Emissions, Emission Reductions, and Costs (section 2). Research Triangle Park, NC. Publication No. EPA-450/3 82-010. April 1982.