



National Pollutant Inventory

Emission Estimation Technique Manual

for

Petroleum Refining

First published in February 1999

**EMISSION ESTIMATION TECHNIQUES
FOR
PETROLEUM REFINING**

TABLE OF CONTENTS

1.0 INTRODUCTION.....	1
2.0 LOCATING EETS IN THIS MANUAL.....	2
2.1 Transfers.....	2
2.2 Reporting Thresholds.....	3
3.0 EMISSION ESTIMATION TECHNIQUES.....	6
3.1 Emission Factors.....	7
3.2 Mass Balance.....	7
3.3 Software Models.....	8
4.0 EMISSIONS TO AIR.....	9
4.1 Combustion Sources.....	9
4.1.1 NPI-Listed Substances.....	10
4.1.1.1 SO ₂ Emissions Using Mass Balance.....	10
4.1.1.2 Emissions of NPI-listed substances Using Emission Factors.....	10
4.1.2 Organic Compound Emissions.....	13
4.1.3 Trace Elements and Inorganics from Combustion Sources.....	14
4.1.3.1 Mass Balance.....	14
4.1.3.2 Emission Factors.....	15
4.2 Refinery Process Sources.....	16
4.2.1 NPI-Listed Substances.....	17
4.2.2 Organic Emissions.....	18
4.2.3 Trace Elements and Inorganics.....	19
4.3 Process Fugitives.....	20
4.3.1 Total VOC Estimation.....	21
4.3.1.1 Total VOC Emission Estimation Methodology.....	21
4.3.1.2 Necessary Data for Estimating VOC Emissions.....	21
4.3.1.3 Definitions for Determining Types of “Service”.....	22
4.3.1.4 Monitoring Equipment.....	22
4.3.1.5 Correlation Equations.....	22
4.3.1.6 Leak/No-Leak Method.....	25
4.3.1.7 Average Emission Factors.....	27
4.3.2 Speciation of VOC Estimates.....	30
4.3.2.1 Speciation Based on Process Stream Composition.....	30
4.3.2.2 Speciation Using Developed Weight Fraction Data.....	31
4.3.3 Process Fugitive Controls.....	32
4.3.3.1 Equipment Modifications.....	32
4.3.3.2 Leak Detection and Repair Programs.....	33
4.4 Tank Farm Fugitives.....	34
4.4.1 Total VOC Estimation.....	34
4.4.2 VOC Speciation Using Facility-Specific Information.....	34
4.4.2.1 Methodology.....	34
4.4.2.2 Emissions from Fixed Roof Tanks.....	35
4.4.2.3 Emissions from Floating Roof Tanks.....	35
4.4.2.4 Calculating Weight Fractions.....	35
4.4.2.5 Calculating Total Losses.....	37
4.4.3 Speciation Using Data from the Literature.....	37
4.5 Loading Losses.....	38
4.5.1 Total VOC Estimation.....	38

4.5.2 Speciation of VOC Estimates.....	39
4.6 Wastewater Emissions to Air.....	39
5.0 EMISSIONS TO WATER.....	40
5.1 Point Source Discharge.....	40
5.2 Diffuse Discharge.....	41
6.0 EMISSIONS TO LAND.....	42
6.1 Groundwater Monitoring.....	42
6.2 Spills.....	43
6.3 On-Site Disposal.....	44
7.0 ASSUMPTIONS & DISCUSSION.....	45
7.1 Air Emissions.....	45
7.1.1 Combustion Sources.....	45
7.1.1.1 NPI-Listed Substances.....	45
7.1.1.2 Organics.....	45
7.1.1.3 Trace Elements.....	45
7.1.2 Refinery Process Sources.....	45
7.1.2.1 NPI-Listed Substances.....	45
7.1.2.2 Organics.....	46
7.1.2.3 Trace Elements.....	46
7.1.3 Process Fugitives.....	47
7.2 Wastewater Emissions.....	48
8.0 REFERENCES.....	49
 APPENDIX A: SUPPLEMENTARY INFORMATION FOR PROCESS FUGITIVE EMISSIONS CHARACTERISATION.....	 50

PETROLEUM REFINING

LIST OF TABLES

Table 1.	Location of EETs for Emissions to Air.....	4
Table 2.	NPI-Listed Substance Emission Factors for Fuel Oil Combustion..	11
Table 3.	NPI-Listed Substance Emission Factors for Gas Combustion.....	12
Table 4.	Emission Factors for Organic Emissions from Oil Combustion....	13
Table 5.	Emission Factors for Organic Emissions from Gas Combustion....	14
Table 6.	Emission Factors for Trace Elements from Fuel Oil Combustion..	15
Table 7.	Emission Factors for Trace Elements from Gas Combustion.....	16
Table 8.	NPI-Listed Substance Emissions from Refinery Process Sources...	17
Table 9.	VOC Speciation Data for Refinery Process Sources.....	18
Table 10.	Total Particulate Emission Factors for Refinery Process Sources....	19
Table 11.	Trace Element Speciation Data for Refinery Process Sources.....	20
Table 12.	Correlation Equations for Process Fugitive Emissions.....	25
Table 13.	Leak/No-Leak Emission Factors for Process Fugitives.....	27
Table 14.	Average Emission Factors for Process Fugitives.....	29
Table 15.	Speciation Data for NPI Substances from Equipment Fugitives.....	31
Table 16.	Summary of Equipment Modifications.....	32
Table 17.	Weight Percent of NPI Substances in Petroleum Products.....	38
Table 18.	Saturation (S) Factors for Calculating Petroleum Liquid Loading Losses	39
Table 19.	Default Speciation Factors for Organics in Refinery Effluent.....	40
Table 20.	Default Speciation Factors for Trace Elements and Inorganics in Refinery Effluent.....	41

1.0 Introduction

The purpose of all Emission Estimation Technique (EET) Manuals in this series is to assist Australian manufacturing, industrial and service facilities to report emissions of listed substances to the National Pollutant Inventory (NPI). This Manual describes the procedures and recommended approaches for estimating emissions from facilities engaged in petroleum refining.

The petroleum refining activities covered in this Manual include processing, storage, handling, and wastewater treatment.

EET MANUAL: Petroleum Refining

HANDBOOK: Petroleum Refining

ANZSIC CODE: 251

This Manual was drafted by Pacific Air & Environment, in conjunction with the NSW Environment Protection Authority, on behalf of the Commonwealth Government. It has been developed through a process of national consultation involving State and Territory environmental authorities, and key stakeholders. Particular thanks are due to the Australian Institute of Petroleum (AIP), and its members for their comments, advice and information.

2.0 Locating EETs in this Manual

In this Manual, Emission Estimation Techniques (EETs) are presented in the following sections:

- Section 4: Emissions to Air;
- Section 5: Emissions to Water; and
- Section 6: Emissions to Land.

Section 4 (Emissions to Air) is subdivided by source categories within the refinery operation. Table 1 details the sources of emissions, and the location of relevant EETs in this Manual.

Section 5 (Emissions to Water) provides an overview of those releases to water that are to be reported under the NPI. Specific guidance on the characterisation of emissions from wastewater treatment is provided.

In a similar manner, Section 6 (Emissions to Land) provides some general guidance on those releases to land that are to be reported under the NPI, as well as specific guidance on the characterisation of releases to land.

You should note that the EETs presented in this Manual relate principally to routine emissions. Emissions resulting from non-routine events are rarely discussed in the literature and there is a general lack of EETs for such events. However, it is important to recognise that emissions resulting from significant operating excursions (eg. spills) will also need to be reported under the NPI.

Any assumptions made regarding the application or derivation of emission data are discussed in Section 7: Assumptions & Discussion.

2.1 Transfers

It is important to remember that the National Environment Protection Measure (NEPM) for the NPI defines an emission as:

"an emission of a substance to the environment whether in pure form or contained in other matter, and whether in solid, liquid or gaseous form".

It includes emission of a substance to the environment from landfill, sewage treatment plants and tailings dams, but does not include (NEPM, Clause 3(3)):

- a) deposit of a substance into landfill; or
- b) discharge of a substance to a sewer or a tailings dam; or
- c) removal of a substance from a facility for destruction, treatment, recycling, reprocessing, recovery or purification.

2.2 Reporting Thresholds

The NPI Guide at the front of this Handbook lists substances reportable under the NPI, along with the associated reporting thresholds. *The NPI Guide* should be consulted to ascertain whether your facility handles, manufactures, or otherwise uses any of the substances in the list, and to determine whether any thresholds have been exceeded. If your facility is found to trigger any thresholds, then emissions to air, water and land must be quantified. You should note that although a particular threshold for an NPI substance may be triggered, an EET may not be currently available. In this situation, it is your responsibility as a reporting facility to apply an EET (ie. either find, or develop one), and to obtain approval for the use of such EETs from your local environmental agency.

Table 1. Location of EETs for Emissions to Air ^a

NPI Substance	EMISSIONS TO AIR											
	Combustion Sources		Refinery Process Sources						Flares	Fugitives	Storage Tanks	
	Oil	Gas	CCU	Fluid Coking	Compressors	Blowdown Systems	VDU Condensers	SRU				
PM ₁₀	4.1.1	4.1.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	N/A	N/A
SO ₂	4.1.1	4.1.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	N/A	N/A
NO _x	4.1.1	4.1.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	N/A	N/A
CO	4.1.1	4.1.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	N/A	N/A
VOC	4.1.1	4.1.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.2.1	4.3.1	4.4.1
Benzene	4.1.2	4.1.2	N/A	4.2.2		4.2.2	4.2.2	N/A	4.2.2		b	b
Toluene	4.1.2	4.1.2	N/A	4.2.2		4.2.2	4.2.2	N/A	4.2.2		b	b
Xylenes	4.1.2		N/A	4.2.2		4.2.2	4.2.2	N/A	4.2.2		b	b
PAH's	4.1.2	4.1.2	4.2.2	N/A		N/A	N/A	N/A	4.2.2		b	b
Acetone	4.1.2		N/A						N/A		b	b
n-Hexane	4.1.2		N/A	4.2.2		4.2.2	4.2.2	N/A	N/A		b	b
Phenol		4.1.2	N/A								b	b
Ethylbenzene	4.1.2		N/A								b	b
Acetaldehyde			N/A	N/A				4.2.2	4.2.2		b	b
Cyclohexane			N/A	4.2.2		4.2.2	4.2.2	N/A	N/A		b	b
Formaldehyde	4.1.2	4.1.2	4.2.2	4.2.2		4.2.2	4.2.2	4.2.2	4.2.2		4.3.2	4.4.2
Antimony	4.1.3	4.1.3	4.2.3	4.2.3				4.2.3			N/A	N/A
Arsenic	4.1.3	4.1.3	4.2.3	4.2.3				4.2.3			N/A	N/A
Beryllium	4.1.3		4.2.3								N/A	N/A
Cadmium	4.1.3		4.2.3	4.2.3				4.2.3			N/A	N/A
Chromium (III) and (VI)	4.1.3	4.1.3	4.2.3								N/A	N/A
Cobalt	4.1.3	4.1.3	4.2.3	4.2.3				4.2.3			N/A	N/A
Copper	4.1.3	4.1.3	4.2.3	4.2.3				4.2.3			N/A	N/A
Lead	4.1.3	4.1.3	4.2.3	4.2.3				4.2.3			N/A	N/A
Manganese	4.1.3	4.1.3	4.2.3	4.2.3				4.2.3			N/A	N/A
Mercury	4.1.3	4.1.3	4.2.3	4.2.3				4.2.3			N/A	N/A

Table 1. Location of EETs for Emissions to Air cont' ^a

NPI Substance	EMISSIONS TO AIR										
	Combustion Sources		Refinery Process Sources						Fugitives	Storage Tanks	
	Oil	Gas	CCU	Fluid Coking	Compressors	Blowdown Systems	VDU Condensers	SRU			Flares
Nickel	4.1.3	4.1.3	4.2.3	4.2.3				4.2.3		N/A	N/A
Selenium	4.1.3		4.2.3	4.2.3				4.2.3		N/A	N/A
Zinc	4.1.3	4.1.3	4.2.3	4.2.3				4.2.3		N/A	N/A
Fluoride	4.1.3		4.2.3	4.2.3				4.2.3		N/A	N/A
Carbon Disulfide			4.2.3	4.2.3				4.2.3		N/A	N/A

^a Blanks indicate either N/A or no data available.

^b Speciation methodology is located in this section.

3.0 Emission Estimation Techniques

Emission estimates of NPI-listed substances to air, water, and land should be reported for each substance that triggers a threshold. The reporting list and detailed information on thresholds are contained in *The NPI Guide*, included at the front of this Handbook.

In general, there are four types of emission estimation techniques (EETs) that may be used to estimate emissions from your facility.

The four types described in *The NPI Guide* are:-

- sampling or direct measurement
- mass balance
- fuel analysis or other engineering calculations
- emission factors

Select the EET, (or mix of EETs), that is most appropriate for your purposes. For example, you might choose to use a mass balance to best estimate fugitive losses from pumps and vents, direct measurement for stack and pipe emissions, and emission factors when estimating losses from storage tanks and stockpiles.

If you estimate your emission by using any of these EET's, your data will be displayed on the NPI database as being of 'acceptable reliability'. Similarly, if your relevant environmental authority has approved the use of emission estimation techniques that are not outlined in this handbook, your data will also be displayed as being of 'acceptable reliability'.

This Manual seeks to provide the most effective emission estimation techniques for the NPI substances relevant to this industry. However, the absence of an EET for a substance in this Manual does not necessarily imply that an emission should not be reported to the NPI. The obligation to report on all relevant emissions remains if reporting thresholds have been exceeded.

You are able to use emission estimation techniques that are not outlined in this document. You must, however, seek the consent of your relevant environmental authority. For example, if your company has developed site specific emission factors, you may use these if approved by your relevant environmental authority.

You should note that the EETs presented in this Manual relate principally to average process emissions. Emissions resulting from non-routine events are rarely discussed in the literature and there is a general lack of EETs for such events. However, it is important to recognise that emissions resulting from significant operating excursions and/or accidental situations (eg: spills) will also need to be estimated. Emissions to land, air and water from spills must be estimated and added to process emissions when calculating total emissions for reporting purposes. The emission resulting from a spill is the net emission, ie.

the quantity of the NPI reportable substance spilled, less the quantity recovered or consumed during clean up operations.

In developing an inventory of emissions for a petroleum refinery, it is important to utilise the best information available to develop emission estimates. Ideally, this data is obtained through source testing of emission points, although it is recognised that, in many situations, this sampling data is not available.

In the specific context of petroleum refining, the EETs that are alternatives to direct measurement are:

- emission factors
- mass balance
- software models

Each of these EETs is discussed briefly in Sections 3.1 to 3.3 below.

3.1 Emission Factors

Emission factors are generally developed through testing a particular source population (eg. various boilers combusting a particular fuel). This information is used to relate the quantity of a pollutant emitted, to some general measure of the activity. For example, boiler emission factors are typically expressed as emissions per quantity of fuel consumed. However, as emissions estimated using emission factors are not derived through testing the actual source, they are subject to uncertainty.

Emission factors require 'activity data', that is combined with the factor to generate the emission estimates. The generic formula is:

$$\text{Emission Factor (mass per unit of activity)} \times \text{Activity Data (unit of activity per time)} = \text{Emission Rate (mass per time)}$$

For example, if the emission factor has units of '*kg pollutant/m³ of fuel burned*', then the activity data required would be '*m³ fuel burned/hr*', thereby generating an emission estimate of '*kg pollutant/hr*'.

3.2 Mass Balance

Mass balance involves the quantification of total materials into and out of a process, with the difference between inputs and outputs being accounted for in terms of releases to the environment, or as part of the facility waste. Mass balance is particularly useful when the input and output streams can be quantified, and this is most often the case for individual process units and operations.

Mass balance techniques can be applied across individual unit operations, or across an entire facility. These techniques are best applied to systems with prescribed inputs, defined internal conditions, and known outputs.

It is essential to recognise that the estimates derived using mass balances are only as good as the values used in performing the calculations. For example, small

errors in data or calculation parameters (eg. pressure, temperature, stream concentration, flow, control efficiencies etc) can result in large errors in the final emission estimations. Additionally, if sampling of input or output materials is conducted, failure to use representative samples will also contribute to the uncertainty of the result.

3.3 Software Models

Emission models are available that predict emission rates for fugitive releases, landfills, lagoons, open dumps, waste piles, land treatment operations, and other source areas. These can be used either as a “screening” tool, or for in-depth investigations requiring site-specific data. A range of other information is, generally, also required to utilise such software packages (eg. for the chemical and/or physical characterisation of specific substances). The use of such software packages has been included, where relevant, for the purpose of characterising and estimating emissions.

While software models frequently require an initial investment of time, they can provide long term benefits because they can be used relatively easily and quickly to estimate emissions.

4.0 Emissions to Air

Emissions to air from petroleum refineries are presented in the following sections:

- Section 4.1: Combustion sources (i.e. furnaces and boilers);
- Section 4.2: Process sources (eg. vacuum distillation, catalytic cracking, sulfur recovery etc.);
- Section 4.3: Process fugitives (that encompass valves, flanges, pumps etc.);
- Section 4.4: Tank farm fugitives;
- Section 4.5: Loading/unloading emissions; and
- Section 4.6: Air emissions from wastewater treatment operations.

4.1 Combustion Sources

The two types of fuels burned at petroleum refineries are oil and gas. Note that emissions from refinery flares are considered separately under refinery processes in Section 4.2.

For the purposes of this Manual, the NPI substances emitted from combustion are divided as follows:

- Section 4.1.1: NPI-Listed substances (NO_x , SO_2 , PM_{10} , CO and total VOCs);
- Section 4.1.2: Organic compound speciation; and
- Section 4.1.3: Trace elements and inorganics (including metals and compounds such as fluorides, ammonia, carbon disulfide etc.).

4.1.1 NPI-Listed Substances

The NPI-listed substances released by combustion sources are:

- Oxides of nitrogen (NO_x);
- Sulfur dioxide (SO₂);
- Particulate matter less than 10 micrometres (PM₁₀);
- Carbon monoxide (CO); and
- Volatile organic compounds (VOCs).

Emission factors are provided for the estimation of these pollutants with the exception of SO₂, for which the preferred estimation technique is mass balance-based on the sulfur content of the fuel.

4.1.1.1 SO₂ Emissions Using Mass Balance

Estimates of SO₂ emissions can be made using the following equation, that assumes 100% conversion of sulfur to SO₂:

$$\text{Emission of SO}_2 \text{ (kg/hr)} = \text{Fuel Usage (kg/hr)} \frac{\text{wt\%S}}{100} * 2$$

Where:

Fuel Usage = the feed rate of fuel (i.e. oil or gas) to the combustion system in kg/hr
wt%S = the weight percent of sulfur (as elemental S) in the fuel

4.1.1.2 Emissions of NPI-Listed Substances Using Emission Factors

Tables 2 and 3 below provide emission factors for use in estimating emissions of the NPI-listed substances from oil and gas combustion sources respectively. The general term 'boiler' is used in these tables, however, the emission factors also apply to furnaces. Additionally, the term 'uncontrolled' indicates that the emission factors assume no pollution control devices are used to reduce the respective pollutants (eg. baghouse or ESP for PM₁₀, Low NO_x Burners for NO_x reduction etc).

Table 2. NPI-Listed Substance Emission Factors for Fuel Oil Combustion ^{a, b}

Oil Type and Firing Configuration	Emission Factors (kg/m ³ oil fired)			
	NO _x ^c	CO	PM ₁₀ ^d	VOC
<i>Boilers > 30 MW</i>				
No. 6 oil fired, normal firing	5.6	0.6	0.71A	0.091
No. 6 oil fired, normal firing, LNB ^e	4.8	0.6	0.71A	ND
No. 6 oil fired, tangential firing	3.8	0.6	0.71A	0.091
No. 6 oil fired, tangential firing, LNB ^e	3.1	0.6	0.71A	ND
No. 5 oil fired, normal firing	5.6	0.6	0.71A	0.091
No. 5 oil fired, tangential firing	3.8	0.6	0.71A	0.091
No. 4 oil fired, normal firing	5.6	0.6	0.71A	0.091
No. 4 oil fired, tangential firing	3.8	0.6	0.71A	0.091
<i>Boilers < 30 MW</i>				
No. 6 oil fired	6.6	0.6	0.86A	0.034
No. 5 oil fired	6.6	0.6	0.86A	0.034
No. 4 oil fired	2.4	0.6	0.86A	0.024
Distillate oil fired	2.4	0.6	0.12	0.024

^a Source: USEPA (1998a). The oil type categories are defined as follows:

No. 5 and 6 Fuel Oil: These are very heavy fuel oils containing significant quantities of nitrogen, sulfur and ash. No. 6 fuel oil is sometimes referred to as Bunker C.

No. 4 Fuel Oil: This is typically a mixture of distillate and residual oils.

Distillate Oil: This is more volatile and less viscous than the other oils, has negligible nitrogen and ash contents, and usually contains less than 0.3 percent sulfur.

^b These emission factors apply to uncontrolled sources, unless otherwise indicated.

^c NO_x emission factors are expressed as NO₂. A more accurate method for estimating NO_x emissions from industrial boilers (i.e. < 30 MW) is to apply the following equation:

$\text{kg NO}_2/\text{m}^3 \text{ oil fired} = 2.47 + 12.53(N)$, where N is the weight percent of nitrogen in the oil.

^d Particulate emission factors for residual oil combustion without emission controls are, typically, a function of fuel oil grade and sulfur content:

No. 6 oil: $A = 1.12(S) + 0.37 \text{ kg/m}^3$, where S is the weight percent of sulfur in the oil.

No. 5 oil: $A = 1.2 \text{ kg/m}^3$

No. 4 oil: $A = 0.84 \text{ kg/m}^3$

Depending on the fuel type burned, the appropriate factor for 'A' should be substituted where shown into the relevant PM₁₀ factor in the table.

^e LNB = Low NO_x Burners

Table 3. NPI-Listed Substance Emission Factors for Gas Combustion^a

Combustion System Type	Emission Factors (kg/10 ⁶ m ³ gas fired)			
	NO _x ^b	CO	PM-10	VOC
<i>Wall Fired Boilers > 30 MW</i>				
Uncontrolled	4480	1344	122	88
Controlled – Low NO _x burners	2240	1344	122	88
Controlled – Flue gas recirculation	1600	1344	122	88
<i>Boilers < 30 MW</i>				
Uncontrolled	1600	1344	122	88
Controlled – Low NO _x burners	800	1344	122	88
Controlled – Flue gas recirculation	512	1344	122	88
<i>Tangential-Fired (All Sizes)</i>				
Uncontrolled	2720	384	122	88
Controlled – Flue gas recirculation	1216	1568	122	88

^a Source: USEPA (1998b). These emission factors are based on the fuel gas at 15 degrees C and 1 atm.

^b NO_x emission factors are expressed as NO₂.

Scaling Emissions According to Heating Value

The emission factors presented in Tables 2 and 3 are based on the volumetric quantity of fuels burned in each boiler/furnace. These factors are based on fuels with the standard heating values listed below:

- Fuel oil No. 4, 5 and 6: 41.8 GJ/m³
- Fuel oil No. 2 and distillate: 39 GJ/m³
- Fuel gas: 37.2 MJ/m³

While it is stated in AP-42 (USEPA, 1997a) that the gas heating value is the higher heating value, no information of this nature is specified with regards to the oil heating values. However, as the gas data refers to the higher heating value, it is assumed that this also holds for the oil heating values.

Emissions calculated using the emission factors provided in Tables 2 and 3 must be scaled according to a ratio of the fuel's actual heating value, to the standard values supplied above. The emission factors provided in the tables should be applied using the following generic formula:

$$\text{Emission (kg/hr)} = \text{Emission Factor (kg/m}^3\text{)} * \text{Fuel Usage (m}^3\text{/hr)} * \frac{\text{Actual Heating Value}}{\text{Standard Heating Value}}$$

It is important to ensure that the units of the actual heating value are consistent with those shown for the standard heating values above. The Australian Institute of Petroleum (AIP) supplied the following higher heating values that can be used as *defaults* in the absence of site specific heating values (AIP, 1997):

- Fuel oil No. 4, 5 and 6: 42 GJ/m³
- Fuel oil No. 2 and distillate: 38.6 GJ/m³
- Fuel gas: 39 MJ/m³

4.1.2 Organic Compound Emissions

There are a range of organic compounds released during the combustion of fuel oil and gas. For those organic compounds on the NPI substance list, emission factors are presented in Table 4 and Table 5 for oil and gas combustion respectively.

It is important to note that the emission factors presented in Tables 4 and 5 reflect the data available in the literature. It is possible that other NPI substances are also emitted, but no information on such emissions is available. Refer to Section 7.1.1.2 for a discussion of these emission factors.

Table 4. Emission Factors for Organic Emissions from Oil Combustion ^a

NPI Substance	Emission Factor (kg/m ³ oil fired)
Benzene	2.57×10^{-5}
Toluene	7.44×10^{-4}
Xylenes ^b	9.01×10^{-4}
Ethylbenzene	7.63×10^{-6}
PAH's	1.43×10^{-4}
Formaldehyde	3.96×10^{-3}
Acetone ^c	1.01×10^{-2}
Polychlorinated dioxins and furans	3.72×10^{-10}
n-Hexane ^c	1.80×10^{-3}

^a Source: USEPA (1998a), unless otherwise indicated.

^b Source: USEPA (1997b).

^c Source: USEPA (1993).

Table 5. Emission Factors for Organic Emissions from Gas Combustion ^a

Organic Compound	Emission Factor (kg/10 ⁶ m ³ gas fired)
Benzene	3.4 x 10 ⁻²
Toluene	5.4 x 10 ⁻²
Acetaldehyde ^b	0.13
Formaldehyde	1.2
Phenol ^b	0.062
PAH's	1.1 x 10 ⁻²
n-Hexane	29

^a Source: USEPA (1998b), unless otherwise indicated.

^b Source: USEPA (1997b).

You should note that, for emissions of NPI-listed substances from the combustion of oil and gas, the emissions calculated using the emission factors provided in Tables 4 and 5 must be scaled based on the fuel's actual heating value (see Section 4.1.1 for a further discussion of this).

4.1.3 Trace Elements and Inorganics from Combustion Sources

Emissions of certain trace elements can be estimated using mass balance, when fuel composition data is available. If such data is unavailable, default emission factors can be used. This Section will be divided into two categories, with the first examining emission estimation using mass balance (ie. where and how it is applicable), and the second relating to emission factors.

4.1.3.1 Mass Balance

Mass balance is the preferred methodology for estimating 'uncontrolled' emissions of metals from fuel and gas combustion. This approach assumes that 100 percent of the trace elements present in the fuels are released into the atmosphere upon combustion (this assumption is discussed further in Section 7.1.1.3).

To use this mass balance methodology, the two key data requirements are:

1. The metal content of the fuels utilised in each boiler and furnace; and
2. The fuel consumption rate for each combustion source.

The above inputs can then be applied using the following equation:

$$\text{Emission Rate (kg/hr)} = \text{Fuel Usage (kg/hr)} * \boxed{\text{Metal Content of Fuel (wt\%)}}$$

$$\text{Annual Emission Rate (kg/hr)} = \text{Emission Rate} * \text{Operational Usage (hrs/yr)}$$

SAMPLE CALCULATION

The following data is known about the fuel and its usage at a refinery:

- the cadmium (Cd) content of the fuel oil is approximately 0.3 ppmwt (parts per million by weight);

- the fuel oil usage of the boiler is approximately 1100 kg/hr.; and
- the boiler is used for 3000 hrs/yr.

Therefore, the emission rate of ‘cadmium and compounds’ (assuming that 100 percent of the cadmium entering the boiler is released in the flue gases) is derived as follows:

$$1100 \text{ kg/hr fuel oil} * 0.3 \text{ kg Cd}/10^6 \text{ kg fuel oil} = 3.3 \times 10^{-4} \text{ kg/hr}$$

The *uncontrolled* emission rate of cadmium and compounds is therefore 3.3×10^{-4} kg/hr.

$$\begin{aligned} \text{Annual Emission Rate} &= 3.3 * 10^{-4} \text{ kg/hr} * 3000 \text{ hr/yr} \\ &= 0.99 \text{ kg/yr} \end{aligned}$$

4.1.3.2 Emission Factors

In the event that insufficient data is available to derive emission estimates of metals using mass balance, the emission factors presented in Table 6 and Table 7 may be used for oil and gas combustion respectively. The oil types relating to Table 6 are discussed in Section 4.1.1.2. The general use of emission factors is discussed in Section 3.1.

Table 6. Emission Factors for Trace Elements from Fuel Oil Combustion ^a

Trace Element (and Compounds)	Distillate Oil Combustion ^b (kg/m ³)	Residual Oil Combustion ^c (kg/m ³)
Antimony	ND ^d	6.3×10^{-4}
Arsenic	7.06×10^{-5}	1.5×10^{-4}
Beryllium	5.03×10^{-5}	3.3×10^{-6}
Cadmium	5.03×10^{-5}	4.8×10^{-5}
Chromium (VI)	ND	3.0×10^{-5}
Cobalt	ND	7.2×10^{-4}
Copper	ND	2.1×10^{-4}
Lead	1.49×10^{-4}	1.8×10^{-4}
Manganese	2.35×10^{-4}	3.6×10^{-4}
Mercury	5.03×10^{-5}	1.4×10^{-5}
Nickel	3.02×10^{-4}	1.0×10^{-2}
Selenium	ND	8.2×10^{-5}
Zinc	ND	3.5×10^{-3}
Fluoride	ND	4.5×10^{-3}

^a Source: USEPA (1997a).

^b ‘Distillate’ also includes No. 2 fuel oil (refer to Section 4.1.1.2).

^c ‘Residual’ includes fuel oil No. 4, 5 and 6 (refer to Section 4.1.1.2).

^d ‘ND’ = No data available.

Table 7. Emission Factors for Trace Elements from Gas Combustion ^a

Trace Element (and Compounds)	Emission Factor (kg/10 ⁶ m ³)
Arsenic	3.2 x 10 ⁻³
Beryllium	1.9 x 10 ⁻⁴
Chromium (VI) ^b	1.1 x 10 ⁻³
Cobalt	1.3 x 10 ⁻³
Copper	1.4 x 10 ⁻²
Cadmium	1.8 x 10 ⁻²
Lead	8.0 x 10 ⁻³
Manganese	6.1 x 10 ⁻³
Mercury	4.2 x 10 ⁻³
Nickel	3.4 x 10 ⁻²
Selenium	3.8 x 10 ⁻⁴
Zinc	4.6 x 10 ⁻¹

^a Source: USEPA (1998a) unless otherwise indicated

^b Source: USEPA (1997b)

You should note that reporting is only required for those substances that trigger reporting thresholds. It is possible that these thresholds are *not* triggered for all of the compounds listed in the tables above. Refer to *The NPI Guide* for more information.

You should also note that for emissions of NPI-listed substances from the combustion of oil and gas, the emissions calculated using the emission factors provided in Tables 6 and 7 must be scaled based on the fuel's actual heating value (see Section 4.1.1 for a further discussion of this).

4.2 Refinery Process Sources

The following refinery operations have the potential to release NPI-listed substances:

- Fluidised Catalytic Cracking Units (FCCU);
- Moving Bed Catalytic Cracking Units (MBCCU);
- Fluid Coking Units;
- Compressor Engines;
- Blowdown Systems;
- Vacuum Distillation Unit (VDU) Condensers – these are also referred to as High Vacuum Units (HVU);
- Sulfur Recovery Units (SRUs); and
- Flaring.

In a similar manner to combustion sources (i.e. Section 4.1), this section will be divided into the following pollutant categories:

- NPI-listed substances (Section 4.2.1);
- Organic species (Section 4.2.2); and
- Metals and inorganics (Section 4.2.3).

4.2.1 NPI-Listed Substances

Table 8 provides emission factors for use in estimating emissions of the NPI-listed substances from non-combustion sources in a petroleum refinery.

Table 8. NPI-Listed Substance Emissions from Refinery Process Sources

Refinery Process Operation	PM ₁₀	SO ₂	NO _x	VOC	CO
FCCU					
- uncontrolled (kg/m ³ feed to the unit)	0.549	1.413	0.204	0.63	39.2
- ESP & CO boiler (kg/m ³ feed to the unit)	0.071	1.413	0.204	neg.	neg.
MBCCU (kg/m ³ feed to the unit)	0.038 7	0.171	0.014	0.25	10.8
Fluid Coking Units					
- uncontrolled (kg/m ³ feed to the unit)	0.765	ND	ND	0.046 ^b	ND
- ESP & CO boiler (kg/m ³ feed to the unit)	0.01	ND	ND	neg.	neg.
Compressor engines					
- reciprocating engines (kg/1000 m ³ gas burned)	Neg.	2S ^c	55.4	21.8	7.02
- gas turbines (kg/1000 m ³ gas burned)	neg.	2S	4.7	0.28	1.94
Blowdown Systems					
- uncontrolled (kg/m ³ refinery feed)	Neg.	neg.	neg.	1662	neg.
VDU Condensers					
- uncontrolled (kg/m ³ vacuum feed)	Neg.	neg.	neg.	0.14	neg.
- controlled (flare or heater) (kg/m ³ vacuum feed)	neg.	neg.	neg.	neg.	neg.
Sulfur Recovery Unit (SRU) ^d					
- 1, uncontrolled (93.5%) (kg/tonne S produced)	ND ^e	139	ND	ND	ND
- 3, uncontrolled (95.5%) (kg/tonne S produced)	ND	94	ND	ND	ND
- 4, uncontrolled (96.5%) (kg/tonne S produced)	ND	73	ND	ND	ND
- 2, controlled (98.6%) (kg/tonne S produced)	ND	29	ND	ND	ND
- 3, controlled (96.8%) (kg/tonne S produced)	ND	65	ND	ND	ND
- unspecified (uncontrolled) ^f (kg/dscm process gas)	ND	ND	ND	0.015	ND
Flares (kg/GJ of flare gas burned)	- ^g	MB ^h	0.029	0.06	0.159

^a Source: USEPA (1997a) unless otherwise indicated. See also Section 7.1.2 for further discussion of the sources of these emission factors.

^b Source: USEPA (1993).

^c S = the refinery gas sulfur content in kg/1000 m³.

^d The percentage efficiencies are the reported elemental sulfur recovery efficiencies of the units for which the emission factors were derived. The numbers at the far left of each row pertain to the number of stages in the SRU. No data was found pertaining to actual emissions from SCOT units.

^e ND = No data available.

^f Source: Taback (1996). This emission factor for VOC emissions is based on the dry standard cubic metre (dscm) feed rate of process gas to the SRU.

^g The emission factors for PM₁₀ from a flare is divided into the following categories:

Non-smoking flare: 0 kg/m³ of gas

Lightly smoking flare: 40 x 10⁻⁶ kg/m³ of gas

Average smoking flare: 177 x 10⁻⁶ kg/m³ of gas

Heavy smoking flare: 274 x 10⁻⁶ kg/m³ of gas

^h MB: Mass balance based on the average S content of the flare gas (see Section 4.1.1.1).

4.2.2 Organic Emissions

There is a limited amount of information on VOC speciation from refinery process sources. Data that has been found in the literature is presented in Table 9. This information is combined with total VOC estimates (i.e. as derived using Table 8) using the following equation:

$$\text{Organic Compound (kg/hr)} = \text{VOC Emission (kg/hr)} * \frac{\text{Speciation Factor (wt\%)}}{100}$$

Table 9. VOC Speciation Data for Refinery Process Sources ^a

Compound	Weight % of VOCs Released from Each Refinery Process Operation					
	CCU ^b	Fluid Coking	Blowdown Systems	VDU Condensers	SRU ^c	Flare ^c
n-Hexane	NA	3.86	3.86	3.86	NA	NA
Cyclohexane	NA	0.08	0.08	0.08	NA	NA
Formaldehyde	51	8.88	8.88	8.88	4.12	0.817
Acetaldehyde	NA	NA	NA	NA	0.67	0.082
Xylenes	NA	0.19	0.19	0.19	NA	0.041
Benzene	NA	0.38	0.38	0.38	NA	0.083
Toluene	NA	0.44	0.44	0.44	NA	0.041
PAHs	0.15 _d (2.9)	NA	NA	NA	NA	0.020

^a Source: USEPA (1993) unless otherwise indicated.

^b CCU is an abbreviation for catalytic cracking units, and includes both FCCUs and Moving Bed CCUs, unless otherwise indicated.

^c Source: Taback (1996)

^d Source: USEPA (1995b). The number in parentheses is applicable to moving bed CCUs, while the number not in parentheses is for FCCUs.

4.2.3 Trace Elements and Inorganics

The information on emissions of trace elements and inorganics from refinery process sources is limited, with the only published data relating to emissions from the following sources:

- catalytic cracking units (i.e. both FCCUs and MBCCUs);
- fluid coking operations; and
- sulfur recovery units (SRUs).

However, it is important to note that other sources may release metals and other compounds, although no data is currently available to quantify these. The assumptions relating to these emissions are discussed in Section 7.1.2.3.

Although PM₁₀ emissions can be estimated using the emission factors presented in Table 8, *total suspended particulate* (TSP) emissions are required to derive estimates of metal releases. In the absence of actual stack test data, the emission factors presented in Table 10 are available to estimate TSP emissions from the refinery sources mentioned above (USEPA, 1997a).

Table 10. Total Particulate Emission Factors for Refinery Process Sources ^a

Refinery Process Operation	Total Particulate Emission Factor (kg/m ³ feed to the unit)
FCCU	
- uncontrolled	0.695
- ESP & CO boiler	0.128
MBCCU	0.049
Fluid Coking Unit	
- uncontrolled	1.5
- ESP & CO boiler	0.0196

^a Source: USEPA (1997a).

No data relating to total particulate emissions from SRUs has been included in Table 10. The reason for this is that the speciation data presented in Table 11 for SRUs (i.e. for carbon disulfide) is actually based on VOC emissions from the SRU. Therefore, this speciation factor should be applied to the equation from Section 4.2.2 above. However, it has been included in this section because it is an inorganic compound. This is discussed further in the Assumptions and Discussion, Section 7.1.2.3.

When total particulate emissions have been estimated, speciation is performed using the weight fractions presented in Table 11, combined with the following equation:

$$ER_i = TSP * (WP_i / 100)$$

Where:

ER_i = The emission rate of the speciated compound "i" from the relevant source (kg/hr);

- TSP = The *total suspended particulates* estimate derived using the emission factors in Table 10 (kg/hr). The exception is the carbon disulfide speciation data, as this must be applied to the total VOC estimate from SRUs (refer Section 4.2.2);
- WP_i = The appropriate weight percent of species “i” provided in Table 11 below.

Table 11. Trace Element and Inorganics Speciation Data for Refinery Process Sources^a

Metal (& Compounds)	CCU ^b (weight % of total particulate matter)		Fluid Coking (weight % of total particulate matter)	SRU ^c (weight % of VOC)
	Uncontrolled	Controlled	Uncontrolled	
Manganese	0.022	ND ^d	0.004	ND
Nickel	0.088	0.031	0.038	ND
Copper	0.02	0.003	0.001	ND
Zinc	0.017	0.006	0.003	ND
Arsenic	0.002	ND	0.144	ND
Selenium	0.002	0.003	0.002	ND
Antimony	0.035	0.002	0.005	ND
Lead	0.046	0.01	0.003	ND
Cobalt	0.002	ND	ND	ND
Cadmium	0.009	0.002	ND	ND
Mercury	0.01	0.001	0.002	ND
Carbon Disulfide	NA ^e	NA	ND	95.2 ^c

^a Source: USEPA (1993).

^b CCU is an abbreviation for catalytic cracker unit, and the factors presented apply to both FCCUs and MBCCUs. The ‘controlled’ data was only available for ESP control.

^c This is actually a speciation factor based on the VOC emission rate from SRUs (refer to Section 7.1.2.3 for further discussion).

^d ND = No data available.

^e NA = Not Applicable.

4.3 Process Fugitives

Process fugitives at a petroleum refinery typically include the following sources:

- valves;
- flanges;
- pumps;
- connectors;
- compressors; and
- drains.

Although the release from each individual source may be small because of the large number of such sources in a refinery, the total emissions from these sources can be significant.

[Note: The methodology presented in this Section is based on USEPA, 1995a].

Emissions from process fugitives are estimated using the following two steps:

1. Total VOC emissions are calculated (refer to Section 4.3.1); and
2. These VOC emission estimates are speciated using appropriate speciation profiles (refer Section 4.3.2).

These steps are discussed further in the following Sections.

Please note that there are two types of definitions used for organic compound emissions from fugitive sources. These are:

- VOCs, which encompass all organic compounds excluding methane (i.e. equivalent to non-methane organic compounds – NMVOCs)
- TOCs, which includes all organic compounds, including methane.

Under the NPI, only emissions of VOCs are required to be reported. However, to calculate emissions of certain organic species, it may also be necessary to calculate emissions of TOC. It is important to consider these definitions when estimating equipment losses using the following methodologies.

4.3.1 Total VOC Estimation

Before emission estimation techniques are discussed, it is important to note that some refineries estimate fugitive losses using various 'in-house' techniques. As noted in Section 3.0, EETs not outlined in this document can be used, provided that consent is obtained from the relevant environmental authority.

4.3.1.1 Total VOC Emission Estimation Methodologies

There are three main techniques that can be utilised to quantify total VOC emissions from process fugitives:

1. Correlation equations;
2. Leak/no-leak emission factors; and
3. Average emission factors.

These methods have been ranked in terms of the level of information required by a facility. Correlation equations require the most data, while average emission factors require the least.

4.3.1.2 Necessary Data for Estimating VOC Emissions

Before any of the EETs presented in this Section can be used for characterising fugitive emissions, the following minimum information is required:

1. The number of each type of component (i.e. valves, flanges, etc.) in each process unit;
2. The service each component is in (i.e. gas, light liquid, heavy liquid); and
3. The time period each component is in that particular service (eg. hours/year).

Depending on the EET chosen, additional information may be required. This is discussed in greater detail in the relevant Section.

4.3.1.3 Definitions for Determining Types of “Service”

The following definitions should be used when determining the type of ‘service’ (i.e. gas/vapour, light liquid and heavy liquid) a particular piece of equipment is in, so that the appropriate emission factors are used:

- *Gas/vapour*: the material is in a gaseous state under operating conditions;
- *Light liquid*: the material is in a liquid state in which the sum of the concentrations of individual constituents with a vapour pressure over 0.3 kilopascals (kPa) at 20_C is greater than (or equal to) 20 weight percent (wt%); and
- *Heavy liquid*: the material does not fall under the classifications for gas/vapour or light liquid service.

4.3.1.4 Monitoring Equipment

Typical monitoring equipment includes a portable flame ionisation detector (FID), designed especially for screening purposes. FIDs are low concentration instruments that can detect from 0.2-10,000 ppm. In general, portable VOC monitoring instruments are equipped with a probe that is placed at the leak interface of a piece of equipment. A pump with the instrument draws a continuous sample of gas from the leak interface area to the sample detector. The instrument response is a screening value in unit of parts per million by volume (ppmv). A detailed discussion on screening of equipment components can be found in USEPA (1995a), Section 3.3.

4.3.1.5 Correlation Equations

This method can only be used if screening values (ppmv) are (or have been) obtained through a fugitive leak screening program. The required screening value (SV) data is collected using a portable FID such as the one discussed in Section 4.3.1.4.

The following points are important to note when using this methodology:

- emission estimates are for ‘total organic compounds’ (TOC) and, as a consequence, a correction must be made to convert the estimates to VOCs (ie to exclude methane);
- these emission factors are on a ‘per source’ basis; and
- each individual screening value must be entered into the correlation equation to predict emissions for an equipment piece. DO NOT average screening values and then enter the average value into the correlation to estimate emissions.

The following steps should be followed to determine fugitive emissions using the correlation equation approach.

Step 1: Measure Leaks from Fugitive Sources

The details of how to use an FID to measure leaks can be obtained from the manufacturer of the FID, or one of the many documents prepared by the USEPA (eg. USEPA 1995a). As not all equipment pieces may be tested, Appendix A provides information on how to select an appropriate sample size for screening components (Step 7 provides additional discussion).

For each piece of equipment tested, the recorded screening value will fall into one of three categories. The correct estimation methodology must then be used for each category as follows:

1. For 'zero' readings (i.e. no emission is detected), Step 2 should be consulted to estimate emissions;
2. For screening values between the lower and upper detection limits of the monitoring device, Step 3 should be used; and
3. For values greater than the upper detection limit of the monitoring device (i.e. a 'pegged' emission reading), Step 4 should be used.

Step 2: Use of Zero Default Factors

If no emissions are detected by the FID (ie. the measured level is below the lower detection limit), then the 'Default Zero Emission Rate' emission factors are used, *unless* the lower detection limit of the monitoring device is greater than 1 ppmv. In this case, half the detection limit is used. (See Table 12).

Step 3: Use of Correlation Factors to Determine Leak

If screening values (SV) are determined through testing (i.e. the measured level is between the lower and upper detection limits), then the 'Correlation Equations' presented in Table 11 are to be used to determine the leak from each relevant component tested.

Step 4: Use of Pegged Emission Rate

If pegged screening values are detected (ie. level is above the upper detection limit of the monitoring device), the 'Pegged Emission Rate' emission factors presented in Table 11 are used.

Step 5: Correct TOC Readings to VOC Estimate

Once emissions have been estimated from each source, the emissions must be converted from TOCs to VOCs. To do this, additional information is required on the approximate weight percent of VOCs and TOCs in the process streams from which the emissions originate. This is then combined with the emission estimate for each equipment component as follows:

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

Where:

- E_{VOC} = The VOC emission rate from the equipment (kg/hr);
 E_{TOC} = The TOC emission rate from the equipment (kg/hr) calculated using the emission factors or correlations from Table 12.

- WP_{VOC} = The concentration of VOC in the equipment in weight percent; and
- WP_{TOC} = The concentration of TOC in the equipment in weight percent.

If a number of equipment pieces can be grouped because they share the same process stream and thus have similar VOC/TOC ratios, TOC emissions can be added for this equipment group prior to performing Step 5, thereby helping to reduce the total number of calculations required.

Step 6: Note Operational Hours

For the specific equipment pieces tested, you should estimate the annual number of operational hours. This information is required to derive annual emissions based on the hourly emission rates.

Step 7: Determine Total VOC Emissions

If all process fugitive sources have been tested, total VOC emissions from all sources can be determined by adding the emissions from each individual equipment component.

In some refineries however, it may not be practical to screen all sources because of safety and/or cost considerations. Appendix A discusses the methodology used to estimate emissions from all components in a refinery when only a fraction of the source population has been screened. Additionally, Appendix A discusses information pertaining to the appropriate sample size that should be used when it is desired to develop refinery specific emission factors based on screening.

Table 12. Correlation Equations for Process Fugitive Emissions ^a

Equipment Type	Default Zero Emission Rate (kg/hr)	Pegged Emission Rate (kg/hr)		Correlation Equation ^b (kg/hr)
		10,000 ppmv	100,000 ppmv	
Connector ^c	7.5×10^{-6}	0.028	0.03	leak = $1.53 \times 10^{-6} (SV)^{0.735}$
Flange	3.1×10^{-7}	0.085	0.084	leak = $4.61 \times 10^{-6} (SV)^{0.703}$
Valve ^d	7.8×10^{-6}	0.064	0.14	leak = $2.29 \times 10^{-6} (SV)^{0.746}$
Open-ended line	2.0×10^{-6}	0.03	0.079	leak = $2.20 \times 10^{-6} (SV)^{0.704}$
Pump Seal	2.4×10^{-5}	0.074	0.16	leak = $5.03 \times 10^{-5} (SV)^{0.610}$
Drain ^e	1.5×10^{-3}	ND ^g	ND	leak = $1.50 \times 10^{-4} (SV)^{1.02}$
Other ^f	4.0×10^{-6}	0.073	0.11	leak = $1.36 \times 10^{-5} (SV)^{0.589}$

^a Source: USEPA (1995a) – Section 2.3.3 unless otherwise indicated. These estimates are for total organic compound emissions, and must therefore be scaled to exclude methane as discussed beneath this table.

^b SV is an abbreviation for Screening Value and is in units of ppmv (parts per million by volume).

^c The category of ‘connector’ pertains to *non-flanged* connectors.

^d Note that the category of valves does not include pressure relief valves, as these are included under the category of ‘other’.

^e Source: Taback (1996) pp. 12.

^f This ‘other’ category should be applied to all equipment types that have not been specifically considered elsewhere in the table. These would include (but are not limited to) loading arms, pressure relief valves, stuffing boxes, vents, compressors and dump lever arms.

^g ND = no data available.

4.3.1.6 Leak/No-Leak Method

As is the case with the correlation approach discussed above, screening using a portable monitoring device is required for this methodology. However, rather than recording discrete screening values, this approach relies on a ‘leak’/‘no leak’ criteria. Note that the criteria used to define whether an equipment component is leaking can vary, although emissions data is only available for a leak definition of 10000 ppmv. As mentioned above, a detailed discussion on screening of equipment components can be found in USEPA (1995a), Section 3.3.

The following steps should be followed to determine fugitive emissions using this approach.

Step 1: Measure Leaks from Fugitive Sources Using FID

A leak is typically defined and recorded if a screening value of ‘greater’ than 10000 ppmv is returned by the monitoring instrument. Therefore, the emission factor chosen from Table 13 will depend on whether the component tested returns a *pass* (i.e. reading \geq 10000 ppmv), or *fail* (i.e. reading $<$ 10000 ppmv).

Step 2: Estimate the VOC Emission Rate

Emissions are estimated for each of the equipment types listed in using the following equation:

$$E_{\text{VOC}} = (F_G * N_G) + (F_L * N_L)$$

Where:

- E_{VOC} = The VOC emission rate for the equipment type (kg/hr);
- F_G = The applicable emission factor for sources with screening values greater than, or equal to 10000 ppmv (kg/hr/source);
- N_G = For the particular equipment type of concern, the number of sources with screening values greater than or equal to 10000 ppmv;
- F_L = The applicable emission factor for sources with screening values less than 10000 ppmv (kg/hr/source);
- N_L = For the particular equipment type of concern, the number of sources with screening values less than 10000 ppmv;

Step 3: Note Operational Hours

For the specific equipment pieces screened, the annual number of operational hours needs to be estimated. This is required to derive annual emissions based on the hourly emission rates.

Step 4: Determine Total VOC Emissions

If all process fugitive sources have been screened, total VOC emissions from all sources can be determined by adding emission rates from each individual equipment component.

In some refineries however, it may not be practical to screen all sources because of safety and/or cost considerations. Appendix A discusses the methodology used to estimate emissions from all components in a refinery when only a fraction of the source population has been screened. Additionally, Appendix A discusses information pertaining to the appropriate sample size that should be used when it is desired to develop refinery specific emission factors based on screening.

Table 13 presents the emission factors required to estimate emissions using the steps discussed above. You should note that 'drains' are not included in this table as no emission factors could be found for such sources. If the drains are screened, and discrete data is recorded (in ppmv), the methodology discussed above in Section 4.3.1 should be used, otherwise the 'average emission factors' presented in Table 13 are required for estimation.

Table 13. Leak/No-Leak Emission Factors for Process Fugitives ^a

Equipment Type	Service	LEAK (≥ 10000 ppmv) Emission Factor (kg/hr)	NO LEAK (< 10000 ppmv) Emission Factor (kg/hr)
Connectors/Flanges ^b	All	0.0375	0.00006
Valves ^c	Gas	0.2626	0.0006
	Light liquid	0.0852	0.0017
	Heavy liquid	0.00023	0.00023
Pump Seals	Light liquid ^d	0.437	0.012
	Heavy liquid	0.3885	0.0135
Compressors	Gas	1.608	0.0894
Pressure Relief Valves	Gas	1.691	0.0447
Open Ended Lines	All	0.01195	0.0015

^a Source: USEPA (1995a). These emission factors are for non-methane VOCs only.

^b 'Connectors' are defined as *non-flanged* connectors.

^c It is important to note that this equipment type category does not include pressure relief valves.

^d The light liquid pump seal factor can be used to estimate leak rates from agitator seals.

4.3.1.7 Average Emission Factors

Where no screening values are available for particular equipment types, the 'average emission factors' presented in this sub-section should be used. This methodology involves applying the following generic algorithm to estimate emissions from all sources in a stream, for a particular equipment type:

$$E_{\text{VOC}} = F_A * WF_{\text{VOC}} * N$$

Where:

- E_{VOC} = Emission rate of VOC from all sources grouped in a particular equipment type and service (kg/hr) (eg valves in light liquid service);
- F_A = Applicable average emission factor for the particular equipment type (from Table 13);
- WF_{VOC} = The average weight fraction of VOC in the stream;
- N = The number of pieces of equipment grouped in the relevant category according to equipment type, service and weight fraction of VOC.

Although the average emission factors are in terms of VOCs, the equation still requires an input regarding the weight fraction of VOC in the process stream (i.e. WF_{VOC}) to account for any non-organic compounds. For example if the stream contains water vapour, You will need to account for this in your calculations. An example calculation is presented at the end of this section illustrating the application of this methodology.

Step 1: Develop an Inventory of the Number and Service Type of Fugitive Sources

The number and service type (refer to Section 4.3.1.3) of each equipment type in the refinery must be determined. This is a prerequisite to the use of this methodology. To simplify data management, spreadsheets can be developed noting the types of equipment and service modes (i.e. gas, light liquid etc.).

Step 2: Group the Inventory into “Streams”

To simplify calculations, it is recommended that the equipment/service mode combinations identified in Step 1 (eg. valves in gas service) be grouped into ‘streams’ according to the approximate weight fraction of VOCs (i.e. WF_{VOC}) in each stream.

A further simplification (if possible) may be to group areas of the refinery according to the ‘average’ weight fraction of VOCs in the process streams. It will be necessary to take account of the various service modes for each equipment type (eg. gas, light liquid etc.) contained within that area.

Another approach may be to make the conservative assumption that all streams are approximately 100% VOCs, thereby making $WF_{VOC} = 1$.

Step 3: Note Operational Hours

For the specific equipment category defined by the above two steps, the number of operational hours needs to be estimated.

Step 4: Use Emission Factors to Estimate Emission Rates

Use the relevant emission factors and the equation given above to calculate the emissions from each equipment type. These emissions should then be added to derive a total emission rate for all equipment pieces quantified using this methodology.

Table 14 presents the emission factors required to estimate emissions using the steps discussed above.

Table 14. Average Emission Factors for Process Fugitives ^a

Equipment Type	Service	Emission Factor (kg/hr/source)
Connectors ^b	Gas	2.50×10^{-4}
	Light liquid	2.50×10^{-4}
	Heavy liquid ^c	4.34×10^{-5}
Flanges	Gas	2.50×10^{-4}
	Light liquid	2.50×10^{-4}
	Heavy liquid ^c	4.68×10^{-5}
Compressor Seals	Gas	0.636
Pump Seals	Light liquid ^d	0.114
	Heavy liquid ^c	3.49×10^{-3}
Valves	Gas	0.0268
	Light liquid	0.0109
	Heavy liquid ^c	9.87×10^{-5}
Open Ended Lines	All	2.30×10^{-3}
Pressure Relief Valves	Gas	0.16
Sampling Connections	All	0.015
Drains ^e	All	0.032
Other ^f	Heavy liquid ^c	5.18×10^{-5}

^a Source: USEPA (1995a) – pp. 2-13, unless otherwise indicated. These emission factors are for non-methane VOCs only.

^b These are defined as *non-flanged* connectors.

^c Source: Taback (1996) – pp. 18.

^d The light liquid pump seal factor can be used to estimate leak rates from agitator seals.

^e Source: Taback (1996) – pp. 12.

^f This 'other' category should be applied to all equipment types in heavy liquid service that have not been specifically considered elsewhere in the table. Note, however, that some equipment types have emission factors applicable to 'All' service types, which includes the heavy liquid category. Therefore, care must be taken to ensure these are NOT included under the 'other' category.

EXAMPLE CALCULATION

The following example illustrates the application of the average emission factor approach:

1. A particular section of a refinery has a count of 300 valves (Step 1);
2. It is ascertained that 200 of these are in gas service (Step 1);
3. Within this smaller group of valves in gas service, it is ascertained that 100 valves are, on average, 80 weight percent VOCs, 10 percent methane, and 10 percent water vapour (Step 2);
4. It is estimated that this group of valves operates for 5500 hours per year (Step 3);
5. The appropriate emission factor for valves in gas service is 0.027 kg/hr/source (from Table 14) (Step 4). Emissions from this group of valves is thus estimated with the following parameters:
 - i) $F_A = 0.027$;
 - ii) $WF_{VOC} = 0.8$ (as this equation parameter does NOT include methane or vapour); and
 - iii) $N = 100$.
6. The final emission estimate for the group of 100 valves specified above is approximately 11,900 kg VOC/year.

The above steps would then be repeated again for the remaining 200 valves that were not included in the above estimate for that section of the refinery. In a similar manner, emissions need to be calculated from other potential fugitive

emission sources in that section, followed by the next refinery 'section', and so on until fugitive emissions from the entire refinery have been quantified.

4.3.2 Speciation of VOC Estimates

Once total VOC emission estimates have been determined, emissions can be speciated into NPI-listed substances according to either of the following two methods:

1. Use process stream composition data; and/or
2. Use limited speciation data in the form of weight fractions developed by USEPA.

The first methodology is likely to give more accurate estimates than using generic weight fractions developed by the USEPA. In addition, the published speciation data is very limited and, therefore, a combination of these two methodologies may be required.

4.3.2.1 Speciation Based on Process Stream Composition

This methodology involves determining the organic composition of each process stream, and applying this data to determine the vapour phase composition. Assumptions are discussed in Section 7.1.3 regarding this methodology.

This EET relies on the following equation to speciate emissions from a single equipment piece:

$$E_i = E_{\text{VOC}} * (WP_i / WP_{\text{VOC}})$$

where:

- E_i = The mass emission rate of NPI substance "i" from the equipment (kg/hr);
- E_{VOC} = The total VOC mass emission rate from the piece of equipment (as determined using the EETs from Sections 4.3.1.1, 4.3.1.2 or 4.3.1.3);
- WP_i = The concentration of NPI substance "i" in the equipment in weight percent;
- WP_{VOC} = The VOC concentration in the equipment in weight percent.

As for the techniques used to estimate total VOC emissions, it may be possible to group the refinery into sections according to process streams with similar compositions. 'Average' composition data could then be derived from these individual process areas and used to speciate VOC emission estimates.

4.3.2.2 Speciation Using Developed Weight Fraction Data

As there is only a limited amount of published data on the speciation of VOC emissions, not all equipment types have been included in Table 15. This methodology can, therefore, only be used for the equipment types identified.

The speciation factors presented in Table 15 can be used to calculate emissions of NPI substances using the following equation:

$$E_i = E_{\text{VOC}} * (WP_i / 100)$$

Where:

- E_i = The mass emissions of NPI substance “i” from the equipment (kg/hr);
- E_{VOC} = The total VOC mass emission rate from the piece of equipment (as determined using the EETs from Sections 4.3.1.1, 4.3.1.2 or 4.3.1.3);
- WP_i = The weight percent of the relevant compound in the vapour released from the equipment, as provided in Table 15.

Table 15. Speciation Data for NPI Substances from Equipment Fugitives

Refinery Source	Compound	Weight Percent in VOCs Released
Flanges	n-hexane	4.76
	cyclohexane	0.14
	xylenes	0.28
	benzene	0.14
	toluene	0.70
Valves	n-hexane	4.76
	cyclohexane	0.14
	xylenes	0.28
	benzene	0.14
	toluene	0.70
Pump seals	n-hexane	11.4
	cyclohexane	0.52
	xylenes	1.34
	benzene	0.52
	toluene	3.10
Compressor seals	n-hexane	5.30
Drains	n-hexane	12.2
	benzene	2.47

^aSource: USEPA (1990). A much greater range of compounds was originally supplied, with the weight fractions all adding to 100%. The compounds shown in the table above are those present on the NPI substance list.

4.3.3 Process Fugitive Controls

This Section provides a general overview of the two principal techniques used in refineries to reduce emissions from process fugitives. These are:

1. Modifying or replacing existing equipment (referred to as 'equipment modification'); and
2. Implementing a leak detection and repair (LDAR) program.

4.3.3.1 Equipment Modifications

There is a range of equipment modifications that can be used to reduce fugitive emissions. In general terms, these involve either installing additional equipment that eliminates or reduces emissions, or replacing existing equipment with seal-less types. Table 15 provides approximate reduction efficiencies for common equipment modifications.

Table 16. Summary of Equipment Modifications ^a

Equipment Type	Modification	VOC Emission Reduction Efficiency (%)
Pump Seals	Sealless Design	100 ^b
	Closed-vent system	90 ^c
	Dual mechanical seal with barrier fluid maintained at a higher pressure than the pumped fluid	100
Compressors	Closed-vent system	90 ^c
Connectors	Weld together	100
Valves	Sealless Design	100
Pressure Relief Devices	Closed-vent system	See footnote d
	Rupture disk assembly	100
Sample Connections	Closed-loop sampling	100
Open-ended Lines	Blind, caps, plug or second valve	100

a Source: USEPA (1995a)

b It is important to note that seal-less design equipment can be a significant source of emissions in the event of equipment failure. No methodology was found to estimate VOC releases in the event of such a failure.

c The actual control efficiency of a closed-vent system is dependent on the percentage of VOC emissions collected, as well as the efficiency of the control device to which the vapours are routed (eg. a flare or a combustion device, such as a furnace)

d The control efficiency of closed vent-systems installed on a pressure relief device may be lower than closed-vent systems used on other sources (ie. pumps and compressors).

For a detailed discussion on each of these modifications, refer to the USEPA (1995a) document, Section 5.2. Note that these equipment modifications are not applicable to the 'correlation equations' and 'leak/no-leak method', as these techniques are based on equipment screening. However, if any equipment emissions are estimated using average emission factors, these reduction efficiencies can be applied as discussed in the following steps.

Step 1: Derive Total Fugitive VOC Emissions

Total VOC emission estimates should be derived using the average emission factor methodology discussed in Section 4.3.1.7.

Step 2: Subtract Relevant Equipment Pieces

Identify those specific equipment pieces that utilise the modifications shown in Table 16. Estimate the uncontrolled emissions from these particular equipment pieces using the emission factors from Section 4.3.1.7. Once emissions from these equipment pieces have been derived, subtract this VOC contribution from the total VOC estimate (derived from Step 1). This avoids any possible confusion with double counting of emission estimates.

Step 3: Incorporate Controlled Equipment Fugitive Emissions

Estimate controlled emission estimates from the equipment pieces identified in Step 2, using the reduction efficiencies from Table 16, and the following equation:

$$\text{Controlled Emission} = \text{Uncontrolled Emission} * (1 - \text{Reduction Efficiency}/100)$$

Once controlled emission estimates have been derived from these equipment pieces, add these controlled emissions estimates to the total VOC emission estimate derived using Step 2.

4.3.3.2 Leak Detection and Repair (LDAR) Programs

An LDAR program is designed to identify pieces of equipment that are emitting sufficient amounts of material to warrant reduction of the emissions through repair. These programs are generally applied to equipment types that can be repaired on-line, (resulting in immediate emissions reduction), and/or to equipment types for which equipment modifications are not feasible.

It is not the aim of this Section to provide a detailed methodology relating to the implementation of an LDAR program, because it is a very complicated and detailed process, and beyond the scope of this Manual. For refineries interested in implementing such a program, please refer to the USEPA (1995a) document, Section 5.3.

If you do not currently have such a program in place, then the appropriate emission estimation technique should be chosen from Section 4.3.1. However, if you are using an LDAR program, then the principal issue relates to the way emissions are estimated for equipment components that are tested (with a time period between testing eg. quarterly or annual testing).

Based on a review of the USEPA (1995a) document, it appears that where an LDAR program is in place, the equipment pieces are tested immediately prior to, and after 'fixing'. The following equation should then be used to estimate emissions for the time period between testing:

$$\text{AER} = (\text{ER}_{\text{INI}} + \text{ER}_{\text{END}}) / 2$$

Where:

- AER = Average emission rate for the equipment type in a particular service mode applicable for the entire time period the equipment is in operation between testing periods (kg/hr);
- ER_{INI} = The emission rate for the equipment type immediately after fixing (i.e. at the start of the period between fixing cycles) (kg/hr);
- ER_{END} = The emission rate estimated for the equipment type immediately prior to fixing (i.e. at the end of the period between fixing cycles) (kg/hr).

This 'average' emission factor is applied to the equipment population tested for each equipment type, with consideration given to the operational hours of the equipment in the period between testing.

4.4 Tank Farm Fugitives

4.4.1 Total VOC Estimation

Storage tank emissions can be estimated using the model developed for the Fuel and Organic Liquid Storage EET Manual, referred to as AUSTANKS. This is a software package that requires information on the storage tanks, typical atmospheric conditions, the contents of the tank, and throughput. Note that for particular inputs, the AUSTANKS program has default values available. However, actual site-specific variables should be used wherever possible. The program, and the accompanying user's manual, can be obtained from your relevant state or territory environment agency.

The following section provides guidance on how total VOC estimates can be speciated so that NPI substances can be estimated.

4.4.2 VOC Speciation Using Facility-Specific Information

4.4.2.1 Methodology

The methodology outlined in this Section uses Raoult's Law together with information on the weight fractions of each NPI substance in the product of concern. Speciated emissions can be estimated using either refinery-specific data for the products stored (the preferred methodology), or average data found in the literature on petroleum products.

4.4.2.2 Emissions from Fixed Roof Tanks

For fixed roof tanks, the emission rate for each individual component can be estimated by:

$$L_{\text{Tkpy},i} = (Z_{i,v})(L_T) \quad (1)$$

Where:

$$\begin{aligned} L_{\text{Tkpy},i} &= \text{emission rate of NPI substance } i \text{ (kg/yr);} \\ Z_{i,v} &= \text{weight fraction of NPI Substance } i \text{ in the vapour, as} \\ &\text{determined using Raoult's Law (kg/kg) - refer to Section 4.4.2.4;} \\ L_T &= \text{total losses for the fixed roof tank, as estimated using} \\ &\text{AUSTANKS (kg/yr);} \end{aligned}$$

For each NPI Substance in the stored liquid, you need to follow equations (3) - (6) from Section 4.4.2.4 to calculate $Z_{i,v}$.

4.4.2.3 Emissions from Floating Roof Tanks

For floating roof tanks, the emission rate of each NPI Substance can be estimated by:

$$L_{\text{Tkpy},i} = (Z_{i,v}) (L_R + L_F + L_D) + (Z_{i,l}) (L_{\text{WD}}) \quad (2)$$

Where:

$$\begin{aligned} L_{\text{Tkpy},i} &= \text{emission rate of NPI Substance } i \text{ (kg/yr);} \\ Z_{i,v} &= \text{weight fraction of NPI Substance } i \text{ in the vapour as} \\ &\text{determined using Raoult's Law (kg/kg) - see Section 4.4.2.4;} \\ L_R &= \text{rim seal losses as estimated using AUSTANKS (kg/yr);} \\ L_F &= \text{roof fitting losses as estimated using AUSTANKS (kg/yr);} \\ L_D &= \text{deck seam losses as estimated using AUSTANKS (kg/yr);} \\ Z_{i,l} &= \text{weight fraction of NPI Substance } i \text{ in the liquid (kg/kg);} \\ L_{\text{WD}} &= \text{withdrawal losses as estimated using AUSTANKS (kg/yr).} \end{aligned}$$

As mentioned in relation to fixed roof tanks, $Z_{i,v}$ is determined using equations (3) - (6) from Section 4.4.2.4. The fraction of the NPI Substance in the stored liquid can be determined using either site-specific information (which is preferred), or using the default substance concentrations presented in Section 4.4.3.

4.4.2.4 Calculating Weight Fractions

In order to use Equations 1 and 2, the weight fraction of each NPI Substance in the liquid and vapour phase is required. While the weight fraction in the liquid may be known from site-specific information or from data shown in Section 4.4.3, the weight fraction in the vapour phase must typically be calculated. Raoult's law forms the basis of this calculation, as it allows the partial pressure of the NPI Substance to be derived. Raoult's law is specified as follows:

$$P_i = (P)(x_i) \quad (3)$$

Where:

$$\begin{aligned} P_i &= \text{partial pressure of NPI Substance } i \text{ (kPa(a));} \\ P &= \text{vapour pressure of pure NPI Substance } i \text{ at the daily average} \\ &\quad \text{liquid surface temperature (kPa(a));} \\ x_i &= \text{liquid mole fraction (kg-mole/kg-mole).} \end{aligned}$$

Determination of Liquid Mole Fractions

Before Equation (3) can be used, the mole fraction of the NPI substance in the liquid (i.e. x_i) must be derived using Equation (4) as follows:

$$x_i = (Z_{i,L}) (M_L) / (M_i) \quad (4)$$

Where:

$$\begin{aligned} x_i &= \text{liquid mole fraction of NPI substance } i \text{ (kg-mole/kg-mole);} \\ Z_{i,L} &= \text{weight fraction of NPI Substance } i \text{ in the liquid (kg/kg);} \\ M_L &= \text{molecular weight of liquid stock (kg/kg-mole);} \\ M_i &= \text{molecular weight of NPI Substance } i \text{ (kg/kg-mole).} \end{aligned}$$

Determination of Vapour Mole Fractions

The liquid mole fraction, and the vapour pressure of the NPI substance at the daily average liquid surface temperature, can then be substituted into Equation (3) to obtain the partial pressure of the NPI substance. The mole fraction of the NPI Substance in the vapour phase can then be determined using the following equation:

$$y_i = P_i / P_{VA} \quad (5)$$

Where:

$$\begin{aligned} y_i &= \text{vapour mole fraction of NPI substance } i \text{ (kg-mole/kg-mole);} \\ P_i &= \text{partial pressure of NPI Substance } i \text{ (kPa(a));} \\ P_{VA} &= \text{total vapour pressure of the liquid mixture (kPa(a)).} \end{aligned}$$

Determination of Vapour Weight Fractions

The weight fractions in the vapour phase are calculated using Equation (6), based on the mole fractions in the vapour phase from Equation (5).

$$Z_{i,V} = y_i M_i / M_v \quad (6)$$

Where:

$$\begin{aligned} Z_{i,V} &= \text{vapour weight fraction of NPI substance } i \text{ (kg/kg);} \\ y_i &= \text{vapour mole fraction of NPI substance } i \text{ (kg/kg-mole) -} \\ &\quad \text{calculated from equation (5);} \\ M_i &= \text{molecular weight of NPI Substance } i \text{ (kg/kg-mole);} \end{aligned}$$

M_v = molecular weight of vapour stock (kg/kg-mole).

4.4.2.5 Calculating Total Losses

The liquid and vapour weight fractions of each desired component, and the total losses can be substituted into either Equation (1) or (2) (depending on tank design), to estimate the individual component losses. Example calculations can be found in Chapter 7.1 of USEPA (1997a).

4.4.3 Speciation Using Data from the Literature

In the event that site specific data on the properties of the stored products is limited or does not exist, the following information may be used to aid in estimating emissions. It should, however, be used with caution, as the actual properties of products stored in refinery tank farms may differ significantly to those presented in the table.

Table 17. Weight Percent of NPI Substances in Petroleum Products ^a

Constituent	Typical Concentration in Petroleum Stocks (weight percent)				
	Petrol	Crude	Jet Fuel	Kerosene	Diesel
n-hexane	4	1.4	5	0.4	0.1
benzene	1.8	0.6	0.6	0.07	0.2
toluene	7	1	3	0.3	0.4
ethylbenzene	1.4	0.4	0.5	0.2	0.2
xylenes	7	1	3	0.9	0.8
cumene	0.5	0.1	0.2	0.07	0.1

^a Source: Taback, (1996), pp. 19.

This table is of limited use, as it is likely that other substances found on the NPI list are also present in petroleum stocks. The identification of these other substances will require a more specific knowledge of your facility's products.

4.5 Loading Losses

4.5.1 Total VOC Estimation

Emissions from the loading petroleum liquid can be estimated (with a probable error of ±30 percent) using the following equation (USEPA, 1997a):

$$L_L = 0.12 \times SPM/T$$

Where:

- L_L = VOC loading loss (kg/m³ of liquid loaded);
- S = a saturation factor - see Table 18 below);
- P = true vapour pressure of liquid loaded (kilopascals (kPa));
- M = molecular weight of vapours (kg/kg-mole); and
- T = temperature of bulk liquid loaded (K (ie °C + 273)).

The saturation factor 'S' accounts for the variations observed in emission rates from the different loading and unloading methods. Table 18 lists suggested saturation factors.

Table 18. Saturation (S) Factors for Calculating Petroleum Liquid Loading Losses ^a

Cargo Carrier	Mode Of Operation	S Factor
Tank trucks and rail	Submerged loading of a clean cargo tank	0.50
Tank cars	Submerged loading: dedicated normal service	0.60
	Submerged loading: dedicated vapour balance service	1.00
	Splash loading of a clean cargo tank	1.45
	Splash loading: dedicated normal service	1.45
	Splash loading: dedicated vapour balance service	1.00
Marine Vessels	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

^a Source: USEPA (1997a).

Emissions from controlled loading operations can be calculated by multiplying the uncontrolled emission rate (as determined using the equation above), by a reduction efficiency term:

$$\text{Controlled Emission} = \text{Uncontrolled Emission} \times (1 - \text{Efficiency}/100)$$

The overall reduction efficiency should account for the capture efficiency of the collection system, as well as both the efficiency, and any downtime of the control device. This data should be obtained from the supplier or manufacturer of the collection system.

4.5.2 Speciation of VOC Estimates

This is performed using the same methodology discussed in Section 4.4.2 in relation to the speciation of VOC emissions from storage tanks. The weight fractions are first derived (ie. as per Section 4.4.2.4), and then combined with the total VOC estimate for loading operations. This enables estimates of specific NPI substances to be quantified.

4.6 Wastewater Emissions to Air

Estimating air emissions from wastewater is data intensive, and requires site-specific data, as well as information regarding the physical and chemical characteristics of the NPI substances in question. The details of the equations, and the input parameters necessary for quantification of emissions to air, are provided in the software package referred to as WATER8 developed by the USEPA. This software, and the associated user manual, can be obtained from the USEPA web site (see Reference 13 in Section 8 of this Manual).

5.0 Emissions to Water

This Section will be divided into two principal parts as follows:

- point source wastewater discharges as released by refinery treatment plants; and
- diffuse wastewater that arises through stormwater, and other miscellaneous run-off from the refinery site that is not captured and treated prior to discharge.

5.1 Point Source Discharge

The following tables should be used to provide 'default' emission data for refinery effluent discharges that are not classified as transfers (transfers include discharging to sewer). Any relevant discussions and assumptions associated with this section are presented in Section 7.2.

Based on discussions with the petroleum refining industry, the 'dissolved organic carbon' (DOC) content of refinery effluents is a known parameter. Hence, the speciation factors for organic compounds in Table 19 are based on this parameter.

A similar parameter to DOC was not identified for trace elements and other inorganics in wastewater effluent. Therefore, trace elements and inorganic compound emissions are expressed as default emission factors in Table 20.

Table 19. Default Speciation Factors for Organics in Refinery Effluent ^a

NPI Substance	Weight Percent of DOC
Toluene	9.2×10^{-4}
Benzene	9.1×10^{-4}
Xylenes	1.4×10^{-3}
Phenol	6.9×10^{-4}
1,2-Dichloroethane	2.7×10^{-4}
Hexachlorobenzene	4.4×10^{-6}
PAH's	1.6×10^{-3}
Styrene	1.0×10^{-4}
Ethylbenzene	1.2×10^{-4}
1,1,2-trichloroethane	3.6×10^{-5}
Chloroform	2.5×10^{-3}

^a Source: Ontario Ministry of the Environment (1992), pp.A-1. See Section 7.2 for more detailed discussion of the sources of this information.

^b The document from which this data was derived indicates a ratio of DOC/COD of 0.267. In the absence of site-specific information regarding DOC, this ratio can be used to determine DOC from measurements of COD.

These speciation factors are applied to this effluent parameter in the following manner:

$$WWE_i = \text{DOC} * (\text{WP}_i/100) * \text{Flow}$$

Where:

- WWE_i = The wastewater emission of component “i” from the treatment plant (kg/hr);
 DOC = The dissolved organic carbon (DOC) content of the treated effluent discharged by the plant (kg/m³);
 WP_i = The weight percent of component “i” as provided in Table 19 above;
 Flow = The wastewater flowrate discharged to the receiving body of water (m³/hr).

The emission factors in Table 20 are applied in the same way as factors are applied to air emissions, with the exception that they are based on the flow of effluent from the treatment plants (ie. the emission factors are kg per m³ of wastewater flow).

Table 20. Default Emission Factors for Trace Elements and Inorganics in Refinery Effluent ^a

NPI Substance	Emission Factors (kg/m ³ of flow)
Zinc	4.4×10^{-4}
Phosphorous	4.1×10^{-7}
Arsenic	6.7×10^{-6}
Chromium (VI)	7.7×10^{-6}
Selenium	3.1×10^{-6}
Nickel	3.6×10^{-6}
Copper	2.9×10^{-6}
Antimony	5.8×10^{-7}
Cobalt	1.6×10^{-6}
Mercury	1.1×10^{-8}
Cadmium	3.3×10^{-7}
Lead	1.9×10^{-6}
Cyanide	7.6×10^{-9}
Ammonia	1.3×10^{-6}

^a Source: Ontario Ministry of the Environment (1992), pp.A-1. See Section 7.2 for more detailed discussion of the sources of this information.

b Any reference to metals in this column relates to the metal and compounds.

5.2 Diffuse Discharge

This is a very complicated and uncertain area for quantification, with little data found in the literature pertaining specifically to refinery operations.

6.0 Emissions to Land

Under the NPI, facilities are required to report on their releases to land. Emissions to land have been defined by the NPI Implementation Working Group as:

All emissions of listed substances, except those which are directed to, and contained by, purpose built receiving facilities are to be reported to the NPI. This applies irrespective of whether the substances' fate is within or outside a reporting facility boundary. All such purpose built facilities are to have the approval of the State or Territory Environmental Authority for the reception of the listed substances.

Emissions to receiving facilities such as secure landfills, sewers, and tailings dams do not need to be reported. Similarly removal of a substance for transfer to another facility for destruction, treatment, recycling, reprocessing, recovery, or purification is excluded. This means, for instance, that if an accidental release of a water-borne pollutant is directed to a temporary bund, or into a watercourse, then it must be reported regardless of whether the emission is detectable at the boundary of the mining lease. If the release is directed to, and stored in, a purpose built facility, (eg. a rubber lined dam), then it does not need to be reported. However, all other emissions of NPI-listed substances except those that are directed to, and contained by, purpose built receiving facilities are to be reported under the NPI, irrespective of whether the substance's fate is within, or outside the reporting facility's boundary.

To characterise emissions to land, three general EETs are discussed here:

- groundwater monitoring
- spills
- on site disposal

6.1 Groundwater Monitoring

Some facilities conduct monitoring of groundwater to characterise releases from the facility. Where available, this monitoring data may be used to assist in the characterisation of releases. This involves determining upstream and downstream concentrations, and using this information, in conjunction with groundwater flow information, to determine the contribution of the facility to pollutant levels in the groundwater.

In terms of meeting NPI reporting requirements, this approach is reasonable in situations where there is no loss of substances (eg due to evaporation) prior to the substance entering the groundwater, and where the time between the release occurring, and the substance entering the groundwater is minimal. Therefore, for those facilities where groundwater monitoring captures all releases to land, such monitoring can be used as a reasonable measure of emissions to the environment. If this is not the case (eg where the rate of transmission through the soil/clay is low, or where there are other routes whereby substances to land are carried offsite, (such as evaporation or surface runoff), it will be necessary to

characterise such releases using the other EET's presented in this Manual.

6.2 Spills

For many facilities, the primary source of releases will be through spills (this may also include intentional spillage due to vessel washdown). Accidental spills can contribute to releases to land (directly), to water (through runoff), and to air.

As discussed above, unless the spilled material is routed to a secure containment facility, the quantity of material spilled, less the quantity collected (or cleaned up), is required to be reported under the NPI. In practical terms, a log of spillages could be maintained detailing the quantities spilled, and the composition of the spill (in particular, the quantities of NPI substances spilled). This log could then form the basic information required to meet NPI reporting requirements.

The quantity spilled can be partitioned into air emissions and releases to land by assuming that all of the light end fraction is volatilised, and the remaining fraction is released into the ground. The time, quantity of spill, temperature and porosity of the soil all play an important part in the estimation of release. The evaporation rate of compounds into the atmosphere is given by the following equation:

$$E_i = 1.2 * 10^{-10} (M(p_i^o)/T) u^{0.78} * 0.89^y$$

Where:

- E_i = Evaporation rate of substance "i" (g/s);
- u = Wind speed over the surface of the spill (cm/s);
- x = Downwind dimension (cm);
- y = Crosswind dimension (cm);
- M = Molecular weight of the substance;
- p_i^o = Vapour pressure of substance "i" at spill temperature T (dyne/cm² = 0.0001 kPa);
- T = Temperature (K).

Once losses to the atmosphere have been quantified, releases to land can be estimated using the following equation:

$$ER_{LAND,i} = Qty_{SPILL} - ((time) * (E_i))$$

Where:

- $ER_{LAND,i}$ = The emission to the land of compound "i";
- Qty_{SPILL} = The quantity of compound in the liquid spilled;
- E_i = The loss through evaporation of substance "i" as estimated using the evaporation equation above; and
- Time = The time period between when the liquid was initially spilled, and eventual clean up.

6.3 On-Site Disposal

Facilities with on-site disposal of wastes will need to consider the discussion in Section 6.0 to determine whether the disposal is classed as a transfer, or as a release to land under the NPI. If the disposal is not a transfer, reporting will be required under the NPI. In a similar manner to spills, the most effective EET is to maintain a record of all such disposal to land and, in particular, the amount of NPI substances contained in the material disposed of in such a manner.

7.0 Assumptions & Discussion

An important point to note with regard to emission factors is that the available data is not always consistent in the literature (eg. more detail is available for certain compounds and sources than for others). In addition, even though an emission factor may not exist for certain compounds from a source, this does not necessarily mean that the substance is not emitted from that source.

7.1 Air Emissions

7.1.1 Combustion Sources

7.1.1.1 NPI-Listed Substances

In the petroleum refining section of USEPA (1997a), Section 5.1, it is indicated that emissions of NPI-listed substances from oil and gas combustion in a refinery can be estimated using the emission factors developed for general oil and natural gas combustion. It must therefore be an intrinsic assumption that these emission factors are applicable to refineries burning fuel oil and fuel gas.

7.1.1.2 Organics

The emission factors presented in Table 4 are based on residual oil combustion. However, in the absence of more appropriate data, it may be assumed that this data also applies to distillate oil combustion.

7.1.1.3 Trace Elements

The following discussion relates to the principle underpinning the mass balance approach. USEPA (1989) suggests that because oil combustion does not generate any bottom ash, it can generally be assumed that 100 percent of the trace elements present in the fuel are released into the atmosphere. It is further stated that emissions of these trace elements would be independent of combustor design, and combustion sector (ie. industrial, utility etc.). While similar comments were not made for gas combustion, it has been assumed that the same assumption applies, because gas combustion does not result in the generation of bottom ash.

The emission factors presented in Table 6 indicate that emissions of beryllium and mercury from residual oil combustion are lower than from distillate oil combustion. These emission factors have been checked with the source document (USEPA, 1998b) and they are correct. However, no explanation can be provided for this discrepancy.

7.1.2 Refinery Process Sources

7.1.2.1 NPI-Listed Substances

The PM₁₀ estimates presented for FCCU, MBCCU, and fluid coking operations are based on a combination of data from USEPA (1997a) and USEPA (1993). This was necessary as USEPA (1997a) only provided data for total particulate from these

operations, while PM₁₀ is reportable under the NPI. USEPA (1993) provided supplementary information regarding the PM₁₀ weight fraction of total particulate for the following operations:

1. FCCU:
 - uncontrolled – 0.79 (weight fraction)
 - controlled – 0.553 (weight fraction)
2. Fluid coking units:
 - uncontrolled – 0.51 (weight fraction)

No data was available regarding the PM₁₀ fraction for controlled fluid coking or MBCCU operations. It was, therefore, assumed that the fraction applicable to controlled emissions from coking is applicable to uncontrolled emissions. In addition, it was assumed that the uncontrolled fraction applicable to FCCU operations is applicable to MBCCU operations.

The VOC emission data for SRUs has been obtained from Taback (1996), as indicated in the footnotes beneath Table 8. This reference did not, however, specify the type of SRU tested. This emission factor has been assumed to generally apply to SRU operations where no other data is available. The units specified in this reference were kg/dscm ‘process gas’. As no other information was supplied with the table, it was assumed that this referred to process gas feed to the SRU.

7.1.2.2 Organics

The speciation data for PAH’s from catalytic cracking units was developed by dividing the emission factor data presented in USEPA (1995b), by the total VOC emission factors from AP-42 (USEPA, 1997a) for refinery catalytic cracking sources.

7.1.2.3 Trace Elements

It is possible that certain trace element emissions will be underestimated using the methodology presented in Section 4.2.3. The principal reason for this relates to the intrinsic assumption that all metals are contained by the particulate released from each refinery source. While this may be a reasonable assumption for some metals, the more volatile ones, such as mercury are likely to be partially present in vapour form. However, insufficient information is currently available to produce better estimates.

The carbon disulfide emission factor was expressed in Taback (1996) as a combined emission factor for CS₂ and methyl mercaptan as these substances coelute. As no other data is available, it has been conservatively assumed that this speciation factor can be used to estimate emissions of CS₂. In addition, it is important to note that this speciation factor must be applied to total VOC estimates from SRUs.

7.1.3 Process Fugitives

Correlation Equations

One questionable aspect of this data is that zero emission rates can be greater than the correlation equation estimates for valves, connectors and drains. Based on some preliminary calculations, the 'zero default' emission factors should be used with screening values of less than 5.2 ppmv, 8.7 ppmv, and 9.6 ppmv for valves, connectors, and drains respectively.

Leak/No-Leak

This approach operates on the principle that components having screening values greater than 10000 ppmv have a different average emission factor than components with screening values less than 10000 ppmv. Although this method is expected to give more reasonable results than the average emission factors, available data indicates that mass emission rates can vary considerably from the rates predicted using these factors (USEPA, 1995a).

Average Emission Factors

This methodology is slightly different than that discussed in the USEPA (1995a) document. The USEPA methodology first converts emission estimates to TOC (i.e. total organic compounds – including methane), and then if required, converts back to VOCs later on. As only VOC estimates are required to be reported under the NPI, the intermediate step has been omitted, and VOC estimates have been derived directly.

The heavy liquid emission factors are different to those presented by the USEPA (1995a) equipment fugitive protocol document. The emission factors have been chosen because they were developed as part of a more recent study for the American Petroleum Institute (as presented in Taback, 1996), and are therefore considered to be more relevant than those provided in the USEPA document.

Speciation

The methodology involving speciation of VOC emissions based on process stream composition (Section 4.3.2.1) is based on the assumption that the weight percent of the organic substances in the equipment, will equal the weight percent of the substance in the released emissions. In general, this assumption is reasonably accurate for single-phase streams containing either gas/vapour material, or liquid mixtures containing constituents of similar volatilities (USEPA, 1995a). The USEPA (1995a) document also indicates that there are no clear guidelines for the determination of which release mechanism is occurring for any given equipment piece, and so the assumptions used with this methodology are generally valid.

7.2 Wastewater Emissions

Tables 19 and 20 were developed based on industry consultation, and a review of available literature on substance levels in refinery wastewater effluents. It was agreed that default values, based on Ontario Ministry of the Environment (1992), should be derived in the event that no better data is available. It was also agreed that the preferred methodology involved presenting the organic effluent data on a speciated basis, using the dissolved organic content (DOC) of refinery effluents.

The default speciation numbers presented in Tables 19 and 20 were determined using test data presented in the Ontario Ministry of the Environment (1992) document. This document provided average effluent concentration levels, as well as the percentage of samples tested, that showed substance concentrations below detection limits. The averages presented were only based on samples with levels exceeding the detection limit, and so account needed to be taken of the samples that showed non-detectable levels. Therefore, using a conservative approach (where it was assumed that samples with non-detectable levels actually contain the compound at half the detection limit), new 'average' effluent concentrations were derived. These average effluent concentrations were then divided by the DOC average presented in the same document to derive speciation fractions.

8.0 References

1. AIP (1997), *AIP Statistical Review*, Pers. Comm. (Barry Challenger, AIP)
2. Ontario Ministry of the Environment (1992) *Background Document on the Development of the Draft Petroleum Refining Sector Effluent Limits Regulation*, Water Resources Branch, Ontario Ministry of the Environment, August 1992 (ISBN 0-7778-0049-7)
3. Taback (1996), *Estimating VOC Emissions from Petroleum Industry Sources*, Hal Taback Company, September 1996 (Course notes presented at AWMA Conference on Emission Estimation, New Orleans, LA, September 1996)
4. USEPA (1989), *Estimating Air Toxic Emissions from Coal and Oil Combustion Sources*, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, (EPA-450/2-89-001)
5. USEPA (1990), *Air Emissions Species Manual – Volume 1 Volatile Organic Species Profiles, Second Edition*, Office of Air Quality Planning and Standards, Research Triangle Park, (EPA-450/2-90-001a).
6. USEPA (1993), *VOC/PM Speciation DBMS*, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, 1993
7. USEPA (1995a), *Protocol for Equipment Leak Emission Estimates*, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, (EPA-453/R-95-017)
8. USEPA (1995b), *Locating and Estimating Air Emissions from Sources of Polycyclic Organic Matter (POM) and Polycyclic Aromatic Hydrocarbons (PAHs)*, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park.
9. USEPA (1997a), *Compilation of Air Pollutant Emission Factors, Volume I: Stationary Sources, Fifth Edition*, Office of Air Planning and Standards, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, 1995 (AirChief CD-ROM, 1997, Version 5.0)
10. USEPA (1997b) *Factor Information Retrieval System (FIRE)*, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, (AirChief CD-ROM, 1997, Version 5.0)
11. USEPA (1998a), *Fuel Oil Combustion*, March 1998 Revision to AP-42 Section 1.3.
12. USEPA (1998b), *Natural Gas Combustion*, September 1998 Revision to AP-42 Section 1.4
13. USEPA Web Site Address, www.epa.gov.

APPENDIX A

**SUPPLEMENTARY INFORMATION FOR PROCESS FUGITIVE EMISSIONS
CHARACTERISATION**

1. Estimating Emissions for Equipment Not Screened when Other Screening Data is Available

Often, there will be a situation where not all components at the refinery site are screened because of cost considerations, or because a particular equipment piece is too difficult or unsafe to screen. These two situations will be discussed below.

Equipment pieces that are unsafe, or too difficult to screen must be included in equipment counts. For these sources, the average emission factors presented in Section 4.3.1.7 should be used.

Where cost considerations play a role in limiting the testing of a particular equipment group, there are certain criteria for determining an adequate sample size so that data can be applied to 'unscreened' equipment. This situation is commonly found in relation to the equipment category of connectors. The following discussion outlines the criteria used by the USEPA when determining an adequate sample size, so that data attained from a limited screening process can be applied to unscreened equipment.

2. Selection of Sample Size for Screening Components.

The following methodology is consistent with the one outlined in the USEPA (1995a) document, Appendix E. Although it is in relation to 'connectors', it may be assumed to apply to the general equipment types defined in Section 4.3.

The purpose of this appendix is to present a methodology for determining how many connectors must be screened, in order to constitute a large enough sample size to identify the actual screening value distribution of connectors in the entire process unit. Please note that the sampling is to be a random sampling throughout the process unit.

The basis for selecting the sample population to be screened is the probability that at least one "leaking" connector will be in the screened population. The "leaker" is used as a representation of the complete distribution of screening values for the entire class of sources. The following binomial distribution was developed to approximate the number of connectors that must be screened to ensure that the entire distribution of screening values for these components is represented in the sample:

$$n = N * [1 - (1 - p)^{1/D}] \quad (A-1)$$

Where:

N = Number of connectors;

D = (fraction of leaking connectors) * N; and

p = 0.95.