

National Pollutant Inventory

Emission Estimation Technique Manual

for

Oil Recycling

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EMISSION ESTIMATION TECHNIQUES FOR OIL RECYCLING

TABLE OF CONTENTS

1.0	INTRODUCTION	1
	1.1 Manual Structure 1.2 Manual Application	1 2
2.0	PROCESS DESCRIPTION	4
3.0	REPORTABLE EMISSION SOURCES	6
	 3.1 Reporting Thresholds 3.1.1 Category 1 3.1.2 Category 2 3.1.3 Category 3 3.2 Emissions to Air 3.2.1 Emission Factors for Releases to Air 3.3 Emissions to Water 3.4 Emissions to Land 	6 8 9 13 13 14
4.0	GLOSSARY OF TECHNICAL TERMS AND ABBREVIATIONS	15
5.0	REFERENCES	16
APP	ENDIX A - EMISSION ESTIMATION TECHNIQUES	17
	 A.1 Direct Measurement A.1.1 Sampling Data A.1.2 Continuous Emission Monitoring System (CEMS) Data A.2 Using Mass Balance A.3 Engineering Calculations A.3.1 Fuel Analysis A.4 Emission Factors 	18 18 21 24 25 25 25 26
APP	ENDIX B - EMISSION ESTIMATION TECHNIQUES: ACCEPTABLE RELIABILITY AND UNCERTAINTY	28
	B.1 Direct Measurement B.2 Mass Balance B.3 Engineering Calculations B.4 Emission Factors	28 28 29 29
APP	ENDIX C - LIST OF VARIABLES AND SYMBOLS	30

EMISSION ESTIMATION TECHNIQUES FOR OIL RECYCLING

LIST OF FIGURES, TABLES AND EXAMPLES

Figure 1 - The Distillation/Chemical Treatment Process for Oil Recycling	5
2 - The Inline Process for Oil Recycling	5
3 - Concentration of Category 1 Substance Required to Trigger Reportir	ng 7
Table 1 - Substances That May Trigger the Category 1 Reporting Thresholds	6
2 - Approximate Fuel Usage Required to Trigger Category 2 Thresholds	8
3 - NPI-listed Category 2 Substances	9
4 - Sources of Air Emissions from Oil Recycling Processes	10
5 - Emission Factors for Waste Oil Re-refineries	13
6 - Stack Sample Test Results	19
7 - Example of CEMS Output for a Hypothetical Furnace Firing Waste Fuel Oil	22
Example 1 - Category 1 Substance Reporting Threshold	7
2 - Using Stack Sampling Data	19
3 - Calculating Moisture Percentage	21
4 - Using CEMS Data	23
5 - Using Fuel Analysis Data	26

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 oil recycling.

This Manual applies to facilities engaged in the recovery of petroleum oils and grease from waste petroleum products. These waste oils consist of engine and transmission lubricants, hydraulic fluids, metalworking fluids, insulating and process fluids and greases.

EET MANUAL:	Oil Recycling
HANDBOOK:	Petroleum & Coal Product Manufacturing
ANZSIC CODE:	2520 and all codes within the 252 ANZSIC code group.

Pacific Air & Environment drafted this Manual on behalf of the Commonwealth Government. It has been developed through a process of national consultation involving State and Territory environmental authorities and key industry stakeholders.

1.1 Manual Structure

This Manual is structured as follows:

- **Section 2** provides a brief overview of the main processes and activities involved in oil recycling.
- Section 3.1 summarises the NPI-listed substances that are triggered, or likely to be triggered for the oil recycling industry. Category 1, 2 and 3 substances are discussed in Sections 3.1.1, 3.1.2 and 3.1.3 respectively. Sections 3.2, 3.3 and 3.4 detail the expected emissions to air, water and land respectively from oil recycling. These sections also detail the sources of these emissions and where emission estimation techniques for each of these sources are to be found.
- **Section 4** provides a glossary of the technical terms and abbreviations used in this Manual.
- **Section 5** provides a list of the references used in the development of this Manual.
- **Appendix A** provides an overview of the four general types of emission estimation techniques: sampling or direct measurement; mass balance; engineering calculations and emission factors, as well as example calculations to illustrate their use. Reference to relevant sections of this appendix is recommended in understanding the application of these techniques with particular respect to the oil recycling industry.
- **Appendix B** provides a discussion of the reliability and uncertainty associated with each of the techniques presented in Appendix A.
- **Appendix C** provides a list of the variables and symbols used in this Manual.

1.2 Manual Application

Context and use of this Manual

This NPI Manual provides a 'how to' guide for the application of various methods to estimate emissions as required by the NPI. It is recognised that the data that is generated in this process will have varying degrees of accuracy with respect to the actual emissions from oil recycling facilities. In some cases, there will necessarily be a large potential error due to inherent assumptions in the various emissions estimation techniques (EETs) and/or a lack of information regarding chemical processes.

EETs should be considered as 'points of reference'

The EETs and generic emission factors presented in this Manual should be seen as 'points of reference' for guidance purposes only. Each has associated error bands that are potentially quite large. Appendix B discusses the general reliability associated with the various methods. The potential errors associated with the different EET options should be considered on a case-by-case basis as to their suitability for a particular facility. Facilities may use EETs that are not outlined in this document. They must, however, seek the consent of their relevant environmental authority to determine whether any 'in house' EETs are suitable for meeting their NPI reporting requirements.

Hierarchical approach recommended in applying EETs

This Manual presents a number of different EETs, each of which could be applied to the estimation of NPI substances. The range of available methods should be viewed as a hierarchy of available techniques in terms of the error associated with the estimate. Each substance needs to be considered in terms of the level of error that is acceptable or appropriate with the use of the various estimation techniques. Also, the availability of pre-existing data and the effort required to decrease the error associated with the estimate will need to be considered. For example, if emissions of a substance are clearly very small, no matter which EET is applied, then there would be little to be gained by applying an EET which required significant additional sampling.

The steps in meeting the reporting requirements of the NPI can be summarised as follows:

Category 1 and 1a Substances:

Identify which reportable NPI substances are used (or handled by way of their incidental presence in ore or materials, or exceeds the bulk storage capacity for 1a), and determine whether the amounts used or handled are above the 'threshold' values and, therefore, trigger reporting requirements. See **Section 3.1.1** of this Manual for guidance on the Category 1 substances which are likely to require reporting for the oil recycling industry.

Category 2a and 2b Substances:

Determine the amount and rate of fuel (or waste) burnt each year, the annual power consumption and the maximum potential power consumption, and assess whether the threshold limits are exceeded. See Section 3.1.2 of this Manual for a discussion of the Category 2 substances which are likely to be triggered for the oil recycling industry.

Category 3 Substances:

Determine the annual emissions to water and assess whether the threshold limits are exceeded. It is unlikely that this NPI Category will require reporting for the oil recycling industry.

Those substances above the threshold values:

Examine the available range of EETs and determine emission estimates using the most appropriate EET.

Generally, it will be appropriate to consider various EETs as alternative options whose suitability should be evaluated in terms of:

- the associated reliability or error bands; and
- the cost/benefit of using a more reliable method.

The accuracy of particular EETs is discussed in Appendix B.

NPI emissions in the environmental context

It should be noted that the NPI reporting process generates emission estimates only. It does not attempt to relate emissions to potential environmental impacts, bioavailability of emissions or natural background levels.

2.0 Process Description

This Manual covers the recovery of petroleum oils and grease from waste petroleum products, as defined under the ANZSIC Code 2520 - Oil Recycling.

The main sources of these waste petroleum products are the automotive, aviation, marine and railroad industries, as well as some industrial processes. These raw materials frequently contain glycols, chlorinated solvents, gasoline, carbon, solid particles and metals. Metals are primarily present in the form of metal-organics but with some metal oxides and sulfides.

There are a number of different oil recycling processes. Used oil processing in Australia generally involves some combination of the following processes, depending on the specific facility:

- Settling/Filtration: This is the basic method for removing free water and solids. The heavy metals and emulsified oil remain in the solution.
- Dehydration processes: Water is removed, usually by heating, and most times the filtration and settling technique is performed as well. Minor cracking (see below) occurs due to the heating and hence some volatile components are also removed.
- Chemical treatment/Demineralisation: Metallic contaminants and additives are removed by the formation of insoluble metallic salts which settle out of solution and can then be filtered. Water is also removed.
- Thermal Cracking: The long chain molecules in the used oils are cracked at high temperatures into shorter chain molecules. The products of cracking range from fuel oils (low intensity cracking) to diesel extender (severe cracking).
- Distillation to produce base oils: The distillation process is usually used in conjunction with pre-treating processes. This pre-treatment usually involves de-watering and the removal of light hydrocarbons, metal contaminants and de-asphalting. The feedstock oil is then distilled into the base oil products.
- Solvent extraction and hydro-treating: Solvent extraction is used to remove aromatic compounds. Hydro-treating reacts unsaturated compounds in the oil with hydrogen and a catalyst at high temperature and pressure to produce an oil that is less likely to oxidise.

Figure 1 and Figure 2 are examples of current methods of processing used oils in Australia. Figure 1 depicts the waste oil distillation/chemical treatment process. Figure 2 shows the Inline process, that uses a propane solvent to dissolve and remove contaminants prior to distillation.

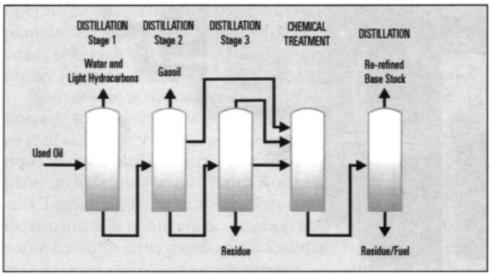


Figure 1 - The Distillation/Chemical Treatment Process for Oil Recycling Source: Australian Institute of Petroleum, 1997

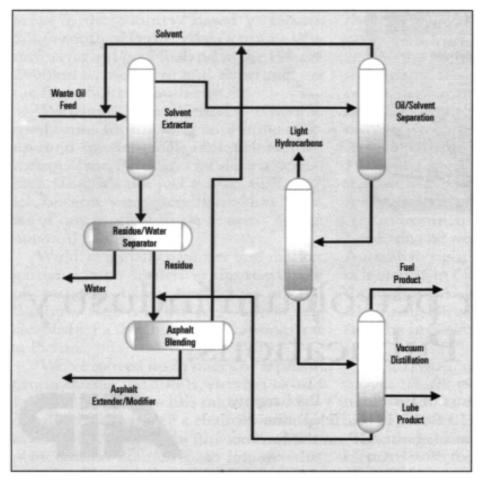


Figure 2 - The Inline Process for Oil Recycling Source: Australian Institute of Petroleum, 1997

3.0 **Reportable Emission Sources**

3.1 **Reporting Thresholds**

3.1.1 Category 1

The reporting threshold for Category 1 substances is exceeded if the activities of a facility involve the use (including handling) of 10 tonnes or more of the substance per year. Therefore, the total amount of Category 1 substances used must be estimated in order to determine whether the threshold is exceeded. A facility is only required to report on these substances for which reporting thresholds have been exceeded. If a reporting threshold is exceeded, then emissions of these substances must be reported for all operations/processes relating to the facility, even if actual emissions are very low or zero.

Table 1 identifies the Category 1 substances that may trigger reporting for the oil recycling industry. It is important to recognise that reporting on Category 1 substances will primarily be triggered by the presence of listed substances in the waste oil.

Category 1 Substances		
Acetaldehyde	Lead & compounds	
Acetone	Magnesium & compounds	
Antimony & compounds	Manganese & compounds	
Arsenic & compounds	n-Hexane	
Benzene	Nickel & compounds	
Beryllium & compounds	Polycyclic Aromatic Hydrocarbons	
Cadmium & compounds	Phenol	
Chlorine	Selenium & compounds	
Chromium (III) compounds	Toluene	
Chromium (VI) compounds	VOCs	
Cobalt & compounds	Xylenes	
Copper & compounds	Zinc & compounds	
Cyclohexane		
Ethylbenzene		

Table 1 - Substances That May Trigger the Category 1 Reporting Thresholds

Due to the variability in the composition of contaminants in used oils, it is not feasible to provide definitive guidance in this Manual on the substances that are likely to trigger reporting. Therefore, facilities will need to consider each of the substances listed above in turn to determine whether or not reporting is required.

Example 1 shows a calculation that can be performed to determine if a Category 1 substance triggers the threshold, for an oil recycling plant that processes 20 million litres of used oil per year.

Example 1 - Category 1 Substance Reporting Threshold

An oil recycling facility processes 20 million litres of oil per year. What mean concentration of a Category 1 substance in the feedstock materials would trigger the 10 tonne threshold?

Total amount of used oil processe Density of used oil	$d = 20 * 10^{6} L/yr = 0.8889 kg/L$
Concentration of Substance	= Quantity of substance (to trigger) Amount of used oil processed
	$=\frac{10 \text{ (tonnes / yr)}}{20*10^{6} \text{ (L / yr)}*0.8889 \text{ (kg / L)}*10^{-3} \text{ (tonnes / kg)}}$
	$= 562 * 10^{-6} \text{ kg/kg} * 10^{6} \text{ ppm.kg/kg} = 562 \text{ ppm}$

Therefore, for a facility handling 20ML of oil per annum, reporting on a particular Category 1 substance is required only if the concentration of the Category 1 substance exceeds the 562 ppm limit.

Figure 3 displays the relation between the quantity of waste oil processed and the Category 1 substance concentration required to trigger the NPI reporting threshold.

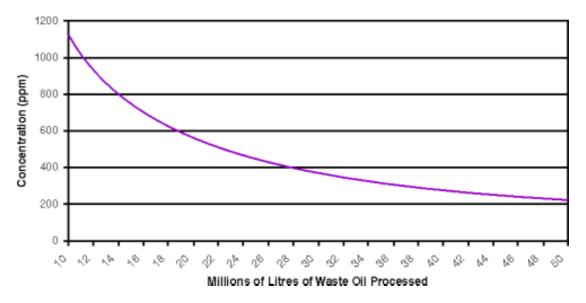


Figure 3 - Concentration of Category 1 Substance Required to Trigger Reporting

3.1.2 Category 2

The Category 2 threshold is based on energy consumption or fuel use. The Category 2a threshold for fuel usage is triggered if:

- a facility burns 400 tonnes or more of fuel or waste per year; or
- a facility burns 1 tonne or more of fuel or waste per hour.

The Category 2b threshold is triggered if:

- a facility burns 2000 tonnes or more of fuel or waste per year; or
- a facility uses 60 000 megawatt hours (MWh) or more of energy in a year; or
- a facility's maximum potential power consumption is rated at 20 megawatts (MW) or more at any time during the year.

Based on these thresholds, the amount of fuel usage required to trigger these thresholds may be calculated (as shown in Table 2). It should be noted that Category 2 threshold calculations should be performed for total fuel usage. If a number of different fuels are used at one facility, the sum of each individual fuel use needs to be calculated to determine whether or not the Category 2 threshold is triggered.

Fuel Type	Category 2a	Category 2b
Natural Gas ^ª	2.06 * 10^7 MJ per reporting year, or at least 5.14 * 10^4 MJ in any one hour in the reporting	1.03 * 10 ⁸ MJ per reporting year
	year	
Fuel Oil ^b	4.44 * 10 ⁵ L per reporting year, or at least	2.22 *10 ⁶ L
	1.11 * 10 ³ L in any one hour in the reporting year	per reporting year

Table 2 - Approximate Fuel Usage Required to Trigger Category 2 Thresholds

^a Assuming natural gas with a gross heating value of 51.4 MJ/kg. Natural gas (NSW) data from the *Natural Gas Technical Data Handbook* (AGL Gas Company (NSW) Limited, 1995).

^bAssuming a density of 900 kg/m³ at 15°C for fuel oil for commercial use (Perry and Green, 1997)

It is possible that a number of oil recycling facilities will exceed the Category 2b reporting threshold on the basis of power consumption at the facility.

If a facility triggers the Category 2a threshold, all Category 2a pollutants need to be reported. If a facility triggers the Category 2b threshold, all Category 2a and Category 2b pollutants need to be reported. The Category 2 substances are listed in Table 3.

Table 3 - NPI-listed Category 2 Substances	
Category 2a Substances	Category 2b Substances
Carbon Monoxide	Arsenic & compounds
Fluoride Compounds	Beryllium & compounds
Hydrochloric Acid	Cadmium & compounds
Oxides of Nitrogen	Chromium (III) compounds
Particulate Matter (PM ₁₀)	Chromium (VI) compounds
Polycyclic Aromatic Hydrocarbons	Copper & compounds
Sulfur Dioxide	Lead & compounds
Total Volatile Organic Compounds	Magnesium Oxide Fume
	Manganese & compounds
	Mercury & compounds
	Nickel & compounds
	Nickel Carbonyl
	Nickel Subsulfide
	Polychlorinated Dioxins & Furans
	PLUS all Category 2a substances

Table 3 - NPI-listed Category 2 Substances

3.1.3 Category 3

Under Clause 13 of the *NPI NEPM*, the reporting threshold for a Category 3 substance is exceeded in a reporting period if the activities of the facility involve the emission to water (excluding groundwater) of:

- 15 tonnes or more per year of Total Nitrogen; or,
- 3 tonnes per year or more of Total Phosphorus.

For oil recycling facilities, it is extremely unlikely there will be licensed discharges to surface or ground waters. Stormwater run-off may trigger NPI reporting requirements, although it is extremely unlikely that this run-off would contain levels of nitrogen or phosphorus that would lead to the triggering of the Category 3 threshold. If, however, your facility has a significant, or potentially significant, release of aqueous nitrogen or phosphorous, you will need to go through the process of determining whether or not Category 3 reporting requirements are triggered for your facility.

3.2 Emissions to Air

The typical emissions to air from oil recycling are summarised in Table 4. Table 4 also provides guidance on the EETs that may be used to characterise these emissions.

Activities	Potential N	PI Emissions	Sources of Information
 Distillation Vacuum Distillation Unit Dehydration Units Solvent Separation Unit Thermal Cracking Unit 	 Antimony & compounds Arsenic & compounds Benzene Beryllium & compounds Cadmium & compounds Cadmium & compounds Carbon disulfide Carbon monoxide Chromium (III) compounds Chromium (VI) compounds Cobalt & compounds Copper & compounds Cyclohexane Fluoride compounds Formaldehyde 	 Lead & compounds Magnesium & compounds Manganese & compounds n-Hexane Nickel & compounds Oxides of Nitrogen Polycyclic Aromatic Hydrocarbons PM₁₀ Selenium & compounds Toluene VOCs Xylenes Zinc & compounds 	 For most facilities with distillation units, it is likely that there will be regulatory or other requirements to conduct, at least periodically, emissions testing on such units. Such sampling data can be used as a basis for emissions estimation. Appendix A of this Manual provides guidance on the use of sampling data for emissions estimation. The Emission Estimation Technique Manual for Petroleum Refining provides guidance on estimating emissions from various petroleum operations, including distillation processes. Section 3.2.1 of the Manual presents emission factors for vacuum distillation units. Direct sampling or continuous emission monitoring data will provide the most accurate data for emissions estimation from point sources such as distillation units. Many facilities currently measure this information for many of the pollutants. Guidance on the use of monitoring data for NPI reporting is provided in Appendix A of this Manual.

 Table 4 - Sources of Air Emissions from Oil Recycling Processes

Activities	Potential N	PI Emissions	Sources of Information
Activities Combustion Processes • Boilers • Furnaces	 Carbon Monoxide Fluoride compounds Hydrochloric Acid Oxides of Nitrogen Particulate Matter (PM₁₀) Polycyclic Aromatic Hydrocarbons Sulfur Dioxide Total Volatile Organic compounds 	 PI Emissions Cadmium & compounds Chromium (III) compounds Chromium (VI) compounds Copper & compounds Lead & compounds Magnesium Oxide Fume Manganese & compounds Mercury & compounds 	For most facilities with combustion units, it is likely that there will be regulatory or other requirements to conduct, at least periodically, emissions testing on such units. Such sampling data can be used as a basis for emissions estimation. Appendix A of this Manual provides guidance on the use of sampling data for emissions estimation. See the <i>Emission Estimation Technique Manual for Combustion in Boilers</i> for guidance on the characterisation of emissions from combustion sources.
	 Arsenic & compounds Beryllium & compounds 	 Nickel & compounds Nickel Carbonyl Nickel Subsulfide 	The <i>Emission Estimation Technique Manual for Petroleum Refining</i> provides specific guidance on estimating emissions from petroleum operations including combustion processes using fuel oil and other refining products.
Storage Tanks	 Acetaldehyde Acetone Benzene Cyclohexane Ethylbenzene Formaldehyde N-Hexane Polycyclic Aromatic Hyde Phenol Toluene VOCs Xylenes 	lrocarbons	The Emission Estimation Technique Manual for Organic Chemical Processing Industries (Section 6.2.3) details how to estimate emissions from various types of tanks. The Manual also provides guidance on the speciation of VOCs.

Table 4 - Sources of Air Emissions from Oil Recycling Processes cont'

Activities	Potential NPI Emissions	Sources of Information
Fugitive Sources	Acetaldehyde	The Emission Estimation Technique Manual for Petroleum Refining
Valves	• Acetone	(Section 4.3) provides guidance the estimation of emissions from
Flanges	• Benzene	each of these sources. The Manual also provides guidance on
Seals	Cyclohexane	the speciation of VOCs.
 Compressors 	• Ethylbenzene	
 Cooling Towers 	• Formaldehyde	
	• N-Hexane	
	Polycyclic Aromatic Hydrocarbons	
	• Phenol	
	• Toluene	
	• VOCs	
	• Xylenes	

Table 4 - Sources of Air Emissions from Oil Recycling Processes cont'

3.2.1 Emission Factors for Releases to Air

There is limited available data on emissions from oil recycling facilities, with the exception of a report from Waste Oil (Waste Oil, 1989). This data provides some emission factors for emissions from a vacuum distillation unit. However, the emission factors are based on the emissions from a vacuum distillation unit from a single US re-refinery and, for this reason, should be used with caution. Table 5 provides the uncontrolled emission factor together with default emission factors for a number of common pollution control options. It is recommended that if actual control efficiencies are known that these be used to determine the 'controlled' emission rates.

Process	VOC
	(kg/ML Oil Processed)
Vacuum Distillation	
Uncontrolled	53
Afterburners ^a	1.6
Biofilter ^b	5.3
Incineration ^c	1.6

Table 5 - Emission Factors for Waste Oil Re-refineries

Source: Waste Oil, 1989

^a Assume afterburner 97% efficiency (Waste Oil, 1989).

^bAssume biofilter 90% efficiency (Waste Oil, 1989).

^cAssume catalytic incineration 97% efficiency (Waste Oil, 1989).

It is likely that speciation of VOC emissions will be required. Please refer to Section 4.3.2 of the *Emission Estimation Technique Manual for Petroleum Refining* for a discussion of the methodologies involved in estimating these emissions.

3.3 Emissions to Water

Most of the liquid releases from oil recycling facilities are likely to be routed to sewer or sent for off-site treatment, recycling or disposal. These effluent releases are classed as transfers under the NPI (see Section 3.4 of this Manual) and, hence, are not required to be reported.

In the unlikely event that wastewater is released to water (eg. after wastewater treatment), this release (and the NPI-listed substances contained in the wastewater) would be required to be reported. Please refer to the *Emission Estimation Technique Manual for Sewage and Wastewater Treatment* for guidance on how to estimate these emissions.

There may be NPI reporting issues associated with stormwater run-off. If stormwater contains NPI-listed substances, most facilities are likely to be required by their relevant State or Territory environment agency to closely monitor and measure these emissions. This sampling data can be used to calculate annual emissions.

3.4 Emissions to Land

Under the NPI, the following are classed as transfers and are not required to be reported:

- discharges of substances to sewer or tailings dam;
- deposit of substances to landfill; and,
- removal of substances from a facility for destruction, treatment, recycling, reprocessing, recovery, or purification.

The definition of transfer has been clarified by the NPI Implementation Working Group as:

"All emissions of listed substances, except those that are directed to, and contained by, purpose built facilities, are to be reported to the NPI. This applies irrespective of whether the substances' fate is within or outside a reporting facility boundary. With respect to receipt of NPI-listed substances, such receiving facilities are to be operating in accordance with any applicable State or Territory government requirements."

Emissions of substances to land on-site include solid wastes, slurries, sediments, spills and leaks, storage and distribution of liquids. Such emissions may contain listed substances. It is expected that, for the oil recycling industry, all of these substances will be sent to sewer, sent off-site for treatment or recycling or sent to landfill. As a consequence, there will be no requirement to report on these emissions. Therefore, it is likely that the only reporting requirements for releases to land will be associated with:

- spills or accidental releases of NPI-listed substances to land (if spills occur, see the *Emission Estimation Technique Manual for Organic Chemical Processing Industries* (Section 9.2) for guidance on how to estimate these releases);
- releases of NPI-listed substances to groundwater (see the *Emission Estimation Technique Manual for Organic Chemical Processing Industries* (Section 9.1) for guidance on how to estimate these releases); and
- on-site disposal, where the activity does not meet the definition provided above.

4.0 Glossary of Technical Terms and Abbreviations

ANZSIC	Australian and New Zealand Standard Industrial Classification
CEMS	Continuous Emission Monitoring System
СО	Carbon Monoxide
EEA	European Environment Agency
EET	Emission Estimation Technique
EFR	Emission Factor Rating
mg	Milligrams
NEPM	National Environment Protection Measure
NO _x	Oxides of Nitrogen
NPI	National Pollutant Inventory
РМ	Particulate Matter
PM ₁₀	Particles that have an aerodynamic diameter equal to or less than 10 micrometers ($\leq 10 \mu m$).
ppmv	Parts per million by volume
SO ₂	Sulfur Dioxide
STP	Standard Temperature and Pressure (0° C and $101.3 * 10^{3}$ Pa)
TSP	Total Suspended Particulates
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound

5.0 References

AGL Gas Company (NSW) Limited, 1995, *Natural Gas Technical Data Book*, Industrial Applications Department - AGL Gas Company (NSW) Limited, Five Dock, Australia.

ANZSIC, 1993, Australian and New Zealand Standard Industrial Classification, Australian Bureau of Statistics & NZ Dept of Statistics 1993, ABS Catalogue No 1292.0.

Australian Institute of Petroleum, 1997. Petroleum Gazette Vol. 32 No. 4/1997, Australian Institute of Petroleum Ltd, Melbourne Vic 3000

Perry, R. and D. Green, 1997, *Perry's Chemical Engineers' Handbook* (7th ed.), McGraw-Hill, New York, USA.

Waste Oil, 1989, *Reclaiming Technology, Utilization and Disposal,* Pollution Technology Review #166, Mueller Associates Inc.

The following Emission Estimation Technique Manuals referred to in this Manual are available at the NPI Homepage (www.npi.gov.au), and from your local environmental protection agency:

Emission Estimation Technique Manual for Combustion in Boilers; Emission Estimation Technique Manual for Fuel and Organic Liquid Storage; Emission Estimation Technique Manual for Petroleum Refining; Emission Estimation Technique Manual for Sewage and Wastewater Treatment; and Emission Estimation Technique Manual for Fugitive Emissions.

Appendix A - Emission Estimation Techniques

Estimates of emissions 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*.

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; and
- emission factors.

Select the EETs (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 EETs, 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 EETs 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 handbook 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 or referenced 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.

The **usage**^a of each of the substances listed as Category 1 and 1a under the NPI must be estimated to determine whether the 10 tonnes (or 25 tonnes for VOCs) reporting threshold is exceeded. If the threshold is exceeded, **emissions** of these Category 1 and 1a substances must be reported for all operations/processes relating to the facility, even if the actual emissions of the substances are very low or zero.

^aUsage is defined as meaning the handling, manufacture, import, processing, coincidental production or other uses of the substances.

A list of the variables and symbols used in this Manual may be found in Appendix C.

A.1 Direct Measurement

You may wish to undertake direct measurement in order to report to the NPI, particularly if you already do so in order to meet other regulatory requirements. However, the NPI does not require you to undertake additional sampling and measurement. For the sampling data to be adequate and able to be used for NPI reporting purposes, it would need to be collected over a period of time, and to be representative of operations for the whole year.

A.1.1 Sampling Data

Stack sampling test reports often provide emissions data in terms of kg per hour or grams per cubic metre (dry). Annual emissions for NPI reporting can be calculated from this data. Stack tests for NPI reporting should be performed under representative (ie. normal) operating conditions. You should be aware that some tests undertaken for a State or Territory license condition may require the test be taken under maximum emissions rating, where emissions are likely to be higher than when operating under normal operating conditions.

An example of test results is summarised in Table 6. The table shows the results of three different sampling runs conducted during one test event. The source parameters measured as part of the test run include gas velocity and moisture content that are used to determine exhaust gas flow rates in m^3/s . The filter weight gain is determined gravimetrically and divided by the volume of gas sampled, as shown in Equation 1 to determine the PM concentration in grams per m^3 . Note that this example does not present the condensable PM emissions.

Pollutant concentration is then multiplied by the volumetric flow rate to determine the emission rate in kilograms per hour, as shown in Equation 2 and Example 2.

Equation 1

 $C_{PM} = C_f / V_{m, STP}$

where:

$C_{_{PM}}$	=	concentration of PM or gram loading, g/m^3
\mathbf{C}_{f}	=	filter catch, g
$V_{\text{m,STP}}$	=	metered volume of sample at STP, m ³

Equation 2

$$E_{PM} = C_{PM} * Q_{d} * 3.6 * [273 / (273 + T)]$$

where:

$E_{_{PM}}$	=	hourly emissions of PM, kg/hr
$\mathbf{C}_{_{PM}}$	=	concentration of PM or gram loading, g/m^3
\mathbf{Q}_{d}	=	stack gas volumetric flow rate at actual conditions, m³/s, dry
3.6	=	3600 seconds per hour multiplied by 0.001 kilograms per gram
Т	=	temperature of the gas sample, °C

Table 6 - Stack Sample Test Results

Parameter	Symbol	Test 1	Test 2	Test 3
Total sampling time (sec)		7200	7200	7200
Moisture collected (g)	$\mathbf{g}_{\text{moist}}$	395.6	372.6	341.4
Filter catch (g)	\overline{C}_{f}	0.0851	0.0449	0.0625
Average sampling rate (m^3/s)		$1.67 * 10^{-4}$	1.67 * 10 ⁻⁴	1.67 * 10 ⁻⁴
Standard metered volume (m ³)	$V_{m, STP}$	1.185	1.160	1.163
Volumetric flow rate (m^3/s) , dry	\mathbf{Q}_{d}	8.48	8.43	8.45
Concentration of particulate (g/m ³)		0.0718	0.0387	0.0537

Example 2 - Using Stack Sampling Data

PM emissions calculated using Equation 1 and Equation 2 (above) and the stack sampling data for Test 1 (presented in Table 6, and an exhaust gas temperature of 150°C (423 K)). This is shown below:

C _{PM}	= = =	C _f / V _{m, STP} 0.0851 / 1.185 0.072 g/m ³
	E_{PM}	$= C_{PM} * Q_{d} * 3.6 * [273/(273 + T)]$ = 0.072 * 8.48 * 3.6 * (273/423 K) = 1.42 kg/hr

The information from some stack tests may be reported in grams of particulate per cubic metre of exhaust gas (wet). Use Equation 3 below to calculate the dry particulate emissions in kg/hr.

Equation 3

$$E_{_{PM}} = Q_{_{a}} * C_{_{PM}} * 3.6 * (1 - moist_{_{R}}/100) * [273 / (273 + T)]$$

where:

E_{PM}	=	hourly emissions of PM in kilograms per hour, kg/hr
\mathbf{Q}_{a}	=	actual (ie. wet) cubic metres of exhaust gas per second, m ³ /s
~	=	concentration of PM or gram loading, g/m^3
	=	3600 seconds per hour multiplied by 0.001 kilograms per gram
moist	_R =	moisture content, %
273	=	273 K (0°C)
Т	=	stack gas temperature, °C

Total suspended particulates (TSP) are also referred to as total particulate matter (total PM). To determine PM_{10} from total PM emissions, a size analysis may need to be undertaken. The weight PM_{10} fraction can then be multiplied by the total PM emission rate to produce PM_{10} emissions. Alternatively, it can be assumed that 100% of PM emissions are PM_{10} ; ie. assume that all particulate matter emitted to air has an equivalent aerodynamic diameter of 10 micrometres or less ie. $\leq 10\mu m$. In most situations, this is likely to be a conservative assumption but it may be a suitable technique to obtain a reasonable characterisation of emissions for the purposes of NPI reporting.

To calculate moisture content use Equation 4.

Equation 4

Moisture percentage =

100 * weight of water vapour per specific volume of stack gas/ total weight of the stack gas in that volume

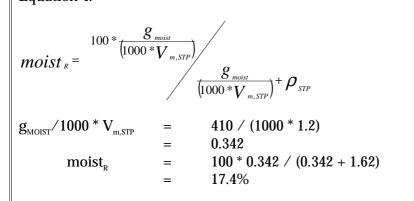
$$moist_{R} = \frac{100 * \frac{g_{moist}}{(1000 * V_{m,STP})}}{\frac{g_{moist}}{(1000 * V_{m,STP})} + \rho_{STP}}$$

where:

moist	, =	moisture content, %
$\mathbf{g}_{\mathrm{moist}}$	=	moisture collected, g
$V_{m,STP}$		metered volume of sample at STP, m ³
ρ_{STP}	=	dry density of stack gas sample, kg/m ³ at STP
		{if the density is not known a default value of 1.62 kg/m^3
		may be used. This assumes a dry gas composition of
		50% air, 50% CO ₂ }

Example 3 - Calculating Moisture Percentage

A $1.2m^3$ sample (at STP) of gas contains 410g of water. To calculate the moisture percentage use Equation 4.



A.1.2 Continuous Emission Monitoring System (CEMS) Data

A continuous emission monitoring system (CEMS) provides a continuous record of emissions over time, usually by reporting pollutant concentration. Once the pollutant concentration is known, emission rates are obtained by multiplying the pollutant concentration by the volumetric gas or liquid flow rate of that pollutant.

Although CEMS can report real-time hourly emissions automatically, it may be necessary to estimate annual emissions from hourly concentration data manually. This Section describes how to calculate emissions for the NPI from CEMS concentration data. The selected CEMS data should be representative of operating conditions. When possible, data collected over longer periods should be used.

It is important to note that, prior to using CEMS to estimate emissions, you should develop a protocol for collecting and averaging the data in order that the estimate satisfies the local environmental authority's requirement for NPI emission estimations.

To monitor SO_2 , NO_x , VOC, and CO emissions using a CEMS, you use a pollutant concentration monitor that measures the concentration in parts per million by volume dry air (ppm_{vd} = volume of pollutant gas/10⁶ volumes of dry air). Flow rates should be measured using a volumetric flow rate monitor. Flow rates estimated based on heat input using fuel factors may be inaccurate because these systems typically run with high excess air to remove the moisture out of the kiln. Emission rates (kg/hr) are then calculated by multiplying the stack gas concentrations by the stack gas flow rates.

Table 7 presents example CEMS data output for three periods for a hypothetical furnace. The output includes pollutant concentrations in parts per million dry basis (ppm_{vd}) , diluent $(O_2 \text{ or } CO_2)$ concentrations in percent by volume dry basis (%v, d) and gas flow rates; and may include emission rates in kilograms per hour (kg/hr). This data represents a snapshot of a hypothetical boiler operation. While it is possible to determine total emissions of an individual pollutant over a given time period from this data, assuming the CEMS operates properly all year long, an accurate emission estimate can be made by adding the hourly emission estimates if the CEMS data is representative of typical operating conditions.

Time	O ₂ content	Concentration				Gas Flow Rate (Q)	Production Rate of Product (A)
	% by volume	SO ₂ (ppm _{vd})	NO _x (ppm _{vd})	CO (ppm _{vd})	VOC (ppm _{vd})	m³/s	tonnes/hour
1	10.3	150.9	142.9	42.9	554.2	8.52	290
2	10.1	144.0	145.7	41.8	582.9	8.48	293
3	11.8	123.0	112.7	128.4	515.1	8.85	270

Table 7 - Example of CEMS Output for a Hypothetical Furnace Firing Waste Fuel Oil

Hourly emissions can be based on concentration measurements as shown in Equation 5.

Equation 5

$$E_i = (C * MW * Q * 3600) / [22.4 * ((T + 273) / 273) * 10^6]$$

where:

$\mathbf{E}_{\mathbf{i}}$	=	emissions of pollutant i, kg/hr
С	=	pollutant concentration, ppm _{vd}
MW	=	molecular weight of the pollutant, kg/kg-mole
Q	=	stack gas volumetric flow rate at actual conditions, m^3/s
3600	=	conversion factor, s/hr
22.4	=	volume occupied by one mole of gas at standard
		temperature and pressure (0°C and 101.3 kPa), m ³ /kg-mole
Т	=	temperature of gas sample, °C
10 ⁶	=	conversion factor, ppm.kg/kg

Actual annual emissions can be calculated by multiplying the emission rate in kg/hr by the number of actual operating hours per year (OpHrs) as shown in Equation 6 for each typical time period and summing the results.

Equation 6

 $E_{kpy,i} = \sum (E_i * OpHrs)$

where:

Emissions in kilograms of pollutant per tonne of product produced can be calculated by dividing the emission rate in kg/hr by the activity rate (production rate (tonnes/hr) during the same period. This is shown in Equation 7 below.

It should be noted that the emission factor calculated below assumes that the selected time period (ie. hourly) is representative of annual operating conditions and longer time

periods should be used for NPI reporting where they are available. Use of the calculation is shown in Example 5.

Equation 7

 $E_{kpt,i} = E_i / A$

where:

${\rm E}_{_{\rm kpt,i}}$	=	emissions of pollutant i per tonne of product produced, kg/t
E	=	hourly emissions of pollutant i, kg/hr
А	=	production, t/hr

Example 4 illustrates the application of Equation 5, Equation 6 and Equation 7.

Example 4 - Using CEMS Data

This example shows how SO_2 emissions can be calculated using Equation 5 based on the CEMS data for Time Period 1 shown in Table 7, and an exhaust gas temperature of 150°C (423 K).

$$\begin{split} E_{SO2,1} &= (C * MW * Q * 3600) / [(22.4 * (T + 273/273) * 10^6] \\ &= (150.9 * 64 * 8.52 * 3600) / [22.4 * (423/273) * 10^6] \\ &= 296 \ 217 \ 907 / \ 34 \ 707 \ 692 \\ &= 8.53 \ kg/hr \end{split}$$
 For Time Period 2, also at 150°C $E_{SO2,2} &= 8.11 \ kg/hr \end{split}$

For Time Period 3, also at 150°C

 $E_{SO23} = 7.23 \text{ kg/hr}$

Say representative operating conditions for the year are:

Period 1	=	1500 hr
Period 2	=	2000 hr
Period 3	=	1800 hr

Total emissions for the year are calculated by adding the results of the three Time Periods using Equation 6:

Emissions, in terms of kg/tonne of product produced when operating in the same mode as time period 1, can be calculated using Equation 7

When the furnace is operating as in time periods 2 or 3, similar calculations can be undertaken for emissions per tonne.

A.2 Using Mass Balance

A mass balance identifies the quantity of substance going in and out of an entire facility, process, or piece of equipment. Emissions can be calculated as the difference between input and output of each listed substance. Accumulation or depletion of the substance within the equipment should be accounted for in your calculation.

Mass balance calculations for estimating emissions to air of NPI-listed substances can be represented conceptually by Equation 8.

Equation 8

E_{kpy,i} = Amount in_i - Amount out_i

where:

E _{kpy,i} =	emissions of pollutant i, kg/yr
Amount $in_i =$	amount of pollutant i entering the process, kg/yr
Amount out _i =	amount of pollutant i leaving the process as a waste
	stream, article or product, kg/yr

The term "Amount out_i " may actually involve several different fates for an individual pollutant. This could include the amount recovered or recycled, the amount leaving the process in the manufactured product, the amount leaving the process in wastewater, the amount emitted to the atmosphere, or the amount of material transferred off-site as hazardous waste or to landfill. A thorough knowledge of the different fates for the pollutant of interest is necessary for an accurate emission estimate to be made using the mass balance approach.

The amount of a particular substance entering or leaving a facility is often mixed within a solution as a formulation component or as a trace element within the raw material. To determine the total weight of the substance entering or leaving the process, the concentration of the substance within the material is required. Using this concentration data, Equation 9 can be applied as a practical extension of Equation 8.

Equation 9

$$E_{kpy,i} = [(Q_{in} * C_{in}) - (Q_{pr} * C_{pr}) - (Q_{rec} * C_{rec}) - (Q_{waste} * C_{waste})] / 10^{6}$$

where:

$\begin{array}{l} E_{\rm kpy,i} &= \\ Q_{\rm in}, Q_{\rm pr}, Q_{\rm rec}, Q_{\rm waste} = \end{array}$	emissions of pollutant i, kg/yr quantity of raw material, product, recycled material or
	waste respectively, that is processed (generally expressed in kg/yr for solids, L/yr for liquids)
$C_{in}, C_{pr}, C_{rec}, C_{waste} =$	concentration of substance i in the raw material, product,
10 ⁶ =	recycled material or waste respectively, that is processed annually (usually mg/kg for solids, mg/L for liquids) conversion from milligrams to kilograms.

Wastewater treatment may precipitate the reportable chemical in a sludge. Facilities are often required to obtain data on the concentration of metals or other substances in sludges as part of their licensing requirement and this data can be used to calculate the emissions as kilograms of sludge multiplied by the concentrations of the substance in the sludge. Although listed substances in sludges transferred off-site do not require reporting, determining this loss can assist with determining other process losses or may require reporting if the sludge is disposed of on-site.

For many chemicals used and emitted during chemical processes, some degradation in treatment may occur so that the entire chemical is not transferred to the sludge. Facilities can estimate the amount of reportable compounds in the sludge by using measured data, or by subtracting the amount biodegraded from the total amount removed in treatment. The amount of removal can be determined from operating data, and the extent of biodegradation might be obtained from published studies. If the biodegradability of the chemical cannot be measured or is not known, reporting facilities should assume that all removal is due to absorption to sludge.

A.3 Engineering Calculations

An engineering calculation is an estimation method based on physical/chemical properties (eg. vapour pressure) of the substance and mathematical relationships (eg. ideal gas law).

A.3.1 Fuel Analysis

Fuel analysis is an example of an engineering calculation and can be used to predict $SO_{2^{2}}$, metals, and other emissions based on application of conservation laws, if fuel rate is measured. The presence of certain elements in fuels may be used to predict their presence in emission streams. This includes elements such as sulfur that may be converted into other compounds during the combustion process.

The basic equation used in fuel analysis emission calculations is the following:

Equation 10

$$E_{kpy,i} = Q_f * C_i / 100 * (MW_p / EW_f) * OpHrs$$

where:

For instance, SO_2 emissions from fuel oil combustion can be calculated based on the concentration of sulfur in the fuel oil. This approach assumes complete conversion of sulfur to SO_2 . Therefore, for every kilogram of sulfur (EW = 32) burned, two kilograms of SO_2 (MW = 64) are emitted. The application of this EET is shown in Example 5.

Example 5 - Using Fuel Analysis Data

This example shows how SO_2 emissions can be calculated from fuel combustion based on fuel analysis results, and the known fuel flow of the engine. $E_{kpy,SO2}$ may be calculated using Equation 10 and given the following:

A.4 Emission Factors

In the absence of other information, default emission factors can be used to provide an estimate of emissions. Emission factors are generally derived through the testing of a general source population (eg. boilers using a particular fuel type). This information is used to relate the quantity of material emitted to some general measure of the scale of activity (eg. for boilers, emission factors are generally based on the quantity of fuel consumed or the heat output of the boiler).

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

$$\operatorname{Emission Factor}\left(\frac{\operatorname{mass}}{\operatorname{unit of activity}}\right) * \operatorname{Activity Data}\left(\frac{\operatorname{unit of activity}}{\operatorname{time}}\right) = \operatorname{Emission Rate}\left(\frac{\operatorname{mass}}{\operatorname{time}}\right)$$

For example, if the emission factor has units of 'kg pollutant/m³ of fuel burned', then the activity data required would be in terms of ' m^3 fuel burned/hr', thereby generating an emission estimate of 'kg pollutant/hr'.

An emission factor is a tool used to estimate emissions to the environment. In this Manual, it relates the quantity of substances emitted from a source, to some common activity associated with those emissions. Emission factors are obtained from US, European, and Australian sources and are usually expressed as the weight of a substance emitted, divided by the unit weight, volume, distance, or duration of the activity emitting the substance (eg. kilograms of sulfur dioxide emitted per tonne of fuel burned).

Emission factors are used to estimate a facility's emissions by the general equation:

Equation 11

$$E_{kpv,i} = [A * OpHrs] * EF_i * [1 - (CE_i/100)]$$

where:

Emission factors developed from measurements for a specific process may sometimes be used to estimate emissions at other sites. Should a company have several processes of similar operation and size, and emissions are measured from one process source, an emission factor can be developed and applied to similar sources. It is necessary to have the site specific emission factor reviewed and approved by State or Territory environment agencies prior to its use for NPI estimations.

Appendix B - Emission Estimation Techniques: Acceptable Reliability and Uncertainty

This section is intended to give a general overview of some of the inaccuracies associated with each of the techniques. Although the National Pollutant Inventory does not favour one emission estimation technique over another, this section does attempt to evaluate the available emission estimation techniques with regards to accuracy.

Several techniques are available for calculating emissions oil recycling facilities. The technique chosen is dependent on available data, and available resources, and the degree of accuracy sought by the facility in undertaking the estimate.

B.1 Direct Measurement

Use of stack and/or workplace health and safety sampling data is likely to be a relatively accurate method of estimating air emissions from oil recycling facilities. However, collection and analysis of samples from facilities can be very expensive and especially complicated where a variety of NPI-listed substances are emitted, and where most of these emissions are fugitive in nature. Sampling data from a specific process may not be representative of the entire manufacturing operation, and may provide only one example of the facility's emissions.

To be representative, sampling data used for NPI reporting purposes needs to be collected over a period of time, and to cover all aspects of production.

In the case of CEMS, instrument calibration drift can be problematic and uncaptured data can create long-term incomplete data sets. However, it may be misleading to assert that a snapshot (stack sampling) can better predict long-term emission characteristics. It is the responsibility of the facility operator to properly calibrate and maintain monitoring equipment and the corresponding emissions data.

B.2 Mass Balance

Calculating emissions from oil recycling facilities using mass balance appears to be a straightforward approach to emission estimation. However, it is likely that few Australian facilities consistently track material usage and waste generation with the overall accuracy needed for application of this method. Inaccuracies associated with individual material tracking, or other activities inherent in each material handling stage, can result in large deviations for total facility emissions. Because emissions from specific materials are typically below 2 percent of gross consumption, an error of only \pm 5 percent in any one step of the operation can significantly skew emission estimations.

B.3 Engineering Calculations

Theoretical and complex equations, or models, can be used for estimating emissions from oil recycling processes. Use of emission equations to estimate emissions from oil recycling facilities is a more complex and time-consuming process than the use of emission factors. Emission equations require more detailed inputs than the use of emission factors but they do provide an emission estimate that is based on facility-specific conditions.

B.4 Emission Factors

Every emission factor has an associated emission factor rating (EFR) code. This rating system is common to EETs for all industries and sectors and therefore, to all Industry Handbooks. They are based on rating systems developed by the United States Environmental Protection Agency (USEPA), and by the European Environment Agency (EEA). Consequently, the ratings may not be directly relevant to Australian industry. Sources for all emission factors cited can be found in the reference section of this document. The emission factor ratings <u>will not</u> form part of the public NPI database.

When using emission factors, you should be aware of the associated EFR code and what that rating implies. An A or B rating indicates a greater degree of certainty than a D or E rating. The less certainty, the more likely that a given emission factor for a specific source or Category is not representative of the source type. These ratings notwithstanding, the main criterion affecting the uncertainty of an emission factor remains the degree of similarity between the equipment/process selected in applying the factor, and the target equipment/process from that the factor was derived.

The EFR system is as follows:

- A Excellent
- B Above Average
- C Average
- D Below Average
- E Poor
- U Unrated

Appendix C - List of Variables and Symbols

Variable	Symbol	Units
Conversion from kilograms to tonnes	10 ³	kg/tonne
Conversion from milligrams to kilograms	106	mg/kg
Density of air	ρ	kg/m ³
Density of material		kg/L
Dry density of stack gas sample	ρ _m	kg/m^3 at STP
Activity rate	ρ_{STP}	units/hr, eg. t/hr
Surface area		m^2
Overall control efficiency	area CE	% reduction in emissions of pollutant i
Filter Catch		
Concentration of pollutant i	C _f	grams leg / I
· · ·	C _i C _i	kg/L
Concentration of pollutant i in material Concentration of substance i in the raw	C_{i} $C_{in}, C_{pr}, C_{rec}, C_{waste}$	kg/L
	$C_{in}, C_{pr}, C_{rec}, C_{waste}$	(usually mg/kg for solids, mg/L for
material, product, recycled material or waste respectively, that is processed		liquids)
annually		
Concentration of PM ₁₀	C	grams/m ³
Uncontrolled emission factor for pollutant i	C _{PM10} EF.	kg of pollutant/tonne
Total emissions of pollutant i per hour	E,	kg/hr
Emissions per tonne	E _{kpt,i}	kilograms of pollutant i per tonne of
	₽ kpt,i	fuel consumed
Annual emissions of pollutant i	E _{kpy.i}	kg/yr
Elemental weight of pollutant in fuel	EW_{f}	kg/kg-mole
Molecular Weight of pollutant i	MW.	kg/kg-mole
Operating hours	OpHrs	hr/yr
Pollutant concentration	ppm _{vd}	volume of pollutant gas/ 10^6 volume of
	PP m _{vd}	dry air
Saturation vapour pressure of pollutant i	P _{sat.i}	kilopascals (kPa)
Total pressure	P _t	kPa
Vapour pressure of pollutant i	P	kPa
Volumetric flow rate,	Q Vap.i	m ³ /s
Volumetric flow rate of stack gas	Q _a	actual cubic metres per second (m^3/s)
		-
Volumetric flow rate of stack gas	Q _d	dry cubic metres per second (m^3/s)
Fuel used		t/hr
Material entering the process	Q_{in} or	kg/hr
	Amount in _i	
Material leaving the process	Q _{out} or	kg/hr
	Amount out _i	$1 \mathbb{D}^{3} / (1 \mathbb{D}^{3})$
Ideal gas constant	R	$kPa.m^3/(kgmol).K$
Standard Temperature & Pressure	STP	0° C (273K) and 1 atmosphere 101.3 kPa
Temperature	Т	°Celsius (°C) or Kelvin (K)
Total suspended particulates or	TSP or	mg/m ³
Total particulate matter (total PM)	PM	
Metered volume at STP	V _{m.STP}	
Total VOC emissions	E _{voc}	kg/L
Moisture collected	g _{moist}	grams
Moisture content	moist _R	%
Percentage weight of pollutant i	Wt%,	%