



National Pollutant Inventory

Emission Estimation Technique Manual

for

**Chemical Product
Manufacture**

First published in December 1999

**EMISSION ESTIMATION TECHNIQUES
FOR
CHEMICAL PRODUCT MANUFACTURE**

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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 chemical product manufacture.

This Manual applies to facilities primarily engaged in the manufacture of cellulose nitrate, recycled plastic, polyethylene, polypropylene, polystyrene, polyvinyl acetate, polyvinyl chloride, synthetic rubber, synthetic resins (except adhesives) and rubber recycling. For guidance on estimating emissions from the manufacture of the basic monomers for chemical products (ie. plastic raw material), please refer to the *Emission Estimation Technique Manual for Organic Chemical Processing Industries*.

EET MANUAL: Chemical Product Manufacture

HANDBOOK: Chemical Product Manufacture

ANZSIC CODE: 2533

Pacific Air & Environment Pty Ltd 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

- **Section 2** discusses the NPI reporting issues associated with the chemical product manufacturing industry. **Section 2.1** discusses the issue of transfers. **Sections 2.2, 2.3 and 2.4** discuss the Category 1, 2 and 3 thresholds respectively in terms of which substances are likely to trigger these thresholds. **Sections 2.5, 2.6 and 2.7** examine the potential emissions to air, water and land, respectively, which are associated with chemical product manufacture.
- **Section 3** examines each of the unit operations or processes, which are relevant to the chemical product manufacturing industry and provides guidance on the application of suitable emission estimation techniques.
- **Section 4** provides a glossary of technical terms and abbreviations used in this Manual.
- **Section 5** provides a list of 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 chemical product manufacturing industry.
- **Appendix B** provides a discussion of the reliability and uncertainty involved with each of the emission estimation techniques presented in **Appendix A**.
- **Appendix C** provides a list of variables and symbols used throughout this Manual.
- **Appendix D** provides emission estimation techniques that supplement those already provided in Section 3.

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 chemical product manufacturing 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 available information of 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:

- For Category 1 and 1a substances, identify which reportable NPI substances are used, produced or stored, if any, and determine whether the amounts used or handled are above the ‘threshold’ values and therefore trigger reporting requirements;
- For 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;
- For Category 3 substances, determine the annual emissions to water and assess whether the threshold limits are exceeded; and
- For 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 Reporting Thresholds and Emissions

2.1 Transfers

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 which 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.”

A number of emissions from the chemical product manufacturing industry are classed as transfers. These are discussed further in **Sections 2.6** and **2.7** of this Manual.

2.2 Category 1

The Category 1 threshold is triggered for a substance if a facility manufactures, imports, processes, co-incidentally produces or otherwise uses 10 tonnes or more of a Category 1 substance. Category 1a substances may also be triggered if a facility:

- Uses more than 25 tonnes of VOC per year; or
- Has a bulk storage facility design capacity greater than 25 kilotonnes.

Chemical product manufacturing facilities may trigger the reporting threshold for a number of Category 1 substances. The specific substances for which reporting is triggered is a highly site-specific issue and each site needs to carefully examine its use of Category 1 substances. Further guidance on Category 1 reporting thresholds is provided in the *NPI Guide*.

A facility is only required to report on the Category 1 substances that trigger thresholds. 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.

2.3 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; 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 1). If site specific information is available for densities of fuels, this information should be used in preference to the values assumed for the results of Table 1.

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.

Table 1 - Approximate Fuel Usage Required to Trigger Category 2 Thresholds

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 year	1.03 * 10 ⁸ MJ per reporting year
Simulated Natural Gas (SNG)^b	1.25 * 10 ⁷ MJ per reporting year, or at least 3.13 * 10 ⁴ MJ in any one hour in the reporting year	6.24 * 10 ⁷ MJ per reporting year
Liquefied Petroleum Gas (LPG)^c	7.87 * 10 ⁵ L per reporting year, or at least 1.97 * 10 ³ L in any one hour in the reporting year	3.94 * 10 ⁶ L per reporting year
Liquefied Natural Gas (LNG)^d	9.47 * 10 ⁵ L per reporting year, or at least 2.37 * 10 ³ L in any one hour in the reporting year	4.73 * 10 ⁶ L per reporting year
Diesel^e	4.44 * 10 ⁵ L per reporting year, or at least 1.11 * 10 ³ L in any one hour in the reporting year	2.22 * 10 ⁶ L per reporting year
Propane^d	2.02 * 10 ⁷ MJ per reporting year, or at least 5.04 * 10 ⁴ MJ in any one hour in the reporting year	1.01 * 10 ⁸ MJ per reporting year
Butane^e	1.98 * 10 ⁷ MJ per reporting year, or at least 4.96 * 10 ⁴ MJ in any one hour in the reporting year	9.92 * 10 ⁷ MJ per reporting year

^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).

^b Assuming natural gas with a gross heating value of 31.27 MJ/kg. Natural gas (NSW) data from the *Natural Gas Technical Data Handbook* (AGL Gas Company (NSW) Limited, 1995).

^c Assuming ideal gas with a density of 508 kg/m³ at 15°C under pressure from the *Natural Gas Technical Data Handbook* (AGL Gas Company (NSW) Limited, 1995)

^d Assuming 100% methane ideal gas with a density of 422.4 kg/m³ at 15°C at its boiling point from the *Natural Gas Technical Data Handbook* (AGL Gas Company (NSW) Limited, 1995)

^e Assuming a density of 900 kg/m³ at 15°C for fuel oil for commercial use (Perry, et al., 1997)

^f Assuming a gross heating value of 50.4 MJ/kg at 25°C and 101.325 kPa (Lide, 1994).

^g Assuming a gross heating value of 49.6 MJ/kg at 25°C and 101.325 kPa (Lide, 1994).

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

Table 2 - Category 2 Substances That Trigger Reporting

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 and 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

2.4 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 Phosphorous.

For chemical product manufacturing 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 unlikely that this run-off would contain levels of nitrogen or phosphorous which 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 need determine whether or not Category 3 reporting requirements are triggered for your facility.

2.5 Emissions to Air

Typical emissions to air from the chemical products manufacturing industry are presented in Table 3.

Table 3 - Emissions to Air from Chemical Product Manufacturing Facilities

Process	Emissions		Sources of Information
Reaction Processes • Monomer storage and feed dissolver tanks • Reactor drum vents • Devolatiliser condenser vent and tanks • Extruder quench vent • Product storage • Recovery units • Tank vents • Spinning processes • Dryers • Wastewater treatment • Reactor vents • Vacuum distillation • Residual drying • Sphere recharging • Final packing of liquids	• Various Category 1 substances depending on the facility. • PM₁₀		Information on many organic chemical process units and specific guidance on the estimation of emissions to air from storage, loading/unloading operations and process vents may be found in the <i>Emission Estimation Technique Manual for Organic Chemical Processing Industries</i>. Guidance on the estimation of emissions to air from wastewater treatment may be found in the <i>Emission Estimation Technique Manual for Sewage and Wastewater Treatment</i>. Guidance on the estimation of emissions from reactor vents, vacuum distillation units, residual drying, sphere recharging and final packing of liquids may be found in Section 3 of this Manual.
Combustion Processes • On-site power / heat / steam generation • Gas Flaring	• Carbon Monoxide • Fluoride Compounds • Hydrochloric Acid • Oxides of Nitrogen • Particulate Matter (PM₁₀) • Polycyclic Aromatic Hydrocarbons • Sulfur Dioxide • Total Volatile Organic Compounds • Arsenic & compounds	• Beryllium & compounds • Cadmium & compounds • Chromium (III) compounds • Chromium (VI) compounds • Copper & compounds • Lead & compounds • Magnesium Oxide Fume • Manganese & compounds • Mercury & compounds • Nickel & compounds • Nickel Carbonyl	Guidance on the estimation of emissions from energy production processes is provided in the <i>Emission Estimation Technique Manuals for Combustion in Boilers and Combustion Engines</i>. Guidance on the estimation of emissions from gas flaring processes is provided in the <i>Emission Estimation Technique Manual for Petroleum Refining</i> (Section 4.1.1.2)

2.6 Emissions to Water

For chemical product manufacturing facilities, it is expected that all the process liquid effluent and waste streams will be:

- Sent to sewer;
- Sent off-site for treatment, recycling or recovery; or
- Recycled through the process.

If wastewater treatment occurs on-site (and the effluent is released to a surface water body), it needs to be examined for potential emissions. Please refer to the *Emission Estimation Technique Manual for Sewage and Wastewater Treatment* for guidance on how to estimate these emissions.

There may also 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.

2.7 Emissions to Land

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 chemical product manufacturing 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 on-site disposal does not meet the definition provided in **Section 2.1** of this Manual.

3.0 Unit Sources / Operations

3.1 Introduction

For the majority of chemical product manufacturing facilities, the *Emission Estimation Technique Manual for Organic Chemical Processing Industries* will provide sufficient guidance on the estimation of emissions. This Manual will consider emissions from the following sources:

- Stripping of gases (**Section 3.2**);
- Reactor vents (**Section 3.3**);
- Vacuum distillation (**Section 3.4**);
- Residual drying (**Section 3.5**);
- Sphere recharging (**Section 3.6**);
- Final packing of liquids (**Section 3.7**); and
- Combustion processes (**Section 3.8**).

For many substances, a facility mass balance is likely to be the most appropriate emission estimation technique for chemical product manufacturing facilities. A discussion and overview of mass balance as an emission estimation technique is provided in **Appendix A.2**. However, it is recognised that, for some facilities, the information necessary to successfully carry out a facility mass balance may not be available. In these situations, default emission factors applied to unit processes may be utilised. Emission factors for a number of different chemical product manufacturing processes are provided in **Appendix D** of this Manual.

The USEPA has provided advice on the preferred and alternative methods for estimating emissions from chemical product manufacturing facilities. These methods are listed in Table 4.

Table 4 - Preferred and Alternative Emission Estimation Methods for Plastic Products Manufacturing Operations

Pollutant	Preferred Emission Estimation Approach (Section in this Manual)	Alternative Emission Estimation Techniques (Section in this Manual)
Category 1 organic compounds and VOCs which are not consumed in chemical reactions (eg. blowing agents, carrier solvents)	Mass Balance (A.2)	Sampling Data (A.1.1) Emission Factors (A.4)
Category 1 organic compounds and VOCs which are consumed in chemical reactions (eg. raw materials)	Sampling Data (A.1.1)	Emission Factors (A.4) Mass Balance (A.2)
Particulate matter (PM ₁₀)	Sampling Data (A.1.1)	Emission Factors (A.4)

Source: Eastern Research Group Inc., 1998

3.2 Scrubbing

3.2.1 General Description

Scrubbing involves the stripping of gaseous products from various unit operations by passing them through a liquid stream to remove impurities and pollutants. The composition of the liquid stream depends on the compound being removed from the vapour stream. Typical vapour streams include combustion products and ammonia.

3.2.2 Emission Estimation Techniques

Chemical product manufacturing facilities may choose to use a mass balance to estimate emissions from scrubbing operations. In the absence of suitable data for mass balance, no other data exists regarding emissions from the stripping of gases from chemical product manufacturing facilities. For guidance on the use of mass balance as an emission estimation technique, please refer to **Appendix A.2** of this Manual.

3.3 Reactor Vents

3.3.1 General Description

When raw materials are mixed in a reactor, gases are also produced. These emissions may contain a variety of NPI-listed substances and need to be estimated if released to the environment.

3.3.2 Emission Estimation Techniques

Chemical product manufacturing facilities may choose to use a mass balance to estimate emissions from reactor vents. For guidance on the use of mass balance as an emission estimation technique, please refer to **Appendix A.2** of this Manual.

Alternatively, if volatile organic liquids are present in reactors, facilities may choose to use an air displacement method for estimating reactor vent emissions. This technique may not be suitable for estimating reaction products but can be used during charging, heating and transfer operations (Ereaut, 1999). Please refer to Section 5.2 of the *Emission Estimation Technique Manual for Organic Chemical Processing Industries* for guidance on the use of the air displacement EET to estimate reactor vent emissions.

3.4 Vacuum Distillation

3.4.1 General Description

NPI listed substances may be emitted due to the general operation of vacuum distillation units at chemical product manufacturing facilities.

3.4.2 Emission Estimation Techniques

Chemical product manufacturing facilities may choose to use a mass balance to estimate emissions from vacuum pumps. In the absence of suitable data for mass balance, no other data exists regarding emissions from vacuum pumps from chemical product manufacturing facilities. For guidance on the use of mass balance as an emission estimation technique, please refer to **Appendix A.2** of this Manual.

3.5 Residual Drying

3.5.1 General Description

When chemical products are left to dry, volatile organic compounds may be released.

3.5.2 Emission Estimation Techniques

At present, there are few emission factors available for residual drying of chemical products, other than those given in Table 11 and Table 14. Chemical product manufacturing facilities may choose to use a mass balance to estimate emissions from drying chemical products. For guidance on the use of mass balance as an emission estimation technique, please refer to **Appendix A.2** of this Manual.

3.6 Sphere Recharging

3.6.1 General Description

Spheres are recharged with water. The water is then left so that the volatile components can be released to air. The water is finally discharged to sewer.

3.6.2 Emission Estimation Techniques

At present, no emission factors exist which are specific to sphere recharging at chemical product manufacturing facilities. Data from environmental license requirements may be used to estimate emissions to air. Any discharges to water are likely to be monitored and these monitoring data may be used to estimate emissions.

Alternatively, facilities may choose to use a mass balance to estimate emissions from sphere recharging. For guidance on the use of mass balance as an emission estimation technique, please refer to **Appendix A2** of this Manual.

3.7 Final Packing of Liquids

3.7.1 General Description

This unit operation involves blowing process lines clean with nitrogen gas.

3.7.2 Emission Estimation Techniques

In the absence of other information, the following general approach may be followed:

1. Assume that, initially, all the lines are full of gas;
2. Assume that all the gas is released to the atmosphere in the cleaning operation (ie. the volume of the lines is released to the atmosphere in each cleaning operation);
3. Convert the volume of gas to a mass using its density and speciate for NPI-listed compounds. For guidance on the speciation of total volatile organic compound emissions, please refer to the *Emission Estimation Technique Manual for Fugitive Emissions*.

During filling of process lines, assuming that the displaced gas is saturated with process liquid, the air displacement EET may be used to conservatively estimate the initial release of gas (Ereaut, 1999). Please refer to Section 5.2 of the *Emission Estimation Technique Manual for Organic Chemical Processing Industries* for guidance on the use of the air displacement EET to estimate reactor vent emissions.

3.8 Combustion Processes

3.8.1 General Description

Combustion processes such as on-site power, heat or steam generation and the flaring of off-gases release a variety of NPI-listed substances.

3.8.2 Emission Estimation Techniques

Guidance on the estimation of emissions from energy production processes may be found in the *Emission Estimation Technique Manuals for Combustion in Boilers and Combustion Engines*. Guidance on the estimation of emissions from gas flaring processes may be found in the *Emission Estimation Technique Manual for Petroleum Refining* (Section 4.1.1.2).

4.0 Glossary of Technical Terms and Abbreviations

ANZSIC	Australian and New Zealand Standard Industrial Classification
CEMS	Continuous Emission Monitoring System
CO	Carbon Monoxide
EEA	European Environment Agency
EET	Emission Estimation Technique
EFR	Emission Factor Rating
Monomer	An organic compound which is used to form polymers by linking with itself.
NEPM	National Environment Protection Measure
NO _x	Oxides of Nitrogen
NPI	National Pollutant Inventory
Polymer	A high molecular-weight organic compound, natural or synthetic, whose structure can be represented by a repeated small unit, the monomer.
PM	Particulate Matter
PM ₁₀	Particulate matter with an equivalent aerodynamic diameter of 10 micrometres or less (ie. ≤10µm)
SO ₂	Sulfur Dioxide
Transfer	Transfers consist of a deposit of a substance into landfill, or discharge of a substance to a sewer or tailings dam, or removal of a substance from a facility for destruction, treatment, recycling, reprocessing, recovery or purification. Emissions classed as transfers are not required to be reported under the NPI.
TSP	Total Suspended Particulate
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compounds

5.0 References

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Eastern Research Group, Inc., 1998, *Emission Inventory Improvement Program – Volume II – Chapter 11 - Preferred and Alternative Methods for Estimating Air Emissions from Plastic Products Manufacturing*, Point Sources Committee, USA, 1998.

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<http://www.epa.gov/ttn/chief/ap42pdf/c06s10.pdf>

The following Emission Estimation Technique Manuals referred to in this Manual are available at the NPI Homepage (<http://www.npi.gov.au>) or from your local Environmental Protection Authority:

Emission Estimation Technique Manual for Combustion in Boilers;

Emission Estimation Technique Manual for Fugitive Emissions;

Emission Estimation Technique Manual for Sewage and Wastewater Treatment;

Emission Estimation Technique Manual for Organic Chemical Processing Industries; and

Emission Estimation Technique Manual for Petroleum Refining.

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* 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; 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 5. 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, which are used to determine exhaust gas flow rates in m³/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 m³. 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 1.

Equation 1

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

where:

$$\begin{aligned} C_{PM} &= \text{concentration of PM or gram loading, g/m}^3 \\ C_f &= \text{filter catch, g} \\ V_{m,STP} &= \text{metered volume of sample at STP, m}^3 \end{aligned}$$

Equation 2

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

where:

$$\begin{aligned} E_{PM} &= \text{hourly emissions of PM, kg/hr} \\ C_{PM} &= \text{concentration of PM or gram loading, g/m}^3 \\ Q_d &= \text{stack gas volumetric flow rate at actual conditions, m}^3/\text{s, dry} \\ 3.6 &= 3600 \text{ seconds per hour multiplied by 0.001 kilograms per gram} \\ T &= \text{temperature of the gas sample, } ^\circ\text{C} \end{aligned}$$

Table 5 - Stack Sample Test Results

Parameter	Symbol	Test 1	Test 2	Test 3
Total sampling time (sec)		7200	7200	7200
Moisture collected (g)	g_{MOIST}	395.6	372.6	341.4
Filter catch (g)	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	Q_d	8.48	8.43	8.45
Concentration of particulate (g/m ³)	C_{PM}	0.0718	0.0387	0.0537

Example 1 - 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 5, and an exhaust gas temperature of 150°C (423 K)). This is shown below:

$$\begin{aligned} C_{PM} &= C_f / V_{m, STP} \\ &= 0.0851 / 1.185 \\ &= 0.072 \text{ g/m}^3 \\ E_{PM} &= C_{PM} * Q_d * 3.6 * [273 / (273 + T)] \\ &= 0.072 * 8.48 * 3.6 * (273 / 423 \text{ K}) \\ &= 1.42 \text{ kg/hr} \end{aligned}$$

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

$$E_{PM} = Q_a * C_{PM} * 3.6 * (1 - \text{moist}_R / 100) * [273 / (273 + T)]$$

where:

E_{PM}	=	hourly emissions of PM in kilograms per hour, kg / hr
Q_a	=	actual (ie. wet) cubic metres of exhaust gas per second, m ³ / s
C_{PM}	=	concentration of PM or gram loading, g / m ³
3.6	=	3600 seconds per hour multiplied by 0.001 kilograms per gram
moist_R	=	moisture content, %
273	=	273 K (0°C)
T	=	stack gas temperature, °C

Total suspended particulates (TSP) are also referred to as total particulate matter (total PM). To determine PM₁₀ from total PM emissions, a size analysis may need to be undertaken. The weight PM₁₀ fraction can then be multiplied by the total PM emission rate to produce PM₁₀ emissions. Alternatively, it can be assumed that 100% of PM emissions are PM₁₀; ie assume that all particulate matter emitted to air has an equivalent aerodynamic diameter of 10 micrometres or less ie. ≤10µm. 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.

$$\text{moist}_R = \frac{100 * \left(\frac{g_{\text{moist}}}{(1000 * V_{m,STP})} \right)}{\left(\frac{g_{\text{moist}}}{(1000 * V_{m,STP})} \right) + \rho_{STP}}$$

where:

moist_R	=	moisture content, %
g_{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 2 - Calculating Moisture Percentage

A 1.2m³ sample (at STP) of gas contains 410g of water. To calculate the moisture percentage use Equation 4.

$$\text{moist}_R = \frac{100 * \left(\frac{g_{\text{moist}}}{1000 * V_{m,STP}} \right)}{\left(\frac{g_{\text{moist}}}{1000 * V_{m,STP}} \right) + \rho_{STP}}$$

$$\begin{aligned} g_{\text{MOIST}} / 1000 * V_{m,STP} &= 410 / (1000 * 1.2) \\ &= 0.342 \\ \text{moist}_R &= 100 * 0.342 / (0.342 + 1.62) \\ &= 17.4\% \end{aligned}$$

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 SO₂, 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 6 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 (O₂ or CO₂) 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.

Table 6 - Example CEMS Output for a Hypothetical Furnace Firing Waste Fuel Oil

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})	m ³ /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

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

Equation 5

$$E_i = (C * MW * Q_{st} * 3600) / [22.4 * ((T + 273)/273) * 10^6]$$

where:

E _i	=	emissions of pollutant i, kg / hr
C	=	pollutant concentration, ppm _{v,d}
MW	=	molecular weight of the pollutant, kg / kg-mole
Q _{st}	=	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
T	=	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:

E _{kpy,i}	=	annual emissions of pollutant i, kg / yr
E _i	=	emissions of pollutant i, kg / hr (from Equation 5)
OpHrs	=	operating hours, hr / yr

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:

$$\begin{aligned} E_{kpt,i} &= \text{emissions of pollutant i per tonne of product produced, kg/t} \\ E_i &= \text{hourly emissions of pollutant i, kg/hr} \\ A &= \text{production, t/hr} \end{aligned}$$

Example 3 illustrates the application of Equation 5, Equation 6 and Equation 7.

Example 3 - Using CEMS Data

This example shows how SO₂ emissions can be calculated using Equation 5 based on the CEMS data for Time Period 1 shown in Equation 5, and an exhaust gas temperature of 150°C (423 K).

$$\begin{aligned} E_{SO_2,1} &= (C * MW * Q_{st} * 3600) / [(22.4 * (T + 273 / 273) * 10^6)] \\ &= (150.9 * 64 * 8.52 * 3600) / [22.4 * (423 / 273) * 10^6] \\ &= 296\,217\,907 / 34\,707\,692 \\ &= 8.53 \text{ kg/hr} \end{aligned}$$

For Time Period 2, also at 150°C

$$E_{SO_2,2} = 8.11 \text{ kg/hr}$$

For Time Period 3, also at 150°C

$$E_{SO_2,3} = 7.23 \text{ kg/hr}$$

Say representative operating conditions for the year are:

$$\begin{aligned} \text{Period 1} &= 1500 \text{ hr} \\ \text{Period 2} &= 2000 \text{ hr} \\ \text{Period 3} &= 1800 \text{ hr} \end{aligned}$$

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

$$\begin{aligned} E_{kpy,SO_2} &= E_{SO_2,1} * \text{OpHrs} + E_{SO_2,2} * \text{OpHrs} + E_{SO_2,3} * \text{OpHrs} \\ &= (8.53 * 1500) + (8.11 * 2000) + (7.23 * 1800) \text{ kg} \\ &= 42\,021 \text{ kg/yr} \end{aligned}$$

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

$$\begin{aligned} E_{kpt,SO_2} &= E_{SO_2} / A \\ &= 8.53 / 290 \\ &= 2.94 * 10^{-2} \text{ kg SO}_2 \text{ emitted per tonne of product produced} \end{aligned}$$

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

A.2 Mass Balance

Mass balances involve examining a process to determine whether emissions can be characterised based on an analysis of operating parameters, material composition, and total material usage. Mass balance involves the quantification of total materials into and out of a process, with the difference between inputs and outputs being accounted for as a release to the environment (to air, water, land) or as part of the facility's waste. Mass balance is particularly useful when the input and output streams can be readily characterised and this is most often the case for small processes and operations.

Mass balance can be applied across individual unit operations (see **Appendix A.2.2**) or across an entire facility (see **Appendix A.2.1**). Mass balance techniques and engineering estimates are best used where there is a system with prescribed inputs, defined internal conditions, and known outputs.

It is essential to recognise that the emission values produced when using mass balance 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, or control efficiencies) can result in potentially large errors in the final estimates. In addition, when sampling of input and/or output materials is conducted, the failure to use representative samples will also contribute to uncertainty. In some cases, the combined uncertainty is quantifiable and this is useful in determining if the values are suitable for their intended use.

A.2.1 Overall Facility Mass Balance

Mass balances can be used to characterise emissions from a facility providing that sufficient data is available pertaining to the process and relevant input and output streams. Mass balances can be applied to an entire facility (see Example 4). This involves the consideration of material inputs to the facility (purchases) and materials exported from the facility in products and wastes, where the remainder is considered as a 'loss' (or a release to the environment).

The mass balance calculation can be summarised by:

Total mass into process = Total mass out of process

In the context of the NPI, this equation could be written as:

Inputs = Products + Transfers + Emissions

where:

Inputs	=	All incoming material used in the process.
Emissions	=	Releases to air, water, and land (as defined under the NPI). Emissions include both routine and accidental releases as well as spills.
Transfers	=	As defined under the NPI NEPM, transfers include substances discharged to sewer, substances deposited into landfill and substances removed from a facility for destruction, treatment, recycling, reprocessing, recovery, or purification.
Products	=	Products and materials (eg. by-products) exported from the facility.

Applying this to an individual NPI substance (substance 'i'), the equation may be written as:

$$\begin{aligned}\text{Input of substance 'i'} = & \text{amount of substance 'i' in product} \\ & + \text{amount of substance 'i' in waste} \\ & + \text{amount of substance 'i' transformed or consumed in process} \\ & + \text{emissions of substance 'i'}.\end{aligned}$$

The mass balance approach can be used for each NPI-listed substance for which the facility has a responsibility to report. Emissions can then be allocated to air, water, and land.

Example 4 provides an example of the application of mass balance.

Example 4 - Overall Facility Mass Balance

A chemical facility receives 1000 tonnes of an NPI-listed solvent product per annum, that is stored on-site. It is known that this solvent product contains 2 percent water that settles during storage, and is drained to sewer. The solubility of the solvent in water is 100 g/kg (ie. 0.1 weight fraction). It is known that 975 tonnes of solvent per annum is utilised in the process, based on actual addition rate data. During the year, it was recorded that 1 tonne of solvent was lost due to spillage, of which 500 kg was recovered and sent for appropriate disposal, with the rest washed to sewer. What quantity of the NPI-listed substance is required to be reported under the NPI?

Considering the water content of the solvent and the solubility of solvent in water the following data can be derived:

Quantity of water received in the solvent annually:

$$\text{Water} = 1000 \text{ tonnes} * (2 / 100) = 20 \text{ tonnes of water (containing 100 g / kg solvent)}$$

The solubility of solvent in this water is 100 g/kg:

$$\text{Therefore, solvent in water} = 20 * (0.1) = 2 \text{ tonnes of solvent}$$

Excluding the water component, the quantity of solvent received annually is:

$$\text{Total solvent (excluding water)} = 1000 * 0.98 = 980 \text{ tonnes}$$

Incorporating the solvent contained within the water component:

$$\text{Total solvent received at facility (including solvent in water)} = 980 + 2 = 982 \text{ tonnes solvent}$$

Once the above quantities have been ascertained, the quantity of solvent released to the environment can be determined as follows:

$$\text{Solvent to sewer} = \text{Drainage from solvent tank} + \text{uncaptured spillage}$$

Example 4 - Overall Facility Mass Balance cont'

$$\begin{aligned} &= 2000 \text{ kg} + 500 \text{ kg} \\ &= 2500 \text{ kg} \\ \text{Captured spillage} &= 500 \text{ kg} \end{aligned}$$

As no solvent was spilled on unsealed ground, there are no emissions to land. Therefore, the emission of solvent to air is derived as follows:

$$\begin{aligned} \text{Air Emission} &= \text{Total solvent received} - \text{sewer release} - \text{captured spillage} \\ &\quad - \text{solvent utilised in the process} \\ &= 982 - 2.5 - 0.5 - 975 \\ &= 4 \text{ tonnes} \end{aligned}$$

Therefore, 4 tonnes of solvent is lost to the atmosphere each year from storage and handling operations. For NPI reporting, it would then be necessary to determine the quantity of NPI substances present in the solvent and to determine the quantities of each of these substances emitted to atmosphere. It is important to note that any emission controls must be taken into account when determining your emissions (eg. the solvent released to air may be routed through an incinerator before being released to the atmosphere).

A.2.2 Individual Unit Process Mass Balance

The general mass balance approach described above can also be applied to individual unit processes. This requires that information is available on the inputs (ie flow rates, concentrations, densities) and outputs of the unit process.

The following general equation can be used (note that scm is an abbreviation for standard cubic metres):

Equation 8

$$E_i = \sum Q_i W_{fi} \rho_i - \sum Q_o W_{oi} \rho_o$$

where:

$$\begin{aligned} E_i &= \text{flow rate of component } i \text{ in unknown stream (kg/hr)} \\ Q_i &= \text{volumetric flow rate of inlet stream, } i \text{ (scm/hr)} \\ Q_o &= \text{volumetric flow rate of outlet stream, } o \text{ (scm/hr)} \\ W_{fi} &= \text{weight fraction of component } i \text{ in inlet stream } i \\ W_{oi} &= \text{weight fraction of component } i \text{ in outlet stream } o \\ \rho_i, \rho_o &= \text{density of streams } i \text{ and } o \text{ respectively (kg/scm)} \end{aligned}$$

Information on process stream input and output concentrations is generally known as this information is required for process control. The loss E_x will be determined through analysis of the process. It should be noted that it is then necessary to identify the environmental medium (or media) to which releases occur.

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 , 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 9

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

where:

- $E_{\text{kpy},i}$ = annual emissions of pollutant i, kg / yr
- Q_f = fuel use, kg / hr
- OpHrs = operating hours, hr / yr
- MW_p = molecular weight of pollutant emitted, kg / kg-mole
- EW_f = elemental weight of pollutant in fuel, kg / kg-mole
- C_i = concentration of pollutant i in fuel, weight percent, %

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 SO₂ 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 9 and given the following:

Fuel flow (Q_f) = 20 900 kg / hr

Weight percent sulfur in fuel = 1.17 %

Operating hours = 1500 hr / yr

$$\begin{aligned} E_{\text{kpy,SO}_2} &= Q_f * C_i / 100 * (MW_p / EW_f) * \text{OpHrs} \\ &= (20\,900) * (1.17 / 100) * (64 / 32) * 1500 \\ &= 733\,590 \text{ kg / yr} \end{aligned}$$

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:

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

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 ‘*m³ 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.

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

Equation 10

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

where :

- $E_{kpy,i}$ = emission rate of pollutant i, kg / yr
- A = activity rate, t / hr
- $OpHrs$ = operating hours, hr / yr
- EF_i = uncontrolled emission factor of pollutant i, kg / t
- CE_i = overall control efficiency of pollutant i, %.

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 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 from chemical product manufacturing 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. In general, site-specific data that is representative of normal operations is more accurate than industry-averaged data, such as the emission factors presented in **Appendix D** of this Manual.

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 chemical product manufacturing 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 chemical product manufacturing 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 ± 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 chemical product manufacturing production processes. EET equations are available for the following types of emissions common to chemical product manufacturing facilities.

Use of emission equations to estimate emissions from chemical product manufacturing 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 will not 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 which 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
Annual emissions of pollutant i	$E_{kpy,i}$	kg / yr
Total emissions of pollutant i per hour	E_i	kg / hr
Uncontrolled emission factor for pollutant i	EF_i	kg of pollutant / tonne
Emissions per tonne	$E_{kpt,i}$	kg of pollutant i per tonne of fuel consumed
Overall control efficiency, (ie Emission reduction control factor)	CE_i	% reduction in emissions of pollutant i
Material entering the process	Q_i	kg / hr
Fuel used	Q_f	kg / hr
Material leaving the process	Q_o	kg / hr
Volumetric flow rate of stack gas	Q_a	actual (ie. wet) cubic metres per second (m^3/s)
Volumetric flow rate of stack gas	Q_d	dry cubic metres per second (m^3/s)
Concentration of pollutant i	C_i	kg / L
Concentration of PM	C_{PM}	g / m^3
Elemental weight of pollutant i in fuel	EW_f	kg / kg-mole
Molecular weight of pollutant i	MW_i	kg / kg-mole
Operating hours	OpHrs	hr / yr
Activity rate	A	units / hr, eg t / hr
Temperature	T	°Celsius (°C) or Kelvin (K)
Standard Temperature & Pressure	STP	0°C (273 K) and 1 atmosphere 101.3 kPa
Filter Catch	C_f	g
Metered volume of sample at STP	$V_{m,STP}$	m^3
Dry density of stack gas sample at STP	ρ_{STP}	kg / m^3
Weight fraction of component i in inlet stream	W_{fi}	
Weight fraction of component i in outlet stream o	W_{oi}	
Density of stream i	ρ_i	kg / m^3
Density of stream o	ρ_o	kg / m^3
Hourly emissions of PM	E_{PM}	kg / hr
Moisture collected	g_{moist}	g
Moisture content	$moist_R$	%
Stack gas volumetric flowrate at actual conditions	Q_{st}	m^3 / s

Appendix D - Emission Factors for Chemical Product Manufacturing

D.1 Introduction

As noted in **Section 3** of this Manual, it is likely that chemical product manufacturing facilities will be able to meet their NPI reporting requirements using mass balance, emissions monitoring and the emissions estimation techniques provided in the *Emission Estimation Technique Manual for Organic Chemical Processing Industries*. There is some published data on specific emissions from the chemical product manufacturing industry. This information is provided here to supplement the emission estimation techniques provided in **Section 3** of this Manual.

In this section, emission factors are presented for the following processes:

- Polyvinyl chloride manufacture;
- Polystyrene manufacture;
- Polypropylene manufacture;
- Synthetic resins manufacture; and
- Synthetic rubber manufacture.

D.2 Polyvinyl Chloride Manufacture

Emission factors for the polyvinyl chloride manufacture process are provided in Table 9. These emission factors are given an emission factor rating of E by the USEPA.

Table 7 - Uncontrolled^a Emission Factors for Polyvinyl Chloride Manufacture

PM₁₀^b (kg/tonne of PVC produced)	Vinyl Chloride^d (kg/tonne of PVC produced)
17.5 ^c	8.5

Source: USEPA, 1995a

^a Assuming no emission control in whole plant.

^b The emission factor published by the USEPA (USEPA, 1995a) is for Total Particulate Matter. In the absence of site-specific particle size distribution data, it can be conservatively assumed that the quantity of PM₁₀ emitted is the same as the quantity of Total Particulate Matter emitted.

^c Emission factor of 0.35 kg / tonne if controlled with fabric filter of 98% collection efficiency (USEPA, 1995a).

^d The emission factor published by the USEPA (USEPA, 1995a) is for gases as vinyl chloride. In the absence of site-specific information, this may be conservatively assumed to equal vinyl chloride.

D.3 Polystyrene Manufacture

The USEPA has published emission factors for the following polystyrene manufacturing processes (USEPA, 1995b):

- Standard batch process;
- Standard continuous process;
- Expandable polystyrene post-impregnation suspension process; and
- In-situ expandable polystyrene process.

The emission factors for batch polystyrene manufacturing processes are provided in Table 8. These emission factors are given an emission factor rating of C by the USEPA (USEPA, 1995b).

Table 8 - Emission Factors for Batch Process of Polystyrene Manufacture

Unit Operation	Emission Factor (kg VOC/tonne product)
Monomer storage and feed dissolver tanks	0.09 ^a
Reactor vent drum vent	0.74 ^b
Devolatiliser condenser vent	0.50 ^b
Devolatiliser condensate tank	0.002 ^a
Extruder quench vent	0.23 ^b
Product storage	- ^c
Total plant	1.55

Source: USEPA, 1995b.

^a Based on fixed roof design.

^b The arithmetic mean of the minimum and maximum values provided by the USEPA (USEPA, 1995b).

^c Emissions are considered negligible (USEPA, 1995b). In the absence of other information, assume zero emissions.

Emission factors for continuous polystyrene manufacturing processes are provided in Table 9. These emission factors have been given an emission factor rating of C by the USEPA (USEPA, 1995b).

Table 9 - Emission Factors for the Continuous Polystyrene Manufacturing Process

Unit Operation	Emission Factor (Uncontrolled Emission Factor) (kg VOC/tonne product)
Monomer storage	0.08
General purpose additives	0.002
High impact additives	0.001
Ethylbenzene storage	0.001
Dissolvers	0.008
Devolatiliser condenser vent ^g	0.05 ^a (0.04) ^{a,b} 2.96 ^c
Styrene recovery unit condenser vent	0.05 ^a 0.13 ^c
Devolatiliser + Styrene recovery unit	0.024 - 0.3 ^f (0.004) ^e
Extruder quench vent	0.01 ^a 0.15 ^{c,e}
Pellet storage	- ^d
General purpose other storage	0.008
High impact other storage	0.007
Total plant	0.21 ^a 3.34 ^c

Source: USEPA, 1995b

^a For plants using vacuum pumps.

^b Condenser is used downstream of primary process condensers. This factor includes emissions from dissolvers.

^c For plants using steam jets.

^d Emissions are considered negligible (USEPA, 1995b). In the absence of other information, assume zero emissions.

^e Plant uses an organic scrubber to reduce emissions. Non-soluble organics are burned as fuel.

^f Lower value based on facility using refrigerated condensers as well as conventional cooling water exchangers; vacuum pumps in use. Higher value for facility using vacuum pumps.

^g Larger plants may route this stream to the styrene recovery section. Smaller plants may find this too expensive.

The USEPA has developed emission factors for the post-impregnation suspension process of polystyrene manufacture. These emission factors are listed in Table 10.

Table 10 - Uncontrolled Emission Factors for the Expandable Polystyrene Post-Impregnation Suspension Process of Polystyrene Manufacture

PM ₁₀ ^a (kg/tonne of polystyrene produced)	VOC Emissions (kg/tonne of polystyrene produced)
18 (0.18) ^b	8.75 ^c

Source: USEPA, 1995b

^a The emission factor published by the USEPA (USEPA, 1995) is for Total Particulate Matter. In the absence of site-specific particle size distribution data, it can be conservatively assumed that emissions of Total Particulate Matter are equal to emissions of PM₁₀.

^b Controlled emission factor, assuming 99% control efficiency (USEPA, 1995b).

^c This is the arithmetic mean of two emission factors provided by the USEPA for this activity (USEPA, 1995b).

Emission factors for the in-situ process of expandable polystyrene manufacture are provided in Table 11. These emission factors in Table 10 and Table 11 are given an emission factor rating of C by the USEPA (1995b).

Table 11 - Emission Factors for the In-Situ Process Expandable Polystyrene Manufacture

Unit Operation	Emission Factor (kg VOC/tonne product)
Mix tank vents	0.13
Regranulator hoppers	- ^a
Reactor vents	1.09 ^b
Holding tank vents	0.053
Wash tank vents	0.023
Drier vents	2.77 ^b
Product improvement vents	0.008
Storage vessel and conveying losses	1.3
Total plant	5.37 ^c

Source: USEPA, 1995b.

^a Emissions are considered negligible (USEPA, 1995b). In the absence of other information, assume zero emissions.

^b Assuming no emission control in whole plant.

^c At plant where all reactor vents and some dryer vents are controlled in a boiler (and assuming 99% reduction), and overall emission rate of 3.75 is estimated.

D.4 Polypropylene Manufacture

Overall process emission factor for the polypropylene manufacturing process are provided in

Table 12. These emission factors are given an emission factor rating of E by the USEPA (1995c).

Table 12 - Uncontrolled^a Emission Factor for the Polypropylene Manufacturing Process

VOC ^c Emission Factor (kg/tonne of polypropylene produced)	PM ₁₀ ^b Emission Factor (kg/tonne of polypropylene produced)
0.35	1.5

Source: USEPA, 1995c

^a Assuming no emission control in whole plant.

^b The emission factor published by the USEPA (USEPA, 1995) is for Total Particulate Matter. In the absence of site-specific particle size distribution data, it can be conservatively assumed that Total Particulate Matter is equal to PM₁₀.

^c The emission factor published by the USEPA (USEPA, 1995a) is for gases as polypropylene. In the absence of site-specific information, this may be conservatively assumed to equal polypropylene.

D.5 Synthetic Resin Manufacture

Emission factors for a number of synthetic fibre manufacturing processes are provided in Table 13. The emission factors have been given an emission factor rating of C by the USEPA (1995d).

Table 13 - Emission Factors for Synthetic Resin Manufacturing

Type of Fibre	VOC Emissions (kg/tonne of fibre spun)	PM ₁₀ Emissions (kg/tonne of fibre spun)
Rayon Viscose	0	- ^k
Cellulose Acetate, filter tow	112 ^a	- ^k
Cellulose acetate and triacetate, filament yarn	199 ^{a,b}	- ^k
Polyester, melt spun		
Staple	0.6 ^c	252 ^e
Yarn	0.05 ^c	0.03 ^c
Acrylic, dry spun		
Uncontrolled	40	- ^k
Controlled	32 ^d	- ^k
Modacrylic, dry spun	125 ^{c,e}	- ^k
Acrylic and modacrylic, wet spun	6.75 ^f	- ^k
Acrylic, inorganic wet spun		
Homopolymer	20.7 ^c	20.7
Copolymer	2.75 ^c	2.75
Nylon 6, melt spun		
Staple	3.93 ^c	0.01 ^c
Yarn	0.45 ^{d,g}	- ^k
Nylon 66, melt spun		
Uncontrolled	2.13 ^h	0.5 ⁱ
Controlled	0.31 ⁱ	0.1 ⁱ
Polyolefin, melt spun	5 ^c	0.01 ^c
Spandex, dry spun	4.23 ^d	- ^k
Spandex, reaction spun	138 ^j	- ^k
Vinyon, dry spun	150 ^d	- ^k

Source: USEPA, 1995d.

^a After recovery from spin cells and dryers

^b If methyl chloride or methanol is used as the solvent in place of acetone, please double this factor.

^c Uncontrolled emissions.

^d After recovery from spin cells

^e After control on extrusion parts cleaning operations

^f After solvent recovery from the spinning washing and drawing stages. This emission contains acrylonitrile and should be speciated if acrylonitrile has triggered the Category 1 threshold.

^g Uncontrolled emission factor is equal to 1.39 kg/tonne.

^h Add 0.1 kg/tonne for plants producing tow or staple. For continuous polymerisation processes, multiply by 1.7. For batch polymerisation processes, multiply by 0.8.

ⁱ After control of spin cells. Add 0.02 kg/tonne for plants producing tow or staple. For continuous polymerisation, multiply by 2.0, for batch polymerisation subtract 0.01 kg/tonne.

^j After recovery by carbon adsorption from spin cells and post-spinning operations of 83% collection efficiency.

^k Emissions are considered negligible (USEPA, 1995d). In the absence of other information, assume zero emissions.

^l For plants with spinning equipment cleaning operations.

D.6 Synthetic Rubber Manufacture

The USEPA has developed a number of emission factors for emulsion synthetic rubber processes. These emission factors have been given an emission factor rating of B by the USEPA and are provided in Table 14.

Table 14 - Emission Factors for Emulsion Processes for the Manufacture of Synthetic Rubber

Process	VOC Emissions kg of VOC/tonne of product
Emulsion Crumb	
Monomer recovery, uncontrolled	2.6
Absorber vent	0.26
Blend / coagulation tank, uncontrolled	0.42
Dryers	2.51 ^a
Emulsion Latex	
Monomer removal condenser vent	8.45
Blend tanks, uncontrolled	0.1

Source: USEPA, 1995e

^a Assuming no emission control in whole plant.