



**National Pollutant Inventory**

# **Emission Estimation Technique Manual**

**for**

**Organic Chemical  
Processing Industries**

*First Published in March 1999*

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**EMISSION ESTIMATION TECHNIQUES  
FOR THE  
ORGANIC CHEMICAL PROCESSING INDUSTRIES**

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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 the organic chemicals processing industries. The Manual can also assist companies producing other products that, as part of their production processes, store, handle, or use organic substances.

EET MANUAL:     Organic Chemical Processing Industries

HANDBOOK:     Organic Industrial Chemical Manufacturing

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The operations and activities covered by this Manual include:

- conversion processes (reactors, both batch and continuous);
- separation processes (distillation, filtration, crystallisation, and extraction);
- equipment leaks (valves, flanges, connectors, pumps);
- transfer operations (product transfer via racks and hoses to tanker truck, rail, or marine vessels);
- storage (tankage and stockpiling);
- wastewater treatment; and
- on-site combustion.

This Manual was drafted by Pacific Air & Environment, in conjunction with the NSW Environment Protection Authority, on behalf of the Commonwealth Government.

The Manual has been developed through a process of national consultation involving State and Territory environmental authorities and key stakeholders. Particular thanks are due to the Plastics and Chemicals Industries Association (PACIA) and its members for their comments, advice and information.

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## 2.0 DO I NEED TO REPORT?

*The NPI Guide*, at the front of this Handbook, provides guidance to help you determine:

- Whether you are required to report under the NPI
- Which substances are to be reported.

Section 2 of *The NPI Guide* details the necessary steps to be taken to determine whether your facility triggers any of the thresholds for NPI-listed substances. A series of worksheets are provided to assist you with this exercise.

### Category 1 and 1a Substances

The reporting criteria for Category 1 and 1a substances, as detailed in Clause 10 of the NPI NEPM, are:

- a Category 1 listed substance is only reportable if 10 tonnes or more of the substance is used per annum;
- the only Category 1a substance is Total Volatile Organic Compounds (VOCs) for which the throughput threshold is 25 tonnes per annum;
- “use” means processed (eg. crude oil throughput, production chemicals, drilling fluids), or coincidental production (eg substances contained in produced formation water, emissions from dehydrator regeneration etc); and
- substances in proprietary mixtures are not reportable unless the substance is specified in a Material Safety Data Sheet or, in the case of any other material, the occupier of the facility could reasonably be expected to know that the substance is contained in the material.

The usage 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.

The total amount of each Category 1 and 1a substance ‘used’ must be calculated in order to determine whether the threshold is exceeded. This involves developing a cumulative total for the use of each NPI substance from various sources.

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

If you estimate your emission by using any of these EET's, your data will be displayed on the NPI database as being of 'acceptable reliability'. Similarly, if your relevant environmental authority has approved the use of 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 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.

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In the specific context of the Organic Chemicals Processing Industry, there are a range of EETs that may be utilised. These may be used individually or in combination (ie. you may use different EETs for different process units or use a combination of measured and estimated emissions to characterise emissions from a specific process unit), depending on data availability. The EETs presented in this Manual, that can be used for characterising releases to air, water, and land are:

- Mass balance (see Section 4);
- Air Displacement (Section 5);
- Specific emission factors for unit sources or operations (Section 6); and
- Direct monitoring (Section 7).

Some additional guidance on characterising releases to water and land is provided in Sections 8 and 9 respectively.

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## 4.0 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 Section 4.3) or across an entire facility (see Sections 4.1 and 4.2). 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.

### 4.1 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 1). 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:

$$\text{Total mass into process} = \text{Total mass out of process}$$

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

$$\text{Inputs} = \text{Products} + \text{Transfers} + \text{Emissions} \quad (1)$$

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:

$$\text{Input of substance 'i'} = \text{amount of substance 'i' in product} + \text{amounts of substance 'i' in waste} + \text{amount of substance 'i' transformed or consumed in process} + \text{emissions of substance 'i'}. \quad (2)$$

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 1 provides an example of the application of mass balance.

### Example 1

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.

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:

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



### Example 1 cont'

Incorporating the solvent contained within the water component:

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

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

Solvent to sewer = drainage from solvent tank + uncaptured spillage  
= 2000 kg + 500 kg  
= 2500 kg

Captured spillage = 500 kg

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:

Air Emission = Total solvent received – sewer release – captured spillage – solvent utilised in the process  
=  $982 - 2.5 - 0.5 - 975$   
= 4 tonnes

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).

## 4.2 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.

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The following general equation can be used (note that scm is an abbreviation for standard cubic metres – refer to Section 7):

$$E_i = \sum Q_i W_{fi} P_i - \sum Q_o W_{oi} P_o \quad (3)$$

Where:

$E_i$	=	flow rate of component i in unknown stream (kg/hr)
$Q_i$	=	Volumetric flow rate of inlet stream, i (scm/hr)
$Q_o$	=	Volumetric flow rate of outlet stream, o (scm/hr)
$W_{fi}$	=	Weight fraction of component i in inlet stream i
$W_{oi}$	=	Weight fraction of component i in outlet stream o
$P_i, P_o$	=	Density of streams i and o respectively (kg/scm)

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.

## 5.0 AIR DISPLACEMENT

Emissions from storage tanks occur during filling and removing (these are commonly referred to as “working” losses) and storage (standing or “breathing” losses). Losses from blending and mixing also include losses due to movement of the material.

Models such as USEPA TANKS 3.0 and the *Emission Estimation Technique Manual for Fuel and Organic Liquid Storage* (discussed further in Section 6.2.3) can be used to calculate emissions from storage tanks and blending and mixing operations.

The Air Displacement EET presented in this section is a simple estimation technique that can be used in place of these models. With this EET, it is assumed that the primary source of emissions from a vessel is through the displacement of saturated vapour during addition of substances into the vessel, such as a mixer (ie. the volume of vapour released is equal to the volume of liquid added). It is further assumed that the volume of vapour displaced from a vessel during filling is saturated with the material filling the tank (ie. the vapour displaced from the vessel is of the same composition as the liquid entering the vessel). This assumption is valid for volatile single components and for some multiple component mixtures.

Further details regarding the application of this EET are provided in Section 5.1 (single component) and Section 5.2 (multiple components). It is important to recognise that the Air Displacement EET relies on information regarding the properties of the material(s) in question (eg vapour pressures, molecular weight, mass fraction) being available.

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## 5.1 “Topping Up”

Emissions arise as a consequence of the displacement of saturated vapour during the addition of substances into a vessel, such as a mixer (ie. the volume of vapour released is equal to the volume of liquid added). The simplest case involves the “topping up” of a substance with the same substance. In this situation, it is assumed that the volume of the substance added is displaced as an equivalent emission of saturated vapour from the mixing tank. (NB: This technique is designed to apply to organic liquids. If required, an EET for emissions from the storage of inorganic acids can be found in the *Emission Estimation Technique Manual for Alumina Refining*).

The equation for calculating the emission of a volatile substance from a storage vessel is as follows:

$$y = x (VP / P) \quad (4)$$

Where:

y	=	vapour mole fraction.
x	=	liquid mole fraction.
VP	=	vapour pressure of component in the tank (kPa). This can be obtained from Material Safety Data Sheets or standard chemical engineering reference books such as Perry’s Chemical Engineers Handbook (7 <sup>th</sup> Edition, Ch 2).
P	=	system pressure (kPa). In most cases, eg for open reactors, this will be ambient pressure (101.3kPa).

## 5.2 Air Displacement Emissions from Mixtures

The composition of vented gases from mixtures may be estimated in a similar manner to that used for single substances. The EET relies on data being available concerning the composition of the mixture (ie. in terms of mass or mole fractions).

If a vessel (eg reactor, mixer) contains a liquid that is a mixture of components A, B, and C at standard temperature and pressure, the vapour space in the mixer, assuming equilibrium has been reached, will be a mixture of components A, B and C. The mole fraction of each component can be calculated using Raoult’s Law:

$$y_i = x_i (VP_i / P) \quad (5)$$

Where

i	=	component A, B or C
y	=	vapour mole fraction
x	=	liquid mole fraction
VP <sub>i</sub>	=	vapour pressure of component i (kPa). This may be obtained

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P = from Material Safety Data Sheets or reference books such as Perry's Chemical Engineers Handbook (7<sup>th</sup> Edition, Ch 2) system pressure (kPa). In open reactors, this will be ambient pressure (101.3kPa).

If a volume (V) of liquid is added to the original mixture, the vapour released through the vent would have the equivalent volume 'V' (at standard temperature and pressure). The composition of the vapour can be derived using Equation 5 above, assuming no chemical reaction. The following example calculation demonstrates how this EET may be applied in practice. The example can be applied to either batch, or continuous processing operations.

For more details on the difference between standard, actual and normal temperature conditions, please refer to Section 7 of this Manual.

## Example 2

A dedicated mixer is used to prepare a mixture of benzene and toluene. The recipe requires that 950 kg of benzene be added to the mixer, followed by 50 kg of toluene. The mixer is closed between batches. The volume of the mixer is 1300 L.

The vessel is not cleaned between batches, and thus, it may be conservatively assumed that the air inside the mixer is saturated with benzene/toluene vapours associated with the liquid mixture. Using the addition quantities, the approximate molar composition of the mixture is determined as follows:

*Step 1: Determine the mole percentages of the components in the mixture*

$$\begin{aligned} \text{No. moles of benzene} &= 950 \text{ kg} / (\text{MW}_{\text{BENZENE}}) \\ &= 950 / 78.11 \\ &= 12.16 \text{ kmoles} \\ \text{No. moles of toluene} &= 50 \text{ kg} / (\text{MW}_{\text{TOLUENE}}) \\ &= 50 / 92.13 \\ &= 0.54 \text{ kmoles} \end{aligned}$$

Therefore, the molar composition of the mixture is:

$$\begin{aligned} \text{Mole percent benzene} &= 12.16 / (12.16 + 0.54) \\ &= 95.7 \% \\ \text{Mole percent toluene} &= 0.54 / (12.16 + 0.54) \\ &= 4.3 \% \end{aligned}$$

*Step 2: Calculate Composition of Vapour Space*

Using Equation 5, the composition of the vapour space is then derived as follows:

$$\begin{aligned} \text{VP}_{\text{benzene}} &= 12.46 \text{ kPa at } 25^\circ\text{C (from Perry's)} \\ \text{VP}_{\text{toluene}} &= 4.97 \text{ kPa at } 25^\circ\text{C (from Perry's)} \\ y_{\text{benzene}} &= x_{\text{benzene}} * \text{VP}_{\text{benzene}} / P \\ &= 0.957 * 12.46 \text{ kPa} / 101.3 \text{ kPa} \\ &= 0.12 \\ y_{\text{toluene}} &= x_{\text{toluene}} * \text{VP}_{\text{toluene}} / P \\ &= 0.043 * 4.97 \text{ kPa} / 101.3 \text{ kPa} \\ &= 0.0021 \end{aligned}$$

So, the resulting vented vapour would have a mole fraction of 0.12 benzene, 0.0021 toluene, and the remainder air.

## Example 2 cont'

### Step 3: Calculate Mass of Benzene and Toluene Released per Filling Operation

It is known that the volume of air releases per fill will equal the volume of benzene and toluene added per mixing batch, which is derived as follows:

The density of benzene at 25°C = 0.872 kg/L

Therefore, the volume added will be = 950 kg/0.872 kg/L = 1090 L

The ideal gas law data can be used to determine the total number of moles exiting the mixer per filling operation. The ideal gas law is as follows:

$$PV = nRT$$

Where:

P	=	Pressure (=101.3 kPa = 1 atm)
V	=	Volume (= 1090 litres (L))
n	=	Number of moles of mixture released
R	=	Ideal gas constant (= 0.082 L atm/mole K)
T	=	Temperature (= 25°C = 298K)

Using the ideal gas law, the total number of moles of vapour mixture released is determined as follows:

$$\begin{aligned}n_{\text{TOTAL}} &= PV/RT \\ &= (1 \text{ atm})(1090 \text{ L})/(0.082 \text{ L.atm/mole K})(298 \text{ K}) \\ &= 44.6 \text{ moles of vapour mixture}\end{aligned}$$

As derived above, the mole fraction of benzene is 0.12, and so the number of moles of benzene released per fill is determined as follows:

$$\begin{aligned}n_{\text{benzene}} &= 0.12 * 44.6 \\ &= 5.35 \text{ moles of benzene}\end{aligned}$$

Using the molecular weight (MW) of benzene, the mass of benzene released per year is calculated below:

$$\begin{aligned}\text{Mass} &= (\text{moles of benzene})(\text{MW of benzene}) \\ &= 5.35 \text{ moles benzene} * 78.11 \text{ g/gmole} \\ &= 418 \text{ g} \\ &= 0.418 \text{ kg}\end{aligned}$$

### Example 2 cont'

In a similar manner to that shown above, the quantity of toluene released per fill is 8.6 grams (0.0086 kg).

Therefore, a total of 0.418 kg and 0.0086 kg of benzene and toluene respectively, is released from the mixer per filling operation. It is important to note that you must take any pertinent emission controls into account when estimating emissions (eg. the waste may be routed through an incinerator that destroys most or all of these organics before they are released to the atmosphere).

If it were known that 300 such mixing batches were performed annually, the quantity of each material released will be derived as follows:

$$\begin{aligned}\text{Annual (uncontrolled) benzene release} &= 0.418 * 300 = 125 \text{ kg/year} \\ \text{Annual (uncontrolled) toluene release} &= 0.0086 * 300 = 2.6 \text{ kg/year}\end{aligned}$$

However, no account has been taken of the actual toluene addition after the benzene has filled the tank. It is assumed that the volume above the benzene is now essentially saturated with benzene vapours only. Therefore, the vapour space composition at this stage is derived as follows

$$\begin{aligned}y_{\text{benzene}} &= x_{\text{benzene}} * VP_{\text{benzene}} / P \\ &= 1.0 * 12.46 \text{ kPa} / 101.3 \text{ kPa} \\ &= 0.123\end{aligned}$$

You should note that it has been assumed that the vapour above the benzene would reach equilibrium before the addition of the toluene, and that the time taken to add the toluene would be such that the toluene would not volatilize sufficiently to affect the composition of the vapour.

The volume of toluene added to the benzene in the vessel is approximately 53 L. Therefore, the subsequent volume expelled from the mixer is also 53 L. Using this data and a similar methodology to that outlined above, the following information is derived:

$$\begin{aligned}n_{\text{TOTAL}} &= 2.2 \text{ moles of vapour expelled from the vessel (using the ideal gas law)} \\ n_{\text{BENZENE}} &= 0.123 * 2.2 \\ &= 0.27 \text{ moles of benzene} \\ \text{Mass} &= 0.27 \text{ moles} * 78.11 \\ &= 21.1 \text{ g benzene}\end{aligned}$$

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**Example 2 cont'**

Using this data, the annual contribution to air emissions from the toluene addition is derived as follows:

$$\begin{aligned}\text{Annual benzene release (from toluene addition)} \\ &= 0.0211 * 300 \\ &= 6.3 \text{ kg}\end{aligned}$$

Therefore, the total annual benzene and toluene emissions from the facility mixing operations are 131.3 kg (ie. 125 + 6.3) and 2.6 kg respectively.



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## 6.0 UNIT SOURCES/ OPERATIONS

In certain situations, it may not be possible to apply the Mass Balance or Air Displacement EETs presented in Sections 4 and 5 of this Manual. It may be necessary to consider unit processes or activities on an individual basis, and to use either direct monitoring, where available, or default emission factors to characterise emissions. In this section, emission factors and other estimation techniques are presented for various unit processes and operations. The unit processes/emission sources considered in this Section are:

- process vents;
- combustion;
- storage vessels;
- fugitive emissions;
- loading/unloading;
- wastewater treatment; and
- gas flaring.

### 6.1 Introduction

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:

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

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

### 6.2 Air Releases

#### 6.2.1 Process Vents

Process vent emissions include emissions from continuous and batch processes released directly to air or through pollution control devices such as flares, incinerators, and/or scrubbers. All such vents should be considered when characterising emissions.

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The most rigorous approach is to measure the emissions using a standard test method, such as USEPA Method 18 for speciated organic compounds or USEPA Method 25A for total organic compounds. These test methods, as well as volatile organic sampling train (VOST), and semi-VOST sampling procedures, are designed to measure organic compounds. However, it should be noted that the National Environment Protection Measure (NEPM) for the NPI specifies that sampling above and beyond what is normally conducted under existing regulatory requirements is not required, hence the methods included in this section are included as suggestions only.

In the absence of source testing data, process vent releases can be calculated through the use of mass balance principles (see Section 4) and/or knowledge of the saturated vapour displaced during, for example, addition of other substances to a vessel or storage container (see Section 5). All approaches however, will require some knowledge of the process vent stream characteristics (eg. flow rate and temperature for using mass balances).

### **6.2.2 Combustion Sources**

Many facilities generate energy and/or steam on-site through the combustion of natural gas and/or fuel oil. Depending on the size of the combustion system(s) at a facility, reporting may be required for Category 2a and/or Category 2b substances. (See *The NPI Guide* for further information). Emission estimation techniques for combustion processes can be found in the *Emission Estimation Technique Manual for Combustion in Boilers*.

### **6.2.3 Storage Vessels**

This section covers storage vessels including tanks and other vessels associated with the storage of NPI-listed substances. Organic liquids in the chemical industry, usually called volatile organic liquids, are composed of pure chemicals or mixtures of chemicals with similar true vapour pressures (for example, a mixture of isopropyl and butyl alcohols). Emissions from organic liquids in storage occur through evaporative losses during storage and as a result of changes in the liquid level.

#### **6.2.3.1 Tanks Greater than 30 Tonnes**

EET's for characterising releases from storage tanks greater than 30 tonnes are presented in the *Emission Estimation Technique Manual for Fuel and Organic Liquid Storage*, which includes the AUSTANKS spreadsheet, or by using the USEPA model referred to as TANKS 3.0. TANKS 3.0 is available free of charge from the USEPA (see reference list).

TANKS 3.0 is a software package that requires information on the physical characteristics of the storage tanks, typical atmospheric conditions (such as wind speeds and temperatures), the contents of the tank and throughput. The limitation of this software is that no speciation of organic emissions is performed. TANKS 3.1

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does not suffer from this limitation. The *Emission Estimation Technique Manual for Petroleum Refining* provides guidance on the speciation of emissions from storage tanks.

#### **6.2.3.2 Tanks Less than 30 Tonnes**

PACIA has advised that emissions from storage tanks of less than 30 tonnes capacity can best be estimated using the Air Displacement EET presented in Section 5 of this Manual. However, should facilities so require, the EETs presented in the *Emission Estimation Technique Manual for Fuel and Organic Liquid Storage* or TANKS 3.0 may be used to characterise such emissions.

#### **6.2.4 Equipment Leaks**

Emissions from equipment leaks result when process fluid (either liquid or gaseous) is lost from various types of equipment. These fugitive sources include valves, pumps, flanges, connectors (ie non-flanged), compressors, sampling connections, open-ended valves, product accumulator vessels, agitators, and instrumentation systems.

In general, the quantity of material released from each individual source is small. However, due to the potentially large number of such sources at a facility engaged in organic chemical processing, total emissions can be significant. Thus, the inclusion of these fugitive emissions sources is important when characterising emissions for the purposes of reporting under the NPI.

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

1. First of all, total emission estimates are made. (This involves identifying all potential sources and classifying each of them by service, annual operating hours per annum, and determining total mass emission rates);
2. Speciation of these mass emission rates using speciation profiles.

Detailed guidance on the characterisation for process fugitives can be found in the *Emission Estimation Technique Manual for Petroleum Refining*.

#### **6.2.5 Loading/Unloading Operations**

Transfer operations have the potential to generate emissions through vapour displacement during the loading of a transfer vehicle. Transfer operations include the loading of liquid products from a transfer rack (ie the collection of loading arms and loading hoses used to fill vessels with product) into a tank truck, rail car, or marine vessel.

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Transfer loading emissions include:

- displacement of residual vapours from a previously loaded product;
- vapours generated from the product being loaded; and
- vapours lost from the transfer piping during the loading cycle.

As with the other sources of volatile organic emissions, releases from loading and unloading need to be speciated to derive the emissions of individual NPI substances.

Emission estimation techniques to characterise emissions from the loading and unloading of organic liquids can be found in the *Emission Estimation Technique Manual for Petroleum Refining*.

### **6.2.6 Wastewater Treatment**

Many of the chemical processes in the organic chemical processing industry use organic compounds as raw materials, solvents, catalysts, and extractants. In addition, many of these processes generate organic by-products during reaction steps. Many of these raw materials, products, and wastes are found in process wastewater.

Emission estimation techniques for volatile emissions from wastewater are provided in a software package developed by USEPA and referred to as WATER 8.

### **6.2.7 Gas Flaring**

EET's to characterise emissions from gas flaring can be found in the *Emission Estimation Technique Manual for Petroleum Refining*.

Emissions can also be characterised through stoichiometric analysis. This involves determining the quantity of flue gas produced, based on the composition of the feed gas, and information regarding combustion conditions (eg amount of excess air). This information can then be combined with flue gas composition information to determine total emissions from this source. Stoichiometric analysis is primarily of use in situations when the composition of the feed gas is known.

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## 7.0 MONITORING

Many facilities conduct monitoring as part of their existing regulatory requirements. Typically, the monitoring is tied directly to the conditions on an environmental licence, and will vary from site to site.

It is important to recognise that facilities also collect a range of other information, beyond stack or liquid effluent testing, that can be used in characterising emissions for the NPI. Typical data collected includes:

- volumetric flow rates (eg products, wastes, wastewater treatment);
- mass flow rates;
- stream composition;
- product and waste composition; and
- production and waste quantities.

In most situations, the use of such data as a basis for calculating emissions will provide the most representative emissions information for a facility and, subject to availability, this data should be used to calculate emissions.

Monitoring data can be expressed in a range of units. The following discussion may be of assistance when converting monitoring results into annual emission estimates for the purposes of the NPI. It is important to remember that the calculation of annual emissions must also take into account the number of hours per year that the source is discharging to the environment.

Stack data is typically presented in terms of either actual flow, or a 'normalised' flow. The difference is that normalised data is standardised to a particular temperature and pressure that are typically 0°C and 1 atm respectively. However, sometimes it may be referenced to 25°C and 1 atm. The following terms can be used when presenting data:

- acm – actual cubic metre (at actual temperature and pressure);
- scm – standard cubic metre (typically at 25°C and 1 atm, although sometimes it may be at 20°C, or even 0°C); and
- Nm<sup>3</sup> – normal cubic metre (typically at 0°C and 1 atm);

It is essential to ascertain under what conditions the source test data was derived before determining annual emission estimates. Two examples of the use of sampling data to characterise annual emissions are presented below. Example 3 is where the concentration of the compound is presented at the same conditions as the measured flow rate while Example 4 is where the concentration and flue gas flows are measured under different conditions.

### Example 3

The following example relates to the situation where the concentration of the compound is presented at the same conditions as the measured flow rate.

The following data is known:

- the flue gas flow from a stack is measured at  $30 \text{ Nm}^3/\text{sec}$ ;
- the measured concentration of benzene in the flue gas is  $0.01 \text{ mg}/\text{Nm}^3$ ; and
- the stack operates 24 hours per day, for 300 days per year.

First of all, the number of seconds per year the stack is emitting is determined:

$$\begin{aligned}\text{No. seconds/year} &= (3600\text{sec}/\text{hour}) * (24\text{hours}/\text{day}) * (300\text{days}/\text{year}) \\ &= 2.6 * 10^7 \text{ seconds/year}\end{aligned}$$

Using this data, the emission is derived as follows:

$$\begin{aligned}\text{Emission} &= (30\text{Nm}^3/\text{sec}) * (0.01\text{mg}/\text{Nm}^3) * (2.6 * 10^7 \text{ sec}/\text{year}) \\ &= 7.8 \text{ kg of benzene per year.}\end{aligned}$$

### Example 4

If the concentration and flue gas flows are measured under different conditions, then additional calculations are required. For example, the following data is known:

- the flue gas flow from a stack is measured at  $100 \text{ acm}/\text{sec}$ ;
- the measured concentration of benzene in the flue is  $0.01 \text{ mg}/\text{Nm}^3$ ;
- the stack operates 24 hours per day for 300 days per year; and
- the conditions at the stack tip are approximately  $150^\circ\text{C}$  and 1 atm.

Using the actual stack data, the 'actual' flue gas flow can be converted to a normalised flow using a ratio of temperatures. Note however that the temperatures must be presented using the absolute temperature scale of Kelvin (ie  $C = 273 \text{ K}$ ). The conversion is then performed as follows (noting that the actual stack conditions are  $150 + 273 = 423 \text{ K}$ ):

$$\begin{aligned}\text{Flue gas (Nm}^3/\text{sec)} &= 100 \text{ acm}/\text{sec} * (273/423) \\ &= 64.5 \text{ Nm}^3/\text{sec}\end{aligned}$$

The emission rate is then derived using the same methodology as outlined in Example 3:

$$\begin{aligned}\text{Emission} &= (0.01 \text{ mg}/\text{Nm}^3) * (64.5 \text{ Nm}^3/\text{sec}) * (2.6 * 10^7 \text{ sec}/\text{year}) \\ &= 16.8 \text{ kg of benzene per year.}\end{aligned}$$

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## 8.0 RELEASES TO WATER

It is important to recognise that, under the NPI, the following are classed as transfers and are not required to be reported (NEPM, Clause 3(3)).

- Discharge of substances to sewer;
- Deposit of substances into landfill; and
- Removal of substances from a facility for destruction, treatment, recycling, reprocessing, recovery, or purification.

Therefore, the first stage in characterising releases to water is to identify those releases that are classed as transfers under the NPI. These releases are not required to be reported under the NPI. Other releases (eg discharges to surface water bodies such as streams and rivers) are required to be reported.

Discharges to water are highly process and site-specific. As a consequence, most facilities perform some monitoring to characterise these releases. While the NPI does not require facilities to conduct monitoring to characterise releases, it is likely that most facilities that discharge to water will have at least some monitoring data that can be used to assist in the characterisation of emissions. Examples to illustrate the application for monitoring data to the calculation of emissions are provided below.

Where no monitoring information is available, guidance on the characterisation of process wastewater releases is provided in *Emission Estimation Technique Manual for Sewage and Wastewater Treatment*.

### Examples

The following two examples will show how emissions can be estimated from point source discharges. Example 5 is relevant for wastewater streams that have a relatively constant daily flow rate, and where the measured concentration of the relevant compound in the stream does not vary greatly. Example 6 is relevant for streams that have more variable flow rates and composition (eg stormwater).

### Example 5

The following information is known regarding the wastewater stream:

- the wastewater stream contains an average acetaldehyde concentration of 500 mg/L;
- the stream is sent to an on-site wastewater treatment plant at a rate of 5 L/minute;
- the stream leaving the plant contains 25 milligrams/L of acetaldehyde (and is discharged to a local water body); and
- the plant operates 24 hours per day for 330 days per year.

Using the data above, determine the quantity of acetaldehyde released from the wastewater treatment plant.

*STEP 1: Determine the annual quantity of wastewater discharged*

$$\begin{aligned}\text{Volume} &= (5 \text{ L/min}) * (60 \text{ min/hour}) * (24 \text{ hour/day}) * (330 \text{ days/year}) \\ &= 2.4 \text{ million L/year}\end{aligned}$$

*STEP 2: Determine the quantity of acetaldehyde exiting the plant*

$$\begin{aligned}\text{Quantity (OUT)} &= (2.4 \text{ million L/year}) * (25 \text{ mg/L}) \\ &= 60 \text{ kg/year}\end{aligned}$$

Therefore, based on these calculations, 60 kg/year of acetaldehyde is discharged from the plant annually (and is required to be reported under the NPI, because the discharge is to a water body).



### Example 6

This example is a little more complex than the previous one, in that it requires the analysis of all monitoring data collated in a year, from which an average can be derived. In this example, samples are taken fortnightly to measure the discharge flow from a site, as well as chromium levels in the discharge. The data collected over a single year are presented in Table 1 below.

The daily release is derived by multiplying the daily flow rate by the measured level of chromium. The annual release can be determined by combining the average daily release shown in the table above, by the number of days the wastewater treatment plant discharges per year.

For the purposes of this example, the plant is assumed to be operational for 300 days per year. Therefore, the annual emission estimate is derived as follows:

$$\begin{aligned}\text{Annual release} &= (1.17 \text{ kg/day}) * (300 \text{ days/year}) \\ &= 351 \text{ kg.}\end{aligned}$$

Thus, it is estimated that 351 kg of chromium is released from the site annually.

**Table 1. Annual Measurement Data**

Measured Flow (10 <sup>6</sup> L/day)	Chromium (µg/L)	Daily Release (kg)
1.660	918	1.52
1.576	700	1.10
1.668	815	1.36
1.760	683	1.20
1.456	787	1.15
1.360	840	1.14
1.828	865	1.58
1.696	643	1.09
1.852	958	1.77
1.656	681	1.13
1.904	680	1.29
1.724	628	1.08
1.476	807	1.19
1.568	729	1.14
1.292	964	1.25
1.208	722	0.87
1.432	566	0.81
1.288	510	0.66
1.320	630	0.83
1.288	630	0.81
1.632	652	1.06
1.768	649	1.15
1.424	695	0.99
1.560	758	1.18
1.692	658	1.11
1.948	970	1.89
	<b>AVERAGE</b>	<b>1.17</b>

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## 9.0 RELEASES TO LAND

Under the NPI, facilities are required to report on their releases to land. The NPI Implementation Working Group has defined emissions to land:

*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 the receipt of NPI-listed substances, such receiving facilities are to be operating in accordance with any applicable State or Territory government requirements.*

Hence, substances sent off-site for destruction, treatment, recycling, reprocessing, recovery, or purification are not required to be reported.

Release to water courses however, must be reported as must any spills that are not contained by purpose built receiving facilities.

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

- groundwater monitoring;
- spills; and
- on-site disposal.

### 9.1 Groundwater Monitoring

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

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

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## 9.2 Spills

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

Unless the spilled material is routed to a secure containment facility, the quantity of material spilled, less any material collected, is required to be reported. In practical terms, a log of spills could be maintained detailing the quantities spilled, and the composition of the spill (in particular, the quantities of NPI substances spilled). This log could then form the basic information required to meet NPI reporting requirements.

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

$$E_i = 1.2 * 10^{-10} (M(p_i^o)/T) u^{0.78} x^{0.89} y \quad (6)$$

Where:

- $E_i$  = evaporation rate of substance "i" (g/s)
- $u$  = wind speed over the surface of the spill (cm/s)
- $x$  = downwind dimension (cm)
- $y$  = crosswind dimension (cm)
- $M$  = molecular weight (from Perry's, or other standard chemical engineering references)
- $p_i^o$  = vapour pressure of substance "i" at spill temperature T (dyne/cm<sup>2</sup> = 0.0001 kPa)
- $T$  = temperature (K)

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

$$ER_{LAND,i} = Q_{ty_{SPILL}} - ((time) * (E_i)) - \text{amount collected or removed} \quad (7)$$

Where:

- $ER_{LAND,i}$  = The emission to the land of compound "i"
- $Q_{ty_{SPILL}}$  = The quantity of compound in the liquid spilled
- $E_i$  = The loss through evaporation of substance "i" as estimated using the Equation 6 above.
- Time = The time period between when the liquid was initially spilled and eventual clean up.

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### 9.3 On-Site Disposal

Facilities with on-site disposal of wastes will need to consider the information presented in Section 9.0 to determine whether the disposal is classed as a transfer or as a release to land under the NPI (if there is a question as to whether on-site disposal is an emission or a transfer, you may need to clarify this matter with your local environmental authority). If the disposal is not a transfer, reporting will be required under the NPI. In a similar manner to spills, the most effective EET would be to maintain a record of all such disposal to land and, in particular, the amount of NPI substances contained in the material disposed of in such a manner.

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## 10.0 REFERENCES

1. The following Emission Estimation Technique Manuals referred to in this Manual can be obtained from Environment Australia:

Emission Estimation Manual for Combustion in Boilers  
Emission Estimation Manual for Petroleum Refining  
Emission Estimation Manual for Fuel and Organic Liquid Storage  
Emission Estimation Manual for Alumina Refining  
Emission Estimation Manual for Sewage and Wastewater Treatment

2. USEPA TANKS 3.0 can be obtained through USEPA's home page, the address of which is [www.epa.gov](http://www.epa.gov).
3. USEPA WATER 8.0 can be obtained through USEPA's home page, the address of which is [www.epa.gov](http://www.epa.gov).
4. Perry, R.H., Green, D.W., Maloney J.O. (1997), 'Perry's Chemical Engineers Handbook – Seventh Edition', McGraw Hill, USA.