



**National Pollutant Inventory**

# **Emission Estimation Technique Manual**

**for**

**Urea Manufacturing**

*First published in June 1999*

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**EMISSION ESTIMATION TECHNIQUES  
FOR  
UREA MANUFACTURING**

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## UREA MANUFACTURING

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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 urea manufacturing.

Urea manufacturing activities covered by this Manual refers to the manufacturing of urea for fertiliser mixtures (prills or granules), animal feed supplements, plastics, adhesives, and other uses.

EET MANUAL:            Urea Manufacturing

HANDBOOK:            Fertiliser Manufacturing

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This Manual was drafted by the NPI Unit of the Queensland Department of Environment and Heritage on behalf of the Commonwealth Government. It has been developed through a process of national consultation involving State and Territory environment authorities and key industry stakeholders.

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## 2.0 Processes and Emissions

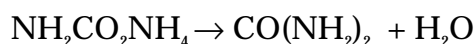
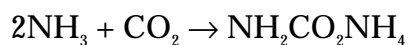
The following section presents a brief description of the urea manufacturing industry and identifies likely sources of emissions of NPI-listed substances.

### 2.1 Process Description

Urea [CO(NH<sub>2</sub>)<sub>2</sub>] is marketed as a solution or in solid form. Most urea solution produced is used in fertiliser mixtures, with a small amount going to animal feed supplements. Most solids are produced as prills or granules, for use as fertiliser or protein supplement in animal feed, and in the plastics industry for urea formaldehyde adhesive and other products.

Urea is produced by reacting carbon dioxide (co-produced with ammonia in the Haber Bosch process) with ammonia. This process involves a combination of up to six major unit operations. These operations, illustrated by the flow diagram in Figure 1, are solution synthesis, solution concentration, solids formation, solids cooling, solids screening, and bagging, and/or bulk shipping. The combination of these processing steps is determined by the desired end products.

In the solution synthesis operation, ammonia (NH<sub>3</sub>) and carbon dioxide (CO<sub>2</sub>) are reacted to form ammonium carbamate (NH<sub>2</sub>CO<sub>2</sub>NH<sub>4</sub>). The carbamate is then dehydrated to yield 70 to 77 percent aqueous urea solution. These reactions are as follows:



The urea solution can be used as an ingredient of nitrogen solution fertilisers, or it can be concentrated further to produce urea.

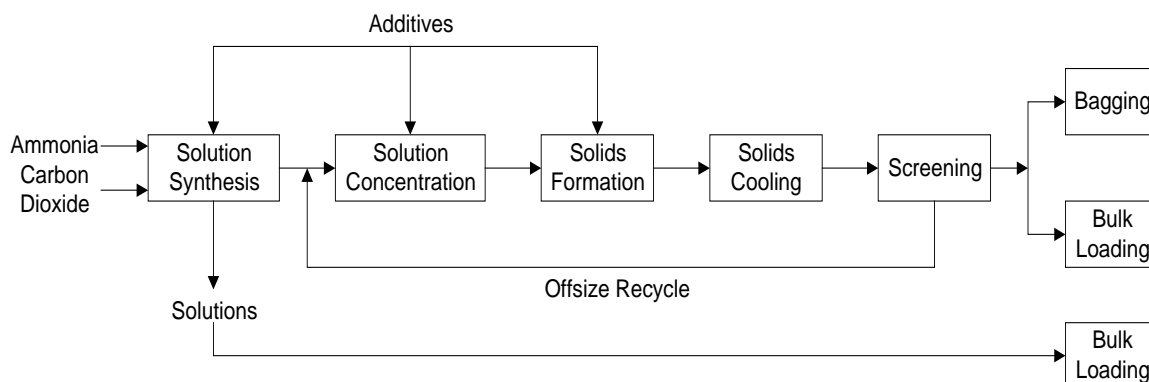
The three methods of concentrating the urea solution are vacuum concentration, crystallisation, and atmospheric evaporation. The method chosen depends upon the level of biuret (NH<sub>2</sub>CONHCONH<sub>2</sub>) impurity allowable in the end product. The most common method of solution concentration is evaporation.

The concentration process produces *melt* for solids formation. Urea solids are produced from the urea *melt* by two basic methods: prilling and granulation. Prilling is a process by which solid particles are produced from the molten urea that is sprayed from the top of a prill tower. As the droplets fall through a countercurrent air flow, they cool and solidify into nearly spherical particles. There are two types of towers used to produce prilled urea: fluidised bed and non-fluidised bed. The major difference is that a separate solids-cooling operation may be required to produce agricultural grade prills in a non-fluidised bed prill tower. **Error! Not a valid bookmark self-reference.** illustrates the prilling process.

Currently, all urea is produced in Australia by prilling although plans are well advanced to convert all production over to granulated product within the next five years. Granular urea is generally stronger than prilled urea, both in crushing strength and abrasion resistance, and is preferred by industry for both agricultural and industrial application.

Granulation methods include; drum, fluidised bed and pan granulation. In drum granulation, solids are built up in layers on seed granules placed in a rotating drum granulator/cooler approximately 4.3 metres in diameter. Pan granulators also form the product in a layering process, but different equipment is used.

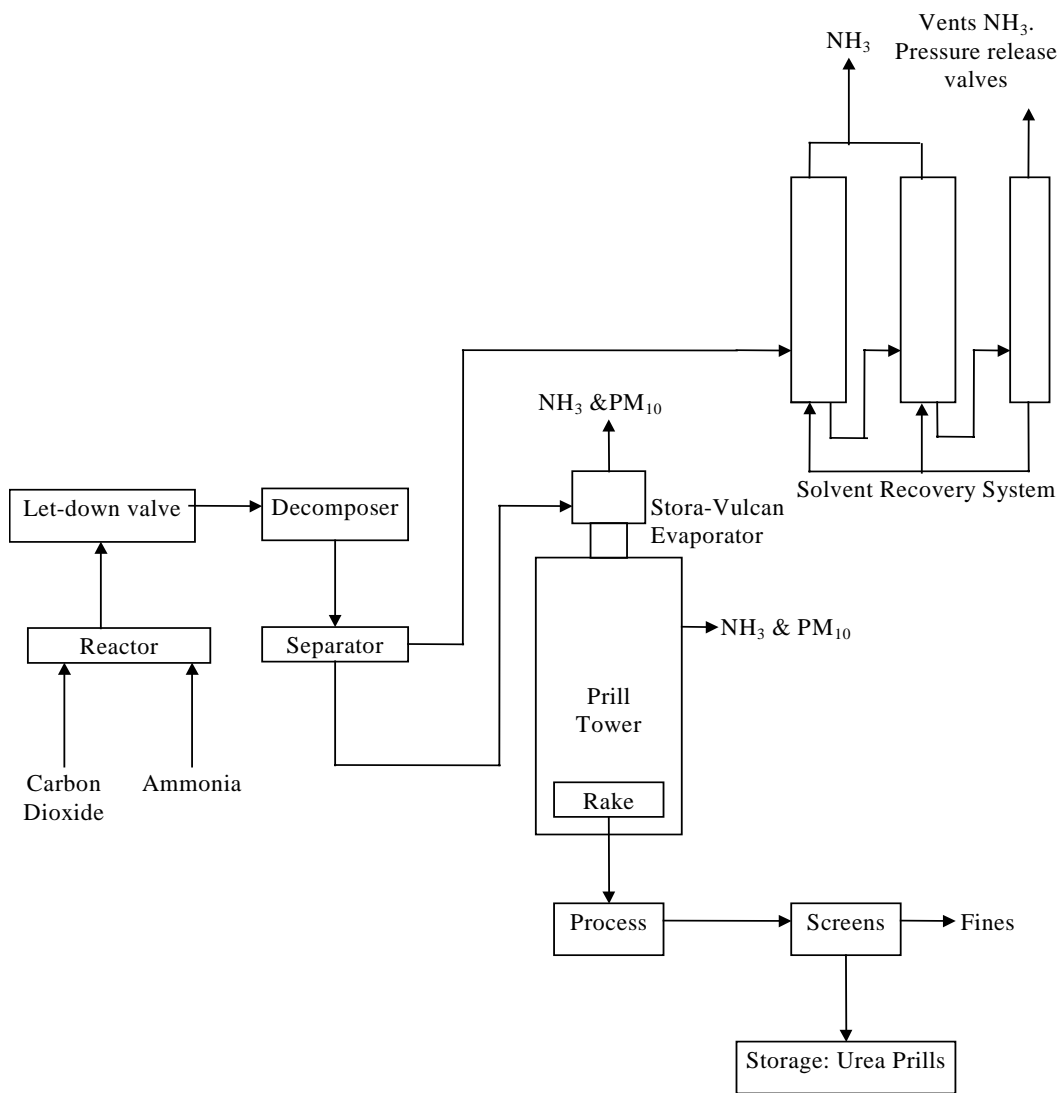
The solids cooling operation is generally accomplished during solids formation, but for pan granulation processes, and for some agricultural grade prills, some supplementary cooling is provided by auxiliary rotary drums. The solids screening operation removes offsize product from solid urea. The offsize material may be returned to the process in the solid phase or be redissolved in water and returned to the solution concentration phase.



**Figure 1 - Major Urea Manufacturing Operation**

Source: USEPA, AP-42, Section 8.2, 1993

Clay coatings are used in the urea industry to reduce product caking and urea dust formation. The coating also reduces the nitrogen content of the product. The use of clay coating has diminished considerably in recent years, being replaced by injection of formaldehyde additives into the liquid or molten urea before solids formation. Formaldehyde reacts with urea to form methylenediurea, which is the conditioning agent. Additives reduce solids caking during storage and urea dust formation during transport and handling.



**Figure 2 - Urea Manufacturing Using a Prill Tower**

Source: Incitec, Gibson Island Works, 1998

Potential emission sources of particulate matter (PM<sub>10</sub>) from the urea manufacturing process represented in Figure 2 are the Prill Tower.

Potential sources of ammonia (NH<sub>3</sub>) from the urea manufacturing process represented in Figure 2 are the prill tower and the Stora-Vulcan Evaporator. Minor emission sources are leaks from pressure release valves and vents including the process water stripper vent, CO<sub>2</sub> vent and ammonia absorber vent.

## 2.2 Emissions to Air

Air emissions may be categorised as either fugitive or point source emissions.

### Fugitive Emissions

These are emissions that are not released through a vent or stack. Examples of fugitive emissions include dust from stockpiles, volatilisation of vapour from vats, open vessels, or spills and materials handling. Emissions emanating from ridgeline roof-vents, louvres, and open doors of a building as well as equipment leaks, and leaks from valves and flanges are also examples of fugitive emissions.

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## Point Source Emissions

These emissions are exhausted into a vent or stack and emitted through a single point source into the atmosphere. Table 1 highlights common air emissions of NPI-listed substances from urea manufacturing processes.

### 2.3 Emissions to Water

Emissions of substances to water can be categorised as discharges to:

- Surface waters (eg. lakes, rivers, dams, and estuaries);
- Coastal or marine waters; and
- Stormwater.

Because of the significant environmental hazards posed by emitting toxic substances to water, most facilities emitting NPI-listed substances to waterways are required by their relevant State or Territory environment agency to closely monitor and measure these emissions. This existing sampling data can be used to calculate annual emissions.

If no wastewater monitoring data exists, emissions to process water can be calculated based on a mass balance or using emission factors.

The discharge of listed substances to a sewer or tailings dam does not require reporting to the NPI. However, leakage and other emissions (including dust) from a tailings storage facility are reportable. (See also Section Three of *The NPI Guide*.)

**Table 1 - Emissions of NPI-Listed Substances from Urea Manufacturing Processes**

Substance	Emission Media		
	To Atmosphere	To Water	Via Solid Waste
Ammonia	X	X	X
Formaldehyde	X	X	X
Methanol	X	X	X
Total Nitrogen		X	
Particulate Matter (PM <sub>10</sub> )	X		
Volatile Organic Compounds (VOCs)	X		

Source: Queensland Department of Environment and Heritage, 1998

### 2.4 Emissions to Land

Emissions of substances to land on-site include solid wastes, slurries, and sediments. Emissions arising from spills, leaks, and storage and distribution of materials containing listed substances may also occur to land. These emission sources can be broadly categorised as:

- surface impoundments of liquids and slurries; and
- unintentional leaks and spills.



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### 3.0 Emission Estimation Techniques

This section presents equations and examples of calculations for estimating emissions of particulate matter (PM<sub>10</sub>), speciated organics (formaldehyde and methanol), and inorganic substances (ammonia, total nitrogen) from Urea Manufacturing processes.

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 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 emission estimation techniques that are not outlined in this Handbook, your data will also be displayed as being of 'acceptable reliability'.

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

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

In general, direct measurement is the most accurate method for characterising emissions and, where available, such data should be used in preference to other EETs presented in this Manual. However, additional direct measurement is not required under the NPI Measure. Direct monitoring may be undertaken as an element of other EETs.

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.

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.

Table 2 lists the variables and symbols used throughout this Manual and indicates the level of information required in estimating emissions of NPI-listed substances from urea manufacturing using the emission estimation techniques illustrated.

**Table 2 - List of Variables and Symbols**

Variable	Symbol	Units
Annual emissions of pollutant i	$E_{kpy,i}$	kg/yr
Hourly emissions of pollutant i	$E_i$	kg/hr or kg/hr/source
Substance entering the process	$Q_{in}$	kg/yr
Substance leaving the process (as an emission, transfer, or in product)	$Q_{out}$	kg/yr
Filter catch	$C_f$	grams
Moisture content	$moist_R$	%
Overall control efficiency	CE	%
Average weight fraction of pollutant i	$WF_i$	%
Number of pieces of applicable equipment type	N	unitless
Volume of sample at standard temperature and pressure	$V_{m,STP}$	$m^3$
Volume of mixture containing pollutant i	$M_i$	kg/yr
Hourly volume of wastewater	$V_w$	L/hr
Stack gas flow rate (actual)	$Q_a$	$m^3/s$
Concentration of pollutant i	$C_i$	ppmv or $g/m^3$ or mg/L or mg/kg
Molecular weight of pollutant i	$MW_i$	kg/kg-mole
Stack gas volumetric flow rate (dry)	$Q_d$	$m^3/sec$
Operating hours	OpHrs	hr/yr
Emission factor for pollutant i	$EF_i$	kg/tonne or kg/units
Activity factor	A	tonnes/hr or units/hr
Temperature	T	$^{\circ}C$

Source: Queensland Department of Environment and Heritage, 1998.

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### 3.1 Using Sampling or Direct Measurement

#### 3.1.1 For Emissions to Atmosphere

##### ***Particulate Matter (PM<sub>10</sub>) Emissions***

Stack sampling test reports often provide emissions data in terms of kg/hr or g/m<sup>3</sup> (dry standard). Annual emissions for NPI reporting can be calculated from this data. Stack tests for NPI reporting should be performed under representative or normal operating conditions. Some tests undertaken for a State or Territory license condition may require that the test be taken under maximum emissions rating, where emissions are likely to be higher than when operating under normal operating conditions. Data from these tests may need to be *scaled back* for NPI reporting purposes.

An example summary of a test method is shown in Table 3. 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 m<sup>3</sup>. The filter weight gain is determined gravimetrically and divided by the volume of gas sampled (as shown in Equation 1) to determine the PM concentration in grams per m<sup>3</sup>.

Pollutant concentration is then multiplied by the volumetric flow rate to determine the emission rate in kilograms per hour, as shown in Equation 2. Example 1 illustrates the application of Equation 1 and Equation 2.

##### **Equation 1**

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

where:

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

##### **Equation 2**

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

where:

$$\begin{aligned} E_{PM} &= \text{hourly emissions of PM, kg/hr} \\ C_{PM} &= \text{concentration of PM or gram loading, g/m}^3 \\ Q_d &= \text{stack gas volumetric flow rate, m}^3/\text{s} \\ 3.6 &= \text{3600 seconds per hour multiplied by 0.001 kilograms per gram} \\ T &= \text{temperature of the gas sample, } ^\circ\text{C} \\ 273 &= \text{273K (0 } ^\circ\text{C)} \end{aligned}$$

**Table 3 - Stack Sample Test Results**

Parameter	Symbol	Test 1	Test 2	Test 3
Total sampling time (sec)		7 200	7 200	7 200
Moisture collected (g)	$g_{\text{MOIST}}$	395.6	372.6	341.4
Filter catch (g)	$C_f$	0.0851	0.0449	0.0625
Average sampling rate ( $\text{m}^3/\text{s}$ )		$1.67 * 10^{-4}$	$1.67 * 10^{-4}$	$1.67 * 10^{-4}$
Standard metered volume ( $\text{m}^3$ )	$V_{\text{m,STP}}$	1.185	1.160	1.163
Volumetric flow rate ( $\text{m}^3/\text{s}$ ), dry	$Q_d$	8.48	8.43	8.45
Concentration of particulate ( $\text{g}/\text{m}^3$ )	$C_{\text{PM}}$	0.0718	0.0387	0.0537

Source: Queensland Department of Environment and Heritage, 1998

**Example 1 - Estimating Particulate Matter ( $\text{PM}_{10}$ ) Emissions**

PM emissions have been calculated using Equation 1 and Equation 2 and the stack sampling data for Test 1 (presented in Table 3, and an exhaust gas temperature of  $150^\circ\text{C}$  ( $423\text{K}$ )). This is shown below:

$$\begin{aligned}
 C_{\text{PM}} &= C_f / V_{\text{m,STP}} \\
 &= 0.085 / 1.185 \\
 &= 0.072 \text{ g}/\text{m}^3 \\
 E_{\text{PM}} &= C_{\text{PM}} * Q_d * 3.6 * [273 / 273 + T] \\
 &= 0.072 * 8.48 * 3.6 * (273/423\text{K}) \\
 &= 1.42 \text{ kg}/\text{hr}
 \end{aligned}$$

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

**Equation 3**

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

where:

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

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

To calculate moisture content use Equation 4.

#### Equation 4

Moisture percentage = 100 % \* weight of water vapour per specific volume of stack gas/ total weight of the stack gas in that volume.

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

where

$moist_R$  = moisture content, %  
 $g_{MOIST}$  = moisture collected, g  
 $V_{m,STP}$  = metered volume of sample at STP, m<sup>3</sup>  
 $\rho_{STP}$  = dry density of stack gas sample, kg/m<sup>3</sup> at STP  
 {if the density is not known a default value of 1.62 kg/m<sup>3</sup> may be used. This assumes a dry gas composition of 50% air, 50% CO<sub>2</sub>}

#### Example 2 - Calculating Moisture Percentage

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

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

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

#### Gaseous Emissions

Sampling test methods can be used to estimate inorganic pollutant emission rates from urea manufacturing processes. Airflow rates can be determined from flow rate metres or from pressure drops across a critical orifice.

Sampling test reports often provide chemical concentration data in parts per million by volume (ppmv).

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If the concentration is known, an hourly emission rate can be determined using Equation 5:

**Equation 5**

$$E_i = (C_i * MW_i * Q_d * 3\,600) / [22.4 * \{(T + 273)/273\} * 10^6]$$

where:

$E_i$	=	total emissions of pollutant i, kg/hr
$C_i$	=	concentration of pollutant i, ppmv
$MW_i$	=	molecular weight of pollutant i, kg/kg-mole
$Q_d$	=	stack gas volumetric flow rate, m <sup>3</sup> /s
22.4	=	volume occupied by 1 mole of ideal gas at standard temperature and pressure (0°C and 101.3 kPa), m <sup>3</sup> /kg-mole
3 600	=	conversion factor, s/hr

Emissions in kilograms per year can be calculated by multiplying the average hourly emission rate (kg/hr) from Equation 5 by the number of operating hours (shown in Equation 6 below) or by multiplying an average emission factor (kg/L) by the total annual amount of material used (L).

**Equation 6**

$$E_{kpy,i} = E_i * OpHrs$$

where:

$E_{kpy,i}$	=	annual emissions in kilograms per year of pollutant i, kg/yr
$E_i$	=	hourly emissions in kilograms per hour of pollutant i, kg/hr
OpHrs	=	annual operating hours in hours per year, hr/yr

Concentration data obtained from source testing may come in a variety of units, including parts per million volume (ppmv), or grams per cubic metre (g/m<sup>3</sup>), and in a variety of conditions, such as wet, dry, or excess O<sub>2</sub>. This may require conversion of concentration data to consistent units for compatibility with the equations given above. Example 3 illustrates the use of Equation 5 and Equation 6.

### Example 3 - Estimating Ammonia Emissions to Atmosphere

This example shows how annual ammonia (NH<sub>3</sub>) emissions can be calculated using the data obtained from a stack or other point-source emission point from a plant manufacturing urea. Using a known ammonia concentration and an exhaust gas temperature of 150°C (423K), hourly emissions are calculated using Equation 5, and annual emissions are calculated using Equation 6.

Given:

$$\begin{array}{llll} C_i & = & 15.4 \text{ ppmv} & MW_i & = & 17 \text{ kg/kg-mole of ammonia} \\ Q_d & = & 8.48 \text{ m}^3/\text{sec} & \text{OpHrs} & = & 1\,760 \text{ hr/yr} \\ T & = & 150 \text{ }^\circ\text{C} & & & \end{array}$$

Hourly emissions of NH<sub>3</sub> are calculated using Equation 5:

$$\begin{aligned} E_{\text{NH}_3} &= (C_i * MW_i * Q * 3600) / [22.4 * \{(T + 273)/273\} * 10^6] \\ &= (15.4 * 17 * 8.48 * 3600) / [22.4 * (423/273) * 10^6] \\ &= 7\,992\,230 / 34\,707\,692 \\ &= 2.303 * 10^{-1} \text{ kg/hr} \end{aligned}$$

Annual emissions of NH<sub>3</sub> are calculated using Equation 6:

$$\begin{aligned} E_{\text{kpy,NH}_3} &= E_i * \text{OpHrs} \\ &= 2.303 * 10^{-1} * 1760 \\ &= 405.33 \text{ kg/yr} \end{aligned}$$

#### 3.1.2 For Emissions to Water

Because of the significant environmental hazards posed by emitting toxic substances to water, most facilities emitting NPI-listed substances to waterways are required by their relevant State or Territory environment agency to closely monitor and measure these emissions. This existing monitoring data can be used to calculate annual emissions by the use of Equation 7.

#### Equation 7

$$E_{\text{kpy},i} = C_i * V_w * \text{OpHrs} / 1\,000\,000$$

where:

$$\begin{array}{ll} E_{\text{kpy},i} & = \text{emissions of pollutant } i, \text{ kg/yr} \\ C_i & = \text{concentration of pollutant } i \text{ in wastewater, mg/L} \\ V_w & = \text{hourly volume of wastewater, L/hr} \\ \text{OpHrs} & = \text{operating hours per year for which data} \\ & \text{apply, hr/yr} \\ 1\,000\,000 & = \text{conversion factor, mg/kg} \end{array}$$

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In applying Equation 7 to water emission calculations, monitoring data should be averaged and only representative concentrations used in emission calculations.

### 3.2 Using Emission Factors

An emission factor is a tool that is 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, for example, kilograms of ammonia emitted per tonne of urea. Emission factors for PM<sub>10</sub>, ammonia, and total nitrogen to water are listed in Table 4 and Table 5.

Equation 8 is used to estimate a facility's emissions from application of emission factors.

#### Equation 8

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

where:

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

Emission control technologies, such as electrostatic precipitators, fabric filters or baghouses, and wet scrubbers, are commonly installed to reduce the concentration of particulates in process off-gases before stack emission. Where such emission abatement equipment has been installed, and where emission factors from uncontrolled sources have been used in emission estimation, the collection efficiency of the abatement equipment needs to be considered.

With regards to emission controls for PM<sub>10</sub>, in the absence of measured data, or knowledge of the collection efficiency for a particular piece of equipment, an efficiency of 90% should be used in the emission factor equation to calculate actual mass emissions. This default should only be used if there is no other available control efficiency.



Application of Equation 8 is illustrated by Example 4.

#### Example 4 - Using Emission Factors

Table 4 shows that 1.46 kg of ammonia are emitted for each tonne of urea produced from an uncontrolled prilling process producing agricultural grade urea. The plant operator estimates that reduction of melt temperature reduces ammonia emissions by 25 percent. It is assumed that the urea manufacturer operates for 1 500 hours per year.

$$\begin{aligned}
 EF_{\text{NH}_3} &= 1.46 \text{ kg/t} \\
 A &= 50 \text{ t/hr} \\
 \text{OpHrs} &= 1\,500 \text{ hr/yr} \\
 E_{\text{KPY,NH}_3} &= A * \text{OpHrs} * EF_i * [1 - (CE_i/100)] \\
 &= 50 * 1\,500 * 1.46 * [1 - (25/100)] \\
 &= 82\,125 \text{ kg/yr}
 \end{aligned}$$

**Table 4 - Emission Factors for Particulate Matter (PM<sub>10</sub>) and Ammonia (NH<sub>3</sub>)**

Type of Operation	PM <sub>10</sub> <sup>a</sup>		Ammonia		Emission Factor Rating
	Uncontrolled kg/tonne <sup>b</sup>	Controlled kg/tonne	Uncontrolled kg/tonne	Controlled kg/tonne	
Solution formation and concentration	ND	ND	9.23	ND	A
Nonfluidised bed prilling					
<i>Agricultural grade</i>	1.71	3.42	0.43	ND	U
<i>Feed grade</i>	1.53	ND	ND	ND	A
Fluidised bed prilling					
<i>Agricultural grade</i>	1.86	0.234	1.46	ND	A
<i>Feed grade</i>	0.432	0.0576	2.07	1.04	A
Drum granulation	ND	ND	1.07	ND	A
Rotary drum cooler	0.2723	0.007	0.0256	ND	A
Bagging	ND	ND	NA	NA	E

Source: Adapted from USEPA, AP-42 section 8.2, 1993 and EFMA, *Production of Urea*, 1995.

<sup>a</sup> PM<sub>10</sub> = particulate matter of aerodynamic diameter less than or equal to 10 micrometres.

ND = No data.

NA = not applicable.

<sup>b</sup> Factor units are kg of substance emitted per tonne of urea produced.

**Table 5 - Emission Factors for Total Nitrogen (N) to Water<sup>a</sup>**

Emission Source	Emission Factor kg/t <sup>b</sup>	Emission Factor Rating
From Existing Plants	0.128	U
From New Plants	0.00228	U

Source: EFMA, *Production of Urea*, 1995

<sup>a</sup> Emissions of total nitrogen only need to be reported for emissions to water. Emissions to sewer or wastewater treatment facilities do not require NPI reporting.

<sup>b</sup> Factor units are kg of total nitrogen emitted per tonne of urea produced.

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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. You are required to have the emission factor reviewed and approved by State or Territory environment agencies prior to its use for NPI estimations.

### 3.3 Using Mass Balance

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

Mass balance calculations for estimating emissions to air of NPI-listed substances can be represented conceptually by Equation 9.

#### Equation 9

$$E_{kpy,i} = \text{Amount in}_i - \text{Amount out}_i$$

where:

$$\begin{aligned} E_{kpy,i} &= \text{emissions of pollutant } i, \text{ kg/yr} \\ \text{Amount in}_i &= \text{amount of pollutant } i \text{ entering the process, kg/yr} \\ \text{Amount out}_i &= \text{amount of pollutant } i \text{ leaving the process as a waste} \\ &\quad \text{stream, article or product, kg/yr} \end{aligned}$$

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

The amount of a particular substance entering or leaving a facility is often mixed within a solution as a formulation component or as a trace element within the raw material. To determine the total weight of the substance entering or leaving the process, the concentration of the substance within the material is required. Using this concentration data, Equation 10 can be applied as a practical extension of Equation 9.

### Equation 10

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

where:

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

Example 4 illustrates the application of Equation 10

#### Example 4 - Using a Mass Balance for NH<sub>3</sub> Emissions

This example shows how NH<sub>3</sub> emissions to air may be calculated using Equation 10 within a urea manufacturing process.

A facility uses 100 000 tonnes of NH<sub>3</sub> per year, which would theoretically produce 176 471 tonnes of urea per year. The facility actually produces 175 000 tonnes of urea, which would only require 99 167 tonnes of NH<sub>3</sub>. The facility operates 340 days per year. Assuming that the only sources of loss are to wastewater and air, the following information is provided from water testing:

Volume of wastewater per year: 100kL/day = (100 \* 10<sup>3</sup>) L/day = (100 \* 10<sup>3</sup> \* 340) L / y

Concentration of NH<sub>3</sub> in water: 2000mg/L

Therefore, the total emissions to both air and wastewater can be calculated using the below equation.

$$\begin{aligned} E_{kpy,NH_3} &= [Q_{in} * C_{in} - Q_{pr} * C_{pr} - Q_{rec} * C_{rec} - Q_{waste} * C_{waste}] / 10^6 \\ &= [100\ 000\ 000 - 99\ 167\ 000 - ((100 * 10^3 * 340 * 2\ 000) / 10^6)] \\ &= 83\ 3000 - 68\ 000 \\ &= 765\ 000\ \text{kg/yr} \end{aligned}$$

Where a facility uses a listed mineral acid or base, with this acid or base being effectively neutralised in use or during wastewater treatment (to a pH of 6 to 8, as required by most State and Territory effluent standards), no emission quantities should be reported. If the acid or base is itself transformed into another listed substance, however, the quantity of this substance coincidentally produced must be determined to assess if a threshold value has been reached. For example, sulfuric acid often yields hydrogen sulfide in effluent streams, which is a listed substance.

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Wastewater treatment may transport the reportable chemical to a sludge. Facilities are often required to obtain data on the concentration of metals or other substances in sludges as part of their licensing requirement and this data can be used to calculate the emissions as kilograms of sludge multiplied by the concentrations of the substance in the sludge. Alternatively, the loss in the sludge can be estimated by Equation (9). Although listed substances in sludges transferred off-site do not require reporting, determining this loss can assist with determining other process losses or may require reporting if the sludge is disposed on-site.

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

### 3.4 Using Engineering and Site-Specific Equations

Theoretical and complex equations or *models* can be used for estimating emissions from urea manufacturing. Inputs for theoretical equations generally fall into the following categories:

- chemical/physical properties of the material involved, such as vapour pressure and vapour molecular weight;
- operating data, such as the amount of material processed and operating hours; and
- physical characteristics and properties of the source, such as tank colour and diameter.

Use of engineering equations to estimate emissions from urea manufacturing processes is a more complex and time-consuming process than the use of emission factors. Engineering 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.

Engineering equations are suitable for estimating emissions from several chemical manufacturing processes. For example, for any process involving a transfer of a chemical species from the liquid phase to the vapour phase, the saturation or equilibrium vapour pressure and exhaust flow rate from the process can be used to establish the upper limit of emissions from that particular process. This is a conservative approach because of the assumption that the total airflow is saturated. An alternative method based on mass transfer kinetics does not assume airflow saturation and results in a lower emission rate estimate than would be obtained assuming saturation. For emissions from fugitive sources such as spills, refer to the *Emission Estimation Technique Manual for Fugitive Emissions*.

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### 3.4.1 Fugitive Emissions

Many of the engineering equations presented in this section are to be applied to estimate emissions of organic compounds. Other than using emission factors or applying the mass balance technique for estimating emissions, there is little information currently available for estimating fugitive emissions of inorganic compounds. However, in urea manufacturing, it may be necessary to estimate emissions of inorganic compounds for NPI-reporting purposes. This is particularly the case for mineral acids and ammonia in the gas/vapour phase.

Emission estimates of inorganic compounds can be obtained for urea manufacturing processes by the following methods:

- develop correlations specific to particular chemical manufacturing processes;
- use a portable monitoring instrument to obtain actual concentrations of the inorganic compounds and then apply the screening values obtained (see paragraph below) into the applicable correlation equation shown in Table 6 and Equation 11; or
- Use the emission factors from Table 7.

Screening data is collected by using a portable monitoring instrument to sample air from potential leak interfaces on individual pieces of equipment. A screening value (SV) is a measure of the concentration of leaking compounds in the ambient air that provides an indication of the leak rate from an equipment piece, and is measured in units of parts per million by volume (ppmv).

Also, surrogate measurements can be used to estimate emissions of inorganic compounds. For example, potassium iodide (KI), or a similar salt solution, is an indicator for equipment leaks from acid process lines at urea plants. Equation 11 illustrates an approach for estimating fugitive inorganic chemical emissions using data from Table 6. An example of this estimation technique is given at Example 5.

#### Equation 11

$$E_{kpy,i} = ER_i * C_i * OpHrs / 100$$

where:

$E_{kpy,i}$	=	mass emissions of pollutant i calculated from either the screening values, correlation equation, or emission factors, kg/yr
$ER_i$	=	emission rate, kg/hr/source
$C_i$	=	concentration of pollutant i in the equipment, %
$OpHrs$	=	operating hours, hr/yr

**Table 6 - Correlation Equations, Default Zero Emission Rates, and Pegged<sup>c</sup> Emission Rates for Estimating Fugitive Emissions**

Equipment Type	Default Zero Emission Rate (kg/hr/source)	Pegged Emission Rates (kg/hr/source)		Correlation Equation (kg/hr/source) <sup>a</sup>
		10 000 ppmv	100 000 ppmv	
Gas valves	$6.6 * 10^{-7}$	0.024	0.11	$LR = 1.87 * 10^{-6} * (SV)^{0.873}$
Light liquid valves	$4.9 * 10^{-7}$	0.036	0.15	$LR = 6.41 * 10^{-6} * (SV)^{0.797}$
Light liquid pumps <sup>b</sup>	$7.5 * 10^{-6}$	0.14	0.62	$LR = 1.90 * 10^{-5} * (SV)^{0.824}$
Connectors	$6.1 * 10^{-7}$	0.044	0.22	$LR = 3.05 * 10^{-6} * (SV)^{0.885}$

Source: Eastern Research Group, 1996.

LR = leak rate.

<sup>a</sup> SV is the screening value (ppmv) measured by the monitoring device. To estimate emissions, use the default zero emission rates only when the screening value (adjusted for background) equals 0.0 ppmv; otherwise use the correlation equations. If the monitoring device registers a pegged value, use the appropriate pegged emission rate.

<sup>b</sup> The emission estimates for light liquid pump seals can be applied to compressor seals, pressure relief valves, agitator seals, and heavy liquid pumps.

<sup>c</sup> When the monitoring device reads a pegged value; for example 10 ppmv for a gas valve, the pegged emission rate of 0.024 kg/hr per source would be used rather than determining the emission rate using a correlation equation, or a default zero emission rate.

### Example 5 - Calculating Fugitive Chemical Leaks

A urea plant operates a light-liquid pump on an 80 percent ammonia solution storage tank. The pump is run for 8 760 hours during the year.

#### ***For a Screening Value of zero ppmv***

$$\begin{aligned} \text{OpHrs} &= 8\,760 \text{ hr/yr} \\ \text{SV (screening value)} &= 0 \text{ ppmv} \\ \text{Default-zero emission rate} &= 7.5 * 10^{-6} \text{ kg/hr/source} \end{aligned}$$

$$\begin{aligned} \text{NH}_3 \text{ emissions} &= ER_x * C_x * \text{OpHrs} \\ &= 7.5 * 10^{-6} * (80/100) * 8\,760 \\ &= 5.26 * 10^{-2} \text{ kg/hr/source} \end{aligned}$$

#### ***For a Screening Value of 20 ppmv***

$$\begin{aligned} \text{OpHrs} &= 8\,760 \text{ hr/yr} \\ \text{SV (screening value)} &= 20 \text{ ppmv} \\ \text{NH}_3 \text{ emissions (kg/hr)} &= 1.90 * 10^{-5} (SV)^{0.824} \\ &= 1.90 * 10^{-5} (20)^{0.824} \\ &= 2.24 * 10^{-4} \text{ kg/hr} \\ \text{NH}_3 \text{ emissions (kg/yr)} &= 2.24 * 10^{-4} * 8\,760 * (80/100) \\ &= 1.57 \text{ kg NH}_3/\text{yr} \end{aligned}$$

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The average emission factor approach is commonly used to calculate emissions when site-specific screening data is unavailable. To estimate emissions using the emission factors in Table 7, the concentration in weight percent of the pollutant of interest within the equipment is needed. This is important because equipment with higher pollutant concentrations tend to have higher emission leak rates. The equipment should be grouped into *streams*, such that all equipment within a *stream* has approximately the same pollutant weight percent.

This approach for estimating emissions allows use of average emission factors in combination with unit-specific data that is relatively simple to obtain. This data includes:

- the number of each type of component in a unit (valve, connector, etc.);
- the service each component is in (gas, light liquid, or heavy liquid);
- the pollutant concentration of the stream; and
- the time period each component was in that service during the NPI reporting year.

Equation 12 can be used to estimate emissions from all of the equipment of a given equipment type in a *stream* using the emission factors from Table 7.

**Equation 12**

$$E_{kpy,i} = EF * WF_i * OpHrs * N$$

where:

- $E_{kpy,i}$  = emission rate of pollutant i from all equipment in the *stream* of a given equipment type, kg/yr
- EF = applicable average emission factor for the equipment type, kg/hr/source
- $WF_i$  = average weight fraction of pollutant i in the *stream*,
- OpHrs = annual operation hours of equipment in the *stream*, hr/yr
- N = number of pieces of the applicable equipment type in the *stream*

Example 6 illustrates the emission factor approach for Streams A and B. Note that Stream A contains water, which is not an NPI-listed substance, and that this is accounted for when total emissions are estimated from Stream A.

### Example 6 - Average Emission Factor Technique

This example shows how annual ammonia (NH<sub>3</sub>) emissions can be calculated from pump seals using the emission factors from Table 7 and Equation 12. The following data is given:

Stream ID	Equipment Count (N)	Emission Factor (kg/hr/source)	Weight Fraction	OpHrs (hr/yr)
A	15	0.0199	0.80	8.760
B	12	0.0199	1.00	4.380

$$E_{\text{kpy,NH}_3} = \text{EF} * \text{WF}_{\text{NH}_3} * \text{OpHrs} * N$$

#### Stream A

$$\begin{aligned} E_{\text{kpy,NH}_3} &= 0.0199 * 0.80 * 8\,760 * 15 \\ &= 2\,092 \text{ kg NH}_3/\text{yr} \end{aligned}$$

#### Stream B

$$\begin{aligned} E_{\text{kpy,NH}_3} &= 0.0199 * 1.00 * 4\,380 * 12 \\ &= 1\,046 \text{ kg NH}_3/\text{yr} \end{aligned}$$

**Table 7 - Emission Factors for Equipment Leaks**

Equipment Type	Service	Emission Factor (kg/hr/source)
Valves	Gas	0.00597
	Light liquid	0.00403
	Heavy liquid	0.00023
Pump seals <sup>a</sup>	Light liquid	0.0199
	Heavy liquid	0.00862
Compressor seals	Gas	0.228
Pressure relief valves	Gas	0.104
Connectors	All	0.00183
Open-ended lines	All	0.0017
Sampling connections	All	0.0150

Source: Eastern Research Group, 1996.

<sup>a</sup> The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.



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## 4.0 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 urea manufacturing facilities. The technique chosen is dependent on available data, 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 Section 3.0 of this Manual.

### 4.1 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 urea 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 the production of urea.

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.

### 4.2 Mass Balance

Calculating emissions from a urea manufacturing facility using mass balance appears to be a straightforward approach to emission estimations. However, it is likely that few Australian industries 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 often result in large deviations of total facility emissions. Because emissions from specific materials are typically below 2 percent of gross consumption, an error of only  $\pm 5$  percent in any one step of the operation can significantly skew emission estimations.

### 4.3 Engineering Calculations

Theoretical and complex equations or *models* can be used for estimating emissions from urea manufacturing processes.

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Use of emission equations to estimate emissions from urea 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.

#### **4.4 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 Section 5.0 of this Manual. 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

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## 5.0 References

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The following Emission Estimation Technique Manuals are available at the NPI Homepage and from your local environmental protection agency (see the front of the NPI Guide for details):

- Emission Estimation Technique Manual for Phosphate Manufacturing;
- Emission Estimation Technique Manual for Ammonium Sulfate Manufacturing;
- Emission Estimation Technique Manual for Synthetic Ammonia Manufacturing; and
- Emission Estimation Technique Manual for Sewage and Wastewater Treatment.