



**National Pollutant Inventory**

# **Emission Estimation Technique Manual**

**for**

## **Phosphate Manufacturing**

*First published in June 1999*

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**EMISSION ESTIMATION TECHNIQUES  
FOR  
PHOSPHATE MANUFACTURING**

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# PHOSPHATE FERTILISER 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 Phosphate Manufacturing.

EET MANUAL:            Phosphate Manufacturing

HANDBOOK:            Fertiliser Manufacturing

ANZSIC CODES :      2531

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 environmental authorities and key industry stakeholders.

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## 2.0 Processes and Emissions

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

### 2.1 Process Description

Phosphate fertilisers are classified into three groups of chemical compounds. Two of these groups are known as superphosphates and are defined by the percentage of phosphorus as phosphorus pentoxide ( $P_2O_5$ ). Normal superphosphates contain between 15 and 21 percent phosphorus as  $P_2O_5$  whereas triple superphosphate contains over 40 percent phosphorus. The remaining phosphate fertiliser group is ammonium phosphate ( $NH_4H_2PO_4$ ).

Phosphoric acid is an important industrial acid used in the manufacture of fertilisers, for the corrosion treatment of metals and in the production of inorganic phosphates, especially detergent and food grade polyphosphates.

Fertiliser grade phosphoric acid is manufactured by treating rock phosphate with excess sulfuric acid, a process that produces considerable amounts of waste calcium sulfate (gypsum). The *Inorganic Chemical Manufacturing* EET Manual contains information on phosphoric acid manufacture, associated emissions, and the techniques for estimating emissions associated with its production.

If phosphoric acid is used, either in place of, or partly as a replacement for sulfuric acid, a higher analysis phosphate fertiliser is produced called *double* and *triple* phosphate. This form of phosphate fertiliser contains more phosphorus (typically to 20 percent as phosphorus). High analysis fertiliser is therefore more economic at locations distant from place of manufacture or supply. To address this shift in demand favouring higher analysis fertiliser, certain Australian manufacturers are producing phosphoric acid to replace sulfuric acid. The weight or bulk of fertiliser required to apply the phosphorus is less than half the single strength form.

High analysis phosphates are also currently imported (especially ammonium phosphates with a high concentration of nitrogen and phosphorus) and often blended with locally produced single strength superphosphate to provide a double strength fertiliser. Single strength superphosphate is under considerable competitive pressure from high analysis forms resulting in flat and even declining demand. It generally contains only 9 percent phosphorus.

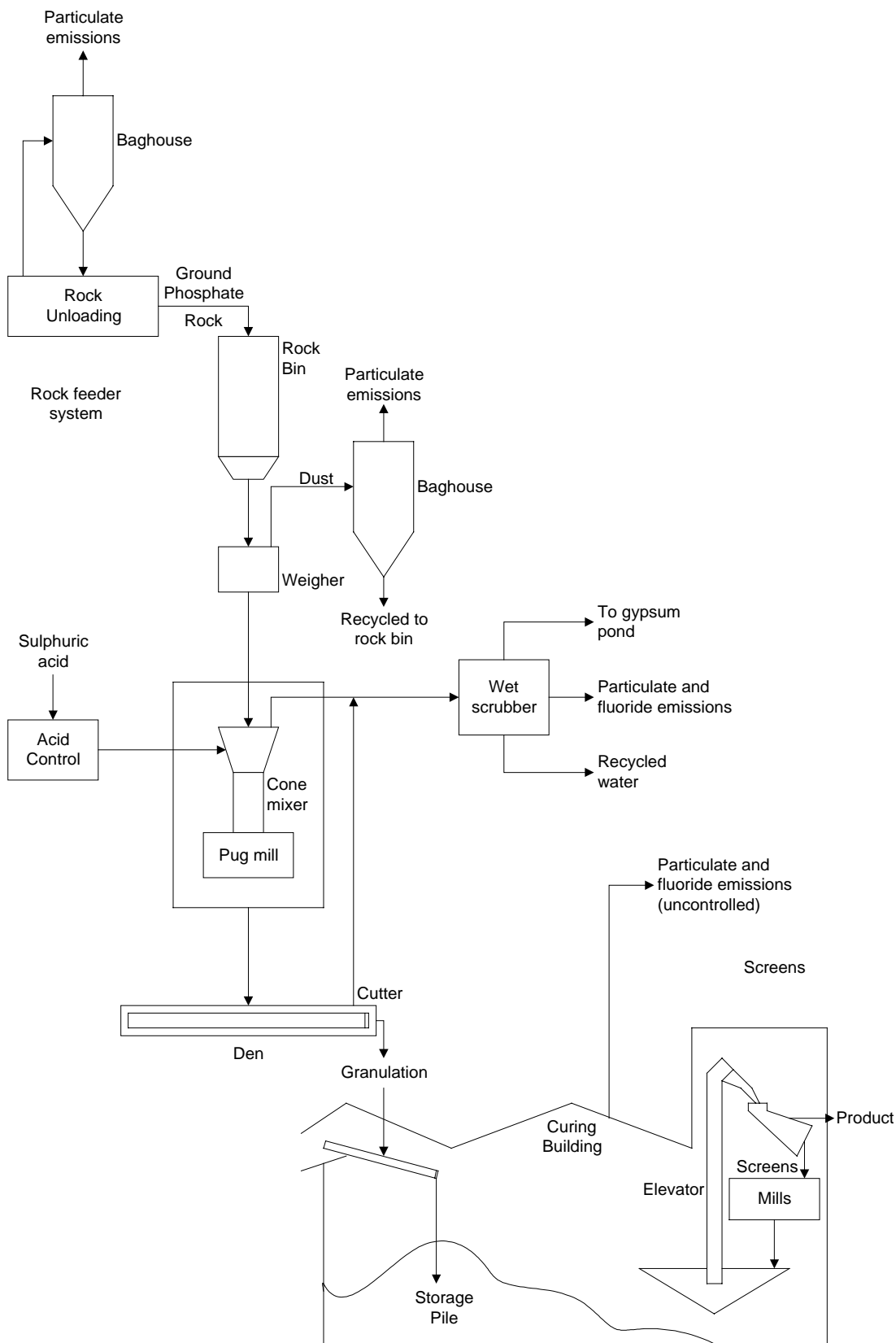
#### 2.1.1 Normal Superphosphate

Normal superphosphates are prepared by reacting ground phosphate rock with 65 to 75 percent sulfuric acid. An important factor in the production of normal superphosphates is the amount of iron and aluminium in the phosphate rock. Aluminium (as  $Al_2O_3$ ) and iron (as  $Fe_2O_3$ ) above five percent imparts an extreme stickiness to the superphosphate and makes it difficult to handle.

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The two general types of sulfuric acid used in superphosphate manufacture are virgin and spent acid. Virgin acid is produced from elemental sulfur, pyrites, as well as industrial gases and is relatively pure. Spent acid is a recycled waste product from various industries, such as copper, zinc, and nickel smelters, which use large quantities of sulfuric acid. Problems encountered with using spent acid include colour, unfamiliar odour, and toxicity.

A generalised flow diagram of normal superphosphate production is shown in Figure 1. Ground phosphate rock and acid are mixed in a reaction vessel, held in an enclosed area for about 30 minutes until the reaction is partially completed, and then transferred, using an enclosed conveyor known as the den, to a storage pile for curing (the completion of the reaction). Following curing, the product is most often used as a high-phosphate additive in the production of granular fertilisers. It can also be granulated for sale as granulated superphosphate or granular mixed fertiliser. To produce granulated superphosphate, cured superphosphate is fed through a clod breaker and sent to a rotary drum granulator where steam, water, and acid may be added to aid in granulation. Material is processed through a rotary drum granulator, a rotary dryer, and a rotary cooler, and is then screened to specification. Finally, it is stored in bagged or bulk form prior to being sold.



**Figure 1 - Normal Superphosphate Process Flow Diagram Showing Emission Sources**  
 Adapted from USEPA, AP 42, Section 8.5.1, 1995

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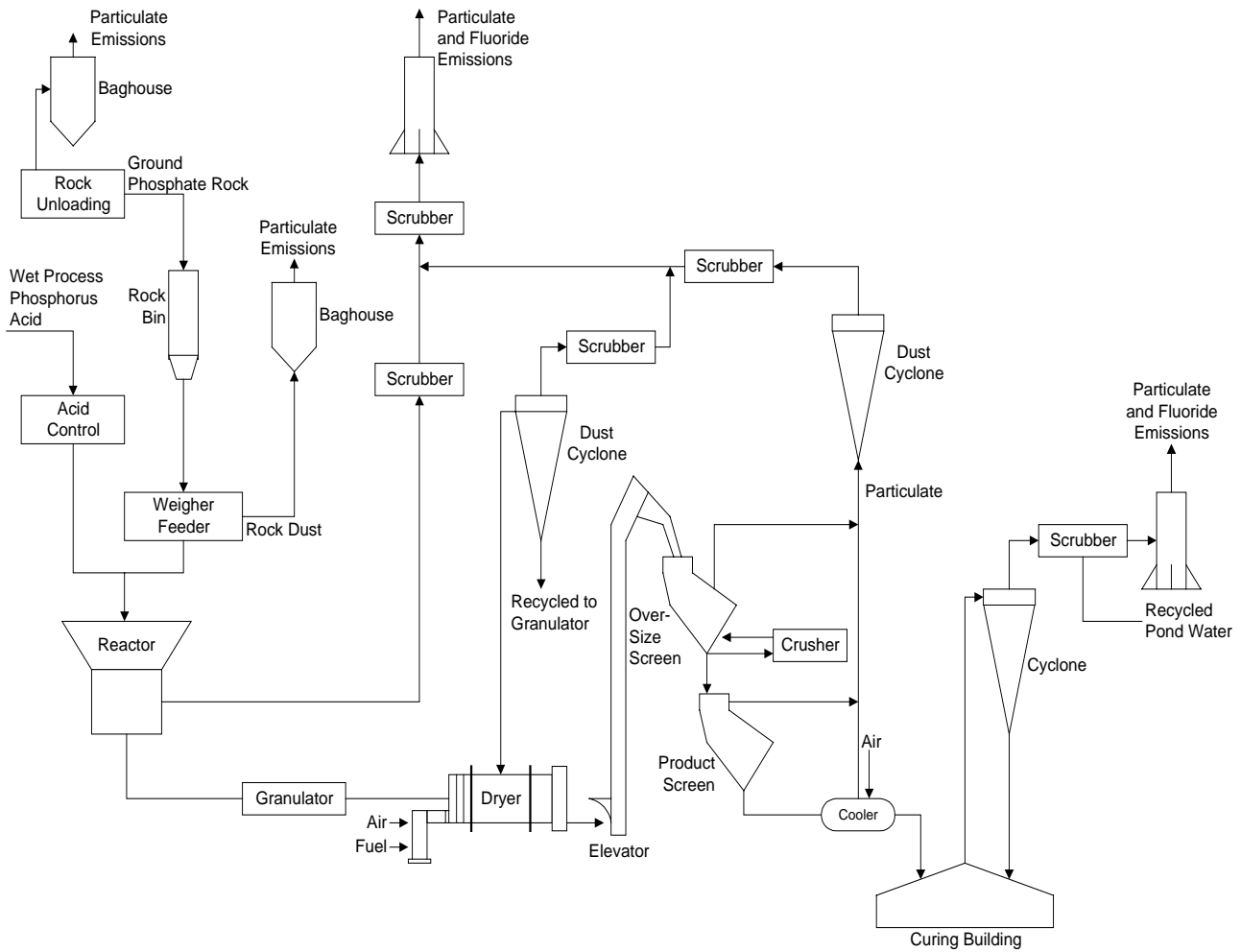
### 2.1.2 High Analysis Superphosphate

High analysis superphosphate is also known as double, triple, or concentrated superphosphate. Two processes have been used to produce high analysis superphosphate: run-of-the-pile (ROP) and granular. The ROP material is essentially a pulverised mass of variable particle size produced in a manner similar to normal superphosphate. Wet-process phosphoric acid (50 to 55 percent  $P_2O_5$ ) is reacted with ground phosphate rock in a cone mixer. The resultant slurry begins to solidify on a slow moving conveyor en route to the curing area. At the point of discharge from the den, the material passes through a rotary mechanical cutter that breaks up the solid mass. Coarse ROP product is sent to a storage pile and cured for three to five weeks. The product is then mined from the storage pile to be crushed, screened, and shipped in bulk.

The granular production method yields larger, more uniform particles with improved storage and handling properties. Most of this material is made with the Dorr-Oliver slurry granulation process, as illustrated in Figure 2. In this process, ground phosphate rock or limestone is reacted with phosphoric acid in one or two reactors in series. The phosphoric acid used in this process is appreciably lower in concentration (40 percent  $P_2O_5$ ) than that used to manufacture ROP product. A small sidestream of slurry is continuously removed and distributed onto dried, recycled fines, where it coats the granule surfaces and builds up its size.

Pugmills and rotating drum granulators have been used in the granulation process. A pugmill is composed of a U-shaped trough, carrying twin counter-rotating shafts, upon which are mounted string blades or paddles. The blades agitate, shear, and knead the liquefied mix and transport the material along the trough. The basic rotary drum granulator consists of an open-ended, slightly inclined rotary cylinder, with retaining rings at each end and a scrapper or cutter mounted inside the drum shell. A rolling bed of dry material is maintained in the unit while the slurry is introduced through distributor pipes set lengthwise in the drum under the bed. Slurry wetted granules are then discharged onto a rotary dryer, where excess water is evaporated and the chemical reaction is accelerated to completion by the dryer heat. Dried granules are then sized on vibrating screens. Oversize particles are crushed and recirculated to the screen, and undersized particles are recycled to the granulator. Product-size granules are cooled in a countercurrent rotary drum, then sent to a storage pile for curing. After a curing period of three to five days, granules are removed from storage, screened, bagged, and shipped.





**Figure 2 - Dorr-Oliver Process for Granular High Analysis Superphosphate Production**

Source: USEPA, AP 42, Section 8.5.2, 1995

### 2.1.3 Ammonium Phosphate

Ammonium phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) is produced by reacting phosphoric acid ( $\text{H}_3\text{PO}_4$ ) with anhydrous ammonia ( $\text{NH}_3$ ). Ammoniated superphosphates are produced by adding normal superphosphate or high analysis superphosphate to the mixture.

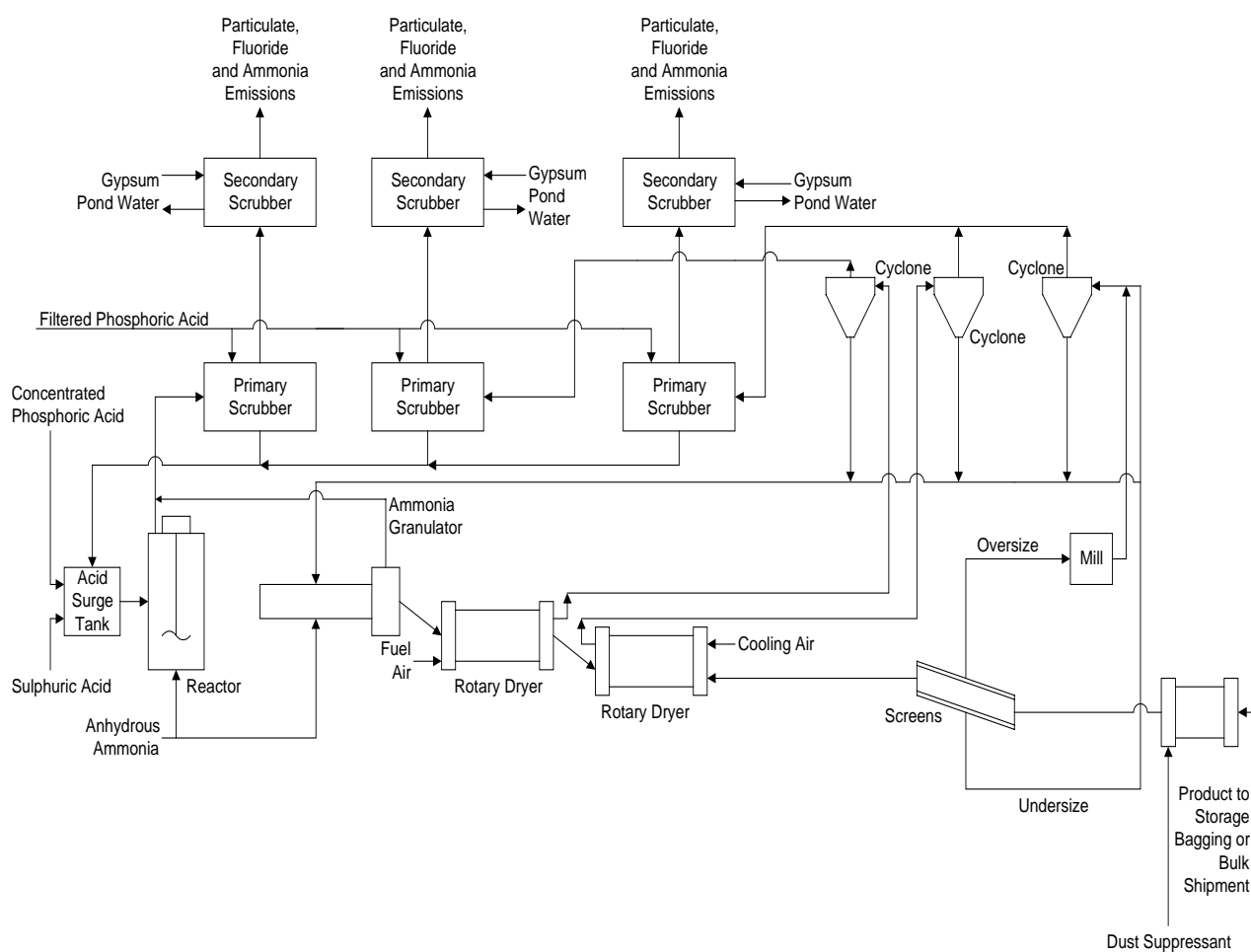
Two basic mixer designs are used by ammoniation-granulation plants: the pugmill ammoniator and the rotary drum ammoniator. The basic rotary drum ammoniator-granulator consists of a slightly inclined open-end rotary cylinder with retaining rings at each end, and a scraper or cutter mounted inside the drum shell. A rolling bed of recycled solids is maintained in the unit.

Ammonia-rich offgases pass through a wet scrubber before exhausting to the atmosphere. Primary scrubbers use raw materials mixed with acids (eg. scrubbing liquor) and secondary scrubbers use gypsum pond water.

In the rotary drum process, phosphoric acid is mixed in an acid surge tank with 93 percent sulfuric acid ( $\text{H}_2\text{SO}_4$ ) which is used for product analysis control, and with recycled acid from wet scrubbers. A schematic diagram of the ammonium phosphate process flow

diagram is shown in Figure 3. Mixed acids are partially neutralised with liquid or gaseous anhydrous ammonia in a brick-lined acid reactor. All of the phosphoric acid and approximately 70 percent of the ammonia are introduced through steam-traced lines to the ammoniator-granulator. Slurry from the reactor is distributed in the bed; the remaining ammonia (approximately 30 percent) is sparged underneath. Granulation, by agglomeration and by coating particulate with slurry, takes place in the rotating drum and is completed in the dryer.

Moist ammonium phosphate granules are transferred to a rotary concurrent dryer and then to a cooler. Before being exhausted to the atmosphere, these offgasses pass through cyclones and wet scrubbers. Cooled granules pass to a double-deck screen, in which oversize and undersized particles are separated from product particles. The product ranges in granule size from one to four millimetres. The oversized granules are crushed, mixed with the undersized granules, and recycled back to the ammoniator-granulator.



**Figure 3 - Ammonium Phosphate Process Flow Diagram**

Source: USEPA, AP 42, Section 8.5.3, 1995.

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## 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.

### 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 Phosphate Manufacturing processes.

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

Substance	Emission Media		
	To Atmosphere	To Water	Via Solid Waste
Ammonia	X	X	X
Sulfates and sulfur dioxide	X		
Total Phosphorus		X	
Fluoride compounds	X	X	X
Particulate Matter (PM <sub>10</sub> )	X		
Volatile Organic Compounds (VOCs)	X		

Source: Queensland Department of Environment and Heritage, 1998

## 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.

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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*.)

## **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>), total VOCs, speciated organics (formaldehyde and methanol), and inorganic substances (ammonia, total nitrogen) from Phosphate 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 Phosphate 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 substance 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	h/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 kilograms per hour or grams per cubic meter (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 cubic meters. 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 cubic meter.

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:

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

##### **Equation 2**

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

where:

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

**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

Queensland Department of Environment and Heritage 1998

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

PM emissions 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  $150^\circ\text{C}$  ( $423\text{K}$ )) are shown below:

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

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 kilograms per hour.

### Equation 3

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

where:

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

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<sub>R</sub> = moisture content, %  
 g<sub>moist</sub> = moisture collected, g  
 V<sub>m,STP</sub> = metered volume of sample at STP, m<sup>3</sup>  
 ρ<sub>STP</sub> = 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 Phosphate 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). Equation 5 can be used to calculate hourly emissions of a substance based on the concentration measurements in the units parts per million:

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**Equation 5**

$$E_i = (C * MW * Q_d * 3\,600) / [22.4 * (T+273/273) * 10^6]$$

where:

$E_i$	=	emissions of pollutant i, kg/hr
$C$	=	pollutant concentration, ppm <sub>vd</sub>
$MW$	=	molecular weight of the pollutant, kg/kg-mole
$Q_d$	=	stack gas volumetric flow rate, m <sup>3</sup> /s, dry
$3\,600$	=	conversion factor, s/hr
$22.4$	=	volume occupied by one mole of gas at standard temperature and pressure (0°C and 101.3 kPa), m <sup>3</sup> /kg-mole
$T$	=	temperature of gas sample, °C

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 of pollutant i, kg/yr
$E_i$	=	total hourly emissions of pollutant i, kg/hr
$OpHrs$	=	annual operating hours, 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 phosphate fertilisers. The hourly emissions of ammonia are calculated using Equation 5, and annual emissions are calculated using Equation 6.

Given:

$$\begin{array}{llll} C_{\text{NH}_3} & = & 15.4 \text{ ppmv} & MW_{\text{NH}_3} & = & 17 \text{ kg/kg-mole of ammonia} \\ Q_d & = & 8.48 \text{ m}^3/\text{sec} & \text{OpHrs} & = & 1\,760 \text{ hr/yr} \\ T & = & 150 \text{ }^\circ\text{C (423K)} & & & \end{array}$$

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

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

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

$$\begin{aligned} E_{\text{kpy,NH}_3} & = E_{\text{NH}_3} * \text{OpHrs} \\ & = 2.303 * 10^{-1} * 1\,760 \\ & = 405.33 \text{ kg of ammonia emitted per year} \end{aligned}$$

#### 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:

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

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

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## 3.2 Using Mass Balance

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

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

### Equation 8

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

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 9 can be applied as a practical extension of Equation 8.

### Equation 9

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

where:

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

Example 4 illustrates the application of Equation 9.

#### Example 4 - Using a Mass Balance for Cobalt Emission

A phosphate fertiliser manufacturer uses phosphate rock as a raw material in the production of a normal superphosphate fertiliser. The rock contains trace amounts of cobalt (Co). The facility uses 143 700 tonnes of phosphate rock per year to manufacture approximately 100000 tonnes of calcium dihydrogen phosphate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ). The concentration of cobalt initially in the phosphate rock is 1.0 mg/kg. The concentration of cobalt in the calcium dihydrogen phosphate is 0.48 mg/kg. Assuming no cobalt is lost to wastewater and there are no recycling activities taking place, annual emissions to air could be determined using Equation 9:

$$\begin{aligned} E_{\text{kpy,Co}} &= [Q_{\text{in}} * C_{\text{in}} - Q_{\text{pr}} * C_{\text{pr}} - Q_{\text{rec}} * C_{\text{rec}} - Q_{\text{waste}} * C_{\text{waste}}] / 10^6 \\ &= [143\,700\,000 * 1.0 - 100\,000\,000 * 0.48 - 0 - 0] / 10^6 \\ &= 96 \text{ kilograms of Co emitted per year.} \end{aligned}$$

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 itself a listed substance and require reporting where annual emissions total 10 tonnes or more.

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

For many chemicals used and emitted during chemical processes, some degradation in treatment may occur so that 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.

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### 3.3 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 phosphate fertiliser. Emission factors relating to the production of phosphate fertiliser are listed in Table 4 to 7.

Equation 10 is used to estimate a facility's emissions from application of emission factors.

#### Equation 10

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

where:

$E_{kpy,i}$	=	emission rate of pollutant i, kg/yr
$A$	=	activity rate, t/hr
$OpHrs$	=	annual operating hours, hr/yr
$EF_i$	=	uncontrolled emission factor of pollutant i, kg/t
$CE_i$	=	overall control efficiency for 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  $PM_{10}$ , 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 10 is illustrated by Example 5.

### Example 5 - Using Emission Factors

Table 4 shows that 1.9 kg of fluorides are emitted from the curing building for each tonne of normal superphosphate produced without a control device in place. If it is assumed that the facility operates for 5 400 hours per year and activity rate is 2 t/hr.

$$\begin{aligned}
 EF_{\text{fluoride}} &= 1.9 \text{ kg/t} \\
 E_{\text{kpy,fluoride}} &= [A * \text{OpHrs}] * EF_{\text{fluoride}} * [1-90/100] \\
 &= 2 \text{ t/yr} * 5\,400 \text{ hr/yr} * 1.9 \\
 &= 20\,520 \text{ kg fluorides emitted per year}
 \end{aligned}$$

**Table 4 - Emission Factors for the Production of Normal Superphosphate**

Emission Point	Pollutant	Emission Factor kg/t of P <sub>2</sub> O <sub>5</sub> produced
Rock Unloading <sup>a</sup>	PM <sub>10</sub> <sup>b</sup>	0.15
Rock Feeding	PM <sub>10</sub>	0.03
Mixer and den <sup>c</sup>	PM <sub>10</sub> Fluoride	0.22 0.10
Curing building <sup>d</sup>	PM <sub>10</sub> Fluoride	3.00 1.9 <sup>e</sup>

Source: USEPA, AP-42, section 8.5.1, 1995.

All emission factors have an uncertainty rating of E unless otherwise noted.

<sup>a</sup> Factors are for emissions from baghouse with an estimated collection efficiency of 99%.

<sup>b</sup> PM<sub>10</sub> = particulate matter no greater than 10 micrometres.

<sup>c</sup> Factors are for emissions from wet scrubbers with reported 97% control efficiency.

<sup>d</sup> Uncontrolled.

<sup>e</sup> Emission Factor Rating = U.

**Table 5 - Emission Factors for Speciated and Total Volatile Organic Compounds from Phosphate Manufacturing<sup>a</sup>**

Listed Substances	Emission Factors <sup>b</sup> kg/tonne of P <sub>2</sub> O <sub>5</sub> Produced
<i>n</i> -Hexane	0.15 * 10 <sup>-3</sup>
Cyclohexane	0.15 * 10 <sup>-3</sup>
Formaldehyde	1.20 * 10 <sup>-3</sup>
Benzene	0.60 * 10 <sup>-3</sup>
Toluene	0.30 * 10 <sup>-3</sup>
Total VOCs	4.35 * 10 <sup>-3</sup>

Source: USEPA 1992, VOC/PM Speciation Data System - Version 1.50

<sup>a</sup> Emission factors are specific to dryer/cooler operations

<sup>b</sup> Emission factor uncertainty rating = U

**Table 6 - Controlled Emission Factors for the Production of High Analysis Superphosphates**

Granular Triple Superphosphate Process	Pollutant	Controlled Emission Factor <sup>a</sup>
		kg/tonne of Product
Rock unloading	PM <sub>10</sub> <sup>b</sup>	0.04
Rock feeding	PM <sub>10</sub>	0.01
Reactor, granulator, dryer, cooler and screens	PM <sub>10</sub>	0.04
	Fluoride	0.12
Curing building <sup>c</sup>	PM <sub>10</sub>	0.08
	Fluoride	0.02

Source: USEPA, AP-42, Section 8.5.2, 1995.

<sup>a</sup> Controlled emission factor rating = E.

<sup>b</sup> PM<sub>10</sub> = Particulate matter with a diameter of less than 10 micrometres.

<sup>c</sup> Factors are for emissions from wet scrubbers with an estimated 97% control efficiency.

**Table 7 - Controlled Emission Factors for the Production of Ammonium Phosphates<sup>a</sup>**

Emission Point	Fluoride kg/tonne of product	PM <sub>10</sub> <sup>b</sup> kg/tonne of product	Ammonia kg/tonne of product	SO <sub>2</sub> kg/tonne of product
Reactor/ ammoniator-granulator	0.02	0.76	ND <sup>c</sup>	NA <sup>d</sup>
Dryer/cooler	0.02	0.75	NA	NA
Product sizing and material transfer <sup>e</sup>	0.001	0.03	NA	NA
Total plant emissions	0.02 <sup>a</sup>	0.34 <sup>a</sup>	0.07 <sup>e</sup>	0.04

Source: USEPA, AP42, section 8.5.3, 1995.

All emission factors have an uncertainty rating of E unless otherwise noted

<sup>a</sup> Emission factor uncertainty rating = A.

<sup>b</sup> PM<sub>10</sub> = Particulate matter with a diameter of less than 10 micrometres.

<sup>c</sup> ND = no data.

<sup>d</sup> NA = not applicable.

<sup>e</sup> Represents only 1 sample

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.

### 3.4 Using Engineering and Site-Specific Equations

Theoretical and complex equations or *models* can be used for estimating emissions from phosphate fertiliser 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.



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Use of engineering equations to estimate emissions from phosphate fertiliser 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 details of the use of vapour pressure and mass transfer based equations, refer to the *Emission Estimation Technique Manual for Fugitive Emissions*.

### 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 Phosphate 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 Phosphate 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 8 and Equation 11; or
- Use the emission factors from Table 9.

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 phosphate fertiliser plants. Equation 11 illustrates an approach for estimating fugitive inorganic chemical emissions using data from Table 8. An example of this estimation technique is given at Example 5.

**Equation 11**

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

where:

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

**Table 8 - 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 6 - Calculating Fugitive Chemical Leaks

A phosphate fertiliser 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**

$$\begin{aligned} \text{OpHrs} &= 8\,760 \text{ hr/yr} \\ \text{SV (screening value)} &= 0 \text{ ppmv} \\ \text{Default-zero emission rate} &= 7.5 * 10^{-6} \text{ kg/hr/source} \\ \\ \text{NH}_3 \text{ emissions} &= \text{ER}_x * \text{C}_x * \text{OpHrs} \\ &= 7.5 * 10^{-6} * (80/100) * 8\,760 \\ &= 5.26 * 10^{-2} \text{ kg/hr} \end{aligned}$$

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

$$\begin{aligned} \text{OpHrs} &= 8\,760 \text{ hr/yr} \\ \text{SV (screening value)} &= 20 \text{ ppmv} \\ \\ \text{NH}_3 \text{ emissions} &= 1.90 * 10^{-5} (\text{SV})^{0.824} \\ \text{Hourly emissions} &= 1.90 * 10^{-5} (20)^{0.824} \\ &= 2.24 * 10^{-4} \text{ kg/hr} \\ \\ \text{NH}_3 \text{ emissions} &= 2.24 * 10^{-4} * 8\,760 * (80/100) \\ \text{Annual emissions} &= 1.68 \text{ kg NH}_3/\text{yr} \end{aligned}$$

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 9, 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 9.

**Equation 12**

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

where:

$$E_{kpy,i} = \text{emission rate of pollutant } i \text{ from all equipment in the } stream \text{ of a given equipment type, kg/yr}$$

$$EF = \text{applicable average emission factor for the equipment type, kg/hr/source}$$

$$WF_i = \text{average weight fraction of pollutant } i \text{ in the } stream,$$

$$OpHrs = \text{annual operation hours of equipment in the } stream, \text{ hr/yr}$$

$$N = \text{number of pieces of the applicable equipment type in the } stream$$

Example 7 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 7 - 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 9 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

$$E_{kpy,NH_3} = EF * WF_{NH_3} * OpHrs * N$$

**Stream A**

$$E_{kpy,NH_3} = 0.0199 * 0.80 * 8\,760 * 15$$

$$= 2\,092 \text{ kg NH}_3/\text{yr}$$

**Stream B**

$$E_{kpy,NH_3} = 0.0199 * 1.00 * 4\,380 * 12$$

$$= 1\,046 \text{ kg NH}_3/\text{yr}$$

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**Table 9 - Emission Factors for Equipment Leaks**

<b>Equipment Type</b>	<b>Service</b>	<b>Emission Factor (kg/hr/source)</b>
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	0104
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 Phosphate 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 Phosphate 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 one specific process may not be representative of the entire manufacturing operation and may provide only one example of the facility's emissions.

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

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 Phosphate Manufacturing facility using mass balance appears to be a straightforward approach to emissions 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 phosphate manufacturing processes.

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Use of emission equations to estimate emissions from Phosphate 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 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

ACTED Consultants, 1997, *Phosphate Fertiliser, Phosphoric Acid, and Calcium Phosphate*, URL: <http://jimi.vianet.net.au/~acted/ammonia.html>.

National Pollutant Inventory Homepage

<http://www.environment.gov.au/epg/npi/home.html>

USEPA, October 1992, *VOC / PM Speciation Data System - Version 1.50*, United States Environmental Protection Agency, Office of Air Quality, Planning and Standards, Research Triangle Park, NC, USA.

USEPA, January 1995, *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, fifth edition, AP-42. Section 8.5.1 Normal Superphosphate*, United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, USA.

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USEPA, January 1995, *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, fifth edition, AP-42. Section 8.5.2 Triple Superphosphate*, United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, USA.

USEPA, January 1995, *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, fifth edition, AP-42. Section 8.5.3 Ammonium Phosphate*, United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, USA.

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