National Pollutant Inventory

Emission Estimation Technique Manual

for

Explosives Manufacturing

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EMISSION ESTIMATION TECHNIQUES
FOR
EXPLOSIVES MANUFACTURING

TABLE OF CONTENTS

EXPLOSIVES MANUFACTURING

LIST OF FIGURES, TABLES AND EXAMPLES

1.0   Introduction

The purpose of all Emission Estimation Technique (EET) Manuals in this series is to assist Australian manufacturing, industrial and service facilities to report emissions of listed substances to the National Pollutant Inventory (NPI). This Manual describes the procedures and recommended approaches for estimating emissions from facilities engaged in the manufacturing of explosives.

EET MANUAL: Explosives Manufacturing

HANDBOOK: Explosives Manufacturing

ANZSIC CODES :   2541

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.

2.0   Processes and Emissions

The following section presents a brief description of the production of explosives, and identifies substances likely to be emitted during this process.

2.1   Process Description

An explosive is a material that, under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of large amounts of heat and gas. There are two major categories, high explosives and low explosives. High explosives are further divided into initiating, or primary, high explosives and secondary high explosives. Initiating high explosives are very sensitive and are generally used in small quantities in detonators and percussion caps to set off larger quantities of secondary high explosives. Secondary high explosives, chiefly nitrates, nitro compounds, and nitramines, are much less sensitive to mechanical or thermal shock, but they explode with great violence when set off by an initiating explosive. The chief secondary high explosives manufactured for commercial and military use are ammonium nitrate blasting agents and 2,4,6-trinitrotoluene (TNT). The production of ammonium nitrate is discussed in this manual.

Low explosives, such as black powder and nitrocellulose, undergo a relatively slow auto-combustion when set off and evolve large volumes of gas in a definite and controllable manner. Many different types of explosives are manufactured in Australia and examples of high (TNT), low (nitrocellulose) explosives and ammonium nitrate fuel oil (ANFO) are discussed below.

2.1.1   TNT Production

TNT may be prepared by either a continuous or a batch process, using toluene, nitric acid, and sulfuric acid as raw materials. The production of TNT follows the same chemical process, regardless of whether batch or continuous methods are used. The flow chart for TNT production is shown in Figure 1. The overall chemical reaction may be expressed as:

$$C_6H_5CH_3 + 3HONO_2 + H_2SO_4 \rightarrow (NO_2)_3C_6H_2CH_3 + 3H_2O + H_2SO_4$$

Toluene	Nitric Acid	Sulfuric Acid	2,4,6 – Trinitrotoluene	Water	Sulfuric Acid
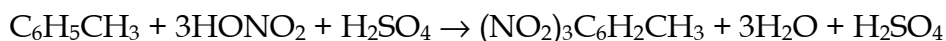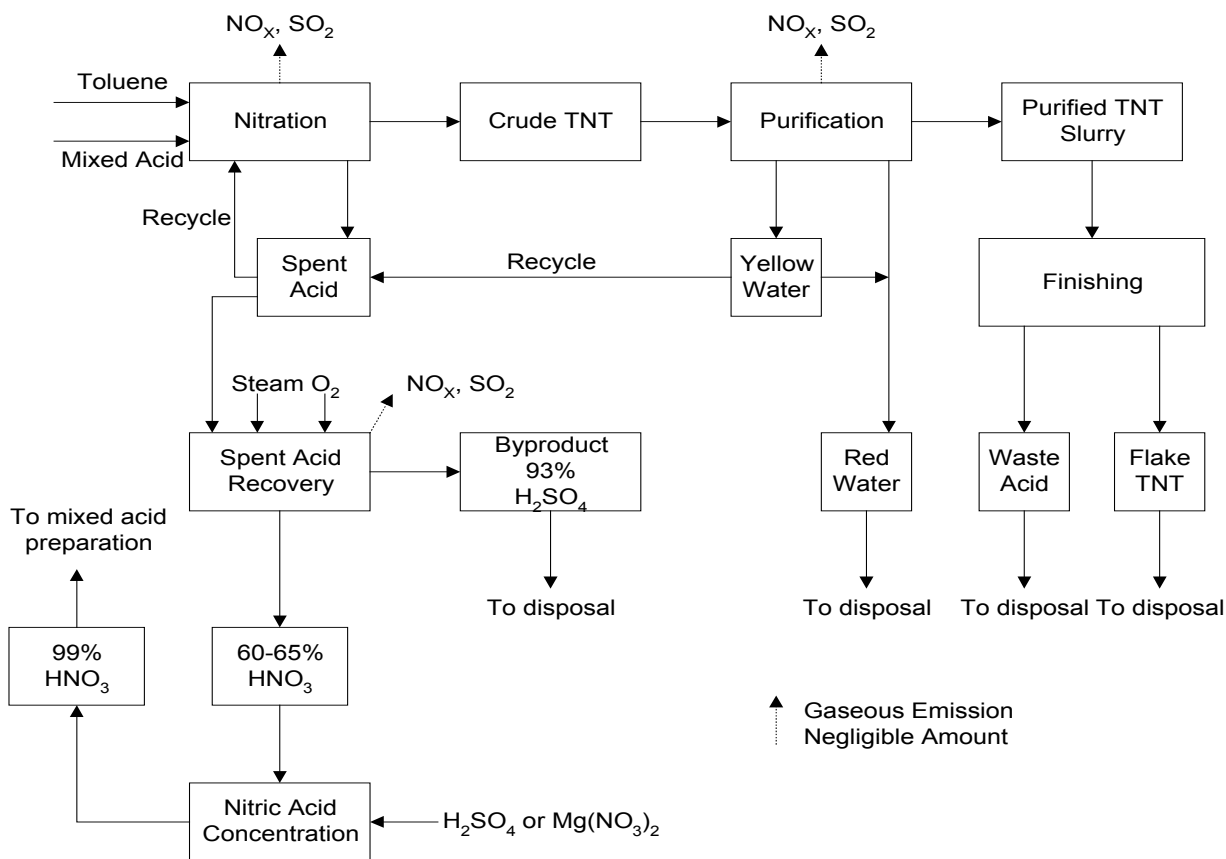
Figure 1 - TNT Production
Source: USEPA, AP-42, Section 6.3, 1995

The production of TNT by nitration of toluene is a 3-stage process performed in a series of reactors, as shown in Figure 2. The mixed acid stream is shown to flow countercurrently to the flow of the organic stream. Toluene and spent acid fortified with 60 percent HNO_3 solution are fed into the first reactor. The organic layer formed in the first reactor is pumped into the second reactor, where it is subjected to further nitration with acid from the third reactor fortified with additional HNO_3. The product from the second nitration step, a mixture of all possible isomers of dinitrotoluene (DNT), is pumped into the third reactor. In the final reaction, the DNT is treated with a fresh feed of HNO_3 and oleum (a solution of sulfur trioxide [SO_3] in anhydrous H_2SO_4). The crude TNT from this third nitration consists primarily of 2,4,6-trinitrotoluene. The crude TNT is washed to remove free acid, and the wash water (yellow water) is recycled to the early nitration stages. The washed TNT is then neutralised with soda ash and treated with a 16 percent aqueous sodium sulfite (Sellite) solution to remove contaminating isomers. The Sellite waste solution (red water) from the purification process is usually emitted as a liquid waste stream, collected and sold, or is concentrated to a slurry and incinerated or taken to landfill. Finally, the TNT crystals are melted and passed through hot air dryers, where most of the water is evaporated. The dehydrated product is solidified, and the TNT flakes packaged for storage or distribution.
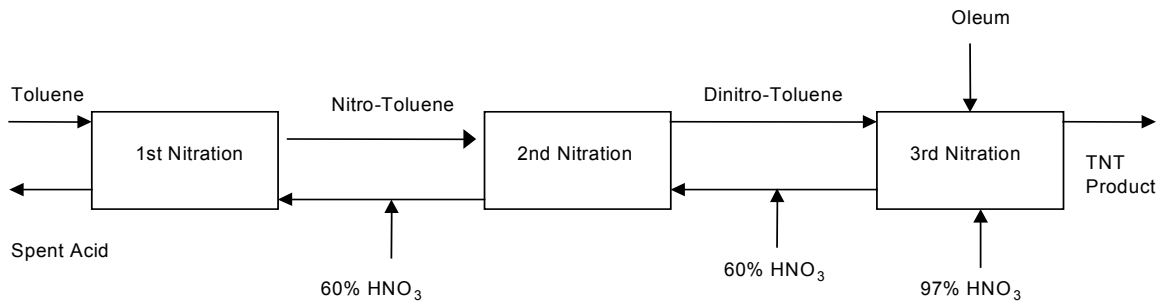
Figure 2 - Nitration of Toluene to Form Trinitrotoluene
Source: USEPA, AP-42, Section 6.3, 1995

2.1.2   Nitrocellulose Production

Nitrocellulose is commonly prepared by a batch-type mechanical dipper process or, more recently, by a continuous nitration processing method. In batch production cellulose in the form of cotton linters, fibres, or specially prepared wood pulp, is purified by boiling and bleaching. The dry and purified cotton linters or wood pulp are added to mixed nitric and sulfuric acids in metal reaction vessels known as dipping pots. The reaction is as follows:

$$(C_6H_7O_2(OH)_3)_i + 3HONO_2 + H_2SO_4 \rightarrow (C_6H_7O_2(ONO_2)_3)_i + 3H_2O + H_2SO_4$$

| Cellulose | Nitric Acid | Sulfuric Acid | Nitrocellulose | Water | Sulfuric Acid |
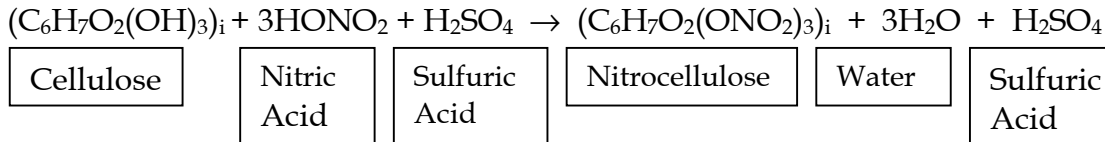
Following nitration, the crude nitrocellulose is centrifuged to remove most of the spent nitrating acids and is put through a series of water washing and boiling treatments to purify the final product.

2.1.3   Ammonium Nitrate Fuel Oil (ANFO) Preparation

Ammonium nitrate fuel oil (ANFO), is a blasting agent composed of ammonium nitrate and liquid hydrocarbons (diesel fuel oil), in the proportion of 6 percent of fuel by weight or by volume, that is, one part of distillate to 16 parts of ammonium nitrate (Hall, R., 1993, p.66).

Loosely poured ANFO has a density of 0.8 - 0.85 grams/cubic metre, but has no water resistance and hence can only be used in dry conditions. Therefore to allow and accommodate different conditions on blast sites, the nature and character of the explosive used need to be varied. ANFO being non-water-resistant, becomes water-resistant if 30%+ emulsion is added to it. At 40% emulsion component the product starts to become

waterproof, as now a layer of emulsion coats each prill particle in the ANFO, preventing water penetration for a short period (TES, 1997, p.53). This blend is called Heavy ANFO.

Possible sources of emissions could be spills and leakage and specific information from the particular distillate in use should be used to calculate emissions for the NPI listed substances.

2.1.3.1 Ammonium Nitrate Manufacturing

The manufacture of ammonium nitrate involves several major unit operations including solution formation and concentration; solids formation, finishing, screening and coating; and product bagging and/or bulk shipping. In some cases, solutions may be blended for marketing as liquid fertilisers.

The number of operating steps employed depends on the end product desired. For example, plants producing ammonium nitrate solutions alone use only the solution formation, solution blending and bulk shipping operations. Plant producing a solid ammonium nitrate product may employ all of the operations.

All ammonium nitrate plants produce an aqueous ammonium nitrate solution through the reaction of ammonia and nitric acid in a neutraliser as follows:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$
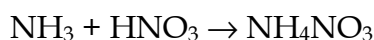
To produce a solid product, the ammonium nitrate solution is concentrated in an evaporator or concentrator. The resulting *melt* contains about 95 to 99.8 percent ammonium nitrate at approximately 149°C. This *melt* is then used to make solid ammonium nitrate products.

Prilling and granulation are the most common processes used to produce solid ammonium nitrate. To produce prills, concentrated *melt* is sprayed into the top of a prill tower. In the tower, ammonium nitrate droplets falls countercurrent to a rising air stream that cools and solidifies the falling droplets into spherical prills. Prill density can be varied by using different concentrations of ammonium nitrate *melt*. Low-density prills, in the range of 1.29 specific gravity, are formed from a 95 to 97.5 percent ammonium nitrate melt, and high-density prills, in the range of 1.65 specific gravity, are formed from a 99.5 to 99.8 percent *melt*. Low-density prills are more porous than high-density prills. Therefore, low-density prills are used for making blasting agents because they will absorb oil. Most high-density prills are used as fertilisers.

The ammonium nitrate prilling process can be divided into 5 major operations:

1. Concentration;
2. Prilling;
3. Drying and cooling;
4. Screening; and
5. Coating.

Rotary drum granulators produce granules by spraying a concentrated ammonium nitrate

melt (99.0 to 99.8 percent) onto small seed particles of ammonium nitrate in a long rotating cylindrical drum. As the seed particles rotate in the drum, successive layers of ammonium nitrate are added to the particles, forming granules. Granules are removed from the granulator and screened. Off-size granules are crushed and recycled to the granulator to supply additional seed particles or are dissolved and returned to the solution process. Pan granulators operate on the same principle as drum granulators, except the solids are formed in a large, rotating circular pan. Pan granulators produce a solid product with physical characteristics similar to those of drum granules.

Although not widely used, an additive, such as magnesium nitrate or magnesium oxide, may be injected directly into the melt stream. This additive serves three purposes: to raise the crystalline transition temperature of the final solid product; to act as a desiccant drawing water into the final product to reduce caking; and to allow solidification to occur at a low temperature by reducing the freezing point of molten ammonium nitrate.

The temperature of the ammonium nitrate exiting the solids formation process is approximately 66 to 124°C. Rotary drum or fluidised bed cooling prevents deterioration and agglomeration of solids before storage and shipping. Low-density prills have a high moisture content because of the lower melt concentration, and therefore require drying in rotary drums or fluidised beds before cooling.

Since the solids are produced in a wide variety of sizes, they must be screened for consistently sized prills or granules. Cooled prills are screened and off-size prills are dissolved and recycled to the solution concentration process. Granules are screened before cooling. Under-size particles are returned directly to the granulator and oversize granules may be crushed and returned to the granulator, or sent to the solution concentration process.

Following screening, products can be coated in a rotary drum to prevent agglomeration during storage and shipment. The most common coating materials are clays and diatomaceous earth. However, the use of additives in the ammonium nitrate *melt* before solidification, as described above, may preclude the use of coatings.

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 (excluding roof vents) or stack and emitted through a single point source into the atmosphere. Table 1 highlights common air emissions of NPI-listed substances from explosives manufacturing processes.

Table 1 - Common Air Emissions of NPI-Listed Substances from the Explosives Manufacturing Processes

Substance
• Sulfur Dioxide (SO_2)
• Carbon Monoxide (CO)
• Particulate Matter (PM_{10})
• Oxides of Nitrogen (NO_x)
• Ammonia (NH_3)
• Nitric Acid (HNO_3)
• Volatile Organic Compounds (VOC)
• Sulfuric Acid (H_2SO_4)

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.

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.

3.0   Emission Estimation Techniques

This sections presents equations and examples of calculations for estimating emissions of particulate matter (PM_{10}), total VOCs, speciated organics and inorganic substances (ammonia, total nitrogen) from the explosives manufacturing processes.

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

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 EETs that are not outlined in this handbook, your data will also be displayed as being of 'acceptable reliability'.

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

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

You should note that the EETs presented in this manual relate principally to average process emissions. Emissions resulting from non-routine events are rarely discussed in the literature, and there is a general lack of EETs for such events. However, it is important to recognise that emissions resulting from significant operating excursions and/or

accidental situations (eg. spills) will also need to be estimated. Emissions to land, air and water from spills must be estimated and added to process emissions when calculating total emissions for reporting purposes. The emission resulting from a spill is the net emission, ie. the quantity of the NPI reportable substance spilled, less the quantity recovered or consumed during clean up operations.

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.

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

Table 2 – List of Variables and Symbols

Variable	Symbol	Units
Total emissions of pollutant i	E_i	kg/hr
Annual emissions of pollutant i	$E_{kpy,i}$	kg/yr
Material entering the process	Q_{in}	L/hr
Material leaving the process (as an emission, transfer, or in product)	Q_{out}	L/hr
Concentration of pollutant i	C_i	ppmv or kg/L
Amount of pollutant i in sludge	AS_i	kg/yr
Process losses of pollutant i	PL_i	kg/yr
Losses in wastewater of pollutant i	WL_i	kg/yr
Temperature correction for temperature differences during test	K_t	dimensionless
Pressure correction for pressure differences during test	K_p	dimensionless
Average concentration of pollutant i	$C_{a,i}$	ppmv
Molecular weight of pollutant i	MW_i	kg/kg-mole
Volumetric flow rate of stack gas	Q_w	wet cubic metres per second (m^3/s)
Volumetric flow rate of stack gas	Q_d	dry cubic metres per second (m^3/s)
Molar volume	M	m^3/kg-mole
Operating hours	OpHrs	hr/yr
Emission factor for pollutant i	EF_i	kg/units
Activity factor	AF	units/hr
Saturation vapour pressure of pollutant i	$P_{sat,i}$	kilopascals (kPa)
Total pressure	P_t	kPa
Density of air	ρ_a	kg/m^3
Evaporation rate of pollutant i	W_i	kg/sec
Gas-phase mass transfer coefficient for VOC species i	K_i	m/sec
Surface area	area	m^2
Vapour pressure of pollutant i	$P_{vap,i}$	kPa
Universal gas constant	R	kPa * m^3 /(kgmol * K)
Temperature	T	K
VOC content of material	C_{VOC}	kg/L
Total VOC emissions	E_{VOC}	kg/L
Density of material	ρ_m	kg/L
Percentage weight of pollutant i	$Wt\%_i$	%

Variable	Symbol	Units
Wind speed	U	km/hr

3.1   Using Sampling or Direct Measurement

3.1.1   For Emissions to Air

Particulate Matter (PM₁₀) Emissions

Stack sampling test reports often provide emissions data in terms of kg/hr or g/m³ (dry). 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 m³. The filter weight gain is determined gravimetrically and divided by the volume of gas sampled (as shown in Equation 1) to determine the PM concentration in grams per m³.

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

Equation 1

$$C_{PM} \quad = \quad C_f \, / \, V_{STP}$$

where:

C_{PM} = concentration of PM or gram loading, g/m³
C_f = filter catch, g
V_{STP} = metered volume of sample at standard
temperature and pressure (at 0°C and 101.3 kPa), m³

Equation 2 can be used to convert the concentration if a substance calculated in Equation 1 to an hourly emission of the substance:

Equation 2

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

where:

E_{PM} = hourly emissions of PM, kg/hr

Q_d	=	stack gas volumetric flow rate, m^3/s		
3.6	=	3600 seconds per hour multiplied by 0.001 kilograms per gram		
T	=	temperature of the gas sample, °C		

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_{MOIST}	395.6	372.6	341.4
Filter catch (g)	C_f	0.0851	0.0449	0.0625
Average sampling rate (m^3/s)		$1.67 * 10^{-4}$	$1.67 * 10^{-4}$	$1.67 * 10^{-4}$
Standard metered volume (m^3)	$V_{m, STP}$	1.185	1.160	1.163
Volumetric flow rate (m^3/s), dry	Q_d	8.48	8.43	8.45
Concentration of particulate (g/m^3)	C_{PM}	0.0718	0.0387	0.0537
Particulate emission rate (kg/hr)	E_{PM}	2.20	1.19	1.65

Source: Queensland Department of Environment and Heritage, 1998

Example 1 illustrates the application of Equation 1 and Equation 2.

Example 1 - Estimating Particulate Matter (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°C (423 K)) are shown below:

C_{PM}	=	C_f / V_{STP}
	=	0.085 / 1.185
	=	0.072 g/ m^3

E_{PM}	=	$C_{PM} * Q_d * 3.6 * [273/(273 + T)]$
	=	$0.072 * 8.48 * 3.6 * [273/(273 + 150)]$
	=	1.42 kg/hr

Emissions can be converted to a yearly basis by multiplying by the yearly hours of operation in units of hr/yr.

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

Equation 3

$$E_{PM} = Q_w * C_{PM} * 3.6 * \left(1 - \frac{moist_R}{100}\right) * \left[\frac{273}{(273+T)}\right]$$

where:

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

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

To calculate moisture content use Equation 4

Equation 4

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

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

where

$moist_R$	=	moisture content, %
g_{moist}	=	moisture collected, g
$V_{m,STP}$	=	metered volume of sample at STP, m^3
ρ_{STP}	=	dry density of stack gas sample, kg/m^3 at STP {if the density is not known a default value of 1.62 kg/m^3 may be used. This assumes a dry gas composition of 50% air, 50% CO_2}

Example 2 - Calculating Moisture Percentage

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

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

$g_{MOIST}/1000 * V_{m,STP} =$ 410 / (1000 * 1.2)

                =   0.342

$moist_R$ =   100 * 0.342 / (0.342 + 1.62)

                =   17.4%

Gaseous Emissions

Sampling test methods can be used to estimate inorganic pollutant emission rates from explosives 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). For gaseous pollutants, the concentration of a pollutant (C_i) can be determined by Equation 5.

Equation 5

      C_i = $K_t * K_p * C_{a,i}$

where:

C_i	=	concentration of pollutant i, ppmv
K_t	=	temperature correction for differences in temperature from STP during sample test
K_p	=	pressure correction for differences in pressure from STP during sample test
$C_{a,i}$	=	average concentration of pollutant i, ppmv

K_t and K_p are correction factors for differences in the temperature and pressure that occur during the sample testing period. For example, the pressure drop as the air flows along the length of the pipe during the stack test. This is illustrated in Example 3 where the temperature does not change over the sample testing period (K_t = 1) but the pressure

reduces, causing K_p to be a factor less than one ($K_p = 0.8$), due to the pressure difference during the sampling test.

The K_t and K_p used here are example values only. Specific values may be found in Chemical Engineering Textbooks.

Equation 6 can be used to calculate hourly emissions of the substance based on the concentration measurements in the units parts per million.

Equation 6

$$E_i \quad = \quad (C_i * MW_i * Q_d * 3600) / [22.4 * \{(T + 273)/273\} * 10^6]$$

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^3/s, dry
3600 = conversion factor, sec/hr
22.4 = volume occupied by one mole of gas at STP (0°C and 101.3 kPa), m^3/kg-mole
T = temperature of gas sample, 0°C
10^6 = conversion factor from ppmv to volume fraction

Emissions in kilograms per year can be calculated by multiplying the average hourly emission rate (kg/hr) from Equation 6 by the number of operating hours (shown in Equation 7 below) or by multiplying an average emission factor (kg/L) by the total annual amount of material used (L).

Equation 7

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

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^3), and in a variety of conditions, such as wet, dry, or excess O_2. 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, Equation 6 and Equation 7.

Example 3 - Estimating Ammonia Emissions to Atmosphere

This example shows how annual ammonia (NH_3) emissions can be calculated using the data obtained from a stack at a plant manufacturing explosives. The concentration of ammonia is calculated using Equation 5, hourly emissions are calculated using Equation 6, and annual emissions are calculated using Equation 7.

Given:

K_t	=	1.0	K_p	=	0.8
$C_{a,i}$	=	15.4 ppmv	MW_i	=	17 kg/kg-mole of ammonia
Q_d	=	8.48 m³/sec	OpHrs=		1760 hr/yr
T	=	25°C (298 K)			

The concentration of ammonia (C_i) is calculated from Equation 5:

$$C_i = K_t * K_p * C_{a,i}$$
$$= 1.0 * 0.8 * 15.4 \text{ ppmv}$$
$$= 12.32 \text{ ppmv}$$

Hourly emissions of NH_3 are calculated using Equation 6:

$$E_{NH3} = (C_i * MW_i * Q_d * 3600)/[22.4 * \{(T + 273)/273\} * 10^6]$$
$$= (12.32 * 17 * 8.48 * 3600)/[22.4 * \{(25 + 273))/273\} * 10^6]$$
$$= (6.39 * 10^6)/(24.45 * 10^6)$$
$$= 0.26 \text{ kg/hr}$$

Annual emissions of NH_3 are calculated using Equation 7

$$E_{kpy, NH3} = E_{NH3} * OpHrs$$
$$= 0.26 * 1760$$
$$= 458 \text{ kg/yr}$$

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 8.

Equation 8

$$E_{kpy,i} = C_i * V * OpHrs/10^6$$

where:

$E_{kpy,i}$	=	emissions of pollutant i, kg/yr
C_i	=	concentration of pollutant i in wastewater, mg/L
V	=	hourly volume of wastewater, L/hr
OpHrs	=	operating hours per year for which data apply, hr/yr
10^6	=	conversion factor, mg/kg

In applying Equation 8 to water emission calculations, monitoring data should be averaged and only representative concentrations used in emission calculations.

3.2   Using Mass Balance

3.2.1   For Emissions to Air

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 of VOCs and speciated organics and inorganics can be made by applying Equation 9.

Equation 9

$$E_i = (Q_{in} - Q_{out}) * C_i$$

where:

E_i	=	total emissions of pollutant i, kg/hr
Q_{in}	=	material entering the process, L/hr
Q_{out}	=	material leaving the process as waste, recycled, or in product, L/hr
C_i	=	concentration of pollutant i, kg/L

The term Q_{out} 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 destinations for the pollutant of interest is necessary for an accurate emission estimate to be made using the mass balance approach. Example 4 illustrates the application of Equation 9.

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Example 4 - Using a Mass Balance for VOC Emissions

This example shows how VOC emissions may be calculated using Equation 9 for non-reactant materials (solvents and absorbents) added during a process operation given the following data:

Q_{in} = 6 L/hr
Q_{out} = 4 L/hr
C_{VOC} = 0.85 kg VOC/L

E_{VOC} = $(Q_{in} - Q_{out}) * C_{VOC}$
= (6 L/hr - 4 L/hr) * 0.85 kg VOC/L
= 1.7 kg VOC/hr

Emissions can be converted to a yearly basis by multiplying by the yearly hours of operation in units of hr/yr.

</div>

Speciated VOC emissions may be estimated by a mass balance approach using Equation 10:

Equation 10

$$E_i = (Q_{in} - Q_{out}) * \rho_m * (wt\%_i)/100$$

where:

E_i = total emissions of pollutant i, kg/hr
Q_{in} = material entering the process, L/hr
Q_{out} = material leaving the process as an emission, transfer, or as an article or product, L/hr
ρ_m = density of material, kg/L
$wt\%_i$ = percentage by weight of pollutant i in material, %

Example 5 illustrates the application of Equation 10.

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Example 5 - Using a Mass Balance to Speciate VOC Emissions
This example shows how pollutant i emissions may be calculated using Equation 10 for a manufacturing process operation given the following data:

Q_{in} = 6 L/hr
Q_{out} = 4 L/hr
ρ_m = 1.09 kg/L
$wt\%_i$ = 25%

E_i = $(Q_{in} - Q_{out}) * \rho_m * (wt\%_i)/100$
= (6 L/hr - 4 L/hr) * 1.09 kg/L * (25/100)
= 0.545 kg/hr

Emissions can be converted to a yearly basis by multiplying by the yearly hours of operation in units of hr/yr.

</div>

3.2.2 For Emissions to Wastewater

If no wastewater monitoring data exists, emissions to process water can be calculated based on a mass balance of the process, shown by Equation 11.

Equation 11

$$E_{kpy,i} = (Q_{in} - Q_{out})$$

where:

$E_{kpy,i}$	=	emissions of pollutant i, kg/yr
Q_{in}	=	amount of pollutant i used, kg/yr
Q_{out}	=	amount of pollutant i incorporated into product + treated on-site + transferred off-site in the reporting year, kg/yr

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.

3.2.3 For Emissions via Solid Waste

Wastewater treatment may transport the reportable chemical to a sludge. Facilities are often required to obtain data on the concentration of metals or and other substances in sludges as part of their licensing requirement and this data can be used to calculate the emissions as kilograms of sludge times concentrations of the substance in the sludge. Alternatively, the loss in the sludge can be estimated by Equation 12. Although listed substances in sludge transferred off-site for waste disposal/treatment do not require reporting, determining this loss may be a necessary step in the application of such a mass balance approach.

Equation 12

$$AS_i = (PL_i - WL_i) * OpHrs$$

where:

AS_i	=	amount of pollutant i in sludge, kg/yr
PL_i	=	process losses of pollutant i, kg/hr
WL_i	=	losses of pollutant i in wastewater, kg/hr
OpHrs	=	operational hours, hr/yr

For many chemicals used and emitted during chemical processes, some degradation in treatment may occur so not all of the chemical is 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.

3.3 Using Engineering and Site-Specific Equations

Theoretical and complex equations or *models* can be used for estimating emissions from explosives manufacturing. Inputs for theoretical equations generally fall into the following categories;
(1) chemical/physical properties of the material involved, such as vapour pressure and vapour molecular weight;
(2) operating data, such as the amount of material processed and operating hours; and
(3) physical characteristics and properties of the source, such as tank colour and diameter.

Use of engineering equations to estimate emissions from explosives 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.

3.3.1 Emissions Using Mass Transfer Kinetics

An EET based on mass transfer kinetics is shown by Equation 13 and Example 6 illustrates the use of this equation.

Equation 13

$$W_i = (MW_i * K_i * area * P_{vap,i}) / (R * T)$$

where:

W_i = evaporation rate of pollutant i, kg/sec

MW_i = molecular weight of pollutant i, kg/kg-mole

K_i = gas-phase mass transfer coefficient for VOC species i, m/sec, $[0.00438 * (0.62138 * U)^{0.78} * (18/MW_i)^{1/3}]/3.2808$

U = wind speed, km/hr

area = surface area, m^2

$P_{vap,i}$ = vapour pressure of pollutant i, kPa

R = universal gas constant at 1 atmosphere of pressure, 8.314 kPa * m^3/(kg-mole * K)

T   =   temperature, K

Example 6 - Using Mass Transfer Kinetics

This example shows how methanol emissions may be estimated using mass transfer kinetics and Equation 13 given the following data:

MW_i = 32 kg/kg-mole
U = 4.5km/hr
area = 0.6 m^2
$P_{vap,i}$ = 13.16 kPa
T = 296 K
R = 8.314 kPa * m^3/(kgmol * K)

First, calculate the mass transfer coefficient, K_i:

K_i = $[0.00438 * (0.62138 * U)^{0.78} * (18/MW_i)^{1/3}]/3.2808$
= $[0.00438 * (0.62138 * 4.5 \text{ km/hr})^{0.78} *$
$(18/32 \text{ kg/kg-mole})^{1/3}]/3.2808$
= 0.0025 m/s

Then, calculate W_i:

W_i = $(MW_i * K_i * \text{area} * P_{vap,i}) / (R * T)$
= $(32 \text{ kg/kg-mole} * 0.0025 \text{ m/sec} * 0.6 \text{ m}^2 * 13.16 \text{ kPa})/$
$\{(8.314 \text{ kPa} * \text{m}^3/(\text{kgmol} * K)) (296 K)\}$
= $2.56 * 10^{-4}$ kg/sec

Emissions from kg/sec can be converted to hourly basis (kg/hr) by multiplying by a conversion factor of (60) and emissions from kg/hr can be converted to a yearly basis by multiplying by the yearly hours of operation in units of hr/yr.

3.3.2   Emissions from Spills

A vaporisation equation can be used to estimate the evaporation rate of a liquid chemical spill if the size area of the spill is known or can be estimated. This is a simple equation and is illustrated by Equation 14.

Equation 14

$$E_i = (MW_i * K_i * area * P_i * 3600 * HR) / (R * T)$$

where:

E_i = emissions of VOC species i from the spill, kg/event

MW_i = molecular weight of VOC species i, kg/kg-mole

K_i = gas-phase mass transfer coefficient for VOC species i, m/sec

area = surface area of spill, m²

P_i = partial pressure of VOC species i (if a pure chemical is spilled) or the partial pressure of chemical i (if a mixture of VOCs is spilled) at temperature T, kPa; the partial pressure of VOC species i (P_i) may be calculated using Equation 15 or Equation 16

3600 = conversion factor, sec/hr

HR = duration of spill, hr/event

R = universal gas constant at 1 atmosphere of pressure, 8.314 kPa * m³/(kg-mole * K)

T = temperature of the liquid spilled, K

P_i may be calculated using Raoult's Law (for ideal solutions) or Henry's Law constants (when gases are dissolved at low concentrations in water). Raoult's Law is given in Equation 15.

Equation 15

$$P_i = m_i * VP_i$$

where:

P_i = partial vapour pressure of VOC species i, kPa

m_i = liquid mole fraction of VOC species i, mole/mole

VP_i = true vapour pressure of VOC species i, kPa

P_i may be calculated using Henry's Law constants and Equation 16.

Equation 16

$$P_i = m_i * H_i$$

where:

P_i = partial vapour pressure of VOC species i, kPa

m_i = liquid mole fraction of VOC species i, mole/mole

$$H_i \quad = \quad \text{Henry's Law constant for VOC species i, kPa}$$

The gas-phase mass transfer coefficient (K_i) may be calculated using Equation 17.

Equation 17

$$K_i \quad = \quad [0.00438 * (0.62138 * U)^{0.78} * (D_i/0.288)^{2/3}]/3.2808$$

where:

K_i = gas-phase mass transfer coefficient for VOC species i, m/sec
U = wind speed, km/hr
D_i = diffusion coefficient for VOC species i in air, cm²/sec

Diffusion coefficients (D_i) can be found in chemical handbooks and are usually expressed in units of square centimetres per second (cm²/s). If a diffusion coefficient is not available for a particular NPI-listed substance, the gas-phase mass transfer coefficient (K_i) may be estimated using Equation 18.

Equation 18

$$K_i \quad = \quad (0.00438 * (0.62138 * U)^{0.78} * (18/MW_i)^{1/3})/3.2808$$

where:

K_i = gas-phase mass transfer coefficient for VOC species i, m/sec
U = wind speed, km/hr
MW_i = molecular weight of VOC species i, kg/kg-mole

Example 7 illustrates the use of Equation 14 through to Equation 18. Emissions are calculated by following Steps 1 and 2.

Example 7 - Calculating Spill Emissions

Toluene is spilled onto the ground outside a building. The following data is given, physical data is derived from *Perry's Chemical Engineers' Handbook*:

- the spill is not detected for 1 hour; it takes an additional 2 hours to recover the remaining Toluene; the duration of the spill (HR), therefore, is 3 hours;
- the average wind speed (U) is 13 km/hr ;
- the ambient temperature (T) is 300 K (27°C);
- the surface area of the spill (area) is 11 m²;
- the molecular weight of Toluene (MW_i) is 92.13 kg/kg-mole; and
- the vapour pressure of Toluene (P_i) at 300 K (27°C) is 4.18 kPa.

Step 1: Using Equation 18, Calculate the Gas-Phase Mass Transfer Coefficient (K_i)

$$K_i = (0.00438 * (0.62138 * U)^{0.78} * (18 /MW_i)^{1/3})/3.2808$$
$$= (0.00438 * (0.62138 * 13)^{0.78} * (18 /92.13)^{1/3})/3.2808$$
$$= 0.0039 \text{ m/s}$$

Step 2: Using Equation 14, Calculate Emissions (E_i)

$$E_{toluene} = (MW_i * K_i * area * P_i * 3\,600 * HR) / (R * T)$$
$$= (92.13 * 0.0039 * 11 \ * \ 4.18 * 3\,600 * 3) / (8.314 * 300)$$
$$= 71.54 \text{ kg toluene spill}$$

3.3.3 Emissions from Fugitive Losses

Many of the engineering equations presented in this section are intended 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 explosives 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 explosives 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 4 and Equation 19, or
- Use the screening values obtained above and apply the emission factors, from Table 5, corresponding to the screening range obtained.

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 explosives plants. Equation 19 illustrates an approach for estimating fugitive inorganic chemical emissions using data from Table 4. An example of this estimation technique is given at Example 8.

Equation 19

$$E_{kpy,i} = ER_i * C_i/100 * OpHrs * \text{number of sources}$$

where:

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

Table 4 - Correlation Equations, Default Zero Emission Rates, and Pegged[c] Emission Rates for Estimating Fugitive Emissions

Equipment Type	Default Zero Emission Rate (kg/hr/source)	Pegged Emission Rates (kg/hr per source)		Correlation Equation (kg/hr per source) [a]
		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[b]	$7.5 * 10^{-6}$	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.

[a] 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.

[b] The emission estimates for light liquid pump seals can be applied to compressor seals, pressure relief valves, agitator seals, and heavy liquid pumps.

[c] 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 8 - Calculating Fugitive Chemical Leaks

An explosive manufacturing plant operates a light-liquid pump on an 80 percent ammonia solution storage tank. The pump is run for 8760 hours during the year.

For a Screening Value of zero ppmv

OpHrs	=	8760 hr/yr
SV (screening value)	=	0 ppmv
Default-zero emission rate	=	$7.5 * 10^{-6}$ kg/hr/source
NH_3 emissions	=	$ER_i * C_i/100 *$ OpHrs * number of sources
	=	$7.5 * 10^{-6}$ kg/hr/source * $(80/100) * 8760$ hr/yr
	=	$5.26 * 10^{-2}$ kg/yr

For a Screening Value of 20 ppmv

OpHrs	=	8760 hr/yr
SV (screening value)	=	20 ppmv
NH_3 emissions (kg/hr)	=	$1.90 * 10^{-5} (SV)^{0.824}$
	=	$1.90 * 10^{-5} (20)^{0.824}$
	=	$2.24 * 10^{-4}$ kg/hr
NH_3 emissions (kg/yr)	=	$2.24 * 10^{-4}$ kg/hr * 8760 hr/yr * $(80/100)$
	=	1.57 kg NH_3/yr

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 5, 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 20 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 5.

Equation 20

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

where:

$E_{kpy,i}$	=	emission rate of pollutant i from all equipment in the *stream* of a given equipment type, kg/yr/source
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* (number of sources)

Example 9 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 9 - Average Emission Factor Technique

This example shows how annual ammonia (NH_3) emissions can be calculated from pump seals using the emission factors from Table 5 and Equation 20. 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	8760
B	12	0.0199	1.00	4380

$$E_{kpy,NH3} = EF * WF_{NH3} * OpHrs * N$$

Stream A

$$E_{kpy,NH3} = 0.0199 * 0.80 * 8760 * 15$$
$$= 2092 \text{ kg/yr}$$

Stream B

$$E_{kpy,NH3} = 0.0199 * 1.00 * 4380 * 12$$
$$= 1046 \text{ kg/yr}$$

3.4   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 explosives.

Equation 21 is used to estimate a facility's emissions from application of emission factors.

Equation 21

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

where:

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

Table 5 - 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 [a]	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.

[a] The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

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} emissions (particulate matter with an equivalent aerodynamic diameter of 10 micrometres or less ie. $\leq 10\mu m$) 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.

Table 6 - Emission Factors for the Open Burning of TNT

Type of Explosive	PM_{10}[a] (kg/t)	Oxides of Nitrogen (NO_x) (kg/t)	Carbon Monoxide (CO) (kg/t)	Benzene (C_6H_6) (kg/t)	Volatile Organic Compounds (VOCs) (kg/t)
TNT	45	75	28	0.04235	0.55

Source: USEPA, AP-42 section 6.3, 1995.
Emission factor units are kg of substance emitted per tonne of TNT burned.
All emission factors are rated U
[a] PM_{10} = Particulate matter of aerodynamic diameter less than or equal to 10 micrometres.

Application of Equation 21 is illustrated by Example 10.

Example 10 - Using Emission Factors

Table 6 shows that 28 kg of carbon monoxide (CO) is emitted for each tonne of the open burning of TNT. If it is assumed that the facility operates for 5400 hours per year and production rate is 5000 t/yr (CE_i = 0).

$$E_{kpy,CO} = [A * OpHrs] * EF_{CO} * [1 - (CE_i/100)]$$
$$EF_{CO} = 28 \text{ kg/t}$$

$$E_{kpy,CO} = 1.08t/hr * 5400 \text{ hr/yr} * 28kg/t * [1 - (0/100)]$$
$$= 163\ 296 \text{ kg/yr}$$

Table 7 - Emission Factors for Explosives Manufacturing of TNT & Nitrocellulose[a, b]

Process	Particulate Matter (PM_{10})[b] (kg/t)	Sulfur Dioxide (SO_2) (kg/t)	Oxides of Nitrogen (NO_x) (kg/t)	Nitric Acid Mist $(100\% HNO_3)$ (kg/t)	Sulfuric Acid Mist $(100\% H_2SO_4)$ (kg/t)
TNT - Batch Process					
Nitration Reactors					
Fume Recovery	-	-	12.5 (3 - 19)	0.5	-
Acid Recovery	-	-	(0.5 - 68)	46	-
Nitric Acid Concentrators	-	-	18.5 (8 - 36)	-	4.5 (0.15 - 13.5)
Sulfuric Acid Concentrators					
Electrostatic Precipitator (exit)	-	7 (2 - 20)	20 (1 - 40)	-	32.5 (0.5 - 94)
Electrostatic Precipitator with Scrubber	-	negligible	20 (1 - 40)	-	2.5 (2 – 3)
Red Water Incinerator					
Uncontrolled	12.5 (0.015 - 63)	1 (0.025 - 1.75)	13 (0.75 - 50)	-	-
Wet Scrubber	0.5	1 (0.025 - 1.75)	2.5	-	-
Sellite Exhaust	-	29.5 (0.005 - 88)	-	-	3 (0.3 - 8)

Table 7 - Emission Factors for Explosives Manufacturing of TNT & Nitrocellulose [a,b] (Cont')

Process	Particulate Matter (PM$_{10}$) (kg/t)	Sulfur Dioxide (SO$_2$) (kg/t)	Oxides of Nitrogen (NO$_x$) (kg/t)	Nitric Acid Mist (100% HNO$_3$) (kg/t)	Sulfuric Acid Mist (100% H$_2$SO$_4$) (kg/t)
TNT -Continuous Process					
Nitration Reactors					
Fume Recovery	-	-	4 (3.35 - 5)	0.5 (0.15 - 0.95)	-
Acid Recovery	-	-	1.5 (0.5 - 2.25)	0.01 (0.005 - 0.015)	-
Red Water Incinerator	0.13 (0.015 - 0.25)	0.12 (0.025 - 0.22)	3.5 (3 - 4.2)	-	-
Nitrocellulose					
Nitration Reactors [c]	-	0.7 (0.04 - 1)	7 (1.85 - 17)	9.5 (0.25 - 18)	-
Nitric Acid Concentrator	-	-	7 (5 - 9)	-	-
Sulfuric Acid Concentrator	-	34 (0.2 - 67)	-	-	0.3
Boiling Tubs	-	-	1	-	-

USEPA, AP-42 section 6.3, 1995.

Emission factor uncertainty rating = C

For some processes, considerable variations in emissions have been reported.

Average of reported values is shown first and the ranges are shown in parentheses.

[a] Emission factor units are kg of substance emitted per tonne of TNT or nitrocellulose produced.

[b] PM$_{10}$ = Particulate matter of aerodynamic diameter less than or equal to 10 micrometres.

[c] For product with low nitrogen content (12%), use high end of range. For products with higher nitrogen content, use lower end of range

Table 8. Emission Factors for Processes in Ammonium Nitrate Manufacturing Plants [a]

Process	Particulate Matter		Ammonia	Nitric Acid
	Uncontrolled (kg/tonne of product)	Controlled [b] (kg/tonne of product)	Uncontrolled [c] (kg/tonne of product)	Controlled [d] (kg/tonne of product)
Neutraliser	0.045 - 4.3 [e]	0.002 - 0.22 [e]	0.43 - 18.0 [d]	0.042 - 1 [e]
Evaporator/concentration operations	0.26	ND	0.27 - 16.7	ND
Solids formation operation				
High density prill towers	1.59	0.60	28.6	ND
Low density prill towers	0.46	0.26	0.13	ND
Rotary drum granulators	146	0.22	29.7	ND
Pan granulators	1.34	0.02	0..07	ND
Coolers and dryers [f]				
High density prill coolers	0.8	0.01	0.02	ND
Low density prill coolers	25.8	0.26	0.15	ND
Low density prill dryers	57.2	0.57	0 - 1.59	ND
Rotary drum granulator coolers	8.1	0.08	ND	ND
Pan granular coolers	19.3	0.158 [d]	ND	ND
Coating operations [g]	< 2.0 [d]	< 0.02 [d]	NA	NA
Bulk loading operations [g]	<0.01 [d]	ND	NA	NA

[a] USEPA, AP-42, Section 8.3 ND = No data, NA = Not applicable, Emission factor uncertainty rating = A (except as noted)

[b] Based on the following control efficiencies for wet scrubbers, applied to uncontrolled emissions: neutralisers, 95%; high density prill towers, 62%; low density prill towers, 43%; rotary drum granulators, 99.9%; pan granulators, 98.5%; coolers, dryers, and coaters, 99%.

[c] Given as ranges because variation in data and plant operations. Factors for controlled emissions not presented due to conflicting results on control efficiency.

[d] Based on 95% recovery in a granulator recycle scrubber.

[e] Emission factor uncertainty rating = B

[f] Factors for coolers represent combined precooler and cooler emissions, and factors for dryers represent combined predryer and dryer emissions.

[g] Fugitive particulate emissions arise from coating and bulk loading operations

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 explosives detonation. 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 3.4 of this Manual.

4.1 Engineering Calculations

Theoretical and complex equations or *models* can be used for estimating emissions from the detonation of explosives.

Use of emission equations to estimate emissions from the detonation of explosives 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.

4.2 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 <u>will not</u> form part of the public NPI database.

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

5.0   References

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

- Emission Estimation Technique Manual for Combustion in Boilers;
- Emission Estimation Technique Manual for Combustion Engines; and
- Emission Estimation Technique Manual for Fuel & Organic Liquid Storage.