National Pollutant Inventory

Emission Estimation Technique Manual

for

Explosives Detonation and Firing Ranges

EMISSION ESTIMATION TECHNIQUES
FOR
EXPLOSIVES DETONATION
AND FIRING RANGES

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EXPLOSIVES DETONATION
AND FIRING RANGES

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1.0   Introduction

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

The activities covered in this Manual apply to facilities primarily engaged in the detonation of explosives through either the use of explosive ordinances, or the discharge of firearms.

HANDBOOK :   Explosives Detonation

ANZSIC CODES :

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 explosives commonly used in industry, and identifies substances likely to be emitted.

2.1   Process Description

An explosion is a physical or chemical phenomenon in which energy is released in a very short time (Ullmann, 1987). Although explosions can be of a mechanical, chemical, nuclear, or electrical origin, chemical explosions are the primary focus of this Manual.

There are a number of different explosives, and the main uses are in weaponry, extraction industries such as mining and quarrying, demolition work, and as a propellant for ammunition. Table 1 outlines the most common explosives, their composition, and general uses.

One of the most commonly used explosives in the mining industry uses a mixture of ammonium nitrate and fuel oil (ANFOs). The main products of the combustion of ANFOs are CO, CO_2, NO_X, PM_{10}, and H_2O. In Australia, it is estimated that the explosives industry uses at least 600 000 tonnes of ANFOs per annum (Dyno Nobel, 1999).

Table 1. Composition and Uses of Common Explosives

Explosive	Composition	Uses
Black powder	75/15/10 Potassium (sodium) nitrate/charcoal/sulfur	Delay fuses
Smokeless powder	Nitrocellulose (sometimes with other materials)	Small arms, propellant
Dynamite, straight	20-60% Nitroglycerine/sodium nitrate/wood pulp/calcium carbonate	Rarely used
Dynamite, ammonia	20-60% Nitroglycerine/ammonium nitrate/sodium nitrate/wood pulp	Quarries
Dynamite, gelatin	20-100% Nitroglycerine	Demolition, construction work, blasting in mines
ANFO	Ammonium nitrate with 5.8-8% fuel oil	Construction work, blasting in mines
TNT	Trinitrotoluene	Main charge in artillery projectiles, mortar rounds, etc.
RDX	$(CH_2)_3N_3(NO_2)_3$ Cyclotrimethylenetrinitroamine	Booster
PETN	$C(CH_2ONO_2)_4$ Pentaerythritol tetranitrate	Booster

Source: USEPA Document AP-42 (1995)

2.2 Emission Sources and Control Technologies

2.2.1 Emissions to Air

Air emissions may be categorised as:

Fugitive Emissions

These are emissions that are not released through a vent or stack. Emissions from the detonation of explosives tend to be the fugitive products of combustion, (eg. carbon monoxide, nitrogen dioxide and sulfur dioxide). Small volumes of other substances (eg. hydrogen sulfide, ammonia and hydrogen cyanide) may also be emitted depending on the type and composition of explosive- used. Emission factors are the usual method for determining losses through fugitive emissions.

Point Source Emissions

These emissions are exhausted into a vent or stack and emitted through a single point source into the atmosphere. However, there are not likely to be any point source emissions resulting from the activities covered in this Manual.

2.2.2 Emissions to Land

Emissions of substances to land (particularly lead) on-site can occur on firing ranges from bullets. Control technologies (eg. bullet traps) can be used to reduce lead emissions to land on firing ranges. If you have installed these control technologies at your facility, or have implemented work practices that reduce emissions, you should multiply the control efficiency of the technology, or the practice adopted, by the appropriate uncontrolled result obtained from an EET outlined in this manual.

3.0 Emission Estimation Techniques

Estimates of emissions of NPI-listed substances to air, water, and land should be reported for each substance that triggers a threshold. The reporting list and detailed information on thresholds are contained in *The NPI Guide* at the front of this Handbook.

In general, there are four types of emission estimation techniques (EETs) that may be used to estimate emissions from your facility. The four types described in the *NPI Guide* are:

- sampling or direct measurement;
- mass balance;
- fuel analysis or other engineering calculations; and
- emission factors.

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

If you estimate your emission by using any of these 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 the activities associated with the detonation of explosives, and the use of firing ranges. However, the absence of an EET for a substance in this Manual does not 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 the other EETs outlined 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

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quantity of the NPI reportable substance spilled, less the quantity recovered or consumed during clean up operations.

3.1 Engineering Calculations

An engineering calculation is an estimation method based on the physical/chemical properties (eg. vapour pressure of the substance), and mathematical relationships (eg. ideal gas law). Example 1 shows how to calculate emissions of carbon monoxide from the detonation of TNT.

Some information is available on the chemical decomposition of explosives, so that the amount of some NPI-listed substances produced from the combustion process (eg. carbon monoxide) can theoretically be calculated.

Example 1 – Estimating Carbon Monoxide Emissions from the Detonation of TNT

The result of the detonation of TNT is represented by the following general reaction series. This reaction forms the basis of the worked example.

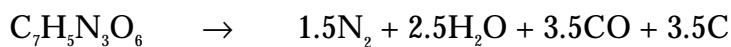The final products of the detonation of TNT:

N $\qquad \rightarrow \qquad$ N$_2$

2H + O $\qquad \rightarrow \qquad$ H$_2$O

C + O $\qquad \rightarrow \qquad$ CO

CO + O $\qquad \rightarrow \qquad$ C$_2$O
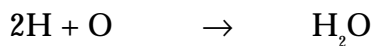
For TNT, the following reaction represents the basic oxidising reaction:
$\qquad$ C$_7$H$_5$N$_3$O$_6$ $\qquad \rightarrow \qquad$ 7C + 5H + 3N + 6O
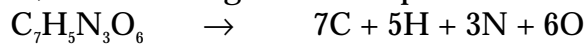
a) $\qquad$ 3N $\qquad \rightarrow \qquad$ 1.5 N$_2$
b) $\qquad$ 5H + 2.5O $\qquad \rightarrow \qquad$ 2.5H$_2$O (3.5O remaining)
c) $\qquad$ 7C + 3.5O $\qquad \rightarrow \qquad$ 3.5CO (all the O is used up) + 3.5C

The overall reaction is:
C$_7$H$_5$N$_3$O$_6$ $\qquad \rightarrow \qquad$ 1.5N$_2$ + 2.5H$_2$O + 3.5CO + 3.5C

Using the basic oxidising reaction, the total CO emissions from the detonation of TNT may be calculated using the following steps:

Total molecular weight of C$_7$H$_5$N$_3$O$_6$ $\qquad$ = (7 * C) + (5 * H) + (3 * N) + (6 * O)

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ = (7 * 12) + (5 * 1) + (3 * 14) + (6 * 16)
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ = 84 $\quad$ + $\quad$ 5 $\quad$ + $\quad$ 42 $\quad$ + $\quad$ 96
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ = 227 kg/kg-mol

Total Molecular weight of CO $\qquad$ = 12 + 16
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ = 28 kg/ kg-mol

Total weight of CO from reaction = 3.5 moles * 28kg/ kg-mol = 98kg

Total CO emissions = (98/227) * 1000kg/t = 431.7 kg of CO produced per tonne of
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ TNT detonated

Source: Explosives Engineering, (1996).

3.2 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 (eg. kilograms of sulfur dioxide emitted per tonne of ANFO detonated).

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

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

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, %

Emission factors developed from measurements for a specific process can 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 factors reviewed and approved by your State or Territory environment agency prior to its use for NPI estimations.

This Manual includes some USEPA data on dust emission factors for blasting in Table 6. This data does not stipulate particle size distribution. Some data is available in Table 5 for an emission factor for a particle size range of 2.5um-15um, stipulating an emission factor of 46.0kg/tonne of rock from blasting. Further particle size measurements may have to be undertaken in order to determine a more accurate emission factor for particulate matter less than 10 micrometres (PM_{10}).

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.

Table 2. Uncontrolled Emission Factors for the Detonation of Explosives
Emission Factor Rating: D (see Section 4.2)

Explosive	Emission Factor (kg/tonne)[a]					
	Carbon Monoxide (CO)	Nitrogen Oxides (NOx)	Ammonia (NH$_3$)	Hydrogen cyanide (HCN)	Hydrogen sulfide (H$_2$S)	Sulfur dioxide (SO$_2$)
Black powder	85	ND	NA	NA	12	NA
Smokeless powder[b]	38	ND	NA	NA	10	NA
Dynamite, straight	141	ND	NA	NA	3	NA
Dynamite, ammonia	32	ND	NA	NA	16	NA
Dynamite, gelatin	52	26	NA	NA	2	1
ANFO	34	8	NA	NA	NA	1
TNT	398	ND	14	13	NA	NA
RDX	98	ND	22	NA	NA	NA
PETN	149	ND	1.3	NA	NA	NA

Source: Adapted from USEPA Document AP-42 (1995)
[a] Units are kilograms (kg) of substance emitted per tonne (tonne) of explosive used.
[b] Ammunition may also contain lead in the bullet casing.
ND - No data available.
NA - Not applicable.

Table 3. Uncontrolled Emission Factors Derived from Thermochemical Calculations for Ammonium Nitrate-Dodecane Fuel Oil (ANFO) Species

Explosive	Emission Factor (kg/tonne)[a]
	Carbon Monoxide (CO)
Ammonium nitrate with Dodecane fuel oil	22

Source: Dyno Nobel
[a] Units are kilograms (kg) of substance emitted per tonne (tonne) of explosive used.

Table 4. Uncontrolled Emission Factors Based on Orica Australia's Powergel Golds, Energan Golds, and ANFO Species for the Small and Large Hole Markets

Explosive	Diameter Small (< 152mm) or Large (> 152mm)	Carbon Monoxide (CO)	Nitrogen Oxide (NO)
Bulk Products			
ANFO	Small	19.6	6
	Large	16.3	3.5
ENERGAN GOLD	Small	4.2	0
	Large	1.3	0
POWERGEL GOLD	Small	16.7	0
	Large	2.3	0
Packaged Products			
AMEX	All diameters	16.3	3.5
POWERGEL	All diameters	9.2	0.2

Source: Orica Australia

[a] Units are kilograms (kg) of substance emitted per tonne (tonne) of explosive used.

Tables 5 and 6 provide particle size distribution information for typical blasting activities and emission factors based on the total area blasted. This may vary from site to site depending on moisture content and other properties of the material blasted.

Table 5. Particle Size Distribution for a Range of Particle Sizes Relating to Blasting, and Estimated Uncontrolled Emission Factors for the Particle Sizes

Activity	Particle Size Ranges[b]	Emission Factor (kg/tonne)[a]
Blasting	0-2.5µm	5.1
	2.5-15µm	46.0
	15-30µm	49.9

Sources: USEPA (1981)

        Axtell & Lowheard, (1981). Improved Emission Factors for Western Surface Coal Mining Sources, Vol. 1. Sampling Methodology and Text Results. EPA Contract No. 68-03-2924.

        Coffey Geosciences Pty Ltd (1999).

[a] Units are kilograms (kg) of substance emitted per tonne (tonne) of explosive used.

[b] PM_{10} emissions relate to emissions from overburden.

Table 6. Uncontrolled Dust Emission Factor for Blasting

Activity	Emission Factor (kg/blast)[a]
Overburden Blasting	$0.00022A^{1.5}$

Sources: USEPA (1988)

[a] Emission factor in (kg/blast) and A is the area to be blasted in m^2.

Example 2 illustrates the use of emission factors for estimating emissions from a firing range.

Example 2 - Estimating Carbon Monoxide Emissions from a Firing Range.

To determine the emissions of carbon monoxide from a firing range, you should initially estimate the number and type of bullets used in a year. For example, 20,000 .223 calibre Remington bullets weighing 40 grains each, and 40,000 .270 calibre Winchester bullets each weighing 90 grains, are used in a year.

To determine the total weight of smokeless powder (nitrocellulose) used at the firing range in a year, you must firstly determine the weight of smokeless powder in each type of bullet, multiply this by the number of bullets of each type used, and then multiply the result by the conversion from grains to kilograms ($6.48 * 10^{-5}$), as indicated below:

Total Weight $= w * cf * n$ (2)

Where w = weight of nitrocellulose in a bullet of a particular calibre;
             cf = conversion factor from grains to kilograms ($6.48 * 10^{-5}$); and,
             n = number of bullets of this particular type used at the range in a year.

  Total Weight $= 54$ grains[1] $*$ $6.48 * 10^{-5}$ $*$ 40 000
                        $= 140$ kg nitrocellulose
                          (.270 Winchester)

  Total Weight $= 22.5$ grains[a] $* 6.48 * 10^{-5} * 20 000$
                        $= 29$ kg nitrocellulose
                          (.223 Remington)

Therefore, the total amount of nitrocellulose used at the firing range in a year is 140kg + 29 kg = 169 kg.

Multiply this figure by the emission factor for carbon monoxide from Table 2.

Emission = weight of explosive $*$ emission factor (g/kg)
                 $= 169$ (kg) $* 38$ (g/kg)
                 $= 6422$ grams
$E_{kpy,co}$ $= 6.422$ kg/yr of carbon monoxide emitted

[a] These weights were obtained from the "ADI Smokeless Powders Handloader's Guide", 2nd Edition, 1996.

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 NPI 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 will depend 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, (eg. the emission factors presented in Section 3.2 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, 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 the 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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