

**To:** Mr. David Krizek, Hudbay Minerals Inc., Copper World, Inc.  
**From:** David E.B. Strohm II, Trinity Consultants  
**Date:** May 30, 2023  
**RE:** Blasting NO<sub>x</sub> Emission Factor (EF) Determination and Documentation

This memorandum documents the source and applicability of the nitrogen oxide (NO<sub>x</sub>) emission factor (EF) used to calculate emissions from blasting with ammonium nitrate and fuel oil (ANFO) at the Copper World Project (Project).

## Background

The Copper World Project is a proposed open-pit mining facility owned and operated by Copper World, Inc. (Copper World), located approximately 28 miles southeast of Tucson, Arizona in Pima County.

Blasting is performed within the Project's open pit's. ANFO blasting agents will be used for nearly all rock breakage in dry ground.

Blasting has the potential to emit NO<sub>x</sub> emissions. Uncontrolled NO<sub>x</sub> emissions from blasting with ANFO are calculated using an emission factor found in *Atmospheric Environment 42* (2008) 7874-7883 "NO<sub>x</sub> Emissions from Blasting Operations in Open-Cut Coal Mining" by Moetaz I. Attalla, Stuart J. Day, Tony Lange, William Lilley, and Scott Morgan. This reference is included in Exhibit 1. The emission factor is 0.9 kg per metric ton based on reported average on page 7881 of the reference, excerpt shown below:

*The average flux level for all the blast plumes measured was 0.9 kg t<sup>-1</sup>.*

The use of this emission factor has recently undergone regulatory scrutiny and has been approved for use by the City of Albuquerque Environmental Health Department for the GCC Rio Grande, Inc. – Tijeras Facility located in Tijeras, NM.

## Emission Factor Development

In 2006, the "NO<sub>x</sub> Emissions from Blasting Operations in Open-Cut Coal Mining" by Moetaz I. Attalla, Stuart J. Day, Tony Lange, William Lilley, and Scott Morgan study was conducted in the Hunter Valley, New South Wales, Australia to develop a new approach to measure acidic gas emissions from blasting in open-cut coal mining.

In the study, portable Differential Optical Absorption Spectroscopy (DOAS) was used to monitor blasts. The DOAS used a spectrometer to determine the NO<sub>2</sub> concentration profile, measured in parts per million meter as a function of time. Data was recorded from the initiation of each blast until the NO<sub>2</sub> concentration profile was no longer distinguishable from the surrounding sky. Ground level measurements were taken using a Greenline 8000 portable gas analyzer, an instrument capable of continuous, simultaneous analysis of O<sub>2</sub>, CO<sub>2</sub>, CO, SO<sub>2</sub>, NO, and NO<sub>2</sub>. The blasts were also videotaped to record the dimensions of the blasts as a function of time as well. Stills from the videos were then used to calculate the volume of each blast plume at specified timestamps.

To estimate the NO<sub>2</sub> concentration from each blast at any given time, the NO<sub>2</sub> concentration profile was divided by the depth of the plume as recorded by the DOAS and measured in the video of the blast. The mass of NO<sub>2</sub> released from each blast was then calculated by multiplying the NO<sub>2</sub> concentration by the volume of the plume. Measurements made on the Greenline 8000 indicated a general trend of increasing NO<sub>2</sub> with increasing NO, with a relative proportion of NO to NO<sub>2</sub> to be 27 to 1. Based on the NO<sub>2</sub> measurements and estimated NO derived from the proportion to NO<sub>2</sub>, the average emission flux of NO<sub>x</sub> from the blasts studied was 0.9 kt/t (0.9 kg/mt).

### Other Agency Approval

The City of Albuquerque Environmental Health Department Air Quality Program (AQP) has reviewed the Title V air permit renewal application for the GCC Rio Grande, Inc. – Tijeras Facility originally submitted in 2021 and follow-up additional information submittals in 2022 and 2023. A draft permit was issued by the AQP on May 17, 2023 which incorporated these NO<sub>x</sub> blasting emission factors.<sup>1</sup> The renewal application and supplemental information included quarry blasting with ANFO, and utilized the NO<sub>x</sub> emission factor derived from the “NO<sub>x</sub> Emissions from Blasting Operations in Open-Cut Coal Mining” of 0.9 kg/mt. The AQP reviewed the methodology and results of the study and determined<sup>2</sup> that this 0.9 kg/mt NO<sub>x</sub> emission factor derived from the study was conservative and reasonable.

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<sup>1</sup> Statement of Basis - Title V Operating Permit, GCC Rio Grande – Tijeras Plant, Permit No. 0532-RN2. Draft issued May 17, 2023. See Section 6, blasting activities, “The NO<sub>x</sub> and SO<sub>2</sub> emission have decreased based on the updated emission factor and calculation. The Facility is in compliance with the NAAQS and NMAAQS.”

<sup>2</sup> Item 7a of City of Albuquerque Environmental Health Department August 5, 2022 letter from Kyle Tumpene to permit file with subject: Concerns with second response to the incompleteness determination for GCC Rio Grande, Inc. – Tijeras Facility Title V Permit #0532-RN1 Renewal (#0532-RN2).

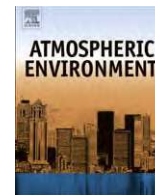
**Exhibit 1**

**Peer Reviewed Reference for  
NO<sub>x</sub> Blasting Emission Factor Development**



Contents lists available at ScienceDirect

# Atmospheric Environment

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## NO<sub>x</sub> emissions from blasting operations in open-cut coal mining

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### ABSTRACT

The Australian coal mining industry, as with other industries is coming under greater constraints with respect to their environmental impacts. Emissions of acid gases such as NO<sub>x</sub> and SO<sub>x</sub> to the atmosphere have been regulated for many years because of their adverse health effects. Although NO<sub>x</sub> from blasting in open-cut coal mining may represent only a very small proportion of mining operations' total NO<sub>x</sub> emissions, the rapid release and high concentration associated with such activities may pose a health risk. This paper presents the results of a new approach to measure these gas emissions by scanning the resulting plume from an open-cut mine blast with a miniaturised ultraviolet spectrometer. The work presented here was undertaken in the Hunter Valley, New South Wales, Australia during 2006. Overall this technique was found to be simpler, safer and more successful than other approaches that in the past have proved to be ineffective in monitoring these short lived plumes. The average emission flux of NO<sub>x</sub> from the blasts studied was about 0.9 kt t<sup>-1</sup> of explosive. Numerical modelling indicated that NO<sub>x</sub> concentrations resulting from the blast would be indistinguishable from background levels at distances greater than about 5 km from the source.

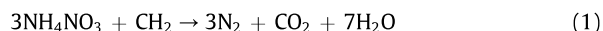
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### 1. Introduction

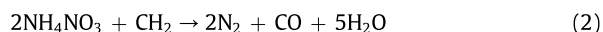
Open-cut coal mining is widespread in the upper Hunter Valley in New South Wales (NSW) with several large mines operating within close proximity to the towns of Muswellbrook and Singleton. Consequently, there is community concern about the potential environmental impacts of mining on nearby populations.

Blasting, in particular, has the potential to affect areas outside the mine boundary and accordingly, vibration and dust emission limits are set in each mine's environmental licence. However, gaseous emissions of environmental concern, such as nitrogen dioxide (NO<sub>2</sub>) may also be released during blasting operations. Currently, there are very little quantitative data relating to the magnitude of these emissions and it is not yet possible to determine if they contribute significantly to ambient levels in the main population centres.

The explosive ammonium nitrate/fuel oil (ANFO) is used almost universally throughout the open-cut coal mining industry. Under ideal conditions, the only gaseous products from the explosion are carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O) and nitrogen (N<sub>2</sub>).



However, even quite small changes in the stoichiometry (either in the bulk material or caused by localised conditions such as moisture in the blast hole, mineral matter or other factors) can lead to the formation of substantial amounts of the toxic gases carbon monoxide (CO) and nitric oxide (NO) as shown.



In addition, some of the NO formed may oxidise in the presence of oxygen (O<sub>2</sub>) to produce NO<sub>2</sub>.

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Often in practice, large quantities of  $\text{NO}_2$  are released from blasts which are observed as intense orange plumes.

Although these gases are not considered in their environmental licences, each mine is required to estimate annual emissions of  $\text{CO}$ ,  $\text{NO}_x$  and  $\text{SO}_2$  for the National Pollutant Inventory (NPI), compiled each year by the Australian government. These estimates are made by multiplying the amount of explosive consumed by an emission factor which is currently  $8 \text{ kg t}^{-1}$  for  $\text{NO}_x$ ,  $34 \text{ kg t}^{-1}$  for  $\text{CO}$  and  $1 \text{ kg t}^{-1}$  for  $\text{SO}_2$  (National Pollutant Inventory, 1999). These emission factors, however, are based on limited overseas data and are subject to high uncertainty.

Most of the studies which have examined  $\text{NO}_x$  formation from blasting have used blast chambers. The results from these studies do not necessarily correlate with what is observed during actual blasts. Few studies have attempted to measure  $\text{NO}_x$  emissions under actual field conditions, presumably because of the practical difficulties involved. Plumes from blasting lack confinement, can be very large in size and are affected by prevailing weather conditions. There is also a large quantity of dust associated with the blast and these factors combine to make physical sampling of the plume very difficult. There are also the obvious safety implications which restrict access to blast sites. Consequently, quantitative measurements of plume characteristics are generally unavailable. Nevertheless, it is important for mine operators, particularly when their operations are close to residential areas, to have some method for assessing  $\text{NO}_x$  formation and more importantly, predicting the severity of the  $\text{NO}_x$  plume. At present predictions of  $\text{NO}_x$  formation are subjective and are based on the blast engineer's knowledge of the area to be blasted (e.g. rock type, area of the mine, presence of water in the holes, etc.) and the ratings obtained from blasts performed under similar conditions. Quantitative flux estimations of  $\text{NO}_x$  released from a blast require measurement of concentration through the plume in both the horizontal and vertical axes.

Some of the options available to make these measurements are given in the following sections.

### 1.1. Physical sampling

Sampling of blasting fumes involves taking a sample of gas from the plume for subsequent analysis, which could be either on site or in an off site laboratory. Although physical sampling could in principle provide sufficient information to characterise a plume, there are a number of serious logistical problems with this approach:

- The size of the plume means that a large number of sample points would be required to sample across the width and height of the plume.
- The force of the explosion and the resulting debris would restrict the proximity of any sampling packages to the initial gas release.
- The potential toxicity of the plume; personnel cannot move through it to take samples, hence sampling stations must be fixed prior to the blast. This means

that the path of the plume must be anticipated before the blast.

### 1.2. Continuous analysis

Another option is to use portable analysers to measure  $\text{NO}_x$  concentrations in real time. There are, however, disadvantages with this approach since a sample of the plume must be presented to the instrument for analysis. Usually a pump draws air through a small diameter tube into the instrument, but to achieve the necessary spatial characterisation of the plume, sample tubes would need to be positioned at various points throughout the plume. Thus many of the problems identified for the physical sampling would also apply to the use of continuous analysers.

### 1.3. Optical methods

There are several optical methods of analysis currently available that may be applicable to field measurements of  $\text{NO}_x$ . These include open-path Fourier Transform Infra-Red Spectroscopy (FT-IR), Correlation Spectroscopy (COSPEC) and Differential Optical Absorption Spectroscopy (DOAS). FT-IR has often been used in air pollution studies (e.g. Levine and Russwurm, 1994). It has also been used in mine situations to measure fugitive methane emissions. Kirchgessner et al. (1993) used open-path FT-IR (op-FT-IR) to estimate methane emissions from open-cut coal mines in the United States. The technique relies on passing a collimated infrared beam through ambient air over a path length of up to several hundred metres. In the Kirchgessner et al. (1993) study, the concentration of methane across the plume was measured then wind speed data and a Gaussian plume dispersion model were used to estimate the methane emission rate from the mine. These authors subsequently developed a modification of their method which improved its accuracy (Piccot et al., 1994, 1996). The improved method was essentially the same as described above except that methane concentrations were measured at several elevations to better characterise the plume.

In principle, open-path FT-IR could be used to measure  $\text{NO}_x$  in blast plumes since it is sensitive to  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{CO}$  along with other gases. Infrared radiation is also strongly absorbed in many parts of the spectrum by both  $\text{CO}_2$  and water which are very likely to be present in high concentrations in blast plumes and this may tend to obscure the  $\text{NO}_x$  signal. High resolution instruments may resolve at least some of the  $\text{NO}_x$  absorption lines, however, a more serious drawback with op-FT-IR is that the infrared beam would be substantially attenuated by the dust thrown up by the blast. In the period immediately after the blast when the dust level is very high it is likely that the IR beam would be completely blocked thus making measurements impossible.

Another well established optical method is Correlation Spectroscopy (COSPEC). The system was first described by Moffat and Milan (1971) and was designed to measure point source emissions of  $\text{SO}_2$  and  $\text{NO}_2$  from industrial plants but found a niche application in the measurement of  $\text{SO}_2$  fluxes from volcanoes (Galle et al., 2002). The COSPEC system utilises a "mask correlation" spectrometer and was designed to measure vertical or slant columns using

sky-scattered sunlight. By traversing beneath plumes with the mobile instrument, the concentration of the column is calculated and, once multiplied by the plume velocity, produces a source emission rate. These instruments are limited to detecting only those species where masks are available. They also suffer from interferences from other atmospheric gases and light scattering from clouds or aerosols that can produce errors in column densities (Chalmers Radio and Space Science, website).

The DOAS technique is a relatively new technique that is gaining widespread acceptance as an air pollution monitoring method. Like the open-path FT-IR method, the DOAS can simultaneously measure concentrations of a number of species over path lengths which typically range from hundreds of metres to kilometres.

A DOAS, configured as an 'active system', Fig. 1, has three main parts – a light emitter, a light receiver and a spectrometer. The emitter sends a beam of light to the receiver (in some cases the emitter and receiver are contained in the same unit and the light beam is reflected off a remotely located passive reflector). The light beam contains a range of wavelengths, from ultraviolet to visible, although instruments are now available with an infrared source, which extends the range of compounds that can be detected. Different pollutant molecules absorb light at different wavelengths along the path between the emitter and receiver. The receiver is connected to the spectrometer which measures the intensity of the different wavelengths over the entire light path and through the data system converts this signal into concentrations for each of the species being monitored.

DOAS instruments are routinely used to measure  $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{O}_3$ .

More recently, advances in miniaturising UV–vis spectrometers has lead to the development of much more compact DOAS units, configured as a passive system (Fig. 1), which have come to be known as "mini-DOAS". The mini-DOAS system has so far been used mainly in the study of  $\text{SO}_2$  fluxes in volcanic emissions (McGonigle et al., 2003).

## 2. Methodology

### 2.1. Field measurements

A portable DOAS (mini-DOAS) manufactured by Resonance Ltd was used in this study. The instrument covers

a spectral range of 280–420 nm and can measure sub-part per million levels of  $\text{NO}_2$  and  $\text{SO}_2$ . The unit, which comprises a telescope, scanning mirrors, calibration cells and a miniature CCD array spectrometer (Ocean Optics USB2000 spectrometer), is housed in a small package which is mounted on a tripod. Calibration of the instrument was carried out using the internal calibration cell. The concentration of the cell was equivalent 50 ppm m. No  $\text{SO}_x$  measurements were undertaken.

Data collection and processing were performed by Ocean Optics OOIBase32 software loaded in a laptop computer. This results in a more compact system that is easier to deploy at mine sites and provides greater flexibility in positioning the instrument in relation to the blast plume.

Prior to each monitored blast, a dark spectrum was collected by blocking light from entering the spectrometer and a scan was performed. To produce a reference spectrum, a further scan was performed in a clear sky background which contained background absorption from  $\text{NO}_2$ . The reference spectrum was required in order to determine the increase in concentration of  $\text{NO}_2$  above ambient levels in the blast plumes.

The plume resulting from each blast was tracked with the spectrometer until the  $\text{NO}_2$  concentration was indistinguishable from the surrounding sky. During each field measurement, the mini-DOAS and a video camera were positioned a safe operating distance from the blast at all times.

$\text{NO}_2$  concentrations in the plume were calculated by subtracting the dark spectrum from the measured spectrum and the reference spectrum using the supplied software.

The results obtained from the mini-DOAS are a path-averaged  $\text{NO}_2$  concentration profile measured in units of parts per million metre (ppm m). The mini-DOAS results must be divided by the path length through the plume to yield a concentration. To estimate the amount of  $\text{NO}_2$  released from each blast it was necessary to multiply the concentration by the volume of the plume. Hence it was necessary to estimate the dimensions of each plume.

All of the blasts monitored were video-taped using at least one, and sometimes two, video recorders. The distances between the cameras and the blast were measured by locating their positions with a handheld GPS receiver.

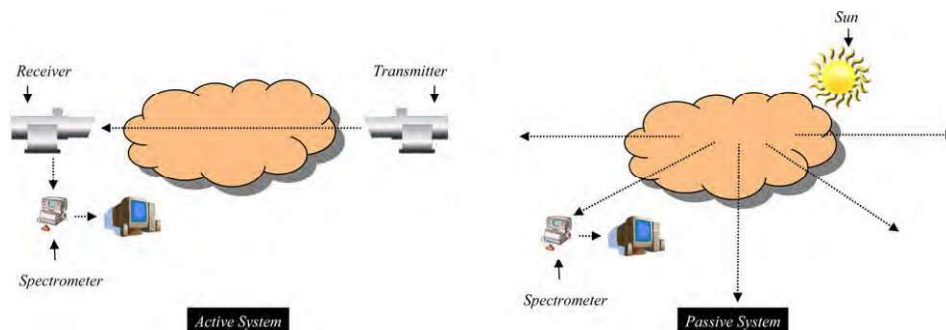


Fig. 1. Schematic diagram of DOAS systems operating in both active and passive modes.

Wind speed and directional data used to plot the directional path of the plume were obtained from a series of meteorological stations located around the mining lease. Simple trigonometry was employed to determine the distance from the video camera to the plume at the corresponding time intervals.

A rudimentary method of photogrammetry was then used to estimate the size of the plume based on still images extracted from the videos. Ratios of the plume to picture size in both the vertical and horizontal planes were made.

Once the plume to camera distance and the constraining angle for the plume is known, a crude three-dimensional estimate of the plume dimension was calculated using basic trigonometric functions. An example of the dimensions determined for a plume using this method is shown in Fig. 2.

Ground level measurements were carried out using a Greenline 8000 portable gas analyser. This instrument is capable of continuous, simultaneous analysis of O<sub>2</sub>, CO<sub>2</sub>, CO, SO<sub>2</sub>, NO and NO<sub>2</sub>. It is battery powered and can operate unattended for up to about 2 h. The instrument was calibrated against a standard gas mixture before each use. Data were logged on a laptop computer connected to the instrument.

For each experiment, the instrument was set up downwind of the blast in a location where the plume was expected to pass, but far enough away to avoid flying debris. The inlet probe was fixed at about 2 m above ground level.

It must be noted that selecting an appropriate location for the instrument was often difficult. In many cases, the wind conditions were quite variable, especially within the pit so it was not always possible to correctly anticipate the path of the blast plume. As well, the layout of the mine pit and safety considerations imposed constraints on where the instrument could be placed. Because of these problems, the plumes from many of the blasts did not pass over the analyser and data was not recorded.

## 2.2. Modelling

A simple modelling exercise was undertaken for this study to determine if the release of NO<sub>2</sub> from a blast could be of detriment to persons exposed to the plume within

5 km of the release. The results of this study are indicative and based on the assumption that the model used is appropriate. Modelling generally relies on local observational data to confirm the performance of the model. The difficulty in measuring emissions from mining blasts has meant that in this case the model is used as an indicator relying on the verifications used in the development of the chosen model. For this reason we have modelled concentrations directly downwind of theoretical blasts with AFTOX (Kunzel, 1991), a USEPA approved dispersion model ([http://www.epa.gov/scram001/dispersion\\_alt.htm#aftox](http://www.epa.gov/scram001/dispersion_alt.htm#aftox)). The original DOS based QuickBasic code was transformed into Excel macros to enable many scenarios to be run.

AFTOX is a Gaussian Puff model developed for the United States Air Force to assess real time toxic chemical releases. The model uses information from US Air Weather Service (AWS) stations to calculate dispersion based on measured atmospheric conditions. As for all Gaussian models, the spread of pollutants is governed by dispersion coefficients in the horizontal ( $\sigma_y$ ) and vertical ( $\sigma_z$ ) directions. These coefficients depend on the atmospheric stability derived from the AWS data. In this study, the scenarios were modelled by predefining the wind speed and atmospheric stability classes. The wind speeds modelled ranged from very low ( $0.5 \text{ m s}^{-1}$ ) to moderate ( $10 \text{ m s}^{-1}$ ). Stability was modelled in six steps representing the standard Pasquill–Gifford stability classes, i.e. A–F, where A, B and C represent unstable conditions (where A is the most unstable), D is neutral and E and F are stable conditions. These stability classes are used to categorise the rate at which a plume will disperse. Unstable conditions might be found on a sunny day with light winds leading to rapid plume dispersion while the stable conditions may occur in clear skies with light winds and perhaps a temperature inversion present. Plume spread is slow in these circumstances.

AFTOX is operated by assuming an emission release from a single location. The emissions can be either continuous or instantaneous. In this study AFTOX was used to describe an area source by representing it as a large number of individual points. The area of the emission (i.e. the area over which the explosives were distributed) was

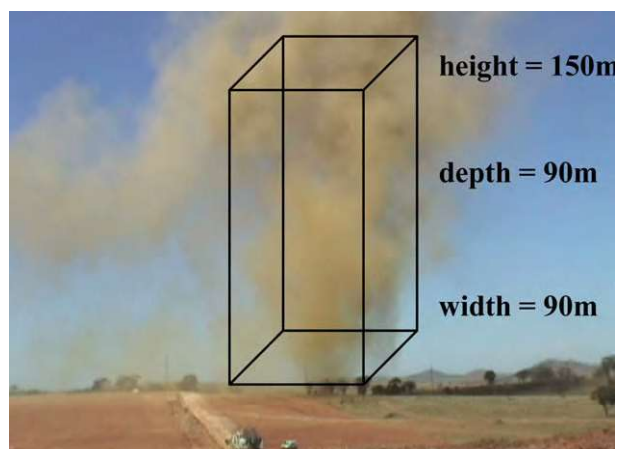


Fig. 2. Blast plume with estimated dimensions.

assumed to be 100 m × 200 m based upon sizes commonly observed during the field measurements. The area was subdivided into 10 m × 10 m units. Each square was represented by a point source with its source at the centre. In total, the area was modelled as 231 separate point sources (see Fig. 3). The total flux of emissions for the source was set at 100 kg. To estimate the maximum concentration and pollutant exposure values, the values should be multiplied by an appropriate scaling factor.

One hundred and twenty scenarios were modelled in which the 100 kg of emissions were spread randomly throughout the source area. A multi-stage process was employed for this task. In the first step, the total maximum number of points emitting was determined. This was defined by a random number between 20% and 80% of the maximum number of sources (in this case 231). The range chosen was an estimate from the portion of blasts that appeared to fume in conditions witnessed during this study. The total emission was then divided by this number. Each portion of the total emission was then placed randomly within the emission area. This process allowed certain points to receive multiple portions of the total emissions enabling the formation of hot spots. An example of one emission grid (Scenario 1 of 120) is displayed in Fig. 4.

Concentrations were determined for each of the 120 emission scenarios at distances of 200 m, 300 m, 400 m, 500 m, 750 m, 1 km, 1.25 km, 1.5 km, 2 km, 2.5 km, 3 km, 4 km and 5 km from the origin of the source. A concentration was determined for a number of discrete times that encompassed the complete plume travelling past the receptor. Further the concentrations were determined at 21 locations 10 m apart in a plane parallel and directly downwind of the source area (see Fig. 3). An average concentration from each of the receptors was determined; in this case with  $N$  equal to 21.

$$C^* = \frac{1}{N} \sum_{i=1}^N C_i \quad (5)$$

The average for each scenario was then used to create an ensemble average and standard deviation for the entire run (i.e.  $N = 120$ ).

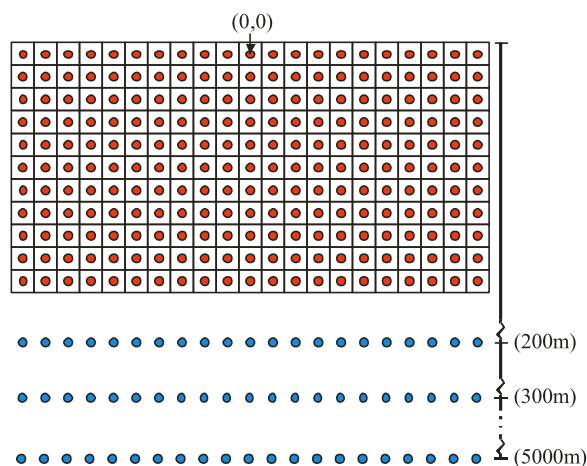


Fig. 3. Emission grid and receptor array setup.

$$\bar{C} = \frac{1}{N} \sum_{j=1}^N C_j^* \quad (6)$$

$$\sigma_{\bar{C}} = \frac{1}{N} \sum_{j=1}^N (C_j^* - \bar{C})^2 \quad (7)$$

$$C_{\max} = \max_{k=1}^N [\bar{C}_k] \quad (8)$$

A dosage expressed in ppm s was determined from the times when the ensemble average plume travelled past the receptors located at each distance downwind of the source. Again  $N$  represents each discrete time step ( $dt$ ) where  $C' \neq 0$ .

$$C_{\text{dose}} = \sum_{k=1}^N (\bar{C}_k) dt \quad (9)$$

The relative variation for the dosage is provided by similarly treating the ensemble standard deviation.

$$\sigma_{\text{dose}} = \sum_{k=1}^N (\sigma_{\bar{C}_k}) dt \quad (10)$$

### 3. Results and discussion

#### 3.1. Field measurements

Plume measurements were made using the mini-DOAS spectrometer at two open-cut mine sites located in the Hunter Valley. The combination of the spectral analysis and the plume estimation technique allowed for  $\text{NO}_2$  concentration and mass flux estimates to be made remotely, totally eliminating the requirement of physical sampling.

An example of the spectral output produced by the mini-DOAS is shown in Fig. 5. The spectral output consists of the  $\text{NO}_2$  concentration (ppm m) as a function of time. The figure also contains a series of photographs depicting the formation of a blast plume at time intervals of 70, 110, 163, 250 and 350 s post-blast initiation. It is worth noting the change in intensity of the colour of plume and size as a function of time.

Reliable concentration measurements with the mini-DOAS may only be made when the spectrometer is aimed into a sky background above the horizon from the point of observation. In this example, a peak concentration of 580 ppm m was achieved in 163 s post-blast initiation (third image from the left). At this time the plume has risen above the horizon from the point of observation. The plume to mini-DOAS distance at this stage is approximately 500 m, with an estimated plume depth of 105 m. This results in a  $\text{NO}_2$  concentration of 5.6 ppm at that particular stage of the plumes' dispersion.

After 350 s, the plume is barely visible and is now estimated to be approximately 650 m from the mini-DOAS unit. The plume depth has increased to 125 m with



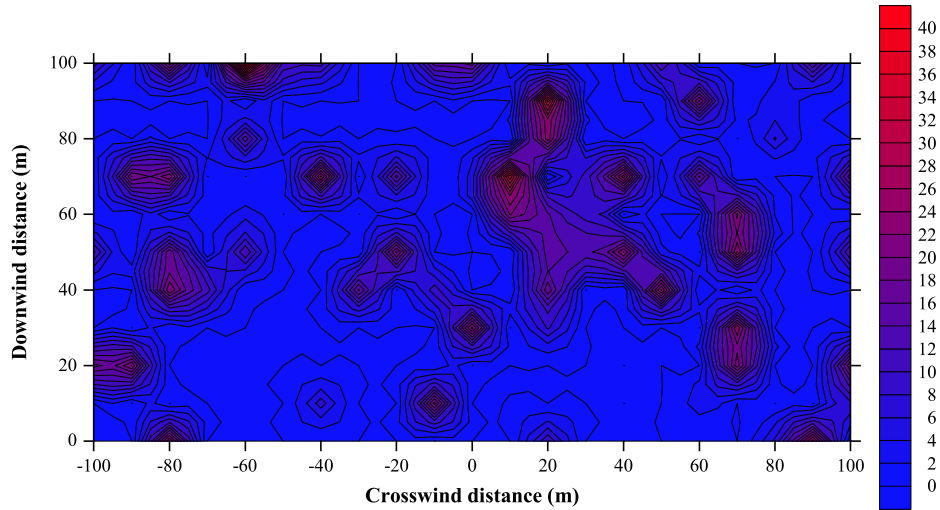


Fig. 4. Example of emission grid for 1 of the 120 scenarios modelled (the scale on the right hand side refers to NO<sub>2</sub> concentration in ppm).

a corresponding increase in plume volume by a factor of two. This expansion of the plume corresponds to a decrease in NO<sub>2</sub> concentration to 2.8 ppm.

At 360 s the plume was no longer visible to the eye and was lost for a short period of time to the mini-DOAS. This, however, was rectified with scanning of the sky with the spectrometer until the invisible plume was tracked for a further period.

Results for all plumes monitored during field work at both mine sites are given in Table 1. The table gives the peak NO<sub>2</sub> concentration as measured by the mini-DOAS above the horizon. Also given in the table is the plume volume at peak concentration and the calculated mass of NO<sub>2</sub> released from the blast. The mass of ANFO typically used in a blast was on average 210 tonnes, ranging from 60 to

565 tonnes. The explosive was distributed over an area of typically 200 m × 100 m containing approximately 200 bole holes with 200 mm diameter and to a depth of 25 m.

From the table the maximum NO<sub>2</sub> concentrations were found to range from 0 to about 7 ppm. This range of concentrations translated to 0–63.3 kg of NO<sub>2</sub> in the plume. However, no correlation can be made between blast charge and NO<sub>2</sub> levels.

During the measurements with the mini-DOAS ground level measurements were also carried out using a portable combustion gas analyser (Greenline 8000) to augment the airborne measurements made by the mini-DOAS. For NO<sub>2</sub> the ground level measures were higher than those observed using the mini-DOAS at higher altitudes. When the results of both measurement methods were applied to

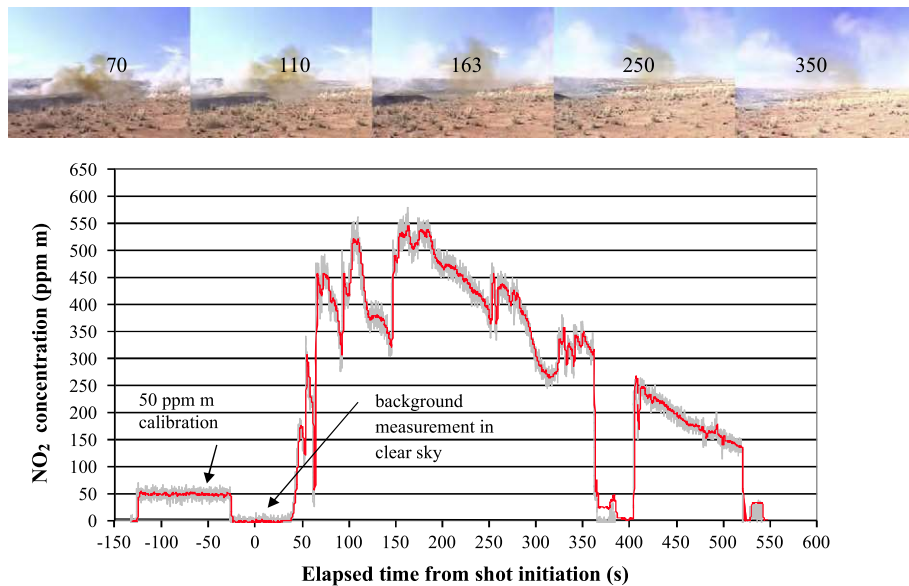


Fig. 5. Typical NO<sub>2</sub> spectrum demonstrating plume colour characteristics relative to concentration level.

**Table 1**  
Through plume measurement results

Date	Total ANFO charge (t)	Peak NO <sub>2</sub> Conc (ppm)	Plume volume (m <sup>3</sup> × 10 <sup>-6</sup> )	Mass of NO <sub>2</sub> (kg)	Emission flux (kg t <sup>-1</sup> ANFO)		
					NO	NO <sub>2</sub>	NO <sub>x</sub>
12/12/2005	281	3.7	1.4	9.9	0.5	0.03	0.6
13/12/2005	150	0.4	5.3	3.7	0.4	0.03	0.4
14/12/2005	119	0.0	0.0	0.0	0.0	0.00	0.0
21/12/2005	229	1.0	4.4	7.9	0.6	0.04	0.6
22/12/2005	211	0.0	0.0	0.0	0.0	0.00	0.0
23/12/2005	222	0.0	0.0	0.0	0.0	0.00	0.0
5/01/2006	177	1.0	0.2	0.4	0.0	0.00	0.0
6/01/2006	275	1.1	15.3	30.6	1.8	0.12	1.9
12/01/2006	225	1.6	6.2	18.3	1.3	0.08	1.4
18/01/2006	169	1.3	1.7	0.2	0.4	0.02	0.4
23/01/2006	139	2.1	4.2	16.7	1.9	0.12	2.0
25/01/2006	155	0.4	4.4	2.9	0.3	0.02	0.4
30/01/2006	132	0.7	5.3	7.1	0.8	0.05	0.9
22/02/2006	224	0.0	0.00	0.0	0.0	0.00	0.0
1/03/2006	194	1.6	20.6	63.3	5.0	0.32	5.3
12/05/2006	362	6.5	1.9	23.3	1.0	0.06	1.1
15/05/2006	131	0.3	3.2	1.7	0.2	0.01	0.2
19/05/2006	168	0.0	0.00	0.0	0.0	0.00	0.0
30/05/2006	100	0.8	0.00	1.0	0.0	0.00	0.0
1/06/2006	365	0.7	3.5	4.9	0.2	0.01	0.2
6/06/2006	145	0.8	11.5	17.5	1.9	0.12	2.0
15/06/2006	60	0.0	0.00	0.0	0.0	0.00	0.0
26/06/2006	254	4.3	0.3	2.1	0.1	0.01	0.2
27/06/2006	212	5.6	0.9	10.0	0.7	0.04	0.7
28/06/2006	241	0.0	0.00	0.0	0.0	0.00	0.0
6/07/2006	565	2.8	2.7	14.0	0.4	0.03	0.4
13/07/2006	184	7.0	1.0	12.6	1.1	0.07	1.2

dispersion modelling techniques strong agreement was observed.

Point measurements which were made on Greenline 8000 indicated that a loose relationship existed between

NO and NO<sub>2</sub> concentration. Although a strong correlation was not found, there is a general trend of increasing NO<sub>2</sub> with increasing NO. It was generally found that the relative proportion of NO to NO<sub>2</sub> from our data set was 27 to 1. This

**Table 2**  
Maximum calculated NO<sub>2</sub> concentrations downwind of source

	200 m	300 m	400 m	500 m	750 m	1000 m	1250 m	1500 m	2000 m	2500 m	3000 m	4000 m	5000 m
WSPD = 0.5 m s <sup>-1</sup>													
Stab A	83.0	30.0	14.4	7.9	2.5	0.9	0.4	0.2	0.1	0.0	0.0	0.0	0.0
Stab B	145.8	69.3	40.8	25.4	10.1	4.8	2.6	1.6	0.7	0.4	0.2	0.1	0.1
Stab C	219.4	122.0	80.8	55.9	26.8	14.3	8.6	5.6	2.8	1.6	1.0	0.5	0.3
Stab D	321.1	201.5	146.0	113.1	64.6	40.2	26.1	18.6	10.5	6.7	4.5	2.4	1.4
Stab E	390.2	267.4	204.3	165.5	109.6	75.9	54.6	41.3	26.4	17.9	12.7	7.1	4.5
Stab F	464.1	339.8	269.0	222.6	154.5	114.9	88.6	69.7	50.4	37.0	27.8	16.7	11.0
WSPD = 3 m s <sup>-1</sup>													
Stab A	78.5	29.1	14.2	7.7	2.4	0.9	0.4	0.2	0.1	0.0	0.0	0.0	0.0
Stab B	137.6	67.7	39.7	25.1	10.0	4.8	2.6	1.6	0.7	0.4	0.2	0.1	0.1
Stab C	211.6	118.7	77.6	55.2	26.0	14.0	8.6	5.6	2.8	1.6	1.0	0.5	0.3
Stab D	312.5	197.9	143.2	110.0	62.5	39.3	26.1	18.2	10.5	6.7	4.5	2.4	1.4
Stab E	383.0	267.0	202.1	162.6	106.3	73.7	54.1	40.3	26.1	17.7	12.5	7.2	4.5
Stab F	461.5	344.6	268.4	220.8	151.1	112.3	86.1	67.6	48.9	36.4	27.5	16.6	11.0
WSPD = 7.5 m s <sup>-1</sup>													
Stab A	62.5	25.5	13.0	7.3	2.3	0.9	0.4	0.2	0.1	0.0	0.0	0.0	0.0
Stab B	111.9	56.1	34.2	22.6	9.4	4.6	2.6	1.6	0.7	0.4	0.2	0.1	0.1
Stab C	173.3	100.4	66.5	47.7	23.8	13.2	8.2	5.4	2.7	1.6	1.0	0.5	0.3
Stab D	261.2	167.9	122.1	92.3	54.8	35.3	23.7	17.2	10.1	6.5	4.4	2.3	1.4
Stab E	325.9	232.2	175.8	139.6	89.5	63.8	46.7	36.0	23.9	16.8	12.1	7.0	4.4
Stab F	394.6	302.7	237.0	194.3	132.2	96.1	73.3	59.0	43.6	33.3	25.7	15.8	10.5
WSPD = 10 m s <sup>-1</sup>													
Stab A	53.0	22.6	11.9	6.9	2.3	0.9	0.4	0.2	0.1	0.0	0.0	0.0	0.0
Stab B	92.3	49.7	31.0	20.9	9.0	4.5	2.5	1.5	0.7	0.4	0.2	0.1	0.1
Stab C	140.1	84.2	57.7	42.1	21.7	12.6	7.9	5.3	2.7	1.6	1.0	0.5	0.3
Stab D	205.5	138.3	102.4	79.9	48.6	31.8	22.1	16.4	9.7	6.4	4.3	2.3	1.4
Stab E	254.0	184.0	143.0	116.4	78.0	56.2	42.6	33.1	22.7	16.0	11.6	6.9	4.4
Stab F	306.8	235.8	189.6	157.9	109.9	82.8	64.5	52.2	40.0	30.9	24.0	15.2	10.2

relationship enabled the estimation of the NO fluxes in the blast plume with a reasonable level of confidence.

The results obtained in this study are the only published quantitative data available on blast plume gas composition that the authors are aware of and it is useful to compare them to the emission factors currently used for NPI estimates.

Based on the NO<sub>2</sub> measurements and estimates of NO, the flux for NO<sub>x</sub> was calculated to be in the range of 0.04–5.3 kg t<sup>-1</sup> ANFO. The average flux level for all the blast plumes measured was 0.9 kg t<sup>-1</sup>. This figure is considerably lower than the current NPI emission factor which is 8 kg t<sup>-1</sup>.

### 3.2. Modelling

Results of the modelling runs are summarised in Table 2 and show the peak NO<sub>2</sub> concentrations (ppm) at various points downwind of the blast for the six atmospheric stability classes considered.

Examples of the modelled data are plotted in Fig. 6 and Fig. 7. In Fig. 6 a plot is displayed for the concentration estimate of one scenario at a distance of 200 m from the source origin and for a wind speed of 2 m s<sup>-1</sup> and a stability class C. In this plot 21 lines are shown representing the dose received directly downwind of the source at the locations displayed in Fig. 3. In this figure it is apparent that there is a considerable difference in the concentration predicted at each of the 21 receptors. It should be noted that the distance of 200 m is defined from the origin of the source area (0, 0) as displayed in Fig. 3. At this distance emission sources at 100 m will cause significantly higher concentrations than those occurring at positions toward the origin. In comparison the concentrations predicted at the receptor array 1 km from the source show more normally defined distributions with maxima occurring towards the middle receptors as a result of crosswind diffusion.

Receptors toward the edge of the sample array receive less crosswind influence and are, therefore, smaller in concentration. Also apparent in these two figures is the considerable difference in the predicted peak concentrations with the values at 1 km up to 25 times lower than at 200 m. When viewing Table 2, the peak values at 5 km approach ambient levels for all but the most stable conditions which are quite commonly over predicted with Gaussian models. For future studies it is recommended that a long path technique on a mining lease boundary may provide both a measure of the model accuracy as well as a direct measure of the impact in areas directly surrounding the mining area.

The data presented in this study represent a dose directly downwind of the source and as such are a worst case scenario for exposure. The averages of the 21 receptors (i.e. the average concentration directly downwind of the source) for each of the 120 scenarios modelled were used to determine the selected data. The number of scenarios modelled was arbitrarily chosen to allow 10 scenarios to be run on each machine in a cluster of 12 computers. The maximum concentration in Table 2 is the maximum ensemble average obtained from the average of the 21 receptors for the 120 scenarios modelled. Maximum concentrations at individual locations directly downwind of hot spots are obviously higher than the values reported in this table.

When viewing Table 2 it is apparent that the peak concentrations drop dramatically as the receptor moves away from the source. It is also apparent that the peak concentrations vary little as a function of wind speed although the plume width will vary. In AFTOX a downwind concentration is determined in two steps. In the first step the size of the initial plume envelope is estimated. In its default mode AFTOX determines the size of the envelope (assumed to be a cylinder of equal height and width) from the magnitude of the emission rate. In this report the size is set at 10 m to match the grid structure used for the area

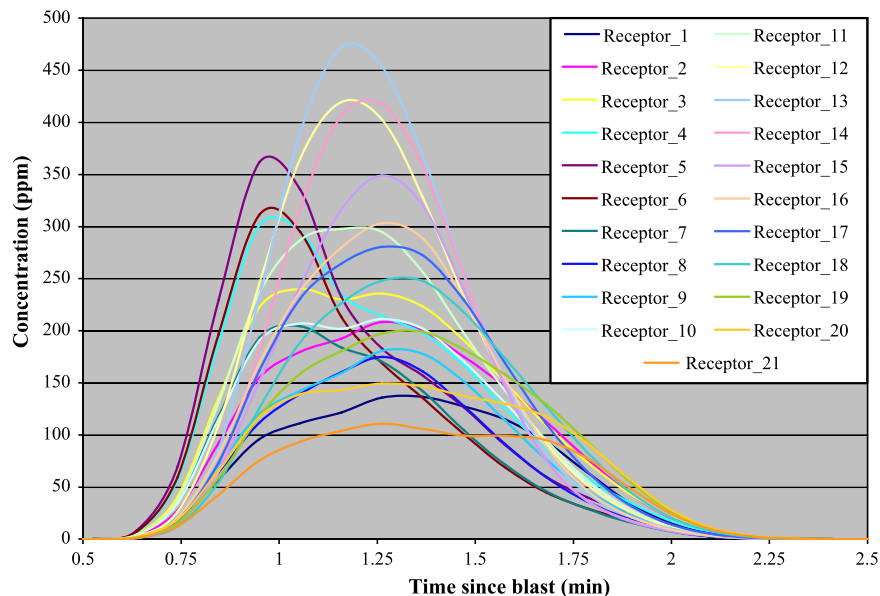


Fig. 6. Calculated NO<sub>2</sub> concentration profiles 200 m from source.

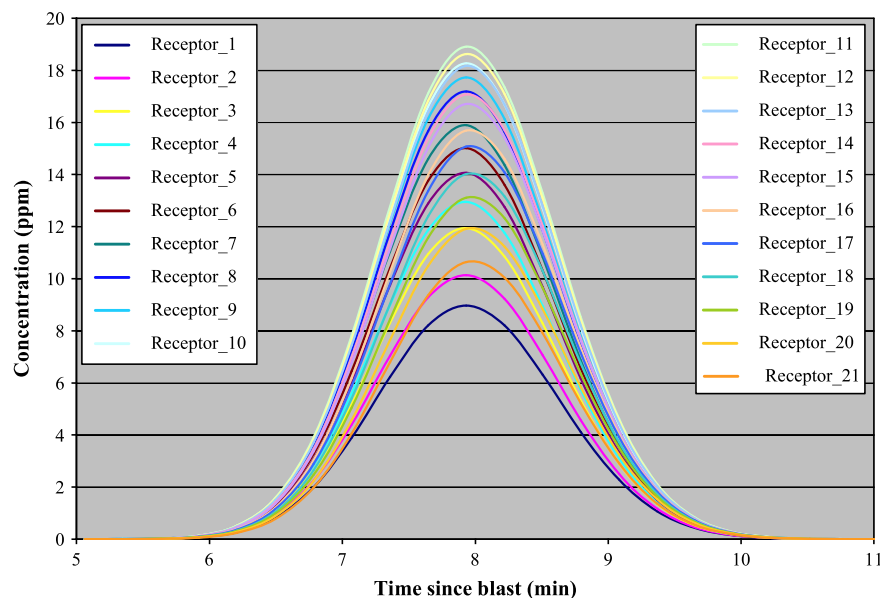


Fig. 7. Calculated  $\text{NO}_2$  concentration profiles 1 km from source.

source. AFTOX in this regard ignores the effect of wind speed on the size of the initial envelope and as such the initial concentration of the plume is identical irrespective of wind speed by ignoring longitudinal (i.e. downwind) spread of the initial release. In the second step the concentration downwind of the initial release is determined by estimating the growth of a puff in three dimensions which in this case explicitly includes longitudinal plume spread which is assumed to be equal to the degree of crosswind spread. The degree of this spread is determined solely from the prescribed atmospheric stability class which ignores any wind speed dependence.

While the peak concentrations are similar, the dose received at a receptor is linearly dependent on wind speed. Emissions released into an atmosphere with higher wind speeds result in a receptor receiving doses for a smaller period of time. It should be noted that some of the differences in the peak concentrations displayed in Table 2 result from the number of discrete time steps used to calculate the concentrations. This was set at 25 intervals between the onset and finish of a plume as it passes by the receptor. This time is dependent on atmospheric stability and the distance from the source. In AFTOX, the puffs are assumed to disperse in the direction of plume travel proportionally with the degree of crosswind spread. As such, portions of the plume arrive before and after the main bulk of the emissions and the effect clearly demonstrated in Figs. 6 and 7. The moderate number of discrete times modelled to capture this effect while generally adequate may have led to a degree of variation particularly at larger distances from the source.

Again it should be noted that the modelled figures assume an area wide flux of 100 kg which is larger than observed in the blast recorded during this study. It should also be noted that while some of the concentrations are high close to the source the concentration at a particular

location occurs for a brief period of time which is determined by the wind speed.

#### 4. Conclusions

A portable open-path spectroscopic method was found to be effective for measuring  $\text{NO}_2$  emissions from blasting. Overall this technique was found to be simpler, safer and more successful than other approaches that in the past have proved to be ineffective in monitoring these short lived plumes.

Quantitative measurements of  $\text{NO}_2$  in plumes from blasting were made at two open-cut mines. The results showed that  $\text{NO}_2$  was present in most of the plumes but in relatively low concentrations (typically ranging between 0 and 7 ppm). The highest concentration measured during all the field campaigns was about 17 ppm at ground level.

Based on field measurements, the emission factor currently used in compiling the Australian National Pollutant Inventory was found to be approximately eight times greater than that observed in our investigation. This would suggest that an over estimation of  $\text{NO}_x$  is made if the current factor is used.

Numerical modelling of the behaviour of plumes resulting from blasting was made to assess the possible downwind concentrations of  $\text{NO}_2$ . These results were compared to ambient  $\text{NO}_x$  measurements made in Muswellbrook.

- Modelling results were consistent with concentration measurements within the plumes at relatively short distances from the blast (i.e. up to about 1 km).
- Ambient monitoring did not detect  $\text{NO}_x$  events that could be attributed to individual blasts. Modelling suggested that these emissions would be very low at

distances greater than 5 km from the blast and may be indistinguishable from background levels; typically of the order of several parts per billion, in most cases.

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