

Attachment 10: Dangers of Toxic Fumes from Blasting
Richard J Mainiero, Marcia L Harris, and James H Rowland III

Dangers of Toxic Fumes from Blasting

**By Richard J. Mainiero, Marcia L. Harris,
and James H. Rowland III**

Abstract

This paper reviews the potential hazards posed by the toxic fumes produced by detonating explosives in surface mining and construction operations. Blasting operations produce both toxic and nontoxic gaseous products; the toxic being mainly carbon monoxide (CO) and the oxides of nitrogen (NO_x). The quantity of toxic gases produced by an explosive is affected by formulation, confinement, age of the explosive, and contamination of the explosive with water or drill cuttings, among others. Techniques to protect workers and the public from the potential hazards of explosive-related toxic fumes are discussed. These include:

- Minimizing the quantity of toxic fumes produced.
- Determining where the fumes may go so workers and neighbors can be moved out of harm's way.
- Preventing the fumes from moving towards workers and neighbors.
- Monitoring the air near workers and neighbors so they can be relocated if fumes appear.
- Ventilating structures or confined spaces until CO falls below a hazardous concentration.

Disclaimer: The findings and conclusions in this report are those of the author(s) and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

Background

Ideally, the gaseous detonation products of explosives would consist of water (H_2O), carbon dioxide (CO_2), and nitrogen (N_2). Due to the kinetics of the chemical reaction, the detonation of explosives in a blasting operation also produces toxic nitrogen dioxide (NO_2), nitric oxide (NO), and carbon monoxide (CO) (ISEE, 1998). The concentrations Immediately Dangerous to Life or Health (IDLH) for NO_2 , NO , and CO are 20, 100, and 1,200 ppm, respectively (NIOSH, 1994). Blasters working in underground or confined environments have long been aware of the hazards of these gases and must ensure adequate ventilation to quickly dilute them below harmful levels. In an effort to protect workers, extensive research has been done on the toxic fumes generated by the detonation of high explosives and many countries have test procedures and formal or informal requirements in place for the maximum permitted fumes production by a given amount of explosives (Streng, 1971, Karmakar and Banerjee, 1984, and International Society of Explosives Engineers, 1998).

Blasters at surface mines and construction operations have not been as concerned about blasting fumes as their counterparts in underground mines, believing that fumes would disperse in the open air (ISEE, 1998). Surface blasters, however, must be aware that toxic fumes have the potential to create hazards in their operations. Large surface mines may detonate up to two million pounds of blasting agent in a single shot. Some of the shots produce a product cloud colored red or orange by the presence of NO_2 (Barnhart, 2004), (Barnhart, 2003), and (Lawrence, 1995). At present it is not known whether the orange cloud contains toxic levels of NO_2 since there have been no published reports of direct measurements. However, in the interest of safety every blaster should assume that any blasting product cloud is unsafe to breathe.

For surface blasting operations, the CO in the gaseous products released immediately after a blast is not of great concern since CO is much less toxic than NO_2 ; the IDLH for CO is 1,200 ppm compared to 20 ppm for NO_2 . For CO , the danger lies with the gas that remains in the ground after the blast. This CO will be released during loading operations or may migrate hundreds of feet through the ground and collect in confined spaces. Since 1988, there have been eighteen documented incidents of CO migration in the United States and Canada; the confined space typically being a home and in one case a sewer manhole vault (NIOSH, 1998), (Eltschlager, Schuss, Kovalchuk, 2001), (NIOSH, 2001), and (Santis, 2001). There have been thirty-nine suspected or medically verified carbon monoxide poisonings, with one fatality. In one incident in Kittanning, Pennsylvania, blasting fumes traveled 450 feet from a coal strip mine into a home, poisoning a couple and their baby. Fortunately, all three recovered following treatment in a hyperbaric chamber (Eltschlager et al. 2001) and (NIOSH, 2001).

Protecting Personnel

There are a number of ways to protect workers and neighbors from toxic fumes produced by blasting operations. Several of these are:

1. Minimize the quantity of toxic fumes produced,
2. Determine where the fumes may go so workers and neighbors may be moved out of the way,
3. Prevent the fumes from moving towards workers and neighbors,
4. Monitor the air near workers and neighbors so they can be relocated if fumes appear, and
5. Ventilating structures or confined spaces until CO falls below a hazardous concentration.

Each of these items will be discussed.

1. Minimize the quantity of toxic fumes produced.

Due to expansion and subsequent cooling of detonation product gasses, the combustion reactions are quenched before they can go to completion. The quenching freezes out CO and NO_x at concentrations higher than those expected for equilibrium. It is not possible to entirely prevent the release of CO and nitrogen oxides (NO_x) in blasting, but the quantities can be minimized. Some factors that lead to excessive CO and NO_x production are incorrectly formulated explosives, use of deteriorated explosives, reaction in diameters below the critical diameter, loading wet boreholes with explosives that are not water resistant, mixing of explosive with drill cuttings at the top and bottom of the hole, and poor confinement (ISEE, 1998), (Rowland III and Mainiero, 2000), (Roberts, Katsabanis, and deSouza, 1992), and (Engsbraten, 1980).

An explosive containing a stoichiometric mix of fuel and oxidizer minimizes the production of CO and NO_x. If there is an excess of fuel, detonation of the explosive or blasting agent will generate increased quantities of CO. If there is not enough fuel, detonation of the explosive or blasting agent will generate increased quantities of NO_x. Figures 1 and 2 illustrate the effect of ANFO fuel oil content on CO and NO_x production.

Explosive manufacturers are careful to balance the oxidizer and fuel in their explosive formulations to minimize fumes production. Blasters must insure the proper compositions for explosives and blasting agents mixed in the field. The performance of modern explosives is controlled by both the composition and the physical structure of the chemical mix. Explosives that are beyond the manufacturer-recommended shelf life or visibly deteriorated should not be used. As some explosives age, ingredients may leak out of the packaging, changing their compositions or their physical structure may break down. Either of these will result in an explosive that may not function as intended by the manufacturer and may produce excessive fumes.

Proper use of explosives and blasting agents is also very important in minimizing toxic fume production. For every explosive or blasting agent there is a minimum charge diameter, commonly referred to as critical diameter, below which it will not detonate properly. Below this critical diameter, the surroundings absorb sufficient energy from the explosion front to quench the detonation. Bulk-loaded blasting agents used in large-scale surface mine blasting do not detonate properly in boreholes of 1-inch diameter or less (ISEE, 1998). If the blasting agent is diluted by mixing with drill cuttings at the top or bottom of the borehole it may not detonate properly and excessive quantities of toxic fumes may be produced (Sapko, 2002). Similarly, the blasting agent may flow into cracks and crevices around the borehole where it may not detonate properly because the width of the cracks and crevices may be below the critical diameter. Incomplete detonation of the blasting agent leads to excessive toxic fumes (ISEE, 1998). Stemming plugs may be placed in the top and bottom of the blasthole to prevent mixture of the blasting agent with drill cuttings or rocks. Flow of the blasting agent into cracks and crevices may be prevented through the use of packaged product or borehole liners.

Production of excessive NO_x during blasting may also be caused by incomplete detonation as a result of loading wet boreholes with an explosive that is not water resistant. When wet boreholes are encountered, the water must be removed or they must be loaded with explosives or blasting agents that are packaged to keep out the water or with a product that is designed to be water resistant. ANFO is not

water resistant and will not shoot properly in wet holes unless it is packaged to resist the water. Emulsion blasting agents are water resistant and may be loaded in bulk in wet boreholes. ANFO/emulsion blends exhibit water resistance to varying degrees depending on the ratio of ANFO to emulsion. The explosive supplier can recommend a mix ratio that is appropriate for a given application.

2. Determine where the blasting fumes are likely to go.

For surface blasting, much of the detonation products can be seen as a cloud of gas and dust coming off the blast. When a surface blast is initiated all workers should be positioned at locations outside of the likely path of the product cloud. Monitoring the wind direction immediately prior to the blast can be useful in accomplishing this. Some mines also have blasting plans that specify a blast should not be initiated if the wind will carry the cloud in the direction of neighbors off mine property. In addition, detonation product gases may be present in the muck pile and may also move into cracks and fissures in the ground. The gases move through the ground and may collect in a nearby confined space such as underground sewers, pipeline trenches, or basements of homes and businesses. As the gases move, CO will be the toxic gas of main interest since NO₂ and indirectly NO are absorbed by the soil. (NO oxidizes to NO₂ which is readily absorbed by the soil.)

In most cases the fumes will spread slowly through the ground in all directions. However, in some cases, pathways exist that allow the gases to move preferentially in one direction. Such pathways may be created by broken rock from an earlier blast (ISEE, 1998), a hill seam (a pathway caused by the movement of rock layers on a hillside) (Eltschlager et. al. 2001) and (NIOSH, 2001), underground utility lines, a French drain, or fractures in the ground (Harris, Sapko, and Mainiero, 2005). A review of available maps and examination of nearby structures should reveal utility lines or French drains that may serve as pathways. Identifying naturally occurring pathways would be much more difficult and it would be impractical to do this for every blast. However, once CO migration has been identified as a problem at a blast site, the blaster may want to consult a geologist for aid in identifying the pathway. Knowledge of the probable pathway will be useful in deciding how to minimize the likelihood of CO migration problems in future blasts.

3. Prevent the fumes from moving towards workers and neighbors.

For surface blasts there is no practical way to change the direction in which the product cloud will move; all a blaster can do is try to ensure that no one will be in the cloud's path. This is not the case for blasting fumes moving through the ground.

Techniques for mitigating the migration of CO were evaluated during blasting research conducted at the NIOSH Pittsburgh Research Laboratory (PRL) (Harris et al. 2005). When no actions were taken to prevent or mitigate CO in the ground, CO was measured for several days in monitoring boreholes after a blast. This has been demonstrated at the PRL site and also during reported incidents in the field. However, when the muck pile is immediately excavated after the shot, the levels of CO measured in monitoring holes are orders of magnitude lower and do not last for a long duration. When negative pressure was applied to a monitoring hole close to the blast location after a blast that was not excavated, the levels of CO measured were comparable with immediate excavation and were of a short duration as well. A reasonable and immediate source of negative pressure is the vacuum from the dust collection system of a drill rig. If a hole is drilled in the near proximity of the blast, the end of the drill boom can

be located on top of the drilled hole and the dust collection system turned on for a period of time. A more extensive system may be constructed using several holes connected to a fan. These techniques need not be applied to every shot but rather only when a problem with CO migration is encountered.

Mucking will remove some gas that is trapped in the muck pile (Harris et al. 2005). Over time CO may migrate beyond the rubble zone and mucking will not remove any CO that has migrated beyond the rubble area. To be effective, mucking should be carried out as soon after the blast as possible.

Blasters' awareness is important in preventing future CO poisonings. Monitoring nearby enclosed spaces for toxic gases before and after blasting still remains the best recommendation for a first approach to intervention and triggering other actions.

4. Monitor the air near workers and neighbors so they can be relocated if fumes appear.

Studies at blasting sites in Amherst, New York (Harris and Mainiero, 2004) and Bristow, Virginia (Harris, Rowland III, and Mainiero, 2004) identified ways to protect people from the CO that may migrate from a blast into nearby homes or other confined spaces. Based on these studies, it was recommended that the blaster place CO monitors in occupied parts of nearby homes and businesses. CO monitors of the type sold in department and hardware stores for home use should be adequate if the instructions on the packaging are followed. These detectors are designed and tested to protect people in their homes from CO poisoning, whatever the source. Each CO migration occurrence is unique and depends on the route of entry, distance of site from CO generation source, and geology. Therefore, possible monitoring of nearby homes or businesses may continue for an extended period of time, from several hours to a few days. Monitoring should continue until CO from the blasting operation no longer enters the home or business. In recent years CO poisonings were most likely prevented by the early warning of a homeowner-installed CO detector. Because of early warning, the source of CO was determined and affected homes were evacuated and closely monitored before anyone could become ill. To the best of our knowledge, no one has had to be treated for blasting-related CO poisoning since the western Pennsylvania incident in April, 2000 (Eltschlager et al. 2001) and (NIOSH, 2001).

It is important that workers follow the confined space requirements of the Occupational Safety and Health Administration when entering a manhole vault, trench, or other confined space near a blasting site (OSHA, 2005). In 1998 a worker was killed and two injured when they entered a manhole vault 45 minutes after a nearby blast. No one had checked the vault for toxic gases prior to entry. The vault contained toxic levels of CO (NIOSH, 1998).

5. Ventilate structures or confined spaces until CO falls below a hazardous concentration.

Once CO is detected in a confined space near a blast site, no one should reenter until safety personnel have stated that it is safe to do so. Local firefighters and other emergency response personnel may be called to assist. These people have been trained and are equipped to deal with toxic atmospheres in homes, businesses, and other confined spaces, and will take appropriate action.

Conclusion

The major toxic gases produced by detonation of commercial explosives and blasting agents are CO and NO_x. These gases may migrate through the ground into the basements of nearby homes and businesses, trenches, manhole vaults, and other confined spaces. NO_x does not migrate through the ground because it is absorbed by the soil as the gases travel. However, NO_x is a concern in surface blasting because it is very toxic; much more toxic than CO. Excessive NO_x production at a blasting site may be evidenced by the presence of an orange or red cloud produced by the blast. The boreholes must be properly loaded to minimize the production of NO_x. To the best of the authors' knowledge, no one knows the concentrations of NO_x in a blasting product cloud but it is best to err on the side of safety and assume the cloud is toxic. People should be kept out of contact with the product cloud. Carbon monoxide is a serious concern because it is not absorbed on passage through the ground. Carbon monoxide may travel up to several hundred feet and collect at toxic levels in a confined space. Carbon monoxide is odorless so there is no obvious indication that a hazard exists. This hazard may be dealt with at several levels. A blaster should use explosives and blasting agents in the manner specified by the manufacturer to minimize the quantity of CO produced. The blaster should attempt to identify any pathways by which gases produced by the detonation may travel from the blast site into homes, businesses, or other confined spaces. If a blaster is aware that there is a likelihood of CO migrating into occupied spaces he/she may minimize the hazard by excavating the blasted rock soon after the blast or may connect a fan to a borehole near the blast to pull the CO out of the ground. The blaster may place home-type CO monitors in homes or businesses near the blast site so occupants will be alerted if CO concentrations rise to unsafe levels. OSHA's confined space regulations must be followed when a worker enters a trench, manhole vault, or other confined space. Firefighters or other emergency personnel may be called in to ventilate any homes or businesses where CO has been detected and determine when a CO hazard no longer exists.

It is very difficult to predict when CO produced by a blast will migrate into homes, businesses, and other confined spaces. It would be impractical to do this for every blast. At present the best defense is to ensure that people are alerted if the air they are breathing contains toxic levels of CO.

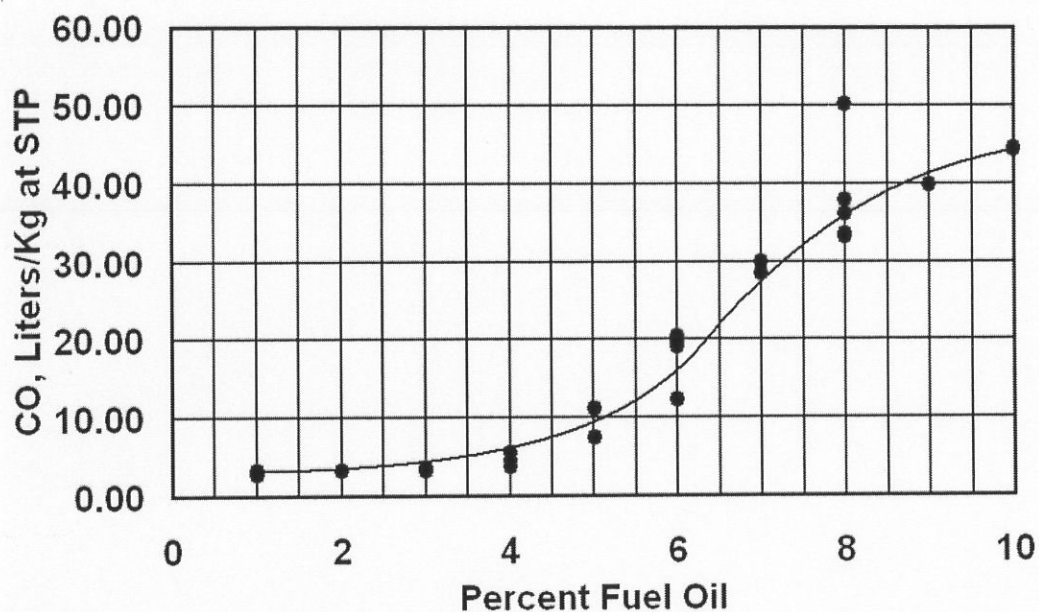


Figure 1. The effect of fuel oil content on the quantity of carbon monoxide produced by detonating ANFO. (Rowland III and Mainiero, 2000)

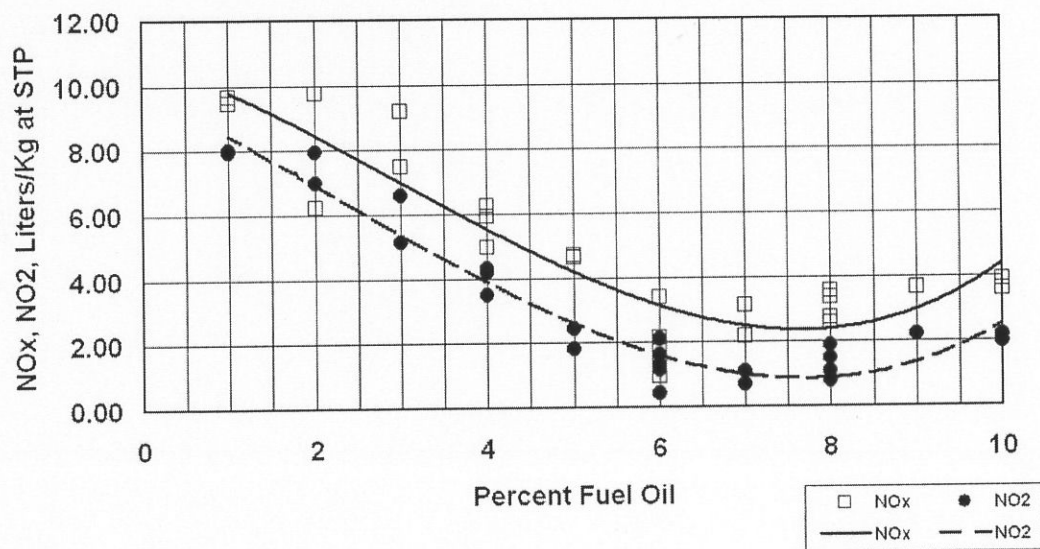


Figure 2. The effect of fuel oil content on the quantity of nitrogen oxides produced by detonating ANFO. (Rowland III and Mainiero, 2000)

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Safety Alert



Explosives

Explosives Inspectorate

Safety Alert No. 44 V2
15 March 2011

Prevention and management of blast fumes

Reference

- A. Queensland Mines Inspectorate Safety Bulletin No. 61
- B. Queensland Explosives Inspectorate Safety Alert No. 28 Post Blast Gases
- C. *Explosives Act 1999* (Qld)
- D. *Coal Mining Safety and Health Act 1999* (Qld)
- E. *Mining and Quarrying Safety and Health Act 1999* (Qld)

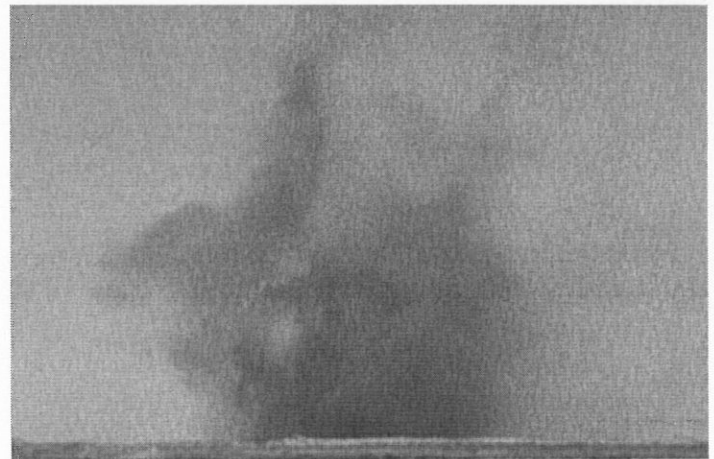


Figure 1 – Oxides of nitrogen generated by blasting

Purpose

1. The purpose of this alert is to make sure that everyone involved in open-cut blasting is aware of the potential for oxides of nitrogen to be generated from the use of ammonium-nitrate-based explosives (see Figure 1). Exposure to oxides of nitrogen can pose a serious health risk.

Scope

2. All Site Senior Executives, drill and blast superintendents, explosives company managers, shotfirers and other relevant people must risk-manage the potential hazards created by post-blast gases.

Background

3. Post-blast fume is a product of combustion from a blast. The products of combustion from a blast may include oxides of nitrogen, ammonia, nitric acid, carbon monoxide and carbon dioxide. These gases are often referred to as fumes. Nitrogen dioxide is visible as a reddish brown colour; the others are not visible.
4. Other than water ingress, known causes for the generation of oxides of nitrogen (including nitrogen dioxide) are:
 - a. incorrect fuel to oxygen ratio
 - b. product pre-compression
 - c. insufficient priming
 - d. acidic soils
 - e. presence of pyrite
 - f. product formulation.

5. Post-blast fume is composed of toxic gases (including oxides of nitrogen) which can be released into the atmosphere in significant quantities from blasting operations. Exposure to even quite low concentrations can pose a serious health risk.
6. The recent wet conditions and increased groundwater with the use of down hole ammonium-nitrate-based products have led to an increase in post-blast gases. Four events have occurred in the past fortnight in open-cut operations. In two of these events, 24 people required treatment and hospital observation for exposure to oxides of nitrogen.

The department has previously provided References A and B in regard to the management of post-blast gases. These are available on its website at:

- a. http://www.dme.qld.gov.au/mines/safety_compliance.cfm (Reference A)
 - b. <http://www.dme.qld.gov.au/mines/safetyalerts.cfm> (Reference B)
7. From 1992 to 2002, the United States of America had eight post-gas events that resulted in injuries to workers and the public, including a fatality.
 8. In the Philippines in 2006, a shotfirer was conducting a post-blast inspection at a quarry when he fell eight metres into a cavity. He was rescued and taken to hospital with apparently only minor injuries. At the time of his recovery, it was noticed that his breathing was laboured, but this information was not passed on to the hospital staff. He died the next day of severe pulmonary oedema (NO_x poisoning), which was not recognised by either the medical team or operational staff.

Issues

9. The operator's safety management system must include all the different control phases for post-blast fumes. The phases are:
 - a. prevention — i.e. how to prevent or minimise post-blast fumes
 - b. management of fumes — i.e. where post-blast fumes extend beyond the exclusion zone
 - c. management of an exposure — i.e. for when people are exposed to fumes.

Prevention

10. To prevent or minimise post-blast fumes, it is necessary to have a knowledge and understanding of ground conditions, water (wet holes and the depth of the water), explosives product and their application, meteorology, and the toxicological effects of the gas.
11. There is a strong correlation between wet ground and the production of excessive fume. The presence of water can degrade the explosive resulting in a poor blast and excess fume.
12. Fume can be reduced if:
 - a. the explosives product selected is correct for the conditions
 - b. holes are dewatered before loading
 - c. sleep times are kept to the minimum time recommended by the manufacturer.
13. An understanding and application of meteorology (i.e. weather conditions, wind speed and direction and stability classes) and gas cloud distributions will enable calculation of how long a gas plume will take to reach a point of interest such as a crib hut, workshop, house.ⁱ Such understanding and application also help determine the dispersion of the gas cloud, how far it will spread sideways, and how the gas concentration will change with distance. The people developing these plans must understand the gas toxicology, exposure to gas and the exposure standards of a gases, such as nitrogen dioxide, particularly high concentration exposures over relatively short periods.

ⁱ Buildings should not be used as shelters, unless they have been assessed by competent persons as safe havens.

Management of fumes

14. Before a gas plume occurs, it is important to have a system for managing a potential incident, including evacuations. The system should include information on wind speed and direction and on whether there is a gas-tight shelter nearby. Communication systems should also be in place, and there should be monitors to record concentrations of toxic fumes.

Management of an exposure

15. Exposure to nitrogen dioxide can result in delayed health effects that may be potentially life-threatening, even though the exposed person may at first appear relatively unaffected. For this reason, anyone who has been exposed to nitrogen dioxide should undergo an immediate medical assessment and a continued period of observation at the advice of the treating doctor.
16. The plan must include a health management plan for an exposure, which needs to be integrated with the local health providers. This should include medical advice to the treating physician. Attached to this alert is a sample advice letter that can be provided to the treating physician. Exposure should be treated seriously and referred for medical treatment based upon an exposure or stated dose.
17. All people involved in the management of blasting activities should review their safety management systems, including standard operating procedures and emergency response plans, to ensure that the management of situations, where clouds of oxides of nitrogen are generated, are properly managed.

Recommendations

1. All people involved in the management of blasting activities should ensure that the management plan for situations where plumes of oxides of nitrogen have been generated has been deployed and is operational. This should include health management and medical management plans.
2. The provision of material safety data sheets relative to the types of products being used should be made readily available to all persons involved in the blasting process.
3. All efforts should be made to reduce the likelihood of the production of post-blast gases during blasting operations.
4. Where doubt exists as to the potential cause of post-blast gases, those involved in the blasting process should contact the supplier of the explosives for further information.
5. Ensure that all relevant people in the organisation receive a copy of this Safety Alert.

The information contained in this Safety Alert is provided for guidance only. It is not to be taken as a statement of law and must not be construed to waive or modify any legal obligations.

Attachment: Information for Treating Doctor

Chief Inspector of Explosives

Southern Region	Central Region	Northern Region
3238 3728	4938 4442	4799 7004
sroexplosives@dme.qld.gov.au	croexplosives@dme.qld.gov.au	nroexplosives@dme.qld.gov.au
	Internet : www.dme.qld.gov.au	

INFORMATION FOR TREATING DOCTOR

Dear Doctor

This patient has been exposed to NOx. This is a gas usually produced on mines after the use of explosives.

NOx consists of multiple combinations of nitrogen and oxygen (N₂O, NO, NO₂, N₂O₄, N₂O₃, N₂O₅). Nitrogen Dioxide (NO₂) is the principal hazardous nitrous fume.

NOx irritates the eyes and mucous membranes primarily by dissolving on contact with moisture and forming a mixture of nitric and nitrous acids. But this is not the only way injury can occur. Inhalation results in both respiratory tract irritation and pulmonary oedema. High-level exposure can cause methaemoglobinaemia. Some people, particularly asthmatics, can experience significant broncospasm at very low concentrations.

The following effects are commonly encountered after NOx exposure:

ACUTE

- cough
- shortness of breath
- irritations of the mucous membranes of the eyes, nose and throat

SHORT TERM

- pulmonary oedema, **which may be delayed from 4 to 12 hours**

MEDIUM TERM

- RADS (Reactive Airways Dysfunction Syndrome)
- in rare cases, bronchiolitis obliterans, which may take from two to six weeks to appear

LONG TERM

- chronic respiratory insufficiency

High-level exposure, particularly associated with methaemoglobinaemia, can cause chest pain, cyanosis and shortness of breath, tachypnoea and tachycardia. Deaths have been reported after exposure and are usually delayed. Even non-irritant concentrations of NOx may cause pulmonary oedema. Symptoms of pulmonary oedema often show until a few hours after exposure and are aggravated by physical effort.

Before transfer to you the patient should have been advised to rest and, if any respiratory symptoms were present, should have been administered oxygen. The patient will need to be treated symptomatically, but as a base line it is suggested that the following may be required:

- spirometry
- chest x-ray
- methaemoglobin estimation.

Because of the risk of delayed onset pulmonary edema, it is recommended that as a precaution the patient be observed for up to 12 hours. As no specific antidote for NOx exists symptoms will have to be treated on their merits.

Information provided by Dr Vern Madden, Health Advantage Toowoomba