



## Mine-Water Leaching of Nitrogen Species from Explosive Residues

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### ABSTRACT

While acid rock drainage (ARD) and metal leaching (ML) are common concerns in mine waters, nitrogen species (nitrate, nitrite, and ammonium) often receive less attention because they are naturally low in most mine rock. Thus, common pre-mining tests for ML-ARD, like acid-base accounting and humidity cells, rarely consider nitrogen leaching. However, common explosives used at minesites often contain large percentages of nitrogen compounds. As a result, only after full-scale mining is underway might unpredicted elevated and potentially toxic levels of nitrogen species appear in drainages. For this reason, pre-mining tests cannot be counted on for accurate predictions, and full-scale case studies become an important source of predictive information.

The case studies in this paper showed the leaching of explosive's nitrogen ranged over approximately two orders of magnitude (0.2-28%). It appears that "wetter" conditions likely contribute to higher percentages, but a quantitative definition of "wetter" is not possible at this time. Also, spatial distances, minesite components, and elapsed times can affect predictions.

### Résumé

Bien que le drainage rocheux acide (DRA) et la lixiviation des métaux (LM) constituent des préoccupations courantes en matière de gestion des eaux de mine, les composés de l'azote (nitrates, nitrites et ammonium) suscitent souvent moins d'intérêt, car leur concentration naturelle est faible dans la plupart des roches exploitées dans les mines. C'est pourquoi les essais habituellement réalisés avant l'exploitation minière afin de déterminer la LM et le DRA, par exemple la détermination du bilan acide-base et l'utilisation de cellules d'humidité, tiennent rarement compte de la lixiviation des composés de l'azote. Toutefois, les explosifs courants utilisés sur les sites miniers présentent souvent de fortes teneurs en composés azotés. Conséquemment, des concentrations élevées et éventuellement toxiques de composés de l'azote, qui n'avaient pas été initialement prévues, pourraient être observées dans les eaux de drainage une fois que l'exploitation minière fonctionne à pleine capacité. Les résultats des essais réalisés avant l'exploitation minière ne sont donc pas fiables au chapitre de l'exactitude des prévisions et l'exécution d'études de cas à grande échelle constitue alors un outil de première importance pour obtenir de l'information prédictive.

Les résultats des présentes études de cas indiquent que la lixiviation de composés de l'azote provenant des explosifs se situe dans une plage d'environ deux ordres de grandeur (de 0,2 à 28 %). Ils semblent indiquer que des « conditions plus humides » contribuent probablement à la présence de concentrations plus élevées, mais il est actuellement impossible d'établir une définition quantitative claire du concept de « conditions plus humides ». Il convient aussi de souligner que les diverses distances, les infrastructures du site minier et la période écoulée peuvent toutes avoir des effets sur les prévisions.

### 1 INTRODUCTION

Mine waters can transport many elements in the Periodic Table, as dissolved species or as natural and anthropogenic compounds. These aqueous concentrations in minesite drainage can be so variable, around the world and across the many types of mines, that no "typical" narrow range can be defined for an element (Morin and Hutt, 1997 and 2001).

One archaic but helpful acronym for minesite-drainage chemistry is ML-ARD (metal leaching and acid rock drainage). Minesite drainage, however, is not always acidic, and carries many more elements than just metals. This paper highlights these facts by discussing aqueous nitrogen species under near-neutral conditions.

Despite the great variability in minesite-drainage chemistry, techniques have evolved over the last century

for site-specific predictions of aqueous concentrations (Figure 1). This includes acid-base accounting and laboratory-based humidity cells. When used together and carefully, they can provide reasonably accurate predictions, and cross-checks for QA/QC. As a result, elevated and potentially toxic levels of many, but not all, elements can be anticipated with these integrated tools.

A good example of where the standard predictive techniques can fail is with nitrogen species (nitrate, nitrite, and ammonium are discussed here). Most rock contains naturally low levels of nitrogen species, so that pre-mining tests like Figure 1 indicate they will produce low aqueous concentrations.

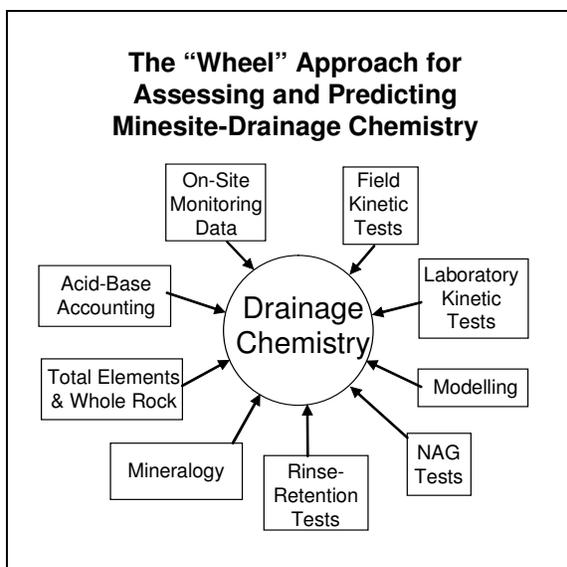


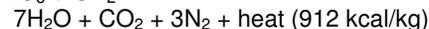
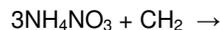
Figure 1. An integrated suite of techniques for predicting minesite-drainage chemistry.

However, common explosives used at minesites contain large percentages of nitrogen compounds. Thus, only after full-scale mining is underway might unpredicted elevated and potentially toxic levels appear in drainages. For this reason, standard pre-mining techniques cannot be counted on for accurate predictions of nitrogen species. Instead, case studies become an important source of predictive information.

## 2 SOME ISSUES FOR PREDICTING NITROGEN SPECIES IN MINESITE-DRAINAGE CHEMISTRY

There are many physical, chemical, and biological issues, both natural and anthropogenic, involved in explaining and predicting nitrogen species in drainage chemistry. For example:

- Nitrogen-bearing mineral phases are often highly soluble, so thermodynamic solubility rarely exerts an influence on their aqueous concentrations. Thus, processes like dilution and kinetics can play significant roles.
- Nitrogen species are redox reactive, so that nitrate, nitrite, and ammonia can convert among themselves, raising concentrations of one while lowering the other. These geochemical conversions often involve biological activity, which is difficult to define and predict within a minesite component.
- Nitrogen species can interact with nitrogen gas in the atmosphere, a tremendously large geochemical source/sink that can rule out conservative geochemical behaviour.
- The chemical compositions of explosives can be highly variable. This includes ANFO (Ammonium Nitrate - Fuel Oil) and proprietary formulations which manufacturers may not reveal. Greatly simplified, ANFO can contain 94%  $\text{NH}_4\text{NO}_3$  and 6% fuel oil (simplified as  $\text{CH}_2$ ), and the explosive reaction is:



However, this reaction is not 100% complete during blasting and thus aqueous nitrogen species can appear in drainages.

- The amounts of remaining, leachable nitrogen species after a blast depend on factors like (1) the handling of explosives, including spillages during handling, and (2) the efficiency of a particular blast, including drilling and packing of holes, sequences of detonations, and reliabilities of detonation. Some holes do not detonate so the explosives remain in the rock for later leaching.
- Another source of nitrogen species at some minesites is the breakdown or treatment of cyanide-related species including cyanate.
- The daily loadings of nitrogen species can reflect the flow of water through the rock and the extent of flushing of rock-particle surfaces by the flowing water.
- Although not always relevant to nitrogen species, explosives can contain a long list of additives such as guar gum, starch,  $\text{Al}_2\text{O}_3$ , calcium nitrate, sodium nitrate, and various hydrocarbons like wax.

Thus, the prediction of nitrogen species in minesites drainages from explosive residue is not as simple as for some other elements (Figure 1). This means that case studies become valuable sources for prediction.

## 3 THE CANADIAN "GOLD STANDARD" FOR PREDICTING NITROGEN SPECIES IN DRAINAGES

Despite the importance of case studies for predicting aqueous nitrogen species, there are actually few well documented ones. The study that is most often referenced in Canada and some other countries was published by Environment Canada in 1988 (Ferguson and Leask, 1988). We have seen this study used even for massive-sulphide sites above the Arctic Circle, so one would assume it was very robust and widely applicable.

In reality, this 1988 study was based on in-field monitoring of five open-pit coal mines in southwestern British Columbia, Canada. Thus, its conclusions might be specific only to:

- coal minesites at higher elevations (1000-2500 m) in mountain ranges,
- in cooler climates (mean monthly temperature of approximately  $-10^\circ\text{C}$  in winter and  $+16^\circ\text{C}$  in summer), and
- with annual precipitation around 0.70 m/yr including snow as 40% of total precipitation as water equivalent.

Nitrogen leaching from each minesite in this 1988 study, through surface water and groundwater, was the sum from various sources. These sources included pits, waste rock, and tailings, which showed that explosive-derived nitrogen was carried by ore and waste rock into other minesite components for later leaching. All nitrogen was assumed to be released within the calendar year of its usage, although some work suggested up to five years was needed for more complete leaching.

Although prior work had shown that 1% to 6% of nitrogen used in the blasting was leached into the

environment, Ferguson and Leask (1988) found that the coal minesites using mostly ANFO under drier conditions lost around 0.2% of the nitrogen to drainages. However, the sites using mostly slurry explosives under wetter conditions lost 2% to 5% with no clear dependence on slurry usage.

The step-wise procedure used in this 1988 study for predicting aqueous concentrations of nitrogen species is summarized in Morin and Hutt (2008). Its strengths and weaknesses are also discussed there. The five general steps were:

- (1) calculate the annually leached nitrogen loading (tonne/year) for the entire minesite, based on annual tonnes of explosive expressed as N and on the type of explosive,
- (2) divide the annually leached nitrogen loading among the minesite components based on some proportion like size or lateral area,
- (3) separate each component's annually leached nitrogen loading into loadings of nitrate, nitrite, and ammonia,
- (4) divide the annual loadings into quarterly loadings weighted by quarterly flow, and
- (5) calculate average quarterly concentrations (mg/L) by dividing quarterly loading by quarterly flow (called daily concentration in the original reference).

Overall, the dominant aqueous nitrogen species was nitrate (75-99% of nitrogen), followed by ammonia (0.5-24%) and nitrite (0-6%).

#### 4 A CASE STUDY OF NITROGEN SPECIES IN DRAINAGE FROM AN UNDERGROUND MINE

Unlike the coal open-pit minesites of Ferguson and Leask (1988), this case study involves an underground metal mine. This mine, with 3100 m of underground workings and 58,000 m of underground drilling, is located in mountainous terrain in western Canada, at approximately 1000 m elevation (Morin and Hutt, 2008). Annual average precipitation is 0.51 m/yr, with 0.20 m/yr of this as snow as water equivalent. Average monthly temperatures range from -9°C in January to +15°C in July.

Sub-freezing temperatures do not affect the mine walls because they are underground. However, they do affect the volume of groundwater flowing into the mine and out the portal, which often ranges from 500,000 to 1,000,000 L/day.

For this case study, nitrogen leaching from explosives, during and after two "campaigns", were monitored during otherwise quiescent times. First, sporadic blasting from November 2005 to February 2006 created new exploration-drilling stations. Second, from June through August 2006, one cross-cut was extended approximately 50 m, producing approximately 2400 t of rock.

Based on simplified chemistry, 50 kg of ANFO and 12.5 kg of proprietary "powder" used at this site contained approximately 18.3 kg of total nitrogen. Initially, this nitrogen was nitrate and ammonium.

For the first campaign using a total of 2300 kg ANFO (~840 kg N), aqueous nitrogen concentrations in mg N/L reached maximums of 11.6 mg/L for nitrate, 0.51 for nitrite, and 11.8 for ammonia. Total organic carbon, presumably from the ANFO, reached 13.3 mg/L.

Overall for the first campaign, approximately 28% of the explosive's nitrogen was eventually leached through the portal (Figure 2). Approximately 51% of this nitrogen was nitrate, 3% nitrite, and 46% ammonia.

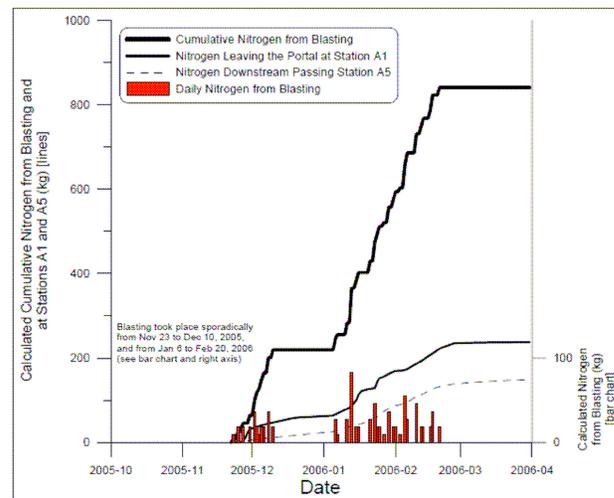


Figure 2. Nitrogen usage from sporadic blasting between November 2005 and February 2006 (daily usage = vertical bars, cumulative usage = uppermost heavy line), and the corresponding cumulative nitrogen loadings at the portal (A1) and approximately 250 m downslope (A5).

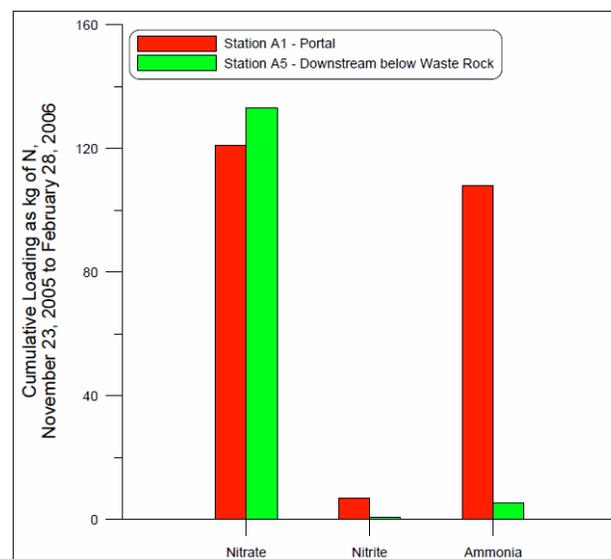


Figure 3. Cumulative loadings of nitrate, nitrite, and ammonia at the portal (A1) and approximately 250 m downslope (A5) between November 23, 2005 and February 28, 2006, showing an overall downstream loss of nitrogen, but an increase in nitrate.

Outside the portal and approximately 250 m downslope, 40% of total leached nitrogen was missing, primarily through a loss of ammonia, while nitrate increased somewhat (Figures 2 and 3). This suggested a complex system including both denitrification and ammonia oxidation.

For the second campaign, approximately 3500 kg of ANFO and "powder" produced lower maximum concentrations (Figure 4), between 1 and 2 mg/L for nitrate and ammonia. Also, only 12% of nitrogen in the explosive was leached, compared to 28% in the first, so there was a distinct difference.

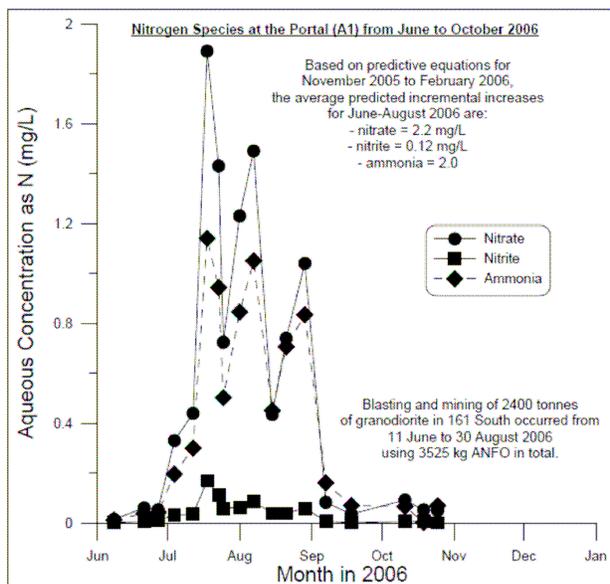


Figure 4. Temporal trends in nitrate, nitrite, and ammonia at the portal after using 3525 kg of ANFO in June-August 2006, showing the predictive equations for November 2005-February 2006 overestimated nitrogen concentrations.

Table 1. Two sets of equations for the prediction of aqueous loadings (kg N/day) of nitrogen species for the underground metal mine of Morin and Hutt (2008).

Average loading of selected nitrogen species (kg N/day) = average explosive usage (kg N/day) \* L/100 \* P/100  
 where L = percentage of leached nitrogen relative to the total amount used (see below), and  
 P = percentage of the selected nitrogen species relative to the sum of nitrate, nitrite, and ammonia (see below)

Blasting Campaign	First		Second	
	L	P	L	P
Nitrate	28%	51.3%	12%	56.0%
Nitrite	28%	2.9%	12%	4.0%
Ammonia	28%	45.8%	12%	40.0%

Morin and Hutt (2008) derived two sets of equations, based on the two blasting campaigns, to predict aqueous loadings of nitrogen species at this site (Table 1). As with the approach of Ferguson and Leask (1988) in Section 3, these loadings can then be divided by flow to obtain aqueous concentrations in mg/L.

## 5 OTHER STUDIES

A commonly referenced paper on nitrogen species is Wiber et al. (1991), which focussed on ammonia, including regulations, sources, and best management practices. It said that 5-15% of ANFO nitrogen leaches into drainages according to surveys, although details were not provided. One detailed case study showed that 12% of ANFO sent into an underground gold mine reported to the mill through ore moisture and mine water. An ammonia mass balance for this site also showed that 9-27% of ammonia was found in the mine water, 26-47% of ammonia was detected in the grinding circuit within the mill, and the remainder was derived from cyanide-related reactions. Thus, the mine component itself was not the sole source of nitrogen species. Later leaching from waste rock and ore rock were additional sources, as also noted by Ferguson and Leask (1988).

Sharpe (2007) repeated the 5-15% from Wiber et al. (1991) and attributed that range to a survey of mines by ICI Explosives. Sharpe also received a personal communication from a retired mining engineer stating that lower estimates in the 2-5% range would be realistic if best practices were followed.

Revey (1996) did not provide case studies, but discussed how quickly ANFO and other explosives could dissolve in water. ANFO was approximately 25% dissolved in six minutes and more than half dissolved in one hour, while water-resistant ANFO was roughly 25% dissolved in one hour. Water gel was about 25% dissolved in six hours, and more than 75% dissolved in six days. Emulsion showed the slowest dissolution, with only about 1% dissolved after six days.

## 6 CONCLUSION

Because of many factors (Section 2), the prediction of the nitrogen species of nitrate, nitrite, and ammonia in minesite-drainage chemistry is more difficult than for some other elements. For example, elevated levels of nitrogen species may not arise from the mined rock, but from the explosives used in mining. The standard predictive techniques used in advance of mining (Figure 1) thus fail to provide early warnings of elevated nitrogen. As a result, full-scale case studies become important as bases of prediction.

Despite the importance of such case studies, few detailed case studies have been published and distributed widely. The most widely quoted case study in Canada was released by Environment Canada in 1988 (Section 3). That study mentioned that previous work had shown that 1-6% of nitrogen used in blasting was leached into drainages. However, case studies of open-pit coal minesites in British Columbia indicated only 0.2% was

leached at drier minesites, and 2-5% at wetter sites. The difference in the percentages of leached nitrogen, between drier and wetter sites, suggest that a significant amount of nitrogen may be stored at the blast site and/or in the blasted rock at the drier site. If so, this stored nitrogen could become mobile later upon contact with water such as during a spring freshet, or could convert to nitrogen gas during long residence times. The dominant aqueous nitrogen species was nitrate (75-99% of nitrogen), followed by ammonia (0.5-24%) and nitrite (0-6%). Environment Canada showed nitrogen could leach from many minesite components, including waste rock, ore, and tailings. Thus, some nitrogen was physically initially carried away from the blast location on rock for later leaching.

A detailed case study from an underground metal mine in British Columbia showed, based on two blasting campaigns, that 12-28% of nitrogen in the explosives was leached by drainages out the portal. Nitrate was 51-56% of the total nitrogen species, ammonia was 40-46%, and nitrite was 3-4%. As this water flowed downslope approximately 250 m below the portal, it lost approximately 40% of the total nitrogen. Most of this loss was ammonia, while nitrate actually increased somewhat. This pointed to a combination of denitrification and ammonia oxidation. Results from this study also highlighted the importance of sampling location when determining nitrogen leaching at minesites. Aqueous samples collected at greater distances downstream from the blasted area can show lower levels of nitrogen. This may also explain, in part, the differences in leaching rates between the various case studies discussed.

Less detailed studies reported that 5-15% of ANFO was leached, while best practices might lower this into the 2-5% range. Also, there were significant differences in dissolution rates of various explosives. As a result, the elapsed time between the blast and the collection of aqueous samples can affect the measured nitrogen levels, depending on the type of explosives used.

Based on this, it is not possible to provide a generic narrow range of nitrogen leaching for prediction, since values here ranged from 0.2% to 28% (two orders of magnitude). The leached nitrogen is obviously dependent on many site-specific factors (Section 2), and there are too few detailed case studies to identify the dominant factors. "Wetter" conditions likely contribute to higher percentages, but a quantitative definition of "wetter" is not possible at this time. Also, spatial distances, minesite components, and elapsed times can strongly affect predictions.

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