

MDAG.com Internet Case Study 29

Leaching of Nitrogen Species during Underground Mining

by K.A. Morin and N.M. Hutt

© 2008 Kevin A. Morin and Nora M. Hutt

www.mdag.com/case_studies/cs29.html

Abstract

The nitrogen species of nitrate, nitrite, and ammonia are not always considered integral parts of minesite-drainage chemistry. This is partly due to their naturally low levels in inorganic rock. However, common explosives used in mining contain nitrogen, and thus can introduce elevated and potentially toxic levels of these species.

The prediction of nitrogen species in minesite-drainage chemistry faces many natural and anthropogenic challenges. For example, their secondary-mineral solubilities are typically high, so that dilution and kinetics are more important than thermodynamic equilibrium. Also, these nitrogen species can convert among each other through redox reactions, sometimes mediated by biological activity, and potentially buffered by the large nitrogen-gas composition of the atmosphere. Furthermore, the exact type of explosive, any spillages, the lack of detonations, and the rate of water movement over rock particles can affect the leached aqueous concentrations of nitrogen species.

Because of these challenges, case studies are valuable for understanding and predicting the leaching of nitrogen species. Surprisingly, there are notably few detailed in-field case studies at minesites. One investigation, involving five open-pit coal minesites in southeastern British Columbia, Canada, found that 0.2 to 6% of the nitrogen in the annual explosives usage appeared in drainages. Most of this nitrogen was nitrate, with significantly lesser ammonia and nitrite. This study was published in 1988, decades ago. However, it is still considered a primary prediction method in Canada, primarily due to the general lack of other similar studies.

In marked contrast to the open-pit coal minesites, this case study focusses on an active underground metal mine in western Canada. This underground mine lies at approximately 1000 m elevation. 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.

Because this is an underground mine, freezing temperatures in winter are not relevant to geochemical processes underground, where the mine walls do not freeze. However, temperatures do affect monthly rates of groundwater recharge. This groundwater flows downwards through up to several hundred of meters of rock to enter the mine, drains along the floor ditch by gravity, and then discharges through the portal. There are approximately 3100 meters of underground workings, mostly in the main adit with four, much shorter, perpendicular cross-cuts deep in the mine.

Starting in late 2005, sporadic, minor blasting and mining created new drilling stations. Average flow at the portal during this first blasting campaign was approximately 600,000 L/day. In mid 2006, a more intensive effort led to the extension of a cross-cut by 50 m, while removing approximately 2400 tonnes of rock. Average portal flow during this second blasting campaign was roughly 916,000 L/day.

Approximately 28% of the explosive's nitrogen was leached and flowed through the portal during the first blasting campaign. In contrast, approximately 12% was leached during the second campaign. The proportional content of nitrate, nitrite, and ammonia in these drainages were 51-56%, 2.9-4.0%, and 40-46%, respectively. Farther downstream, there was a net loss of 40% of nitrogen, with ammonia and nitrite decreasing substantially, while nitrate increased in concentration.

1. Introduction

The aqueous “inorganic” nitrogen species of nitrate, nitrite, and ammonia are not always included in the concept of minesite-drainage chemistry. This partly stems from their typical low to negligible levels within in situ mine rock. However, they can become important, and sometimes toxic, components of drainage chemistry, because they are introduced by common explosives used in mining.

There are many challenges 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. Also, 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. Furthermore, these species can interact with nitrogen gas in the atmosphere, a tremendously large geochemical sink that can rule out conservative geochemical behaviour.

If those were not enough, other challenges, more anthropogenic in nature, arise in the assessment and prediction of nitrogen species in minesite-drainage chemistry. These include:

- the types of explosives, which include ANFO (Ammonium Nitrate - Fuel Oil) and proprietary formulations which manufacturers may not reveal (illustrated in this case study below);
- the handling of explosives, including spillages during handling;
- the efficiency of the 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);
- the flow of water through the rock; and,
- the extent of flushing of rock-particle surfaces by the flowing water.

2. Previous Relevant Studies

Probably due to these and other challenges in Section 1, detailed studies for the prediction of nitrogen species in minesite-drainage chemistry are few. Surprisingly, a study released decades ago (Ferguson and Leask, 1988) is often a major reference used for nitrogen-species predictions in technical studies and environmental assessments, especially in Canada where it was published.

The study by Ferguson and Leask (1988) was based on in-field monitoring conducted at five open-pit surface mines for coal 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°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, through surface water and groundwater, was the sum from various sources, including pits, waste rock, and tailings. However, the coal minesites were not significant sources of phosphorus. The average annual incremental increase in total phosphorus was -0.011 mg/L (a decrease) to $+0.173$ mg/L, with an average of 0.044 mg/L.

Ferguson and Leask (1988) assumed all nitrogen was released within the calendar year of its usage. However, they mentioned some work suggesting nitrogen may require five years or more before it was substantially leached. This would complicate the following equations.

Prior work had shown 1% to 6% of nitrogen used in blasting would be released to the environment through surface and ground waters. ANFO used under dry conditions released the lower amounts, whereas slurry explosives used under wet conditions general released more. Ferguson and Leask (1988) evaluated this further, typically based on instantaneous sampling for water chemistry on a monthly or less frequent basis. Loadings (concentrations multiplied by flows) were calculated from flows sometimes interpolated from other days or locations. Maximum flows were in May and June, due to snowmelt, decreasing to minimum flows in the winter.

Overall, Ferguson and Leask (1988) found the coal minesites using little to no slurry explosives, in dry conditions, lost around 0.2% of the annual explosive's nitrogen to the environment annually. Those sites using 20-70% slurry explosives lost around 2-5%, with no clear dependence on slurry percentage.

Ferguson and Leask (1988) recommended the following approach for predicting nitrogen-species loadings and concentrations. It has been expanded here for clarity.

A) Calculate the annual leached-nitrogen loading for the entire minesite, based on annual explosive usage.

- for up to 1% of explosive as slurry:

annual leached-nitrogen loading as N (e.g., t of N/yr) = 0.2% of ANFO as N (t of N/yr)

-for 1-20% slurry usage (no data points were in this range, so less reliable):
 annual leached-nitrogen loading as N = (0.1% of ANFO as N) + (8.5% of slurry as N)

- for more than 20% slurry usage (data were actually independent of slurry usage in this range):
 annual leached-nitrogen loading as N = (0.94% of ANFO as N) + (5.1% of slurry as N)

B) Divide the annual site-wide leached-nitrogen loading among the minesite components and catchments, based on some proportion like size or lateral area.

C) Divide the localized, component-specific annual leached-nitrogen loading into loadings of nitrate, nitrite, and ammonia.

Ferguson and Leask (1988) reported that proportions of the nitrogen species were notably variable, with 75-99% nitrate, 0-6% nitrite, and 0.5-24% ammonia. Thus, the corresponding mean values would not be reliable predictors, but were used anyway. For more than 3 mg/L of total nitrogen, the mean values were 95% nitrate, 1% nitrite, and 4% ammonia. For less than 0.5 mg/L of total nitrogen, the mean values were 83% nitrate, 2% nitrite, and 15% ammonia. Farther downstream in the receiving environment, which included upstream baseline nitrogen species, the percentages were again variable: 67-99% nitrate (mean of 87%), 0-6% nitrite (mean of 3%), and 1-27% ammonia (mean of 10%).

D) Calculate average and weighted quarterly loadings of the leached nitrogen species.

The preceding annual loadings of nitrogen species for each minesite component can be divided by four to obtain the average quarterly loadings. However, because flows were not identical in each quarter, Ferguson and Leask (1988) recommended that the average quarterly loading be multiplied by weighting factors reflecting local quarterly flows. The weighting factors were:

	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec
Effluents	0.2	3.1	0.3	0.4
Receiving water	0.5	1.8	1.0	0.7

E) Calculate the variable daily aqueous concentration

The weighted seasonal loading can be multiplied by the ratio of (daily flow / quarterly flow) to estimate the weighted daily loading (Ferguson and Leask, 1988). This assumed a linear and proportional relationship. The weighted daily loading could then be divided by the daily flow to obtain the daily concentrations, after mathematical unit conversion to mg/L. However, because of the mathematical approach used here by Ferguson and Leask (1988), the daily concentration in mg/L will be identical for each day in the quarter.

3. Case Study of Nitrogen Leaching from an Active Underground Mine

3.1 Introduction

Although the case studies of Ferguson and Leask (Section 2) were open-pit coal minesites, this case study of “Mine A” focusses on an underground metal mine. Located in mountainous terrain in western Canada, this underground mine lies at approximately 1000 m elevation. 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 $+15^{\circ}\text{C}$ in July.

Because this is an underground mine, freezing temperatures in winter are not relevant to geochemical processes underground, where the mine walls do not freeze. However, temperatures do affect monthly rates of groundwater recharge. This groundwater flows downwards through up to several hundred of meters of rock to enter the mine, drains along the floor ditch by gravity, and then discharges through the portal.

Exploration mining at this site was carried out mostly in the 1960's, with some work extending into the 1980's. This produced approximately 3100 meters of underground workings and 58,000 m of underground drilling in 165 holes. The main adit was approximately 2000 m long. Four perpendicular cross-cuts, near the distant end of the main adit and the ore zone, ranged from roughly 100 to 500 m in length. In the 1980's, the portal was buried and there was no access until 2005.

In 2005, the portal was excavated, some ponded water was drained, and the underground workings were renovated. Drainage-chemistry monitoring at the portal, from 1981 through 2007, showed notably steady aqueous concentrations. Thus, the leaching of most elements has not been disturbed by underground activity. This was not the case for nitrogen species.

Starting in late 2005, sporadic, minor blasting and mining created new drilling stations. In mid 2006, a more intensive effort led to the extension of a cross-cut by 50 m, while removing approximately 2400 tonnes of rock. This case study examines the leaching of nitrogen species during and after these two blasting campaigns.

3.2 Sporadic Blasting in Late 2005 and Early 2006

Sporadic blasting started in November 2005 to February 2006. Before this, aqueous concentrations of nitrate, nitrite, and ammonia were generally around or below detection limits at the portal of the main adit at Mine A (Station A1). Detection limits were typically 0.005 mg N/L for nitrate and ammonia, and 0.001 mg N/L for nitrite.

However, because the explosives contained nitrogen, aqueous concentrations of the three nitrogen species often became detectable after November. Through November to February, maximum concentrations for nitrate, nitrite, and ammonia reached 11.6, 0.51, and 11.8 mg N/L, respectively. This section examines the blasting activity, and resulting nitrogen-species concentrations, in order to predict the future nitrogen concentrations during mining of the next

campaign of blasting (Section 3.3).

The explosives were ammonium nitrate-fuel oil (ANFO) and a proprietary “powder”. The ANFO reportedly contained 92% ammonium nitrate (NH_4NO_3). The powder was proprietary and the manufacturer declined to reveal its formulation. The powder’s MSDS sheets said it contained 0-75% ammonium nitrate, 0-50% sodium nitrate, 10-30% ammonium chloride, and several other nitrate and ammonium compounds. For these predictions, we assumed the powder was on average 50% ammonium nitrate.

One “round” of blasting used approximately 12.5 kg of powder and 50 kg of ANFO. Based on the preceding ammonium-nitrate contents, and on the presence of two moles of nitrogen in one mole of ammonium nitrate, one round would contain approximately 18.3 kg of total nitrogen (N), initially as nitrate and ammonium. Partial rounds to many rounds of blasting occurred on various days, in a generally random pattern (Table 1; see also the Notes at the end of that table).

Table 1. Blasting Schedule in the Main Adit from November 2005 to February 2006 (see Notes at the bottom of the table)		
Blasting dates:		
<u>Date</u>	<u>Shift (Night/Day)</u>	<u>Description (see Notes at the end)</u>
<u>2005</u>		
Nov 23	N	slash
Nov 25	N	raise round
Nov 27	D	round
Nov 30	N	2 slashes
Dec 2	N	2 rounds
Dec 3	D	raise round
Dec 4	D	slash
Dec 5	D	raise round
Dec 6	D	round
Dec 8	D	oversize
Dec 8	N	lifters
Dec 10	N	lifters
<u>2006</u>		
Jan 6	N	round & slash
Jan 7	N	slash
Jan 11	N	round & slash
Jan 13	D	2 drift rounds, 1 raise round, slashes
Jan 13	N	re-blast
Jan 15	N	round
Jan 16	N	re-blast
Jan 21	D	slash
Jan 21	N	?
Jan 23	N	drift round, raise round, slashes
Jan 24	D	re-blast
Jan 25	N	re-blast

Date	Shift (Night/Day)	Description (see Notes at the end)
Jan 27	D	slashes
Jan 29	D	round
Jan 29	N	re-blast
Jan 31	N	loose
Feb 1	N	re-blast
Feb 3	N	slashes
Feb 5	D	2 drift rounds
Feb 5	N	oversize
Feb 6	D	raise round and slash
Feb 10	D	round & slash
Feb 10	N	re-blast
Feb 12	N	raise round
Feb 13	D	re-blast
Feb 16	N	raise round
Feb 17	D	raise round
Feb 17	N	drift round
Feb 20	D	round
Note: "re-blast" and "oversize" are small blasts.		
"Slash" is about 1/2 the size of "round".		
raised round = over head blast		
drift round = horizontal blast		
One round requires ~12.5 kg of powder and 50 kg of ANFO		

Some of the ammonium and nitrate in the explosives would have converted to nitrogen gas after detonation. Also, depending on the flow rates over water through the blasted rock, not all of the nitrogen may have been flushed out. In any case, occasional monitoring of flow and chemistry at Mine A's portal (Station A1) and farther downstream (Station A5) were used to reconstruct the release of nitrogen species in the drainage waters. This required some assumptions, because monitoring data were not always collected on days close to blasting days. For this reason, we used the averages of the closest previous and subsequent dataset for days with no data. During the Christmas 2005 break with no blasting, we used the December 20 data to represent all days until the next blast on January 6. During this period, average flow from the portal was approximately 600,000 L/day.

As a result, the nitrogen content of the explosives could be summed through time to create a cumulative curve in kg N (Figure 1). The sum of nitrate, nitrite, and ammonia loadings (concentrations multiplied by flow) at A1 (portal) and A5 (downstream) were also summed for comparison. Concentrations of total nitrogen at A1 and A5 were also available, but the sum of nitrogen species was typically greater at A1 and were used instead. This showed that aqueous concentrations of nitrogen species generally responded to blasting within a few days and that the sum at A1 was on average 28% of the explosives' nitrogen content. This can be seen in Figure 2, where A1 nitrogen loadings multiplied by 3.6 ($= 1 / 0.28$) generally matched the explosives curve. The leaching of 28% of the explosive's nitrogen through the portal substantially exceeds the 0.2-6% reported by Ferguson and Leask for open-pit coal mines (Section 2).

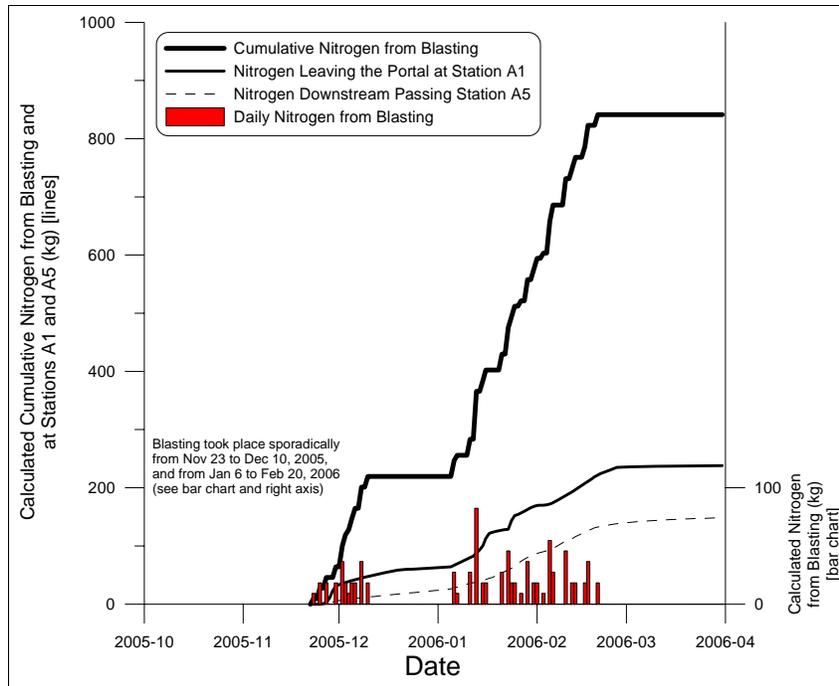


Figure 1. Cumulative Nitrogen Usage (Nitrate plus Nitrite plus Ammonia) from the Underground Blasting Program, and Corresponding Cumulative Aqueous Nitrogen Loadings at Stations A1 (Portal) and A5 (Downstream).

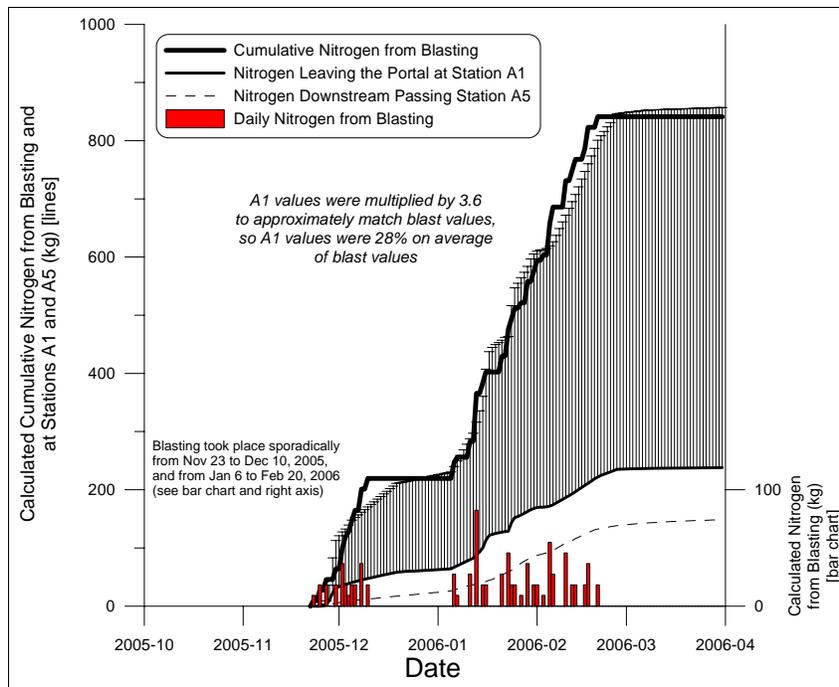


Figure 2. Cumulative Aqueous Nitrogen Loadings at Station A1 Multiplied by a Factor of 3.6 (Vertical Lines), to Show A1 (Portal) Typically Reflects 28% of the Cumulative Nitrogen Usage from Blasting.

Overall, the cumulative curve for A5 was 16% of the explosives curve (Figure 1). However, A5, when adjusted by $(1 / 0.16)$:

- 1) does not match the explosives curve well except for the final cumulative amount (Figure 3),
 - 2) A5 shows a loss of 40% of nitrogen observed at A1, and
 - 3) as discussed below A5 confirms loss of selected nitrogen species.
- As a result, predictions downstream at A5 would be more complex.

Of the total nitrogen (sum of nitrate, nitrite, and ammonia) at the portal (A1), nitrate as N represented 51.3% of the total, nitrite as N 2.9%, and ammonia as N 45.8% (Figure 4). Thus, the nitrate and ammonia are roughly equal and dominant, resembling the original explosives. This is notably different from the findings of Ferguson and Leask (Section 2), who found nitrate was a much higher percentage at the expense of ammonia.

Farther downstream at A5, the percentages of nitrite and ammonia were substantially lower (0.5% and 3.9% of total N, respectively, more typical of those from Ferguson and Leask). However, the absolute concentration of nitrate at A5 was actually higher than at A1, that is, it increased downstream (Figure 4). Overall, this represented a net loss of 40% of the summed nitrogen species between A1 and A5. Thus, complex ammonia-oxidation and perhaps denitrification processes may be operating below the portal.

Based on this round of blasting, the approach for general predictions of nitrogen species at the portal is summarized in Table 2. This assumes future explosives, blasting, and underground water movement will be generally similar and proportional to conditions at that time (see the “challenges” listed in Section 1). Thus, average loadings of individual species in kg N/day were estimated from average explosives usage. Concentrations in mg/L could then be calculated based on predicted flows from the underground.

3.3 Blasting and Mining in Mid 2006

Subsequent exploration work provided an opportunity to test the reliability of the predictive equations in Table 2. From June 11 to August 30, 2006, one cross-cut was extended approximately 50 m southward by mining approximately 2400 t of rock. Over the 80 days, 3525 kg of ANFO (44 kg ANFO/day) was used. Based on the previously estimated content of Mine A’s ANFO, this was equivalent to 14 kg N/day on average. Over this same period, average flow at the portal (Station A1) was approximately 916,000 L/day, roughly 50% higher than the flow during the previous blasting campaign (Section 3.2).

Based on Table 2, the predicted average incremental increases in nitrate, nitrite, and ammonia would be 2.2, 0.12, and 2.0 mg N/L. At the portal, incremental increases were not actually seen until early July, and fell off sharply after blasting ended (Figure 5). In July and August, the average concentrations of nitrate, nitrite, and ammonia were 0.98, 0.069, and 0.70 mg N/L, compared to prior concentrations well below 0.1 mg N/L.

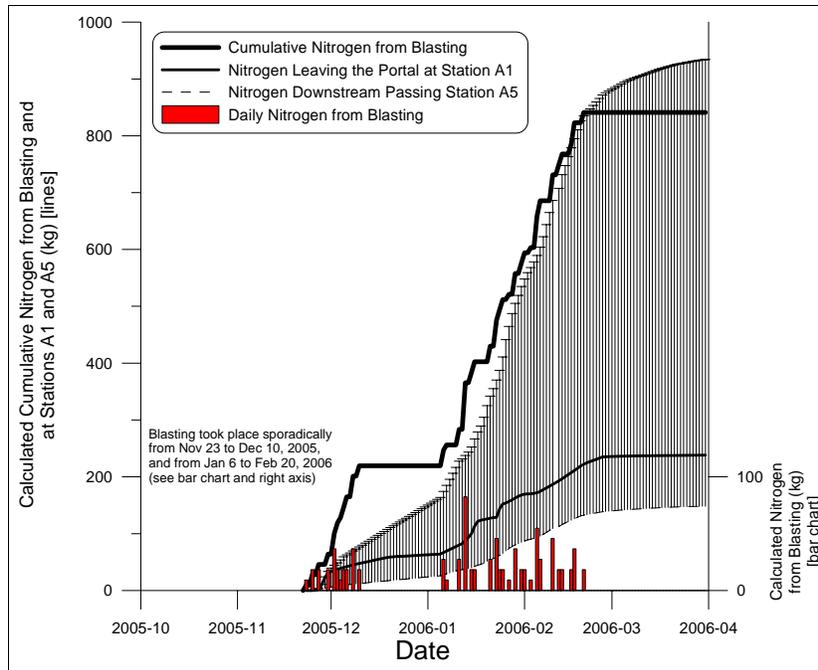


Figure 3. Cumulative Aqueous Nitrogen Loadings at Station A5 (Downstream) Multiplied by a Factor of 6.3 (Vertical Lines), to Show A5 Only Roughly Reflects 16% of the Cumulative Nitrogen Usage from Blasting.

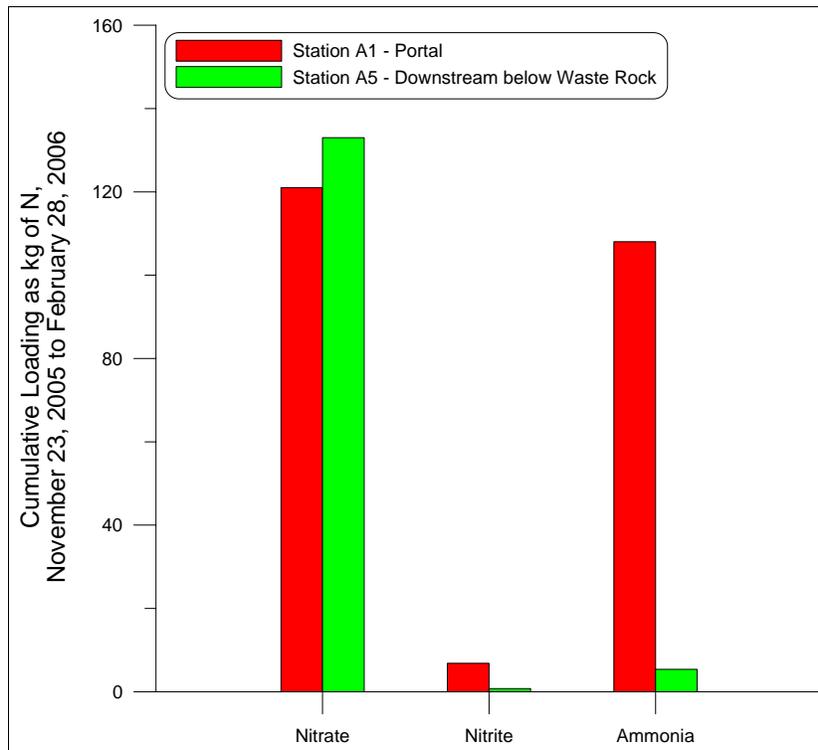


Figure 4. Cumulative Loadings of Nitrate, Nitrite, and Ammonia at Stations A1 (Portal) and A5 (Downstream) Between November 23, 2005 and February 28, 2006.

Table 2. Predictions of Average Aqueous Nitrogen Species at the Portal, Based on Blasting Data from November 2005 to February 2006		
<i>Predictive Equation Requiring Input of Factors "L" and "P"</i>		
Average loading of selected nitrogen species (kg N/day) = Average explosives usage (kg N/day) * L/100 * P/100,		
where L = percentage of leached nitrogen relative to the total amount used in the explosives, and P = percentage of the selected nitrogen species relative to the sum of nitrate, nitrite, and ammonia		
Nitrogen Species	<u>L</u>	<u>P</u>
Nitrate	28%	51.3%
Nitrite	28%	2.9%
Ammonia	28%	45.8%

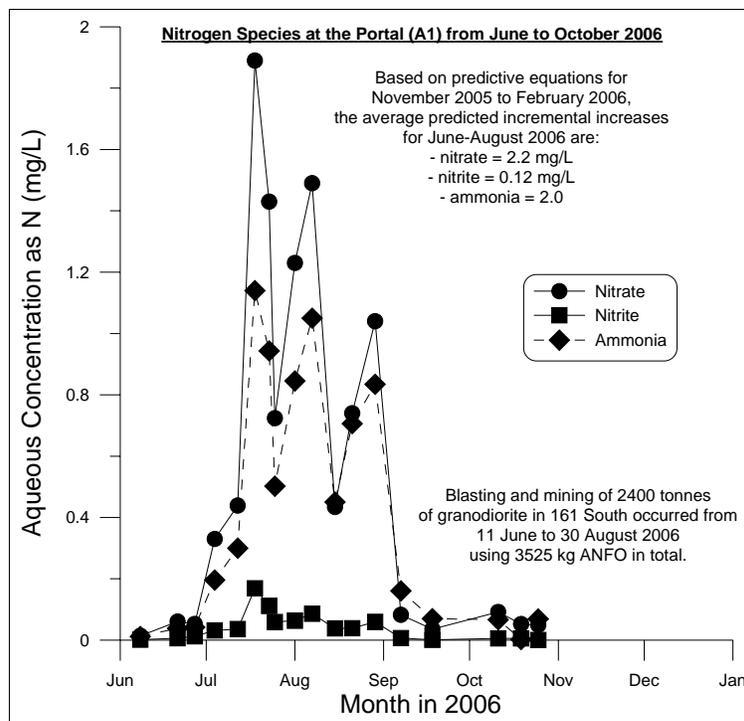


Figure 5. Temporal Trend in Nitrate, Nitrite, and Ammonia at the Portal After Using 3525 kg of ANFO for Mining in June-August 2006.

Thus, Table 2 overestimated incremental increases roughly by factors of 2 to 3, which is considered an acceptable safety factor for environmental protection. To match better the actual concentrations, the total leached amount of nitrogen decreased from 28% in the first blasting campaign (Section 3.2) to 12% for this second campaign. This is still substantially higher than values reported by Ferguson and Leask for open-pit coal mines (Section 2). Then, the relative proportions of nitrate, nitrite, and ammonia are adjusted. The best-fit factors for both blasting campaigns are compiled in Table 3.

Table 3. Predictions of Average Aqueous Nitrogen Species at the Portal, Based on Two Campaigns of Blasting in Underground Mine A				
<i>Predictive Equation Requiring Input of Factors "L" and "P"</i>				
Average loading of selected nitrogen species (kg N/day) = Average explosives usage (kg N/day) * L/100 * P/100,				
where L = percentage of leached nitrogen relative to the total amount used in the explosives, and P = percentage of the selected nitrogen species relative to the sum of nitrate, nitrite, and ammonia				
Blasting Campaign	November-February		June-August	
	<u>L</u>	<u>P</u>	<u>L</u>	<u>P</u>
Nitrate	28%	51.3%	12%	56.0%
Nitrite	28%	2.9%	12%	4.0%
Ammonia	28%	45.8%	12%	40.0%

4. References

Ferguson, K.D., and S.M. Leask. 1988. The Export of Nutrients from Surface Coal Mines Environment Canada Regional Program Report 87-12. Dated March, 1988. 127 p.