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Thank you, Robyn
The Diavik Waste Rock Project: Persistence of contaminants from blasting agents in waste rock effluent

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ABSTRACT

During mining operations, explosives are used to fragment rock into workable size fractions. Mine-water chemistry can be affected by blasting agent residuals, including NH3, NO3, NO2, Cl-, and ClO4. At the Diavik diamond mine, Northwest Territories, Canada, waste rock generated from open-pit and underground mining is stockpiled on site. Three large-scale test piles measuring 60 by 50 m at the base and 15 m in height, along with four 2 × 2 m lysimeters each 2 m in height, were constructed at Diavik as part of a comprehensive research program to evaluate the quality of water emanating from waste rock stockpiles. Ongoing monitoring of the water chemistry since 2007 shows that blasting residuals comprise a large proportion of the dissolved constituents in the initial pore water and effluent. Leach tests conducted on freshly blasted rock from Diavik indicate the mass of N released corresponds to a 5.4% N loss from the blasting explosives; this mass is in the range for N loss reported for blasting operations at Diavik during the period when the test piles were constructed. The total mass of N released from the lysimeters was also within this range. The three large-scale test piles have only released a small fraction of the N estimated to be contained within them. Blasting of waste rock contributes SO2 to effluent through the oxidation of sulfide minerals in the rock during the blast. During the initial flush of water, the test pile that contained waste rock with the higher S content was observed to release higher concentrations of SO2 than the test pile with lower S content waste rock. Mass-balance calculations based on the ratios of SO2 to total N can be used to estimate the relative contributions of sulfide oxidation within the test piles and SO2 released when S in the host rock is oxidized during blasting. These calculations provide an estimate of S mass released during the first flush of the test piles.

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1. Introduction

1.1. Background

Mining generates and moves the greatest volume of materials in the world (ICOLD, 1996). At mine sites around the globe, explosives are used to fragment rock into workable size fractions. In 2009, mining consumed 87% of explosives used in the United States, excluding military use (USGS, 2009). Ammonium nitrate mixed with fuel oil (ANFO) is the primary blasting agent used in the mining industry (80%) versus alternatives such as 2,4,6-trinitrotoluene (TNT), nitroglycerine, and perchlorate salts. Although relatively inexpensive and safe to transport, store, and use, ammonium nitrate is hygroscopic. Increases in moisture content can cause the explosive to lose efficacy, potentially resulting in detonation failures (Pommen, 1983) and the eventual release of undetonated explosives to the environment. Emulsion explosives are similar in composition to ANFO, but include an aqueous solution supersaturated with respect to ammonium nitrate prill surrounded by an immiscible fuel oil. This formulation decreases the dissolution of ammonium nitrate in water (Egły and Neckar, 1964). Emulsions contain 20–30% total N (Ntotal) and are usually blended with ANFO for applications in wet blast holes (Pommen, 1983). Ore and waste rock are blasted using ANFO emulsion explosives at the Diavik diamond mine (Diavik), Canada. Explosives are detonated with a boosting agent that contains ClO4, which can release Cl− during detonation (Aziz, 2006).

Nitrate has low toxicity to aquatic life (Pommen, 1983) and is an important nutrient source for aquatic plants; however, elevated concentrations of NO3 can lead to eutrophication if other requirements such as light and P are abundant (Stumm and Morgan, 1996). Nitrite and NH3 are toxic to fish at low concentrations (CWQG, 1987). In addition to blasting, sources of NO3 and NH3 to the environment include agricultural activity, wastewater disposal, and landfills.

Perchlorate can have harmful effects to human health at concentrations in the low µg L⁻¹ range (Cox, 1994; NRC, 2005; Ting et al., 2006). Perchlorate has been found in surface water and groundwater surrounding explosive processing plants, military testing sites, mine sites, and sites where fireworks have been detonated (Susarla et al., 1999; Motzer, 2001; ITRC, 2005; Jackson et al., 2005; Parette et al., 2005; Sanchez et al., 2005; Schaefer et al., 2007; Wilkin et al., 2007).

Ammonium nitrate is highly soluble in water, rapidly dissociating into NO₃⁻ and ammonium (NH₄⁺). Ammonium can further dissociate to NH₃ in alkaline conditions (Clark, 1981):

\[
\text{NH}_4\text{NO}_3 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{NH}_4\text{OH} + \text{H}^+ \quad (1)
\]

\[
\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \quad (2)
\]

Under aerobic conditions, NH₃ is oxidized to the unstable intermediate N species NO₂ by the Nitrobacter group of nitrifying bacteria (Koren et al., 2000):

\[
2\text{NH}_3^+ + 3\text{O}_2 \rightarrow 2\text{NO}_2^- + 2\text{H}_2\text{O} + 4\text{H}^+ \quad (3)
\]

Nitrite is further oxidized to NO₃⁻ by the Nitrosomonas group of nitrifying bacteria (Sawyer and McCarty, 1967):

\[
2\text{NO}_2^- + 2\text{O}_2 \rightarrow 2\text{NO}_3^- \quad (4)
\]

Under aerobic conditions, NO₃⁻ persists in solution and is not readily adsorbed by soils or aquifer materials (Baalsrud and Baalsrud, 1954). Reducing conditions and sufficient soluble organic C are required for denitrification by heterotrophic bacteria including Pseudomonas, Paracoccus, Flavobacterium, Alcaligenes, and Bacillus spp. (Koren et al., 2000). Denitrification by autotrophic bacteria, such as Thiobacillus denitrificans, reduces NO₃⁻ to N₂(g) with the oxidation of sulfate or organic C at neutral pH (Schedel and Almeda, 2007; Wilkin et al., 2007).

Three large-scale test piles were constructed at Diavik to assess the hydrology, temperature, and (bio)geochemical reactions in waste rock piles in permafrost terrains (Smith et al., this issue-a, this issue-b) (Fig. 1). Two of the test piles, measuring 60 by 50 m at the base and 15 m in height, are constructed of run of mine waste rock resting at the angle of repose. The Type I test pile contains 0.035 wt.% S and the Type III test pile contains 0.053 wt.% S (lower than the operational S target of >0.08 wt.% S; Smith et al., this issue-a). A third test pile (the Covered test pile) was constructed based on a reclamation concept for the Type III waste rock at Diavik. The configuration consists of 13 m of Type III waste rock (average of 0.082 wt.% S) covered with a 1.5 m of glacial till and then 3 m of Type I waste rock. The test piles are underlain by an impermeable high-density polyethylene (HDPE) liner, which collects effluent water at their respective bases. This water is directed to instrumentation huts by gravity flow through polyvinyl chloride (PVC) drain lines with mineral insulated (MI) heating cable set to maintain temperatures between 5 and 10 °C to facilitate the collection of water samples. Water in the instrumentation huts flows through a series of flow through cells, where water samples are collected and continuous measurements of pH, electrical conductivity (EC), and flow rates are obtained.

Four lysimeters were constructed in the upper 2 m of waste rock (referred to as active zone lysimeters; AZLs) at a site adjacent to the test piles to provide detailed information on the hydrology and geochemistry within the thermally active layer near the pile surface (Fig. 1). These lysimeters were constructed using 2 m diameter × 2 m high HDPE tanks; two are filled with sub-samples of Type I waste rock from the same haul truck load with an average of 0.017 ± 0.0095 wt.% S (n = 2) (Type I east and west lysimeters) and two with Type III waste rock from the same haul truck load with an average of 0.035 ± 0.015 wt.% S (n = 2) (Type III east and west lysimeters). Drainage from the AZLs is directed to an instrumentation trailer through gravity flow where the effluent pH, EC, temperature, and flow rate are continuously monitored. Full details on the design, construction and instrumentation of the test piles

and AZLs are provided by Smith et al. (this issue-b). Pham et al. (this issue) provides a discussion of the thermal regime within the test piles, and Neuner et al. (this issue) and Fretz et al. (2011) provide discussions of hydrologic processes controlling infiltration through the test piles and the AZLs.

2. Methods of investigation

2.1. Laboratory leach test methods

Eight laboratory leach tests were completed using recently blasted (within 3 months) Type I waste rock collected from the open pit at the Diavik site in September 2009. The samples were from the same blast pattern at the mine site. Leach tests (LT1 through LT8) consisted of 100 g of run-of-mine un-crushed waste rock sieved to <20 mm. Waste rock was mixed with 1 L of Milli-Q-grade water in a pre-washed HDPE bottle placed on a bench top orbital shaker (Model 3520, Lab-Line Instruments, USA) at 40 rpm for 48 h and were completed in triplicate. Mean values were calculated and were labelled according to the sample (e.g., LT1 through LT8). Water samples were collected using a sterile 30 mL polyethylene (PE) syringe placed in the leach test bottle. Water was then passed through 0.45 μm cellulose-acetate membrane filters into pre-washed HDPE sample bottles that had been triple-rinsed with sample water prior to filling. This water passed through the basal drains prior to entering the sampling system and thus was exposed to O2(g). Pore-gas concentrations within the lysimeters were not measured; however, testing in the large-scale waste rock piles indicated that O2(g) and CO2(g) concentrations throughout the test piles were at atmospheric levels (Amos et al., 2009). The pH measurements were made using a combination electrode (Orion ROSS Ultra® 8156, Thermo Scientific, USA) calibrated using pH 7, 4, and 10 or 1.68 standard buffer solutions. Eh measurements were made with a Pt redox electrode (Orion 96-78; Thermo Scientific, USA) checked against ZoBell’s (Nordstrom, 1977) and Light’s solutions (Light, 1972). Alkalinity measurements were made using a Hach digital titrator with brom cresol green/methyl red indicator and 0.16 N H2SO4. Field measurements were completed using a Hach spectrophotometer DR/8400 for the determination of NH3 (NH3–N; salicylate method) and blanks into the protocol.

2.2. Field characterization methods

At each sampling location, pH, EC, temperature, and alkalinity were determined for water collected from the sampling cell system. Water samples were collected from flow-through cells using 0.64 cm PE tubing attached to a sterile 60 mL PE syringe. The water was passed through 0.45 μm cellulose-acetate membrane filters into pre-washed HDPE sample bottles that had been triple-rinsed with sample water prior to filling. This water passed through the basal drains prior to entering the sampling system and thus was exposed to O2(g). Pore-gas concentrations within the lysimeters were not measured; however, testing in the large-scale waste rock piles indicated that O2(g) and CO2(g) concentrations throughout the test piles were at atmospheric levels (Amos et al., 2009). The pH measurements were made using a combination electrode (Orion ROSS Ultra® 8156, Thermo Scientific, USA) calibrated using pH 7, 4, and 10 or 1.68 standard buffer solutions. Eh measurements were made with a Pt redox electrode (Orion 96-78; Thermo Scientific, USA) checked against ZoBell’s (Nordstrom, 1977) and Light’s solutions (Light, 1972). Alkalinity measurements were made using a Hach digital titrator with brom cresol green/methyl red indicator and 0.16 N H2SO4. Field measurements were completed using a Hach spectrophotometer DR/8400 for the determination of NH3 (NH3–N; salicylate method) and Cl– determined using ion chromatography (IC; DX600, Dionex, USA). All concentrations of NO3–, NO2–, and Cl– were determined using ion chromatography (IC; DX600, Dionex, USA). All concentrations of NO3– and NO2– are expressed as mg L–1 NO3––N and mg L–1 NO2––N, respectively. Concentrations of NH4+(NH4–N; salicylate method) were determined using a Hach spectrophotometer DR/8400 (SMEWW, 2005).

2.3. Perchlorate analysis

Water samples were collected from flow-through cells and filtered as described above, then frozen at −20 °C until analysis at the University of Waterloo. The analytical method for perchlorate followed the procedure described by Snyder et al. (2005), with an additional step involving the addition of 18O-labelled ClO4– to all standards and samples to assess matrix interferences. Each water sample was prepared by elution through an OnGuard II barium cartridge and an OnGuard II hydronium cartridge (Dionex, USA) to remove high concentrations of SO42– and polyvalent...
cations, such as Ca and transition metals, from sample matrices. The cartridge extracts were analyzed using high performance liquid chromatography (HPLC; Agilent 1100, Agilent Technologies, Mississauga, Canada) with electrospray tandem mass spectrometry (LC/MS/MS; 4000 Q Trap, Applied Biosystems, Foster City, USA) operated in electrospray ionization (ESI) negative mode. The following conditions were found to provide the optimum signal: curtain gas –10 arbitrary units (a.u.), turboionspray voltage –4500 V, temperature 750 °C, nebulizer gas 55 a.u., auxiliary gas (turb) 60 a.u., and collision gas 8 a.u. Four multiple reaction monitoring transitions were determined: m/z 99–83 and m/z 101–85 for native ClO\textsubscript{4}\textsuperscript{−}, and m/z 107–89 and m/z 109–91 for enriched ClO\textsubscript{4}\textsuperscript{−}.

Perchlorate was quantified using the internal standard technique. Instrument calibration was performed using a 10-point linear regression with \(1/x^2\) weighting. Measured responses were corrected for the recovery of internal standards added to both standards and unknown samples. Method blanks were analyzed and calibration checks conducted every 10 samples. Perchlorate was not detected in the method blank samples and instrument calibration blank samples. The analytical precision was checked by analyzing duplicate samples following the entire preparation procedure. The relative standard deviation of duplicates was less than 5% and the error less than 0.2%. The instrument and practical precision was less than 5% and the error less than 0.2%. The instrument and practical precision was less than 5% and the error less than 0.2%. The instrument and practical precision was less than 5% and the error less than 0.2%.

### 3. Results and discussion

#### 3.1. Laboratory leach tests

The concentrations of NO\textsubscript{3}—N and NO\textsubscript{2}—N followed similar trends in all of the leach tests; however, higher concentrations of both species were observed in leach test LT1 and lower concentrations in LT7 and LT8 (Table 1). The NH\textsubscript{4}—N was below detection (<0.02 mg L\textsuperscript{−1}) for all leach test samples. For the eight laboratory leach tests conducted on the freshly blasted waste rock, N\textsubscript{Total} concentrations averaged 0.46 mg L\textsuperscript{−1} (4.6 mg N kg\textsuperscript{−1} waste rock), with lower concentrations observed in two samples (LT7 and LT8; Table 1). All leach tests had similar SO\textsubscript{2}\textsuperscript{−} concentrations with the exception of higher levels in LT1 and LT8. Chloride concentrations were similar for all leach tests with the exception of higher concentrations in LT1.

Six leach tests (LT1 through LT6) had similar ratios of N\textsubscript{Total} to Cl\textsuperscript{−}, SO\textsubscript{2}\textsuperscript{−} to N\textsubscript{Total} and SO\textsubscript{2}\textsuperscript{−} to Cl\textsuperscript{−}, whereas values for leach tests LT7 and LT8 were lower (Table 2). Leach test LT1 had the highest concentrations of Cl\textsuperscript{−}, N\textsubscript{Total} and SO\textsubscript{2}\textsuperscript{−}, resulting in a higher than average ratio of N\textsubscript{Total} to Cl\textsuperscript{−}, and a lower than average ratio of SO\textsubscript{2}\textsuperscript{−} to Cl\textsuperscript{−}. The ratio of SO\textsubscript{2}\textsuperscript{−} to N\textsubscript{Total} was consistent with average ratios (Table 2). Leach test LT7 had the lowest N\textsubscript{Total} concentration, and leach test LT8 had the second lowest N\textsubscript{Total} concentration (after LT7) (Table 1).

The differences in the observed N\textsubscript{Total} released likely reflect variations in leachable blasting residuals in the waste rock samples attributable to differences in the blasting activity, with samples derived from locations in the vicinity of blast holes having higher concentrations of blasting residuals than those located further away. Similarly, the variation in SO\textsubscript{2}\textsuperscript{−} released during the leach tests was likely due to differences in the mass of S exposed to the explosion during blasting. These differences could be a result of variations in the proximity of the sample to the blast hole or the original S content of the rock, with higher SO\textsubscript{2}\textsuperscript{−} concentrations expected for samples with a higher original S mass. Humidity cell leaching experiments completed on Type I and Type III waste rock show that SO\textsubscript{2}\textsuperscript{−} to N\textsubscript{Total} ratios are greater for samples with a greater S content relative to samples with a lower S content (unpublished data).

#### 3.2. Diavik field site

#### 3.2.1. Blasting residuals in the active zone lysimeters

Drainage commenced in the Type I AZLs in the spring of 2008. Both the Type I east and west AZLs maintained near neutral conditions for the duration of the study (Fig. 2). The blasting residuals attained maximum concentrations of NO\textsubscript{3}—N, NO\textsubscript{2}—N, NH\textsubscript{3}—N, and ClO\textsubscript{4}\textsuperscript{−} in the Type I west and east AZLs in early 2008 (Fig. 2; Table 3), with the exception of NO\textsubscript{3}—N and ClO\textsubscript{4}\textsuperscript{−} in the Type I east which had maximums in 2010. The maximum ClO\textsubscript{4}\textsuperscript{−} concentration may have occurred in samples not analyzed from 2008 with high concentrations of other blasting residuals. Concentrations of Cl\textsuperscript{−}, SO\textsubscript{2}\textsuperscript{−} and NO\textsubscript{2}—N decreased sharply at the end of August and beginning of September 2008, indicating flushing of the blasting residuals initially present in the Type I AZLs. The concentrations of these components remained low for the remainder of 2008. Although the concentrations of dissolved NH\textsubscript{3}—N and NO\textsubscript{2}—N also decreased sharply in September 2008, low concentrations persisted in the effluent. Concentrations of dissolved SO\textsubscript{2}\textsuperscript{−} increased early in 2009 and 2010. The absence of Cl\textsuperscript{−} during these years suggests that most of the SO\textsubscript{2}\textsuperscript{−} was derived from in situ sulfide-mineral oxidation within the AZLs.

A sharp decline in Cl\textsuperscript{−} concentrations occurred after approximately 153 L of flow through the Type I west AZL. The volume of flow prior to the decline in Cl\textsuperscript{−} concentrations was lower (77 L) in the Type I east AZL. However, the record of flow measurements was less comprehensive for the Type I east AZL. In addition, the Type I east AZL was damaged during placement of waste rock in the lysimeter, requiring a repair, but leading to greater uncertainty in the Type I east AZL flow measurements.

The sharp decline in Cl\textsuperscript{−} concentrations that occurred after 77 L in the Type I east AZL and 155 L in the Type I west AZL probably represent the first flush of recharge water. The total volume of the Type I AZLs is 5.7 m\textsuperscript{3}. Neuner et al. (this issue) estimated the total porosity of the Diavik waste rock to be 0.25, and that 18%
of this porosity is associated with the matrix, corresponding to a bulk matrix porosity of 0.05 computed for the volume of the AZL. Using these values, the calculated matrix volume of the Type I lysimeters is 0.256 m$^3$ (256 L). The volume of water that passed through the Type I west AZL prior to the sharp decline in the concentrations of blasting residuals observed in September 2008 represents approximately 59% of the matrix porosity volume. Flow in the Type I east AZL prior to the sharp decline in Cl$^-$ concentrations corresponds to 30% of the matrix porosity volume, suggesting that all of the flow through the Type I east AZL may not have been recorded. Alternatively, it may reflect differences between hydrologic properties of the Type I waste rock placed in these lysimeters, and the subsequent influence of surface infiltration and flushing.

Five artificial rainfall events were applied to the Type III AZLs in 2007, increasing the rainfall to 115% of the annual mean rainfall (Neuner et al., this issue). A 53 mm artificial rainfall event was applied on August 12, 2008; this event included the addition of a LiCl tracer. As a consequence of the artificial rainfall events, flow through the Type III AZL was greater than observed for the Type I AZLs. The addition of the LiCl tracer to the Type III AZLs precludes the use of Cl$^-$ to identify the first flush of water from these lysimeters.

The Type III east AZL maintained near neutral (pH ~ 6) conditions in 2007, but the pH decreased to <4.5 in 2008 and remained low for the remainder of the study. The pH in the Type III west AZL decreased through 2007 to pH 4 and remained low (pH < 4.5) through 2010 (Fig. 3). From 2007 to 2010, the NH$_3$–N, NO$_2$–N, and ClO$_4^-$ concentrations in effluent from the Type III AZLs followed trends similar to those observed in the Type I AZLs: high concentrations in 2007, maximum concentrations during the mid-summer of 2008, a sharp decrease in concentrations at the end of August through the beginning of September 2008; and subsequently lower concentrations through 2009 and 2010 (Fig. 3). Maximum concentrations of ClO$_4^-$ and NO$_3$–N were observed in 2007, whereas NO$_2$–N and NH$_3$–N were at their maximum in 2008. Concentrations of Cl$^-$ and SO$_4^{2-}$ reached maximum concentrations in 2010 (Table 3). The Type III west AZL effluent contained maximum concentrations of NO$_3$–N, NH$_3$–N, ClO$_4^-$, and Cl$^-$ in 2008 and maximum concentrations of NO$_2$–N and SO$_4^{2-}$ in 2010.

The tracer test initiated on the Type III AZLs in 2008 makes it difficult to distinguish the decrease in Cl$^-$ concentrations associated with the first flush through these AZLs. However, the sharp decline in the concentrations of other blasting-derived constituents, including NO$_3$–N, NH$_3$–N, and ClO$_4^-$, at the end of August probably represents the conclusion of the first flush of water through the finer grained matrix in these lysimeters. This decline corresponds to a flow volume of 155 L in both AZLs. The Type III AZLs have an internal volume of 3.4 m$^3$. Based on the parameters estimated by Neuner et al. (this issue), the bulk matrix porosity

### Table 2

<table>
<thead>
<tr>
<th>Leach test</th>
<th>N$_{\text{Total}}$/Cl$^-$</th>
<th>Cl$^-$/N$_{\text{Total}}$</th>
<th>Cl$^-$/SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LT1</td>
<td>3.8</td>
<td>0.24</td>
<td>5.1</td>
</tr>
<tr>
<td>LT2</td>
<td>2.2</td>
<td>0.06</td>
<td>5.4</td>
</tr>
<tr>
<td>LT3</td>
<td>1.1</td>
<td>0.04</td>
<td>4.8</td>
</tr>
<tr>
<td>LT4</td>
<td>1.7</td>
<td>0.10</td>
<td>6.8</td>
</tr>
<tr>
<td>LT5</td>
<td>1.6</td>
<td>0.03</td>
<td>5.0</td>
</tr>
<tr>
<td>LT6</td>
<td>1.3</td>
<td>0.03</td>
<td>5.4</td>
</tr>
<tr>
<td>Average (LT1 through LT6; n = 18)</td>
<td>1.2</td>
<td>0.91</td>
<td>5.5</td>
</tr>
<tr>
<td>LT7 (n = 3)</td>
<td>0.8</td>
<td>0.03</td>
<td>27</td>
</tr>
<tr>
<td>LT8 (n = 3)</td>
<td>0.5</td>
<td>0.003</td>
<td>42</td>
</tr>
</tbody>
</table>


![Fig. 2. Blasting residual concentrations for the Type I west and east active zone lysimeters.](image-url)
of these lysimeters is estimated at 0.17 m$^3$ (170 L). The volume of water that passed through the lysimeters prior to the sharp decline in the concentrations of blasting residuals observed in September 2008 represents approximately 91% of the matrix porosity volume. The concentration of Cl$^-$ sharply increased and decreased after the first flush, at the beginning of September. Chloride concentrations after this time were influenced by both Cl$^-$ from the tracer test and blasting residuals.

Fig. 3. Blasting residual concentrations for the Type III west and east active zone lysimeters.
The maximum concentrations of Cl\(^-\) and SO\(_4^{2-}\) increased in 2009 and 2010 in the Type III east AZL and in the Type III west AZL (Fig. 3). Because Cl-containing minerals are very soluble and the potential for adsorption of Cl\(^-\) is low, transport of Cl\(^-\) through the AZLs is expected to be conservative. The N\(_{Total}\) to Cl\(^-\) ratios remained relatively constant in 2007 but declined in 2008, 2009, and 2010, possibly due to the addition of Cl\(^-\) during the tracer test. These observations suggest that although transformations may

![Fig. 4. Blasting residual concentrations for the Type I test pile drain.](image)

**Table 4**

Maximum concentrations of SO\(_4^{2-}\), Cl\(^-\), NH\(_3\)–N, NO\(_2\)–N, and NO\(_3\)–N in the basal drains of the Type I, Type III and Covered test piles.

<table>
<thead>
<tr>
<th>Basal drain</th>
<th>SO(_4^{2-}) (mg L(^{-1}))</th>
<th>Cl(^-) (mg L(^{-1}))</th>
<th>NH(_3)–N (mg L(^{-1}))</th>
<th>NO(_2)–N (mg L(^{-1}))</th>
<th>NO(_3)–N (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>1200</td>
<td>2800</td>
<td>410</td>
<td>7.9</td>
<td>2000</td>
</tr>
<tr>
<td>Type III south</td>
<td>2950</td>
<td>230</td>
<td>54</td>
<td>3.7</td>
<td>720</td>
</tr>
<tr>
<td>Covered</td>
<td>3530</td>
<td>245</td>
<td>10</td>
<td>13</td>
<td>380</td>
</tr>
</tbody>
</table>

have occurred between N species, the overall transport of N_{Total}
was conservative. The transport of ClO_4^- and N_{Total} initially resident
in the AZLs suggests that the period of release of constituents present
on the rock ended in August 2008. The subsequent increase in
SO_4^{2-} concentrations and ratios of SO_4^{2-} to N_{Total} in the Type III AZLs
in 2009 was probably due to \textit{in situ} sulfide-mineral oxidation.

3.2.2. Blasting residuals in the experimental test piles

Intermittent flow was observed in the test pile basal drains over
the study period (2007–2010). Because of the cold winter tempera-
tures at the Diavik site, the entire thickness of both the Type I and
Type III test piles fell below freezing each winter. Each spring, as
the temperatures in the test piles rose, flow commenced in the

![Fig. 5. Blasting residual concentrations for the Type III north basal drain and Type III south basal drain.](http://dx.doi.org/10.1016/j.apgeochem.2012.04.008)
basal drains and increased throughout the summer before decreasing in September (Fretz et al., 2011). As the test piles warmed from the margins inward, increased regions of the test piles contributed water to the drains. The initial drainage was probably derived from the shorter flow paths originating on the sides (batteries) of the test piles, with longer flow paths associated with the central portion of the test piles reporting later in the year. Furthermore, the Type III test pile received additional recharge through three artificial rain-fall experiments in each of 2006 and 2007, including two tracer tests conducted in 2007 (Neuner et al., this issue). The artificial rainfall was applied only to the tops of the test piles and not to the test pile batteries. Consequently, flow to the Type III test pile basal drains was substantially greater than flow to the Type I test pile basal drain.

3.2.2.1. Blasting residuals in the Type I test pile basal drain. Significant water flow began to report to the Type I test pile basal drain in 2008. In 2009 and 2010, concentrations of blasting residuals increased gradually from May until October when they increased sharply as the volume of flow decreased. The maximum concentrations of blasting residuals in the effluent occurred in November 2010 (Fig. 4 and Table 4).

3.2.2.2. Blasting residuals in the Type III test pile basal drains. The Type III test pile has two outflow drains (north and south). Flow to the Type III test pile basal drains commenced in 2007, with increased flow in subsequent years varying in response to changes in annual precipitation and temperature fluctuations. As the Type III test pile warmed during each field season, the pH decreased and concentrations of the blasting residuals NO\textsubscript{3}\textsuperscript{—N}, NH\textsubscript{3}\textsuperscript{—N}, SO\textsubscript{4}\textsuperscript{2—}, Cl\textsuperscript{—}, and ClO\textsubscript{4} increased (Fig. 5). Concentrations of blasting residuals reached a maximum in August 2008 (Table 4) in the Type III north basal drain, and subsequently declined and remained low throughout 2009. The concentrations of blasting residuals in the effluent from the Type III south basal drain peaked in October 2009 and remained elevated until the end of the field season. In 2010, Cl\textsuperscript{—}, N\textsubscript{Total}, and SO\textsubscript{4}\textsuperscript{2—} concentrations followed similar trends but at lower levels. Elevated concentrations at the end of the sampling session indicate contributions derived from longer flow paths and sources of blasting residuals not previously contributing to the pile drainage.

3.2.2.3. Blasting residuals in the Covered test pile basal drain. The Covered test pile had limited outflow in 2007, but concentrations of blasting residuals increased from September to January 2008 when flow declined and then ceased (Fig. 6). Flow resumed in September 2008 with the maximum concentrations of Cl\textsuperscript{—} and elevated concentrations of NO\textsubscript{3}\textsuperscript{—N} and SO\textsubscript{4}\textsuperscript{2—}. Flow continued until June 2009. Flow recommenced in August 2009 through the end of May 2010 when the maximum concentrations of N\textsubscript{Total} and SO\textsubscript{4}\textsuperscript{2—} were recorded (Table 5). Flow recommenced in July 2010 and continued for the remainder of the study.

3.2.3. Nitrogen species

Nitrogen is present in the ANFO emulsion explosives used at Diavik as NH\textsubscript{3} and NO\textsubscript{3}. The results of the leach test conducted on samples of recently blasted rock indicate the presence of NO\textsubscript{3}\textsuperscript{—N} and NO\textsubscript{2}\textsuperscript{—N} (Table 1); concentrations of NH\textsubscript{3}\textsuperscript{—N} were below detection. In the summers, when temperatures within the test piles rise to a maximum of 15 \degree C, the presence of detectable concentrations of NO\textsubscript{3}\textsuperscript{—N} indicates the nitrification of NH\textsubscript{3} to NO\textsubscript{2}. Elevated concentrations of NO\textsubscript{3}\textsuperscript{—N} were observed concurrent with maximum concentrations of NH\textsubscript{3}\textsuperscript{—N} and NO\textsubscript{2}\textsuperscript{—N}, suggesting oxidation of NO\textsubscript{2} to NO\textsubscript{3}. As the first flush of water advanced through the test piles, un-detonated blasting residuals, principally NH\textsubscript{3} and NO\textsubscript{3} with trace amounts of NO\textsubscript{2}, as well as SO\textsubscript{4}\textsuperscript{2—} ClO\textsubscript{4}, and Cl\textsuperscript{—}, were transported through the unsaturated waste rock. Nitrate can be removed by denitrification; however, reducing conditions...
and a sufficient supply of a labile electron donor are required. Denitrification by heterotrophic bacteria, e.g., Pseudomonas, Paracoccus, Flavobacterium, Alcaligenes, and Bacillus spp., requires a labile source of organic C (Koren et al., 2000). The organic C content of the Diavik waste rock piles is low. In addition, bacteria such as T. denitrificans reduce NO$_2^-$ to N$_2$G. Coupled with the oxidation of sulfide or organic C at neutral pH, however, this reaction does not seem to have resulted in extensive denitrification within the AZLs or test piles. The presence of elevated concentrations of NO$_3^-$—N were consistent with the high concentrations of O$_2$(g) present (Amos et al., 2009) and absence of labile organic C.

### 3.2.3.1. Ammonia

Concentrations of NH$_3$—N were only determined once in water collected from the Type III AZLs in 2007. The 2007 NH$_3$—N concentration was 2.6 mg L$^{-1}$ in the Type III west AZL and 2.9 mg L$^{-1}$ in the Type III east AZL. Ammonia reached maximum concentrations of 8.7 mg L$^{-1}$ in the Type III east AZL in late July and 3.5 mg L$^{-1}$ in the Type III west AZL in early August of 2008. In 2009, the NH$_3$—N concentration in the Type III east AZL effluent reached a maximum of 2.6 mg L$^{-1}$ in 2009 and 3.5 mg L$^{-1}$ in 2010. The Type III east AZL effluent NH$_3$—N concentration reached 6.6 mg L$^{-1}$ in 2009 and 9.0 mg L$^{-1}$ in 2010. Ammonia concentrations in the Type I east and west AZLs reached maximum values of 0.8 and 1.7 mg L$^{-1}$, respectively, in 2008. In 2009 and 2010, NH$_3$—N concentrations remained low (<0.5 mg L$^{-1}$) in both the Type I east and west AZLs.

Concentrations of NH$_3$—N in the Type III south drain were low in early 2007 and increased to a maximum of 23 mg L$^{-1}$ in July 2007. The Type III north drain reached maximum NH$_3$—N concentrations in August 2007 at 34 mg L$^{-1}$. The NH$_3$—N concentrations progressively decreased through to the end of November 2007 when flow ceased due to low temperatures.

In 2008, the NH$_3$—N concentrations attained maximum values of 31 mg L$^{-1}$ in the Type III north drain in July and 15 mg L$^{-1}$ at the Type III south drain in August. The NH$_3$—N concentrations remained low through 2009 with the exception of the Type III south drain, which increased in October to its maximum and remained elevated until the end of the field season. Throughout 2010 NH$_3$—N concentrations in the Type III south drain were <6 mg L$^{-1}$. The NH$_3$—N concentrations in the Type III south drain in 2010 followed a similar trend as in 2009, with low NH$_3$—N concentrations followed by much higher concentrations (54 mg L$^{-1}$) in October. These higher concentrations were attributed to an increase in the volume of waste rock affected by water flow, and, therefore, an increase in sources of blasting residuals. Elevated NH$_3$—N concentrations corresponded to increases in NO$_2^-$—N, NO$_3^-$—N, Cl$^-$, and SO$_4^{2-}$. Overall, effluent from the test pile basal drains had higher NH$_3$—N concentrations than effluent from the AZLs.

Flow in the Type I test pile began in May 2008. The maximum NH$_3$—N concentration (36 mg L$^{-1}$) was observed in September 2008 followed by a decrease (to 5.7 mg L$^{-1}$) for the remainder of the year. In 2009, NH$_3$—N concentrations in the Type I basal drain remained <5.0 mg L$^{-1}$ with the exception of one sample (at 10 mg L$^{-1}$). In 2010, concentrations increased through the field season and reached a new maximum of 410 mg L$^{-1}$ in November.

The Covered test pile had a low volume of flow from September 2007 to January 2008. Flow recommenced in September 2008 and continued through to the end of 2009. Ammonia concentrations increased over time to a maximum of 10 mg L$^{-1}$ in April 2009 before decreasing for the remainder of the year. In 2010, concentrations reached a minimum of 1.0 mg L$^{-1}$ in July and increased to 6.6 mg L$^{-1}$ by the end of November.

### 3.2.3.2. Nitrite

Nitrite was not detected (<0.05 mg L$^{-1}$) in any of the Type III AZLs in 2007. In 2008, concentrations were below detection in the Type III east and west AZLs prior to late September, and then increased to reach concentrations of 7.3 and 22 mg L$^{-1}$, respectively. In 2009 and 2010 the concentration of NO$_2^-$—N were below detection with the exception of spikes in concentrations (6–10 mg L$^{-1}$) in August 2009 and July 2010. The NO$_2^-$—N concentration in the Type I west AZL reached a maximum of 7.7 mg L$^{-1}$ in July 2008. Concentrations of NO$_2^-$—N in the Type I east AZL reached a maximum of 0.3 mg L$^{-1}$ in late September 2008 and end of July 2010. Increases in NO$_2^-$—N coincide with increases in NH$_3$—N and NO$_3^-$—N.

Maximum NO$_2^-$—N concentrations in the Type III east and west AZLs were detected in May 2008 in the Type III east AZL and 3.7 mg L$^{-1}$ in May 2008. In 2009 and 2010 the concentration of NO$_2^-$—N were below detection except for a few spikes in concentrations (10 mg L$^{-1}$) in late August 2008 and early September 2009. The concentration of NO$_2^-$—N was below detection in the Type III north and south basal drains for most of 2010, with the exception of September where a maximum concentration of 1.6 mg L$^{-1}$ was detected in the south drain. In 2010, concentrations were also below detection in both drains, with the exception of July when low concentrations of ~1 mg L$^{-1}$ were measured in both the north and south drains.

The NO$_2^-$—N concentration in the Type I test pile reached a maximum value of 6.5 mg L$^{-1}$ in late August 2008. Concentrations in 2009 were low when flow resumed in May, and remained below detection until October when the concentration increased to 6.5 mg L$^{-1}$. In 2010, NO$_2^-$—N concentrations were elevated in comparison to previous years. The maximum concentration of 7.9 mg L$^{-1}$ was detected in October when the peaks of other blasting residuals were observed at this location.

Effluent from the Covered test pile had low (<2 mg L$^{-1}$) to undetectable concentrations of NO$_2^-$—N in 2007. The peak NO$_2^-$—N concentration of 13 mg L$^{-1}$ occurred in September 2008 before decreasing to below detection. Concentrations were detectable in late 2009, but remained low (<1 mg L$^{-1}$) and returned to below detection through 2010.

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**Table 5**

<table>
<thead>
<tr>
<th>Location</th>
<th>Estimated mass of explosives used (kg)</th>
<th>Mass loading of N from explosives (kg)</th>
<th>Mass loading of N released (kg)</th>
<th>% of estimated residual N released from 2007 to 2010</th>
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<td>AZLs</td>
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<tr>
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<td>11</td>
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</tr>
<tr>
<td>Type I west</td>
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<td>0.02 g</td>
<td>2.0</td>
</tr>
<tr>
<td>Type I east</td>
<td>2.7</td>
<td>0.93</td>
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</tr>
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<td>Basal drains</td>
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The measurement of low NO$_3$—N concentrations in the leach tests, combined with the consistent observation of low initial NO$_3$—N concentrations and subsequent increases to concentrations exceeding 1 mg L$^{-1}$ in the field studies, suggests that NO$_3$—N was derived from the nitrification of NH$_3$. This reaction is catalyzed by chemolithotrophic nitrifying bacteria (e.g., *Nitrobacter* spp.), and the delayed appearance of NO$_3$—N in the effluent from the AZLs and the test pile basal drains may represent the time required to establish a viable population of nitrifying species.

### 3.2.3.3. Nitrate

Nitrate concentrations reached a maximum of 600 mg L$^{-1}$ in the Type III west AZL and 340 mg L$^{-1}$ in the Type III east AZL in 2007 (Fig. 3). In 2008, water was collected in all four AZLs. The maximum NO$_3$—N concentrations were similar in the two Type III AZLs (560 mg L$^{-1}$ in the west AZL and 640 mg L$^{-1}$ in the east AZL) and in the Type I east AZL (480 mg L$^{-1}$); however, high NO$_3$—N concentrations of 2400 mg L$^{-1}$ were observed in the Type I west AZL. As greater volumes of the AZLs began to contribute to flow, portions containing higher concentrations of blasting residues were likely encountered, thereby releasing the higher concentrations observed. Nitrate concentrations in all four AZLs remained lower (<300 mg L$^{-1}$) for the remainder of 2008, all of 2009 and 2010.

In 2007, the concentrations of NO$_3$—N in the Type III test pile north and south basal drain effluent increased from May through August (maximum of 365 mg L$^{-1}$ in the north drain and 170 mg L$^{-1}$ in the south drain), followed by a decrease through to the end of October when flow ceased (Fig. 5). These high concentrations probably represent contributions from the batters of the Type III test pile. In 2008, the concentrations were much lower with a maximum of 30 mg L$^{-1}$ in the Type III test pile north drain and 66 mg L$^{-1}$ in the Type III south drain. Concentrations remained low through 2009, with the exception of the Type III south drain that increased in October to the maximum reported concentration (720 mg L$^{-1}$) and remained elevated until the end of the field season. Similar trends were observed in 2010, with the maximum of 660 mg L$^{-1}$ occurring in October. This increase in NO$_3$—N late in the season is likely attributable to the increasingly large contributions to flow from the central portions of the test pile, which had not previously contributed to the flow to the basal drains. In all years following 2007, the concentrations of N species increased during the late fall when larger portions of the test piles were flushed with water, and during periods of higher flow rates.

Discharge from the Type I test pile had elevated NO$_3$—N concentrations in 2008 (up to 210 mg L$^{-1}$). Similar to the Type III test pile, the high NO$_3$—N concentrations in the initial flow reporting to the Type I test pile basal drain probably were derived from the batters of the Type I test pile. Nitrate concentrations were lower at the beginning of 2009, but increased in September to a maximum of 430 mg L$^{-1}$ at the end of the field season. In July 2010, NO$_3$—N concentrations were lower, at <50 mg L$^{-1}$, but steadily increased through the field season to the highest concentrations observed at this location (2000 mg L$^{-1}$).

Only a limited number of water samples were collected from the Covered test pile from August 2007 to January 2008 due to low flow volumes. The samples that were collected had NO$_3$—N concentrations ranging from 250 to 380 mg L$^{-1}$ (Fig. 6). In 2008, NO$_3$—N concentrations in the Covered test pile effluent increased from 103 to 340 mg L$^{-1}$ within the first month of flow, then decreased and remained stable between 250 and 320 mg L$^{-1}$ through 2010.

### 3.2.4. Nitrogen mass loading

Nitrogen is released from undetonated explosives left residual on rock in the area surrounding a blast hole. In mining operations, the mass of explosives required to break a quantity of rock is referred to as the powder factor. Powder factors vary depending on the lithology, hardness and competence of the rock. The mass of N used to blast a mass of rock (N$_{used}$) can be estimated based on the powder factor used in the blast. Measurements of the total mass of undetonated N in effluent can be used to estimate the loss of N during blasting, referred to as nitrogen loss (N$_{loss}$). Data from two surface mines indicate the mass of undetonated N associated with blasting typically ranges from 0.1% to 6% N$_{loss}$/N$_{used}$ (Pommen, 1983). The average N$_{loss}$ at Diavik during the construction of the experimental waste rock piles was also within this range (DDMI, 2006). The average concentration of N$_{loss}$ (0.59 mg L$^{-1}$) in the leach tests corresponds to a 5.4% N loss from the blasting explosions (Table 5), which is in the range for N loss observed at Diavik over the period between 2003 and 2005 (DDMI, 2006), before N loss mitigation measures were initiated.

The concentrations of blasting residuals decreased over time to very low concentrations in the AZLs. Assuming that the majority of available blasting residuals were flushed from the AZLs, the mass loading can be used to determine the amount of un-detonated explosive remaining in the waste rock after blasting. The total mass of N released was 0.040 kg N in the Type III west AZL and 0.022 kg N in the Type III east AZL (Table 5). Combining an average powder factor (total explosives (kg) per total tonnage (t)) estimate of 0.32, for the AZL construction period, with the mass of rock in each AZL, indicates that the explosives used to blast the rock in the Type I AZLs contained 1.1 kg of N and 0.93 kg N was contained in the explosives used to blast the rock in the Type III AZLs. Comparing the mass of N contained in the explosives to the mass of N present in blasting residuals flushed from the AZLs indicates that un-detonated explosive was 3.7% of the original mass in the Type III west AZL and 2.0% of the original mass in the Type III east AZL. The total mass of N released from the Type I west AZL was 0.11 kg N, and the mass of N released from the Type I east AZL was 0.042 kg N (Table 5). These masses correspond to 12% of un-detonated explosives in the Type I west AZL and 4.6% in the Type I east AZL. The increased mass of N present at the Type I east AZL may be attributed to a larger mass of un-detonated explosives associated with the rock in this lysimeter prior to construction, suggesting that the distribution of un-detonated explosives in waste rock piles may be heterogeneous.

The total mass of N released from the Type III test pile (sum of the Type III north and south drains) was 35.2 kg N (Table 5). The Type I test pile released a total mass of 31.9 kg N. These values correspond to a release of 0.45% of the residual N contained in the Type III test pile and 0.43% of the residual N contained in the Type I test pile. A total mass of 43.5 kg N was released from the Covered test pile, which corresponds to 0.23% of the residual N. The low release of N$_{total}$ from the waste rock test piles indicates that a significant mass of explosive residuals remains within the test piles, probably because at the time of this publication flow has yet to report from large portions thereof. The N$_{total}$ mass released from the test piles is anticipated to initially increase as reaction products from previously un-flushed waste rock are released and report to the basal drainage system, before declining as the initial N is flushed from the waste rock.

### 3.2.5. Perchlorate

Perchlorate can be derived from accelerants, typically NaClO$_4$ and KClO$_4$, used in blasting materials. The range of ClO$_4^-$ concentrations observed in mine wastewaters is similar to concentrations observed in municipal water supplies affected by anthropogenic ClO$_4^-$ (Tikkanen, 2006). Perchlorate concentrations in the test piles followed a similar trend to other blasting residuals at all sampling locations. Perchlorate concentrations reached a maximum of 16 µg L$^{-1}$ in effluent from the Type III east AZL and 23 µg L$^{-1}$ from the Type III west AZL in 2007 (Fig. 3). In 2008, ClO$_4^-$ concentrations

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reached maximum values in July in the Type III east (38 µg L⁻¹) and west (18 µg L⁻¹) AZLs and decreased to <8 µg L⁻¹ for the remainder of 2008, 2009, and 2010. In 2008, ClO₄⁻ concentrations reached a maximum of 3.7 µg L⁻¹ in effluent from the Type I east AZL, but were much higher, at 130 µg L⁻¹ in the Type I west AZL (Fig. 2). Perchlorate concentrations decreased and remained low (<10 µg L⁻¹) through 2008 and for all of 2009 and 2010.

Perchlorate concentrations in the Type III test pile exhibited temporal trends similar to other blasting residuals (Fig. 5). In 2007, the ClO₄⁻ concentrations reached a maximum of 12 µg L⁻¹ in the Type III north drain and 10 µg L⁻¹ in the Type III south drain (Fig. 5). Concentrations draining from the Type III test pile remained low through 2008 and 2009, except for an increase in ClO₄⁻ concentrations in the south drain, similar to other blasting residuals at the end of October 2009 and 2010.

The ClO₄⁻ concentrations in the Type I test pile effluent increased throughout 2008, reaching a maximum of 14 µg L⁻¹ in October (Fig. 4). In 2009 and 2010, ClO₄⁻ concentrations increased at the end of the field season, similar to Cl⁻, NO₃⁻—N and SO₄²⁻. The maximum ClO₄⁻ concentration in 2009 was 21 µg L⁻¹. The ClO₄⁻ concentration increased through 2010 to 340 µg L⁻¹, the maximum concentration observed at this location. Perchlorate concentrations ranged between 6 and 25 µg L⁻¹ in the Covered test pile for the duration of the study, following similar trends to other blasting residuals (Fig. 6). Overall, the maximum ClO₄⁻ concentrations in all piles corresponded with the highest NO₃⁻—N and Cl⁻ concentrations, further demonstrating the coincidence of the maximum concentrations of blasting agents in the effluent.

### 3.2.6. Chloride

Chloride is present in the rock deposited in the waste rock pile and from blasting residuals. Release and transport of Cl⁻ can be used to indicate the first flush of water through the AZL and test piles, where irregular concentrations represent flushing along different flow paths.

The maximum concentrations of Cl⁻ in the Type I AZLs occurred at the onset of flow in the spring of 2008 with 140 mg L⁻¹ in the Type I east AZL and 370 mg L⁻¹ in the Type I west AZL. The Cl⁻ concentration remained low for the remainder of the study. The Cl⁻ concentrations in the Type III AZLs followed a similar trend to NO₃⁻—N and SO₄²⁻ in 2007 and early 2008. Chloride concentrations after August 2008 were variable as a result of additional Cl⁻ applied to the Type III AZLs from the LiCl tracer test. The maximum concentration of Cl⁻ prior to the breakthrough of the tracer test was 230 mg L⁻¹ in the east AZL and 130 mg L⁻¹ in the west AZL.

In 2007, Cl⁻ concentrations exhibited trends similar to those for NO₃⁻—N, with a maximum concentration of 110 mg L⁻¹ in the Type III north drain and 25 mg L⁻¹ in the Type III south drain. In September 2007, Cl⁻ was released within a suite of tracers applied to the Type III test pile, which obscured trends in Cl⁻ concentrations in 2008. During 2008, Cl⁻ concentrations remained low in the Type III test pile reaching a maximum of 9.9 mg L⁻¹ in the north drain and 32 mg L⁻¹ in the south drain; although low, these concentrations may have been affected by the Cl⁻ tracer applied in September 2007. Concentrations remained low through early 2009 and 2010, with the exception of the water collected from the south drain that increased to 227 mg L⁻¹ in October 2009 and 200 mg L⁻¹ in October 2010, similar to other blasting residuals.

Chloride concentrations in water collected from the Type I test pile in 2008 were similar to concentrations observed for the Type III test pile in 2007, with a maximum concentration of 140 mg L⁻¹. Chloride concentrations were low (<10 mg L⁻¹) through 2009, but in late 2009 elevated concentrations, to a maximum of 540 mg L⁻¹ were observed, similar to trends in other blasting residuals. In 2010, concentrations increased as temperatures in the test pile increased and reached a maximum of 2800 mg L⁻¹.

Chloride concentrations from the Covered test pile reached peaks of 130 mg L⁻¹ in January 2008 and 240 mg L⁻¹ at the beginning of the 2008 field season. The Cl⁻ concentration in the Covered test pile effluent decreased to approximately 90 mg L⁻¹ through 2009 and decreased slightly through 2010 to ~50 mg L⁻¹.

### 3.2.7. Sulfate predictions

Ratios of N_Total to Cl⁻ for the Type III test pile for 2007–2008 were constant, and show a slight excess of Cl⁻ in 2009–2010, possibly due to the tracer test initiated in 2007. The ratios of N_Total to

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**Fig. 7.** Type III south (left) and north basal drain (right) ratios of N_Total to Cl⁻, SO₄²⁻ to N_Total, and SO₄²⁻ to Cl⁻.

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Cl\(^{-}\) in 2007–2008 were consistent and highly correlated, suggesting N species and Cl\(^{-}\) were derived from the test pile (Fig. 7). Ratios of SO\(_4^{2-}\) to N\(_{\text{Total}}\) in the effluent from the Type III test pile were relatively uniform in 2007 and averaged 6.3 ± 0.89 in the north drain effluent and 7.2 ± 1.23 in the south drain effluent (Fig. 7). Sulfate concentrations increased as temperatures in the test piles increased and corresponded to increases in N\(_{\text{Total}}\) mass. In 2008, the SO\(_4^{2-}\) to N\(_{\text{Total}}\) ratio increased and averaged 25 ± 6.7 in effluent from the north drain and 20 ± 7.0 from the south drain. Sulfate concentrations in 2008 were not correlated as strongly to the N\(_{\text{Total}}\) mass. In 2009, the ratios became more erratic, suggesting the potential impact of SO\(_4^{2-}\) sources in addition to blasting residues. However, at the end of October 2009 the increase in SO\(_4^{2-}\) concentrations in the south drain effluent reflected the increase in other blasting residuals.

The coincident rise of SO\(_4^{2-}\) with other blasting agents suggests the initial release of SO\(_4^{2-}\) in 2007 was mainly derived from sulfide oxidation during the blasting of rock (Figs. 8 and 9). During a blast, a small amount of sulfide in the rock is oxidized, and the product is subsequently mobilized when exposed to water. Thus, the SO\(_4^{2-}\) to N\(_{\text{Total}}\) ratios from 2007 can be used to estimate the concentration of SO\(_4^{2-}\) attributable to blasting in subsequent years when concentrations are more erratic, and to determine the proportion released due to in situ sulfide oxidation. The ratio of SO\(_4^{2-}\) to N\(_{\text{Total}}\) observed in 2007 in the Type III test pile was compared to the N\(_{\text{Total}}\) concentrations from 2008 to 2010 to estimate the mass of SO\(_4^{2-}\) derived from blasting, thereby differentiating the sulfide oxidation during blasting from subsequent in situ sulfide oxidation. This comparison suggests that the SO\(_4^{2-}\) in the Type III test pile effluent through 2008 and most of 2009 was largely derived from in situ sulfide oxidation. The SO\(_4^{2-}\) concentration peak in October 2009 in the Type III south drain effluent corresponded to the increase in other blasting residuals. The majority of this SO\(_4^{2-}\) probably originated in areas of the test pile remote from the basal drains, and migrated along longer flow paths. The predicted SO\(_4^{2-}\) concentrations (Figs. 8 and 9) at this time show a deficit, potentially due to the loss of SO\(_4^{2-}\) to the formation of secondary minerals, principally jarosite which remove SO\(_4^{2-}\). At these high SO\(_4^{2-}\) concentrations, geochemical speciation calculations suggest equilibrium of the effluent water with respect to jarosite.

Ratios of SO\(_4^{2-}\) to N\(_{\text{Total}}\) from the Type III AZL during the initial flush in 2008 were 6.7 ± 0.65 in the west and 7.25 ± 0.48 in the east (Fig. 10). These ratios were similar to the Type III test pile basal drains in 2007. As more water arrived at the base of the Type III AZLs, the SO\(_4^{2-}\) to N\(_{\text{Total}}\) ratio became more erratic; this is similar to the pattern observed in the Type III test pile, suggesting that the SO\(_4^{2-}\) contribution from in situ sulfide mineral oxidation exceeded the contribution from blasting residuals.

Ratios of SO\(_4^{2-}\) to N\(_{\text{Total}}\) from the Type I waste rock were much lower than those from the Type III test pile and Type III AZL effluent (Fig. 10). The Type I test pile contains a lower mass of S and the volume of water that reported to the drain was significantly less than in the Type III test pile. The overall average ratio of SO\(_4^{2-}\) to N\(_{\text{Total}}\) (3.3 ± 1.6) suggests that much of the SO\(_4^{2-}\) reporting to the Type I test pile basal drain was released during blasting. The overall average SO\(_4^{2-}\) to N\(_{\text{Total}}\) ratios observed for the Type I AZLs were 2.2 ± 1.6 in the west and 2.0 ± 0.93 in the east. The Type I AZL effluent is similar to that observed for the Type I test pile effluent, suggesting that blasting is the principal source of SO\(_4^{2-}\) for this location as well.

In 2007, the SO\(_4^{2-}\) to N\(_{\text{Total}}\) ratio in the effluent from the Covered test pile was similar to the SO\(_4^{2-}\) to N\(_{\text{Total}}\) ratio measured in the effluent from the Type III test pile basal drains (Fig. 11). Flow ceased in January 2008 and resumed in August 2008. The Covered test pile effluent had consistent concentrations of blasting residuals versus SO\(_4^{2-}\) over time, with a slight increase in the SO\(_4^{2-}\) to N\(_{\text{Total}}\) ratio in the fall of 2008. The SO\(_4^{2-}\) to N\(_{\text{Total}}\) ratio steadily in-

![Fig. 8. Type III south basal drain predictions of SO\(_4^{2-}\) from in situ oxidation versus oxidation during blasting.](image8.png)

![Fig. 9. Type III north basal drain predictions of SO\(_4^{2-}\) from in situ oxidation versus oxidation during blasting.](image9.png)

increased from 4 to 11 from 2007 to 2009. The total volume of water reporting to the base of the Covered test pile from 2007 to 2009 was similar to the volume draining from the Type III test pile in 2007. The $SO_2^-$ to $N_{\text{Total}}$ ratio in the effluent from the Covered test pile is anticipated to increase as more water migrates to the drain and the initial mass of blasting residuals is flushed from the pile. The Type III AZLs and Type III test pile basal drains had similar $SO_2^-$ to $N_{\text{Total}}$ during the initial flush of water through each experiment. As in situ sulfide mineral oxidation increased, the ratios became more erratic. The Type I AZL and Type I test pile basal drains had lower $S$ content than the Type III sample locations and thus had lower and more consistent $SO_2^-$ to $N_{\text{Total}}$ ratios.

4. Conclusions

Substantial concentrations of $N$ species, $ClO_4^-$, and $Cl^-$ have been derived from the release of undetonated explosives and blasting residuals from waste rock at Diavik. The concentrations of these blasting residuals were used as a resident tracer to indicate the first flush of water through experimental waste rock piles. The breakthrough of these components indicated volumes that were similar to estimates of the matrix porosity within the AZLs. Irregular concentrations and gradual dissipation of blasting residuals provided an indication of the test pile heterogeneity and the relative contributions of portions of the test piles along different flow paths. As the temperature within the test piles increased and larger portions of the test pile contributed to flow, increased concentrations of blasting residuals were observed. The initial release of $SO_2^-$ was a result of the oxidation of sulfide minerals during blasting and was highly correlated to blasting residuals. After the dissipation of the blasting residuals, additional $SO_2^-$ was derived from the in situ oxidation of sulfide minerals. The release of $SO_2^-$ during blasting was dependant on the mass of sulfide present within the rock. In this experiment, Type III waste rock released higher ratios of $SO_2^-$ to $N_{\text{Total}}$ than Type I waste rock. The mass of sulfide released during blasting was estimated using the ratio of $SO_2^-$ to $N_{\text{Total}}$ thus providing a novel approach for estimating the mass of $S$ released during the first flush of the piles.

Fig. 10. $SO_2^-$ to $N_{\text{Total}}$ ratios for Type III east and west AZLs (left) and Type I east and west AZLs (right).

Fig. 11. $SO_2^-$ to $N_{\text{Total}}$ ratios for Type I, Type III south, and Covered test pile basal drains.

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