

From: Virtue,Robyn-Lynne [CEAA]

Sent: June 25, 2012 10:11 AM

To: 'Gunter Muecke'; 'Jamie.Archibald'; 'Stevan.Dimitrijevic@'; Haddon,David [CEAA]; 'Kelly.McGee'; Myles,Debra [CEAA]; 'stellastrat

Cc: DGR Review / Examen DFGP [CEAA]

Subject: Request for Paper on blasting residuals

Hello Panel Members,

As per your request, copy of the paper "The Diavik Waste Rock Project: Persistence of contaminants from blasting agents in waste rock effluent". Bailey et al. 2012 is being sent to you for your information.

Thank you, Robyn

Contents lists available at [SciVerse ScienceDirect](#)

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

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

Brenda L. Bailey^a, Lianna J.D. Smith^{a,b}, David W. Blowes^{a,*}, Carol J. Ptacek^a, Leslie Smith^c, David C. Segó^d

^a Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, ON, Canada N2L 3G1

^b Rio Tinto (Diavik Diamond Mines Inc.), Yellowknife, NT, Canada X1A 2P8

^c Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, BC, Canada V6T 1Z4

^d Department of Civil and Environmental Engineering, University of Alberta, Edmonton, AB, Canada T6G 2W2

ARTICLE INFO

Article history:

Available online xxx

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 NH_3 , NO_2^- , NO_3^- , Cl^- , and ClO_4^- . 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 SO_4^{2-} 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 SO_4^{2-} than the test pile with lower S content waste rock. Mass-balance calculations based on the ratios of SO_4^{2-} to total N can be used to estimate the relative contributions of sulfide oxidation within the test piles and SO_4^{2-} 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.

© 2012 Elsevier Ltd. All rights reserved.

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 (Egly and Neckar, 1964). Emulsions contain 20–30% total N (N_{Total}) 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 ClO_4^- , 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 NO_3^- can lead to eutrophication if other requirements such as light and P are abundant (Stumm and Morgan, 1996). Nitrite and NH_3 are toxic to fish at low concentrations (CWQG, 1987). In addition to blasting, sources of NO_3^- and NH_3 to the environment include agricultural activity, wastewater disposal, and landfills.

* Corresponding author. Tel.: +1 519 888 4878; fax: +1 519 746 7484.

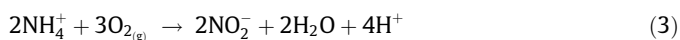
E-mail address: blowes@uwaterloo.ca (D.W. Blowes).

Perchlorate can have harmful effects to human health at concentrations in the low $\mu\text{g L}^{-1}$ 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 NO_3^- and ammonium (NH_4^+). Ammonium can further dissociate to NH_3 in alkaline conditions (Clark, 1981):



Under aerobic conditions, NH_3 is oxidized to the unstable intermediate N species NO_2^- by the *Nitrobacter* group of nitrifying bacteria (Koren et al., 2000):



Nitrite is further oxidized to NO_3^- by the *Nitrosomonas* group of nitrifying bacteria (Sawyer and McCarty, 1967):



Under aerobic conditions, NO_3^- 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 NO_3^- to $\text{N}_{2(\text{g})}$ coupled with the oxidation of sulfide or organic C at neutral pH (Schedel and Truper, 1980; Sanmugasunderam et al., 1987; Kuenen et al., 1992).

Remediation systems have been developed to remove N species from waste water disposal sites and landfills (Blowes et al., 1994; Diamadopoulos et al., 1997; Robertson et al., 2000, 2009), but few studies have addressed the removal of N species from mill and mine effluents. Koren et al. (2000) demonstrated microbial treatment methods for the removal of NH_3 and NO_3^- from simulated mill and mine effluent with low nutrient content. Zaitsev et al. (2008) demonstrated the removal of NH_3 and NO_3^- from two underground mine water samples using fixed-bed biofilm reactors at low temperatures. However, these studies do not discuss the release of N species from waste rock piles.

Waste rock is commonly stockpiled on the ground surface, where both undetonated explosives and blasting residuals within the waste rock can be flushed by rain water, snowmelt, or groundwater. At locations where waste rock or ore contain sulfide minerals, such as pyrite (FeS_2) and pyrrhotite (Fe_{1-x}S), these minerals may be oxidized during blasting, potentially releasing SO_4^{2-} to the environment (Briggs and Kelso, 2001). Nitrate and NH_3 released from the use of explosives are usually attributed to ammonium nitrate spillage or incomplete detonation and subsequent dissolution (Cameron et al., 2007). These sources result in releases of NO_3^- and NH_3 in mine effluent. The objectives of this study are to determine the concentrations of blasting agents, their residuals, and S oxidation products resulting from blasting in drainage water derived from waste rock test piles located at the Diavik diamond mine.

1.2. Site description

Diavik is located 300 km north of Yellowknife, Northwest Territories (64°29'N; 110°18'W; elevation 440 m), on a 20 km² island in the oligotrophic Arctic lake Lac de Gras. The study area is in the continuous permafrost region with a mean annual air temperature

of -9.2°C within a range of 27°C in July to -44°C in January/February (1998–2007 data; Environment Canada, 2010). This study area is located in a semi-arid climate, receiving an average mean annual precipitation of 280 mm from 1998 to 2007 of which 65% occurred as snow (Environment Canada, 2010).

At Diavik, an open pit and underground diamond mine, the economic ore body is diamondiferous kimberlite. The host rock consists of granite and granite pegmatite, both containing irregular xenoliths of biotite schist. These host rocks are cut by diabase dikes. The granites contain only trace sulfides, and are considered non-acid generating with little neutralization potential. The granite consists mainly of K-feldspar [KAlSi_3O_8], albite [$\text{NaAlSi}_3\text{O}_8$], and quartz [SiO_2], with <5% each of biotite [$\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$] and muscovite [$\text{KAl}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$] (Jambor, 1997). The biotite schist (<0.42 wt.% S) contains locally disseminated pyrrhotite with lesser amounts of pyrite, sphalerite, and chalcopyrite and has little neutralization potential; therefore, it is considered potentially acid generating (Smith et al., this issue-a). The biotite schist aluminosilicate mineral assemblage consists mainly of quartz (20–50%), albite (35–55%), and biotite (10–25%). Waste rock at the mine site is classified and segregated according to S content: Type I (<0.04 wt.% S), Type II (0.04–0.08 wt.% S), and Type III (>0.08 wt.% S). The mine is expected to generate a 120 Mt waste rock pile over the course of production. Although the S content of the Diavik waste rock is low, the carbonate mineral content is also very low, providing little neutralizing capacity (Jambor, 1997; Smith et al., this issue-a).

1.3. Test pile instrumentation

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 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 \times 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

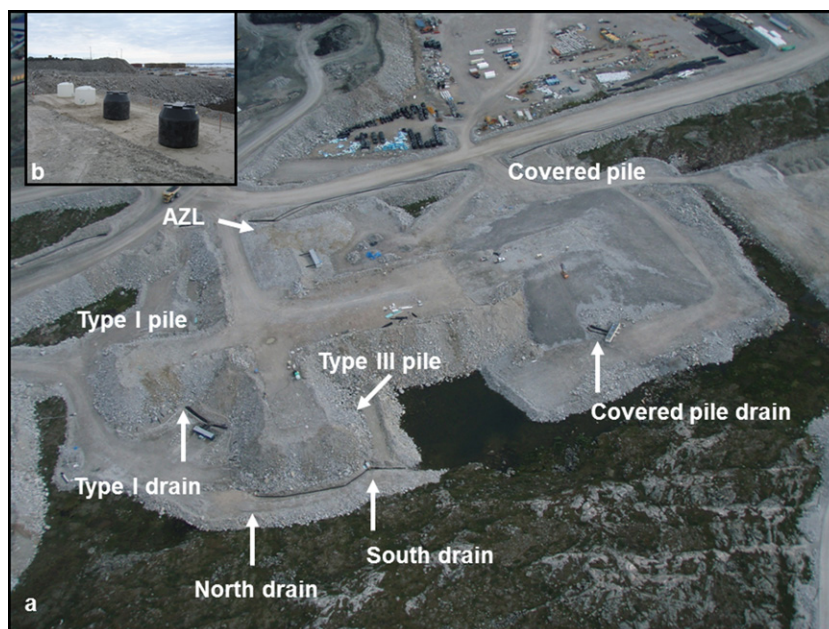


Fig. 1. Aerial view of the Diavik Waste Rock Research Facility: (a) locations of the Type I test pile, Type III test pile, Covered test pile, and AZLs; (b) high density polyethylene barrels used in the construction of the AZLs before rock placement.

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 and sample triple-rinsed HDPE bottles. The samples were refrigerated at 4 °C until analysis at the University of Waterloo. Concentrations of SO_4^{2-} , NO_3^- , NO_2^- , and Cl^- were determined using ion chromatography (IC; DX600, Dionex, USA). All concentrations of NO_3^- and NO_2^- are expressed as $\text{mg L}^{-1} \text{NO}_3^- \text{-N}$ and $\text{mg L}^{-1} \text{NO}_2^- \text{-N}$, respectively. Concentrations of NH_3 ($\text{NH}_3\text{-N}$; salicylate method) were determined using a Hach spectrophotometer DR/8400 (SMEWW, 2005).

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 $\text{O}_{2(g)}$. Pore-gas concentrations within the lysimeters were not measured; however, testing in the large-scale waste rock piles indicated that $\text{O}_{2(g)}$ and $\text{CO}_{2(g)}$ 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. E_h 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 bromocresol green/methyl red indicator and 0.16 N H_2SO_4 . Field measurements were completed using a Hach spectrophotometer DR/8400 for the determination of NH_3 ($\text{NH}_3\text{-N}$; salicylate method) concentrations for selected samples (SMEWW, 2005). Additional non-acidified, filtered samples were refrigerated at 4 °C until analysis at the University of Waterloo for inorganic anion concentrations (SO_4^{2-} , NO_3^- , NO_2^- , and Cl^-) by ion chromatography (IC; DX600, Dionex, USA). All concentrations of NO_3^- and NO_2^- are expressed as $\text{mg L}^{-1} \text{NO}_3^- \text{-N}$ and $\text{mg L}^{-1} \text{NO}_2^- \text{-N}$, respectively. Quality control and quality assurance were assessed by evaluating several standards covering the range of measured concentrations, and incorporating both field replicates and blanks into the protocol.

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 ^{18}O -labelled ClO_4^- 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 SO_4^{2-} 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 (turbo) 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_4^- , and m/z 107–89 and m/z 109–91 for enriched ClO_4^- .

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 detection limits were 0.02 and 0.05 $\mu\text{g L}^{-1}$, respectively.

3. Results and discussion

3.1. Laboratory leach tests

The concentrations of NO_3^- -N and NO_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_3 -N was below detection ($<0.02 \text{ mg L}^{-1}$) for all leach test samples. For the eight laboratory leach tests conducted on the freshly blasted waste rock, N_{Total} concentrations averaged 0.46 mg L^{-1} (4.6 mg N kg^{-1} waste rock), with lower concentrations observed in two samples (LT7 and LT8; Table 1). All leach tests had similar SO_4^{2-} 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_{Total} to Cl^- , SO_4^{2-} to N_{Total} and SO_4^{2-} to Cl^- , whereas values for leach tests LT7 and LT8 were lower (Table 2). Leach test LT1 had the highest concentrations of Cl^- , N_{Total} , and SO_4^{2-} , resulting in a higher than average ratio of N_{Total} to Cl^- , and a lower than average ratio of SO_4^{2-} to Cl^- . The ratio of SO_4^{2-} to N_{Total} was consistent with average ratios (Table 2). Leach test LT7 had the lowest N_{Total} concentration, and leach test LT8 had the second lowest N_{Total} concentration (after LT7) and second highest SO_4^{2-} concentration (after LT1) (Table 1).

Table 1
Leach test concentrations of Cl^- , NO_2^- -N, NO_3^- -N, sum of N species (NO_3^- -N and NO_2^- -N), and SO_4^{2-} . NH_3 -N was below detection in all leach test samples ($<0.02 \text{ mg L}^{-1}$).

Leach test	Cl^- (mg L^{-1})		NO_2^- -N (mg L^{-1})		NO_3^- -N (mg L^{-1})		N_{Total} (mg L^{-1})		SO_4^{2-} (mg L^{-1})	
	Average	St. dev.	Average	St. dev.	Average	St. dev.	Average	St. dev.	Average	St. dev.
LT1	1.49	0.14	0.054	0.006	1.27	0.11	1.32	0.06	7.19	0.69
LT2	0.67	0.04	0.003	0.0003	0.33	0.03	0.33	0.03	1.80	0.14
LT3	0.53	0.12	0.006	0.001	0.59	0.13	0.60	0.13	2.88	0.72
LT4	0.22	0.04	0.002	0.0004	0.37	0.08	0.37	0.08	2.53	0.07
LT5	0.22	0.07	0.002	0.0005	0.35	0.11	0.35	0.11	1.76	0.71
LT6	0.36	0.12	0.003	0.0003	0.45	0.14	0.45	0.14	2.45	0.77
LT7	0.13	0.02	0.001	0.0001	0.10	0.01	0.10	0.01	2.76	0.47
LT8	0.28	0.04	0.002	0.0001	0.13	0.02	0.13	0.02	5.73	0.89
Average	0.49	0.44	0.009	0.017	0.45	0.37	0.46	0.38	3.39	1.98

The differences in the observed N_{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_4^{2-} 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_4^{2-} 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_4^{2-} to N_{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_3^- -N, NO_2^- -N, NH_3 -N, and ClO_4^- , in the Type I west and east AZLs in early 2008 (Fig. 2; Table 3), with the exception of NO_2^- -N and ClO_4^- in the Type I east which had maximums in 2010. The maximum ClO_4^- concentration may have occurred in samples not analyzed from 2008 with high concentrations of other blasting residuals. Concentrations of Cl^- , SO_4^{2-} , and NO_3^- -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_3 -N and NO_2^- -N also decreased sharply in September 2008, low concentrations persisted in the effluent. Concentrations of dissolved SO_4^{2-} increased early in 2009 and 2010. The absence of Cl^- during these years suggests that most of the SO_4^{2-} was derived from *in situ* sulfide-mineral oxidation within the AZLs.

A sharp decline in Cl^- concentrations occurred after approximately 153 L of flow through the Type I west AZL. The volume of flow prior to the decline in Cl^- 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^- 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^3 . Neuner et al. (this issue) estimated the total porosity of the Diavik waste rock to be 0.25, and that 18%

Table 2Leach test ratios of N_{Total} to Cl^- , SO_4^{2-} to N_{Total} , and SO_4^{2-} to Cl^- .

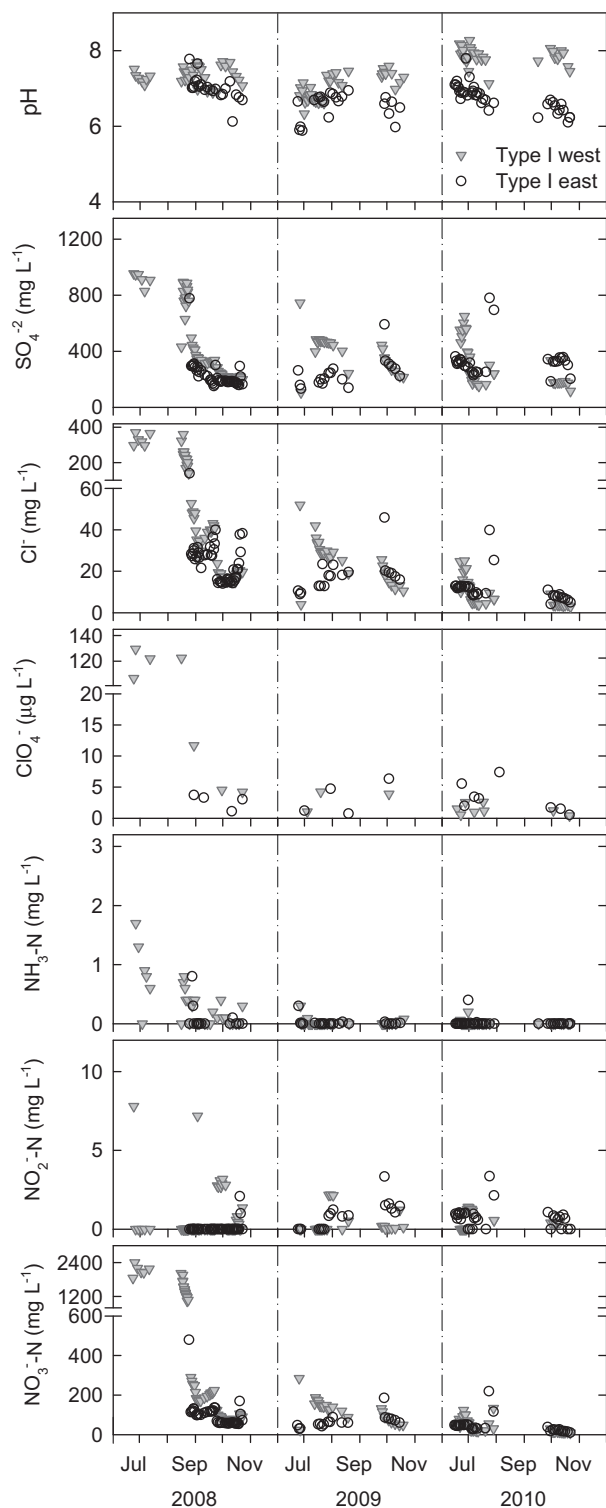
Leach test	$N_{\text{Total}}:\text{Cl}^-$		$\text{SO}_4^{2-}:N_{\text{Total}}$		$\text{SO}_4^{2-}:\text{Cl}^-$	
	Average	St. dev.	Average	St. dev.	Average	St. dev.
LT1	3.8	0.24	5.1	0.22	4.5	0.13
LT2	2.2	0.06	5.4	0.03	2.7	0.08
LT3	1.1	0.04	4.8	0.22	5.5	0.15
LT4	1.7	0.10	6.8	1.40	11.6	1.74
LT5	1.6	0.03	5.0	0.59	8.0	0.90
LT6	1.3	0.03	5.4	0.04	6.8	0.18
Average (LT1 through LT6; $n = 18$)	1.2	0.91	5.5	0.42	6.6	3.01
LT7 ($n = 3$)	0.8	0.03	27	2.5	21	2.6
LT8 ($n = 3$)	0.5	0.003	42	0.88	20	0.28

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 two 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 ($\text{pH} \sim 6$) 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 $\text{pH} 4$ and remained low ($\text{pH} < 4.5$) through 2010 (Fig. 3). From 2007 to 2010, the $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$, 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 $\text{NO}_3\text{-N}$ were observed in 2007, whereas $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ 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 $\text{NO}_3\text{-N}$, $\text{NH}_3\text{-N}$, ClO_4^- , and Cl^- in 2008 and maximum concentrations of $\text{NO}_2\text{-N}$ 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 $\text{NO}_3\text{-N}$, $\text{NH}_3\text{-N}$, 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

**Fig. 2.** Blasting residual concentrations for the Type I west and east active zone lysimeters.**Table 3**Maximum concentrations of SO_4^{2-} , Cl^- , $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NO}_3\text{-N}$ in the AZLs.

AZL	SO_4^{2-} (mg L^{-1})	Cl^- (mg L^{-1})	$\text{NH}_3\text{-N}$ (mg L^{-1})	$\text{NO}_2\text{-N}$ (mg L^{-1})	$\text{NO}_3\text{-N}$ (mg L^{-1})
Type I east	780	140	0.8	3.4	480
Type I west	950	370	1.7	7.7	2400
Type III east	8580	660	9.0	9.0	640
Type III west	13300	870	4.3	28	600

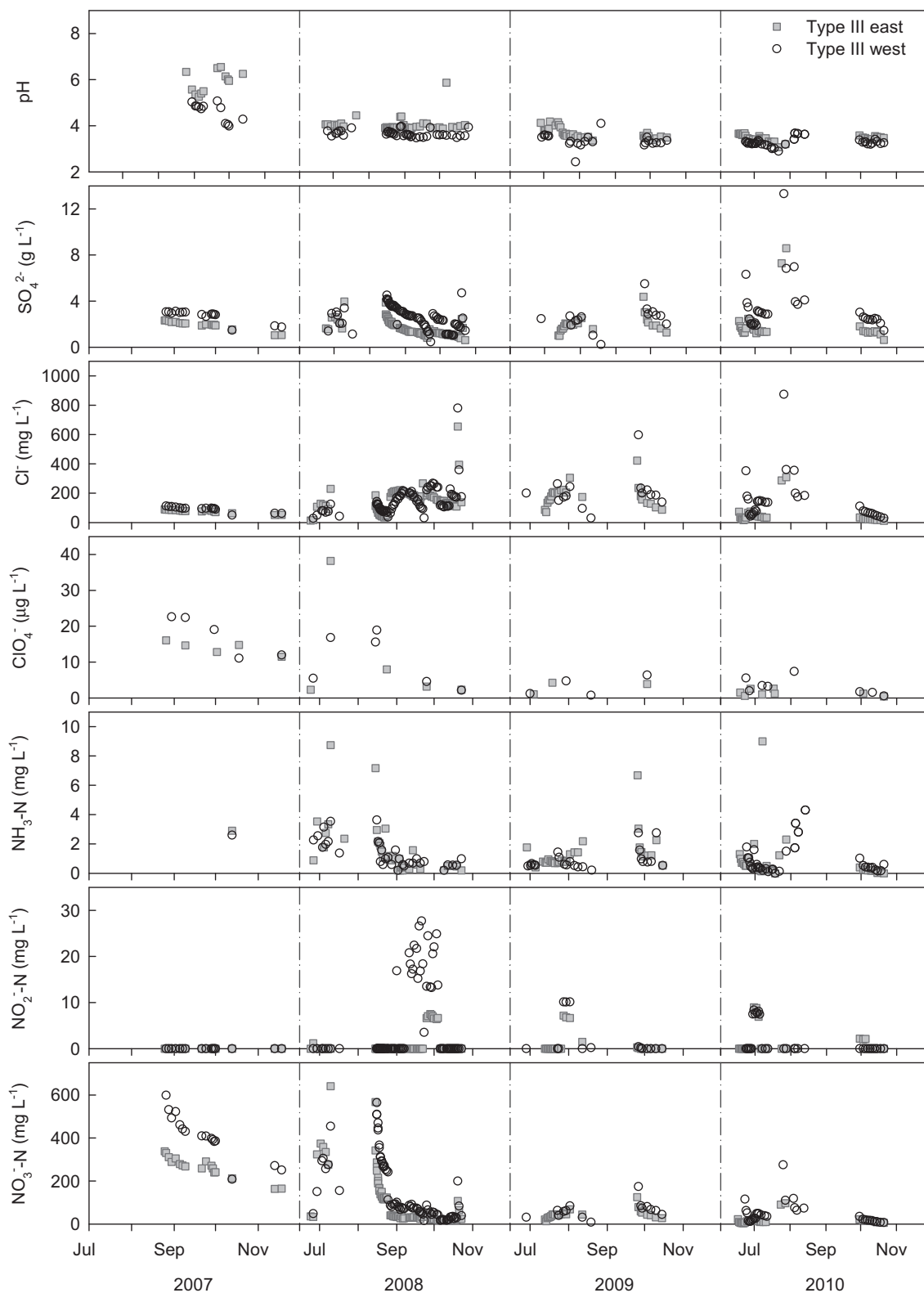


Fig. 3. Blasting residual concentrations for the Type III west and east active zone lysimeters.

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.

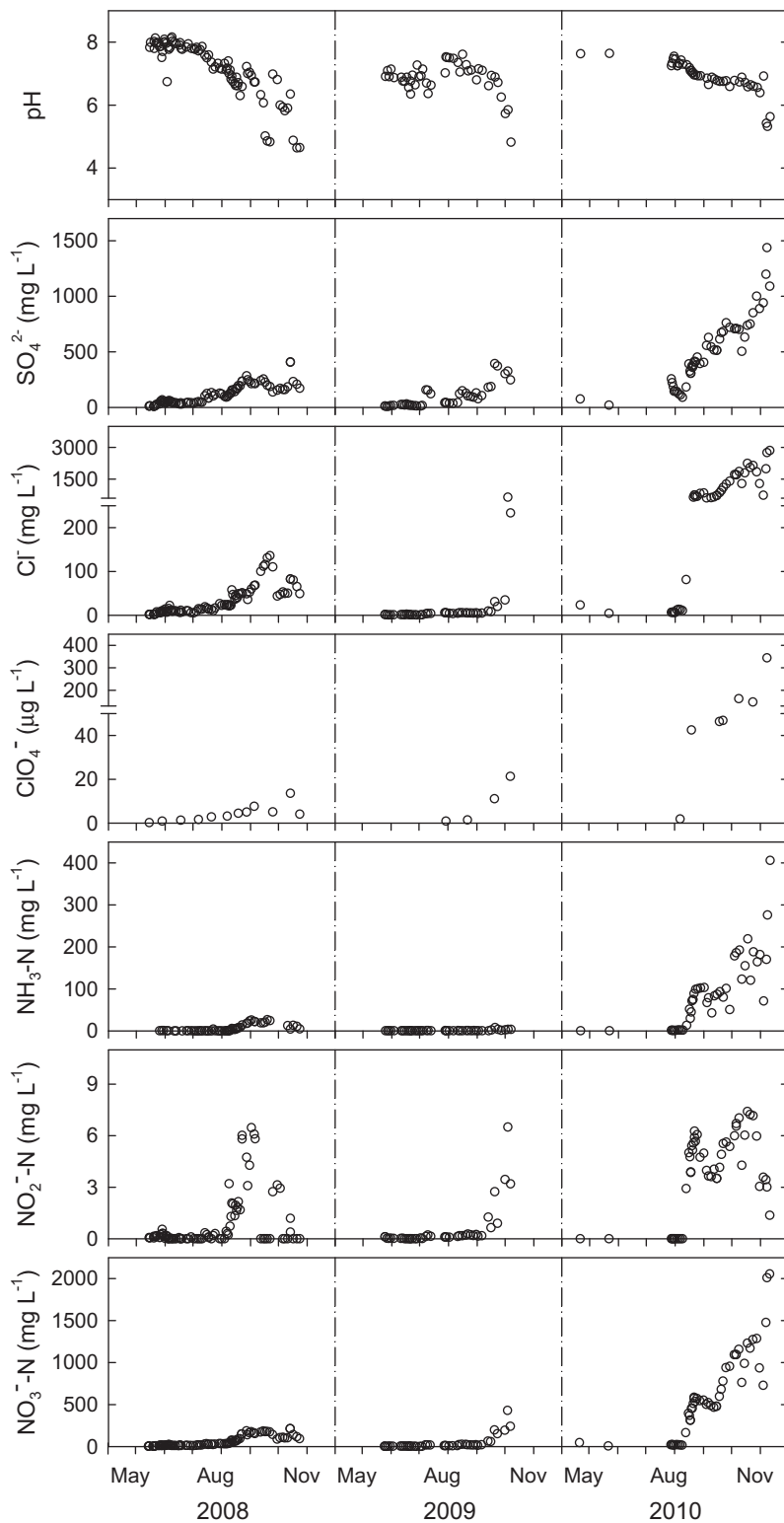


Fig. 4. Blasting residual concentrations for the Type I test pile drain.

Table 4

Maximum concentrations of SO_4^{2-} , Cl^- , $\text{NH}_3\text{-N}$, $\text{NO}_2^- \text{-N}$, and $\text{NO}_3^- \text{-N}$ in the basal drains of the Type I, Type III and Covered test piles.

Basal drain	SO_4^{2-} (mg L^{-1})	Cl^- (mg L^{-1})	$\text{NH}_3\text{-N}$ (mg L^{-1})	$\text{NO}_2^- \text{-N}$ (mg L^{-1})	$\text{NO}_3^- \text{-N}$ (mg L^{-1})
Type I	1200	2800	410	7.9	2000
Type III south	2950	230	54	3.7	720
Covered	3530	245	10	13	380

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

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 *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 temperatures 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

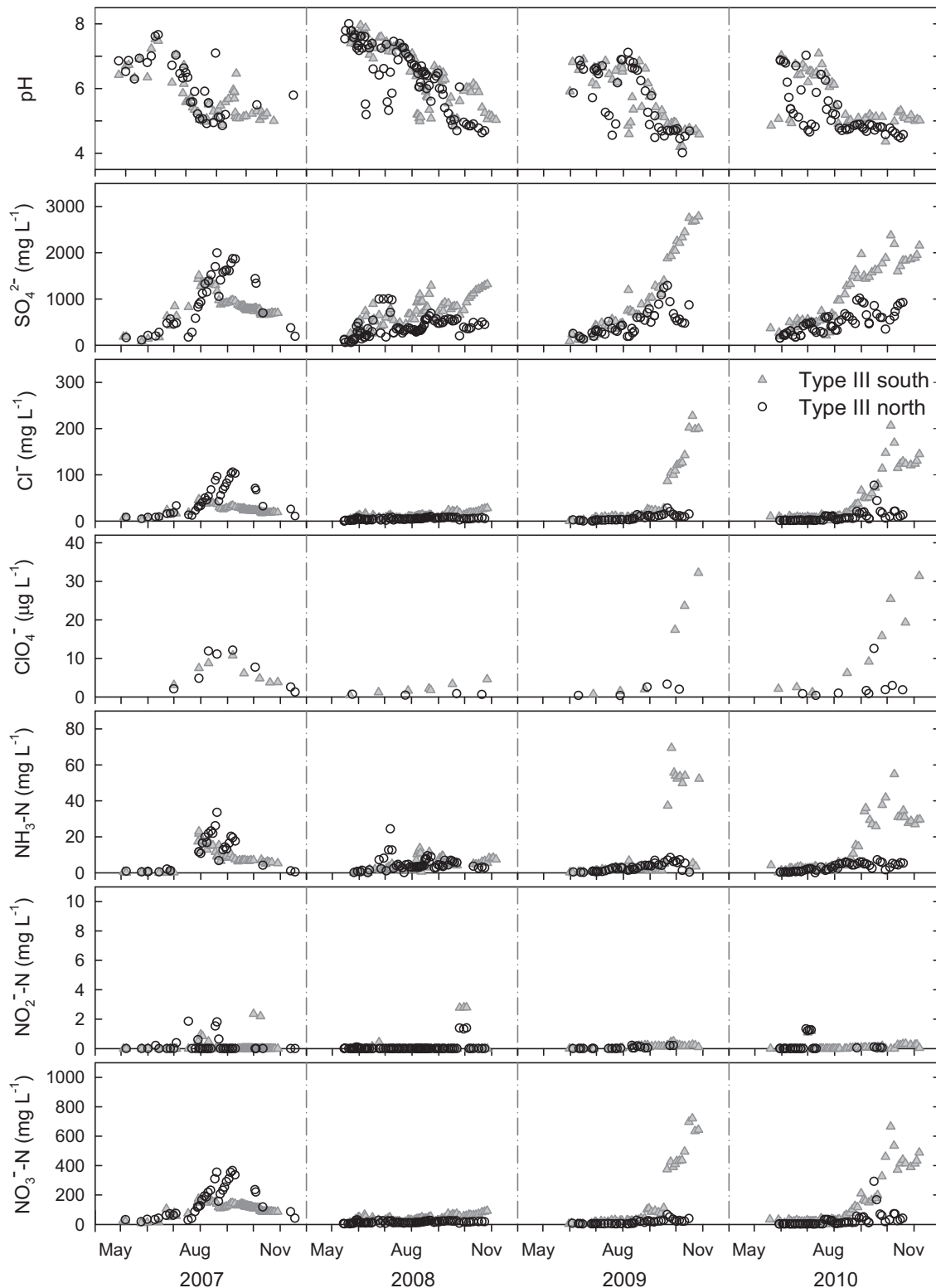


Fig. 5. Blasting residual concentrations for the Type III north basal drain and Type III south basal drain.

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 (batters) 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 rainfall 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 batters. 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_3^- -N, NH_3 -N, SO_4^{2-} , Cl^- , and ClO_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^- , N_{Total} , and SO_4^{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^- and elevated concentrations of NO_3^- -N and SO_4^{2-} . Flow continued until June 2009. Flow recommenced in August 2009 through the end of May 2010 when the maximum concentrations of N_{Total} and SO_4^{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_4^+ and NO_3^- . The results of the leach test conducted on samples of recently blasted rock indicate the presence of NO_3^- -N and NO_2^- -N (Table 1); concentrations of NH_3 -N were below detection. In the summers, when temperatures within the test piles rise to a maximum of 15 °C, the presence of detectable concentrations of NO_2^- -N indicates the nitrification of NH_3 to NO_2^- . Elevated concentrations of NO_3^- -N were observed concurrent with maximum concentrations of NH_3 -N and NO_2^- -N, suggesting oxidation of NO_2^- to NO_3^- . As the first flush of water advanced through the test piles, un-detonated blasting residuals, principally NH_3 and NO_3^- with trace amounts of NO_2^- , as well as SO_4^{2-} , ClO_4^- , and

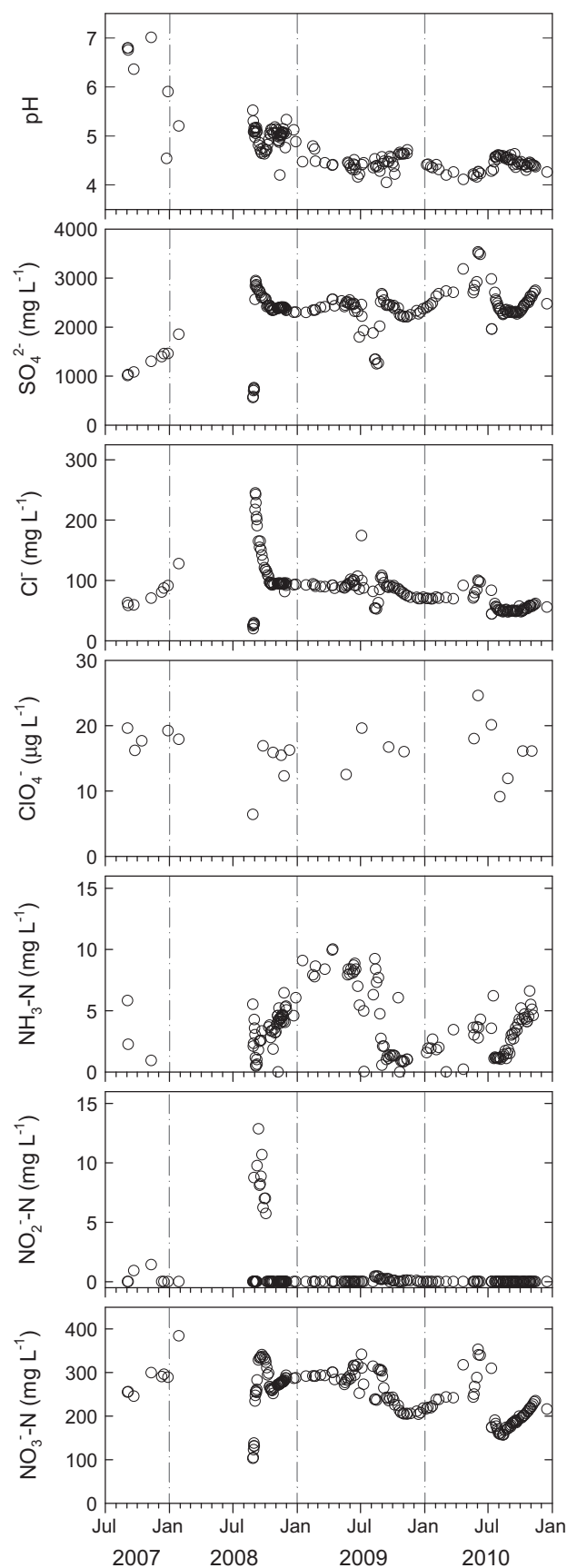


Fig. 6. Blasting residual concentrations for the Covered test pile basal drain.

Cl^- , were transported through the unsaturated waste rock. Nitrate can be removed by denitrification; however, reducing conditions

Table 5
Summary of mass loadings and explosives released from laboratory leach tests, 2 m × 2 m AZLs, and basal drains from large-scale test piles.

Location	Estimated mass of explosives used (kg)	Mass loading of N from explosives (kg) N_{used}	Mass loading of N released (kg) $(NH_4^+ + NO_3^- + NO_2^-) N_{loss}$	% of estimated residual N released from 2007 to 2010
<i>Leach test AZLs</i>	31 mg	11 mg	0.59 mg	5.4
Type III west	3.2	1.1	0.040	3.7
Type III east	3.2	1.1	0.022	2.0
Type I west	2.7	0.93	0.11	12
Type I east	2.7	0.93	0.042	4.6
<i>Basal drains</i>				
Type III	22,000	7800	35.2	0.45
Type I	21,000	7500	31.9	0.43
Covered	54,000	19,000	43.5	0.23

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_3^- 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 west 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 north 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_3^- -N, NO_2^- -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 3.0 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 test pile north drain were 1.8 mg L⁻¹ in 2007 and 0.65 mg L⁻¹ in 2008, whereas NO_2^- -N concentrations in the Type III test pile south drain reached 3.7 mg L⁻¹ in 2007 and 2.8 mg L⁻¹ in 2008. The concentration of NO_2^- -N was below detection in both the Type III north and south basal drains for most of 2009, with the exception of September when 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.

The measurement of low NO_2^- -N concentrations in the leach tests, combined with the consistent observation of low initial NO_2^- -N concentrations and subsequent increases to concentrations exceeding 1 mg L^{-1} in the field studies, suggests that NO_2^- -N was derived from the nitrification of NH_3 . This reaction is catalyzed by chemoautotrophic nitrifying bacteria (e.g., *Nitrobacter sp.*), and the delayed appearance of NO_2^- -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 residuals were likely encountered, thereby releasing the higher concentrations observed. Nitrate concentrations in all four AZLs remained lower ($<300 \text{ mg L}^{-1}$) 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 $<50 \text{ mg L}^{-1}$, 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% $N_{\text{Loss}}/N_{\text{Used}}$ (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 explosives (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 $16 \mu\text{g L}^{-1}$ in effluent from the Type III east AZL and $23 \mu\text{g L}^{-1}$ from the Type III west AZL in 2007 (Fig. 3). In 2008, ClO_4^- concentrations

reached maximum values in July in the Type III east ($38 \mu\text{g L}^{-1}$) and west ($18 \mu\text{g L}^{-1}$) AZLs and decreased to $<8 \mu\text{g L}^{-1}$ for the remainder of 2008, 2009, and 2010. In 2008, ClO_4^- concentrations reached a maximum of $3.7 \mu\text{g L}^{-1}$ in effluent from the Type I east AZL, but were much higher, at $130 \mu\text{g L}^{-1}$ in the Type I west AZL (Fig. 2). Perchlorate concentrations decreased and remained low ($<10 \mu\text{g L}^{-1}$) 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 ClO_4^- concentrations reached a maximum of $12 \mu\text{g L}^{-1}$ in the Type III north drain and $10 \mu\text{g L}^{-1}$ 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 ClO_4^- concentrations in the south drain, similar to other blasting residuals at the end of October 2009 and 2010.

The ClO_4^- concentrations in the Type I test pile effluent increased throughout 2008, reaching a maximum of $14 \mu\text{g L}^{-1}$ in October (Fig. 4). In 2009 and 2010, ClO_4^- concentrations increased at the end of the field season, similar to Cl^- , NO_3^- -N and SO_4^{2-} . The maximum ClO_4^- concentration in 2009 was $21 \mu\text{g L}^{-1}$. The ClO_4^- concentration increased through 2010 to $340 \mu\text{g L}^{-1}$, the maximum concentration observed at this location. Perchlorate concentrations ranged between 6 and $25 \mu\text{g L}^{-1}$ in the Covered test pile for the duration of the study, following similar trends to other blasting residuals (Fig. 6).

Overall, the maximum ClO_4^- concentrations in all piles corresponded with the highest NO_3^- -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 NO_3^- -N and SO_4^{2-} 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 NO_3^- -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 ($<10 \text{ mg L}^{-1}$) 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 $\sim 50 \text{ mg L}^{-1}$.

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

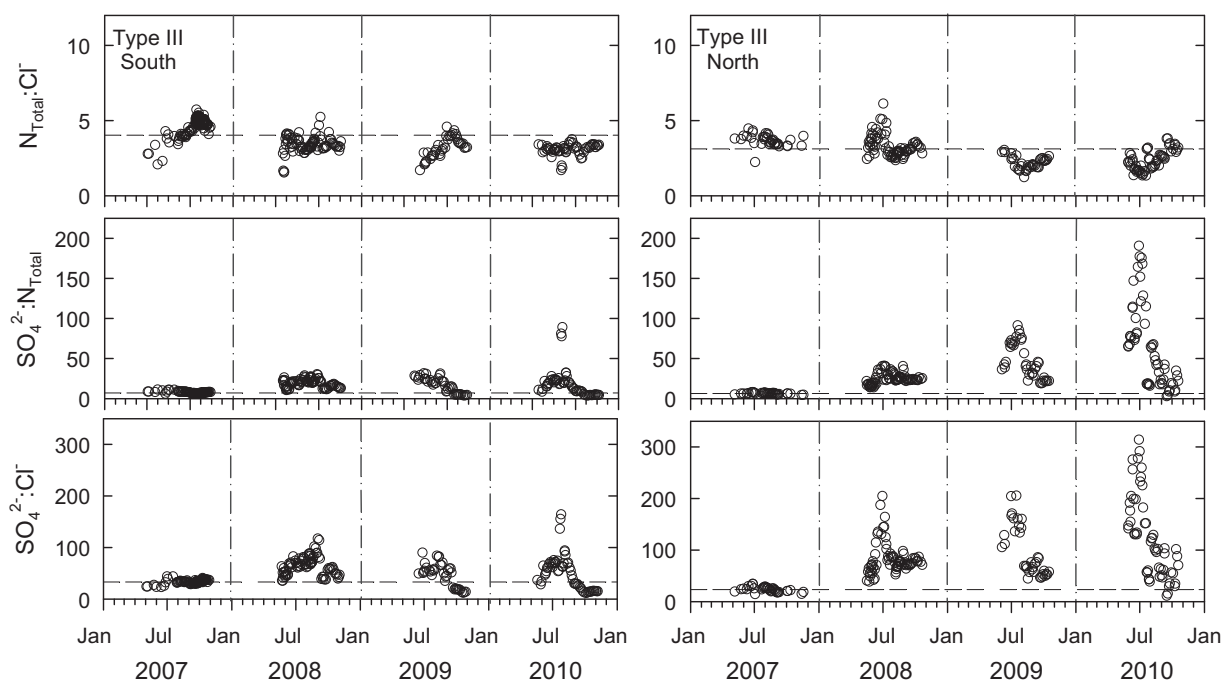


Fig. 7. Type III south (left) and north basal drain (right) ratios of N_{Total} to Cl^- , SO_4^{2-} to N_{Total} , and SO_4^{2-} to Cl^- .

Cl^- in 2007–2008 were consistent and highly correlated, suggesting N species and Cl^- were derived from blasting residuals flushed through the test pile (Fig. 7). Ratios of SO_4^{2-} to N_{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_{Total} mass. In 2008, the SO_4^{2-} to N_{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_{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_{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_{Total} observed in 2007 in the Type III test pile was compared to the N_{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

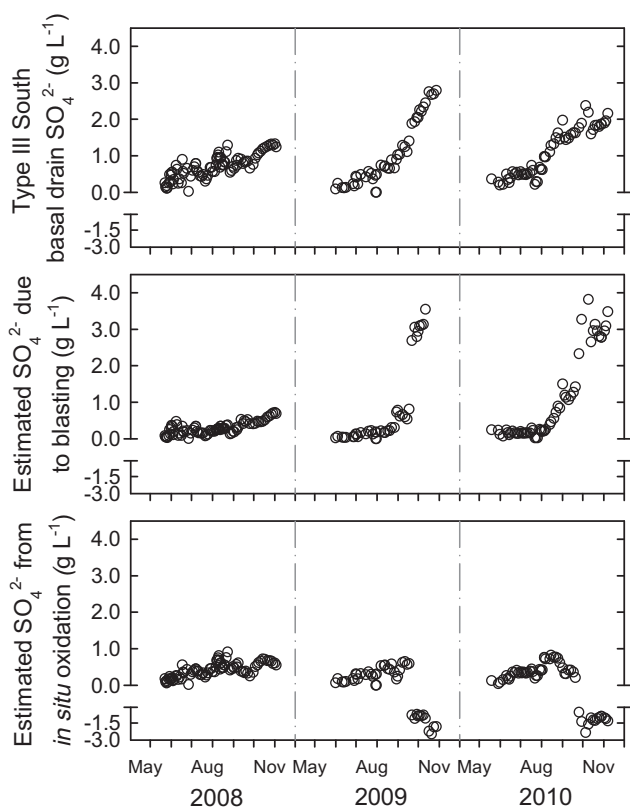


Fig. 8. Type III south basal drain predictions of SO_4^{2-} from *in situ* oxidation versus oxidation during blasting.

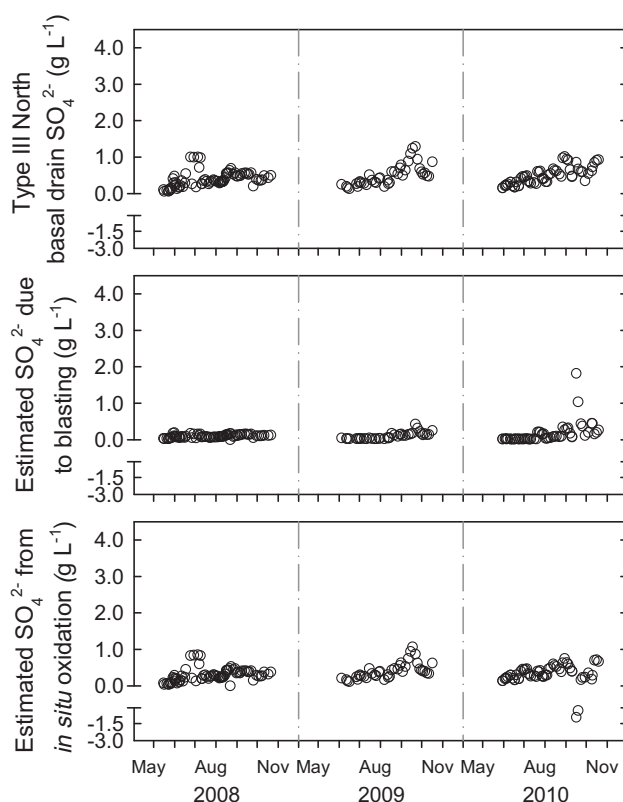


Fig. 9. Type III north basal drain predictions of SO_4^{2-} from *in situ* oxidation versus oxidation during blasting.

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_{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_{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_{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_{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_{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_{Total} ratio in the effluent from the Covered test pile was similar to the SO_4^{2-} to N_{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_{Total} ratio in the fall of 2008. The SO_4^{2-} to N_{Total} ratio steadily in-

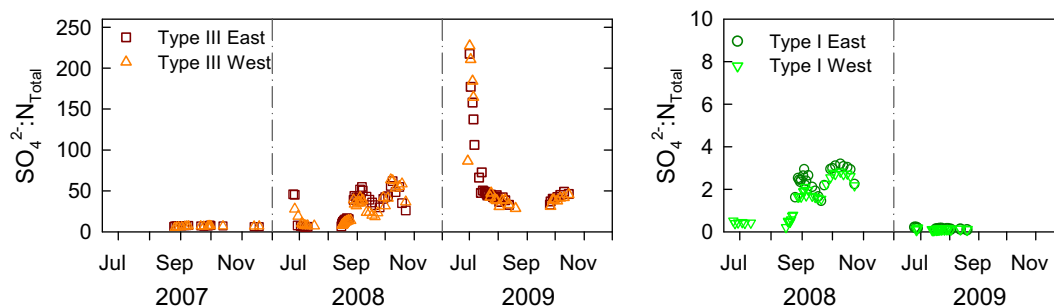


Fig. 10. SO_4^{2-} to N_{Total} ratios for Type III east and west AZLs (left) and Type I east and west AZLs (right).

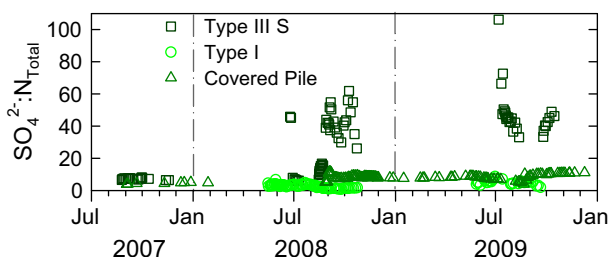


Fig. 11. SO_4^{2-} to N_{Total} ratios for Type I, Type III south, and Covered test pile basal drains.

creased 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_4^{2-} to N_{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_4^{2-} to N_{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_4^{2-} to N_{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_4^{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_4^{2-} was derived from the *in situ* oxidation of sulfide minerals. The release of SO_4^{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_4^{2-} to N_{Total} than Type I waste rock. The mass of sulfide released during blasting was estimated using the ratio of SO_4^{2-} to N_{Total} , thus providing a novel approach for estimating the mass of S released during the first flush of the piles.

Acknowledgments

The authors thank Jeff Bain, Laura Groza, Corina McDonald, Michael Gupton, Matthew Neuner, Steve Momeyer, Nathan Fretz, Nam Pham, Stacey Hannam and Richard Amos for their contributions to the project. Funding for this research was provided by a Natural Sciences and Engineering Research Council of Canada (NSERC) Collaborative Research and Development Grant; Diavik Diamond Mines Inc.; a Canadian Foundation for Innovation (CFI) Innovation Fund Award; the Mine Environment Neutral Drainage (MEND) Program; the International Network for Acid Prevention (INAP); and an Ontario Research Fund – Research Excellence Award. Also, scholarships provided by the Northern Scientific Training Program (NSTP), and the Association of Canadian Universities for Northern Studies (ACUNS) awarded to Brenda L. Bailey. The authors thank Roger Herbert and Philip Verplanck for their thorough and helpful reviews of this manuscript.

References

- Amos, R.T., Blowes, D.W., Smith, L., Sego, D.C., 2009. Measurement of wind-induced pressure gradients in a waste rock pile. *Vadose Zone J.* 8, 953–962.
- Aziz, C., 2006. Alternative causes of wide-spread, low concentration perchlorate impacts to groundwater. In: Gu, B., Coates, J.D. (Eds.), *Perchlorate Environmental Occurrence, Interactions and Treatment*. Springer, Boston, MA, USA (Chapter 4).
- Baalsrud, K., Baalsrud, K.S., 1954. Studies on *Thiobacillus denitrificans*. *Arch. Microbiol.* 20, 34–62.
- Blowes, D.W., Robertson, W.D., Ptacek, C.J., Merkley, C., 1994. Removal of agricultural nitrate from tile-drainage effluent water using in-line bioreactors. *J. Contam. Hydrol.* 15, 207–221.
- Briggs, T.J., Kelso, I.J., 2001. Ammonium nitrate–sulfide reactivity at the Century Zn–Pb–Ag mine, northwest Queensland, Australia. *Explor. Min. Geol.* 10, 177–190.
- Cameron, A., Corkery, D., MacDonald, G., Forsyth, B., Gong, T., 2007. An investigation of ammonium nitrate loss to mine discharge water at diavik diamond mines. In: *EXPLO 2007 – Blasting: Techniques and Technology, Proc.*; Wollongong, NSW. Australasian Institute of Mining and Metallurgy Publication Series, pp. 21–33.
- Clark, G.B., 1981. *Basic Properties of Ammonium Nitrate Fuel Oil Explosives (ANFO)*. Colorado School of Mines Quart., vol. 76, No. 1.
- Cox, C., 1994. Statistical issues for animal studies of developmental neurotoxicity. In: Weiss, B., O'Donoghue, J.L. (Eds.), *Neurobehavioral Toxicity: Analysis and Interpretation*. Raven Press, New York, NY, USA, pp. 93–101.
- Canadian Water Quality Guidelines (CWQG), 1987. Canadian Council of Resource and Environment Ministers, Environment Canada, March 1987, Ottawa.
- Diavik Diamond Mine Inc. (DDMI), 2006. Revised Ammonia Discussion Paper. Technical Report Submitted to Mackenzie Valley Land and Water Board May 15, 2006.
- Diamadopoulos, E., Samaras, P., Dabou, X., Sakellaropoulos, G.P., 1997. Combined treatment of landfill leachate and domestic sewage in a sequencing batch reactor. *Water Sci. Technol.* 36, 61–68.
- Egly, R.S., Neckar, A.E., 1964. Ammonium Nitrate-containing Emulsion Sensitizers for Blasting Agents, US Patent No. 3 161 551.
- Environment Canada, 2010. Monthly Data Report for Ekati A, Northwest Territories, Bulk Data 1998–2007. <http://climate.weatheroffice.ec.gc.ca/climateData/canada_e.html>.
- Fretz, N., Momeyer, S., Smith, L., Blowes, D., Sego, D., Amos, R., 2011. Diavik Waste Rock Project: unsaturated water flow. In: *Tailings and Mine Waste 2011 Proc.*, Vancouver, BC, 6–9 November, 2011.
- International Commission on Large Dams (ICOLD), 1996. *A Guide to Tailings Dams and Impoundments: Design, Construction, Use and Rehabilitation*. ICOLD Bulletin (United Nations Environment Programme), No. 106.

- Interstate Technology and Regulatory Council (ITRC), 2005. Perchlorate: Overview of Issues, Status, and Remedial Options. PERC-1. ITRC, Washington, DC. <<http://www.itrcweb.org/Documents/PERC-1.pdf>>.
- Jackson, W.A., Anandam, S.K., Anderson, T., Lehman, T., Rainwater, K., Rajagopalan, S., Ridley, M., Tock, R., 2005. Perchlorate occurrence in the Texas Southern High Plains aquifer system. *Ground Water Monit. Remed.* 25, 137–149.
- Jambor, J.L., 1997. Mineralogy of the Diavik Lac de Gras Kimberlites and Host Rocks. Report to Diavik Diamond Mines Inc..
- Koren, D.W., Gould, W.D., Bedard, P., 2000. Biological removal of ammonia and nitrate from simulated mine and mill effluents. *Hydrometallurgy* 56, 127–144.
- Kuenen, J.G., Robertson, L.A., Tuovinen, O.H., 1992. The genera *Thiobacillus*, *Thiomicrospira*, and *Thiosphaera*. In: Balows, A., Trüper, H.G., Dworkin, M., Harder, W., Schleifer, K.-H. (Eds.), *The Prokaryotes*, vol. 3. Springer, New York, pp. 2638–2657.
- Light, T.S., 1972. Standard solution for redox potential measurements. *Anal. Chem.* 44, 1038–1039.
- Motzer, W.E., 2001. Perchlorate: problems, detection, and solutions. *Environ. Forensics* 2, 301–311.
- Neuner, M., Smith, L., Blowes, D.W., Segó, D.C., Smith, L.J.D., Gupton, M., this issue. The Diavik Waste Rock Project: water flow through waste rock in a permafrost terrain. *Appl. Geochem.*
- Nordstrom, D.K., 1977. Thermochemical redox equilibria in ZoBell's solution. *Geochim. Cosmochim. Acta* 41, 1835–1841.
- National Research Council (NRC), 2005. Health Implications of Perchlorate Ingestion. The National Academy Press, Washington, DC, pp. 3–198.
- Parette, R., Cannon, F.S., Weeks, K., 2005. Removing low ppb level perchlorate, RDX, and HMX from groundwater with cetyltrimethylammonium chloride (CTAC) pre-loaded activated carbon. *Water Resour.* 39, 4683–4692.
- Pham, N., Segó, D.C., Arenson, L.U., Blowes, D.W., Amos, R.T., Smith, L., this issue. The Diavik Waste Rock Project: measurement of thermal regime in a waste rock pile under permafrost environment. *Appl. Geochem.*
- Pommen, L.W., 1983. The effect on Water Quality of Explosives use in Surface Mining. Vol. 1 Nitrogen Sources, Water Quality, and Prediction and Management of Impacts. British Columbia Ministry of the Environment, Victoria, British Columbia, MOE, Tech. Rep. 4.
- Robertson, W.D., Blowes, D.W., Ptacek, C.J., Cherry, J.A., 2000. Long-term performance of in situ reactive barriers for nitrate remediation. *Ground Water* 38, 689–695.
- Robertson, W.D., Ptacek, C.J., Brown, S.J., 2009. Rates of nitrate and perchlorate removal in a 5-year-old wood particle reactor treating agricultural drainage. *Ground Water Monit. Remed.* 29, 87–94.
- Sanchez, C.A., Crump, K.S., Krieger, R.I., Khandaker, N.R., Gibbs, J.P., 2005. Perchlorate and nitrate in leafy vegetables in North America. *Environ. Sci. Technol.* 39, 9391–9397.
- Sanmugasunderam, V., Lakshmanan, V.I., Christison, J., McKim, M., 1987. Can microorganisms be used to control nitrate levels in mining process effluents? *Hydrometallurgy* 18, 383–395.
- Sawyer, C.N., McCarty, P.N., 1967. *Chemistry for Sanitary Engineers*, second ed. McGraw-Hill Book Company, New York, NY, USA.
- Schaefer, C.E., Fuller, M.E., Condee, C.W., Lowey, J.M., Hatzinger, P.B., 2007. Comparison of biotic and abiotic treatment approaches for co-mingled perchlorate, nitrate, and nitramine explosives in groundwater. *J. Contam. Hydrol.* 89, 231–250.
- Schedel, M., Truper, H.G., 1980. Anaerobic oxidation of thiosulfate and elemental sulfur in *Thiobacillus denitrificans*. *Arch. Microbiol.* 124, 205–210.
- Standard Methods for the Examination of Water and Wastewater (SMEWW), 2005. American Public Health Association, Washington, DC.
- Smith, L.J.D., Blowes, D.W., Jambor, J.L., Smith, L., Segó, D.C., Neuner, M., this issue-a. The Diavik Waste Rock Project: particle-size distribution and sulfur characteristics of low-sulfide waste rock. *Appl. Geochem.*
- Smith, L.J.D., Moncur, M.C., Neuner, M., Gupton, M., Blowes, D.W., Smith, L., Segó, D.C., this issue-b. The Diavik Waste Rock Project: design, construction and instrumentation of field-scale experimental waste rock piles. *Appl. Geochem.*
- Snyder, S.A., Vanderford, B.J., Rexing, D.J., 2005. Trace analysis of bromate, chlorate, iodate, and perchlorate in natural and bottled waters. *Environ. Sci. Technol.* 39, 4586–4593.
- Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry*, third ed. J. Wiley, New York.
- Susarla, S., Collette, T.W., Garrison, A.W., Wolfe, N.L., McCutcheon, S.C., 1999. Perchlorate identification in fertilizers. *Environ. Sci. Technol.* 33, 3469–3472.
- Tikkanen, M.W., 2006. Development of a drinking water regulation for perchlorate in California. *Anal. Chim. Acta* 567, 20–25.
- Ting, D., Howd, R.A., Fan, A.M., Alexeeff, G.V., 2006. Development of a health protective drinking water level for perchlorate. *Environ. Health Perspect.* 114, 881–886.
- United States Geological Survey (USGS), 2009. *Minerals Yearbook*, vol. I. Metals & Minerals, pp. 23.1–23.3.
- Wilkin, R.T., Fine, D.D., Burnett, N.G., 2007. Perchlorate behavior in a municipal lake following fireworks displays. *Environ. Sci. Technol.* 41, 3966–3971.
- Zaitsev, G., Mettanan, T., Langwaldt, J., 2008. Removal of ammonium and nitrate from cold inorganic mine water by fixed-bed biofilm reactors. *Min. Eng.* 12, 10–15.