



# Assessing the fate of explosives derived nitrate in mine waste rock dumps using the stable isotopes of oxygen and nitrogen

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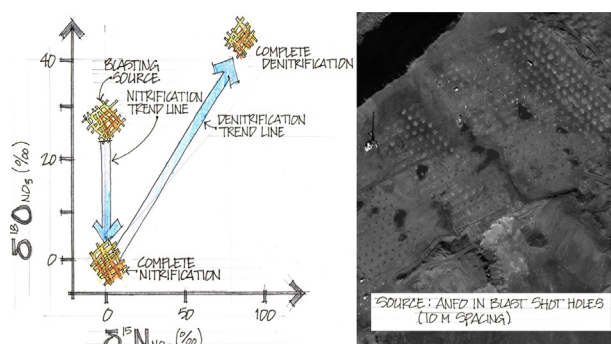
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## HIGHLIGHTS

- $\text{NH}_4\text{NO}_3$  used in blasting is an important source of  $\text{NO}_3$  contamination.
- Blasted waste rock dump samples were analyzed for  $\text{NO}_3$  and its stable isotopes.
- Isotopes showed the extent of nitrification of  $\text{NH}_4\text{NO}_3$  in oxic zones in dumps.
- Isotopes showed the extent of denitrification in anoxic zones in dumps.
- Isotopes provided estimates of the  $\text{NO}_3$  concentrations prior to denitrification.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) mixed with fuel oil is a common blasting agent used to fragment rock into workable size fractions at mines throughout the world. The decomposition and oxidation of undetonated explosives can result in high  $\text{NO}_3$  concentrations in waters emanating from waste rock dumps. We used the stable isotopic composition of  $\text{NO}_3$  ( $\delta^{15}\text{N}$ - and  $\delta^{18}\text{O}$ - $\text{NO}_3$ ) to define and quantify the controls on  $\text{NO}_3$  composition in waste rock dumps by studying water-unsaturated and saturated conditions at nine coal waste rock dumps located in the Elk Valley, British Columbia, Canada. Estimates of the extent of nitrification of  $\text{NH}_4\text{NO}_3$  in oxic zones in the dumps, initial  $\text{NO}_3$  concentrations prior to denitrification, and the extent of  $\text{NO}_3$  removal by denitrification in sub-oxic to anoxic zones are provided.  $\delta^{15}\text{N}$  data from unsaturated waste rock dumps confirm  $\text{NO}_3$  is derived from blasting.  $\delta^{15}\text{N}$ - and  $\delta^{18}\text{O}$ - $\text{NO}_3$  data show extensive denitrification can occur in saturated waste rock and in localized zones of elevated water saturation and low oxygen concentrations in unsaturated waste rock. At the mine dump scale, the extent of denitrification in the unsaturated waste rock was inferred from water samples collected from underlying rock drains.

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## 1. Introduction

Nitrate ( $\text{NO}_3$ ) contamination of surface and groundwater is a global environmental problem. Loading of nitrogen (N) to surface and

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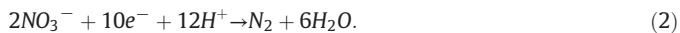
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groundwater is generally attributed to the use of fertilizers, release of biological waste from agriculture or municipal sources, landfill effluent, and elevated levels of atmospheric N deposition (c.f., Benkovitz et al., 1996; Hallberg, 1989; Power and Schepers, 1989; Seiler et al., 1999; Wakida and Lerner, 2005). These anthropogenic N inputs can result in  $\text{NO}_3^-$  concentrations that exceed the drinking water limit of 10 mg  $\text{NO}_3^-$ -N  $\text{L}^{-1}$  (WHO, 2004; Health Canada, 2014; U.S. EPA, 2009) and contribute to the eutrophication of water bodies (Deutsch et al., 2006; Kaushal et al., 2011).

Worldwide, approximately 65% of  $\text{NH}_4\text{NO}_3$  is used in agricultural fertilizer applications, with the remainder used for explosives (Chemical Economics Handbook, 2016). In the mining industry,  $\text{NH}_4\text{NO}_3$  is often mixed with fuel oil to create explosives (referred to as ANFO). The  $\text{NH}_4\text{NO}_3$  in ANFO is soluble in water and dissociates into dissolved  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . The release of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  to the environment from explosives during mining is generally attributed to  $\text{NH}_4\text{NO}_3$  spillage or incomplete detonation and subsequent dissolution (Cameron et al., 2007; Pommen, 1983). Under oxic conditions,  $\text{NH}_4^+$  can undergo nitrification to  $\text{NO}_3^-$  as described by:



Although nitrification is a multi-step oxidation process facilitated by autotrophic microorganisms (e.g., Nitrosomonas and Nitrobacter), the evolution of dissolved N species during and after blasting is poorly understood. Under oxygen-depleted conditions, dissolved  $\text{NO}_3^-$  can be irreversibly reduced to  $\text{N}_2$  via bacterial denitrification (c.f., Appelo and Postma, 2005; Kendall, 1998). The electron transfer processes for complete denitrification from dissolved  $\text{NO}_3^-$  to gaseous  $\text{N}_2$  can be described by:



Denitrification is carried out by several different enzymes, leading to different intermediates:



Sub-oxic to anoxic conditions can exist in unsaturated mine waste rock dumps (Mahmood et al., 2017) and in saturated waste rock (Dockrey et al., 2015). Denitrification is a potential  $\text{NO}_3^-$  removal mechanism in both of these environments.

Soluble  $\text{NO}_3^-$  is transported through and out of the waste rock by recharging percolating waters. Bailey et al. (2013), Mahmood et al. (2017), and Villeneuve et al. (2017) interpret  $\text{NO}_3^-$  transport through waste rock as conservative (i.e., non-reactive) due to typically well-oxygenated conditions in unsaturated rock dumps. The concentrations of  $\text{NO}_3^-$  in freshly blasted waste rock can be great and highly variable. Mahmood et al. (2017) report mean measured porewater  $\text{NO}_3^-$ -N concentrations of  $497 \pm 854$  mg  $\text{L}^{-1}$  in a fresh coal waste rock dump. Dockrey et al. (2015) report  $\text{NO}_3^-$ -N concentrations in coal waste rock seepages from 5 to over 100 mg  $\text{L}^{-1}$  depending on the size and age of the waste rock dump. Measured dissolved concentrations from seepage outflow at a diamond mine were 2000 mg  $\text{NO}_3^-$ -N  $\text{L}^{-1}$  and 410 mg  $\text{NH}_3$ -N  $\text{L}^{-1}$  (Bailey et al., 2013). Concentrations of dissolved  $\text{NO}_3^-$ - and  $\text{NH}_3$ -N in mine effluent from uranium mines ranged from 60 to 80 and 53 to 350 mg  $\text{L}^{-1}$ , respectively (Schmidt and Moffett, 1979), many times higher than the drinking water exceedance limits.

The  $\text{NO}_3^-$  inputs resulting from mining can affect surface waters. For example, the Elk River watershed drains 4450 km<sup>2</sup> of the Rocky Mountains to the Kootenay River and Koochanusa Reservoir (Fig. 1). This valley is a major steelmaking coal production region in Canada (Goodarzi et al., 2008). During the 1960s and 1970s, mean N ( $\text{NO}_3^-$ -N +  $\text{NO}_2^-$ -N) concentrations in the Elk River south of Sparwood (Fig. 1) were <0.01 mg  $\text{L}^{-1}$  (Clark and Peppin, 1984; McDonald, 1987). Rising trends in riverine  $\text{NO}_3^-$  concentrations were observed in the early 1980s (Ferguson and

Leask, 1988; McDonald, 1987; Pommen, 1983), and data from 2009 indicated continued increases in  $\text{NO}_3^-$  +  $\text{NO}_2^-$ -N concentration in the Elk River south of Sparwood (Fig. 1) to 0.5–1.4 mg  $\text{L}^{-1}$ , varying seasonally (Dessouki and Ryan, 2010). In smaller order streams in mine sub-catchments, the  $\text{NO}_3^-$ -N concentrations were greater. For example, Villeneuve et al. (2017) show mean yearly  $\text{NO}_3^-$  concentrations in West Line Creek (Fig. 1) increasing from 6.5 mg  $\text{L}^{-1}$  in 1994 to 38.5 mg  $\text{L}^{-1}$  in 2006 and then decreasing slightly to 26.7 mg  $\text{L}^{-1}$  in 2014. The increasing concentrations of  $\text{NO}_3^-$  in the Elk River were correlated to the volume of waste rock produced in the Elk Valley (Strategic Advisory Panel on Selenium Management, 2010). Ferguson and Leask (1988), Mahmood et al. (2017), and Villeneuve et al. (2017) attribute the source of this riverine  $\text{NO}_3^-$  to N-based explosives used in rock blasting.

The dual-isotope approach ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  in  $\text{NO}_3^-$ ) has been successfully used to fingerprint distinctive  $\text{NO}_3^-$  sources, define  $\text{NO}_3^-$  transport pathways, and identify N biotransformation processes (e.g., nitrification and denitrification) in groundwaters, lakes, and marine environments (c.f., Aravena and Robertson, 1998; Böhlke et al., 2002; Brandes et al., 1998; Einsiedl et al., 2005; Lehmann et al., 2003; Voss et al., 2001; Wassenaar, 1995). The stable isotopes of N and O (and H and C) have also been used to discriminate between types of explosives (Widory et al., 2009) and to characterize the fate of  $\text{NO}_3^-$  from blast rock used as fill to build roadways (Degnan et al., 2015). The dual-isotope approach has not, however, been applied to characterize the  $\text{NO}_3^-$  source term or the N transformation processes that might be occurring in mine waste rock.

A multi-disciplinary research and development program was initiated by Teck Resources in 2012 to investigate the influence of mining on the fate and transport of solutes (specifically Se,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , Cd) from low sulfide–high carbonate mine dumps in the Elk Valley, British Columbia, Canada. As part of this study, Mahmood et al. (2017) report  $\text{NO}_3^-$  in the dumps in the Elk Valley is derived from blasting practices. They used nitrate isotope analyses at one dump to show that nitrification of the ANFO contributes to  $\text{NO}_3^-$  loading within the waste rock dump. They did not, however, study the post-blasting evolution of dissolved N species as it relates to the nitrification process or address potential denitrification. The current study greatly extends the findings of Mahmood et al. (2017) by conducting additional geochemical investigations at nine coal waste rock dumps located in the Elk Valley to generate an improved (i.e., water-saturated and unsaturated environments) interpretation of the N system in saturated and unsaturated waste rock dumps. Determining the source(s) and evolution of  $\text{NO}_3^-$  in contaminated systems is generally difficult due to the common presence of multiple N sources, overlapping isotopic source values, and complex biologically mediated reactions (Aravena et al., 1993; Granger et al., 2008; Mengis et al., 2001; Vavilin and Rytov, 2015; Xu et al., 2015). In the case of mine waste rock, however, one source of  $\text{NO}_3^-$  dominates: ANFO. This simplicity in source provides an opportunity to examine the isotope fractionation of both N and O during and after blasting (e.g., the  $\text{NO}_3^-$  source term) and any post hoc denitrification. In the latter case, the observed degree of isotopic fractionation can also be used, with the measured  $\text{NO}_3^-$  concentration, to estimate the  $\text{NO}_3^-$  source concentration prior to the onset of denitrification. We hypothesized the application of the stable isotopes of  $\text{NO}_3^-$  could be used to define the  $\text{NO}_3^-$  source term, determine under which mine environments denitrification occurs, as well as quantify the extent of denitrification and the original  $\text{NO}_3^-$  source concentrations.

## 2. Study sites and methods

### 2.1. Study sites and sampling

Mining of high- to low-volatile bituminous coal from the Mist Mountain Formation of the Jurassic-Cretaceous Kootenay Group, has been ongoing in the Elk Valley, southeastern British Columbia, Canada since the

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