Determination of the Rate of Release of Nitrates from Waste Rock, Tailings and Kimberlite in Field Conditions – A Case Study

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Abstract

This paper presents a case study on the determination of the release rate of nitrates from waste rock, tailings and kimberlite using field kinetic tests (FKT). The FKT cells were monitored over a period of 3 years. The results of the study discussed in this paper include particle size distribution, mineralogy, percentages of leached nitrates, trends in leached nitrates (seasonal variability) and nitrates leaching rates. Geogenic nitrogen, also detected in basalt and kimberlite, is also discussed in this paper. The purpose of the study was to inform the development of a sustainable nitrates management plan.

Keywords: Field kinetic tests, nitrates, kimberlite, tailings, waste rock

Introduction

Nitrates are readily soluble in water and in this context constitute the aqueous phases of materials containing ammonium nitrate from explosives. However, establishing a direct link between blasting residues and nitrates entering the water system is extremely difficult to achieve. This is mainly because of the complexity of the deportment of nitrogen species following a blast, microbial activity that metabolises nitrate and ammonia and the lack of techniques to "fingerprint" nitrogen in residues to the nitrogen in explosives. The study used FKT monitored over a period of 3 years to establish the sources of elevated levels of nitrates in surface water at a mine and to determine the rate of release of nitrates from waste rock, tailings and kimberlite. The purpose of the study was to inform the development of a sustainable nitrates management plan for the mine.

The study site was characterised by extreme winter conditions with temperatures ranging between -15˚C and 10˚C. Maximum temperatures average 23˚C in summer with a mean annual rainfall of 750 mm. Snowfalls are frequent and common between May and September.

Methods

The study established discrete FKT cells of blasted and unblasted waste rock, kimberlite and tailings. The cells were made of 1m^3 polyvinyl chloride (PVC) barrels loaded with approximately 3.5 tonnes of test material. The cells were leached with rainwater from direct precipitation. The leachates were collected in 1.5L sample bottles and overflow from the sample bottles collected in 5L buckets.

The data collected during sampling included the date of sampling, volume of leachate collected in the sample bottles and buckets, temperature, pH, electrical conductivity and nitrate concentrations in the leachates.

Geochemical analysis undertaken on sub samples of the test materials included particle size distribution, mineralogical analysis by X-ray diffraction and batch leach test. Geogenic nitrogen in drill core samples of basalt (waste rock) and kimberlite were analysed using automated (MetroOhm) Ion Chromatography.

Results and Discussion

Particles size distribution

Blasted waste rock consisted of 62% gravel, 24% sand, 12% silt and 2% clay. Blasted kimberlite was 84% gravel and 16% sand. Tailings was 88% sand and 12% gravel. Blasted waste rock was characterised by a finer particle fraction relative to the rest.

Particle size distribution is expected to have a significant influence on nitrate leaching rates in the materials. The nitrates in the materials occur mainly as mixed salts within the friable matrix (clay, silt and sand) and on the surfaces of the gravels following blasting.

Mineralogy

Silicate minerals, mainly plagioclase, smectite and diopside, dominated the waste rock, kimberlite and tailings mineralogy, Table 1. Calcite was present in kimberlite and tailings. X-ray diffraction did not identify any nitrogen bearing minerals.

pH of leachates

An increase in pH from neutral to alkaline occurred in the leachate from all the materials over time, Figure 1, except UBWR sample that appears to be going acidic in the December 2017 data. The increase in pH is attributed to the dissolution and weathering of calcite, diopsite and aluminosilicates that contributed to the overall neutralisation potential in the leachates.

Nitrogen species

The dominant nitrogen species leached from the materials was nitrate. The concentrations of nitrite (<0.1 mg/kg N) and ammonium (0.4 – 5.6 mg/kg N) were substantially lower than the concentrations of nitrate (0.4 – 26 mg/kg N) in the leachates. Ammonium will convert to nitrite, and nitrate under oxidising conditions, such as aeration or excavation, while nitrate will convert to ammonium under reducing circumstances.

Table 1. *Mineralogical composition of waste rock, kimberlite and tailings.*

Mineral Group	Mineral Name	Formula	BWR	UBWR	UBWRN	KMB	Tailings
Dissolving	Calcite	$CaCO_3$				1.3	3.0
Fast weathering	Diopside	$CaMgSi_2O_6$	23	24	26	21	16
Intermediate	Biotite	$K(Mg,Fe)_3\ ((OH)_2AlSi_3O_{10})$				8.1	14
weathering	Chlorite	$(Mg,Fe)_5Al(AlSi_3O_{10})(OH)_8$	5.3	5.2	4.1	8.8	15
	Enstatite	$MgSiO_3$	2.1	5.3	8.2		
	Heulandite	$CaAl_2Si7O1_8(H2O)_6$	1.8	2.2	2.3		
	Natrolite	$Na_2Al_2(Si_3O_{10})(H_2O)_2$				1.1	
	Scolecite	$CaAl_2Si_3O10(H_2O)_3$		11		1.9	
	Stilbite	$NaCa_2Al_5Si_{13}O_{36}\ 14H_2O$	4.9	5.1	2.8		
Slow weathering	Kaolinite	$Al_2Si_2O_5(OH)_4$				2.9	5.7
	Plagioclase	$(Na,Ca)(Si,Al)_4O_8$	43	32	34	9.5	3.1
	Smectite	$CaMg_2AlSi_4(OH)_2H_2O$	19	16	22	45	43
Very slow weathering	Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	1.8				

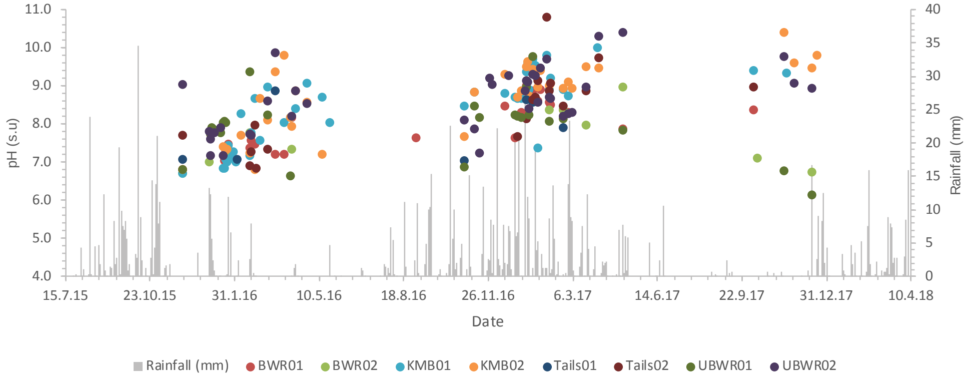

Figure 1 *Graph showing change in pH over time for blasted waste rock (BWR), kimberlite (KMB), tailings (Tails) and unblasted waste rock (UBWR).*

***Table 3.** Percentage of nitrates leached from the leachable content in the materials.*

Description of test materials	FKT Cell	Total leached NO_3 as N from bulk leaching (mg/kg)	Total leached NO_3 as N from FKT (mg/kg)	Percentage of leached NO_3 as N (%)
Blasted waste rock	BWR01	26	2.5	9.6
	BWR02		0.96	3.7
Blasted Kimberlite	KMB01	5.6	3.9	69
	KMB02		1.8	32
Tailings	Tails01	5.6	0.02	0.35
	Tails02		0.62	11
Un-blasted waste rock	UBWR01	0.4	0.049	12
	UBWR02		0.084	21

Percentages of leached nitrates

Kimberlite leached out the highest percentage of nitrates, 32-69%, of its leachable nitrate content, Table 3. Blasted waste rock leached out 3.7-9.6% while unblasted waste rock leached out 12-21%. The difference in particle size distribution accounted for the variability in the blasted and unblasted waste rock leaching rates. The unblasted waste rock had a higher gravel and sand content (88-93% gravel and 7-12% sand) relative to the blasted waste rock (62% gravel, 24% sand). The tailings leached 0.35- 9.4% of its leachable nitrate content.

Figure 2 to Figure 5 show the trends in leached nitrates from 2015 to 2017. The highest concentrations of leached nitrates occurred in the first rainy season in summer, October 2015 to April 2016. The leached concentrations dropped steadily in the subsequent rainy seasons, with little or no nitrates recorded in the leachates by the third year of leaching.

The trends showed that nitrates leached from the waste rock, kimberlite and tailings during summer from October to April. Insufficient to no leachates emanated from the materials during winter from May to September due to frozen conditions and lack of rainfall.

In reality, as deposition continues with the addition of more materials on the dumps and stockpiles, a continuous source of nitrates is maintained rather than depleted.

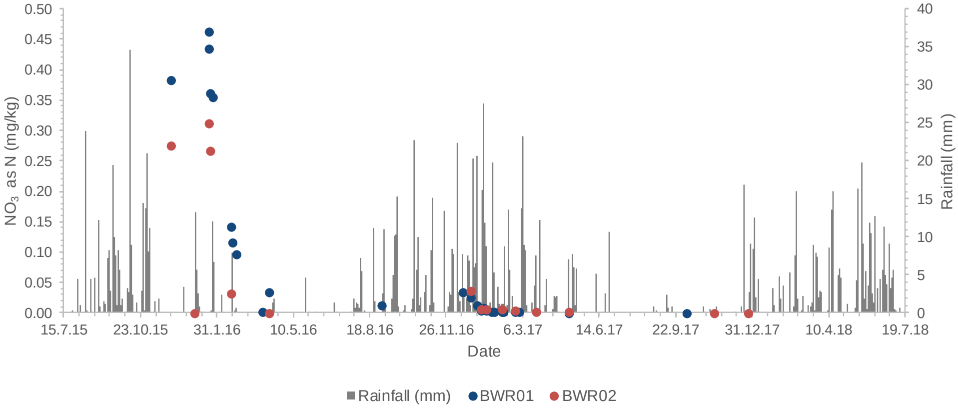

***Figure 2.** Graph showing change in nitrate concentration in leachate from blasted waste rock (BWR).*

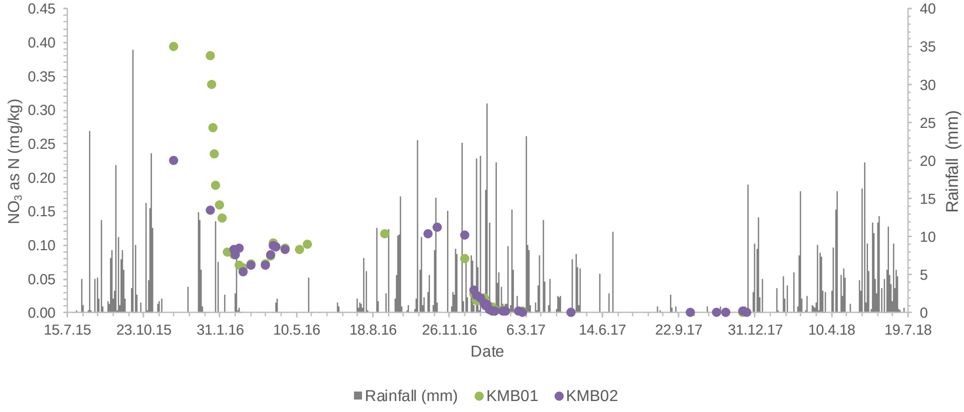

Figure 3 *Graph showing change in nitrate concentrations in leachate from Kimberlite (KMB).*

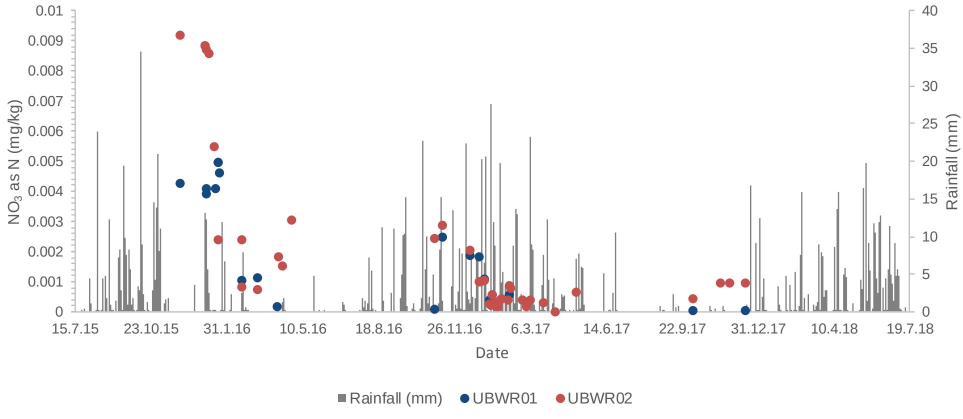

Figure 4 *Graph showing change in nitrate concentrations in leachate from unblasted waste rock (UBWR).*

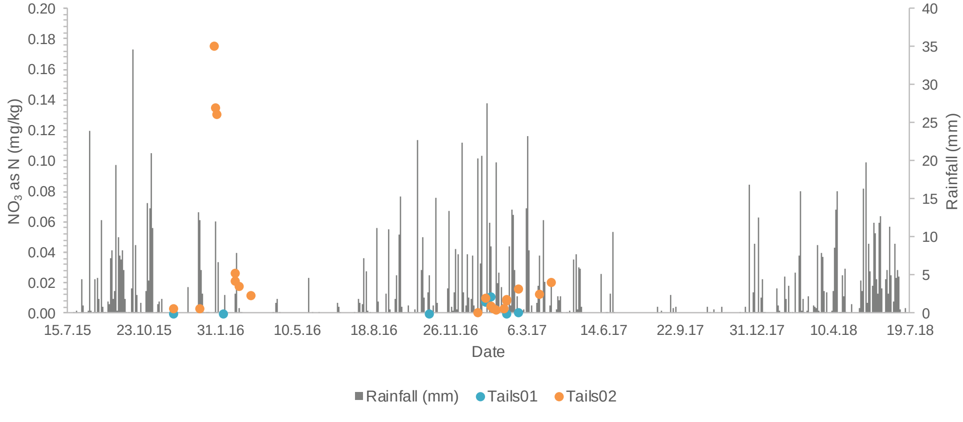

Figure 5 *Graph showing change in nitrate concentrations from leachate from tailings (Tails).*

Nitrate leaching rates

Blasted kimberlite (0.0002-0.024 mg/kg/day N) and waste rock (0.0001-0.019 mg/kg/day N) had high nitrate leaching rates relative to the tailings (0.0002-0.008 mg/kg/day N) and unblasted waste rock (0.0001-0.0024 mg/kg/day N), Table 2.

The study established the nitrate leaching rates to be as follows in decreasing order:

Blasted kimberlite > blasted waste rock > tailings > unblasted waste rock

The nitrate leaching rates of the waste rock, kimberlite and tailings were related to the particle size distribution in the materials rather than to the material types. Particle size distribution influences the size and distribution of the voids within the materials, which serve as pathways and storage spaces for fluids and gases contained in and moving through the material. The nitrates in the materials occur mainly as mixed salts within the friable matrix and on the surfaces of the larger particle fractions following blasting.

In reality, while the tailings nitrate leaching rates may be representative of the actual tailings conditions, the waste rock and kimberlite nitrate-leaching rate may be slightly lower than the actual waste rock dump and kimberlite stockpile because the actual dumps/stockpiles are characterised by a larger particle size fractions than the test materials.

Geogenic nitrogen

Various studies indicate that geogenic nitrogen contributes to ecosystem nitrogen saturation (more nitrogen available than required by biota), which leads to nitrogen leaching and elevated concentrations of nitrate in surface and groundwater (Dahlgren 1994, Holloway et al 2002). Release of nitrogen through weathering occurs at ecologically significant rates, with nitrogen release rates ranging from 10-20 mol N cm^2 s^{-1} corresponding to nitrogen fluxes of 4-37 kg N ha^{-1} yr^{-1} (Holloway et al., 1999).

This study detected geogenic nitrate nitrogen of a range of 0.09 – 1.3 mg/L N in the leachate from un-weathered basalt and kimberlite. However, the quantified concentrations of the geogenic nitrates in un-blasted basalt and kimberlite were significantly low (> 5 times lower) relative to the quantified concentrations in the blasted basalt and kimberlite. Although insignificant relative to the explosives source, geogenic nitrogen occurs in the basalt and kimberlite and contribute to the nitrate loadings into the system.

Conclusions

The study established the nitrate leaching rates, associated with the particle size distribution, to be as follows in decreasing order:

Blasted kimberlite > blasted waste rock > tailings > un-blasted waste rock

Table 2. *Nitrate leaching rates from the FKT cells.*

Description of test material	FKT Cell	NO3 leaching rates (mg/kg/day)	
		Min	Max
Blasted waste rock	BWR01	0.0001	0.019
	BWR02	0.0001	0.018
Blasted Kimberlite	KMB01	0.0002	0.023
	KMB02	0.0002	0.024
Tailings	Tails01	0.0003	0.008
	Tails02	0.0002	0.008
Unblasted waste rock	UBWR01	0.0001	0.0024
	UBWR02	0.0001	0.0024

The study recommended nitrate reduction at source through improved handling, storage and blasting practices. The study also recommended that the stockpiling of kimberlite ore over an extended period, especially during the summer rains, should be minimised.

The predominant nitrogen species leached from the cells was nitrate. Although the concentrations of leached ammonium and nitrites were substantially lower than leached nitrates, ammonium will convert to nitrite, and nitrate under oxidising conditions, while nitrate will convert to ammonium under reducing circumstances. Therefore, all the nitrogen species are monitored in surface and groundwater.

Although insignificant relative to the nitrates from explosives, geogenic nitrogen contribute to the overall nitrate loading into the surface water system from the basalt and kimberlite.

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