Field-scale denitrifying woodchip bioreactor treating high nitrate mine water at low temperatures

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Abstract A field-scale woodchip bioreactor was installed at the Kiruna iron ore mine (northern Sweden) for the removal of NO_3^- in mine and process water originating from the use of ammonium nitrate based explosives. Over a period of two years, the woodchip bioreactor removed an average incoming NO_3^- concentration of 22.0±0.3 mg N L^{-1} to below detection limits (0.06 mg N L^{-1}) at bioreactor temperatures above 5°C and hydraulic residence times between 1.9-2.6 days. As the hydraulic residence time in the system was decreased to 1 day and/or the bioreactor temperature decreased to below 5°C, NO_3^- removal was incomplete. The bioreactor acted as an overall sink and source of NO_2^- and NH_4^+, respectively, with low level ammonium production (< l mg N L^{-1}) observed during the test period. The direct application of a woodchip bioreactor for the removal of NO_3^- in leachate produced from waste rock deposits in subarctic climates is limited by the variability and timing of leachate production.

Key words Woodchip bioreactor, nitrate removal, neutral mine drainage, low temperatures

Introduction

A substantial amount of the ammonium nitrate-based explosives used in mining never detonate; a study of the explosives used in Swedish mines (Lindeström 2012) indicates that the amount of undetonated explosives reaches 10-20% of the total explosives used. Ammonium nitrate residues are retained on waste rock masses and are highly soluble in water. Following the deposition of the waste rock masses on the ground surface, nitrogen compounds are leached as the undetonated explosive residues come into contact with percolating rainwater and/or snowmelt. Consequently, waste rock piles are sources of nitrogen (N) primarily in the form of nitrate (NO_3^-), with less amounts of ammonium (NH_4^+) and nitrite (NO_2^-) (Lindeström 2012). Excess release of NO_3^- to aquatic ecosystems may lead to the eutrophication of water bodies. In addition, ammonia (NH_3) is toxic to aquatic ecosystem when present at high concentrations.

Denitrification, the sequential reduction of NO_3^- to nitrogen gas (N_2) via the intermediate species NO_2^-, NO, and N_2O, is together with anaerobic ammonium oxidation (ANAMMOX) the only process that may serve as an environmental sink for NO_3^-. Denitrification is exemplified with glucose as the carbon substrate/electron donor in reaction (1):

$$NO_3^- + \tfrac{5}{24}C_6H_{12}O_6 \rightarrow \tfrac{1}{2}N_2 + HCO_3^- + \tfrac{1}{4}H_2CO_3 + \tfrac{1}{2}H_2O \qquad (1)$$
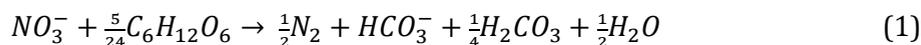
Compared to ionized species of nitrogen, N_2 is inert and largely unavailable as a source of nitrogen for the majority of living organisms. Bioreactors containing organic carbon and promoting heterotrophic denitrification are low maintenance and low cost techniques for

NO_3^- removal that have been applied to various NO_3^- contamination settings (e.g. Woli et al. 2010, Warneke et al. 2011). However, most of the studies have been performed at relatively high temperatures not relevant in climates where temperatures may be close to, or below, 0°C for extended periods. In addition, few have been applied to mine settings. In this study, a field-scale denitrifying woodchip bioreactor constructed in the subarctic climate at the Kiruna mine (northern Sweden) was installed for the removal of NO_3^- from mine drainage and process water. The objective of the study was to determine the potential of a denitrifying woodchip bioreactor as a treatment method for the removal NO_3^- from waste rock leachate at temperatures expected in a subarctic climate. For an overview of the denitrifying bioreactor technology, the reader is referred to Schipper et al. (2010).

Methods

The bioreactor was constructed at the Kiruna iron ore mine (northern Sweden) in close proximity to a clarification pond at the mine site. Construction of the bioreactor took place in May and June 2015.

Bioreactor material and construction

The bioreactor was constructed below ground by the excavation of a 1.10 m deep, 44.0 m long, and 6.65 m wide trench with a trapezoidal cross-section (Figure 1). 1.0 m high mounds of waste rock material surrounded the trench, resulting in an effective depth of 2.10 m. The bottom of the trench (including surrounding mounds) was lined with a 1.5 mm thick impermeable high-density polyethylene geomembrane to eliminate any hydraulic contact with the surrounding soil. Five "inner walls" of plywood were placed within the trench in ~8.5 m intervals (W1-W5, Figure 1), with the intention of forcing the water to flow along the bottom of the bioreactor. The inner walls were fixated by steel I-beams that were placed on top of the walls.
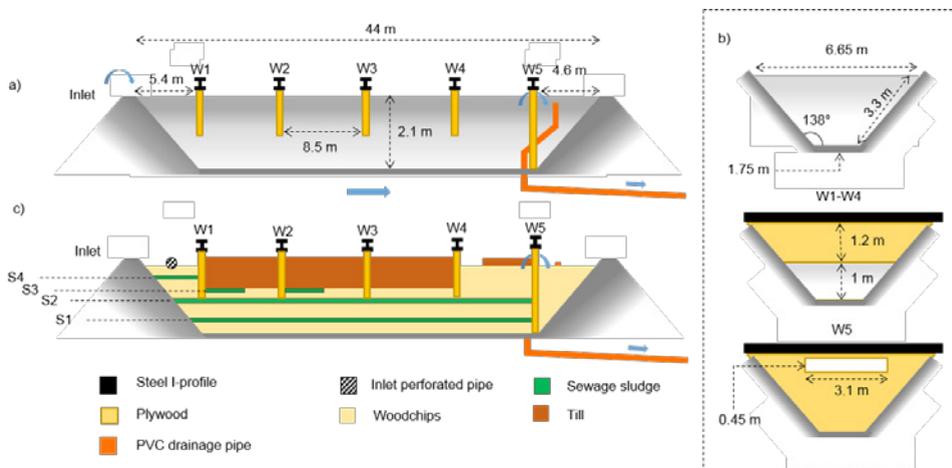
Figure 1 Longitudinal (a) and cross-sectional (b) dimensions of the bioreactor. W1-W5 are inner walls designed to force the flow below the ground surface. Sequencing of bioreactor filling is seen in (c). Direction of flow is left to right.

W5 covered the entire cross-section of the bioreactor (Figure 1b) and featured an adjustable rectangular weir intended for controlling the water level in the bioreactor. The inlet was constructed using a perforated pipe that was placed perpendicular to the direction of flow in the bioreactor. The bioreactor was drained at the outlet using polyvinyl chloride (PVC) pipes emerging at the surface (Figure 1c). The inlet and outlet was designed to spread the flow of water in the bioreactor, reducing advection velocities, which have been shown to promote higher NO_3^- removal rates (see Herbert and Nordström 2016).

The bioreactor was filled with pine woodchips (porosity 0.54) and digested sewage sludge at a sludge:woodchip ratio of 1:84 on a volume basis. Woodchips were purchased at a local lumber mill, and served as the carbon source for (heterotrophic) denitrification (see reaction 1). Woodchip sized fragments (approximately 0.5 cm x 1 cm x 3 cm w/b/l) were used as they provided a high permeability environment in comparison to smaller sized fragments, e.g. sawdust, minimizing the risk of clogging pores and bypassing of flow, and in addition enabling a high process volume. The sewage sludge was shipped from the Uddebo waste water plant in Luleå (northern Sweden) and was used as an initial source of denitrifying microorganisms catalyzing reaction 1. The digested sewage sludge was mixed with water (1:10 on a volume basis) in a slurry, and added in layers at 50 cm and 100 cm above the geomembrane (S1 and S2 in Figure 1c). In addition, sewage sludge (not slurry) was (partially) added to the top surface of the woodchips in the first ~20 m of the bioreactor (S3 and S4 in Figure 1c). Geotextile was used to cover the top surface of the woodchips, and was partially covered by a layer of glacial till (primarily silty-sand, but also with larger cobbles <300 mm, and with detrital organic matter) as seen in Figure 1c. The geotextile was used as to prevent the till material from migrating into the woodchips, while the glacial till served three purposes: (1) minimizing the atmospheric contact with the bioreactor interior, (2) forcing water to flow in the more permeable woodchip material along the bottom of the bioreactor, and (3) decreasing the infiltration of precipitation to the bioreactor interior which would have a dilutive effect. Additionally, temperature probes (Campbell Scientific T107, 16 in total) were embedded within the mixture of woodchips and sewage sludge during construction.

The bioreactor was fed with water from the outlet of the clarification pond using a submergible pump, and a ball valve was used to adjust the input flow rate to the bioreactor. The ability to adjust the input flow rate allowed for controlling the hydraulic residence time (HRT) of the system. During the emplacement of the glacial till, the bioreactor was saturated with water from the clarification pond. Pore water was then slowly recirculated for 10 days (cf. Nordström and Herbert 2016) to allow the denitrifying microbial community to develop, before the bioreactor outlet was opened and through-flow commenced.

Bioreactor operation

The bioreactor test period extended for the duration of two field seasons, referred to as the first and second operational year, respectively. The first operational year extended between the 22nd of June 2015 following the completion of the bioreactor, and the 20th of November 2015. Between the 20th of November 2015 and the 9th of May 2016, referred to as the winter intermission, there was no flow through the bioreactor. Temperature measurements did,

however, show that temperatures at 1-2 m depth in the bioreactor were well above 0°C during the winter intermission. The second operational year extended between the 9th of May 2016 as average daily air temperatures increased above 0°C and through-flow was commenced, and the 21st of October 2016 when the test period of the bioreactor was terminated. The theoretical HRT of the bioreactor system, calculated as the pore volume divided by the flow rate, was adjusted several times during the operation of the bioreactor (see Table 1).

Table 1 *Theoretical hydraulic residence times (HRT) in the bioreactor system (day 0 = 22nd of June 2015)*

Days of operation	Theoretical HRT [days]
-10-0	Recirculation
0-45	2.6
46/51-52	No flow − Pump malfunction
53-151	1.9
152-321	No flow − winter intermission
322-370	2.6
371-428	2.3
429-487	1

Sampling and analysis

Influent and effluent water from the bioreactor were sampled by the mining company LKAB approximately two times a week. Once a month, an extended sampling and analysis was carried out where, in addition to the weekly samples, dissolved and surface emission of gases (N_2O, CH_4) were sampled. Water samples were analyzed for NO_3^-, NO_2^-, NH_4^+, pH, alkalinity, total organic carbon (TOC), and other major inorganic anions by LKAB's accredited laboratory services following standardized analytic procedures. Samples (50 mL) intended for the analysis of dissolved gases were injected into a 100 mL serum vial containing 1 mL $ZnCl_2$ (50% w/v) as a preservative. The emission of surface gases was sampled using static gas chambers emplaced upon the woodchip surface at 2 m and 37 m (three at each location) from the bioreactor inlet. Dissolved and surface gas samples were shipped via ground transport (4-7 days) to Uppsala (central Sweden) for analysis. Following 24-72 hours of headspace equilibration at room temperatures (22°C), ~45 mL headspace of the dissolved gas samples were then collected and injected into a pneumatically pre-sealed, non-evacuated (air-filled), 22 mL PerkinElmer™ glass vial, so that the atmosphere was replaced in the vial. Dissolved and surface gas samples were analyzed together using a gas chromatograph equipped with an electron capture detector (Clarus 500GC, Perkin Elmer, CT, USA).

Data analysis

Cumulative production/removal was calculated in R (R Core Team 2015) on a daily basis from the observed difference in influent and effluent concentrations of NO_3^-, NO_2^-, NH_4^+,

and TOC, respectively. The influent/effluent concentrations were assumed to vary linearly between observations.

Results and discussion

For the duration of the test period of the bioreactor, the influent water (average pH 8.1) had an average NO_3^- concentration of 22.0±0.3 mg N L^{-1}, which was reduced to below detection limits (0.06 mg N L^{-1}) at temperatures above ~5°C and at theoretical HRTs between 1.9-2.6 days (Figure 2a, Table 1).
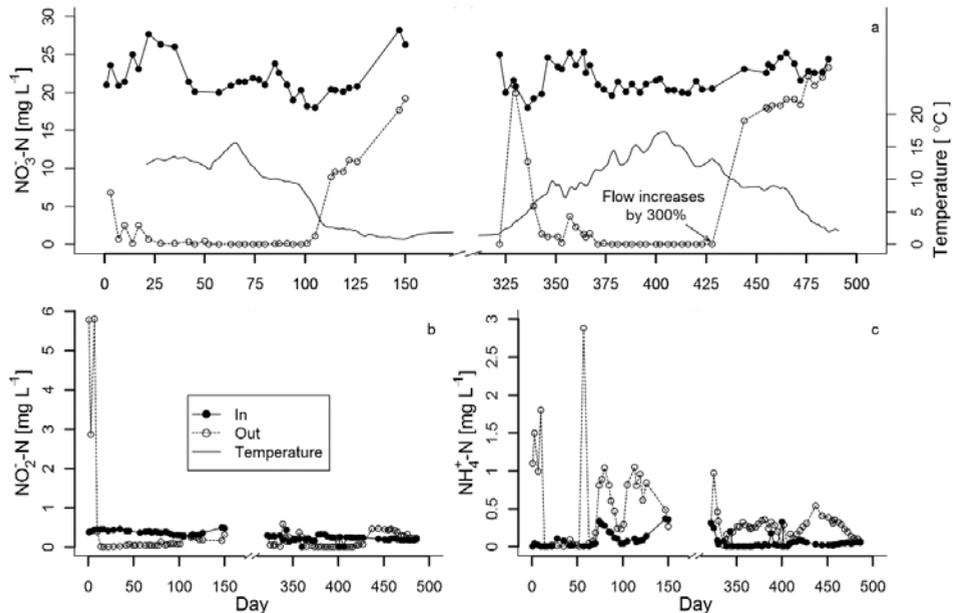
Figure 2 *Time series (days since start of bioreactor) of influent (full symbols) and effluent (open symbols) concentrations of nitrate (a), nitrite (b), and ammonium (c). Mean daily average bioreactor temperature is shown in (a) as line with no symbols.*

The cumulative removal of NO_3^- amounted to 5131 kg N during the operational periods, with 53.7% and 46.3% reduced during the first and second operational years, respectively, and with an average daily removal of 16.2±0.4 kg N as NO_3^- (calculated as concentration multiplied by daily flow rate). The daily mass removal of NO_3^- increased with bioreactor temperature, and decreased with the HRT of the system (Figure 2a, Table 1). Effluent alkalinity generally increased/decreased with the magnitude of NO_3^- removal in the system. The production of alkalinity (HCO_3^-) is indicative of heterotrophic denitrification (see reaction 1).

NO_2^- concentrations in the incoming water were generally greater than in the effluent (Figure 2c). The exceptions to this was following the bioreactor start-up (days 1-7) and following the decrease in HRT to 1 day on day 429 (Figure 2c). For the entire duration of the test period, there was a net removal of 8.4 kg N as NO_2^- in the bioreactor. However, up until day 131,

the bioreactor was a net source of NO_2^- due to the initial high effluent NO_2^- concentrations (Figure 2b).

The bioreactor was a net source of NH_4^+ with a total production of 116.1 kg N as NH_4^+, and with a daily average production of 0.4±0.05 kg N as NH_4^+. The majority (68.6%) of the total produced NH_4^+ was emitted during the first operational year when greater NH_4^+ concentrations were observed (Figure 2c). The ratio between NH_4^+ production (effluent – influent NH_4^+ concentrations) and NO_3^- removal by denitrification (influent – effluent NO_3^- concentrations) was on average 3.8%, initially being 7.4% following the bioreactor start-up (days 1-10). At the onset of snowmelt during the second operational year following the winter intermission, the production of NH_4^+ relative to the reduced NO_3^- was 48.5±14.5% (days 325-329) due to the low removal of NO_3^- relative to the high effluent concentrations of NH_4^+ (Figures 2a, 2c).

The production of N_2O (data not shown) was on average 0.10±0.05% of the NO_3^- reduced as bioreactor temperatures were above 5°C. As temperatures decreased below 5°C, or the HRT decreased to 1 day, the N_2O production relative to the NO_3^- reduced increased and constituted ~100% of the reduced NO_3^-. Increased N_2O concentrations in effluent, as the bioreactor temperature decreased to below 5°C, were due to incomplete removal of NO_3^-.

Influent sulfate (SO_4^{2-}) concentrations were on average 1137.7 mg L^{-1} and sulfate reduction generally commenced whenever NO_3^- removal yielded NO_3^- concentrations below detection limits (0.06 mg N L^{-1}). The H_2S development was more prominent during the first operational year, as noted by smell.

High concentrations of organic carbon are commonly observed following the start-up of woodchip bioreactors (e.g. Gibert et al. 2008, Hoover et al. 2016). During the test period, the bioreactor was a net source of organic carbon, emitting a total amount of 5845 kg organic carbon (TOC) with an average daily emission of 21.4±4.4 kg TOC. 75.2% of the total emission of organic carbon occurred during the first year of operations, and 50% before day 47. The initial high export of organic carbon from the bioreactor may be reduced by using weathered instead of "fresh" woodchips (cf. Hoover et al. 2016).

Application of the technique to waste rock deposits

The emission of NO_3^- from explosive residues retained on waste rock masses is controlled by the water flow through the waste rock. In direct proximity to the woodchip bioreactor described in this study, the NO_3^- export from two experimental waste rock deposits 35m x 35m x 8m (w/b/h) (~3267 m^3) was determined (see Herbert and Nordström, these proceedings). During the operational period of the bioreactor, the cumulative NO_3^- export from the two (duplicate) experimental waste rock deposits was calculated as 2.4-3.2 and 12.3-25.3 kg N. The results from this study shows that a woodchip bioreactor of similar design could remove NO_3^- in leachate from 6.67-6.94 Mm^3 of waste rock under a period of two years in a subarctic climate. This estimate is only a minimum since the longevity of the treatment in the woodchip bioreactor is likely exceeding the two year test period (cf. Robertson 2010).

However, leachate from the two experimental waste rock deposits was mainly produced during snowmelt (see Herbert and Nordström, these proceedings) when bioreactor temperatures were below 5°C and NO_3^- removal was observed to be incomplete in the bioreactor with a comparatively high production of NH_4^+ and N_2O relative to the NO_3^- reduced (Figure 2). In addition, the observed intermittent production of large volumes of leachate (see Herbert and Nordström, these proceedings) would result in low HRTs in the bioreactor when most of the NO_3^- originating from explosive residues is emitted, resulting in a comparatively low removal of NO_3^- (see above). Periods of no leachate production would instead result in (excessively) high HRTs in the bioreactor. The results from this study suggest that periods of stagnancy (high HRTs) and complete removal of NO_3^- in the bioreactor could potentially trigger sulfate reduction (see above) and other undesirable reactions (e.g. methanogenesis).

Conclusions

During the two year test period, the woodchip bioreactor reduced a net amount of 5131 kg N as NO_3^- and 8.4 kg N as NO_2^- in mine drainage and process water originating from the use of ANFO explosives, with the net production of 116.1 kg N as NH_4^+. Influent NO_3^- (22.0±0.3 mg L^{-1}) was reduced to below detection limits (0.06 mg N L^{-1}) at HRTs between 1.9-2.6 days and bioreactor temperatures above 5 °C, with a daily removal rate of 16.2±0.4 kg N as NO_3^-. As the HRT was decreased to 1 day and/or bioreactor temperature decreased to below 5°C, NO_3^- removal was incomplete. During the first year of operation, the bioreactor was a net source of NO_2^- and a substantial amount of organic carbon was emitted from the bioreactor. The direct application of a denitrifying woodchip bioreactor to remove NO_3^- in leachate from waste rock deposits in subarctic climates is limited by the variability and timing of leachate production. These problems could, however, be circumvented by delaying and evenly distributing leachate delivery to the bioreactor over the operational period.

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