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Determination of major biogeochemical processes in a denitrifying woodchip bioreactor for treating mine drainage

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ABSTRACT

At the Kiruna iron ore mine in northern Sweden, mine drainage and process water contain elevated concentrations of nitrate (NO_3^-) from the use of ammonium nitrate fuel oil explosives. In order to investigate the treatment capacity of a denitrifying woodchip bioreactor technique for the removal of NO_3^- through denitrification, a bioreactor was installed at the mine site in 2015 and operated for two consecutive years. Neutral-pH mine drainage and process water containing 22 mg NO_3^--N and 1132 mg SO_4^{2-} (average) was passed through the bioreactor which was filled with a reactive mixture of pine woodchips and sewage sludge, at treatment temperatures ranging between 0.8 and 17 °C. At bioreactor temperatures above ~5 °C, NO_3^- removal proceeded to below detection limits (0.06 mg N L^{-1}) without substantial production of nitrite (NO_2^-), ammonium (NH_4^+), nitrous oxide (N_2O), or methane (CH_4). The relative production of NH_4^+ and N_2O to the NO_3^- reduced increased as bioreactor temperatures decreased below ~5 °C. Based on the resultant changes in alkalinity and pH from the production of bicarbonate (HCO_3^-) and carbonic acid (H_2CO_3), a stoichiometric mass balance model indicated that denitrification, nitrate reduction to ammonium (DNRA), sulfate reduction, and fermentation were the major biogeochemical processes controlling pH, alkalinity and nitrogen, sulfur and carbon concentrations in the system. It is suggested that fermentation changed from being mainly butyrate producing to acetate producing with time, triggering a decline in biogeochemical process diversity and leaving denitrification as the sole major electron accepting process.

1. Introduction

Ammonium nitrate (NH_4NO_3) is the most common explosive used in the mining industry (Forsyth et al., 1995) and is highly soluble in water. Due to spillage during storage, transport, and loading of the explosives, as well as the incomplete detonation of the explosives (Revey, 1996), NH_4NO_3 dissolves in mine drainage and process water and is eventually discharged to the environment, primarily in the form of nitrate (NO_3^-) (Lindeström, 2012). Excess release of NO_3^- to aquatic ecosystems can be hazardous as it may induce eutrophication leading to hypoxia, or may be transformed into ammonium (NH_4^+) or ammonia (NH_3). NH_4^+ is more easily incorporated into biomass than NO_3^- (Rittmann and McCarty, 2001), leading to increased risks of eutrophication, and may further be transformed into NO_2^-/NO_3^- through nitrification, an oxygen consuming reaction, both leading to increased risks of hypoxia in aquatic ecosystems. NH_3 is additionally toxic to aquatic biota at high concentrations (EPA, 2013).

Denitrification provides the possibility of completely transforming NO_3^- into nitrogen gas (N_2), a comparatively inert form of nitrogen (N) that is unavailable for uptake by most living organisms. The stoichiometric definition of net denitrification is exemplified in reaction (1) using glucose ($C_6H_{12}O_6$) as the carbon substrate/electron donor

$$NO_3^- + \frac{5}{24}C_6H_{12}O_6 \rightarrow \frac{1}{2}N_2 + HCO_3^- + \frac{1}{4}H_2CO_3 + \frac{1}{2}H_2O \quad (1)$$

Denitrification occurs under the sequential reduction of NO_3^-, NO_2^-, NO, and N_2O to N_2, and is known to be "leaky", such that intermediate NO_x species may accumulate.

Woodchip bioreactors have been identified as effective technologies for the removal of NO_3^- from contaminated water (e.g. Moorman et al., 2010; Robertson and Merkley, 2009; Warneke et al., 2011a). For a general overview of the woodchip bioreactor technology, the reader is refered to Schipper et al. (2010). In terms of the reactive material in the bioreactor, wood products (e.g. sawdust and woodchips) have increasingly been used as an electron source for denitrification due to the high content of carbon (electron donor) available at low cost (Schipper et al., 2010), and due to the longevity of the material (Moorman et al., 2010; Robertson and Merkley, 2009; Robertson, 2010; Warneke et al., 2011a).

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In this study, a pilot-scale woodchip bioreactor was installed in the subarctic climate at the Kiruna iron ore mine (northern Sweden) with the purpose of removing NO_3^- in mine drainage and process water originating from the use of ammonium-nitrate fuel oil explosives (ANFO). To the best of our knowledge, this is the first woodchip bioreactor that has been tested for the removal of NO_3^- from mine water.

The objectives of the study were to determine the predominating biogeochemical processes controlling pore water composition in the system. Furthermore, a mass balance approach was applied to nitrogen and sulfur in order to calculate changes in the carbonate speciation, and hence pH, based on reaction stoichiometry.

2. Material and methods

2.1. Study site

This study was conducted at the Kiruna iron ore mine, operated by the mining company Luossavaara-Kiirunavaara Aktiebolag (LKAB), and located in the subarctic climate of northern Sweden, Kiruna (67°51′N 20°13′E). The mean annual air temperature in the region of the study site was −3 °C for the period 1961–1990 (SMHI, 2017).

Mine drainage and process water are released through a clarification pond into the recipient Mettä Rakkurijärvi lake that drains through the Rakkuri river system into the Kalix River (LKAB, 2016), and ultimately to the Baltic Sea. The ore and waste rock has a low sulfide mineral content, and hence the pH of the site drainage is close to neutral at 8.05 ± 0.04. The water has relatively high concentrations of nitrogen (N) from the use of ammonium-nitrate fuel oil (ANFO) explosives (LKAB, 2016). In 2015, ~5,7 Mm^3 of mine and process water was released into the Mettä Rakkurijärvi lake, with an average NO_3^- concentration of 27.8 mg N L^{-1} (LKAB, 2016).

The bioreactor in this study was constructed near the point where water was discharged from the clarification pond to the recipient. Construction took place during May and June 2015.

2.2. Bioreactor design

The bioreactor was designed as a subsurface system: a ~1.1 m deep trench with trapezoidal cross-section was excavated and enclosed by ~1 m high mounds of waste rock material originating from the Kiruna iron ore mine. The total depth was 2.1 m. At the ground surface, the bioreactor was 44 m long and 6.65 m wide (see dimensions in Fig. 1a and b). The bottom of the trench was covered with a 1.5 mm thick impermeable geomembrane (high-density polyethylene, HDPE) serving as an impermeable boundary and preventing the leakage of water to the surrounding soil.

Five "inner walls" of plywood (W1–W5, Fig. 1a and b) were constructed and placed at 8.5 m intervals, demarcating six compartments (C1–C6, Fig. 1a), with the purpose of forcing water flow below the surface of the bioreactor (i.e. avoiding surface flow). The inner walls were fixated by their own weight and by the additional weight of steel I-beams that were placed on top of the walls (Fig. 1b).

W1–W4 measured 1.2 m in height, extending from approximately 0.1 m above the bioreactor surface to 1 m above the trench floor (Fig. 1b). W5 covered the entire cross section of the bioreactor and featured a rectangular weir (Fig. 1b) with an adjustable cross-sectional area intended for regulation of the water table in the bioreactor.

Water from the clarification pond was delivered to the bioreactor using a submersible pump placed at the clarification pond outlet, and a ball valve was used to adjust the input flow rate (Q) to the bioreactor system. The inlet water from the clarification pond was spread across the width of the bioreactor using a perforated PVC drainage pipe so that flow would be distributed as evenly as possible over the width of the bioreactor.

The outlet was constructed as a basal drain connected to a polyvinyl chloride (PVC) pipe extending to the surface of the bioreactor, emerging at 0.9 m from W5 (in the direction of flow, see Fig. 1a). The elevation at the top of the vertical drainage pipe was adjustable and regulated the water level in the bioreactor. The distribution of water over the width of the bioreactor at the inlet, and the broad-crested weir near the outlet, were both efforts to minimize preferential flow and reduce the advective velocity within the bioreactor; these are two factors that have been shown to maximize contact between the treated solution and the reactive material (Herbert et al., 2014; Nordström and Herbert, 2017).

The bioreactor featured 20 observation points referred to as A1–A20. A1 and A20 was the inlet and the outlet, respectively. A2-A19 were PVC pipes attached in different configurations on the inner walls of the bioreactor, and of two different designs used for pore water sampling. A3, A7, A11, A15, and A18 were sampled according to the BAT sampling technique (see Torstensson, 1984). The remaining PVC pipes ended in a 10 cm screen covered in a polyester plastic net filled with medium grained sand that worked as a filter to prevent smaller particles from passing through the well screens.

2.3. Bioreactor material

Previous column studies have shown that a mixture of pine woodchips and sewage sludge created a suitable biogeochemical environment for the promotion of denitrification at temperatures relevant at the study site (see Nordström and Herbert, 2017). Decorticated pine woodchips (porosity 0.54, estimated in the laboratory) were retrieved from a nearby sawmill, and digested sewage sludge was shipped from the Uddebo waste water plant, Luleå, northern Sweden. A digested form of sewage sludge was used as a source of denitrifying bacteria and was selected in preference of activated sewage sludge as it was easier to transport and handle.

Woodchips and sewage sludge were deposited in layers when filling the bioreactor. In total, 2.5 m^3 of digested sewage sludge and ~210 m^3 of decorticated pine woodchips were added to the bioreactor, yielding a sludge-woodchip ratio of 1:84 on a volume basis. The woodchips were emplaced and gently compressed using an excavator, while the sewage sludge was deposited manually. A sewage sludge slurry (sludge:water volume ratio ~1:10) was poured over the woodchips in layers located 50 cm and 100 cm above the geomembrane (S1–S2; Fig. 1c). Approximately 10 Liters of slurry were added per square meter of the woodchip surface. In addition, sludge (not slurry) was dispersed on the wood chip surfaces in the first three compartments (C1–C3, Fig. 1a). Note that no sewage sludge (or slurry) was added to compartment C6 in the bioreactor.

The accumulated thickness of the layers of pine woodchips and sewage sludge in C1, C5, C6 and C2–C4, was ~1.7 m and 1.2 m, respectively. The mixture of pine woodchips and sewage sludge was then covered with a geotextile as to minimize the contact with the atmosphere. In compartments C2–C4, 0.9 m of glacial till (primarily silty-sand with detrital organic matter, but also with larger cobbles < 300 mm) was placed, and compressed, on top of the geotextile using an excavator. The purpose of the till layer was primarily for forcing the flow to pass through the more permeable woodchip material and minimize gas exchange (O_2, CO_2, N_2O, CH_4) between the bioreactor interior and the surrounding atmosphere. The till layer also decreased the infiltration of precipitation into the permeable woodchip material, which would lead to a dilution effect. The geotextile underlying the till prevented the till from migrating into the woodchip material and thereby risking a decrease in permeability. During the placement of the glacial till, the bioreactor was saturated with water from the clarification pond at a flow rate of 2 L s^{-1}.

2.4. Bioreactor operation

After the saturation of the bioreactor system, the pore water was slowly recirculated for 10 days (cf. Nordström and Herbert, 2017) to