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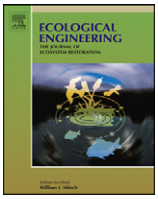

Efficacy of a denitrification wall to treat continuously high nitrate loads

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ABSTRACT

Denitrification walls have been proven as an effective, long-term method for remediating nitrogen in groundwater underneath agricultural lands. Utilizing walls to provide large N load reductions requires targeting a significant portion of agricultural effluent. One approach for more efficient application of walls is to locate them adjacent to zones with high groundwater flow, although treatment efficacy in these conditions is uncertain. In this study, a large wall (168 m^3) receiving high N loads was assessed using a well transect array for hydraulic and water quality evaluations and media were collected from within the wall to evaluate enzyme activity with flow distance. Porewater velocity through the wall was rapid (1.7 m day^{-1}) with short detention times (1.7–1.9 days), yet the wall treated 100 ± 28 m^3 of groundwater per day, effectively removing 228 ± 155 kg of total N per year. Maximum nitrate-N removal rates per media volume (4.9–5.5 g-N m^{-3} d^{-1}) were at the upper end of published values. Rapid reduction of potential denitrification rates in media samples from 4.89 g N m^{-3} d^{-1} to undetectable within a quarter of the wall length suggests that nitrate-N depletion drove a rapid reduction in denitrifying enzymes. Based on a carbon mass balance, dissolved organic C leaching was initially the largest C export process and the longevity of total bioavailable C was estimated as 23 ± 5.9 years. These results indicate the ability of walls to reduce high N-loads over long timespans.

1. Introduction

Agriculture is the most extensive source of nitrate-N to groundwater and increases in nitrate-N within shallow groundwater due to modern agricultural practices have been well documented (Andersen and Kristiansen, 1984; Hallberg, 1989; Hill, 1983; Hudak, 2000; Nolan and Stoner, 2000; Nolan, 2001; Puckett et al., 1999; Refsgaard et al., 1999; Breemen et al., 2002). The efficiency of N applied and ultimately consumed by humans or livestock is generally low, with approximately 33% of all N added to agroecosystems consumed by humans or livestock, while 65% is lost to the atmosphere or aquatic ecosystems (Galloway et al., 2003; Smil, 2001, 2002). Additionally it has been estimated that in the US, farmers typically over fertilize with N by 24 to 38% (Babcock and Blackmer, 1992; Trachtenberg and Ogg, 1994). As a result of this low efficiency, nitrate-N concentrations in shallow groundwater underneath agricultural lands exceed the maximum contaminant level (MCL = 10 mg L^{-1}) in 19% of samples nationwide (Nolan and Stoner, 2000). In addition to fertilizer efficiency improvements, edge of field remediation processes can help achieve water quality standards for N.

Denitrification is a microbial process that mitigates nitrate-N pollution by reducing nitrate-N to N_2 or N_2O in hypoxic conditions utilizing an electron donor such as organic carbon. Several techniques have been utilized to increase the denitrification rate in agricultural effluent by adding a C amendment such as woodchips or sawdust. These include ‘denitrification beds’ and ‘denitrification walls’, both of which are termed denitrification bioreactors (Schipper et al., 2010). Denitrification beds are often containerized treatment systems consisting of wood chips-alone, treating concentrated discharges from natural or tile-drainage systems. Denitrification walls are traditional permeable reactive barriers (PRBs) inserted vertically into the ground to intercept groundwater flow. Denitrification is stimulated in these PRBs by adding an organic carbon amendment such as sawdust or woodchips to stimulate the denitrification process and reduce effluent nitrate-N concentrations.

Scaling-up denitrification walls for widespread application to reduce groundwater nitrate-N require efficiently maximizing treatment area and volume. When denitrification walls are installed in aquifers with low porewater velocities, volumetric treatment rates are low and N-limiting conditions are more likely

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Abbreviations: DEA, denitrification enzyme activity; MBC, microbial biomass carbon; TKN, total Kjeldahl nitrogen; TMDL, total maximum daily load; PRB, permeable reactive barrier; DOC, dissolved organic carbon.

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to occur in a fraction of the groundwater flow-length within the wall. One technique to increase treatment efficiency is to deploy denitrification walls to target zones of high porewater velocities, such as adjacent to a ditch or in riparian areas where groundwater discharges to surface water. This will reduce the occurrence of N-limiting conditions and allow for high volumetric treatment rates and greater reductions in nitrate-N loading rates. In this study, this concept was evaluated by the construction of a relatively large denitrification wall (168 m^3) immediately adjacent to a stream where high porewater velocities and nitrate concentrations directed a high nitrate load through the wall.

2. Materials and methods

2.1. Site location and construction

The study area was located in a 65 ha container nursery in Alachua, Florida that sells plants for the landscape market, which are all grown in containers partially buried in the soil. The nursery is located in a watershed (Fig. 1a), which has total maximum daily load (TMDL) restrictions for nitrate-N (Hallas and Magley, 2008). Soils in the groundwatershed of the denitrification wall are excessively to moderately well drained and consist of >93% sand sized particles to ~2 m depth overlying a clay aquitard 2–2.4 m below the surface (USDA, 1985). Excessive N leaching from the bottom of the plant container drains through the surface soils in to a shallow aquifer resulting from a subsurface clay aquitard. This shallow groundwater is transported laterally towards the edge of the property where declining surface elevations exposes the aquitard and forces groundwater to the surface in numerous seepage slopes. The denitrification wall was installed adjacent to this break in elevation, approximately 14 m upgradient from a small stream, which begins as a significant seepage discharge (Fig. 1a). The lowest depth of the wall was installed a few inches in to the clay-rich aquitard to prevent groundwater bypass. The shallowest depth was 1.8 m above that at a height which for two years had been the highest water table measured within an adjacent well. The final dimensions of the wall are 55 m long, 1.7 m wide and 1.8 m deep (168 m^3).

The denitrification wall was constructed on September 30th, 2009. A washed and sieved quartz sand (Edgar Minerals, Inc., Edgar, Florida) was mixed with pine sawdust in a 1:1 ratio by volume. The sand and sawdust were mixed above ground, and then as soil and groundwater were excavated along the trench, the sand-sawdust media was rapidly placed in the excavated pit. The C content of the final sand-sawdust mixture was 7.4 ± 0.7%. After construction, four subsamples were collected of the final mixture within the trench.

2.2. Nitrogen and dissolved organic C groundwater measurements

Monitoring wells were installed to the bottom of the denitrification wall in three parallel transects using U.S. environmental protection agency (USEPA) guidelines (USEPA, 2008) (Fig. 1b). Wells were placed upgradient, within (center), and downgradient of the wall in three transects to monitor nitrate-N, total Kjeldahl N (TKN), and dissolved organic C loading as well as groundwater temperature, dissolved oxygen, porewater velocity, direction and elevation.

Water samples were collected within each well weekly for 20 weeks and then monthly thereafter for 660 days after construction after purging two well volumes using a submersible pump (Mini Typhoon® DTW, Proactive Environmental Products, Bradenton, FL). Samples were collected and either filtered through a 0.45 μm membrane filter (Pall Corporation, Port Washington, NY), then acidified or unfiltered and acidified directly, stored on ice and transported to the laboratory. Unfiltered samples were digested using a block digester and analyzed colorimetrically for TKN (EPA Method 351.2) on an autoanalyzer (Seal Analytical, West Sussex, UK). Filtered samples were analyzed for nitrate-nitrite colorimetrically (EPA Method 353.2) after cadmium reduction on an autoanalyzer (Seal Analytical, West Sussex, UK). Total organic C (TOC) was determined using EPA Method 415.1, after combustion as non-purgable organic C on an infrared gas analyzer (Shimadzu Corp, Kyoto, Japan). Dissolved oxygen was measured directly in the wells by slowly raising and lowering an YSI multi-probe (556 MPS, YSI Incorporated, Yellow Springs, Ohio) throughout the groundwater column.

2.3. Hydraulic measurements

Effective porosity of the wall was determined in triplicate as the fraction of saturated water volume drained at field capacity (33 kPa) (Ahuja et al., 1984; Timlin et al., 1999) in a laboratory study using recreated cores of sand and sawdust in the same ratios and same bulk density as the wall. Cores were vacuum saturated in tempe cells (Soil Moisture Equipment Co., Santa Barbara, CA), then allowed to drain to a porous surface for 72 h. This field capacity measure of effective porosity has been determined as a better predictor of the mobile groundwater volume in wall media than total porosity (Barkle et al., 2007).

The focusing of groundwater through permeable reactive barriers (PRBs) has been hampered by decreases in hydraulic conductivity due to construction, thus instigating bypass flow (Barkle et al., 2007; Schipper et al., 2004). The hydraulic conductivity (K_{sat}) was therefore determined in all nine wells using the Hvorslev slug-test method as described in the following equation (Fetter, 2001).

$$K_{sat} = \frac{r^2 \ln(L_e/R)}{2L_e t_{37}}$$

In this equation, K_{sat} is the saturated hydraulic conductivity $[\mathrm{L\,T^{-1}}]$, r is the well casing radius [L], L_e is the length of the well screen [L], R is the borehole radius, and t_{37} is the time it takes for the water level to fall to 37% of initial head change.

Porewater velocity and direction were measured periodically in wells at 0.4, 0.8 and 1.2 m from the bottom of the denitrification wall using a heat-pulse flowmeter (GeoFlo Model 40, Kerfoot Technologies, Mashpee, MA). The direction and velocity readings of the flowmeter are calibrated by pumping a known velocity and direction in a tank containing the well screen surrounded by the same standard sand filter pack used in the field well installation. This procedure yielded an r^2 for velocity of 0.999 and a standard deviation for direction of ± 2 degrees around the true value. Heat-pulse groundwater flowmeters have been field-verified as accurate representations of porewater velocity and direction as compared to piezometer gradients with average velocity uncertainties of only 0.02–0.04 m d^{-1} and direction uncertainties of 4.9–7.4 degrees (Alden and Munster, 1997).

Water level elevations and temperature were measured hourly over 462 days by pressure transducers placed in the wells (Global Water. Gold River, CA). To provide a confirmation on the flowmeter results and a more continuous measurement of groundwater mobility, porewater velocities were determined using Darcy's law based on measured head gradients from transducers, K_{sat}, and effective porosity.