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Deciphering and modeling the physicochemical drivers of denitrification rates in bioreactors☆

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ABSTRACT

Denitrification bioreactors have served as effective artificial N sinks by stimulating denitrification and remediating excessive nitrate. Predictions on bioreactor performance will be improved by quantifying the relationship between denitrification rates and causal factors which vary by geography (temperature), land-use intensity (NO_3 concentration) and media type (carbon quality, quantity, and surface area). Experimental mesocosms filled with different wood media types (oak, pine), particle sizes and wood–sand volume ratios were exposed to flowing high-nitrate groundwater across a range of seasonal groundwater temperatures (8–24 °C) to determine the influence of these coarse but utilitarian parameters on bioreactor performance. To increase the transferability and specificity of findings, a multivariate analysis was used to quantify relationships between denitrification rates, microbial biomass, temperature, media surface area to volume ratio and metrics of C quality to guide de novo media selection and performance predictions. There were no strong differences in hydraulic conductivity, media consumption rates, and TKN flux between different treatments although increasing the wood–sand volume ratio alone produced significant increases in denitrification rates and undesirable DOC leaching. Fluxes of DOC and TKN also increased with higher hydraulic loading rates. Denitrification rates were unresponsive to nitrate concentration and most strongly influenced by groundwater temperature ($Q_{10} = 4.7$), although carbon bioavailability and media surface area were uniquely predictive of denitrification rates. Bioreactor performance will therefore be most strongly influenced by geographical variations in temperature, although within a specific location, bioreactor media selection will influence denitrification rates.

1. Introduction

The use of N-based fertilizer will need to increase to meet future demands for agricultural crops (Tenkorang and Lowenberg-DeBoer, 2009), yet existing N application rates have been implicated as the main source of coastal eutrophication (Howarth and Marino, 2006) and a significant contributor to the growth of large hypoxic dead zones in regions such as the Gulf of Mexico (Goolsby and Battaglin, 2000) and Chesapeake Bay (Hagy et al., 2004). Producing sufficient crops to feed a growing planet will require efficient food production in combination with innovative and sustainable practices to protect aquatic ecosystems. The long-term success of carbon-based denitrification bioreactors (Long et al., 2010; Moorman et al., 2010; Robertson et al., 2008) to create hotspots of biological denitrification (Warneke et al., 2011a), and cost-effectively and efficiently remove nitrate (NO_3) from groundwater with limited maintenance, indicates this technology is a feasible treatment option. Denitrification bioreactors have generally taken the form of; lined beds filled with woodchips used to treat point sources of agricultural effluent, and denitrification walls where wood chips or sawdust were mixed with the soil in a permeable reactive barrier (PRB) to treat non-point sources (Schipper et al., 2010). To supplement the application of denitrification walls where non-point N is the concern (Schmidt and Clark, 2012a,b), factors affecting denitrification wall performance were examined.

Bioreactor denitrification rates are influenced by a variety of factors including the relatively immutable site specific factors

Abbreviations: CPS, coarse pine sawdust treatment; FPS, fine pine sawdust treatment; OS, oak sawdust treatment; LCI, lignocellulose index; LOI, loss on ignition; MBC, microbial biomass carbon; NDF, neutral detergent fiber; PRB, permeable reactive barrier; ShrP, shredded pine treatment; TKN, total Kjeldahl nitrogen; DOC, dissolved organic carbon.

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such as the groundwater temperature and influent nitrate concentration and the type and properties of media. Previous research has indicated that wood media sustains adequate denitrification rates over longer time spans and has fewer adverse effects (N_2O emissions, TKN, DOC export) as compared to more labile media (maize cobs, wheat straw, green waste) (Cameron and Schipper, 2010; Long et al., 2010; Schipper and Vojvodic-Vukovic, 2001; Warneke et al., 2011c). As a result, wood has been the most common media used. Denitrification wall media has included; hardwood (Robertson et al., 2000) and softwood sawdust (Schipper and Vojvodic-Vukovic, 1998; Schmidt and Clark, 2012a,b) wood chips (Jaynes et al., 2008) and with volume mix ratios of wood to sand ($\nu_{\text{wood}}/\nu_{\text{total media}}$; wood volume ratio) of 0.20 (Robertson and Cherry, 1995; Schipper et al., 2004), 0.50 (Schipper and Vojvodic-Vukovic, 1998) and 1.0 (Fahrner, 2002). Predictions on bioreactor performance and denitrification rates within a specific site can be improved by assessing and quantifying influential media properties which affect nitrate removal rate, microbial biomass and denitrification enzyme activity. Additionally, some bioreactors have been hampered by the occurrence of unintended negative consequences that may be correlated to media properties such as undesirable variations in hydraulic conductivity (Schipper et al., 2004), as well as excess dissolved organic C (DOC) and total Kjeldahl N (TKN) export (Cameron and Schipper, 2010; Schmidt and Clark, 2012a,b). Determining the impacts resulting from variations in commonly available wood types (oak, pine), sizes (sawdust, chips, etc.) and wood volume ratio will improve predictions on groundwater denitrification rates and the potential occurrence of adverse effects in denitrification walls.

Bioreactor guidelines based on wood type, particle size and wood volume ratios may have a pragmatic, albeit limited utility because general wood properties which could affect denitrification rate and microbial populations (C availability, surface area/porosity) can vary due to differences in species, age (Robertson, 2010), plant components, preparation methods, and climate of the growing region (Kilpelainen et al., 2003). The profuse application of bioreactors can be facilitated by predictions based solely on measurable physicochemical drivers of microbial properties and nitrate reduction rates. Previous researchers have made inferences on the influence of wood surface area and C bioavailability on denitrification rates in bioreactors utilizing metrics of wood grain size (Cameron and Schipper, 2010), respirable C (Schipper and Vojvodic-Vukovic, 2001; Warneke et al., 2011b,c) and C:N ratio (Greenan et al., 2006). Warneke et al. (2011c) showed that respirable C was positively correlated with denitrification rate, although the specific properties of the media that influence C respiration weren't determined. Guiding de novo media selection requires determining the proximate causal wood media properties which influence denitrification rate and microbial activity. Greenan et al. (2006) observed that media which had a lower C:N ratio and presumably lower lignin content tended to have higher denitrification rates, although this relationship wasn't quantified. Quantifying and interpreting foundational C bioavailability metrics which are uniquely correlated with denitrification rate will improve our understanding of microbial processes and facilitate predictions of bioreactor performance.

The influence of media surface area on denitrification rates has also been examined. The surface area in a given volume (surface area to volume ratio) of wood media could plausibly influence denitrification rates due to an increased area for extracellular enzyme exposure and bacterial colonization. Because the surface area to volume ratio is inherently related to grain size, researchers have compared media of differing grain sizes and they have found a weak to non-detectable influence on denitrification rates (Cameron and Schipper, 2010; Robertson et al., 2000). Grain size is not always a strong determinant of the surface area due to variations in the effective porosity of the wood, therefore surface area alone needs to be quantified to accurately decipher this relationship.

Predictions on bioreactor performance based on wood media properties alone will need to incorporate the variability in groundwater temperature and influent nitrate concentrations at installation sites, which both affect denitrification reaction kinetics (Cameron and Schipper, 2010; Elgood et al., 2010; Robertson et al., 2008; Robertson, 2010; van Driel et al., 2006a,b; Warneke et al., 2011b,c). The correlation between temperature and denitrification rates has been hypothesized as an exponential relationship with a doubling of denitrification rates every 10 °C (Q_{10} = 2.0), although Q_{10} values for denitrification rates have varied by an order of magnitude (0.16–4.95) (Cameron and Schipper, 2010; Elgood et al., 2010; Robertson et al., 2008; Warneke et al., 2011c). Similarly, the relationship between nitrate concentration and denitrification rate has been hypothesized to be non-linear following Michaelis–Mentin kinetics. Some studies have failed to confirm this (Robertson, 2010; Warneke et al., 2011b), while another study found a strong influence of nitrate concentration on denitrification rates (Christianson et al., 2012). Further controlled studies will be required to quantify these relationships.

In the following study, nitrate-N removal rates were evaluated in experimental mesocosms filled with different wood media types, sizes and wood volume ratios for 246 days. Water samples were collected at several locations within the mesocosm to assess the influence of declining nitrate-N concentrations on the kinetics of the denitrification reaction. Groundwater temperature was measured during each sampling event to determine the covariance of temperature and each treatment. The differences in nitrate-N removal rates and the occurrence of adverse effects (low hydraulic conductivity, DOC and TKN export) were evaluated between treatments (type, size, and volume ratio) to provide pragmatic guidelines on bioreactor implementation utilizing commonly available wood media. Empirical relationships between predictive metrics of bioreactor media (total C, C:N ratio, surface area and fiber quality) were quantified to determine whether C quality and/or quantity significantly increases TKN and DOC production, microbial biomass and experimental and laboratory measures of denitrification rates. Because metrics of surface area, C quality and quantity may be cross-correlated, a step-wise multivariate analysis was utilized to filter cross-correlated variables and construe the parameters which had discrete and strong contributions to measured nitrate-N removal rates and estimates of microbial biomass. From these results a statistical model was developed to provide transferable predictions on bioreactor performance from measurable predictor variables.

2. Materials and methods

2.1. Experimental design

Groundwater from underneath an agricultural property described in Schmidt and Clark (2012a,b), with an average nitrate-N concentration of 7.5 ± 0.73 mg L^{-1} continuously flowed vertically through PVC mesocosms (diameter 15.2 cm, length 152 cm) filled with different wood types, particle sizes and volume ratios ($\nu_{\text{wood}}/\nu_{\text{total media}}$) for 246 days (Fig. 1). The groundwater was pumped from a well to a sealed bladder contained within a water bath, protected from atmospheric exposure, and discharged through the treatments via precisely controlled head gradients (Fig. 1). The experimental unit was covered with a tent and each individual external component was wrapped with reflective and