Effect of biochar, hydraulic residence time, and nutrient loading on greenhouse gas emission in laboratory-scale denitrifying bioreactors

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ABSTRACT

Increased adoption of denitrifying bioreactors to mitigate nutrient export in agricultural drainage can improve water quality but also raises concerns about potential unintended consequences of widespread implementation. Greenhouse gas (GHG) emissions, especially as nitrous oxide (N_2O) produced during denitrification, are of particular concern. To gain understanding of the variables controlling bioreactor GHG production, the effects of nutrient loading, hydraulic residence time, and biochar addition on emissions of N_2O, methane (CH_4), and carbon dioxide (CO_2) were tested in 6550 cm^3 laboratory columns. Biochar, an organic carbon pyrolysis product, was hypothesized to reduce GHG emissions, as has been reported with its use as an agricultural soil amendment. GHG fluxes were measured during 5-day trials using the closed dynamic chamber technique. The 36 combinations of three media types (woodchips, 10% biochar, and 30% biochar), three residence times (3, 6, and 12 h), and four influent formulations, all combinations of high and low nitrogen as nitrate (16.1 and 4.5 mg NO_3-N L^{-1}) and phosphorus as orthophosphate (1.9 and 0.6 mg PO_4-P L^{-1}) concentrations, were tested in triplicate. Treatment effects were assessed with linear mixed effects models. Biochar addition, particularly at the 30% rate, was found to increase N_2O and CO_2 emissions and the proportion of removed NO_3-N released as N_2O-N. However, quantified GHG flux rates were not environmentally concerning. Methane fluxes were negligible, and CO_2 fluxes were not considered to increase net GHG emissions. Nitrous oxide fluxes normalized to surface area averaged 2.92 mg N_2O-N m^{-2} d^{-1}, and 98% of measured fluxes were within the range previously reported for woodchip bioreactors and considered acceptable.

1. Introduction

The establishment of denitrifying bioreactors among accepted agricultural best management practices (BMP) to reduce nitrogen (N) export in drainage waters is underpinned by a growing body of research establishing N removal efficiencies (e.g., Addy et al., 2016) and relating performance to design parameters including bed volume, dimensions, and target hydraulic residence time (HRT) (Christianson et al., 2013; Christianson et al., 2011a; Sharrer et al., 2016). Maximizing removal of nitrate as nitrogen (NO_3-N) has been the primary focus of bioreactor development, but current work increasingly focuses on mitigating potential negative environmental impacts of bioreactors. Pollution swapping potential, the trade-off between enhancing NO_3-N removal and producing environmentally harmful byproducts, is often acknowledged, quantified, and incorporated into assessment of bioreactor performance (Christianson et al., 2017; Healy et al., 2012, 2015; Warneke et al., 2011a,b). These byproducts include greenhouse gases (GHGs),

methylmercury (CH_3Hg^+), and excess dissolved organic carbon. GHG emissions, specifically nitrous oxide (N_2O) produced via incomplete denitrification, were among the earliest identified concerns regarding widespread bioreactor implementation (Schipper et al., 2010), and have since been quantified in several laboratory- (Bock et al., 2015; Feyereisen et al., 2016), pilot- (Warneke et al., 2011b), and field-scale systems (Elgood et al., 2010; Moorman et al., 2010; Warneke et al., 2011a; Woli et al., 2010). Although problematic rates of N_2O flux have not been reported, the high variability of GHG emissions from agricultural soils (e.g., Mathieu et al., 2006; Oertel et al., 2016) suggests flux dynamics could complicate efforts to estimate average or cumulative emissions from denitrifying bioreactors. Given the expense and technical challenges of measuring GHG flux with high spatial or temporal resolution, few controlled experiments to determine the effect of bed conditions on GHG emissions in bioreactors have been conducted. However, such experiments could provide valuable insight into the factors controlling bioreactor GHG production and potentially inform

system design aimed at minimizing emissions.

Substrate engineering is one approach to mitigating bioreactor GHG emissions. Modifying the typical woodchip substrate of bioreactors by adding biochar, an organic carbon pyrolysis product developed as a soil amendment, merits investigation because significant reductions in GHG emissions from agricultural soils have resulted from biochar application (Florinsky et al., 2004; Kookana et al., 2011; Saarnio et al., 2013; Sohi et al., 2010). However, instances of biochar increasing N_2O emissions have also been reported (Bruun et al., 2011; Yanai et al., 2007). Biochar has also been shown to reduce leaching of NO_3-N, phosphorus as orthophosphate (PO_4-P), and organic carbon from soils (Beck et al., 2011), potentially providing additional opportunities to mitigate pollution swapping in bioreactors. General characteristics of biochar that induce changes in soil properties include high specific surface area, micropore volume, cation exchange capacity, and water holding capacity (Kookana et al., 2011; Lehmann et al., 2011; McLaughlin et al., 2009). These biochar-induced changes in turn affect soil biological and physiochemical processes driving nutrient cycling and GHG emissions (Anderson et al., 2011). Different mechanisms of N_2O flux suppression related to these characteristics have been reported. Clough and Condron (2010) describe the ability of alkaline biochar to raise pH which favors production of N_2 over the accumulation of N_2O during denitrification. Saarnio et al. (2013) found that biochar indirectly decreased N_2O emissions through its effect on increasing soil moisture. However, Case et al. (2015) reported that biochar suppressed N_2O emissions in a completely saturated sandy loam, suggesting a mechanism unrelated to the effect on soil water holding capacity.

Perhaps unsurprisingly, reports of the effect of biochar on GHG emissions in woodchip bioreactors have been mixed. A simple laboratory batch experiment showed that biochar-amended woodchips produced less N_2O than woodchips alone in gastight bioreactor columns (Bock et al., 2015; Easton et al., 2015), whereas no effect of biochar on N_2O production was observed by Christianson et al. (2011c) in a benchtop study with flow-through columns. Yet aside from its effect on GHG flux, biochar may hold potential to increase NO_3-N removal in bioreactors. Pluer et al. (2016), Hassanpour et al. (2017) and Bock et al. (2015; 2016) observed greater NO_3-N removal rates in both laboratory and field bioreactors amended with biochar than with woodchips alone. Furthermore, an economic analysis applying an empirical model of bioreactor NO_3-N removal developed from a pilot-scale experiment (Bock et al., 2016) suggests biochar addition may be cost-effective given sufficient drainage area and NO_3-N loading to the bioreactor, where the benefits of enhanced NO_3-N removal outweigh the additional monetary cost of the biochar (DeBoe et al., 2017). However, as noted by Christianson and Schipper (2016), these results require validation in field testing. Nonetheless, additional investigation of the ability of biochar to enhance bioreactor function is warranted.

The objective of this study was to quantify the effect of biochar amendment on diffusive flux of N_2O, methane (CH_4), and carbon dioxide (CO_2) from woodchip bioreactors while simultaneously evaluating the effects of nutrient loading rate and HRT over time. The hypothesis that biochar addition lowers GHG emissions relative to woodchips alone was tested across different HRTs and nutrient loading rates in bioreactor columns under controlled laboratory conditions; simultaneously, the effect of biochar on NO_3-N and PO_4-P removal was also evaluated and is reported elsewhere (Coleman, 2017).

2. Methods

The effect of media type, HRT, and NO_3-N and PO_4-P loading rate on GHG (N_2O, CH_4, and CO_2) flux was tested using horizontal flow-through denitrifying bioreactor columns $6560 \pm 30 \, cm^3$ in volume (Fig. 1). The three media types tested were woodchips (W), woodchips with a 10% biochar by volume (B_{10}), and woodchips with 30% biochar by volume (B_{30}). Three target HRTs (3, 6, and 12 h) were tested, which encompassed the range of 4–8 h recommended to meet a target load

reduction of 45% (Christianson et al., 2011b; Christianson et al., 2013). Four formulations of artificial agricultural drainage, each combination of representative high and low NO_3-N ($16.1 \, mg \, L^{-1}$ and $4.5 \, mg \, L^{-1}$) and PO_4-P ($1.9 \, mg \, L^{-1}$ and $0.6 \, mg \, L^{-1}$) concentrations, were continuously pumped through the columns during testing. All 36 combinations of media type, HRT, and influent formulation were tested in triplicate using 12 columns reused over nine trials. In each trial, a single combination of media and HRT was tested, and each of the four influent concentrations was pumped through three independent replicate columns.

2.1. Column design

Bioreactor columns $6560 \pm 30 \, cm^3$ in volume were constructed from 10.2 cm (4 in) inner diameter (i.d.) schedule 40 PVC pipe (see Fig. 1). A 45° wye with a 5.1 cm i.d. branch and 10.2 cm socket connections was installed approximately 70% of the length toward the outlet to function as a gas sampling port. A short section of 5.1 cm PVC was cemented to the branch of the wye to accommodate a removable socket cap, which was used to isolate the headspace during GHG flux measurement. The wye was uncapped so that the bioreactor column headspace freely exchanged with the atmosphere between GHG measurements. Endcaps with removable threaded plugs were affixed to each end of the column with PVC primer and cement and pipe thread sealant to maintain a gas- and watertight seal. Couplings with barbed tube fitting adaptors were installed in the threaded plugs and attached to inlet tubing supplying the column-bioreactors with nutrient solution or outlet tubing freely draining effluent. As shown in Fig. 1, the inlet coupling was located near the top of the horizontally-oriented column at a height of 9.75 cm from the bottom, and the outlet coupling was at a height of 7.5 cm, just above the height of the fill media, to control the volume of water contained in the column and leave a headspace sufficient for gas sampling. During the trials, the nutrient solutions pumped through the columns using two peristaltic pumps (Masterflex, Cole-Parmer, Vernon Hills, IL). Details of the experimental design are also reported in the companion study of nutrient removal by Coleman (2017).

2.2. Experimental treatments

Organic carbon media included locally-sourced woodchips of mixed hardwood species and biochar produced from pine (*Pinus sp.*) feedstock (Biochar Now, Carbondale, CO). To avoid confounding effects of the "first flush" of labile nutrients and organic C associated with bioreactor startup (Abusallout and Hua, 2017; Sharrer et al., 2016), the woodchips had been aged outdoors exposed to ambient temperatures and precipitation for approximately one year, though the biochar was fresh. The biochar was manufactured by a two-stage pyrolysis process where low oxygen conditions are maintained and the feedstock is held briefly (< 1 min) at 500–700 °C followed by up to 14 min at 300–550 °C. The material consisted of two size fractions by volume, 80% with dimensions approximately 1.5 cm by 1 cm by 0.5 cm and the remaining 20% a fine dust fraction ranging 10–100 μm. For each trial, $5000 \pm 100 \, cm^3$ (1900 ± 38 g) of fresh woodchips were used for each column. For the B_{10} and B_{30} treatments, $500 \pm 10 \, cm^3$ (162 ± 4 g) or $1500 \pm 10 \, cm^3$ (485 ± 4 g) of biochar was combined thoroughly with the woodchips to produce a homogeneous mixture before filling the columns. The biochar filled the interstitial spaces between the woodchips, so the column headspace remained constant across treatments, reducing the likelihood that differences in headspace volume or geometry would affect flux measurements. Prior to the start of each trial, the columns filled with new media were primed with the same nutrient solution as would be used for testing by filling and draining them three times over five days, followed by a triple rinse with deionized water. Previously, the woodchips were inoculated with microbes by incorporating a small amount of native soil (< 2% by volume).