



## Research article

## Performance of an under-loaded denitrifying bioreactor with biochar amendment

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## ABSTRACT

Denitrifying bioreactors are recently-established agricultural best management practices with growing acceptance in the US Midwest but less studied in other agriculturally significant regions, such as the US Mid-Atlantic. A bioreactor was installed in the Virginia Coastal Plain to evaluate performance in this geographically novel region facing challenges managing nutrient pollution. The 25.3 m<sup>3</sup> woodchip bed amended with 10% biochar (v/v) intercepted subsurface drainage from 6.5 ha cultivated in soy. Influent and effluent nitrate-nitrogen (NO<sub>3</sub>-N) and total phosphorus (TP) concentrations and flowrate were monitored intensively during the second year of operation. Bed surface fluxes of greenhouse gases (GHGs) nitrous oxide (N<sub>2</sub>O), methane (CH<sub>4</sub>), and carbon dioxide (CO<sub>2</sub>) were measured periodically with the closed dynamic chamber technique. The bioreactor did not have a statistically or environmentally significant effect on TP export. Cumulative NO<sub>3</sub>-N removal efficiency (9.5%) and average removal rate (0.56 ± 0.25 g m<sup>-3</sup> d<sup>-1</sup>) were low relative to Midwest tile bioreactors, but comparable to installations in the Maryland Coastal Plain. Underperformance was attributed mainly to low NO<sub>3</sub>-N loading (mean 9.4 ± 4.4 kg ha<sup>-1</sup> yr<sup>-1</sup>), although intermittent flow, periods of low HRT, and low pH (mean 5.3) also likely contributed. N removal rates were correlated with influent NO<sub>3</sub>-N concentration and temperature, but decreased with hydraulic residence time, indicating that removal was often N-limited. GHG emissions were similar to other bioreactors and constructed wetlands and not considered environmentally concerning. This study suggests that expectations of NO<sub>3</sub>-N removal efficiency developed from bioreactors receiving moderate to high NO<sub>3</sub>-N loading with influent concentrations exceeding 10–20 mg L<sup>-1</sup> are unlikely to be met by systems where N-limitation becomes significant.

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## 1. Introduction

Artificial drainage of poorly-drained soils increases agricultural productivity and promotes soil conservation, but elevated concentrations of nitrogen (N) and phosphorus (P) are often detected in drainage waters. A large body of research links agricultural drainage to increased N and P export to water bodies and resultant water quality degradation (e.g., David et al., 2015; Dinnes et al., 2002; Ikenberry et al., 2014). Agricultural nutrient losses are exacerbated by accelerated removal of water from the soil profile via both surface (ditches) and subsurface (tile) drainage, which reduces the opportunity for plant uptake, soil sorption, and nutrient cycling. With over 36.8 million ha of tile-drained cropland

in the US according to the 2012 census of agriculture (USDA NASS, 2012), various best management practices (BMPs) to reduce the water quality impact have been developed, including the use of control structures to adjust in-field water table height, riparian buffers, and denitrifying bioreactors.

Denitrifying bioreactors are structural BMPs that intercept N-enriched drainage water and support naturally-occurring soil microorganisms that convert nitrate-nitrogen (NO<sub>3</sub>-N) into inert dinitrogen gas (N<sub>2</sub>), thereby removing bioavailable N before it enters a water body. This process, heterotrophic denitrification, occurs under anaerobic conditions in the presence of sufficient NO<sub>3</sub>-N and organic carbon. Denitrifying bioreactors utilizing woodchip substrate are increasingly accepted drainage BMPs in the Midwest, as evidenced by their incorporation into state-level nutrient reduction strategies in the Upper Mississippi River Basin (IA EPA, 2015; IDALS, 2014; MN PCA, 2014) and the development of a USDA-NRCS conservation practice standard (USDA-NRCS, 2015). However, less work has been done outside of the Corn Belt to evaluate the utility

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of bioreactors in meeting water quality goals in other agriculturally significant areas of the United States. This work contributes to early efforts to adapt bioreactors to agricultural systems in the Mid-Atlantic to meet Chesapeake Bay water quality improvement goals.

Expanding on previous research on biochar-amended woodchip bioreactors (Bock et al., 2015, 2016; Easton et al., 2015), a field-scale woodchip bioreactor with a 10% (v/v) addition of pine-feedstock biochar was installed in a high-priority nutrient management area in Virginia identified by the Chesapeake Bay Total Maximum Daily Load (TMDL). Biochar was selected as a supplemental source of organic carbon based on evidence from laboratory-scale experiments that biochar amendment reduces  $\text{N}_2\text{O}$  production and increases N and P removal in woodchip bioreactors (Bock et al., 2015; Easton et al., 2015), and the results of a pilot-scale experiment suggesting that biochar may increase N removal with moderate to high influent  $\text{NO}_3\text{--N}$  concentrations ( $>10\text{ mg L}^{-1}$ ). The bioreactor was monitored from March 2015 to December 2016 to quantify  $\text{NO}_3\text{--N}$  removal, total P (TP) removal, and emissions of the greenhouse gases (GHGs) nitrous oxide ( $\text{N}_2\text{O}$ ), methane ( $\text{CH}_4$ ), and carbon dioxide ( $\text{CO}_2$ ). This system provides a unique case study of bioreactor performance at the lower limits of N loading and pH reported in the literature that is pertinent to adapting bioreactor designs to US Mid-Atlantic agroecosystems. However, while the application is targeted to address a regional water quality issue, this use of a bioreactor with a relatively small drainage network and acid soils has relevance beyond the United States to similar agricultural landscapes. Additionally, this work is among the early investigations of biochar amendment in field-scale bioreactors, along with Hassanpour et al. (2017) and Pluer et al. (2016).

## 2. Materials and methods

### 2.1. Site description and bioreactor design

A denitrifying bioreactor was installed in August 2014 to treat subsurface drainage on a farm located in the tidal portion of the Rappahannock River Basin in Middlesex County, VA, in the Coastal Plain physiographic region. The bioreactor is  $25.3\text{ m}^3$  and intercepts a 15.24 cm (6 in) terra cotta tile drain serving as the outlet to a 6.5 ha drainage area. The drainage area is comprised of acid soils (pH 4.6–5.1), approximately 60% of which are poorly drained (30% Myatt loam and 30% an equal mixture of Bertha and Daleville loams), while the remaining 40% are moderately well drained (20% Slagle silt loam, 15% Nansemond loamy fine sand, and 5% other [Soil Survey Staff, accessed 4/6/2017]). The field was planted in soy 2014 to 2016, and per agronomic recommendations no fertilizer was applied.

The bioreactor is approximately 5.8 m long, 5.3 m wide, and 0.8 m deep. The sides and bottom of the bed are lined with impermeable polyethylene, and the top is covered with permeable landscaping fabric. The bed was not covered with a layer of soil, as is typical, to maximize the potential for GHG emissions and reduce the chance of underestimating fluxes from a limited number of measurements. Water-level control structures (AgriDrain Corp.) connect the tile to the bed at the inlet and govern flow at the outlet by the positioning of removable stoplogs. To minimize preferential flow and maximize effective volume, the influent is distributed by a manifold that spans the width of the bed, which consists of 15.24 cm (6 in) PVC pipe with 0.6 cm (0.25 in) perforations connected by a tee to the inlet control structure. During installation, the bed was filled with 90% locally sourced mixed hardwood woodchips and 10% biochar (v/v), which was incorporated with the woodchips as they were added (Biochar Solutions Inc., Carbondale, CO). The biochar, which previously had been demonstrated to enhance  $\text{NO}_3\text{--N}$  removal (Bock et al., 2016), was

produced from a pine feedstock via a two-stage pyrolysis where feedstock is held for  $<1\text{ min}$  at  $500\text{--}700\text{ }^\circ\text{C}$  under low oxygen conditions, after which the temperature is reduced to  $300\text{--}550\text{ }^\circ\text{C}$  and held for up to 14 min. The final product consists of two size fractions produced by passing the biochar through an auger, yielding a material consisting of about 80% particles approximately 1.5 cm long by 1 cm wide by 0.5 cm and 20% as a fine dust fraction on the order of  $10\text{--}100\text{ }\mu\text{m}$ .

### 2.2. Data collection

#### 2.2.1. Water chemistry monitoring and sampling

Aqueous grab samples were collected in triplicate from both flow control structures and a piezometer within the bed approximately every two to four weeks between December 2014 and November 2016 on a total of 31 occasions (on 8 others the bed was dry). An automated monitoring and sampling system installed April 2015 collected flow-weighted inlet and outlet water samples and recorded rainfall and bed outflow, on 15- to 60-min intervals. The automated system consisted of two 24-bottle autosamplers (6712, Teledyne Isoco); a rain gauge (674 module, Teledyne Isoco); pressure transducer (720 module, Teledyne ISO) installed in the outlet control structure; and a power source consisting of two deep cycle marine batteries in parallel recharged by a 110-W solar panel. Additionally, two capacitance probes (WT-HR Data Logger, Tru-Track, Intech Instruments LTD) recorded water levels and temperatures in the inlet and outlet control structures at 15- to 30-min intervals.

Detected flow triggered simultaneous sampling from the inlet and outlet at a rate of one 200 ml sample per every  $5\text{ m}^3$  of effluent, with four 200 ml samples per 1000 ml bottle. Fresh sample bottles were prepared with 5 ml of 10% concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to achieve a sample pH  $<2$  and prevent degradation at ambient temperature following the method of Burke et al. (2002). Testing of field spikes and comparison with refrigerated samples provided evidence that the acid preservation ensured stable  $\text{NO}_3\text{--N}$  and TP concentrations for up to two weeks in the field (data not shown). Grab samples were field-filtered with  $0.45\text{ }\mu\text{m}$  nylon filters, transported on ice, and subsequently stored at  $4\text{ }^\circ\text{C}$  until analyzed, typically within 48 h. Acid-preserved, autosampler-collected samples were transported and stored at ambient temperature until adjusted to neutral pH with 0.5 M sodium hydroxide (NaOH) solution using an autotitrator (Easy pH Titrator System, Mettler Toledo), after which they were filtered and analyzed or stored at  $4\text{ }^\circ\text{C}$  until analysis. Samples collected between January and March 2015 were analyzed colorimetrically by spectrophotometer (Thermo Scientific Orion AquaMate 7000 Vis Spectrophotometer) to quantify combined  $\text{NO}_3\text{--N}$  and nitrite-nitrogen ( $\text{NO}_2\text{--N}$ ), collectively  $\text{NO}_x\text{--N}$ , (chromotropic acid method, Orion AQUAFast method ACR007) and TP (ascorbic acid/persulfate digestion method, ACD095). Beginning April 2016, samples were analyzed by flow injection analysis (FIA, QuikChem 8500, Lachat Instruments) with the cadmium reduction method for  $\text{NO}_x$  (Lachat method 10-107-04-1-A) and the ascorbic acid method with prior persulfate digestion for TP (Lachat method 10-115-01-4-C). A subset of the grab samples was analyzed for ammonium ( $\text{NH}_4\text{--N}$ ) with the salicylate method by either spectrophotometer (ACR012) or FIA (10-107-06-5-J) but were consistently below the method detection limit ( $0.1\text{ mg L}^{-1}$ ), so quantification was discontinued. Note that in subsequent discussion  $\text{NO}_x\text{--N}$  will be referred to as  $\text{NO}_3\text{--N}$ , because  $\text{NO}_2\text{--N}$  is relatively unstable and  $\text{NO}_3\text{--N}$  is the dominant form of dissolved N observed in tile drainage waters (Williams et al., 2015). Additionally, because all samples were filtered prior to analysis, TP more precisely refers to total filterable phosphorus.

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