

INFLUENCE OF BIOCHAR AMENDMENTS ON DENITRIFICATION BIOREACTOR PERFORMANCE

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Abstract: As a soil amendment, biochar can provide environmental benefits like increased soil cation exchange capacity, microbial growth and soil water retention, in addition to its role as a long-term store of carbon in terrestrial ecosystems. This suggests that biochar can also be a useful addition to treatment systems aiming to reduce nutrient loadings in agricultural drainage. One possible such application for biochar is inclusion as fill denitrification bioreactors for agricultural drainage, where woodchips (carbon source) allow enhanced denitrification as drainage water laden in nitrate (electron acceptor) flows through the woodchip bioreactor. It was hypothesized that biochar additions could improve nitrate removal and decrease ammonium losses from woodchip denitrification bioreactors. This was explored with lab-scale column experiments consisting of woodchips mixed with two application rates of biochar (7% and 14% biochar by dry weight) which was produced from *Pinus radiata* feedstock. Biochar was pyrolysed at a peak temperature of either 380°C or 550°C to investigate effects of different temperature-derived chars on nitrate removal (i.e. more labile carbon remaining in lower temperature char). A nitrate solution was pumped through the columns and outlet stream samples were analysed for ammonium-N and nitrate-N while head space samples were analysed for nitrous oxide. Initial results indicated that there was no observable difference in nitrate removal between the woodchip control and the woodchip plus biochar columns. The columns containing biochar also seemed to release more ammonium upon start-up than the woodchip control though this trend was not significant ($p=0.36$).

Despite the recent research interest in biochar, there are still many unanswered questions regarding possible biochar applications in the environment or detrimental effects of such applications. As a soil amendment, biochar can provide environmental benefits like increased soil cation exchange capacity, microbial growth and soil water retention, in addition to its role as a long-term storage of carbon in terrestrial ecosystems. In other words, within the soil there is a wide range of beneficial biochar applications, but the derivative impacts upon water quality have not been explored. It is possible that, in addition to biochar's favourable impacts upon certain soils, biochar amendments may provide extra treatment power for water quality technologies.

From an agricultural perspective, nitrate-nitrogen (NO_3^- -N) losses in agricultural drainage are a major cause of water quality impairment for many regions world-wide (USEPA, 2007; Horizons Regional Council, 2007). The new innovation of wood-based enhanced-denitrification treatment (i.e. denitrification bioreactor) for such pollution is being trialled in several such impaired agricultural locations (Jaynes et al., 2008; Schipper et al., 2010; Chun et al., 2010). By routing nitrate-laden agricultural drainage through these bioreactor trenches

filled with woodchips, denitrification can proceed at high rates allowing field-scale treatment of NO_3^- -N loads.

It is well established that biochar in soils can adsorb many cations including dissolved ammonium and phosphate (Lehmann et al., 2006; Lehmann et al., 2002; Beaton et al., 1960). Moreover, biochar's adsorption capacity has proven effective for water treatment with Mizuta et al. (2004) reporting that bamboo powder charcoals sorption affinity for nitrate-nitrogen was even higher than that of commercial activated carbons (average diameter of 80 and 35 μm and BET surface area of 400 and 850 m^2/g , for the biochar and activated carbon, respectively). Trialling biochar as a nitrate treatment for agricultural drainage is a natural next step.

In addition to possible NO_3^- adsorption, biochar's ability to adsorb ammonium (NH_4^+ -N) is another potential benefit of these amendments to denitrification systems (Lehmann et al., 2002; Hua et al., 2009; Honma et al., 2001), though it is important to note that different chars may be capable of adsorbing NO_3^- versus NH_4^+ (positively vs. negatively charged chars, respectively). Wood-based denitrification systems can have significant NH_4^+ and dissolved/total organic carbon (DOC/TOC) flushes upon start-up depending upon the type of carbonaceous material utilized (Christianson et al., 2010; Gibert et al., 2008; Greenan et al., 2006). The ability to reduce these potential initial losses before they leave the system would greatly increase the overall treatment effectiveness of denitrification bioreactors.

Enhanced microbial activity provides additional rationale to investigate biochar amendments in water treatment systems (Yoshizawa et al., 2005; Ogawa et al., 2008). In a wastewater treatment study, a treatment using bamboo charcoal as a biological medium for microbial growth led to similar reductions of DOC and TOC compared with a more conventional wastewater treatment (three-phase fluidized bed biofilm) (Ohata and Yoshizawa, 2008). Using FE-SEM, the documentation of microbial growth on the char concurrent with DOC removal led the authors to conclude that the DOC was bioremediated by biofilm covering the char surface. Based on this evidence, it is plausible that biochar additions may increase denitrifier activity within a drainage bioreactor and/or microbially reduce TOC start-up flushes.

A final consideration for biochar amendments to denitrification systems is the potential effect on nitrous oxide (N_2O) emissions. Though the end product of denitrification is usually benign dinitrogen gas (N_2), the intermediary product N_2O may also be released. In soil systems, Sohi et al. (2009) and Yanai et al. (2007) documented that char additions could reduce N_2O emissions upon wetting/drying. However, Yanai et al. (2007) also found that biochar additions increased N_2O emissions from soil at high water contents. The main mechanism for reduced N_2O emissions with biochar treatments is alterations of soil physical properties related to pore size redistribution (Sohi et al., 2009), better soil aeration, and potentially more stable carbon (Rondon et al., 2005; Lehmann et al., 2006). As it is critical to maintain sufficient hydraulic conductivity of denitrification fill media, biochar particles should be roughly the same size as the original woodchip material meaning that pore size/space will not be significantly modified. Therefore, reductions in N_2O emissions may not occur in denitrification bioreactors containing biochar amendments.

It is well established that biochars produced at different temperatures and from different feedstocks possess varying physical and chemical properties. Pyrolysis temperature affects biochar functionality with higher temperature chars being more aromatic (more stable carbon,

less reactivity) and having higher alkalinity (liming potential). For additions to denitrification systems, it is perhaps the lower temperature chars that could be most useful as these chars tend to have relatively more aliphatic functional groups (i.e. microbially-available carbon). At increasing pyrolysis temperatures, mass recovery decreases while percent carbon increases, generally resulting in lower carbon recoveries. Increasing temperatures also make nitrogen in the biochar less available.

Our hypothesis was that biochar amendments would improve bioreactor performance by both increasing the amount of NO_3^- -N removed and by decreasing the amount of NH_4^+ -N leached through adsorption to negative surface charged sites. More specifically, it was thought that biochar additions could increase NO_3^- -N removal by serving as an additional carbon source for denitrifiers and/or by increasing microsites for microbial activity. Due to the particle size similarity between the biochar and woodchips, it was further hypothesized that N_2O emissions would be similar between biochar and control treatments.

Methods

Three biochar-woodchip treatments and one woodchip-only control were tested in either duplicate or triplicate using ten preserving jars (Agee brand; 1 L nominal volume; 16 cm total depth) modified to serve as flow-through columns. The woodchip-only control consisted of *Pinus radiata* woodchips, freshly chipped, with this same feedstock used to produce the biochar. The treatments are as described in Table 1 with two application rates of biochar produced at 380°C (“380H” and “380L”) and only a high application rate for biochar produced at 550°C (“550”). Woodchips were dried at 70°C until they reached a constant weight to determine moisture content.

Table 1: Properties of woodchip control and three biochar treatments used in column testing

	Control: Pine Woodchips (n=3)	380° High Application Rate: 380H (n=3)	380° Low Application Rate: 380L (n=2)	550° High Application Rate: 550 (n=2)
Dry Weight Woodchips (g)	183.7	154.9	171.8	155.2
Dry Weight Biochar (g)	NA	25.0	12.5	25.0
Mixture % Biochar (dry wt)	0	13.9	6.8	13.9
Bulk Density of Biochar/Woodchip Mixture (g/L)	183.7	179.9	180.2	184.3
Porosity	0.6	Assumed to be similar to the control		

For each column, woodchips (*Pinus radiata*) were mixed with 10 g soil (wet weight, Tokomaru silt loam) and either 25 g or 12.5 g biochar for the high and low application rates, respectively. These application rates of biochar were chosen to minimize the number of production runs. The column filling and operation as well as sample analysis procedures were similar to that reported by Christianson et al. (*In preparation*) and more detail is provided in that paper. In brief, the columns underwent alternating high and low retention times (14.1, 4.1, 13.4, 5.2, and 14.4 hours) with an inflow nitrate solution of approximately 20 mg NO_3^- -N/l. The retention times were changed by raising or lowering the level of solution within the column with a 15 cm solution depth corresponding to the high retention times and 5 cm depth corresponding to the low retentions. Outflow samples were analyzed for NO_3^- -N and NH_4^+ -N with methods from Kamphake et al. (1967) and Searle (1975). Nitrous oxide headspace

samples were collected from individual pore volumes after the first and last two pore volumes of each retention time stage and were analyzed with a Shimadzu GC-17A gas chromatograph equipped with a ^{63}Ni -electron capture detector. Gas data were converted to mass values using the ideal gas law and the headspace volume at each stage.

Results

Outlet stream NO_3^- -N concentrations from all treatments were all higher than the inflow solution at the beginning of the test indicating mineralization of organic nitrogen from the carbon material upon start-up (Figure 1). After this start-up, none of the treatments had NO_3^- -N outlet concentrations noticeably different from each other. However, there was a noticeable stage effect for all the treatments. During the first stage, biochar outlet concentrations stabilized at a mean of 14.0 mg NO_3^- -N /L for all three treatments. The third and fifth stages which were also high retention time stages and had NO_3^- -N outlet concentrations stabilize at means of 9.5 and 11.8 mg NO_3^- -N /L, respectively. The low retention time stages (stage 2 and 4), had outlet concentration means of 17.2 and 19.7 mg NO_3^- -N /L, respectively, which were noticeably higher than for the high retention time stages.

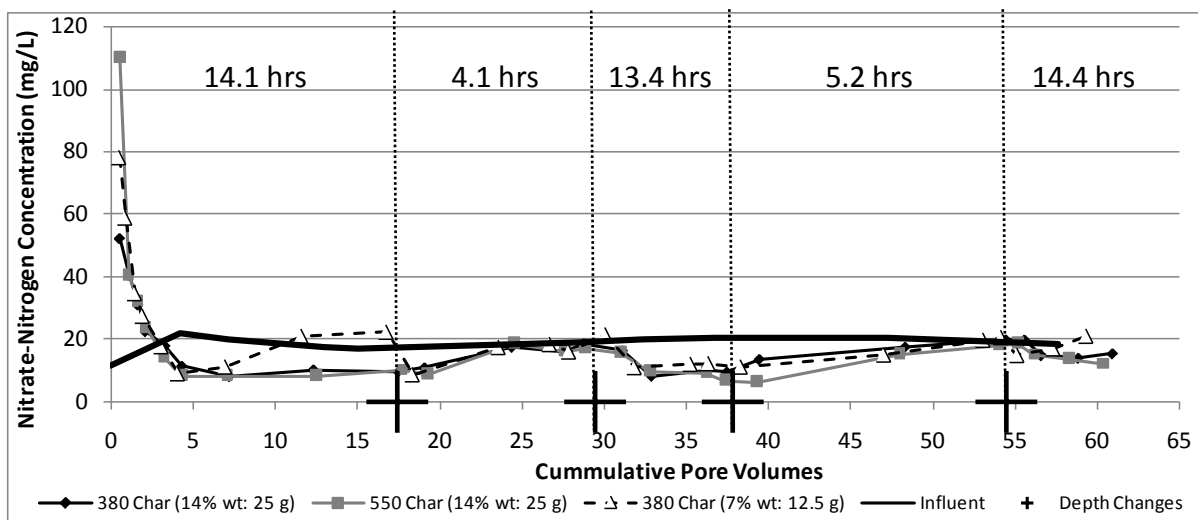


Figure 1: Outlet stream NO_3^- -N concentrations from three biochar treatments in a column experiment; changes in stage marked with crosses and dotted lines with the retention time of that stage noted

The NO_3^- -N outlet stream concentrations of the biochar treatments were not different from the woodchip control with the total cumulative masses not significantly different between treatments ($p = 0.91$). Figure 2 shows the percent difference in cumulative nitrate mass emitted from the woodchip control with positive percentages indicating the biochar treatment had higher removal than the control (i.e. lower mass emitted than the control). This result was contrary to the hypothesis in that biochar additions did not consistently enhance NO_3^- removal. The overall mean differences from the control in total mass NO_3^- -N emitted were 2.0, -5.7, and -10.1% for the 380H, 550, and 380L treatments, respectively.

Increased NO_3^- leaching losses from biochar/soil mixtures have been documented from chars generated from feedstock's high in organic nitrogen. Singh et al (2010) and Hyland et al. (2010) both reported that soil amended with biochar made partially with poultry manure at low temperatures (400°C and 300°C , respectively) had increased NO_3^- -N leaching compared to higher temperature chars and to the controls. This indicates that biochar feedstock and

pyrolysis temperature have an effect upon the potential for NO_3^- leaching losses at least in soil systems (Hyland et al., 2010).

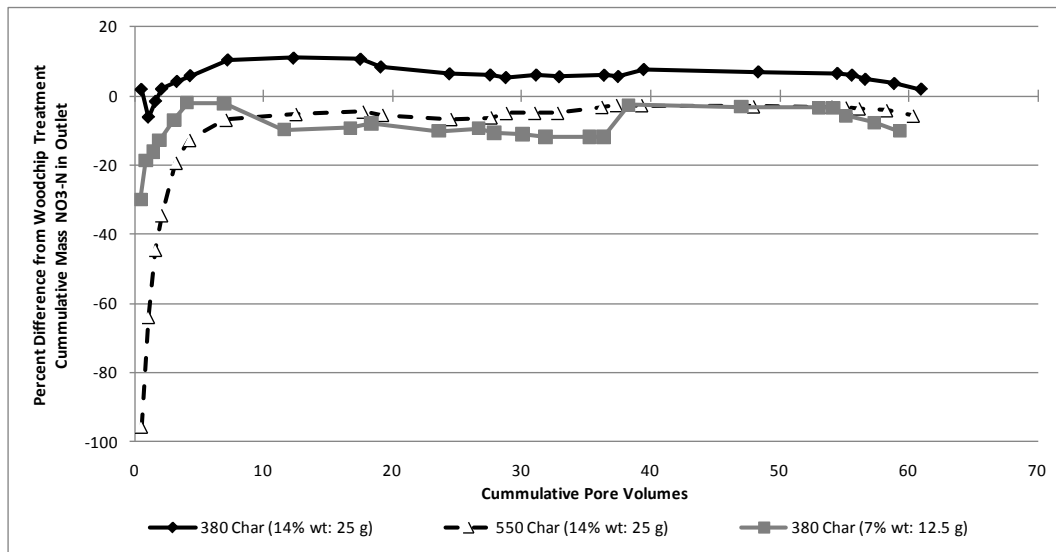


Figure 2: Percent difference from the woodchip control in cumulative outlet NO_3^- -N mass for three biochar treatments; positive percentages indicate the biochar treatment had higher removal than the control

There was a noticeable difference in the outlet stream concentrations of NH_4^+ -N released during the start-up phase between the woodchip control and the biochar treatments (Figure 3). However, the total cumulative mass NH_4^+ -N released between these four treatments was not significantly different ($p=0.36$). In an ammonium leaching study with biochar/soil mixtures (pyrolysis temperature 300°C), Hyland et al. (2010) documented a 7% char application rate increased NH_4^+ -N leaching losses for three feedstock treatments. However, at higher pyrolysis temperatures (i.e. 600°C) this same application rate significantly decreased NH_4^+ -N losses for oak and paper mill waste chars; poultry manure + sawdust biochar amended soil still showed increased NH_4^+ -N losses even at a pyrolysis temperature of 600° (7% application rate) (Hyland et al., 2010). Such differences in NH_4^+ -N losses and pyrolysis temperature were not documented here.

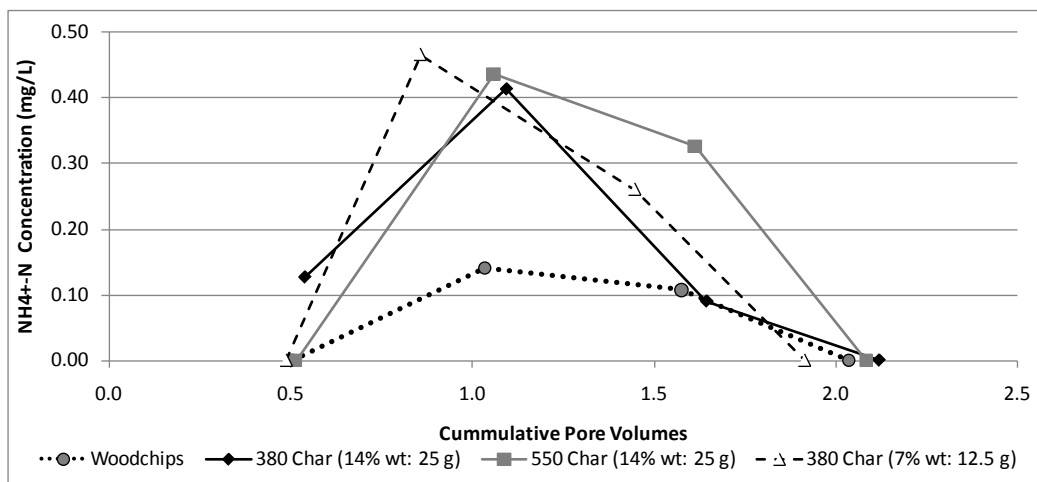


Figure 3: NH_4^+ -N outlet stream concentrations released by three biochar treatments and the woodchip control during the initial stage of the column experiment

For all treatments, there were noticeable spikes in N₂O-N mass produced when the retention time was dropped to approximately 4-5 hours (i.e. saturated depth was dropped) at approximately 17 and 38 cumulative pore volumes (Figure 4; control not shown). Similar to the NO₃⁻-N results, there were no differences between biochar treatments and the woodchip control for N₂O-N emissions, though only one replicate from each treatment was analyzed for N₂O-N so statistical differences could not be evaluated. The cumulative mass of N₂O-N produced for the woodchip, 380H, 550, and 380L treatments were 12.6, 26.3, 7.8, and 15.1 µg N₂O-N, respectively. Singh et al. (2010) found that in an initial wetting/drying cycle, soils amended with poultry manure + rice hull biochar (pyrolysis temperature 400°) had higher N₂O emissions compared to a sand control likely due to the high N content of the char, which is not the case of the current study. However, by the third cycle of wetting/drying, the biochar amended soils all had decreased N₂O emissions compared to the control (Singh et al., 2010). This work did not continue long enough to corroborate this trend.

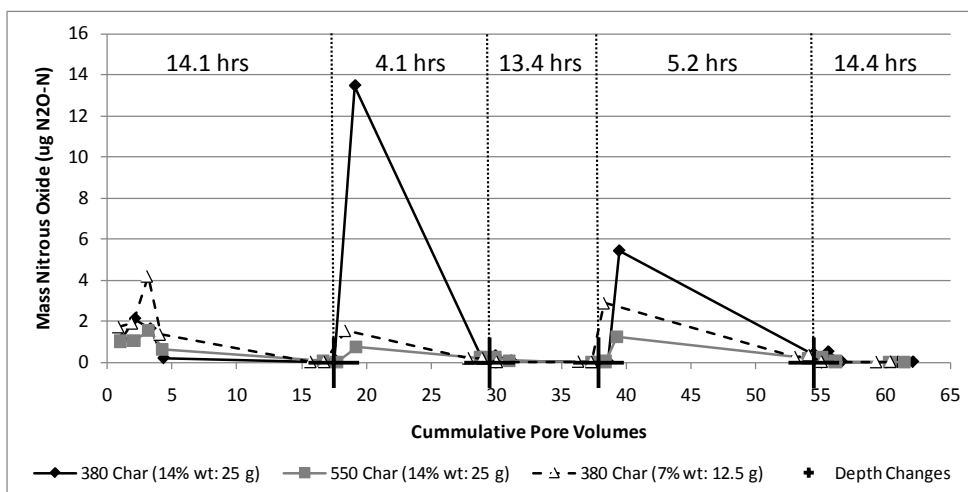


Figure 4: Nitrous oxide-nitrogen mass produced for biochar treatments from column experiment (n=1) (control not shown)

Summary and Conclusions

It was thought that biochar amendments could enhance performance for water quality, nutrient removal technologies. A column study was done to test the effects of biochar addition to woodchips upon water (i.e. NO₃⁻-N and NH₄⁺-N) and air quality (i.e. N₂O-N). Overall, there was a nitrate removal effect for changes in depth/retention time with deeper saturated depths and higher retention times resulting in higher nitrate removal. However, there was no difference between treatments in nitrate removal performance (cumulative mass in outlet stream, p = 0.91). This indicated the biochar did not provide additional microsites or enhance carbon availability, though these parameters themselves were not directly measured. There were numerically higher mass losses of NH₄⁺-N from the biochar treatments (not significant); this was also contrary to the hypothesis. Nitrous oxide emissions from the treatments were correlated with the changes in retention time stage, but as these gas samples were not replicated, significance between treatments could not be determined. Numerically, the treatment of 380° C biochar applied at the high rate produced over twice as much total N₂O-N as the woodchip treatment.

In this study, longevity and performance over elapsed time was not tested. This could be a significant factor as aged biochar seems to be able to significantly positively affect nitrogen losses from soils. Singh et al. (2010) documented that regardless of initial increased N₂O emissions and NO₃⁻-N leaching losses for some biochar treatments, aged biochar treatments

(four different feedstocks after four months), showed much less N₂O emissions and NH₄⁺-N leaching compared to the control. It was thought the “aging” effect of biochars significantly increases adsorption capacity through increased oxidation reactions on the char surface. Another consideration is that with *in situ* denitrification bioreactor volumes averaging approximately 140 m³ (L. Christianson, unpublished data), even a 1% addition of biochar, which is much lower than the rates used here, would require levels of biochar production only practical from a commercial plant.

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