Optimization of Denitrifying Bioreactor Performance with Agricultural Residue-Based Filter Media

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EXECUTIVE SUMMARY

This report describes experiments conducted by the USDA-Agricultural Research Service (USDA-ARS) to investigate the performance of agriculturally derived residue materials in denitrifying bioreactors. This included a comparison of the materials to wood chips at two temperatures, 59 and 35°F (15 and 2°C), identified as Run 1 and Run 2, respectively, in continuous flow column experiments. The investigation measured nitrate removal, microbial abundance and dissolved nitrous oxide gas. In a separate experiment, the hydraulic conductivity of the various materials was determined in a 12-inch diameter by 8-foot long permeameter constructed for this project.

This report was initially written 2/28/2014, after the experimental work was completed but prior to the results having been analyzed and published in peer-reviewed journal articles. The body of this report following the Executive Summary is the initial report. The next paragraphs summarize the findings of the peer-reviewed journal articles and provide direction in obtaining more details from them.

The first peer-reviewed scientific journal article included the rich set of data gathered from the two experiment column runs (Feyereisen et al., 2016). This article compares the nitrate removal performance of wood chips (WC), corn cobs (CC), barley straw (BS), corn stover (CS), and WC+CC (a segment of wood chips followed by a segment of corn cobs) treatments, investigates the microbial communities within each medium, and reports the production of nitrous oxide for each treatment. Briefly, the nitrate-N removal rates of the five treatments ranged from 35 to 1.4 grams of nitrate-N per day per cubic meter of medium (g N d⁻¹ m⁻³) for Run 1 and were ranked as follows: CC > CC+WC > BS = CS > WC. Removal rates were lower for the colder Run 2, ranging from 7.4 to 1.6 g N d⁻¹ m⁻³ with similar rankings: CC ≥ CC+WC = CS ≥ BS > WC. The abundance of microbial genes associated with denitrification was greater for the agricultural residues than for the WC for Run 1. For Run 2, the abundance was greater for CS and BS than for WC. At the colder temperature, Run 2, nitrous oxide production was a higher percentage of nitrate-N removed than for Run 1, 7.5 versus 1.9 percent, respectively, when averaged across all treatments. The conclusion of this article was that a compartment of agriculturally derived material in front of a wood chip bioreactor would provide increased nitrate-N removal rates with less impact of total carbon (C) losses compared to using an agricultural material alone.

A second peer-reviewed scientific journal article on the column experiment was accepted for publication on April 20, 2017 (Feyereisen et al., 2017). The article compares nitrate-N removal, microbial denitrifier gene abundance, and nitrous oxide production of two CC treatments. The treatments were CC by themselves and CC followed by a chamber containing an inert plastic biofilm carrier (PBC), identified as the CC and CC-PBC treatments. The total nitrate-N load removal averaged across Runs 1 and 2 was statistically greater for the CC-PBC treatment than for the CC treatment, 54 versus 44 percent, respectively. The nitrate-N removal rate for Run 1 was significantly greater for CC-PBC but the same for the Run 2. Outlet nitrate-N concentrations were less for CC-PBC for Run 1 but the same for Run 2. Total organic C concentrations and loads were the same for both CC and CC-PBC for both runs. Cumulative nitrous oxide production was less for CC-PBC for Run 1 but the same for Run 2. The amount of nitrous oxide production averaged across both treatments and both Runs was 0.9 percent of the amount of nitrate-N removed. Denitrifying bacteria colonized the PBC material but the
A third peer-reviewed scientific journal article documents the methods, materials, and results of the hydraulic conductivity testing of wood chips, corn cobs, corn stover, and barley straw (Feyereisen and Christianson, 2015). The hydraulic conductivities of the materials ranged from 1.9 to 1.1 inches per second (in/s), or in metric units 4.8 to 2.8 cm/s. Although there were no significant differences among materials, the value for wood chips was elevated with respect to the agricultural materials. During the work, multiple tests of the same materials showed that barley straw in particular became compressed, dramatically reducing flow. It is also important to note that the materials tested were fresh. The expectation is that the results would change after media breaks down in a bioreactor.

The abstracts and interpretive summaries of the aforementioned articles may be located on the internet via the link in the reference section of this report. In the future, the articles in their entirety may be accessible from the linked site.

The results of this project have informed two additional research efforts to increase the rate of nitrate-N removal in Minnesota tile drainage water. An additional column experiment, funded by the Minnesota Department of Agriculture, was conducted by a Master of Science (M.S.) student at the University of Minnesota using three treatments that included corn cobs and three that used wood chips. In order to enhance the rate of removal of nitrate-N from tile drainage water in a field setting in southwestern Minnesota, the study combined the findings from this additional column experiment with those of the present experiment. Thus, the impact of the relatively modest project that is the subject of this report has continued well beyond the project’s scope.

**PROJECT OBJECTIVES**

1. Identify agriculturally derived materials that will maintain required hydraulic properties in a bioreactor.
2. Improve the nitrate-N removal rate of bioreactors using agriculturally derived materials rather than wood chips, including at temperatures just above freezing.
3. Investigate the cost for bioreactors using agriculturally derived materials and compare to the cost for wood chip bioreactors.
BACKGROUND

Wood-chip denitrifying bioreactors are a promising technology to mitigate subsurface drainage nitrate-nitrogen losses. Drainage water is routed through these denitrifying bioreactors, where anaerobic microbes reduce nitrate-N to nitrogen gas that ultimately escapes to the atmosphere (Figure 1). This study demonstrates that agricultural residue-based materials – e.g. stover, straw, cobs – used as filter media can improve the performance and decrease the size of bioreactors, and potentially lower their cost. Additionally, a large fraction of annual subsurface drainage and nitrate-N loss occurs during the spring snowmelt when soil temperatures are just above freezing (Jin and Sands, 2003). The cold temperatures tend to reduce microbial activity and negatively affect reactor efficiency. USDA-ARS tested the cold-temperature effectiveness of bioreactors with agricultural residue-based materials, which contain carbon that is more labile than in wood chips.

DESCRIPTION OF WORK PERFORMED

A system to pump water through eighteen PVC column bioreactors, 6-in. diameter by 19 in. long) filled with various agriculturally derived media was designed, constructed, and instrumented (Figures 2 and 3). The system was situated in a temperature-controlled chamber. Chemicals were added to water filtered by reverse osmosis to reflect the chemistry of agricultural drainage water in Minnesota. A method was developed to fill and mix chemicals in two water-holding tanks in the temperature-controlled chamber before transferring the water to a single, larger inlet tank.

Materials and combinations of materials tested included corn cobs (CC), corn stover (CS), barley straw (BS), corn cobs followed by a plastic biofilm carrier (PBC) material (Kaldnes™-K3, Veolia Water Technologies AB - AnoxKaldnes, Lund, Sweden) (CC-PBC), corn cobs followed by wood chips (CC-WC), and wood chips (WC), which served as a control (Figure 4). The CC-PBC columns were constructed with an additional 9.5-inch length of 6-inch diameter PVC pipe added atop the primary column; water flow was first through the primary vessel, which was filled with corn cobs, and then through the additional chamber, which was filled with the PBC material (Figure 3b). The PBC material, invented for use in wastewater treatment in moving or packed bed reactors, maximizes surface area for bacterial growth. The PBC material was included because previous testing by others showed comparable performance to using a carbon source material by itself (Saliling et al., 2007) and promising performance in cold conditions (Welander and Mattiasson, 2003). The CC-WC columns were filled to two-thirds (2/3) full with corn cobs with the remaining one-third (1/3) filled with wood chips. Moisture, ash, carbon, hydrogen, and nitrogen contents for the four carbonaceous materials in pre- and post-test condition were determined by the Agricultural Utilization Research Institute’s (AURI) analytical laboratory in Marshall, MN, using ASTM test methods (Table 1).

The columns with media that had been saturated, drained, and inoculated with top soil taken from a field at the U of M – St. Paul campus that has a history of manure application, ensuring a robust supply of microbes. The porosity of the bioreactor columns was checked prior to
initiating the experiment. They were then operated for 25 weeks at a temperature of approximately 60°F (Run 1), dismantled, re-packed and operated for another 28 weeks at 35°F (Run 2). During these periods, the volume of water passing through each column was measured several times per week. Water samples were collected three times per week, and water for dissolved gas testing sampled every four weeks.

This project resulted in more than 4,000 water samples collected, processed, stored, analyzed, and archived as well as over 800 gas samples collected, processed and analyzed. At the completion of both runs, each column was unpacked and media samples were collected for DNA testing of the microbial biomass.

One objective of this study was to characterize the hydraulic properties of agriculturally derived materials. The permeability of a material, known as its hydraulic conductivity in the case of water flow, is dependent on the size and volume of pore spaces between the particles and the size of the neck connecting the pores. Determination of hydraulic conductivity is made by transporting water through the material and measuring friction losses at a number of flow rates. The design of the flow-through column bioreactors did not permit testing of the hydraulic conductivity of the candidate materials as had originally been proposed. Thus, USDA-ARS, AURI, and MCR&PC personnel agreed in May 2012, to provide additional funds to build a separate test apparatus, known as a permeameter, to test the hydraulic conductivity of the candidate materials in their raw state. The AURI and the MCR&PC agreed to provide funds for student labor while ARS provided funds for the pump and materials. During June and July 2012, the permeameter was designed and built on the turfgrass research plots on the University of Minnesota – St. Paul campus (Figure 5). Testing of the materials was nearly completed prior to the winter freeze. In January 2013, the permeameter was re-erected in the BioAg Engineering building on the U of M – St. Paul campus. Completion of the hydraulic conductivity testing, which is now performable regardless of weather, occurred during the spring semester 2013.

The bioreactor experiment provided ancillary opportunities for four undergraduate students to have research experiences under the U of M’s Undergraduate Research Opportunity Program (UROP). Two students tested a 50/50 mixture of corn cobs and wood chips; one student added three bioreactor columns to the second denitrification run and the other student tested the hydraulic conductivity of the mixture. Two additional students did investigation of hydraulic conductivity of larger wood chip particle sizes, comparing vertical and horizontal orientation of the permeameter tube using an inert tracer (bromide, Br	extsuperscript{-}). The students each presented a poster that summarized their work at the U of M’s Undergraduate Research Symposia held on April 19, 2013 (Appendices A and B), and April 16, 2014 (Appendices C and D).

RESULTS

Material Properties.

Physical and chemical properties of the agriculturally derived residue materials are observable in Table 1.
Table 1. Properties of the bioreactor test media.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Particle Size Description</th>
<th>Moisture Content† (%)</th>
<th>Ash Content† (%)</th>
<th>Carbon† (%)</th>
<th>Nitrogen† (%)</th>
<th>C:N Ratio†</th>
<th>Hydrogen† (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood Chips</td>
<td>Sieve Size (mm) Mass (%)</td>
<td>Initial 2.98 Run 1 4.51 Run 2 4.12</td>
<td>Initial 0.39 Run 1 3.52 Run 2 5.71</td>
<td>Initial 50.0 Run 1 48.9 Run 2 46.4</td>
<td>Initial 0.19 Run 1 0.28 Run 2 0.33</td>
<td>Initial 263 Run 1 172 Run 2 141</td>
<td>Initial 5.94 Run 1 5.82 Run 2 5.52</td>
</tr>
<tr>
<td>Corn Stover</td>
<td>Particle Length (cm) Mass (frctn)</td>
<td>Initial 4.24 Run 1 4.31 Run 2 4.19</td>
<td>Initial 4.47 Run 1 19.62 Run 2 12.76</td>
<td>Initial 46.2 Run 1 44.0 Run 2 44.1</td>
<td>Initial 0.66 Run 1 0.79 Run 2 0.63</td>
<td>Initial 70 Run 1 55 Run 2 70</td>
<td>Initial 5.76 Run 1 5.28 Run 2 5.40</td>
</tr>
<tr>
<td>Barley Straw</td>
<td>Particle Length (cm) Mass (frctn)</td>
<td>Initial 3.92 Run 1 4.15 Run 2 4.23</td>
<td>Initial 8.87 Run 1 21.48 Run 2 21.10</td>
<td>Initial 44.6 Run 1 42.9 Run 2 41.8</td>
<td>Initial 0.42 Run 1 0.85 Run 2 0.93</td>
<td>Initial 106 Run 1 51 Run 2 45</td>
<td>Initial 5.56 Run 1 5.23 Run 2 5.15</td>
</tr>
<tr>
<td>Corn Cobs</td>
<td>Particle Length Numeric Frctn (±0.5 cm) (%)</td>
<td>Initial 4.17 Run 1 4.50 Run 2 4.03</td>
<td>Initial 2.98 Run 1 12.55 Run 2 11.08</td>
<td>Initial 48.1 Run 1 43.0 Run 2 42.7</td>
<td>Initial 0.58 Run 1 0.81 Run 2 0.67</td>
<td>Initial 83 Run 1 53 Run 2 64</td>
<td>Initial 5.88 Run 1 5.17 Run 2 5.21</td>
</tr>
<tr>
<td>PBC‡</td>
<td>2.5 cm diameter by 1.0 cm long 584 m² surface area per m³</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

† Source of data: AURI Analytical Laboratory.

‡ Plastic Biofilm Carrier (PBC).
**Bioreactor Column Tests.**

The calculation of nitrate-N removal performance of the treatments involves the nitrate-N concentration reduction of and the rate of water flow through each column, which is affected by the volume of void or pore space in the column. The total pore space in the column is known as one “pore volume.” The length of time that it takes for the volume of water equal to one pore volume to flow through the column is called the hydraulic residence time (HRT). An attempt was made to pack the various materials such that the void space was similar so that the HRT would be a nominal 12 hours. However, the inherent differences in particle size, aspect ratio, and compressibility of the materials, and pump variability resulted in some differences in HRTs (Table 2).

Table 2. Hydraulic residence times for Run 1 and Run 2.

<table>
<thead>
<tr>
<th>Run</th>
<th>Period</th>
<th>Temp (°F)</th>
<th>CS</th>
<th>CC</th>
<th>CC-WC</th>
<th>BS</th>
<th>WC</th>
<th>CC-PBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5/2 – 5/29/12</td>
<td>60.9</td>
<td>11.9</td>
<td>11.9</td>
<td>12.7</td>
<td>10.8</td>
<td>13.8</td>
<td>11.8</td>
</tr>
<tr>
<td>1</td>
<td>6/22 – 7/18/12</td>
<td>59.3</td>
<td>12.5</td>
<td>11.9</td>
<td>11.4</td>
<td>11.3</td>
<td>14.4</td>
<td>11.3</td>
</tr>
<tr>
<td>2</td>
<td>2/6 – 4/19/13</td>
<td>35.0</td>
<td>11.1</td>
<td>13.1</td>
<td>11.8</td>
<td>11.7</td>
<td>13.6</td>
<td>13.2</td>
</tr>
</tbody>
</table>

In order to evaluate the nitrate-N removal performance of the treatments, periods of time were selected during each run where the nitrate-N concentrations into and out of the columns and hydraulic residence times were relatively stable. The periods chosen in Run 1 were May 2 – 29, 2012 (28 days) and June 22 – July 18, 2012 (29 days). Between these periods, nitrate-N inlet concentrations fluctuated outside reasonable limits, rendering the data unusable. During Run 2, the experiment operated with consistent results for the period from February 6 – April 19, 2013 (73 days). Failure of the peristaltic pump ended the stable period in Run 2.

For Run 1, the nitrate-N removal rates of the agricultural residue treatments were greater than for wood chips and were from highest to lowest: CC-PBC > CC > CC-WC > BS > CS > WC. The reason for the enhanced nitrate-N removal for the CC-PBC treatment could be the biofilm formation on the PBC material, which was observed when the columns were disassembled, provided additional nitrate-N processing capacity and/or the additional residence time in the PBC chamber, provided additional time for nitrate reduction to occur. In either case, simply adding a volume of space filled with a porous inert material, e.g. lava rock, after the bioreactor bed has the potential to improve bioreactor nitrate-N removal performance beyond that of the bioreactor itself.

Between the 1st and 2nd periods of Run 1 an observable decline in nitrate-N removal rates occurred for the barley straw, corn stover, and wood chip treatments (Table 3). The reductions for the barley straw and corn stover were consistent with what other researchers have found. Soares et al. (1998) observed that the nitrate-N removal rate for wheat straw, a medium very similar to barley straw, declined within one week of operation and that weekly additions of fresh straw were required to maintain performance. The average nitrate-N removal rate for the wood chips (Run 1, 1st period) was similar to what others have found in lab studies (Greenan et al., 2009; Healy et al., 2012). The nitrate-N removal rate for the 2nd period of Run 1
was lower primarily because there were some samplings during which the outlet nitrate-N concentration exceeded the inlet concentration. The sporadic performance of the wood chips remains a mystery of this experiment. The chips came from a freshly removed and chipped green ash tree on the University of Minnesota’s St. Paul campus. The chips had been oven dried prior to being saturated, inoculated, and packed into the columns.

The nitrate-N removal rates were much less for all media candidates for Run 2 than Run 1 (Table 3). This expected temperature effect was the result of reduced biological activity at colder temperatures. Also, cold water has the potential to hold more dissolved oxygen (DO) than warm water (Table 4). The additional oxygen entering the columns under the colder temperatures delayed the establishment of the anaerobic conditions that support dissimilatory denitrification. The denitrifying microbes initially use DO to respire and then, when DO concentrations deplete, begin reducing nitrate. Dissolved oxygen readings taken on days of water sampling on one column per treatment throughout most of the experiment indicate greater inlet DO concentrations for Run 2 compared to Run 1, but that the column outflow DO concentrations between the runs was similar (Table 4). It is worth noting that DO readings were difficult to obtain and inconsistent readings during Run 2 resulted in repairs to the instrument and loss of data during the stable period used for the nitrate-N removal rate calculations. The greater DO levels were related to greater oxidation-reduction potential (ORP) measurements for Run 2 (Table 5).

| Table 3. Nitrate-N removal rates for the treatments for Run 1 and Run 2. |
|---------------------------------|--------|------------|------------|------------|--------|--------|
| Run Period                      | Temp (°F) | CS (g N d⁻¹ m⁻³)† | CC (g N d⁻¹ m⁻³) | CC-WC (g N d⁻¹ m⁻³) | BS (g N d⁻¹ m⁻³) | WC (g N d⁻¹ m⁻³) | CC-K (g N d⁻¹ m⁻³) |
| 1 5/2 – 5/29/12                 | 60.9    | 24.6       | 35.3       | 29.3       | 30.1   | 5.6    | 40.2     |
| 1 6/22 – 7/18/12                | 59.3    | 20.2       | 35.9       | 27.8       | 22.0   | 1.4    | 40.5     |
| 2 2/6 – 4/19/13                 | 35.0    | 5.5        | 7.0        | 6.4        | 5.0    | 1.8    | 9.4      |

† grams of nitrate-N per day per cubic meter of medium.

The nitrate-N removal rates for Run 2 were reduced from four to seven times compared to Run 1 for the agricultural residue treatments and about three times for the wood chip treatment (Table 3). Nonetheless, the treatments with corn cobs exhibited nitrate-N removal rates at the cold temperatures above that of wood chips at the warmer temperature. The results of the cold test indicate that some nitrate-N can still be removed during the coldest portion of the drainage flow, i.e. spring snow melt.

The nitrate-N concentrations of the water exiting each of the six treatments varied widely throughout Run 1 (Figure 6) and Run 2 (Figure 7). However, the concentration reductions were quite consistent with greatest to least reductions for Run 1 as follows: CC-PBC > CC > CC-WC > CS > BS > WC. The Run 2 concentration reductions were much less than those from Run 1, an effect of the lower operating temperature and reduced rate of biological activity. The relative order of nitrate-N concentration reductions among the treatments was the same as for Run 1.
Table 4. Dissolved oxygen readings for Run 1 and Run 2.

<table>
<thead>
<tr>
<th>Run</th>
<th>Period</th>
<th>Temp (°F)</th>
<th>Inlet</th>
<th>CS</th>
<th>CC</th>
<th>CC-WC</th>
<th>BS</th>
<th>WC</th>
<th>CC-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5/2 – 5/29/12</td>
<td>60.9</td>
<td>5.5</td>
<td>0.9</td>
<td>1.2</td>
<td>1.3</td>
<td>0.9</td>
<td>0.9</td>
<td>1.2</td>
</tr>
<tr>
<td>1</td>
<td>6/22 – 7/18/12</td>
<td>59.3</td>
<td>5.9</td>
<td>1.7</td>
<td>2.0</td>
<td>1.7</td>
<td>1.8</td>
<td>1.7</td>
<td>1.9</td>
</tr>
<tr>
<td>2</td>
<td>5/3 – 5/13/13</td>
<td>35.0</td>
<td>8.4</td>
<td>0.8</td>
<td>1.3</td>
<td>1.0</td>
<td>0.9</td>
<td>0.9</td>
<td>1.2</td>
</tr>
</tbody>
</table>

† parts per million.
Readings represent measurements on water sampling days of one column only for each treatment. The DO probe was providing inconsistent results during Run 2 until it was repaired and returned to service on 5/3/13.

Table 5. Average oxidation-reduction potential (ORP) readings for Run 1 and Run 2.

<table>
<thead>
<tr>
<th>Run</th>
<th>Period</th>
<th>Temp (°F)</th>
<th>CS</th>
<th>CC</th>
<th>CC-WC</th>
<th>BS</th>
<th>WC</th>
<th>CC-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5/2 – 5/29/12</td>
<td>60.9</td>
<td>169</td>
<td>192</td>
<td>186</td>
<td>185</td>
<td>231</td>
<td>148</td>
</tr>
<tr>
<td>1</td>
<td>6/22 – 7/18/12</td>
<td>59.3</td>
<td>222</td>
<td>102</td>
<td>191</td>
<td>245</td>
<td>203</td>
<td>149</td>
</tr>
<tr>
<td>2</td>
<td>2/6 – 4/19/13</td>
<td>35.0</td>
<td>281</td>
<td>381</td>
<td>375</td>
<td>314</td>
<td>390</td>
<td>363</td>
</tr>
</tbody>
</table>

† millivolts.

Total organic carbon (TOC) concentrations tended to be greater for the agricultural residue treatments compared to the wood chip treatment, which was expected (Table 6). There was a reduction in TOC concentrations for all treatments between Runs 1 and 2, consistent with the concept of an initial “flush” of carbon upon startup of a denitrifying bioreactor (Healy et al., 2012; Fenton et al., 2014). The relatively high TOC concentration of the inlet water during the first period of Run 1 is unexplained as is its potential influence on the outlet concentrations. The TOC concentrations for Run 2 were remarkably similar and reflected the lower level of biological activity under the colder temperature.
Table 6. Average effluent total organic carbon concentrations for Runs 1 and 2.

<table>
<thead>
<tr>
<th>Run</th>
<th>Period</th>
<th>Temp (°F)</th>
<th>Inlet Water</th>
<th>CS</th>
<th>CC</th>
<th>CC-WC</th>
<th>BS</th>
<th>WC</th>
<th>CC-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5/2 – 5/29/12</td>
<td>60.9</td>
<td>17.1</td>
<td>15.1</td>
<td>40.2</td>
<td>26.6</td>
<td>18.2</td>
<td>12.9</td>
<td>39.3</td>
</tr>
<tr>
<td>1</td>
<td>6/22 – 7/18/12</td>
<td>59.3</td>
<td>7.6</td>
<td>9.3</td>
<td>23.1</td>
<td>11.0</td>
<td>8.9</td>
<td>8.6</td>
<td>18.0</td>
</tr>
<tr>
<td>2</td>
<td>2/6 – 4/19/13</td>
<td>35.0</td>
<td>8.7</td>
<td>10.1</td>
<td>10.1</td>
<td>10.1</td>
<td>9.8</td>
<td>9.9</td>
<td>10.2</td>
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</tbody>
</table>

At the completion of each of the tests, the porosity of each column was re-measured and the media sampled for microbial DNA testing by a collaborating ARS scientist from the National Laboratory for Agriculture and the Environment (NLAE) in Ames, IA. After sampling, the media were dried and weighed. Ideally, comparison of the initial and final media weights and carbon contents would provide a measure of how rapidly each medium degraded and lend to a relative estimate of service life in a field bioreactor. Unfortunately, an accurate comparison could not be made from these tests due to the addition of the soil inoculant. During the porosity checks pre- and post- test, unmeasured quantities of soil particles were drained from the columns. Also, soil remained attached to the insides of the chamber caps at the conclusion of the test. Thus, although the mass and carbon content of medium, and the mass of soil, in each column was known, the mixture of medium and soil at the end of the experiment prevented a separate measure of each. In the future, column inoculation will be performed by mixing in carbonaceous materials taken from an existing, active bioreactor so that the mass and carbon contents of the media can be fully accounted for at the conclusion of the test.

**Hydraulic Conductivity Testing.**

The saturated hydraulic conductivities of the three agricultural materials and wood chips, adjusted for water temperature ranged from 1.9 to 1.1 inches per second (in/s), or in metric units 4.8 to 2.8 cm/s, with the order from highest to lowest: WC > CS > CC > BS. The corn stover results were greater than expected; apparently, the structure of the stalk particles and occasional pieces of cob created a network of pore spaces that permitted flow better than the other residues. Over time, the expectation is reduced hydraulic conductivities due to settling, compaction, and reduction of particle size due to biological breakdown. For at least one replication of each medium, the water was drained from the permeameter vessel after an initial test, then the vessel was re-filled with water and the test re-run. Most affected by the retesting was the barley straw, losing 30 percent of its conductivity. After reopening the vessel after retesting, the barley straw appeared to have compressed. In a field situation, the compression is expected to cause flow problems. An example of a graph of the permeameter data is shown in Figure 8, just prior to the appendices to this report.
POTENTIAL BENEFIT TO MINNESOTA ECONOMIC/ENVIRONMENTAL DEVELOPMENT

Agricultural residues were tested to determine their bio-physical suitability to replace wood chips as the bed medium in denitrifying bioreactors. In addition to physical performance, the economics of using agricultural residues to reduce nitrate-N loads would need to be comparable to or better than wood chips. Given the greater nitrate-N removal rates of agricultural residues, there may be opportunities to reduce the size of the bioreactor unit, or to increase nitrate-N removal effectiveness within a given bioreactor footprint. However, the agriculturally derived materials will need replenishing more often than wood chips, thus increasing the associated maintenance costs. Nonetheless, the proximity of agricultural residues to an edge-of-field bioreactor is a significant incentive to design a way to use them successfully and cost efficiently.

COST ANALYSIS

The approach taken for this cost analysis was to start with a detailed analysis for woodchip bioreactors done by others (Christianson et al., 2013) and modify it for agricultural residues. Christianson et al. (2013) itemized the present value costs per acre associated with installing a bioreactor and with maintaining it over a 40-year lifetime, using a discount rate of four percent. The researchers provided a minimum – maximum range of costs to build a bioreactor that would treat 50 acres using two semi-truckloads of woodchips. The approach taken here is that certain costs will be the same for woodchips or agricultural residues: design engineering, control structures, miscellaneous materials, seeding/mowing, and maintenance labor and materials. Cost differences between woodchips and agricultural residues exist for the cost of the media and contractor’s fees for the installation and replacement of the media.

For the purposes of the current analysis, assumptions are necessary with respect to the dimensions of the bioreactor, cost of the media, and the media replacement interval. Given that the nitrate-N removal rate is greater for agricultural residues, the assumption made is that either the bioreactor can be made smaller in footprint or that a greater percentage of drainage water can be treated and thus more pounds of nitrogen per acre (lb N/ac) can be removed within the same-sized footprint. An estimate of the service life of the materials tested in the columns cannot be given based on the current study as discussed above. However, it can be inferred from the concentration data that corn cobs will last longer than corn stover which will last longer than barley straw. Others have found that corn cobs have maintained their biological and hydraulic performance over a 23-month period (Cameron and Schipper, 2010). For simplicity’s sake and because corn cobs performed better than the other residues tested, corn cobs will be used in the cost analysis. In view of the preceding sentences, the assumptions identified in Table 7 were made to carry out the analysis.
Table 7. Assumptions made for cost analysis of a denitrifying bioreactor with a medium of corn cobs.

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Corn Cobs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioreactor Bed Medium</td>
<td>Same as for Wood Chips</td>
</tr>
<tr>
<td>Size of Bioreactor Bed</td>
<td></td>
</tr>
<tr>
<td>Nitrate-N Load, lb N/ac/y</td>
<td>28</td>
</tr>
<tr>
<td>Nitrate-N Load Removal</td>
<td></td>
</tr>
<tr>
<td>Case A, %</td>
<td>37.5†</td>
</tr>
<tr>
<td>Case B, %</td>
<td>50‡‡</td>
</tr>
<tr>
<td>Medium Replacement Interval, y</td>
<td>4‡</td>
</tr>
<tr>
<td>Cost of Medium</td>
<td></td>
</tr>
<tr>
<td>Minimum, $/ton</td>
<td>0</td>
</tr>
<tr>
<td>Maximum, $/ton</td>
<td>87‡‡</td>
</tr>
</tbody>
</table>

† Value for wood chips from Christianson et al. (2013).
‡‡ Value assumes greater rate of removal for corn cobs compared to wood chips.
‡ Comparison value for wood chips is 20 y.
‡‡ Cost obtained from University of Minnesota – Morris, where corn cobs are used as a boiler fuel (James Barbour, personal communication).

The total present value costs for installation and maintenance of a wood chip bioreactor for a minimum and maximum cost scenario came from Christianson et al. (2013). The total present value costs (TPVC) for a corn cob bioreactor range from less than that of a wood chip bioreactor at the minimum case to greater than that of a wood chip bioreactor at the maximum case (Table 8). Replacement intervals shorter than four years would increase the cost of maintaining a corn cob bioreactor; until better information is available about the life expectancy of corn cobs as a bed medium, the uncertainty of this estimate is high.

The cost of installing and maintaining a bioreactor is only one facet of cost. Professionals and policy makers are often looking to express the effectiveness of nutrient removal practices in terms of the cost per unit mass removed (i.e. $/lb N removed) in order to compare practices. In order to calculate this value for the current study, one must divide the equal annual cost (EAC) by the estimated mass of nitrate-N annually removed by the bioreactor. The EAC is the annual payment calculated over a 40-year bioreactor life at the given four percent discount rate for the TPVCs for the wood chip and corn cob bioreactors, using the following formula (Eq. 1)(Christianson et al., 2013):

$$EAC = TPVC \times \frac{(i(1+i)^n)/(1+i)^n - 1)}$$  

where $i$ is the discount rate and $n$ is 40 years. Table 8 shows the EACs for the minimum and maximum cases for WC and CC. Christianson et al. (2013) used a “Midwestern-representative load” of 28 lbN/ac/year and a mean nitrate-N load reduction of 37.5 percent to determine the mass of N removed annually by a wood chip bioreactor. In the current study, two cases are shown for a corn cob bioreactor: Case A, in which the same load reduction was used (37.5%), and Case B, in which a greater load reduction of 50 percent was assumed (Table 9). The cost for removing 1 lb N with a wood chip bioreactor ranged from $0.60 – 1.24 and from $0.49 – 2.06 for the corn cob bioreactor with the same load reduction. The numbers are reasonable compared to other best management practices (BMPs). Improving the performance of the bioreactor by one-third (1/3), thus increasing the load reduction to fifty percent, lowered the
cost range of removing 1 lbN to $0.37 – 1.55. Improved performance of corn cobs could well be shown in future field testing because of the increased effectiveness observed in the cold temperature testing in this study. The numbers show that placing an accurate value on the corn cob medium is important to get a fair comparison of N removal with wood chips.

Table 8. Total present value costs for a denitrifying bioreactor designed to treat 50 acres.

<table>
<thead>
<tr>
<th>Item</th>
<th>WC, Minimum ($/ac)</th>
<th>CC, Minimum ($/ac)</th>
<th>WC, Maximum ($/ac)</th>
<th>CC, Maximum ($/ac)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Installation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Media</td>
<td>47.02†</td>
<td>0.00</td>
<td>47.02</td>
<td>14.57</td>
</tr>
<tr>
<td>Contractor Fees</td>
<td>11.21</td>
<td>11.21</td>
<td>40.02</td>
<td>40.02</td>
</tr>
<tr>
<td>Design</td>
<td>0.00</td>
<td>0.00</td>
<td>12.81</td>
<td>12.81</td>
</tr>
<tr>
<td>Materials</td>
<td>24.04</td>
<td>24.04</td>
<td>84.11</td>
<td>84.11</td>
</tr>
<tr>
<td>Cost of installation</td>
<td>82.27</td>
<td>35.25</td>
<td>183.95</td>
<td>151.50</td>
</tr>
<tr>
<td><strong>Maintenance &amp; Replacement</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Replacement</td>
<td>26.58</td>
<td>49.99</td>
<td>39.75</td>
<td>243.33</td>
</tr>
<tr>
<td>Labor and materials</td>
<td>16.22</td>
<td>16.22</td>
<td>34.44</td>
<td>34.44</td>
</tr>
<tr>
<td>Cost of maintenance &amp; replacement</td>
<td>42.80</td>
<td>66.21</td>
<td>74.18</td>
<td>277.77</td>
</tr>
<tr>
<td>Total present value cost of installation, maintenance &amp; replacement</td>
<td><strong>125.07</strong></td>
<td><strong>101.45</strong></td>
<td><strong>258.13</strong></td>
<td><strong>429.26</strong></td>
</tr>
</tbody>
</table>

† Values for WC are from Christianson et al. (2013).

†† Wood chip costs from Christianson et al. (2013) were based on two semi-truck loads at $975 material cost and $200 transportation cost for each load.

Comparison is made between wood chips (WC) and corn cobs (CC). Assumed replacement intervals are 20 years for wood chips and 4 years for corn cobs. The discount rate used to bring the maintenance costs back to year 0 was 4%. See other assumptions in text above.
Table 9. Estimated cost of nitrate-N removal based on minimum and maximum cost projections to install and maintain a denitrifying bioreactor.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Annual Nitrate Load (lbN/ac)</th>
<th>Nitrate Removed (%)</th>
<th>Nitrate Removed (lbN/ac/y)</th>
<th>EAC Min ($/ac/y)</th>
<th>EAC Max ($/ac/y)</th>
<th>Cost per lbN removed Min ($/lbN)</th>
<th>Cost per lbN removed Max ($/lbN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC</td>
<td>28</td>
<td>37.5%</td>
<td>10.5</td>
<td>6.32</td>
<td>13.04</td>
<td>0.60</td>
<td>1.24</td>
</tr>
<tr>
<td>CC –</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case A</td>
<td>28</td>
<td>37.5%</td>
<td>10.5</td>
<td>5.13</td>
<td>21.69</td>
<td>0.49</td>
<td>2.06</td>
</tr>
<tr>
<td>CC –</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case B</td>
<td>28</td>
<td>50.0%</td>
<td>14.0</td>
<td>5.13</td>
<td>21.69</td>
<td>0.37</td>
<td>1.55</td>
</tr>
</tbody>
</table>

Assumptions taken from Christianson et al. (2013) are found in the report text above.

CONCLUSIONS

This study began with a set of three objectives focused on comparing agricultural residues versus wood chips as media candidates for denitrifying bioreactors in these areas: hydraulic properties, nitrate-N removal performance, and cost. The work demonstrated that at least in the short term, the hydraulic conductivities of corn cobs and corn stover is near that of wood chips, warranting further study over a longer service life. The nitrate-N removal performance of all three agricultural residues was superior to that of wood chips at two temperatures spanning the expected range of ground temperatures in Minnesota. Total carbon losses were greater for agricultural residues than for wood chips; field monitoring to better understand any potential downstream water quality concerns is recommended. The cost comparison was favorable for one of the agricultural residues with respect to wood chips; however, the key unknowns that affect this result are the load reduction performance in a field situation, the length of service life, and actual producer cost of the agriculturally derived medium.

FUTURE NEEDS/PLANS

A logical next phase of the project would be to select the most promising material and build a pilot scale bioreactor at a field location. Since the properties of the agricultural residues are different from those of wood chips (i.e. greater nitrogen removal rates, lower hydraulic conductivities, and shorter service life), success in the field is dependent upon overcoming design and engineering challenges. These challenges include, for example, ease of filling, emptying, flow routing, protection from freezing, and affordability. The successful project team will include appropriate engineering expertise, a plan to adequately monitor performance of the system for a few years, and input from project partners, stakeholders, and producer-cooperators.
REFERENCES


Figure 1. Schematic of a denitrifying bioreactor designed to reduce the nitrate-nitrogen concentration of agricultural drainage water.

Figure 2. Eighteen bioreactor columns racked and plumbed in a temperature controlled chamber.
Figure 3. Bioreactor column schematics: (a) Standard; (b) With additional chamber for plastic biofilm carrier material (PBC).
Figure 4. Materials tested.
Figure 5. Permeameter built in June and July, 2012, for hydraulic conductivity testing. Insets: Column packed with corn cobs (A) and corn stover (B); column laid horizontally for removal of barley straw (C).
Figure 6. Lab test results of the first denitrification test run, which was conducted at 61°F. The treatments that included two media were: CC-WC, initial 2/3 of column was corn cobs and the final 1/3 was wood chips; CC-PBC (“CC-Kaldnes” in legend), corn cobs filled the primary 19-in. long column and plastic biofilm carrier (PBC) filled an additional 10-in. length of column added atop the primary column. Pictures of the media are shown in Figure 4.
Figure 7. Lab test results of the second denitrification test run, which was conducted at 35°F. The treatments that included two media were: CC-WC, initial 2/3 of column was Corn Cobs and the final 1/3 was wood chips; CC-PBC (“CC-Kaldnes” in legend), corn cobs filled the primary 19-in. long column and plastic biofilm carrier (PBC) filled an additional 10-in. length of column added atop the primary column; CC-WC mix, corn cobs and wood chips mixed together 50%-50% by oven-dry weight prior to packing in the columns. The CC-WC mix treatment was added for Run 2 as an Undergraduate Research Opportunity Project (UROP) student project. Pictures of the media are shown in Figure 4.
Figure 8. Permeameter data for 16 runs of three different materials. The legend key is explained as follows: Each item in the legend represents one complete flow test. A hydraulic conductivity coefficient is calculated for each flow test; the slope of the line represents the hydraulic conductivity in units of cm per second (cm/s). The initial characters indicate the test media in the vessel during the flow test: WC = Wood Chips; C Stover = Corn Stover; B Straw = Barley Straw. The number following the characters represents the number of times the permeameter vessel had been filled.

The letters a, b, and c indicate separate flow tests for a given column of material. For example, the permeameter vessel was filled the 3rd time with wood chips (WC-3); the first flow test was indicated as “WC-3a.” A second flow test was performed with the same wood chips in the vessel and was indicated as “WC-3b.”
Appendix A

(a) pH by Treatment: Run 1

(b) pH by Treatment: Run 2

Appendix A. Outflow pH by treatment for: (a) Run 1; (b) Run 2.
Appendix B  Noah Slocum’s University of Minnesota UROP poster.

**Comparison of Three Agricultural Residue-Based Filter Media for Use In a Denitrifying Bioreactor**

*Noah Slocum*

Faculty Advisor: Gary Feyereisen, Bioproducts & Biesystems Engineering and USDA-ARS

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**Introduction**

Nitrogen (N) is an essential nutrient for plant growth; however, unintended nutrient losses from cropping systems cause environmental concern. Nitrogen from soil organic matter is typically converted in the soil to nitrate (N$_{3}^{-}$), which is dissolved in the soil water and then taken up by the plants that are not incorporated through the plant roots remain in solution and are not host to soil particles, which have a slightly negative electrical charge.

Subsurface drainage systems are needed in the Midwest to remove excess water that can hinder crop production. These drainage systems not only convey excess water but also dissolve nitrate-$_{N}$, which is a water quality concern for both humans and marine animals. It can lead to phenomena like the Gulf of Mexico Hypoxic Zone (Fig. 4), where the additional N$_{3}^{-}$ results in a chain of events that cause depleted oxygen levels with subsequent negative consequences to marine life.

Denitrifying bioreactors are a promising technology to help mitigate the surplus of nitrate-$_{N}$ (Fig. 1). However, the leakage of nitrogen is reduced through filter media, typically a mix of wood chips, wherein anaerobic microorganisms convert dissolved nitrate-$_{N}$ to dinitrogen gas. In this experiment, three agricultural residues were tested to determine their comparative effectiveness as denitrifying bioreactor filter media. The three residues tested were corn cob, wood chip, and a 50/50 mixture of the two.

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**Methods**

Corn cob, wood chip, and a 50/50 by weight mixture of the two were packed in to three 13 x 30 cm PVC columns each (Fig. 3) so that there were nine columns total. Each column was inoculated with soil samples from nearby fields. A solution containing 20 mg/L concentration of nitrate-$_{N}$ was pumped through each column at a rate equivalent to anhydrous ammonia (42% of 12 hours using a peristaltic pump. This was performed continuously a period of 20 weeks. The entire apparatus was held in a cooler to keep the ambient temperature at a constant 2°C to mimic conditions common to the Midwestern US in springtime snowmelt.

Water samples were taken three times per week from each column to measure nitrate-$_{N}$ concentration pre- and post-treatment. The flowrate through each column was monitored daily.

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**Results**

After the temperature of the apparatus had been lowered to 2°C, the average post-treatment nitrate-$_{N}$ concentration of the woodchip medium was lower than that of both the mixture medium and corn cob medium (Fig. 4). Over a period of 14 weeks, the average post-treatment nitrate-$_{N}$ concentration was 4.6 mg/L for the woodchip medium, 4.1 mg/L for the mixture medium, and 4.2 mg/L for the corn cob medium, as compared to an average pre-treatment nitrate-$_{N}$ concentration of 21.4 mg/L for each medium.

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**Conclusions**

- Nitrate-$_{N}$ removal rates for the tested media, from greatest to least were: Corn Cob, Corn Cob–Wood Chip Mixture, Wood Chips.
- Lowering the ambient temperature to 2°C has a visibly effect (reduction) on the microbial activity in each medium.
- The mixture medium regularly behaved more like the wood chip medium than the corn cob medium, suggesting that microbial activity occurred more frequently with the wood chips than the corn cob, possibly because of the larger amount of surface area available to host microbial activity per unit volume of woodchip than per unit volume of corn cob.
- Further experimentation could be performed to determine the relationship between the amount of surface area per unit volume of a filter media and the feasibility of that medium to host microbial activity.

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**Acknowledgments**

Funding for this project was kindly provided by the University of Minnesota Undergraduate Research Opportunities Program, the USDA Agricultural Research Service Soil and Water Research Unit, the MN Agricultural Utilization Research Institute and the MN Corn Growers Association.
Appendix C Madison Rogers’ University of Minnesota UROP poster.

Hydraulic Flow Characteristics of a Promising Bioreactor Media
Madison Rogers
Faculty Advisor: Gary Feyereisen

Denitrifying Bioreactors

Agricultural practices tend to use nutrients that can be harmful towards the surrounding lakes and streams. A tile drainage system is a popular way to route excess water from agricultural fields into the surrounding surface waters. Unfortunately, the runoff of nitrogen (N) is having a large impact on water quality, and contributes to a hypoxic zone at the Mississippi River basin, the Gulf of Mexico [Fig. 1].

A denitrifying bioreactor is a practical, cost-effective design that helps reduce the nitrate-N levels in water runoff from agricultural fields (Fig 2). It is an excavation, filled with a carbonaceous filter medium, into which the drainage is routed. Anaerobic conditions in the bioreactor bed convert nitrate-N (NO₃⁻) to nitrogen gas (N₂) following the reaction

5NO₃⁻ + 10H⁺ → 5NO₂⁻ + 10H₂O

2NO₂⁻ + 3H₂O → 2NO₃⁻ + 4H⁺ + CO₂

Figure 2: Design layout of a denitrifying bioreactor

Finding the Most Effective Carbon Media

The type of media used in a denitrifying bioreactor can affect the amount of nitrogen removed, the flow of water through the bioreactor, and cost. One of the most commonly used media is woodchips, due to their accessibility, fairly low cost, and long service life. However, corn cobs have shown to have double the nitrate removal rate of woodchips. Corn cobs tend to have adverse effects of using more organic material to the system.

Focusing my project on hydraulic conductivity, I chose to mix the two types of media in hopes of gaining a balance of properties that would provide excellent nitrate removal rates along with efficient hydraulic conductivity. In terms of water flow, through the best material, uniform flow is desired so that all water may equilize contact time with the medium. Also, particle and pore sizes of the medium need to support sufficient flow rate to meet the bioreactor design.

Methods

All together, eight trials were completed, four in the horizontal, four in the vertical position. The flow velocities (Q) were plotted as a function of the hydraulic gradient (dH/dx). The hydraulic conductivity can be calculated using Darcy’s Law, K = Q/A·dH/dx. Darcy’s flow assumes a linear relationship, however, in this situation, that is not the case. To solve this, the natural log is taken of each function, which then goes into a linear relationship (Fig. 5).

Figure 4: Value on permeameter outflow which is used to control the flowrate of the water

Figure 5: Permeameter in horizontal position

Figure 6: Graph of hydraulic conductivity of corn cob/wood chip

Results and Discussion

The hydraulic conductivity of the Corn Cob/Wood Chips mix (CKW) while the permeameter was in the horizontal position was more than in the vertical position (Table 1). In general, greater porosity and/or larger pores will help to greater hydraulic conductivity, because with more space for water to flow through, the water will pass with less resistance. Higher conductivity in the horizontal position could be related to these items:

1. Setting - The media was packed into the column in the vertical position, it would have settled when allowed, creating a void between the media and tube, permitting water to take the path of least resistance.
2. Design - The permeameter not was designed for horizontal flow, slight modifications were made to allow change in position to work.

Table 1: Varied vs Horizontal Hydraulic Conductivity

<table>
<thead>
<tr>
<th>Position</th>
<th>Hydraulic Conductivity (cm/s)</th>
<th>Standard Deviation (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical</td>
<td>3.02</td>
<td>0.13</td>
</tr>
<tr>
<td>Horizontal</td>
<td>3.50</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Compared to the average values previously obtained for wood chips (WC), alone, the mix conductivity was lower (Table 2). On the contrary, the mix conductivity was not statistically different from corn cob alone (CC). Since the mix had a lower hydraulic conductivity, it can be assumed that corn cobs have a greater impact on the hydraulic conductivity than woodchips.

When comparing the columns after each trial, corn cobs were extremely swollen, which caused the pore space to decrease, inevitably causing a decrease in conductivity.

Table 2: Hydraulic Conductivity of Media in Vertical Position

<table>
<thead>
<tr>
<th>Media Type</th>
<th>Hydraulic Conductivity (cm/s)</th>
<th>Standard Deviation (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn Cob and Wood</td>
<td>3.02</td>
<td>0.13</td>
</tr>
<tr>
<td>Wood Chips</td>
<td>5.81</td>
<td>1.27</td>
</tr>
<tr>
<td>Corn Cob</td>
<td>2.81</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Conclusions

- The results of the vertical and horizontal mix of CKW are statistically different; the horizontal position has a 14% faster conductivity.
- The hydraulic conductivity of WC is statistically the same as CC.
- The hydraulic conductivity for WC is approximately 49% faster than mix, and 52% faster than CC.
- Each of these aspects affect the design of a denitrifying bioreactor in need and the amount of area needed to optimize flow rates and nitrate removal of the nutrients.

Figure 3: Hypotheses zone of Gulf of Mexico and Gulf of Mexico area of 2014

Figure 4: Permeameter in vertical position

Figure 5: Permeameter in horizontal position

Figure 6: Graph of hydraulic conductivity of corn cob/wood chip
Appendix D Rebecca Mattson’s University of Minnesota UROP poster.

The Effect of Increased Biomass Size on the Hydraulic Conductivity of a Bioreactor

Rebecca Mattson

Faculty Advisor: Gary Feyenson

Denitrifying Bioreactors

The hypoxia that exists at the outfall of the Mississippi River into the Gulf of Mexico is a problem attributed, in part, to the increased use of fertilizers in the Midwest. The rise of fertilizer use is a repercussion of the goal to maximize agricultural production. Nitrogen (N) is a main component in fertilizer. Several researchers note that this increase in fertilizer has caused an increase in nitrate-N runoff. 2-5 Denitrifying bioreactors are an effective and useful technology in removing nitrate-N from agricultural run-off before it flows into tributaries. Bioreactors address the nitrate-N pollution problem caused by increased production; an increased need to sustain population growth. Placing bioreactors in agricultural drainage ditches instead of the edges of fields would make the technology easier to access and maintain.

How the Permeameter Operates

Dr. Gary Feyenson and his team built a 30-cm diameter by 2.5-m long permeameter over the summer of 2012. This device performs tests on different carbon media types to determine their hydraulic conductivities. It was moved into the site South Building on the St. Paul Campus and rebuilt over January 2013.

To determine the feasibility of drainage ditches and to compare the large particle size hydraulic conductivity results to previous results, the permeameter was tested in the vertical position (Fig. 4) and the horizontal position (Fig. 5).

The packing procedure was consistent with previous research and is as follows:

1. Fill a 5 gal. bucket with sanded woodchips, collect a sample, weigh the bucket, pack down each 5 gal. bucket of woodchips into the cylinder using an 8 kg weight and tarp twist.
2. Fill the cylinder with water at a steady pace from the bottom up and let sit for 24-96 hours.
3. Turn on pump, and open outlet water valve to head differences ranging from 0.5 to 25 cm.
4. Measure flow rates at specific head difference measured by the manometer, a bucket, and stopwatch.
5. Measure porosity; empty water out of column by opening outlet hole, and weigh each bucket.

Results and Discussion

Larger biomass significantly increased the hydraulic conductivity of the permeameter compared to previous trials in both the vertical and horizontal positions. The percent of biomass that was larger than a 254-mm mesh was more than 65% larger. Although the error increases when the conductivity is corrected for change in viscosity due to temperature, the hydraulic conductivity is still statistically significant. This is detailed in the table below (Table 1).

<table>
<thead>
<tr>
<th>Table 1: Conductivities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated Hydraulic Conductivity, k, adjusted for water-temperature porosity (cm/s)</td>
</tr>
<tr>
<td>Vertical Average</td>
</tr>
<tr>
<td>Horizontal Average</td>
</tr>
</tbody>
</table>

The large standard deviation for the hydraulic conductivity of the horizontal test could be attributed to:
- Flows inconsistent with the linear model at low flow rates
- Possible open cavities, which could increase flow rate

The dry bulk density and the average flow porosity are much different than the previous data. Larger particles cannot be packed as tightly, leaving more space between them and increasing porosity and lowering dry bulk density, outlined in Table 2.

<table>
<thead>
<tr>
<th>Table 2: Material Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
</tr>
<tr>
<td>Density (kg/m3)</td>
</tr>
<tr>
<td>Average flow porosity</td>
</tr>
<tr>
<td>Percent Median Larger than 254-mm mesh</td>
</tr>
</tbody>
</table>

Conclusions

The data collected is promising for the future use of bioreactors in drainage ditches. It is clear that the increased biomass size increased the hydraulic conductivity. Increased hydraulic conductivity is the most crucial factor in moving the system to ditches, to accommodate more flow over a larger distance. Future research should focus on the type of flow expected in the system from agricultural runoff to see expected results based on flow rates. Another step would be to examine bioreactor holding time and nitrate-N removal in the system with the use of larger biomass.

Acknowledgements

Funding for this project was generously provided by the Cariotis Foundation Undergraduate Research Endowment; the Minnesota Legislative Special Session Area 38F; the University of Minnesota Faculty Early Career Grant Program; and the USDA National Institute of Food and Agriculture Hatch Program. Funding for this project was provided by Dr. Gary Feyenson and Dr. Fei Shi.
Appendix E  Grace Polverari’s University of Minnesota UROP poster.

Bromide Tracer Testing for Efficiency of a Bioreactor Permeameter

Grace A. Polverari

Faculty Advisor: Gary Feyereisen

The Issue
The Upper Midwest consists mainly of farming land that utilizes fertilizers and other nutrient rich supplements to grow crops. The nutrient surplus is often leached from the ground when the snow melts in the spring, bringing it to the drainage ditches about 6 feet under the ground and from here it eventually transported to the Mississippi River. The Mississippi River transports the excess nitrate-nitrogen to the Gulf of Mexico and further transports the Gulf of Mexico, especially along the Louisiana coast. The nutrient enrichment of the water creates an environment in which algae thrive, then die off, bacteria feeding on the algae deplete the dissolved oxygen in the water. This creates an area of hypoxia beneath the surface where most fish and sea life are unable to live, the term “hypoxic zone” refers to this area (Fig. 1).

The Solution
Denitrification is the process of removing the nitrate nitrogen from the water before it reaches streams and the Mississippi River. One specific way to use a bioreactor (Fig. 2) in practice, identifying bioreactors that are placed in the drainage ditch hold the water for 44 hours before it finally moves through them and re-enters to local streams, allowing the water to be in contact with the carbon medium long enough for the nitrate-nitrogen to be converted to N2 gas by bacterial metabolism. Bioreactors are a cost effective relative to other nitrate-nitrogen reduction techniques, an efficient and simple way to reduce the nutrient pollution in agricultural runoff.

Methods and Analysis
For this experiment, a test bioreactor/permeameter (Fig. 1) on St. Paul Campus was used. Bromide anion is a non-reactive tracer chemical that can be detected in water at different concentrations by using an ion specific electrode (ISE). For this experiment, three different types of flow were tested at four trials for each type. The three types included a slow vertical flow, a fast vertical flow and a fast horizontal flow. Water that was pumped from a tank ran through the top of the permeameter (inflow) to the bottom of the permeameter (outflow). To perform this bromide tracer test, the column was first packed full of woodchips that were of uniform size (>2.5 cm diameter). The method used was a slug method in which a large quantity of bromide tracer solution (12 g of bromide tritiated) was injected into the apparatus inflow, and the time started right after the slug was injected. Water samples and flow rates were collected at 30 minute intervals. The bromide samples were analyzed using the ISE to find the concentration at the time of different pore volumes throughout each run.

To analyze the data, the bromide concentrations were normalized and analyzed as a function of pore volume (Fig. 3). The flow rates were calculated using Darcy’s Law: X = QL/Ah. Using flow rates and bromide concentrations given by the ISE, the load distribution was calculated, graphed (Fig. 4), and used to estimate the Moore Dispersion Index number (MDI) (Table 1). The equation shown as (MDI = P/R) as Modified (c/a) / Wastewater Engineering: Treatment and Reuse.

Results and Conclusion
After normalizing the curves and combining the four tests for each flow, it’s shown that there is very little variability in the vertical flows, and a more significant amount of variability in the horizontal flow (Fig. 5). Start time issues may have caused the peaks to occur at different pore volumes. Overall, the curves are fairly narrow and don’t contain significant outliers. Each flow yielded an average MDI number less than or very close to two (Table 1) calculated using an MDI graph (example in Fig. 4). The MDI number is a type of analysis that shows a testing permeameter is efficient and plug flow is occurring with very little dispersion if the final number has value less than two. It’s proven that this permeameter is effective and that previous and future data collected from it is relevant.

Table 1: Average MDI Values and Standard Deviations

<table>
<thead>
<tr>
<th>Flow Type</th>
<th>MDI Ave. (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical Slow</td>
<td>2.02 (0.39)</td>
</tr>
<tr>
<td>Vertical Fast</td>
<td>1.77 (0.13)</td>
</tr>
<tr>
<td>Horizontal Fast</td>
<td>1.72 (0.11)</td>
</tr>
</tbody>
</table>

Acknowledgements
Funding for this project was provided by the University of Minnesota, Land O’Lakes, Inc., Department of Agriculture and the USDA Agricultural Research Service Soil and Water Research Unit.

Credit for the hypoxic zone image (Fig. 1) photo for the agricultural drainage management systems took place at http://hydrologyanddrainage.ca/sites/default/files/2016-04/Pressure.png and the USDA Agriculture Research Service Soil and Water Research Unit.
Appendix F  Student workers, clockwise beginning with upper left:  Taylor Hoffman; Elizabeth Petesch; Noah Slocum; Madison Rogers.  Madison is standing on the permeameter stand in its new location in the Biosystems and Agricultural Engineering Building on the U of M’s St. Paul campus.