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



By:

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Table of Contents

Acknowledgements	3
Executive Summary	4
Project Objectives	5
Background	6
Description of Work Performed	6
Results	
Material Properties	7
Bioreactor Column Tests	9
Hydraulic Conductivity Testing	12
Potential Benefit to Minnesota Economic/Environmental Development	13
Cost Analysis	13
Conclusions	16
Future Needs/Plans	16
References	17
Appendix A Graphs of effluent pH for Runs 1 and 2	25
Appendix B Student research project poster	26
Appendix C Student research project poster	27
Appendix D Student research project poster	28
Appendix E Student research project poster	29
Appendix F Student worker photographs	30

List of Tables

Table 1	Properties of the bioreactor test media	8
Table 2	Hydraulic residence times for Run 1 and Run 2	9
Table 3	Nitrate-N removal rates for the treatments for Run 1 and Run 2	10
Table 4	Dissolved oxygen readings for Run 1 and Run 2	11
Table 5	Average oxidation-reduction potential readings for Run 1 and Run 2	11
Table 6	Average effluent total organic carbon concentrations for Run 1	
	and Run 2	12
Table 7	Assumptions made for cost analysis	14
Table 8	Total present value costs for a bioreactor with wood chips versus	
	corn cob media	15
Table 9	Estimated cost of nitrate-N removed	16

List of Figures

Figure 1	Schematic of a denitrifying bioreactor	18
Figure 2	Photos of eighteen bioreactor columns in controlled temperature chamber	18
Figure 3	Bioreactor column schematics	19
Figure 4	Photos of materials tested	20
Figure 5	Permeameter stand in original field location	21
Figure 6	Inlet and outlet nitrate-N concentration over time for Run 1	22
Figure 7	Inlet and outlet nitrate-N concentration over time for Run 2	23
Figure 8	Graph of hydraulic conductivity tests	24

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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: $CC \ge CC+WC = CS \ge$ 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 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

number of gene copies was less on the PBC outlet end than on the CC inlet end of the CC-PBC columns. The conclusions of the article were that the additional chamber of PBC after CC marginally improved the nitrate removal performance and nitrous oxide production was less for CC-PBC at the warmer temperature. The added chamber of PBC did not result in organic C removal from the effluent and did not improve performance at low temperatures. Another unidentified factor limited nitrate removal, since nitrate and carbon were present in the effluent.

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 becomes 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 entireties 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⁻). 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. Pro	Operties of th	Description	Lest meur	d.	Carbant	Nitragont	C.N. Datiat	Lludra gan [†]
Treatment	Particle Size	Description	Moisture Content [†]	Asn Content [†]	Carbon	Nitrogen	C:N Ratio	Hydrogen
			(%)	(%)	(%)	(%)		(%)
Wood Chips	Sieve Size	Mass	Initial	Initial	Initial	Initial	Initial	Initial
	(mm)	(%)	2.98	0.39	50.0	0.19	263	5.94
	> 38	0						
	25 - 38	3	Run 1	Run 1	Run 1	Run 1	Run 1	Run 1
	19 - 25	5	4.51	3.52	48.9	0.28	172	5.82
	13 - 19	25						
	6 - 13	50	Run 2	Run 2	Run 2	Run 2	Run 2	Run 2
	< 6.4	16	4.12	5.71	46.4	0.33	141	5.52
Corn Stover	Particle Length	Mass	Initial	Initial	Initial	Initial	Initial	Initial
	(cm) Stalk	(frctn)	4.24	4.47	46.2	0.66	70	5.76
	5 – 10	0.25	Run 1	Run 1	Run 1	Run 1	Run 1	Run 1
	10 – 15	0.25	4.31	19.62	44.0	0.79	55	5.28
	15 – 20	0.26						
	Leaves		Run 2	Run 2	Run 2	Run 2	Run 2	Run 2
	0-10	0.04	4.19	12.76	44.1	0.63	70	5.40
	10 – 15	0.05						
	15 – 20 Cobs	0.09						
	<= 2.5	0.02						
	2.5 – 6	0.02						
	7 – 10	0.02						
Barley	Particle Length	Mass	Initial	Initial	Initial	Initial	Initial	Initial
Straw	(cm)	(frctn)	3.92	8.87	44.6	0.42	106	5.56
	0-10	0.16						
	10-20	0.51	Run 1	Run 1	Run 1	Run 1	Run 1	Run 1
	20 – 30	0.20	4.15	21.48	42.9	0.85	51	5.23
	30 - 40	0.08						
	40 – 50	0.05	Run 2	Run 2	Run 2	Run 2	Run 2	Run 2
			4.23	21.10	41.8	0.93	45	5.15
Corn Cobs	Particle Length	Numeric	Initial	Initial	Initial	Initial	Initial	Initial
		Frctn	4.17	2.98	48.1	0.58	83	5.88
	(±0.5 cm)	(%)						
	2	2	Run 1	Run 1	Run 1	Run 1	Run 1	Run 1
	3	7	4.50	12.55	43.0	0.81	53	5.17
	4	19						
	5	29	Run 2	Run 2	Run 2	Run 2	Run 2	Run 2
	6	28	4.03	11.08	42.7	0.67	64	5.21
	7	6						
	8	4						
	9	3						
	TÜ	Ţ						
	Sieve Size	Mass Passing						
	(mm)	(%)						
	38.1	88						
	25.4	20						
	19.1	1						
PBC‡	2. 5 cm diamete 584 m ² surface a	r by 1.0 cm long area per m ³	n/a	n/a	n/a	n/a	n/a	n/a

Table 1 Properties of the bioreactor test media

⁺ 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).

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

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

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).

Run		Temp	CS	СС	CC-WC	BS	WC	СС-К
	Period	(°F)			(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

Table 3. Nitrate-N removal rates for the treatments for Run 1 and Run 2.

⁺ 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.

Run	Period	Temp	Inlet	CS	СС	CC-WC	BS	WC	СС-К
		(°F)				(ppm)†			
1	5/2 – 5/29/12	60.9	5.5	0.9	1.2	1.3	0.9	0.9	1.2
1	6/22 – 7/18/12	59.3	5.9	1.7	2.0	1.7	1.8	1.7	1.9
2	5/3 – 5/13/13	35.0	8.4	0.8	1.3	1.0	0.9	0.9	1.2

+ 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.

Run	Period	Temp	CS	CC	CC-WC	BS	WC	СС-К
		(°F)			(mV)	†		
1	5/2 – 5/29/12	60.9	169	192	186	185	231	148
1	6/22 - 7/18/12	59.3	222	102	191	245	203	149
2	2/6 - 4/19/13	35.0	281	381	375	314	390	363

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

† 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.

Run	Period	Temp	Inlet Water	CS	СС	CC-WC	BS	WC	СС-К
		(°F)				(mg L ⁻¹)			
1	5/2 – 5/29/12	60.9	17.1	15.1	40.2	26.6	18.2	12.9	39.3
1	6/22 — 7/18/12	59.3	7.6	9.3	23.1	11.0	8.9	8.6	18.0
2	2/6 – 4/19/13	35.0	8.7	10.1	10.1	10.1	9.8	9.9	10.2

Table 6. Average effluent total organic carbon concentrations for Runs 1 and 2.

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 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.

Assumption	
Bioreactor Bed Medium	Corn Cobs
Size of Bioreactor Bed	Same as for Wood Chips
Nitrate-N Load, lb N/ac/y	28
Nitrate-N Load Removal	
Case A, %	37.5*
Case B, %	50**
Medium Replacement Interval, y	4*
Cost of Medium	
Minimum, \$/ton	0
Maximum, \$/ton	87**

Table 7. Assumptions made for cost analysis of a denitrifying bioreactor with a medium of corn cobs.

⁺ 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 x $(i(1+i)^n/((1+i)^n - 1))$

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

(1)

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.

	WC,† Minimum	CC, Minimum	WC,⁺ Maximum	CC, Maximum
ltom	winning	iviiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii		Waximum
item		(\$/	dC)	
Installation				
Media	47.02**	0.00	47.02	14.57
Contractor Fees	11.21	11.21	40.02	40.02
Design	0.00	0.00	12.81	12.81
Materials	24.04	24.04	84.11	84.11
Cost of installation	82.27	35.25	183.95	151.50
Maintenance & Replacement				
Replacement	26.58	49.99	39.75	243.33
Labor and materials	16.22	16.22	34.44	34.44
Cost of maintenance &				
replacement	42.80	66.21	74.18	277.77
I otal present value cost of				
installation, maintenance &				
replacement	125.07	101.45	258.13	429.26

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

⁺ 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.

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

Table 9. Estimated cost of nitrate-N removal based on minimum and maximum cost projections to install and maintain a denitrifying bioreactor.

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.

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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).







Corn Cobs (CC)



Corn Stover





Barley Straw



CC + Plastic Biofilm Carrier

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.

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. Outflow pH by treatment for: (a) Run 1; (b) Run 2.

Appendix B Noah Slocum's University of Minnesota UROP poster. USDA **Comparison of Three Agricultural Residue-Based Filter Media** for Use In a Denitrifying Bioreactor Noah Slocum Faculty Advisor: Gary Feyereisen, Bioproducts & Biosystems Engineering and USDA-ARS Introduction Methods Results Nitrogen (N) is an essential nutrient for plant growth; Corn cob, woodchip, and a 30%/30%-by-weight After the temperature of the apparatus had been lowered to 2°C, the average post-treatment however, unintended nutrient losses from cropping mixture of the two were packed in to three 15 x 50 cm PVC nitrate-N concentration of the wood chip medium was higher than that of both the mixture medium and corn cob medium (Fig. 4). Over a period of 14 weeks, the average post-treatment systems cause environmental concern. Nitrogen from soil columns each (Fig. 3) so that there were nine columns organic matter or fertilizers is typically converted in the total. Each column was inoculated with soil samples from nitrate-N concentration was 49.6 mg/L for the wood chip medium, 48.3 mg/L for the mixture soil to the nitrate ion form (NO,), which is dissolved in nearby fields. A solution containing a 30 mg/L medium, and 42.9 mg/L for the corn cob medium, as compared to an average pre-treatment the soil water and then taken up into the plant. Jons that concentration of nitrate-N was pumped through each nitrate-N concentration of 51.4 mg/L for each medium. are not transported through the plant roots remain in column at a rate equivalent to a hydraulic residence time of solution and are not held to soil particles, which also have 12 hours using a peristaltic pump. This was performed a slightly negative electrical charge. continuously for a period of 20 weeks. The entire apparatus - 12 Mar was held in a cooler so as to keep the ambient temperature ----Subsurface tile drainage systems are needed in the at a constant 2 °C to mimic conditions common to the Midwest to remove excess water that can hinder crop Midwestern US in springtime snowmelt. production. These drainage systems not only convey Water samples were taken three times per week from excess water but also dissolved nitrate-N, which is a water each column to measure nitrate-N concentration pre- and quality concern for both humans and marine animals. It post-treatment. The flow rate through each column was contributes to phenomena like the Gulf of Mexico hypoxic monitored daily. zone (Fig. 1), where the additional N results in a chain of events that causes depleted oxygen levels with subsequent negative consequences to marine life. The corn cob medium was observed to have an average nitrate-N removal rate greater than Denitrifying bioreactors are a promising technology that of the mixture medium or wood chip medium (Fig. 5). The nitrate-N removal rate for each to help mitigate the outflow of nitrate-N (Fig. 2). medium was calculated in units of grams of nitrate-N removed per cubic meter of medium per Subsurface tile drainage effluent is routed through a filter day. Over a period of 14 weeks, the average nitrate-N removal rate was 7.81 g/m³/d for the corn medium, typically a bed of wood chips, where anaerobic cob medium, 3.03 g/m³/d for the mixture medium, and 1.69 g/m³/d for the wood chip medium. microbes convert the dissolved nitrate-N to innocuous N. Inconsistencies in the patterns described were most likely a result of variations in the nitrate-N gas. In this experiment, three agricultural residues were concentration of the inlet solution. tested to determine their comparative effectiveness as denitritying bioreactor filter media. The three residue media tested were corn cob, wood chip, and a 30%/30% Conclusions mixture of the two. Nitrate-N removal rates for the tested media, from greatest to least were: Corn Cobs > Corn Cob-Wood Chip Mixture > Wood Chips. Page 3. Schematic of a PVC increasion solar · Lowering the ambient temperature to 2° C had a visible effect (reduction) on the microbial activity in each medium. · The mixture medium regularly behaved more like the wood chip medium than the corn Inflow Control Outflow Control cob medium, suggesting that microbial activity occurred more frequently with the wood chips than the corn cobs, 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 Nitrogen poes Further experimentation could be performed to determine the relationship between used NO₂ 4N los the amount of surface area per unit volume of a filter medium and the favorability of that medium to host microbial activity. Figure 1: Water syst Centrifying Nonector Bed Actions Funding for this project was kindly provided by the University of Minnesota Undergraduate Research Opportunities Program, the USDA Agricultural Research Service Soil and Wister Research Unit, the M Figure 2: Schematic of a typical denitrifying bioreactor arch Unit, the MN Arrighteni Utilization Research Institute and the MN Core Generate Association

Appendix C Madison Rogers' University of Minnesota UROP poster.

Appendix D Rebecca Mattson's University of Minnesota UROP poster.

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

Denitrifying Bioreactors

The hypoxia that exists at the outflow of the Mississippi River into the Gulf of Mexico is a problem attributed, in part, to the increased use of fertilizers in the Midwest¹. 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 upturn in nitrate-N runoff^{1, 2, 3}. 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 increase needed to sustain population growth. Placing bioreactors in agricultural drainage ditches instead at the edges of fields would make the technology easier to access and maintain.

Figure 1: Design layout of a denitrifying bioreactor

A denitrifying bioreactor is a practical and cost effective technology that reduces nitrate-N levels in water runoff from agricultural fields (Fig. 1). Tile drainage systems naturally run to drainage ditches. When converted to a bioreactor, ditches are filled with a carbon-based filter medium, into which tile drainage is routed. Anaerobic microbes in the bioreactor bed convert nitrate-N (NO3⁻) to nitrogen gas (N2), shown below, reducing outflow loading.

 $5C + 4NO_3^- + 2H_2O \longrightarrow 2N_2 + 4HCO_3^- + CO_2$

Identifying Larger Particle Sizes

Bioreactors have been extensively studied. Many variables have been researched in depth or are currently under investigation. One under-tested variable is the biomass particle size. I hypothesized that the conductivity of the bioreactor would increase due to the increased biomass size. Increased conductivity and therefore flow rate increases the potential for bioreactors in drainage ditches due to the increased water quantity and flow distances.

I chose to focus my research on the effect of increased biomass size on the permeameter hydraulic conductivity. To investigate. I created a mesh sieve (1" diagonal dimension) to separate acceptable woodchips from smaller chips. All woodchips used were sampled and sent through a particle size distribution to determine the percentage of particles that were greater than 1-in² (25.4-mm). The distribution also facilitated simpler comparison to previous work.

Figure 3: Particle Size Distribution

How the Permeameter Operates

Dr. Gary Feyereisen 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 BBE South Building on the St. Paul Campus and rebuilt over January 2013.

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

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

1. Fill a 5 gal. bucket with sieved woodchips, collect a sample, weigh the bucket, pack down each 5 gal. bucket of woodchips into the column using an 8-kg weight and tamp twice.

2. Fill the column 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 0.5-25 cm. 4. Measure flow rates at specific head difference

measured by the monometer, a bucket, and stopwatch

5. Measure porosity: empty water out of column by opening outlet hose, and weighing each bucket.

Methods

Figure 5: Permeameter in

horizontal position

The procedure was run a total of eight times: four trials in the horizontal and 4 in the vertical position. The flow velocities, flow rate over the area (Q/A), were plotted as a function of the hydraulic gradient, the change in head over the length (Dh/L). Darcy's Law, k = QL/Adh , was used to calculate the hydraulic conductivity (k). Darcy's flow assumes a linear relationship, however the data is better fit by a power function. To display the relationship more intuitively, the natural log is taken of the flow velocity and the hydraulic gradient (Fig. 6).

Results and Discussion

Larger biomass significantly increased the hydraulic conductivity of the permeameter compared to previous trails in both the vertical and horizontal positions. The percent of biomass that was larger than a 25.4-mm mesh was more than 45% 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 1: Conductivities Saturated Saturated Hydraulic Hydraulic Conductivity, k', adjusted Conductivity for water temperature (cm/s) ± st.dev. k, (cm/s) ± st.dev. 8.73 (1.48) b Vertical Average 6.69 (0.98) b Horizontal 10.68 (3.27) a 17.23 (5.30) a Average 3.02 (0.13) b 3.28 (0.22) b Chritianson Mean values in a column followed by the same letter are not statistically different at α =0.10 Mean values in a column followed by the same letter are not statistically different at α =0.05

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, that could increases 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

Table 2: Material Properties

	Mattson	Feyereisen & Christianson ⁴
Dry Bulk Density (kg/m ³)	177	220
Average Flow porosity	51	46
Percent Media Larger than 25.4-mm Mesh	53	5

Conclusions

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 longer distance

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.

Acknowledgments

space between them and increasing porosity and lowering dry bulk density, outlined in Table 2.

	Mattson	Feyereisen & Christianson ⁴
Dry Bulk Density (kg/m ³)	177	220
Average Flow porosity	51	46
Percent Media Larger than 25.4-mm Mesh	53	5

The data collected is promising for the future use of bioreactors in drainage

Future research should focus on the type of flow expected in the system

Appendix E Grace Polverari's University of Minnesota UROP poster.

Bromide Tracer Testing for Efficiency of a Bioreactor Permeameter

Grace A. Polverari

Results and Conclusion

Faculty Advisor: Gary Feyereisen

<u>The Issue</u>

The Upper Midwest composed mainly of farming land that utilizes fertilizer and other nutrient rich supplements to grow crops. The nutrient surplus is often leeched from the ground when the snow mells in the spring, bringing it to the drainage tile about 6 feet under the ground and from here it is eventually transported to the Mississippi River. The Mississippi River transports the excess nitrate-nitrogen to the Mississippi River Basin and furthermore the Gulf of Mexico especially along the Louisiana coast. The nutrient enrichment of the water creates an environment in which algae thrive, then tie off; bacteria feeding on the algae deplete the dissolved oxygen in the water. This creates an area of hypoxia underneath the surface where most fish and sea life are unable to live; "the term "Hypoxic Zone" refers to this area (Fig. 1).

Figure 1: Gulf of Mexico Hypoxic Zone

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 is to use a bioreactor (Fig. 2). In practice, denitrifying bioreactors that are placed in the drainage tile hold the water for 4+ hours before it finally moves through them and rerouted 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 bollution in agricultural runoff.

Figure 2: Bioreactor/ Permeameter on St. Paul Campus

For this experiment, a test bioreactor/permeameter (Fig. 1) on St. Paul Campus was used. Bromide anion is a nonreactive 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 permeamater (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 anion solution (12 g of bromide total) was injected into the apparatus inflow, and the time started right after the slug was injected. Water samples and flow rates were collected at certain pore volumes. The bromide samples were analyzed using the ISE to find the concentration at the time of different pore volumes throughout each run.

Methods and Analysis

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 Flow: K = QL/Abh. Using flow rates and bromide concentrations given by the ISE, the load distribution was calculated, graphed (Fig. 4), and used to calculate the Morrill Dispersion Index number (MDI) (Table 1). The equation shown as (MDI) = P90/P101 in Metcalf Eddy's Wastewater Engineering. Treatment and Reuse.

After normalizing the curves and combining the four trials 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. 3). 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 proves a testing permeameter is efficient and plug flow is occurring with very little dispersion if the final number has a value of less than two. It's proven that this permeameter is effective and that previous and future data collected from it is relevant.

Funding for this project was provided by the University of Minnesota Undergraduate Research Opportunities Program and the USDA Agricultural Research Service Soil and Water Research Unit.

Credit for the Hypoxic zone image (Figure 1) goes to the agricultural drainage management systems task force at http://hostedweb.cfaes.ohiostate.edu/usdasdru/ADMS/Gallery/INloss%20in%20MS%20Rr%20Dr%20Basin2.jpg

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.