Report to the Minnesota Department of Agriculture: Anaerobic Woodchip Bioreactor for Denitrification, Herbicide Dissipation, and Greenhouse Gas Mitigation

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Denitrification in Field Anaerobic Bioreactor Under Rainfall and Snowmelt Regimes

Several conservation practices have been promoted to mitigate nitrate loss to waterways. Among them, a woodchip bioreactor system that has been tested in several locations in the Midwest and has yielded reasonable reductions of nitrate concentration and load. The system is based on using woodchips as a carbon source and the ability of certain bacteria (facultative anaerobic denitrifiers) to use nitrate for respiration under low oxygen conditions. The woodchips used in this experiment consist of a mix of maple and red oak. Red oak makes up 12.5% of woodchips by weight. Under such conditions, oxygen is quickly consumed first, and then microbes switch to nitrate as an electron acceptor in the respiration metabolism. Depending on the local conditions, nitrate can be completely transformed into dissolved dinitrogen gas in the tile drainage water that eventually escapes to the atmosphere.

As an alternative to aerobic respiration, denitrification is a microbial metabolism through which nitrate is transformed to nitrogen gas with several intermediate compounds in absence of oxygen as summarized in the following reactions:

$$NO_3^- \,(+V) \rightarrow NO_2^- \,(+III) \rightarrow NO\,(+II) \rightarrow N_2O\,(+I) \rightarrow N_2\,(0)$$

The compounds listed in the reaction from left to right are: nitrate, nitrite, nitric oxide, nitrous oxide, and nitrogen gas with, in parenthesis, their associated oxidation state.

Flow Processes: Two major flow processes need to be taken into account when considering the woodchip bioreactor system:

- Advective flow through the woodchip material and

- Diffusion flow across biofilm membranes and into bacteria cells where contaminant reduction occurs.

These two types of flow rate can be very different by orders of magnitude. Their effects are quantifiable in terms of exiting flow rate and reduction of nitrate concentration.

Site Description and Methods

Soils: At the Dodge County site, the soil is made up of Maxfield silty clay loam (Fine-silty, mixed, superactive, mesic Typic Endoaquolls) that covers the entire field. Patterned tile is at 80 ft spacing and 4.0 ft depth. Field is gently sloping to the south, with 1-2 percent grade. Bioreactor is located across the road, bordering adjoining property, south of the field.

Crop Rotation, Primary Tillage and Fertilizer Application: Crop rotation includes one year of soybean followed by two years of corn. Soybeans were planted in 2006 and 2009. Field operations include fall moldboard, and anhydrous ammonia applied/injected with N-serve at 150 lbs/ac for corn following soybeans. 200 lbs/ac of P_2O_5 and 200 lbs/ac of K_2O were applied the following spring. There was no fertilizer application for the soybean year.

Monitoring: Site has a contributing area of 26 ac with a bioreactor of 240 ft long, 6 ft deep, and 3.5 ft wide. The bioreactor trench is capped with 2.0 ft of topsoil over 4.0 ft of of woodchips. This site used two flow monitoring systems: a.) weir flow with AgriDrain system, and b.) ISCO area-velocity flow unit (ISCO 2150). Area-velocity ring and probe units were installed upstream and downstream of the AgriDrain flow box. These were connected to data loggers that downloaded data on a regular basis. AgriDrain data stream was transferred via a radio system (MiniSat). At Dodge County site, the inlet flow box contains three compartments. Flow from the field comes into the first compartment; second compartment directs flow into bioreactor; third compartment is connected to bypass system for high flow rates. Flow height was measured with pressure transducers at both the first and second compartments and converted into flow rate via a rating curve calibrated at the University of Illinois, Urbana-Champaign. Flow heights from ISCO measurements closely matched the AgriDrain system.

Automated Sampler: Using ISCO (2150) automated sampler, sampling scheme with the bioreactors consist of 24-hr sampling with 8 sub-samples every 3-hour period. Each sub-sample was 0.127 qt, which gives a total of 1.01 qt per bottle. Two collection bottles were filled every day, one with acid preservatives (H_2SO_4 to keep samples at pH 2.0) and the other without acid preservatives. Acid bottles were tested for nitrate + nitrite (N+N) and total phosphorus (Tot P) while the 7th day non-acid bottle was tested for nitrite, soluble phosphorus, and ammonia. The other 6 non-acid sampling bottles were for total suspended solids (TSS). The sampling scheme was changed from 1-day bottle in 2009 to 2-day bottle in 2010.

Bioreactor Parameters: Other parameters to assess bioreactor efficiency included: hydraulic residence time, temperature, pH, dissolved oxygen, and oxido-reduction potential. Hydraulic Residence Time (HRT) provides the length of time a parcel of water was flowing through the bioreactor. HRT is a key indicator of needed contact time with the bacterial community to process contaminants. HRT is calculated as a ratio of total water volume to the flow rate across the bioreactor; volume calculation is bioreactor physical volume multiplied by porosity of the woodchip material.

HRT was calculated based on two methods: 1/ probabilistic distribution curve of HRT based on average daily flow rates (1-hour flow rate record or shorter), and 2/ field experiment using Bromide tracer.

Snowmelt and Tile Flow

Monitoring included two snowmelt periods (2010 and 2011) and two rainfall seasons (2009 and 2010). Nitrate load reduction during snowmelt period was 26% (2010) and 10% (2011) (Table 1.1). The two snowmelt events demonstrated the capability of the bioreactor under cold conditions. The snowmelt flow depth was 1.59 in. in 2010, 20% of the annual total value of 7.91 in. of flow depth. 2011 snowmelt flow depth was 2.88 in. with a lower nitrate load reduction of 10.2%.

AgriDrain control structures allow variable water height control (changes in head) that can force nearly all of the incoming tile flow through the bioreactor. This was employed during the 2011 snowmelt, as nearly all tile flow was forced through the bioreactor using the maximum stop log height.

The snowmelt load reduction was inversely proportional to flow depth. When combined, the two snowmelt events (2010-11) yielded a total nitrate load reduction of 15.3%. This combined snowmelt nitrate load reduction is comparable to the sum of May and June 2010 load reductions.

Impact of Precipitation

Total precipitation for 2009 was 30.4 in., which is less than the 30-year normal precipitation for this area (33.6 in., Owatonna-MN, 1981-2010). Bioreactor flow for 2009 was 9.92 in. with 5.47 in. through the bypass and 4.45 in. through the bioreactor. Total precipitation for 2010 was 41.7 in., which is 8.1 in. greater than 30-year normal. Bioreactor flow for 2010 was 15.8 in. through the bypass and 9.45 in. through the bioreactor (Table 1.3).

During high flows, nitrate load reduction decreases significantly. From April 2009 to November 2009, nitrate load reduction was 48%, but it fell to 21% in 2010 during the same time period due to a significant increase in rainfall. Rainfall amount in 2010 was 11.3 in. greater than that of 2009. Flow depth and precipitation were extremely high from September to November 2010 decreasing the percent load reduction.

The HRT was much smaller in 2010 (14.4 hours) compared to that of 2009 (21 hours); flow rate was faster in 2010 and the nitrate load reduction was 50% smaller. Nitrate reduction decreases during the rising limbs of a hydrograph and around the peak flow, but usually recovers during the falling limbs or between the peaks (Figure 1.1). Infrequently a large reduction occurred within the peak flow period (June 6, 2009) and contributed to load reduction. Commonly, rising limb periods were associated with shorter HRT and smaller load reductions[1].

For both snowmelt and growing season, two versions of nitrate load reduction are presented: 1/ one representing reduction at the bioreactor level by taking into account inflow and outflow only, and 2/ the other taking into account untreated load through the bypass (Table 1.2 and 1.4)

Temperature Gradients

Temperature gradient between the surrounding soil and the bioreactor trench during snowmelt suggests that heat energy was transferred to the bioreactor from surrounding soil, and may have contributed to load reduction in 2010 and 2011[2]. Other parameters such as dissolved oxygen, redox potential, and pH support the occurrence of denitrification from April to November 2010. During this timeframe there was a reducing environment when water in the bioreactor remained stagnant; small amounts of harmful gas (H_2S and CH_4) may have been

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[1] *In 2009, nitrate load reduction normalized to flow depth were 1.54 and 1.59 lbs.ac^{-1}.in^{-1} for rising and falling limbs, respectively. In 2010, the values were 0.73 lbs.ac^{-1}.in^{-1} for rising limbs and 1.04 lbs.ac^{-1}.in^{-1} for falling limbs.*

[2] *Welander and Mattiason (2003) pointed the usefulness of bioreactor as they found out a weak relationship between denitrification rate and temperature, which can be interpreted as the ability of the system to perform under cold temperature.*

released into the water column. Strong rotten egg smell was detected at the outlet of the bioreactor during no flow periods, an evidence of sulfate reducing bacteria activity.

Longevity of Woodchips

The longevity of the woodchips is related to the continuous presence of water in the bioreactor; the key is to keep as much woodchip volume as possible under water, as long as possible. Upper 12-18” of 48” woodchip lens experiences the greatest frequency of fluctuating water level, and therefore the highest degradation rate. The bioreactor was established in 2007, and by 2011 the C/N ratio of the upper layer 12-18” decreased by 25%. However, the bottom layer decreased only by 1.5% for the same period.

Conclusion

The nitrate load reduction occurred during snowmelt, rainfall seasons, and late in the season. There was no difference for nitrate concentrations between soybean year (2009) and corn year (2010). The rainfall patterns and associated tile flow made more difference in terms of nitrate load reduction between those two years than any other parameters.

Increase of rainfall or snowmelt and subsequent flow depths don’t overwhelm the bioreactor practical, minimum design standards, but the hydrograph flow patterns do.

On an annual basis, rainfall and flow quantity are inversely proportional to load reduction. This holds on a monthly basis if rainfall sets trend pattern. This trend was more obvious in 2010 growing season with regard to monthly load reduction.

Atrazine and Acetochlor Dissipation in A Bioreactor Under Flowing Conditions: Adsorption Reactor Model

The herbicides Atrazine and Acetochlor are commonly used with corn-soybean farming system in the Midwest to control weeds. Adsorption reactor models were used to assess the ability of the bioreactor to dissipate herbicides[3]. These two herbicides as well as their metabolites have been detected in groundwater, drainage water, and surface water in the region[4]. Based on the latest publication of a woodchip bioreactor (Ilhan et al. 2011) and this Minnesota experiment, the most likely process for herbicide dissipation within the bioreactor is adsorption on the woodchip.

The Minnesota experiment explores the adsorbing capacity and defines the limitations of woodchip material with Atrazine and Acetochlor. The Minnesota experiment provides both field data and modeling to confirm the strong relationship between these two herbicides and woodchip material properties.

Rodriguez-Cruz et al. (2007b) have investigated the role of wood component on adsorbing herbicides based on K_{ow} coefficient (indicative of herbicide hydrophobicity [5]), wood property, and ionic property of herbicides, in that order of importance. Rodriguez-Cruz et al. (2007b) have investigated the role of wood components on adsorbing herbicides based upon both wood and

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[3] *Mode of actions of Atrazine and Acetochlor as herbicide is summarized as inhibition of photosynthesis and disruption of protein synthesis in target plant, respectively (Scheebaum, 2006).*

[4] *The common metabolites of Atrazine are de-ethyl atrazine (DEA), de-isopropyl atrazine (DIA), or hydroxyl atrazine (HA) whereas those of Acetochlor are ethane sulfonic acid (ESA) and oxalic acid (OXA).*

[5] *The logarithm of octanol-water partition coefficient (log K_{ow}) for acetochlor and atrazine is 4.14 and 2.50, respectively. It refers to the degree of attraction of herbicide to octanol rather than to water.*

herbicides properties. They tested four herbicides, among them was alachlor; alachlor and acetochlor belong to the same family of herbicides and are the closest in terms of physico-chemical properties. They tested herbicides against nine types of wood including oak, walnut, and maple. Lignin content of the wood types was found to be a key parameter in determining herbicide adsorption. Lignin content of the wood type selected ranged from 18.2 to 26.9%. Batch equilibrium method (not kinetic, i.e., flowing method) was applied to establish adsorption capacity for each herbicide against the types of woods and their relative lignin content[6].

Field Site Description and Methods: Rice County site is a relatively flat field, with two plots. One plot with a managed pattern-tiled drainage system (6.65 acres) and the other plot is a conventional pattern-tiled drainage system (15.6 acres). The bioreactor is part of the managed drainage plot (6.65 acres). Bioreactor is 90 ft long, 3 ft wide and 6.0 ft deep (2.0 ft top soil and 4.0 ft of woodchip)[7]. This field is in a corn-soybean rotation, with soybeans in 2007, 2009, and 2011.

For the herbicide experiment, nearby ditch water was filtered and pumped at a flow rate of 4.0 gpm into the woodchip bioreactor[8]. A known concentration of herbicide was injected into the bioreactor for an experiment during September-October 2010. Based on the bioreactor

[6] *Adsorption of herbicides on wood material has been explored by various researchers among which are works by Rodriguez-Cruz et al. (2007b), Bra's et al. (1999), Shukla et al. (2002), Mackay et Gschwend (2000), Trapp et al. (2001), and Boving and Zhang (2004).*

[7] *The porosity of the woodchip is estimated at 0.57 from laboratory experiment. Soil on this site is made up mostly of Dundas silty loam (fine-loamy, mixed, superactive, mesic Mollic Endoaqualfs). Patterned tile is set-up at 40 ft distance between tiles and buried at 4.0 ft below ground surface. Field is gently undulating to the south 0-1 percent slope with a 8.0-ft deep ditch located immediately adjacent to the south side of the field. Location of bioreactor is directly at the south end of the field within the ditch buffer zone.*

[8] *The system was changed to handle 6 pairs of 1-L glass bottles for collecting water samples. One bottle of each pair was left plain for collecting herbicide sample while the other was acidified for nitrate and total phosphorus samples. The sampling cycle was 6-day with a sub-sampling schedule of 0.127 qt every 3 hour per day*

volume (5284 gal), the flow rate insured a 24-hour residence time before discharging water back into the ditch. This steady flow rate system was built with several components (please see appendix).

The motivation behind the herbicide concentrations[9] is based on values reported by a MDA project (Highway 90, 2008) and from a review article of herbicide in tile-drainage by Kladivko et al (2001). The employed concentration values are bracketed between those of the MDA project (Highway 90, 2008) and the maximum values reported by the Kladivko review article, 0.5 ppb (acetochlor) and 11 ppb (alachlor), respectively. A fixed amount of nitrate was added to herbicide-nitrate solution to maintain a final concentration of 1.0 mg/L of NO_3-N. Two 6.5-gal glass jars were used weekly to transport the herbicide-nitrate solution mixture to the field site.

Details of chemical tests are presented in footnotes[10,11]. Array of thermocouples for recording temperature data and probes for bioreactor parameters were installed. In the center of the bioreactor, three probes were inserted through an access hatch. Data from thermocouples and parameter probes were logged, and the output sent to a data storage system on a 20-minute time interval.

<u>The Adsorption Reactor Approach:</u> There are three reasons to use adsorption reactor model approach for this investigation:

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[9] *Target acetochlor concentrations are 2.0, 3.5, 7.5 ppb; atrazine concentrations are 80% of those of acetochlor. The mother solution used for the herbicide was the formulation in Harness (Xtra 5.6L, Syngenta, EPA reg. No 524-485) with 372 g/L of acetochlor and 300 g/L of atrazine*

[10] *Ammonia, Nitrate, Nitrite, Total Suspended Solids, Soluble and Total phosphorus were tested in a commercial laboratory using EPA standard tests (Minnesota Valley Testing Laboratory, Inc. at New Ulm, MN). The same laboratory was contracted for herbicides analysis based on a battery of tests called MDA List 1 (acetochlor and atrazine included) that determines concentration levels of 22 herbicides and two metabolites of atrazine (DEA and DIA). Laboratory testing limit was 0.5 ppb for all herbicides*

[11] *Nitrate test checks if the herbicides will inhibit denitrification due to their potential toxicity to the facultative anaerobic bacteria; total phosphorus is tested to ascertain trends of phosphorus load reduction observed in rainfall and snowmelt events prior to the herbicide experiment.*

1. Time: Field work is dependent upon cooperation from the farmer, field researchers, but, most importantly, untimely weather patterns. Modeling adsorption relationships can confer field research robustness and assist with new ways to approach the unknown with fewer dependable variables. Modeling can be conducted during the winter months.
2. Finances: field experiments are expensive and require greater travel time; in addition, there are few and fewer opportunities to work near the University of Minnesota – Saint Paul Campus.
3. See footnotes[12]:

It is assumed in this article that no biotransformation has occurred in the bioreactor for herbicide dissipation, at least, at the laboratory detection limit of 0.5 ppb. As suggested by the literature cited, adsorption would be the main process by which the herbicides can be transformed. In addition, research identified hydrophobicity of the herbicide (higher affinity to alcohol compared to water) and wood lignin content as the key drivers for herbicide sorption onto the wood matrix.

<u>Two Models to Fit Herbicide Adsorption to Woodchip Material</u>: Originally, the following mathematical models were classified as fixed-bed sorption models and applied to activated carbon columns, but the principle behind the derivation of the models allow their use for most adsorptive processes: two adsorption models, Bohart-Adams (Trgo *et al.*, 2011;

[12] *Additional reasons for choosing the adsorption reactor model: 1/ classical sorption models such as Freundlich or Langmuir cannot assess adsorption in a dynamic system with flowing water (Bernardin, 1985); 2/ adsorption reactor models became necessary as it will be shown in the herbicide concentration results that no metabolite of atrazine was detected at the 0.5 ppb detection limit.*

Keerthiranayana & Bandyopadhyay, 1997) and Yoon and Nelson (1984) were selected for this work.

Herbicide, Nitrate, and Total Phosphorus Load Reduction Results: All load values reported in this section are presented with respect to the managed drainage plot area of 6.6 acres[13]. Overall nitrate load reduction was 47%. The reduction decreased steadily from the first to the third cycle, 69%, 43%, and 33% with decreasing water temperature and air temperature throughout the month of October 2010. The corresponding loads at inlet and outlet were 1.61 and 0.85 lbs NO_3-N/ac, respectively. Associated concentrations of nitrite for 2nd and 3rd cycle increased on average from 0.047 to 0.578 ppm NO_2-N at inlet to outlet, respectively. Some relative accumulation of nitrite has occurred during the herbicide experiment although concentrations have remained below the upper limit set by EPA in aquatic system (1.0 ppm NO_2-N).

Total phosphorus average load reduction was 79%. The corresponding loads at inlet and outlet were 0.025 to 0.005 lbs/ac at inlet and outlet, respectively. This is a significantly higher load reduction compared to other events (range of 10% - 35%) from this site. Nearly 100% of the total phosphorus was in the soluble form (99%). It was measured and analyzed that the incoming total phosphorus concentrations decreased across the three week-long runs, as phosphorus was not part of the weekly herbicide-nitrate solution spiked into the bioreactor.[14].

[13] *Based on the tipping bucket flow data across the three-cycle period, the average flow rate and the associated HRT is 4.41 gpm and 20.5 hours (target: 24 hours), respectively. Inlet nitrate concentrations span from 6.5 ppm to 14.0 ppm taking into account that the incoming water flow was spiked with 1.0 mg NO_3-N /L. Effluent concentrations remained below the MCL of 10 ppm NO_3-N for the 1st and 2nd cycle; the 3rd cycle effluent concentrations reached the MCL values.*

[14] *Since this reduction is in the high range and that most of the phosphorus is soluble it is suggested that biological reduction of phosphorus has occurred (Denitrifying Phosphorus Accumulating Organisms -- DNPAO) and the microorganisms can sustain their uptake activity under anoxic conditions (Kuba et al., 1996b).*

Target concentrations of acetochlor were 2.0, 3.5, 7.5 ppb, but the measured averages were 1.78, 2.98, 6.63 ppb for the first, second, and third week-long runs, respectively. Again, one of the motivations for the choice of the influent concentrations was based on the laboratory detection limit set at 0.5 ppb[15].

Acetochlor Field Results: Load of acetochlor was reduced by 70% through the bioreactor across the three concentration runs[16](Figure 2.1).

Acetochlor Modeling Results: Herbicide effluent concentrations were fitted to a linear equation and the fitting parameters were derived from each concentration equation (Table 2.1 and 2.2). The first cycle had the lowest regression coefficient for the fit; this low r-square was due to the unstable flow rate that ended up higher than the target value (4.0 gpm) on three of 6 days[17]. Wood adsorption capacity value was calculated from wood density measured in the laboratory[18]. Based on B&A model, only about 10% of the adsorption capacity (N_o parameter) of the woodchip was used for this experiment. Time of exhaustion of the woodchip ($C = C_o$) from the same model is reported as 7, 12, and 10 days for 1st, 2nd, and 3rd run, respectively. Comment: The bioreactor should have been able to dissipate more herbicide mass based on

[15] *The relative error at each concentration is at 25%, 14%, and 7% for 2.0, 3.5, 7.5 ppb, respectively; thus, any lower concentrations than those applied through the bioreactor could not have given any reasonable assessment of the process.*

[16] *Area-normalized loads are 4.8 x10^{-4} lbs/ac and 1.4 x10^{-4} lbs/ac at inlet and outlet, respectively. The set of laboratory test did not allow the detection of metabolites from acetochlor. Since the experiment was run under dynamic conditions (flowing water), classical adsorption isotherms for batch equilibrium (Freundlich and Langmuir) could not be applied, thus simulation models based on adsorption reactor was chosen to characterize the process.*

[17] *The situation resulted in early breakthrough of effluent concentration on the second day of the first cycle. The flow rate variability through the three cycles has impacted cumulated mass of acetochlor adsorbed on the woodchip matrix. Average flow rate (4.73, 4.31, 3.86 gpm for 1st, 2nd, and 3rd cycle, respectively) has generated different slopes on curve of cumulative mass per cycle.*

[18] *Wood density measured in the laboratory is 16.2 lbs/cuft*

residual adsorptive capacity and herbicide mass adsorbed on woodchip, but as shown in the previous paragraph flow rate had a large impact on adsorbed herbicide mass.

Comparison of the Two Models: The difference between the two models is the formulation of the concentration used for the linear equation. The Y&N linear model uses $C/(C_o-C)$ in contrast with C/C_o as in B&A model. The regression coefficient mirrors that of the B&A model with the 1st cycle having a low value compared to the two other cycles. The two main parameters obtained from the Y&N linearization are the rate coefficient, K_{yn}, and τ, which is the time to reach a 50% concentration breakthrough (half-life of adsorption capacity). According to Y&N, the τ model parameter is 5.3, 7.0, 6.8 days for 1st, 2nd, and 3rd run, respectively[19].

Atrazine Field Results: Similar to the situation with acetochlor the target spiked values for atrazine were not attained via the injector and flow rate combination. The overall dissipation of atrazine is 53% with area-normalized loads of 3.1×10^{-4} lbs/ac and 1.4×10^{-4} lbs/ac at inlet and outlet, respectively (Figure 2.2).

Atrazine Modeling Results: The results of B&A model gave atrazine a better fit for the 1st cycle ($r^2 = 0.52$ compared to $r^2 = 0.32$ for acetochlor) while the two other cycles had high regression coefficients (Table 2.3 and 2.4). The amount of adsorbed herbicide is less than 11% of woodchip adsorption capacity. A large fraction of adsorption sites remained unused due to the relatively low flow rate. For the Y&N model, the first run fit is again lower than the two

[19] *Time for acetochlor concentration breakthrough ($C = 0.9\ C_o$) with the Y&N model is higher than predicted by B&A since the values are 9, 18, 14 days for 1st, 2nd, and 3rd run, respectively.*

following runs in terms of regression coefficient. The K_{yn} parameter is comparable to that of acetochlor within the same order of magnitude[20].

Conclusions: Two adsorption reactor models were used to assess the ability of the woodchip material in the bioreactor to dissipate herbicides. Both Bohart-Adams and Yoon-Nelson models provided parameterization of the bioreactor effluent concentrations for the two herbicides. *Both models showed that breakthrough time of herbicide concentrations can be shortened despite a large residual adsorbing capacity of the wood material*; it can be explained by the flow rates that influence adsorption capacity for such dynamic system. B&A models have given average wood matrix adsorption exhaustion time of 9.5 and 7.5 days for acetochlor and atrazine, respectively, compared to the 6-day duration at each concentration. For Y&N, breakthrough times ($C = 0.9\ C_o$) were 14 and 10 days for acetochlor and atrazine, respectively. Acetochlor showed a stronger affinity to the woodchip for the adsorption process compared to atrazine. Atrazine reached a concentration breakthrough ($C = C_o$) at the end of the 1st cycle.

[20] *The B-A parameter gave smaller values compared to those of acetochlor (average: 3.7 days vs. 6.4 days), but closer together (standard deviation: 0.46 vs. 0.94). Root Mean Square Deviation remains close to the same range as those of acetochlor and time for concentration breakthrough ($C = 0.9\ C_o$) are 8, 13, 10 days for 1st, 2nd, and 3rd cycle, respectively.*

Abstract for:
Impacts of denitrification beds on total greenhouse gas emissions

Agricultural drainage waters can be a source of nitrate (NO_3^-) contamination. Once released to aquatic ecosystems, NO_3^- can be converted to nitrous oxide (N_2O), which is a potent greenhouse gas (GHG). On-site denitrification beds (DBs) or woodchip bioreactors can be used to reduce NO_3^- and therefore reduce GHG impacts. However, unintended consequences of DBs include the production of N_2O and other GHGs which may be released in dissolved form in bioreactor effluents and thereby offset the GHG benefits of NO_3^- removal. We measured dissolved NO_3^-, N_2O, methane (CH_4), and carbon dioxide (CO_2) in influent and effluent water from two DBs filled with woodchip substrates at two different agricultural fields in southern Minnesota, USA (Dundas and Claremont, MN). We also measured emissions of GHGs to the atmosphere from the soils directly above the DBs.

The DBs at both sites decreased dissolved NO_3^- and increased dissolved CH_4 concentrations. The DB in Dundas decreased dissolved N_2O concentration; however the DB in Claremont increased N_2O concentration. Neither DB affected soil surface GHG emissions. After accounting for the global warming potential (GWP) of NO_3^- driven N_2O and dissolved GHG emissions, which was expressed as CO_2 equivalents (eq.), the DB in Claremont increased the average growing season GHG emissions by 37.2 lbs CO_2 eq. ac^{-1}, whereas the DB in Dundas reduced GHG emissions by 5.53 lbs CO2eq. ac^{-1}. The difference in overall GHG impact was mainly due to the contrasting effects of the two different DBs on dissolved N_2O. The data suggest that the DB at Dundas allowed for more complete denitrification of NO_3^- to di-nitrogen (N_2) gas whereas the DB in Claremont did not promote complete denitrification. This result may have been due to differences in hydraulic residence time, pH, or other factors between the two sites. Future studies are required to determine optimium design and operating parameters to minimize overall GHG emissions from DBs.

Appendix

1. A sand-bag dam across the ditch located at 350 ft downstream of bioreactor and 3.0 ft high above water level keeping enough water to fill the water tower.A pump (Pacer Electric Drive Pump, 110 gom, 2.0 HP, 2-in.) with intake in the ditch water; A 500 gal capacity water tower lifted 14.0 ft above ground,
2. A set of pipe and plumbing system connecting the components,
3. A set of pipe, water filter, and injector manifold with adjustable check valve; this valve was the main component used to adjusting for the target flow rate.
4. A fixed mixing ratio injector fed by a 6.5 gal glass jar filled with herbicide solution (DOSATRON 14 DMZ 3000; 0.5-14.0 gpm flow rate range, dilution ratio of 0.03% - 0.3 %);
5. A set of water filters at intake before water tower (Spraying Systems, Co., liquid strainer Model 430 ML, pressure 110 psi) and before the mixing injector; the manifold had two branches with a filter each branch.
6. A PVC pipe for direct delivery of spiked water to bioreactor inlet. A submersible pump was installed inside the inlet station to rid of field water in case of a rainfall event (Wayne Submersible Stainless Steel Cast Iron Pump, 72.0)

Tables for Denitrification in Field Anaerobic Bioreactor

Under Rainfall and Snowmelt Regimes

Table 1.1. Flow depth through the bioreactor during snowmelt in 2010 and 2011. Bypass is the difference between inflow and outflow depths. Inflow and outflow rates are obtained directly from the ISCO unit.

Station	2010	2011
Inflow, in.	3.37	5.13
Outflow, in.	1.59	2.88
Bypass, in.	1.79	2.24
% Bypass	53.0%	43.8%

Table 1.2. Nitrate load and load reduction for snowmelt in 2010 and 2011. Load for both inflow and outflow uses the same outflow depth (Table 1.1), but different concentrations: inlet and outlet concentrations. Bioreactor reduction refers to the load difference between the inflow and outflow loads. Watershed load reduction refers to the amount reduced through the bioreactor reported to the load at inflow and bypass.

Station	2010	2011
Inflow, lbs/ac	5.40	10.40
Outflow, lbs/ac	4.01	9.37
Bypass, lbs/ac	6.07	7.13
% Reduction (Bior.)	26%	10%
% Reduction (Wshd.)	12%	6%

Table 1.3. Flow depth through the bioreactor at Dodge County during growing season. Units are in cm. Proportion of precipitation (March-November) that became flow in 2009 and in 2010 was 33% and 44%, respectively. For 2010, the amount of precipitation includes April to November since March snowmelt was reported in previous table.

Year	Outflow, in.	Bypass, in.
2009	5.47	4.45
2010	6.34	9.45

Table 1.4. Nitrate load for 2009 and 2010 for growing season.

STATION	2009	2010
Inflow, lbs/ac	17.45	24.75
Outlfow, lbs/ac	9.11	19.43
Bypass, lbs/ac	17.11	26.95
% Bior. Reduction	48%	21%
%Wshed Reduction	24%	10%

Figure for Denitrification in Field Anaerobic Bioreactor

Under Rainfall and Snowmelt Regimes

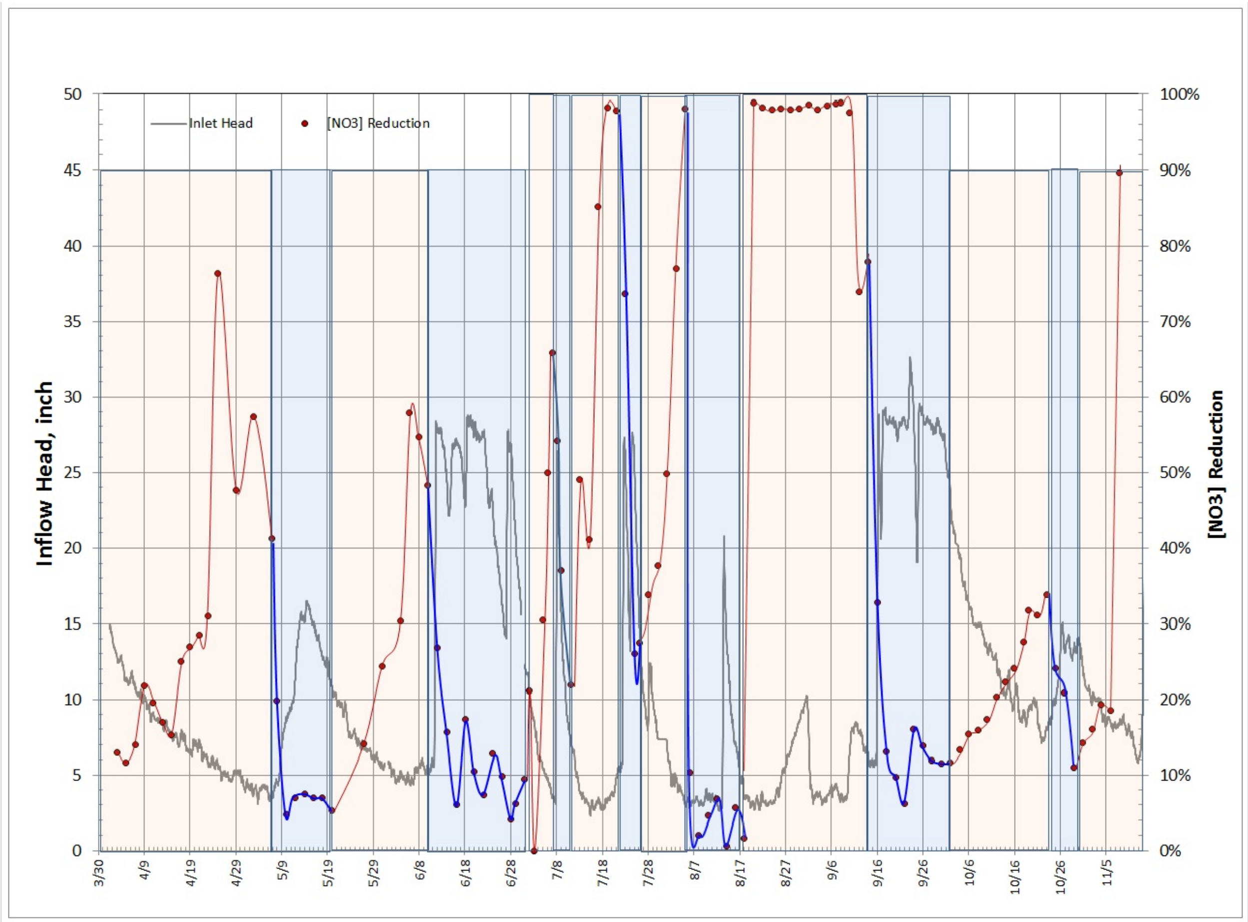

Figure 1.1. Hydraulic head at inlet of bioreactor and nitrate concentration reduction for 2010. Nitrate reduction values were connected with red and blue lines for falling limbs (or between the peaks) rising limbs (or around the peak), respectively. Light colored areas refer to falling limbs and dark-colored areas are related to rising limbs. There is an increasing trend for nitrate reduction rate "between the peaks" period and decreasing trend "during the peak" flow period. Period between mid-August and mid-September had low flow.

Tables for Atrazine and Acetochlor Dissipation in A Denitrifying Field Bioreactor Under Flowing Conditions: Adsorption Reactor Model

Table 2.1. Linear equations per cycle of Acetochlor experiment based on Bohart-Adams model. The units proposed by Keerthinarayana and Bandyopadhyay (1997) were used in this linearization (mg, cm^3, and hr).
K is a rate constant and N_o is adsorptive capacity. Wood adsorption is derived from difference between inlet and outlet concentration reported to woodchip mass per unit volume.

Conc., ppb	ACETOC. B-A Linear Equation	Regr. Coeff, r^2	% BTC (C/Co) at 6 Days	Time of Exhaust., days	Avg No, ppb	% Site Occupied
2.0	y = 0.0197x - 3.3275	0.33	61%	7.0	43.5	11%
3.5	y = 0.0055x - 1.5812	0.92	45%	11.9	113.4	7%
7.5	y = 0.0090x - 2.0542	0.76	47%	9.7	185.1	10%

Table 2.2. Linear equations per cycle of Acetochlor experiment for Yoon-Nelson model (Equation #6 in text). The units proposed by Lin and and Huang (2000) were used in this linearization (mg/L, hr). K_{yn} is a rate constant and τ is time when 50% concentration breakthrough is reached.

Cycle	Acetochlor Linear Equation	Regr. Coeff, r^2	K_{yn}, hr^{-1}	τ, hr	τ, day	Days to C/Co =0.90
1st	Y = 0.0258 X - 3.2825	0.32	0.0258	127.2	5.3	8.9
2nd	Y = 0.0082 X - 1.3874	0.92	0.0082	169.2	7.0	18.3
3rd	Y = 0.012 X - 1.9472	0.78	0.0120	162.3	6.8	14.6

Table 2.3. Linear equations per cycle of Atrazine experiment based on Bohart-Adams model.

Conc., ppb	ATRAZ. B-A Linear Equation	Regr. Coeff, r2	% BTC (C/Co) at 6 Days	Time of Exhaust., days	Avg No, ppb	% Site Occupied
1.8	y = 0.0188x - 2.5862	0.52	100%	5.7	25.6	10%
2.6	y = 0.0047x - 1.0750	0.80	67%	9.5	60.5	6%
6.0	y = 0.0090x - 1.5795	0.78	75%	7.4	96.0	11%

Table 2.4. Linear equations per cycle of Atrazine experiment for Yoon-Nelson model
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Cycle	Atrazine Linear Equation	Regr. Coeff, r^2	K_{yn}, hr^{-1}	τ, hr	τ, day	Days to C/Co =0.90
1st	Y = 0.024 X - 2.2825	0.30	0.0240	95.1	4.0	7.7
2nd	Y = 0.0096 X - 0.722	0.79	0.0096	75.2	3.1	12.9
3rd	Y = 0.012 X - 1.9472	0.82	0.0154	93.4	3.9	9.9

Figures for Atrazine and Acetochlor Dissipation in A Denitrifying Field Bioreactor Under Flowing Conditions: Adsorption Reactor Model

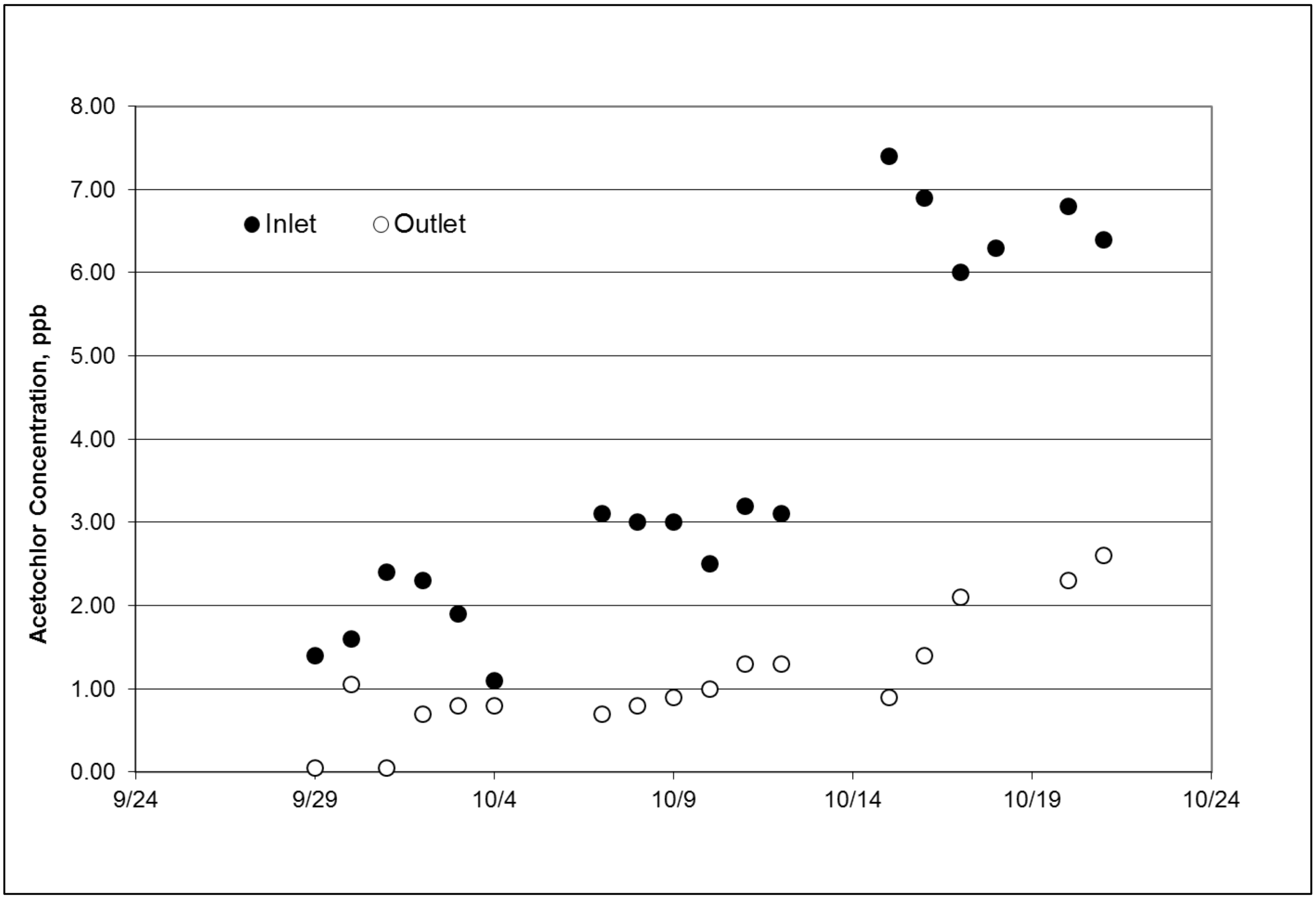

Figure 2.1. Concentrations of acetochlor from bioreactor inlet and outlet. Since the inlet concentrations were not uniform, the associated statistics are given as follows: 1^{st} cycle average: 1.78 ppb (Coefficient of variation: 29%), 2^{nd} cycle average: 2.98 (CV: 8%), and 3^{rd} cycle average: 6.63 ppb (CV: 8%). Incoming concentrations did not reach target due to the removal of a mixer unit installed right after the mixing injector and before the bioreactor inlet flow box. During trial startups, the mixer consistently slowed the flow and prevented the system from reaching the target flow rate of 15.0 L min^{-1}

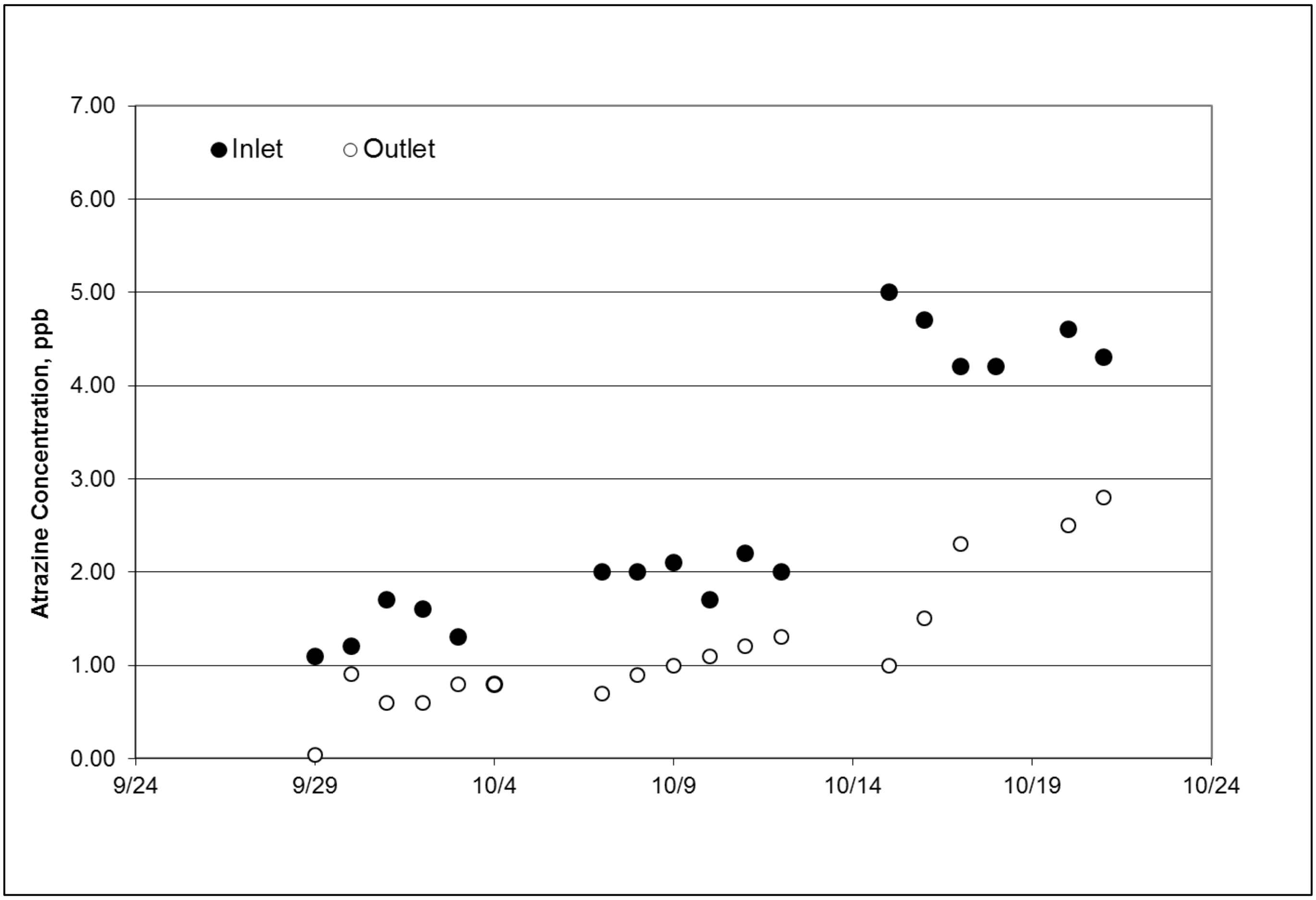

Figure 2.2. Concentrations of atrazine from bioreactor inlet and outlet. Since inlet concentrations were not uniform, the associated statistics are given as follows: 1st cycle average: 1.28 ppb (Coefficient of variation: 26%), 2nd cycle average: 2.00 (CV: 8%), and 3rd cycle average: 4.50 ppb (CV: 7%).