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## Nitrogen balance in and export from agricultural fields associated with controlled drainage systems and denitrifying bioreactors

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## ABSTRACT

Nitrate loss from drainage tiles across the cornbelt of the upper midwestern US is a result of intensive agriculture with limited crop diversity, extensive periods of fallow soil, and the need for high fertilizer applications to corn, all located on a hydrologically modified landscape. Two methods proposed to reduce tile nitrate export are managed or controlled drainage to limit tile flow and bioreactors to enhance denitrification. Nitrogen budgets and tile flow monitoring were conducted over two- to three-year periods between 2006 and 2009. We estimated N budgets in a seed corn-soybean rotation farming system near DeLand, east-central Illinois, USA, with free (FD) and controlled drainage (CD) patterned tile systems. In addition, wood chip filled trenches (bioreactors) were installed below the CD structures, one lined with plastic and one unlined. We measured daily tile flow and nitrate-N ( $\text{NO}_3\text{-N}$ ) concentrations and calculated cumulative N loss from the tile water at both FD and CD areas for a period of three cropping years. We also monitored the tile flow and nitrate concentration in inlet and outlet of the bioreactor associated with a CD system and evaluated the efficiency of the bioreactor for two cropping years. Most components of the N balance were unaffected by CD (yields and therefore N harvested, surface soil denitrification), and there was a negative N balance in the soybean cropping year ( $-165$  and  $-163 \text{ kg N ha}^{-1}$  at FD and CD areas, respectively), whereas seed corn cropping in the following year resulted in positive N balances ( $29$  and  $34 \text{ kg N ha}^{-1}$  at FD and CD areas, respectively). For two years, the overall N balances were  $-136$  and  $-129 \text{ kg N ha}^{-1}$  at FD and CD areas, respectively, consistent with other recent corn belt studies showing a small net depletion of soil organic N. Controlled drainage greatly reduced tile N export, with a three-year average loss of  $57.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  from FD compared to  $17 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  for CD. There was high uncertainty in denitrification measurements and thus the fate of missing N in the CD system remained unknown. Nitrate reduction efficiency of the bioreactor varied greatly, with periods where nearly 100% of the nitrate was denitrified. The overall efficiency of the bioreactor associated with the CD system in reducing the tile N load was 33%. When nitrate was non-limiting, the nitrate removal rate of the bioreactor was  $6.4 \text{ g N m}^{-3} \text{ d}^{-1}$ . Little  $\text{N}_2\text{O}$  emission was found from the bioreactor bed and is not thought to be a problem with these systems. Both the tile bioreactor and controlled drainage greatly reduced tile nitrate export in this leaky seed corn and soybean agricultural field.

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### 1. Introduction

Agricultural intensification is recognized as a major source of increased N concentrations in surface and ground waters (McIsaac and Libra, 2003; Puckett, 1995). Increased nitrate loading in the Mississippi River has been thought to be a primary cause of the large hypoxic zone in the Gulf of Mexico (Rabalais et al., 2001; USEPA,

2008). A number of studies in the Midwest have developed field N budgets to evaluate the effects of agricultural practices on N leaching losses (e.g., David et al., 1997; Gentry et al., 1998; Andraski et al., 2000; Jaynes et al., 2001) that are the source of riverine N loads. David et al. (1997) evaluated agricultural N fluxes and sources of river nitrate in a predominantly tile-drained agricultural watershed in east-central Illinois and reported that about 49% of the field inorganic N pools was leached through tile drains and seepage and was exported by the Embarras River. Estimating the net N inputs for a period of 20 years, McIsaac and Hu (2004) reported that 100% of the residual N, the remaining N in soil after harvest, was discharged to the rivers in a tile-drained region of Illinois.

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Most of the cropland in the Midwest is intensively tile-drained and corn (*Zea mays* L.) soybean (*Glycine max* L.) rotations are the predominant cropping system (USEPA, 2008). Because N fertilizer management alone is not likely to reduce nitrate pollution sufficiently (Jaynes et al., 2001; Hong et al., 2007), additional methods of nitrate removal from subsurface drainage water are needed (USEPA, 2008). One possible method is controlled drainage (CD), sometimes called drainage water management, where structures are placed in tile lines to control the outlet depth and allow water to be temporarily backed up into the field (Gilliam et al., 1979; Skaggs and Youssef, 2008; Cooke et al., 2008). Many of these systems have been installed in the upper Midwest and southern Ontario, and the reports available suggest they greatly reduce the volume of tile flow and concomitantly the amount of nitrate (e.g., Lalonde et al., 1996; Fausey et al., 2004; Drury et al., 2009). Wetlands placed at the end of tile lines have also been shown to be an effective method to reduce tile export of nitrate, but can be quite costly to build (Kovacic et al., 2000; USEPA, 2008).

Other edge-of-field methods such as setting up riparian buffer strips in areas where lateral seepage is the dominant flow (Blattell et al., 2009; Woodward et al., 2009) or constructing denitrification walls or trenches to intercept flow (Schipper and Vojvodic-Vukovic, 2001; Jaynes et al., 2008) fosters biological denitrification to remove nitrate. Use of denitrifying biofilters or bioreactors at the end of the pipe is common for treating industrial wastewater or reducing pollution from landfill sites (e.g., He et al., 2007; Morita et al., 2007), and have now been proposed for controlling tile nitrate losses. There have been some results from installation of trenches and bioreactors to reduce nitrate loss due to agriculture (Blowes et al., 1994; Schipper et al., 2010), as well as recent evaluations conducted under laboratory conditions (Greenan et al., 2009; Chun et al., 2009) or to establish field-scale flow and transport parameters (Chun et al., 2010).

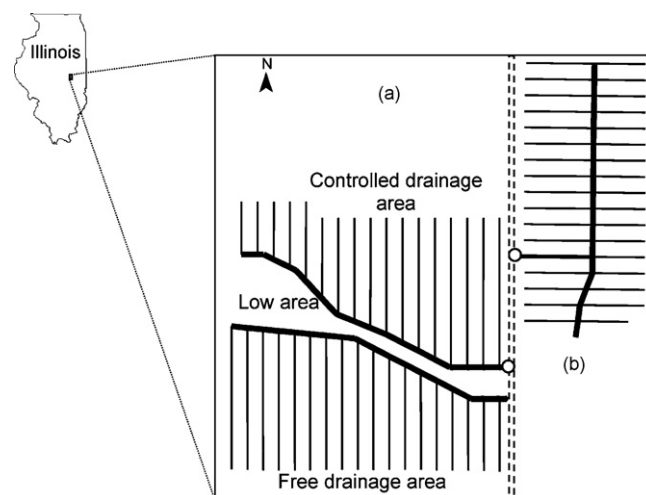
Many of the systems (both walls, trenches and bioreactors) that have been designed to remove nitrate have proposed using sawdust or wood chips as the carbon (C) source to promote denitrification, and have reported that these systems did or could reduce the nitrate concentration in water flowing through the C bed (Schipper and Vojvodic-Vukovic, 2001; Jaynes et al., 2008; Greenan et al., 2009). One question concerning the use of bioreactors is the degree of  $N_2O$  production. If the nitrate is fully reduced to  $N_2$ , then there is no environmental degradation. However, if nitrate is only reduced to  $N_2O$ , a powerful greenhouse gas, then one environmental problem could be substituted for another. Greenan et al. (2009) in their laboratory column study with wood chips reported little  $N_2O$  emission and indicated complete denitrification to  $N_2$ .

In the study reported here, reductions in tile nitrate loss were evaluated from CD and subsurface, end of tile denitrifying bioreactors. The study was conducted on typical corn and soybean fields with patterned tile drainage. We also sought to determine the effect of the drainage management on the overall field N balances. Therefore, the objectives of our study were to (1) compare the field N balance with free drainage (FD) and without the CD system, (2) determine the reduction in tile nitrate export due to CD, and (3) measure how efficient a tile bioreactor was in reducing the N load.

## 2. Materials and methods

### 2.1. Site description

We selected a private farm located near DeLand (40°7'18"N 88°38'42"W) in Piatt County, east-central Illinois, USA, for this study. This farm is a part of a watershed that is predominantly



**Fig. 1.** Layout of the study farm in east-central Illinois, showing the west (a) and east (b) fields separated by a drainage ditch (dashed double line). Thin lines represent the tile drain laterals with the thick lines the headers. Circles denote the bioreactors. A low area separated the free and controlled drainage systems on the west field. The header for the east field was located to take advantage of the small slope present on the field with the lowest area well within the drainage system.

(>90%) in row-crop agriculture, with extensive tile-drainage. Sable (fine-silty, mixed, superactive, mesic Typic Endoaquolls) silty clay loams and closely related Ipava (fine-silty, smectitic, mesic Aquic Ariudolls) are the dominant soils (Mollisols) in the studied areas. The field has a flat topography that requires tile drainage for agricultural production. The area has a humid continental climate with average temperature and annual precipitation of 11.0 °C and 996 mm, respectively. The drainage systems on this farm were installed in fall 2003. Two of the systems west of the drainage ditch, an 11 ha system and a 13-ha system separated by a small low area (Fig. 1), were used for calculating N balances for two cropping years (2007 and 2008). For this study, the 11-ha system was retrofitted with a control structure and a bioreactor was installed at the end of the tile line before it entered the ditch. We also added a control structure and a bioreactor to a 14-ha system on the east side of the drainage ditch. The spacing between the tile drains was 34.5 m for both controlled and free drainage areas and at both east and west fields. For the 2007 crop year, the studied fields on the east and west sides of the ditch were planted with seed corn and soybean, and in 2008 crop year, the fields were planted with soybean and seed corn, respectively.

### 2.2. Water table management

Since we did not have extensive time required to develop water balance relationships in advance of treatments for the three different study areas, the study design could not be set up as a classic paired watershed study. We are assuming that both systems on the west side of the ditch would have similar water and N balances given that they drain the same field, were farmed in the same manner by the same operator and have a similar intensity of drainage. In order to compare the effect of controlled and free drainage on N balances and N loss through drainage, one of these systems was operated in control drainage mode and the other in free drainage mode. The outlet level for the free drainage system was set at the tile depth for the duration of the study, while the outlet level of the controlled system was raised to within 15 cm of the soil surface on or close to November 1st of each year, and lowered back down to the level of the tile on or close to March 15th of the following year.

### 2.3. Soil temperature and moisture

After the completion of farmer's fall field work in 2007, temperature probes and automated soil moisture sensors with dataloggers were installed in strategic areas of the west field to measure soil temperature at 5 cm and soil volumetric water content at 5 and 20 cm. Two dataloggers (Decagon Em5b) and set of sensors (Decagon EC-5 (2) and ECT) were installed in each CD and FD areas of the field. The locations of the four dataloggers and sensors were set up ensuring a good representation of the fields. Soil moisture content above 0.4 represents saturated or nearly saturated conditions, which typically occurs after major rainfall events. Monitoring was carried out from mid-December 2007 to early May 2008 with the dataloggers removed from the fields before the cultivation of spring crop. These data were collected to help determine when and where denitrification might be occurring in the CD and FD areas, and to examine whether controlling the drainage altered the surface soil moisture content.

### 2.4. Tile flow monitoring

Tile flow was measured continuously throughout the study period by using flow structures (MULTI MINI-SAT<sup>TM</sup> Field Station, Automata) that were equipped with V-notch weirs and pressure transducers with dataloggers at the inlets and outlets of the bioreactors. Water samples were collected weekly or biweekly from both the inlets and outlets of the bioreactors when the tiles were flowing. These water samples were filtered through 0.45  $\mu\text{m}$  membrane filters and were analyzed for nitrate concentrations using EPA Method 353.1, a colorimetric automated hydrazine reduction method (USEPA, 1978). The measured data were linearly interpolated to obtain daily values during the study period. These data were used to calculate the drainage loss from the west field, as a component of N budgets, and to determine the effectiveness of the controlled drainage system. For the east field bioreactor, there were two major, short-term flow events during June and July of 2008 where high flows occurred in response to intense rainfall and samples were not collected. During those high flow periods, we assumed that the N load entering the bioreactor was the same as the load leaving, because the retention time was likely short (<1 h). We had three years (October 2006 to September 2009) of tile flow and N load for both FD and CD systems in the west field and two years of data (October 2007 to September 2009) for the CD system in the east field.

### 2.5. Tile bioreactors

Below each of the tile control structures on the controlled drainage tile systems on the east and west fields, bioreactor trenches (30.5 m long, 0.91 m wide, and 1.5 m deep in the west field and 12.2 m long, 3.0 m wide, and 2.1 m deep in the east field), hereafter referred to as 'denitrification beds' were excavated and filled with mixed species wood chips, processed from fallen trees and pruned limbs, obtained from municipal storage piles in nearby Monticello, Illinois. All wood chips were <5 cm in diameter, with 32% <0.63 cm, 34% between 0.63 and 1.27 cm, 28% between 1.27 and 2.54 cm, and 6% between 2.54 and 5 cm. As part of studies to evaluate different bioreactor design and dimensions in various locations in Illinois, the bed in the east field had a clear, 4-mm-thick polyethylene lining at the bottom and sides, to prevent seepage, whereas the bed in the west field had no lining. The east bioreactor also did not have a layer of soil placed over the wood chips, whereas the west bioreactor did have a soil layer. The bioreactor was installed in the west field in fall 2006 and in the east field in fall 2007.

### 2.6. Laboratory incubation for measuring soil denitrification

Focusing on the spring and early summer of 2008, soil denitrification rates were measured to determine the release of  $\text{N}_2\text{O}$  and  $\text{N}_2$  from the soils in response to tile management. Denitrification was measured eight times from March to June 2008 (March 12 and 21, April 7 and 11, May 9 and 13, and June 5 and 9). The acetylene ( $\text{C}_2\text{H}_2$ ) inhibition technique with static core was used for measuring N gas flux in non-ponded areas of the fields (Mosier and Klemmedtsson, 1994). Three replicate soil cores from three locations at each CD and FD area and a low area that separated two drainage systems were taken on each sampling date. Soil cores (10 cm length and 2.7 cm diameter) were extracted using a PVC soil corer. The lower end of the corer was sharpened to ease ground insertion and reduce soil compaction. The corers had holes on their sides to facilitate diffusion of gases into and out of soil pores. Two samples were taken randomly from 0 to 10 cm depth, one for treatment with  $\text{C}_2\text{H}_2$  and the other without  $\text{C}_2\text{H}_2$  as a control. Upon extraction, an intact soil core was placed in a canning jar, and  $\text{C}_2\text{H}_2$  (generated by reacting  $\text{CaC}_2$  with  $\text{H}_2\text{O}$ ) was added to the jar headspace to yield a final volumetric concentration of 10%. By creating a strong  $\text{C}_2\text{H}_2$  gradient, diffusion of  $\text{C}_2\text{H}_2$  from the jar headspace into soil pores would be accelerated and the  $\text{C}_2\text{H}_2$  level in the soil core atmosphere reached the minimum concentration (0.1%, v/v) needed for quantitative inhibition of  $\text{N}_2\text{O}$  reduction. Jars were incubated in the lab at field soil temperature, and their headspace gas was sampled at 0, 0.5, 1, 2, and 4 h. Gas samples were analyzed using a gas chromatograph (Varian-3600 with a  $^{63}\text{Ni}$  ECD) to quantify the concentration of  $\text{N}_2\text{O}$ . The N gas flux was calculated using regression coefficients obtained from plotting  $\text{N}_2\text{O}$  concentrations against sampling time. Gravimetric soil moisture content was determined by drying the remaining field moist soil at 105 °C for 48 h and reweighing. Bulk density was determined for each soil core based on the total mass of oven-dried soil and the volume of the core. Denitrification rates were calculated using the  $\text{N}_2\text{O}$  flux and bulk density.

### 2.7. Soil nitrate and ammonium concentrations

Soil samples were collected from the CD and FD areas in the west field in 2007 following harvest. Six soil cores were collected from each CD and FD area at three depths (0–20, 20–50, and 50–100 cm) on October 9, 2007. Four soil cores (0–10 cm) were collected at each location during the sampling of the eight laboratory incubation experiments (see above) and extracted for  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$ . The soil samples were stored in a cooler of ice until transporting to the laboratory. Soil cores were immediately processed by taking 30 g of well-homogenized soil and extracting it with 150 ml 1 M KCl after shaking for 1 h. After settling, extracts were filtered through Whatman GF/F (0.7  $\mu\text{m}$ ) glass fiber filters. Extracts were stored at  $-20^\circ\text{C}$  until analysis. Soil extracts were analyzed for exchangeable ammonium ( $\text{NH}_4\text{-N}$ ) and nitrate ( $\text{NO}_3\text{-N}$ ) concentrations on a Lachat QuikChem 8000 flow injection analyzer (Lachat Instruments/Hach Company, Loveland, CO) with minimum detection limits of 0.005 and 0.050  $\text{mg N L}^{-1}$ , respectively.

### 2.8. Gas flux measurement

Measurement of N gas fluxes was conducted at both denitrification beds. Three gas sampling chamber bases were placed one week prior to gas sampling at each bed; one near the inlet, another in the center of the bed, and the other near the outlet of each denitrification bed. Gas samples were collected at 0, 10, 20, and 30 min intervals using vented chambers every two weeks from April to June 2009. The chambers were made from 8-in. PVC rounded end



caps with ID of 22 cm and volume of 3995 cm<sup>3</sup>. The vent tube was 1.5 mm (ID). Nitrous oxide concentrations were measured using a gas chromatograph (GC-2014, Shimadzu, Kyoto, Japan) with an ECD detector and flux was calculated using the regression coefficients obtained from N<sub>2</sub>O concentrations against sampling time. While taking gas samples for N<sub>2</sub>O measurement, CO<sub>2</sub> flux was also measured at each chamber by a LI-COR instrument (LI-8100, LI-COR Inc.) directly in the field three times during June 2009 in order to assess the decomposition rate of wood chips in the bioreactor.

### 2.9. Nitrogen budget estimation

We calculated an N balance in the west field for the 2007 and 2008 cropping years. The N balance was estimated by subtracting the outputs of total amount of N removed in harvested grain, drainage losses, and denitrification from the inputs or sources of mineral N for the field including chemical N fertilizer, biological N<sub>2</sub> fixation, and atmospheric N deposition. We followed methods detailed in Gentry et al. (2009). The data on crop harvest yields and applied fertilizer were obtained from the farmer. We also measured N content in grain harvest and aboveground parts of both corn and soybean. The soybean crop was sampled during the late growth stage to determine N accumulation in the aboveground portion of the plants. The plants were divided into two portions; the stalk-stem with leaves and pods with immature seed. The dried biomass was weighed and laboratory analysis indicated 2.2% N in the leaves and stems and 5.3% in the undeveloped pods. The total aboveground N accumulation was measured to be 274 kg N ha<sup>-1</sup>. This N concentration (corresponding to 35% protein) was equal to the commonly assumed percentage used in N calculations (Gentry et al., 2009). Soybean grain samples were taken just before harvest and the N content was measured and found to be 6.5%. The soybean grain yield was 4.0 Mg ha<sup>-1</sup> and harvest equated to an N export of 258 kg N ha<sup>-1</sup>. Corn samples were taken just before the 2008 harvest. The grain harvest was calculated to be 5.4 Mg ha<sup>-1</sup> (seed corn) with an N concentration of 1.8% equating to an N export of 82 kg N ha<sup>-1</sup>.

Loss of N through tile drainage was estimated by the cumulative load in the inlets of the bioreactors at the control structures.

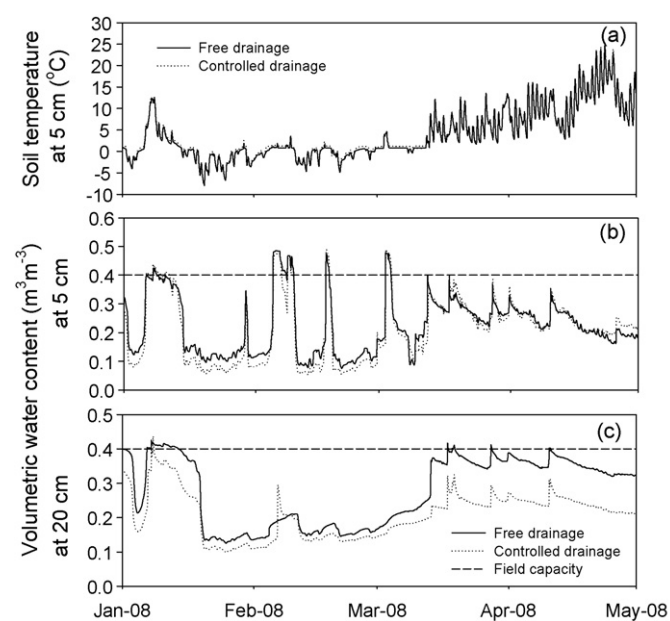


Fig. 2. Soil temperature at 5 cm (a) and volumetric water content at 5 (b) and 20 cm (c) depths at free and controlled drainage areas for the west field in 2008.

The denitrification loss for the CD area was estimated by subtracting its drainage loss from that of the FD area, whereas that for the FD area was estimated by using the sum of simulated daily denitrification values for the study period using the DNDC model. As discussed later, we have no direct measurement of the denitrification loss as a result of CD. We have previously calibrated and applied the DNDC model for this area (Tonitto et al., 2007; David et al., 2009). In mid-November 2008, the farmer applied diammonium phosphate and anhydrous ammonia at a combined rate of 152 kg N ha<sup>-1</sup>. Biological N<sub>2</sub> fixation by soybean crop was estimated as the 60% of N in aboveground soybean biomass. Wet deposition of atmospheric nitrate and ammonium were calculated using the precipitation data by an on-site recording rain gage supplemented by four National Weather Service Cooperative weather stations for verification and to fill in missing data. Inorganic N concentrations in precipitation were measured by the National Atmospheric Deposition Program that has a site near Bondville, IL (25 km east of our study location). Atmospheric dry deposition was assumed to be 70% of the total inorganic N in precipitation. The N balance estimation does not account for the losses to shallow groundwater, ammonia volatilization, and changes in soil organic N pools.

## 3. Results and discussion

### 3.1. Soil temperature, moisture, and precipitation

Soil temperatures at the 5 cm depth ranged from  $-8^{\circ}\text{C}$  in January to  $25^{\circ}\text{C}$  in April (Fig. 2a). However, there was no significant variation in soil temperature between FD and CD areas. Fluctuation of soil moisture content at 5 cm was high throughout the measurement period (January–April, 2008), exceeding the field capacity of 0.4 of this soil type (Hansen et al., 1980) at several instances (Fig. 2b). We found that the surface soil moisture content at the CD area was lower compared to that in the FD area. There was less fluctuation of soil moisture at 20 cm depth at both CD and FD areas (Fig. 2c), some peaks being near or below the field capacity. The soil moisture at 20 cm in the CD area was lower than that in the FD area. The total precipitation amount during cropping years 2007, 2008, and 2009 were 84, 128 and 99 cm, respectively and thus the crop year 2008 remained much wetter than 2007 and 2009 (Fig. 3a). The soil moisture differences between the FD and CD areas were the reverse of what we expected. However, the water table was likely not increased to within 20 cm of the soil surface in the CD area where we made our measurements, and during winter and spring with limited evapotranspiration with high rainfall small scale field effects seemed to be much greater than any effect of CD on surface soil moisture contents.

### 3.2. Tile flow and drainage N loss

The pattern of daily tile flow and cumulative N load for both the FD and CD areas on the west side of the ditch for the period of three years (2006–2009) are presented in Fig. 3b and c and the data are summarized in Table 1. The CD was extremely effective in reducing tile flow with a three-year average of 10.7 cm of flow compared to 41 cm from the FD. The cumulative drainage N loss from the CD area was lower throughout the study period (Fig. 3c). The three-year average NO<sub>3</sub>-N flux was 57.2 kg N ha<sup>-1</sup> for the FD area, and was reduced to 17.0 kg N ha<sup>-1</sup> for the CD, an overall reduction of 70%. The drainage loss values for the FD area were close to the previous findings of 38 and 64 kg N ha<sup>-1</sup> for 1995 and 1996 cropping years, respectively by Gentry et al. (1998) for a 40-ha watershed in the same region with similar cropping (seed corn) and free drainage management practices. Drury et al. (1996) measured

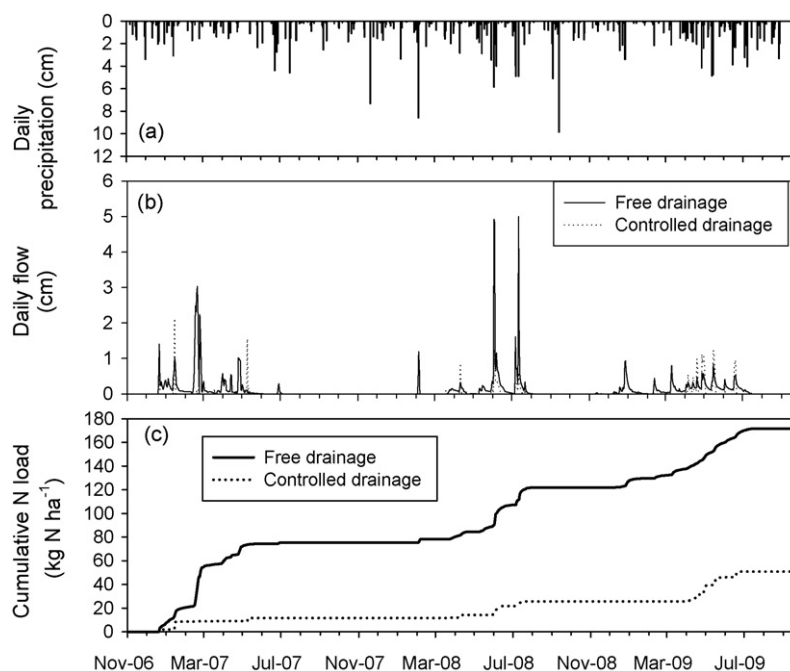


Fig. 3. Daily precipitation at the study site (a), daily tile flow (b), and cumulative N load (c) in free and controlled drainage areas of the west field.

nitrate leaching through free and controlled drainage-subirrigation systems for three years, and reported that the annual nitrate loss was reduced 43% from 25.8 kg N for the conventional FD system to 14.6 kg N for the CD system. Lalonde et al. (1996) measured reductions in NO<sub>3</sub>-N loads between 41 and 96% for various years and heights of the water table. Fausey et al. (2004) reported a five-year average reduction of the nitrate load with CD of about 45%. Finally, Drury et al. (2009) reported an average reduction in the nitrate load with CD of 44%. The average reduction in drainage loss in the CD system during the five-year period in our study was within the range of these reported values, although on the higher end. Some of this difference with other published removal percentages may be that the two tile systems we compared performed differently, and therefore would not have equal flow if both were operated with free drainage. This could have caused us to overestimate the effectiveness if the FD system would have had greater flow than the CD operated in a free drainage mode. The soil moisture results were contrary to our assumption that moisture content would be higher in CD areas compared to that in FD areas, which may account for some of the differences in flow. The fate of the missing tile drainage water and nitrate is probably increased shallow groundwater flow to the ditch. Given that the soils in this study area are C rich Mollisols, we speculate that much of the nitrate in this shallow groundwater flow was likely denitrified, as we found in seepage water from a wetland previously studied in a nearby watershed (Larson et al., 2000). However, this is a weakness in our N mass balance as we have no direct measurement of the fate of the missing N.

### 3.3. Denitrification loss

The soil denitrification values determined at various dates are given in Table 2. Denitrification was rarely observed during the early period of spring (March 12 and 21, April 7 and 11), probably because of the minimal activities of denitrifying bacteria owing to the cold temperature. Denitrification was not detected in any soil samples taken from the FD area and only four samples out of 22 samples from the CD area during this period (Table 2). The exchangeable soil inorganic N was 61.7 and 75.8 kg N ha<sup>-1</sup> with most of the N as nitrate (data not shown) in various soil layers (0–100 cm). We expected that denitrification would occur after soil temperature increased in late spring and early June. However, in May and June, denitrification was not detected in 63% of the total samples. The detected denitrification values were highly variable ranging from 61 to as high as 3011 g N ha<sup>-1</sup> d<sup>-1</sup> possibly including some hotspots, and such high variability was consistent with the findings of Folunso and Rolston (1984), Parkin et al. (1987), and Christensen et al. (1990). We did find some of the most consistently high denitrification rates during late spring in the low area between the CD and FD areas (Table 2), which may reflect the movement of nitrate rich water flowing to the ditch due to the water table management.

We compared median values for each date to the simulated denitrification rates obtained from modeling (DNDC model) for the study period (Fig. 4). For this purpose, climate, soil, and farming management information of the study site were used to run the DNDC model for the FD area. Although high peaks of denitrification

Table 1  
Annual and average tile flow and nitrate-N yields from the free and controlled drainage systems in the west field.

Year	Free drainage (FD)		Controlled drainage (CD)	
	Flow (cm)	Nitrate-N yield (kg N ha <sup>-1</sup> )	Flow (cm)	Nitrate-N yield (kg N ha <sup>-1</sup> )
2007	47.6	75.5	6.3	11.7
2008	39.6	46.3	9.3	14.0
2009	36.4	49.7	16.6	25.2
Three-year average	41.2	57.2	10.7	17.0

**Table 2**

Soil denitrification rates measured in free drainage (FD) and controlled drainage (CD) areas, as well as the low area between the FD and CD areas.

Drainage areas	g N ha <sup>-1</sup> d <sup>-1</sup>							
	March 12	March 21	April 7	April 11	May 9	May 13	June 5	June 9
FD	0	0	0	0	0	575	37	0
FD	0	0	0	0	0	265	665	246
FD	0	0	0	0	0	0	585	0
FD	0	0	0	0	0	0	1336	0
FD		0	0	0	0	870	0	0
FD		0	0	0	0	104	0	0
Low area	0	0	0	0	606	443	404	944
Low area	0	0	0	0	184	231	1336	3011
Low area	0	0	0	0	213	358	0	92
Low area	0	0	0	0	332	445	0	124
Low area		0	0	0	0	0	316	190
Low area		0	0	0	0	0	61	78
CD	0	0	0	0	0	0	0	0
CD	0	0	0	0	0	0	0	0
CD	0	0	0	0	586	0	763	0
CD	0	515	0	0	484	0	1323	0
CD		0	604	0	0	124	0	0
CD		0	462	408	0	379	0	0

occurred in November and December 2006, they were similar to the measured denitrification values in May and June 2008. The median values for the CD area were all zero and for the FD area ranged from 0 to 311 g N ha<sup>-1</sup> d<sup>-1</sup> (Fig. 4). However, when using the interquartile ranges, the fourth quartiles of the denitrification values ranged from 124 to as high as 1323 g N ha<sup>-1</sup> d<sup>-1</sup> for the CD area too (Table 2), indicating high variability and uncertainty. Since our measured values were not sufficient to simulate denitrification for the entire study period, the simulated total denitrification values (2.1 kg N ha<sup>-1</sup> in 2007 and 5.0 kg N ha<sup>-1</sup> in 2008) were used in calculating the N budgets (Table 3). We anticipated identifying a relation between denitrification and temperature, soil moisture content, and soil inorganic N content that could be used to estimate the quantity of denitrification occurring throughout a season. However, we discontinued denitrification measurements because

fluxes in most of the samples during a four-month period were below detection. Finally, the moisture content in the upper soil (0–10 cm) of the CD was not different than the FD and therefore we did not expect to measure greater denitrification rates than the FD area.

### 3.4. Field level nitrogen budget

Nitrogen budgets were calculated separately for the 2007 and 2008 cropping years (Table 3). In 2007, biological N<sub>2</sub> fixation (164 kg N ha<sup>-1</sup>) was the dominant input and soybean harvest (258 kg N ha<sup>-1</sup>) was the main output for both FD and CD areas. There were no biomass or yield differences between the crops grown in the FD and CD areas, so we used the same lumped average harvest values for both FD and CD areas. The second most

**Table 3**

Estimated N balance for the free drainage and controlled drainage areas of the west field for the 2007 and 2008 crop years.

	Free drainage (kg N ha <sup>-1</sup> )			Controlled drainage (kg N ha <sup>-1</sup> )		
	Input	Output	Balance	Input	Output	Balance
2007 (Soybean)						
Atmospheric deposition	7			7		
N <sub>2</sub> fixation	164			164		
Grain harvest		258			258	
Denitrification		2 <sup>a</sup>			64 <sup>b</sup>	
Tile nitrate loss		76			12	
Total	171	336	-165	171	334	-163
2008 (Seed corn)						
Atmospheric deposition	10			10		
Fertilizer N	152			152		
Grain harvest		82			82	
Denitrification		5 <sup>a</sup>			32 <sup>b</sup>	
Tile nitrate loss		46			14	
Total	162	133	29	162	128	34
Combined years						
Atmospheric deposition	17			17		
N <sub>2</sub> fixation	164			164		
Fertilizer N	152			152		
Grain harvest		340			340	
Denitrification		7 <sup>a</sup>			96 <sup>b</sup>	
Tile nitrate loss		122			26	
Total	333	469	-136	333	462	-129

<sup>a</sup> Values estimated by simulation using the DNDC model.

<sup>b</sup> Values obtained by subtracting the controlled drainage tile loss from the free drainage loss.

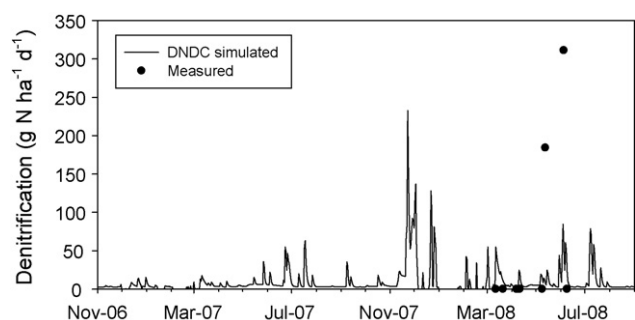


Fig. 4. Simulated (DNDC) and measured denitrification values for the west field, free drainage.

important export of N from the FD area was the drainage loss ( $76 \text{ kg N ha}^{-1}$ ) through tile drains. The FD system had much higher drainage loss compared to the CD system ( $12 \text{ kg N ha}^{-1}$ ), suggesting approximately  $64 \text{ kg N ha}^{-1}$  more denitrification with the CD system. However, the fate of missing N is unknown because of the high uncertainty in measured field denitrification values, and that we did not determine the fate of the water held back by the system, or the nitrate in it. Much of the denitrification in the water held back in the CD likely occurred in subsurface flow to the ditch rather than in the surface soils because we did not observe denitrification that occurred in the surface soil in most of the soil samples (Table 2). In addition, the volume weighted nitrate concentration was  $14.1 \text{ mg N L}^{-1}$  in the FD area, compared to  $15.6 \text{ mg N L}^{-1}$  in the CD. This again suggests limited denitrification within the CD area. For this reason, we used the annual simulated denitrification values for 2007 and 2008 (Fig. 4 and Table 3) of 2 and  $5 \text{ kg N ha}^{-1}$  for the FD area, which were close to the annual denitrification values reported by David et al. (2009). Because of the depletion of soil residual N from the previous year's fertilized corn field and no application of fertilizer N to the soybean crop, a high negative balance was observed for both FD ( $-165 \text{ kg N ha}^{-1}$ ) and CD ( $-163 \text{ kg N ha}^{-1}$ ) areas.

For the 2008 seed corn year the dominant input was fertilizer N ( $152 \text{ kg N ha}^{-1}$ ) for both FD and CD areas. Similarly, corn harvest was the major output ( $82 \text{ kg N ha}^{-1}$ ). The drainage loss ( $46 \text{ kg N ha}^{-1}$ ) was the second largest output from the FD area compared to 14 from the CD that suggested a denitrification value of  $32 \text{ kg N ha}^{-1}$  in the CD system. There was a net balance of 29 and  $34 \text{ kg N ha}^{-1}$  for the FD and CD areas for the cropping year 2008. Combining both the cropping years, a net negative balance was found in both FD ( $-136 \text{ kg N ha}^{-1}$ ) and CD ( $-129 \text{ kg N ha}^{-1}$ ) areas. Such negative balances were also recently reported for the Big Ditch watershed ( $-67 \text{ kg N ha}^{-1}$ ) near our study site, again with a dominantly corn–soybean rotation (Gentry et al., 2009).

### 3.5. Nitrogen fluxes at the denitrification beds and N removal efficiency

We monitored tile flow and  $\text{NO}_3\text{-N}$  concentrations in drainage water both at inlets and outlets for each bioreactor. However, because of the unlined nature of the denitrification bed in the west field, there was almost no outflow throughout the study period and we could not evaluate the efficiency of the system. Therefore, we utilized the adjoining east field with a similar type of cropping pattern and management for comparison, which had a similar denitrification bed but with plastic lining along the sides and bottom. Tile monitoring data on  $\text{NO}_3\text{-N}$  concentrations in inlet and outlet of the bioreactor are presented in Fig. 5a. Nitrate-N concentrations in the inlet tile water ranged from 2.8 to  $18.9 \text{ mg L}^{-1}$ , which decreased to 0.1 to  $14.6 \text{ mg L}^{-1}$  in the outlet. The nitrate reduction

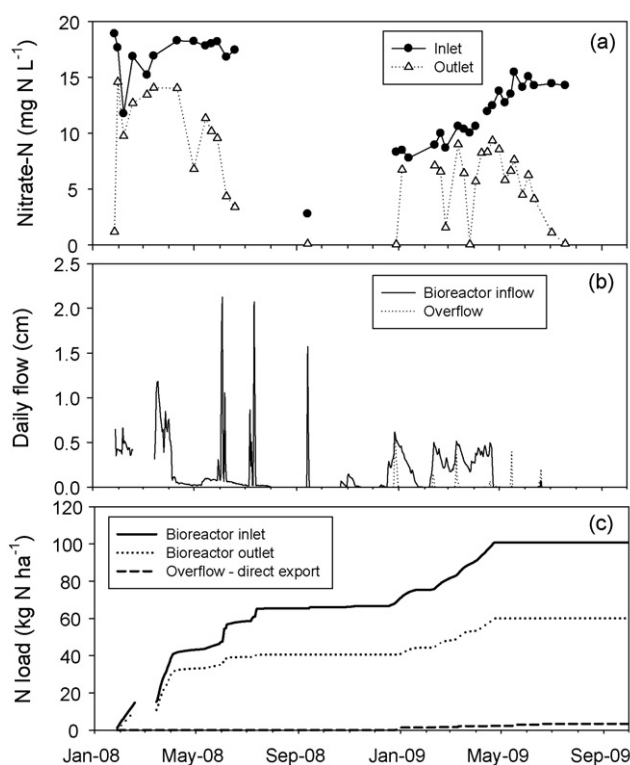
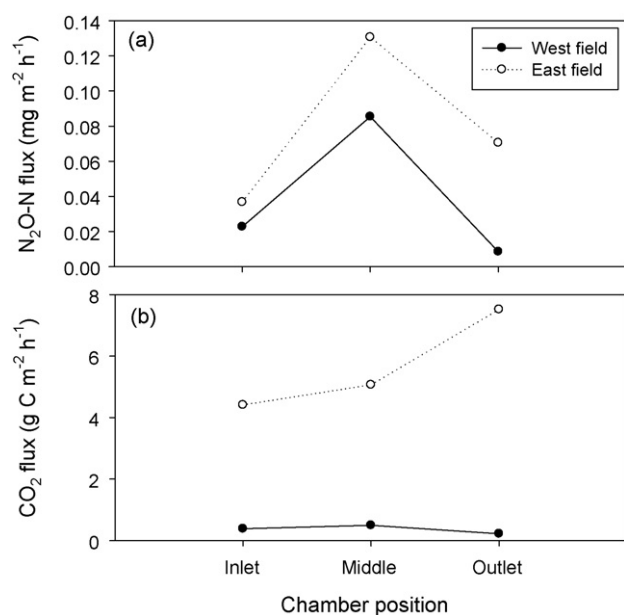


Fig. 5. Nitrate-N concentrations in the inlet and outlet of the east field bioreactor (a), daily flow (b), and cumulative N loads (c).

efficiency of the bioreactor varied greatly, ranging from 12 to 99.5%, and there were several instances where nearly 100% of the  $\text{NO}_3\text{-N}$  was reduced by the bioreactor filter. We also calculated the nitrate removal rate of the bioreactor considering various weir heights and the volume of the denitrification bed. When assuming that the nitrate was non-limiting, the nitrate removal rate was  $6.4 \text{ g N m}^{-3} \text{ d}^{-1}$ . The daily flows at the inlet and outlet were the same throughout the study period (Fig. 5b), which is attributed to the lining of the bioreactor so that there was no leakage of water inside the denitrification bed. The bioreactor system in the east field also had a structure for bypass flow to the drainage ditch. Therefore, we also determined flow and cumulative N load for the overflow water (Fig. 5b and c). The cumulative N load in the outlet ( $50.9$  and  $19.0 \text{ kg N ha}^{-1}$ ) was lower compared to the inlet ( $66.2$  and  $38.0 \text{ kg N ha}^{-1}$ ) in 2008 and 2009, respectively. The bioreactor therefore removed 23% of the nitrate in 2008, and 50% in 2009, for an overall two-year removal of 33% ( $17.1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ). Jaynes et al. (2008) found that a denitrification wall filled with wood chips along a tile line reduced nitrate loads by 55% ( $29 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) in Iowa. The results from our study and Jaynes et al. (2008) are the only two upper midwestern field scale systems that we are aware of.

We expected that the efficiency of the bioreactor was likely limited by retention time of tile water in the wood chip bed. To estimate retention time we used an estimated pore space of 65% of the bed volume, determined by R.A. Cooke (unpublished data). The height of the water in the denitrification bed was held at 61 cm during all of 2009, and varied between either 61 or 100 cm in 2008. For the average flow of  $0.15 \text{ cm d}^{-1}$ , the retention time was 1.4 and 2.8 h for the 61 and 100 cm heights, respectively. At a higher flow of  $0.5 \text{ cm d}^{-1}$ , the retention time was estimated at 26 and 50 min for 61 and 100 cm heights, respectively. The short retention times at high flows no doubt greatly reduced the efficiency of the bioreactor. However, there was not a significant correlation of nitrate removal





**Fig. 6.** Measured mean N<sub>2</sub>O (a) and CO<sub>2</sub> (b) fluxes from the denitrification bed in the west and east fields during 2009. The bioreactor at the west field had the uppermost surface layer filled with soil while that at the east field had the surface layer filled with wood chips.

and retention time using all of our data. We found that there were three time periods with high flows and high nitrate removal that followed prolonged dry periods, which may have led to a pool of labile C that could support rapid denitrification for a limited time period. If those were excluded from our correlation analysis, there was a significant correlation ( $r=0.44$ ,  $p=0.03$ ,  $n=24$ ) of retention time versus nitrate removal percentage. Chun et al. (2010) studied a nearby bioreactor (Decatur, IL) using an experimental single dose of nitrate and found 47% removal with a retention time of 4.4 h. These results demonstrate the challenge of designing a bioreactor that is large enough to provide retention times long enough for more complete nitrate removal from a tile system, where the flows may not be well known.

Another possible area of concern with the tile bioreactors is that they may be so anaerobic that sulfate is reduced (after all nitrate is removed, which is what we anticipated to occur), and methyl mercury could be formed. We also analyzed inlet and outlet samples for sulfate and chloride. In several instances, nitrate in outlet was close to zero and sulfate was also much less in the outlet compared to the inlet (data not shown). This could support formation of methyl mercury. However, in most samples nitrate was not reduced to zero (Fig. 5a), so that sulfate was not reduced. It seems that if complete nitrate removal did not occur, then sulfate reduction was not observed. This does remain an area of concern however, and further monitoring is required (along with direct mercury measurements) to fully understand the conditions in the bioreactor.

A final concern is the possibility of N<sub>2</sub>O emission from the denitrification beds. However, our results indicated that the observed N<sub>2</sub>O fluxes were negligible ranging from as low as 0.01–0.13 mg m<sup>-2</sup> h<sup>-1</sup> (Fig. 6a), indicating that the denitrification process was going fully to N<sub>2</sub>, rather than being evolved as N<sub>2</sub>O. This can be attributed to the degree of anaerobic conditions in the denitrification beds. However, the N<sub>2</sub>O emission could have been underestimated due to the fact that we did not measure potential for N<sub>2</sub>O to leave the bed in dissolved form. There was no consistent pattern of N<sub>2</sub>O fluxes among the chambers placed near the inlets

and outlets and center part of the beds, and given the low flux differences within the bioreactors the differences are not meaningful (Fig. 6a). Greenan et al. (2009) also found in their laboratory study with wood chips a negligible release of N<sub>2</sub>O. The proportion of nitrate converted to N<sub>2</sub>O while passing through the denitrification beds was as low as 0.00004 (0.004%, close to the minimum value reported by Greenan et al., 2009), indicating that the denitrification beds caused negligible N<sub>2</sub>O production.

On the other hand, CO<sub>2</sub> fluxes showed a distinct pattern in the denitrification beds filled with soil and wood chips on the top in the west and east fields, respectively. The flux ranged from 0.2 to 0.5 g C m<sup>-2</sup> h<sup>-1</sup> at west bed, and ranged from 4.4 to as high as 7.5 g C m<sup>-2</sup> h<sup>-1</sup> from the bed (Fig. 6b) filled with wood chips up to the surface. These results indicated that the gases were venting up from the bottom, and substantial decomposition of the wood was occurring, no doubt causing the anaerobic concentrations and reduction of nitrate. Even at these rates, which were enhanced by the warm temperatures, it would take many years for the wood to fully decompose. Previous studies also reported that the C source provided with wood materials would last many years ranging from at least five years (Schipper and Vojvodic-Vukovic, 2001) to as long as above 15 years (Robertson et al., 2008). Our study results support the previous understanding of the bioreactors with respect to mitigate nitrate pollution in agricultural tile drainage. The bioreactors produce anaerobic conditions (as evidenced by sulfate reduction) where nitrate is reduced fully to N<sub>2</sub>, with concomitant release of CO<sub>2</sub>. Although N<sub>2</sub>O was detectable, the concentrations and resulting fluxes were extremely low. These results indicate that there is little concern of N<sub>2</sub>O release from these bioreactor systems.

#### 4. Conclusions

We estimated and/or measured N fluxes at a field scale and attempted to compare the N balances between CD with a denitrifying bioreactor and free drainage systems for a period of two cropping years. We did not find any differences in crop yields and most N fluxes in the CD area compared to the FD, and could not detect an increase in surface soil denitrification during one winter and spring period. However, CD greatly reduced tile flow and tile N export compared to the FD area. We speculate that the backed-up tile water likely flowed to the ditch, with denitrification occurring along the flow path. Documenting the fate of this water and nitrate during CD is an important and critical research need. The tile bioreactor combined with CD on the east field also greatly reduced nitrate export from the tile system. Managed drainage and lined denitrification beds have a great potential for reducing tile nitrate export to streams through increased denitrification.

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