Published September 16, 2015

Journal of Environmental Quality

TECHNICAL REPORTS

SURFACE WATER QUALITY

Characterizing the Performance of Denitrifying Bioreactors during Simulated Subsurface Drainage Events

Natasha Bell, Richard A. C. Cooke,* Todd Olsen, Mark B. David, and Robert Hudson

Abstract

The need to mitigate nitrate export from corn and soybean fields with subsurface (tile) drainage systems, a major environmental issue in the midwestern United States, has made the efficacy of field-edge, subsurface bioreactors an active subject of research. This study of three such bioreactors located on the University of Illinois South Farms during their first 6 mo of operation (July–Dec. 2012) focused on the interactions of seasonal temperature changes and hydraulic retention times (HRTs), which were subject to experimental manipulation. Changes in nitrate, phosphate, oxygen, and dissolved organic carbon were monitored in influent and effluent to assess the benefits and the potential harmful effects of bioreactors for nearby aquatic ecosystems. On average, bioreactors reduced nitrate loads by 63%, with minimum and maximum reductions of 20 and 98% at low and high HRTs, respectively. The removal rate per unit reactor volume averaged 11.6 g NO_3–N m^{-3} d^{-1} (range, 5–30 g NO_3–N m^{-3} d^{-1}). Multiple regression models with exponential dependencies on influent water temperature and on HRT explained 73% of the variance in NO_3–N load reduction and 43% of the variance in its removal rate. Although concentrations of dissolved reactive phosphorus and dissolved organic carbon in the bioreactor effluent increased relative to the influent by an order of magnitude during initial tests, within 1 mo of operation they stabilized at nearly equal values.

Core Ideas

- Bioreactors successfully reduced nitrate loads from drainage tiles.
- Nitrate removal rate was independent of hydraulic residence time.
- Initially high DRP and DO were reduced after a month of operation.
- Temperature and residence time explained 85% of the variance in N load reduction.
- Temperature and residence time explained 66% of the variance in N removal rate.

One of the most pressing environmental issues, the eutrophication of waterways, is often associated with nutrient application on agricultural fields. Despite improvements in nitrogen (N) use efficiency on agricultural systems, total reactive N loss is expected to grow substantially in the coming decades (Tilman et al., 2001; Eickhout et al., 2006). Increased nitrate N (NO_3^-–N) leaching into the Mississippi River has been linked to the growing formation of the "Dead Zone" in the northern Gulf of Mexico (Turner and Rabalais, 2003). Subsurface (tile) drainage across the midwestern United States, which has permanently altered the hydrological cycle in the Mississippi River Basin, has been implicated in this phenomenon (David et al., 2010). Tile drains serve to quickly flush excess water from agricultural fields and therefore do not allow for natural attenuation of nitrate levels through the soil column before being exported to local surface waters. Illinois is one of the most extensively tile-drained states, with a total drained area of approximately four million hectares (Kalita et al., 2007).

Several methods have been proposed to mitigate nitrate leaching from tile drains, including constructed wetlands and drainage water management (Northcott et al., 1999; Kovacic et al., 2000; Zuercher et al., 2000; Miller et al., 2002; Verma et al., 2010; Woli et al., 2010). One fairly new management practice is the use of subsurface denitrifying bioreactors. Bioreactors are trenches filled with carbon (C) material (usually wood chips) that intercept tile-drained water before it enters local water bodies. Under anoxic conditions, denitrifying bacteria in the bioreactor bed respire nitrate and transform it into inert nitrogen gas. Bioreactors to treat agricultural waters have been studied for almost 20 yr. Much of the early work on bioreactors was done at the University of Waterloo, Canada (van Driel et al., 2006a,b). Blowes et al. (1994) constructed two 200-L fixed bed bioreactors consisting of coarse sand and varying forms of organic C (tree bark, wood chips, and leaf compost) used to treat nitrate from agricultural runoff. The rate of nitrate removal was sufficiently rapid (<1–2 d) to maintain low effluent nitrate concentrations throughout the variations in residence times. Nitrate removal continued at temperatures below 8°C,

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J. Environ. Qual. 44:1647–1656 (2015)
doi:10.2134/jeq2014.04.0162
Received 14 Apr. 2014.
Accepted 2 June 2015.
*Corresponding author (rcooke@illinois.edu).

N. Bell and R.A.C. Cooke, Dep. of Agricultural and Biological Engineering, Univ. of Illinois Urbana-Champaign, 1304 W. Pennsylvania Ave., Urbana, IL 61801; T. Olsen, M.B. David, and R. Hudson, Dep. of Natural Resources and Environmental Sciences, Univ. of Illinois Urbana-Champaign, 1102 S. Goodwin Ave., Urbana, IL 61801.
Assigned to Associate Editor T.Q. Zhang.

Abbreviations: DO, dissolved oxygen; DOC, dissolved organic carbon; DRP, dissolved reactive phosphorus; HRT, hydraulic retention time.

suggesting that denitrification is possible throughout most of the growing season.

Schipper and Vojvodic-Vukovic (1998) constructed a denitrification wall by digging a trench (35 m long, 1.5 m × 1.5 m) that intercepted groundwater. The excavated soil was mixed with sawdust (40 m^3) as a C source. After 1 yr, the average concentration entering the wall was between 5 and 16 mg NO_3–N L^{-1} (high = 22 mg NO_3–N L^{-1}); the concentration within the wall was between 0.6 and 2 mg NO_3–N L^{-1}. This wall has subsequently been monitored for a total of 5 yr, with no decrease in observed performance.

Researchers at the University of Illinois have been working on the characterization of bioreactor performance and the development of design standards for them. Cooke et al. (2001) and Doheny (2002) tested various C sources and retention times to determine the necessary design criteria for a bioreactor system that could adequately treat tile drainage water. Wood chips and corn cobs were found to be the most economically viable C sources for use in a bioreactor system. A retention time of approximately 8 h was found to be sufficient in lowering nitrate concentrations from 20 to 5 mg NO_3–N L^{-1}. Wildman (2002) found that field-scale systems were more efficacious than would have been predicted by extrapolating from the laboratory studies. He attributed this result to lower levels of oxygen saturation in the water entering the field systems. Appleford et al. (2008) developed a procedure to characterize the population of microorganisms contributing to denitrification in bioreactors. They reported that denitrification is mediated primarily by bacterial populations; however, fungi enhance the process by breaking down the wood chips into C forms that are more readily available to the bacteria. Chun et al. (2010) developed a pulse test to determine flow and transport parameters for field-scale bioreactors. Using the Random Walk method, they successfully modeled nitrate transport through a 6.1 m × 6.1 m bioreactor. Verma et al. (2010) developed annual performance curves relating load reduction to loading density (treated area per unit bioreactor surface area) for two watersheds in Illinois.

In general, bioreactors have been shown to significantly reduce nitrate loads on sites in Canada (Ontario), New Zealand, and the United States (Iowa and Illinois) (Blowes et al., 1994; van Driel et al., 2006a; Jaynes et al., 2008; Greenan et al., 2009; Robertson et al., 2009; Chun et al., 2010; Moorman et al., 2010; Schipper et al., 2010; Woli et al., 2010; Warneke et al., 2011b; Christianson et al., 2012). Bioreactors provide many potential advantages that make them a strong candidate for implementation as a best management practice across the midwestern United States because they require no modification of current practices, no land needs to be taken out of production, there is no decrease in drainage effectiveness, they require little to no maintenance, they use proven technology, and they can last for up to 20 yr (Cooke et al., 2001).

Although bioreactors have been shown to effectively reduce nitrate loads from fields, there is still much unknown about the factors that drive their performance (Christianson et al., 2012; Schipper et al., 2010; Warneke et al., 2011b; Woli et al., 2010). Also, potential negative effects of bioreactor use have been observed, such as the methylation of mercury, extreme declines in effluent dissolved oxygen, and high concentrations of organic matter in bioreactor effluent (Shih et al., 2011; Warneke et al., 2011c; Christianson et al., 2012). Before bioreactors can be implemented on a wide scale, their performance characteristics and potential unintended side effects should be more clearly understood. The overall goal of this study was to characterize the response of woodchip-based subsurface tile bioreactors to varying environmental conditions through time. Specifically, the objectives of this study were (i) to characterize seasonal temperature effects on nitrate removal efficacy of bioreactors at varying hydraulic retention times (HRTs), (ii) to observe changes in water quality parameters between influent and effluent waters of bioreactors and assess whether these changes have the potential to be harmful to the local environment, and (iii) to characterize transient characteristics of bioreactors during the startup period.

This study serves as the only field experiment in which influent nitrate concentration and HRT were held constant to determine the effects of influent water temperature on bioreactor performance. The results are being incorporated into the bioreactor design and evaluation model developed by Cooke and Bell (2014).

Materials and Methods

Site Description

The experiments were performed on three fields, each with an area of 1 ha, at the University of Illinois Urbana-Champaign Research Farm located just south of the campus in Champaign County, IL (40°4′18.68″ N 88°12′45.0″ W). Champaign is located in the central part of the state, which is the region with the greatest concentration of subsurface drainage (David et al., 2010; Cooke and Verma, 2012). The watershed encompassing the study area can be classified as agricultural, with >90% of the area under row-crop agriculture (Woli et al., 2010). The area has a humid continental climate, with average annual high and low temperatures of 16.5 and 5.4°C, respectively, and average annual precipitation of 1051 mm. The fields are primarily made up of Drummer silty clay loam and Flanagan silt loam.

On 10 May 2011 and 16 May 2012, corn (*Zea mays* L.) was planted on all three study fields. Approximately 224 kg ha^{-1} (200 lbs $acre^{-1}$) of N (anhydrous ammonia 82–0-0) was applied before planting for both years.

Drainage System and Subsurface Bioreactor Design

A tile drainage system was installed in each field during the late spring of 2012, with varying spacing and depths, as part of a separate study on the effect of drainage depth and spacing on the quality of drain outflow. The drainage system in the northwestern field was installed with a spacing of 18.3 m and a depth of 0.8 m, the drainage system in the northeastern field was installed with a spacing of 12.2 m and a depth of 1.1 m, and the drainage system in the southwestern field was installed with a spacing of 24.4 m and a depth of 1.1 m. Drainage effluent from the northeastern field was directed into a nearby pond, and drainage effluent from the northwestern and southwestern fields was directed into an existing main that empties into a drainage ditch located southwest of the study area.

During the early summer of 2012, three fixed-bed, in-field bioreactors were installed on the University of Illinois Research Farm, one for each study field. The schematic outline of these bioreactors is shown in Fig. 1. They were designed in accordance with guidelines established by the University of Illinois (Cooke and Bell, 2014). In this routine, 30 yr of historic weather data are used to determine the daily drain flow with a 10% probability of exceedance, and this value was used to optimize bioreactor dimensions based on residence time and flow rate considerations. Before being filled with wood chips, each excavated bioreactor trench was lined along the bottom and sides with clear, 0.25-mm-thick polyethylene plastic to prevent seepage of water from the bioreactors directly into the surrounding soil. Wood chips were of mixed species and were obtained from the local municipal landscape recycling center. They were similar in size to that reported by Woli et al. (2010). Each bioreactor trench measured 6.10 m long × 1.1 m wide × 1.4 m deep. The bioreactors were not covered with a layer of soil; wood chips were directly exposed to the atmosphere.

Four-chamber Agri Drain structures (Agri Drain Corp.) were installed at the outlet of each drainage system. These structures serve to divert flow from the field into the structure and to control the flow rate of water from the structure to the bioreactor by adding or removing sliding boards (stop logs) between compartments, thus altering the head difference. These structures allow for bypass flow, although there was no bypass flow during this study. The top board between the third and last compartment was fitted with a V-notch weir to accurately measure the flow rate of water exiting the bioreactor.

Data Collection and Analysis

Due to limited precipitation, there was no tile flow at this site during the spring, summer, and fall of 2012. It was therefore decided to run the experiments with N-spiked pond water. The bioreactors were operated in batch mode fashion with no water flowing through them between runs. Before each experimental run, water was pumped from a nearby pond into a 3785-L (1000 gal) tank located adjacent to each bioreactor. Each experimental run lasted between 10 and 12 h, and runs were conducted once or twice per week, on average, from July to December 2012. Because the pond water contained NO_3–N concentrations below the detection threshold, each tank was spiked with potassium nitrate before each run. Experimental runs occurring from 7 to 10 August were inadvertently spiked to a concentration of approximately 3 mg NO_3–N L^{-1} instead of the desired concentration of approximately 12 mg NO_3–N L^{-1}. Data from these runs were not included in any graph or analysis where nitrate was the dependent variable. Runs occurring from 14 August to 14 December were spiked to a concentration of approximately 12 mg NO_3–N L^{-1}. Flow of water from the tanks into the bioreactors was controlled to achieve HRTs of 2, 4, 6, or 8 h by metering the water through a Plexiglass V-notch weir structure that was calibrated at the hydrologic lab of the Agricultural and Biological Engineering Department at the University of Illinois. The timing and targeted HRT for each experimental run are given in Table 1. For each run, water was

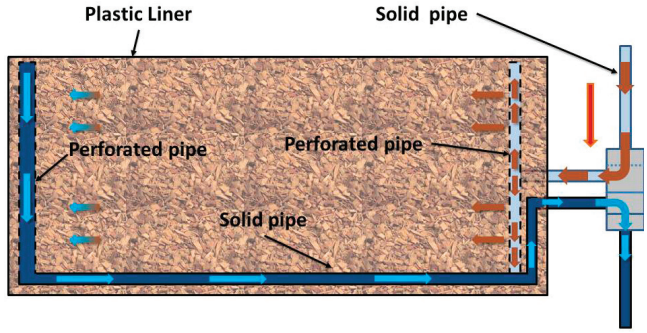

Fig. 1. Overhead-view schematic of bioreactor bed and four-chamber Agri Drain structure for each of the three bioreactors.

maintained at the flow rate corresponding to the particular HRT being tested. Flow rate was calculated as

$$Q = \frac{V\varphi}{\tau} \quad [1]$$

where V denotes flow volume (wetted volume consisting of both wood chips and voids), φ denotes drainable porosity, τ denotes hydraulic retention time, and Q denotes flow rate (L s^{-1}).

A drainable porosity of 0.7 was assumed based on previous laboratory trials from the University of Illinois (unpublished data). The flow volume was estimated based on flow depth,

Table 1. Schedule of experimental runs and associated target hydraulic retention times.

Hydraulic retention time	Date
2 h	18 July
	27 July
	10 Aug.
	17 Aug.
	4 Sept.
	27 Sept.
	18 Oct.
4 h	2 July
	12 July
	17 July
	26 July
	21 Aug.
	6 Sept.
	11 Oct.
	14 Dec.
6 h	9 Aug.
	14 Aug.
	15 Aug.
8 h	31 Aug.
	18 Sept.
	8 Nov.
	20 July
	23 July
	7 Aug.
	23 Aug.
	13 Sept.
	4 Oct.
	9 Nov.
	4 Dec.

which was maintained at 0.6 m throughout the course of these experimental pump runs. Target HRTs for each experimental run were randomly scheduled so as not to bias bioreactor efficacy data. Each experiment consisted of triplicate runs; that is, during each experiment all three bioreactors were operating concurrently at the same HRT and were treated as replicates.

During each experimental run, grab samples of both influent and effluent water were collected from the AgriDrain structure. For each bioreactor, influent water samples were collected approximately every 2 h, beginning at the start of each run, for a total of four samples per experimental run. These four samples were combined into one composite, 500-mL HDPE Nalgene sample bottle, which represented an average influent water sample for that entire experimental run. Effluent water samples were collected at 2-h intervals, beginning after one HRT had elapsed, for a total of four samples per experimental run. These samples were combined into one composite, 500-mL Nalgene sample bottle, which represented an average effluent water sample for that entire experimental run. All samples were kept on ice during the sampling day and then transported to a refrigerator with temperature maintained at 4°C until laboratory analysis. During the same times that grab samples were obtained from both influent and effluent water, a YSI Professional Plus handheld multiparameter meter with Quatro cable attachment was deployed to record values for dissolved oxygen (DO), pH, and water temperature. Within 1 wk of sample collection, the 500-mL composite water samples were analyzed at the Biogeochemistry Laboratory at the University of Illinois for chloride, sulfate, NO_3^-–N, dissolved organic carbon (DOC), dissolved reactive phosphorus (P) (DRP), and total P (TP). In the laboratory, the sample was divided into four aliquots. Aliquot A was unfiltered, preserved with H_2SO_4 (pH <2), and refrigerated at 4°C until analysis for TP and total Kjeldahl N (the sum of organic and ammoniacal N), which occurred within 2 to 6 mo. Aliquots B, C, and D were filtered through a 0.45-μm nitrocellulose filter and analyzed within 1 to 3 wk. Aliquot B was unpreserved and frozen until analysis for nitrate, chloride, and sulfate. Aliquot C was preserved with H_2SO_4 and was kept at 4°C until analyzed for DOC. Aliquot D was kept at the same temperature but was unpreserved until analyzed for DRP.

Nitrate, chloride, and sulfate concentrations were determined using a Dionex DX-120 ion chromatograph with minimum detection limits of 0.1 mg NO_3–N L^{-1}, 2 mg Cl L^{-1}, and 2 mg SO_4 L^{-1}. Dissolved reactive P was analyzed colorimetrically via flow injection analysis using the Lachat 8000 series. Detection limits were 10 μg NH_4–N L^{-1} and 5 μg P L^{-1}, respectively. Dissolved organic C was analyzed using a Shimadzu TOC-Vcsn analyzer with a minimum detection limit of 0.5 mg DOC L^{-1}. Total P was analyzed using a sulfuric acid and ammonium persulfate digestion technique. This digestion process converts organic P into orthophosphate, which was then analyzed colorimetrically with the Lachat 8000 using flow injection analysis. Water samples for total Kjeldahl N analysis were digested with sulfuric acid, copper sulfate, and potassium sulfate in an aluminum block digestor using the Lachat BD-46. This digestion process converts organic N compounds into ammonium, which was then analyzed by flow injection using the Lachat 8000. Water samples were processed, stored, and analyzed in accordance with approved methods (APHA, 1998). Organic P is the difference between TP and DRP.

Reweighted least squares models that use the least median of squares estimator for outlier diagnostics (Rousseeuw and Leroy, 1987) were fitted to the bioreactor performance data using the Trend Surface Analysis program developed by Cooke et al. (1994). Bioreactor performance was evaluated based on the relationship between both percent NO_3–N load reduction and NO_3–N removal rate and HRT and influent water temperature. Percent load reduction was calculated as the difference between influent load and effluent NO_3–N load per run divided by influent load. Removal rate was calculated as the difference in concentration between influent and effluent NO_3–N per run multiplied by flow rate and divided by saturated volume of the bioreactor. Adjusted coefficients of determination (R^2) values were used to measure how well the independent variable(s) of each model predicted bioreactor performance. Data were plotted using the OriginPro (OriginLab) data analysis and graphing software.

Results and Discussion

N Removal and Dynamics

Average concentrations (i.e., the average from samples taken from each of the three bioreactors), removal rates, and load reductions during the study period are shown in Fig. 2 and 3. In each instance, variations between the three bioreactors are shown with error bars.

Influent and effluent concentrations are shown in Fig. 2. Average influent concentrations ranged from <0.1 mg NO_3–N L^{-1} during initial runs (i.e., the runs before the pond water was spiked to 17 mg NO_3–N L^{-1} during the last experimental run in December 2012). Average effluent concentrations ranged from 0 to 13 mg NO_3–N L^{-1}. Percentage load reductions are shown in Fig. 3. The average maximum concentration reduction achieved was 98%, which corresponded to an 8-h HRT. The average minimum concentration reduction achieved was 20%, which corresponded to a 2-h HRT. The average concentration reduction achieved over all runs was 63%.

These concentrations and percent reductions are typical to those measured in systems using tile-drained water (as opposed to pumped surface water, as in this experiment). Woli et al. (2010) measured NO_3–N influent concentrations ranging from 2.8 to 18.9 mg L^{-1} and NO_3–N effluent concentrations ranging from 0.1 to 14.5 mg L^{-1} for a subsurface bioreactor treating tile-drained water on a field in central Illinois. Robertson and Merkley (2009) observed NO_3–N influent concentrations between 3 and 11 mg L^{-1} during the nongrowing season (Dec.–May) and concentrations of <2 mg L^{-1} during midsummer for an in-stream bioreactor in Ontario. Overall, the mean NO_3–N removal amount was 3.8 mg L^{-1} for that system. For four field-scale drainage bioreactors in Iowa, Christianson et al. (2012) observed annual flow-weighted influent NO_3–N concentrations ranging from 1.2 to 15.2 mg L^{-1} and flow-weighted effluent concentrations ranging from 0.6 to 11.6 mg L^{-1}. Moorman et al. (2010) observed influent nitrate concentrations of 20 to 25 mg NO_3–N L^{-1} entering a wood chip bioreactor in Iowa, with effluent concentrations

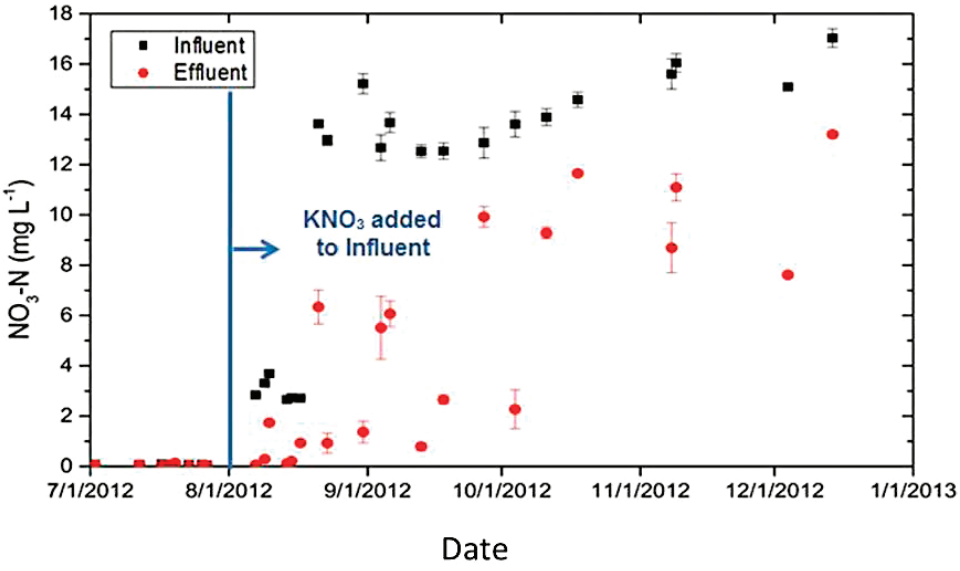

Fig. 2. Mean (n = 3) influent and effluent nitrate concentrations (± SD) in wood chip bioreactors. The dashed line indicates the time after which the influent was spiked with potassium nitrate.

reaching 10 mg NO_3–N L^{-1} or below after a HRT of about 24 h. From a wood-based bioreactor in a cornfield in southern Ontario, van Driel et al. (2006a) measured a mean influent NO_3–N concentration of 11.8 mg L^{-1} and a mean removal rate of 3.9 mg L^{-1}.

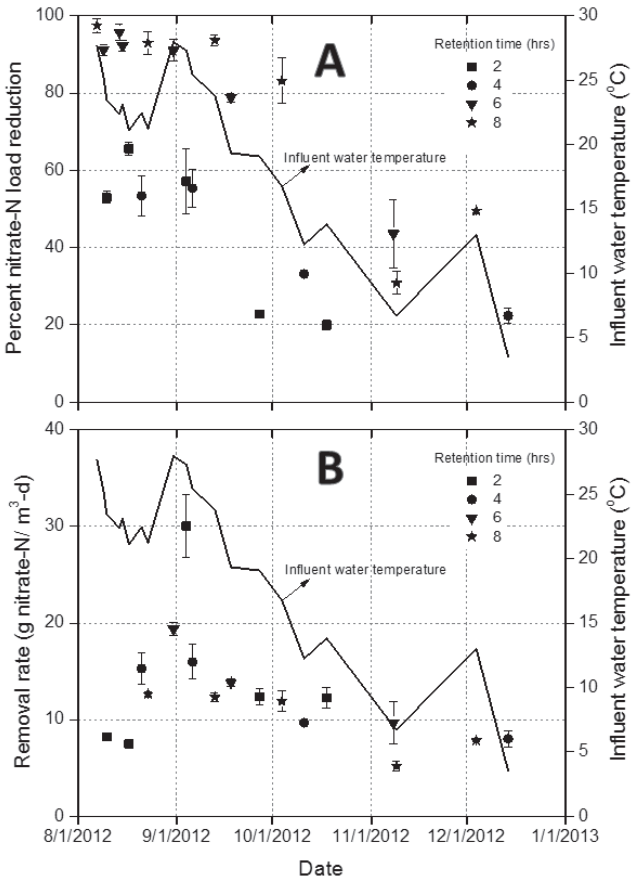

Fig. 3. Effect of water temperature on mean (n = 3) nitrate load reduction (± SD) (A) and nitrate removal rate (± SD) (B) in wood chip bioreactors operated at different hydraulic residence times.

Nitrate removal, shown in Fig. 3, was most likely limited by nitrate concentration during the initial runs when influent concentrations were low. Robertson and Merkley (2009) and Warneke et al. (2011c) reported that removal rate is not limited when effluent NO_3–N concentrations exceed 0.5 mg L^{-1}. When this threshold was exceeded, the highest removal rate of 30 g NO_3–N m^{-3} d^{-1} corresponded to an HRT of 2 h, and the lowest removal rate of approximately 5 g NO_3–N m^{-3} d^{-1} corresponded to an HRT of 8 h. The highest removal rate occurred at the highest water temperature, and the lowest removal rate occurred at the next to lowest water temperature over the study period. In appears, therefore, that removal rate is a stronger function of water temperature than of flow rate when not N limited. The average nitrate removal rate was 11.6 g NO_3–N m^{-3} d^{-1}.

Removal rates fell within the range of values reported by other wood chip bioreactor studies. Christianson et al. (2012) observed removal rates ranging from 0.4 to 7.8 g NO_3–N m^{-3} d^{-1} from four field-scale drainage bioreactors in Iowa. Christianson et al. (2013) reported removal rates ranging from 0.4 to 1.1 g NO_3–N m^{-3} d^{-1} from yet another bioreactor in Iowa. Robertson et al. (2009) measured removal rates in the range of 2 to 16 g NO_3–N m^{-3} d^{-1} in the sixth and seventh years of operation of a wood particle reactor treating agricultural tile drainage in southern Ontario. Warneke et al. (2011a) calculated an average removal rate of 8.7 g NO_3–N m^{-3} d^{-1} from a denitrification bed treating effluent discharged from a glasshouse in New Zealand. In a laboratory experiment testing various C substrates for nitrate removal capabilities, Warneke et al. (2011c) measured removal rates ranging from 1.3 g NO_3–N m^{-3} d^{-1} from wood chips to 6.2 g NO_3–N m^{-3} d^{-1} from corn cobs. Although corn cobs removed N at a rate three times that of wood chips, corn cobs are not recommended as a substrate for subsurface bioreactors except in a mixture with woodchips due to dissolved N_2O release and substantial C consumption by nondenitrifiers. Warneke et al. (2011b) also observed an increase in removal rates as temperatures increased. Woli et

al. (2010) calculated an average nitrate removal rate of 6.4 g NO_3–N m^{-3} d^{-1} in a field bioreactor located in central Illinois. Removal rates for denitrification walls, however, seem to be much lower than those for denitrification beds (Schipper et al., 2010). For a denitrification wall in Iowa, Jaynes et al. (2008) reported an average removal rate of 0.62 g NO_3–N m^{-3} d^{-1} over four plots and 5 yr of study.

Removal rates increased from August to September and then decreased from September to December (Fig. 3). The initial increase in removal rate could be attributed to the gradual establishment of denitrifying bacterial communities over that period. Declining temperatures (and thus increasing concentrations of dissolved oxygen) most likely contributed to decreased microbial activity, resulting in decreasing removal rates from September to December, similar to previous studies (Christianson et al., 2011; Christianson et al., 2013; Elgood et al., 2010; Robertson and Merkley, 2009; Schipper et al., 2010; Shih et al., 2011; Warneke et al., 2011a). The removal rate curve mirrors the typical response of an under damped transient system; that is, removal rate begins near zero, increases to a peak, then gradually decreases to a stable rate (~10 g NO_3–N m^{-3} d^{-1}). Removal rate is dependent on temperature; however, removal rate is not strongly dependent on HRT, as evidenced by the overlap of the points for all the HRTs in Fig. 4. Therefore, after removal reaches a stable, continuous rate, approximately equivalent loads of NO_3–N will be removed in a given time period, regardless of HRT, for any given influent water temperature. Hydraulic retention time is of importance, however, because a greater percentage of the effluent concentration is reduced with increasing HRT.

Removal efficiency of nitrate decreased as flow rate increased, as indicated by percent load reduction (Fig. 3). During any given time, high percent load reductions occurred during experimental runs with longer HRTs (i.e., slow flow rates). Also, percent nitrate load reduction decreased over time as temperatures decreased, regardless of HRT. These results agree with general trends observed by others, notably Greenan et al. (2009) and Robertson and Merkley (2009).

Other Water Quality Parameters and Potential Adverse Effects

Dissolved reactive P effluent concentrations were higher than influent concentrations for nearly all runs (Fig. 4). Dissolved reactive P effluent concentrations for the first three experimental runs were an order of magnitude higher than influent concentrations. However, in subsequent runs influent and effluent DRP concentrations did not differ substantially. We do not know the cause of the initial extreme increase of DRP concentration in the effluent. It may have been due to desorption of DRP from soil particles mixed in with the wood chips or P leached from the wood chips. However, the sustained increase in concentration of effluent DRP as compared with influent DRP could also be due to biological processes at work. Although the DRP effluent concentrations stabilized and were not substantially different from the influent concentrations after 1 mo of operation, they were almost invariably higher than the influent concentrations, and they started trending upward by the end

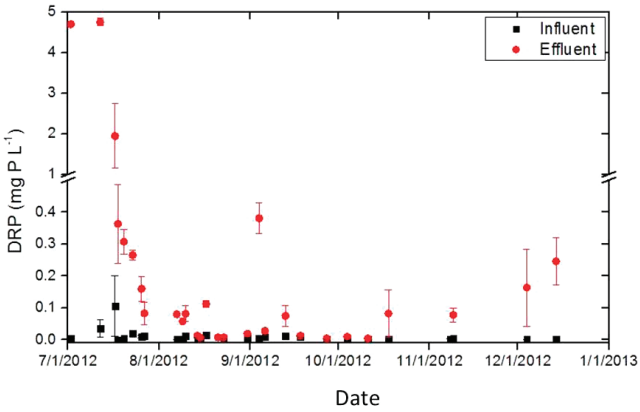

Fig. 4. Mean (n = 3) Influent and effluent dissolved reactive P (DRP) concentrations (± SD) in wood chip bioreactors.

of the experiment. These increasing DRP levels may be a cause for concern in terms of negative water quality effects on the surrounding environment. There is, therefore, a need for long-term evaluation of P transport from bioreactors.

Plots of dissolved oxygen, water temperature, and pH values for influent and effluent water over the course of the experiment are given in Fig. 5. Average pH of the influent

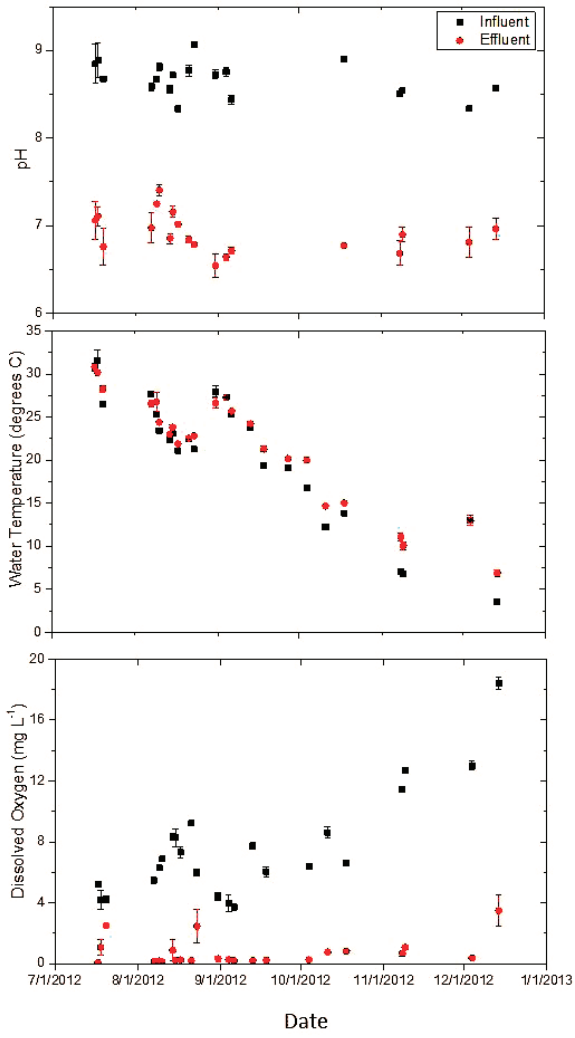

Fig. 5. Mean (n = 3) dissolved oxygen, water temperature, and pH values (±SD) for influent and effluent water in wood chip bioreactors.

was 8.6, whereas the average pH of the effluent was 6.9. The pH response to denitrification appears to be due to the composition of the denitrifier community (Dörsch et al., 2012) or the nature of the organic substrate (Drtil et al., 1998). The minimum effluent pH recorded was 6.5, which lies within the range of 6.5 to 9, to which an aquatic community can be briefly exposed without resulting in an unacceptable effect (USEPA, 1976). Effluent water temperature was found to be approximately 1°C higher than influent water temperature for 80% of the experimental runs. Influent water temperatures exceeded 30°C in July and dropped to below 5°C in December. The decrease in NO_3–N removal rate could be attributed to this decline in influent water temperature. Robertson et al. (2009), Elgood et al. (2010), and Warneke et al. (2011a) also documented increases in NO_3–N removal rates with increasing temperatures. However, denitrification appeared to continue even when influent temperatures reached <5°C. During this sampling period, the minimum influent temperature reached 3.5°C in December. Maximum effluent temperature reached 31.6°C near the beginning of experimental runs.

Dissolved oxygen concentrations in influent water averaged 7.5 mg DO L^{-1}, whereas DO concentrations in effluent water averaged 0.8 mg DO L^{-1}. Influent DO concentrations increased from 4 mg DO L^{-1} in July to close to 20 mg DO L^{-1} in December. This increase in DO concentration could have contributed to a decrease in nitrate removal over time because DO depletion must occur before the onset of denitrification (Robertson and Merkley, 2009). Warneke et al. (2011c) also noticed a significant decrease of DO in effluent water from different C substrates, ranging from 7.1 mg DO L^{-1} in influent to 1.3 mg DO L^{-1}. Although influent DO concentration significantly increased over the study period for these experimental runs, effluent DO concentrations remained below 3 mg DO L^{-1} over that same period.

Christianson et al. (2012) obtained similar results in a study evaluating the performance of four field-scale bioreactors in Iowa. Dissolved oxygen concentrations were highest in the early spring months (≥8.5 mg DO L^{-1}) and lowest in summer (≤5 mg DO L^{-1}). They observed that, regardless of influent DO concentration, effluent DO concentration was always reduced to <2.4 mg DO L^{-1}.

The effluent DO concentrations observed in these studies are below the water quality criteria established by the USEPA (USEPA, 1976), which indicates a daily minimum DO concentration of 5.0 mg L^{-1} for early life stages of aquatic wildlife species. However, bioreactors typically flow out into small streams or drainage ditches, and these water bodies tend to have high reaeration coefficients (Melching and Flores, 1999). In addition, Goswami et al. (2008) found that tile-drained water makes up <20% of the total flow in drainage channels in central Illinois.

Although Goswami et al. (2008) observed that tile-drained water makes up <20% of total flow, on average, in drainage channels in central Illinois, there were periods, particularly during the recession section of flow events, when tile flow was as much as 90% of stream flow. Low bioreactor effluent DO values could be a cause for concern, particularly if bioreactors are widely adopted.

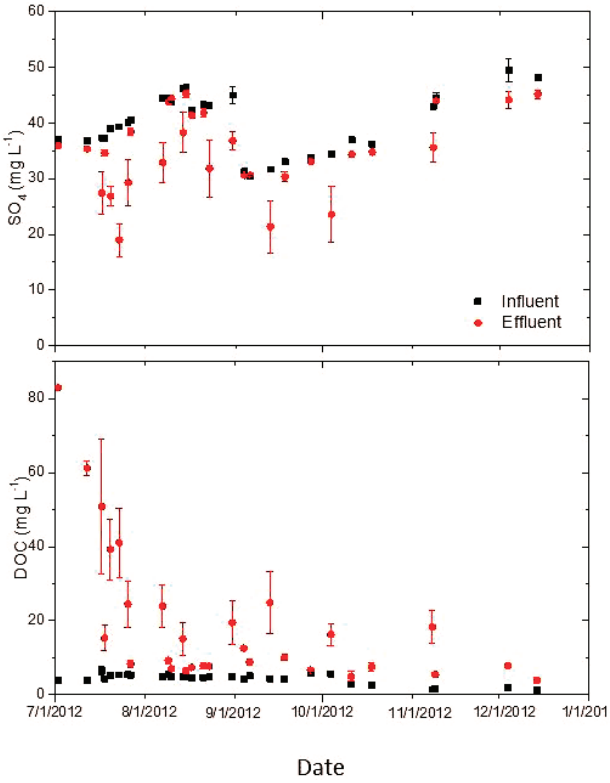

Fig. 6. Mean (*n* = 3) dissolved organic C DOC and sulfate concentration of influent and effluent water in wood chip bioreactors.

Effluent DOC concentrations were significantly higher than influent DOC concentrations, especially during the first month of bioreactor operation (Fig. 6). After 5 mo of operation, effluent DOC concentration decreased from approximately 80 mg C L^{-1} to <10 mg C L^{-1}. Extremely high DOC values at the beginning of bioreactor operation were likely due to the initial flushing of labile C from wood chips. This trend and range of DOC values agree with those found in similar studies (Blowes et al., 1994; Schipper et al., 2010; Warneke et al., 2011c).

In the majority of cases (83% of total runs), sulfate reduction occurred (Fig. 7). Sulfate reduction may result in

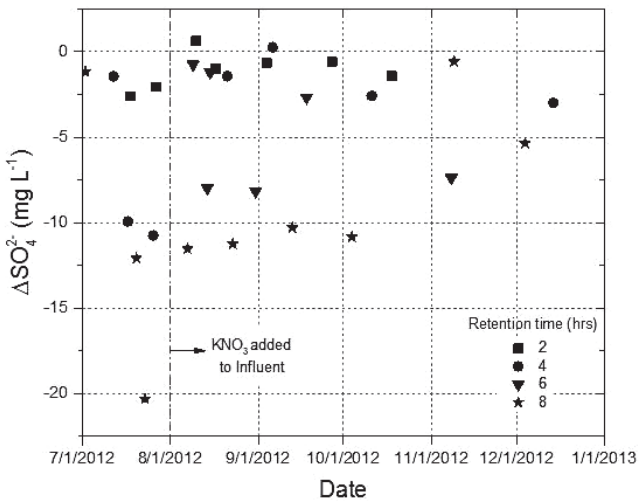

Fig. 7. Changes in mean (*n* = 3) sulfate concentrations between influent and effluent water and corresponding hydraulic retention times in wood chip bioreactors operated at different hydraulic residence times. The dashed line indicates the time after which the influent was spiked with potassium nitrate.

conditions that are favorable for the formation of methyl mercury (King et al., 2002). Reduction of the most sulfate occurred during experimental runs with a target HRT of 8 h (Fig. 7). Eight-hour HRT experimental runs were also associated with the largest percent reduction of nitrate load. This pattern is to be expected because more energetically favored electron acceptors, such as oxygen and nitrate, must first be consumed before the onset of sulfate reduction. Shih et al. (2011) observed sulfate reducing conditions in a streambed bioreactor in southern Ontario. They found the highest level of sulfate reduction, a loss of 10 to 15 mg L^{-1} sulfate, occurred during the early fall when nitrate removal was complete. Robertson and Merkley (2009) concluded that sulfate reduction appeared to be inhibited in the presence of 0.5 to 1 mg L^{-1} NO_3–N. For this study, in most instances the nitrate concentration of the effluent exceeded 1 mg L^{-1} NO_3–N (Fig. 3). Blowes et al. (1994) noticed a sulfate decrease of up to 38 mg L^{-1} in one of the trials of their barrel experiments. Christianson et al. (2012) documented sulfate reduction for two bioreactor sites in Iowa, most notably in winter months when influent nitrate was reduced to nearly zero.

Another potentially adverse effect is the production of nitrous oxide (N_2O) resulting from incomplete denitrification. Although N_2O was not measured in these bioreactors, Woli et al. (2010) and Herbstritt (2014) found that the levels of N_2O produced in similar bioreactors in central Illinois did not exceed levels produced in nearby corn fields.

Nitrite concentrations were not measured in this study. Although nitrite rapidly oxidizes to nitrate in oxygenated waters (Hem, 1985), given the low bioreactor effluent DO values, nitrite is likely present. The failure to measure nitrite concentrations added uncertainty to the evaluation of bioreactor effectiveness. It is recommended, therefore, that nitrite concentrations be measured in future bioreactor studies.

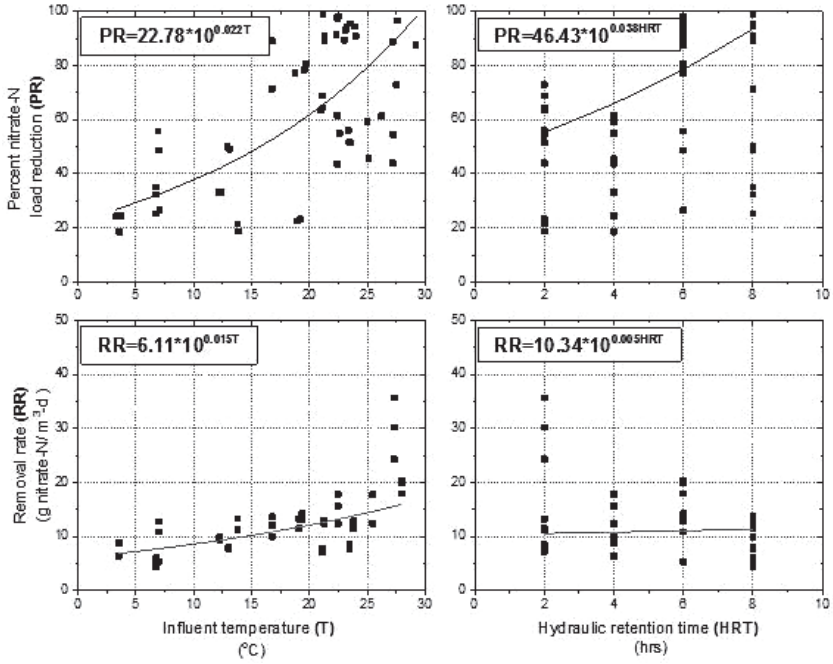

Fig. 8. Plots of hydraulic retention time and influent water temperature versus nitrate removal rate and percent nitrate load reduction in wood chip bioreactors. PR, percent NO_3^-–N load reduction; RR, removal rate.

Statistical Analyses and Model Development

Weighted least squares regression analyses of bioreactor performance (removal rate and percent NO_3^-–N load reduction) were performed for two independent variables (HRT and influent temperature). Reweighted least squares simple regression models, which detected and removed outliers (resulting in lower residuals and higher coefficients of determination), are presented in Fig. 8. Although exponential and linear models for the data exhibited almost equal coefficients of determination, residuals of the exponential models were consistently lower than residuals of the linear models. Therefore, the exponential models were chosen to represent these data. Influent water temperature explained the majority of the variance in both percent NO_3^-–N load reduction and removal rate, with coefficients of determination of 0.74 and 0.65, respectively. Hydraulic retention time explained 75% of the variance in percent nitrate load reduction and only 8% of the variance in removal rate.

For both models, the inclusion of two independent variables (as opposed to only one) resulted in a model with

Table 2. Coefficients and summary statistics of reweighted exponential (linearized) regression models for percentage nitrate load removed and removal rate.

	Coefficients	SE	*P* value
Removal rate ($RR = 5.97 \times 10^{0.016T}$)			
Intercept	0.776	0.078	<0.001
HRT†	−0.001	0.009	0.93
Temperature	0.016	0.003	<0.001
	$R^2 = 0.43$		
Percent load reduction ($LR = 16.14 \times 10^{0.018T} \times 10^{0.047HRT}$)			
Intercept	1.208	0.060	<0.001
HRT	0.047	0.006	<0.001
Temperature	0.018	0.002	<0.001
	$R^2 = 0.73$		

† Hydraulic retention time.

better fit. Parameters and coefficients of determination for the two variable fits are given in Table 2. A slope of almost zero for HRT for the removal rate model indicates that HRT does not seem to influence removal rate. However, as HRT increases percent nitrate load reduction increases because load reduction is the product of removal rate and residence time. Similar slopes for influent water temperature in both models suggest that temperature has the same degree of impact on bioreactor performance whether it is measured as percent load reduction or removal rate. Considering the models presented here, percent NO_3^-–N load reduction can be more accurately predicted than removal rate using the input parameters of influent water temperature and HRT.

Christianson et al. (2012) concluded that temperature and nitrate concentration were the most important factors affecting percent bioreactor nitrate load reduction and nitrate removal rate, respectively. Analyses also indicated that load reductions were significantly affected by HRT. However, the study recommended more field-scale performance data from bioreactors of different designs and from multiple locations around the Midwest to further enhance understanding of nitrate removal in bioreactor systems.

Implications and Conclusions

This study was conducted during the first 8 mo after installation of the bioreactors. The results, therefore, are not generally representative of long-term performance. The study revealed how effectively in-field wood chip bioreactors reduce nitrate at various HRTs and influent water temperatures. Changes in water quality parameters were assessed, and exponential models to predict bioreactor performance as a function of HRT and influent water temperature were developed. This study serves as the only controlled field experiment in which influent nitrate concentration and HRT were held constant to determine the effects of influent water temperature on bioreactor performance. Important questions and concerns regarding the potential and widespread implementation of bioreactors across the country were addressed. These results demonstrate that bioreactors to treat subsurface drainage are an effective means to reduce nitrate loads while producing minimal adverse impacts on water quality. However, more long-term studies over a variety of landscapes should be performed to ensure that bioreactors are not solving one environmental issue while creating others.

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