

Technical Report No: 13-04

**COMPARISON OF DENITRIFICATION POTENTIAL
AROUND A TILE DRAIN AND IN AQUIFER SEDIMENTS:
OAKES, ND**

by

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May 2013

**North Dakota Water Resources Research Institute
North Dakota State University, Fargo, North Dakota**

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ABSTRACT

Denitrification, the microbial reduction of nitrate (NO_3^-) in groundwater, has three requirements: limited oxygen, bacteria capable of mediating the reaction, and electron donors for the bacteria to use in the redox reactions. The critical factor for aquifer denitrification is the concentrations of electron donors. Without an adequate supply of electron donors, bacteria cannot reduce concentrations of either oxygen or NO_3^- .

Artificial drainage within agricultural areas may allow contaminants to bypass, or increase conveyance through, reduced areas in which denitrification is likely to occur. This contributes to elevated NO_3^- yields as it is discharged directly into surface water. Depending on site geology, however, bacterial biofilms capable of NO_3^- reduction may cultivate within the tile drainage. This study aims to quantify and compare the potential for denitrification, as well as denitrification rates, within tile drainage and aquifer sediments at the Best Management Practices (BMP) site, within the Oakes Irrigation Test Area (OITA) near Oakes, North Dakota.

For the aquifer sediment study, sediment samples (n=43) were collected from 10 locations at the BMP site. All samples were analyzed for the following potential electron

donors: organic carbon, ferrous iron, manganese, and inorganic sulfide. A subset of samples was analyzed for organic sulfur, but all were below detection limits (<0.01%). Samples were also analyzed for texture and color. For the subsurface drainage study, a nutrient tracer test was conducted within a drain tile transect at the BMP site. Sediment samples (n=6) from the gravel pack surrounding the tile drains were analyzed in the same manner as the aquifer sediments.

The major finding was that the biofilm accumulation within the gravel pack surrounding the tile drains contains adequate electron donor concentrations. However, when compared with denitrification rates occurring in the aquifer sediments, the tracer test in the drain tile produced no observable denitrification. Secondary findings indicated that electron donors are correlated with one another and electron donor concentrations are inversely correlated with grain size in the aquifer sediments.

INTRODUCTION

The use of drain tiles for subsurface drainage has several advantages, including increased cropped acreage (Pavelis 1987), earlier planting seasons, increased crop yields (Eidman 1997), and decreased compaction of soil (Spaling and Smit 1995). Subsurface drainage may also reduce the use of and need for pesticides and fungicides by improving crop quality, thereby reducing the susceptibility of a crop to pests (Fraser and Fleming 2001). Drain tiles may also have disadvantages, such as increased peak flows during storm events (Robinson and Rycroft 1999), increasing nutrient concentrations in agricultural runoff (Downing et al. 1999) and they may become obstructed, resulting in reduced hydraulic efficiency. Obstructions can include silt deposits, roots, or sludge deposits and biofilms associated with bacterial activity (Ford 2005). Obstructions associated with bacterial activity involve the oxidation-reduction (“redox”) cycling of sulfur (S), iron (Fe), and manganese (Mn) (Ford 2005) with oxygen in the drain tile. However, NO_3^- , like oxygen, is also a strong oxidant and it may be denitrified with these same elements (Korom 1992). Denitrifying bacteria have been confirmed in drain tiles (Ivarson and Sojak 1978, Knighton 1997) and biological clogging of drainage systems has improved water quality in situations involving extended retention time (Rowe and VanGulck 2004). Some investigators have speculated that denitrification may be occurring in the tile drain system in the Oakes Irrigation Test Area (OITA) (Knighton 1997, Casey et al. 2002, Derby et al. 2009, Sawatsky 2009). Significant denitrification has also been known to occur in North Dakota aquifers (Korom et al. 2005, Korom et al. 2012). In this paper it is hypothesized that within the saturated zone, substantially more of the NO_3^- reduction in the OITA is occurring within the aquifer sediments at the site,

rather than within the drain tiles. The aquifer sediments within the saturated zone of the OITA, not the drain tiles, are able to reduce NO_3^- at a rate which could be beneficial to water quality.

Agricultural Tile Drainage

Since the first recorded installation of drain tiles in 1835, the reclamation of land by subsurface drainage has transformed the American landscape (Framji and Mahajan 1969). Today, it is estimated that within the Mississippi basin alone, drainage pipes lie in the subsurface of an estimated 40-70 million acres (Hey 2001). The use of subsurface drainage continues to grow in the Midwest and has converted up to 30% of poorly drained wetlands to agricultural areas (Pavelis 1987). The recent wet cycle within the Red River Valley basin of North Dakota has caused tile-drainage to be installed within the region at a rapid pace (Figure 1). One drain tile installer within the region has reported installing more than 20 million feet of tile in the Red River Valley since 2005 (Nodak Electric 2011).

Overall, subsurface drainage remains a major pathway for nutrient (N and P) loss to surface waters (Blann et al. 2009). Subsurface drainage delivers nutrients to surface water via different pathways, and at different magnitudes. Enrichment of surface waters with nutrients is common in regions where intensive agriculture is practiced; the greatest riverine NO_3^- fluxes are observed from basins draining extensively drained agricultural regions (McIsaac and Hu 2004).

The eutrophication of downstream water bodies may be attributed to the leaching of NO_3^- and P out of the soil through subsurface drains (Dinnes et al. 2002). As

subsurface drainage reclaims more land for agricultural production, it also creates environmental hazards on a global scale.

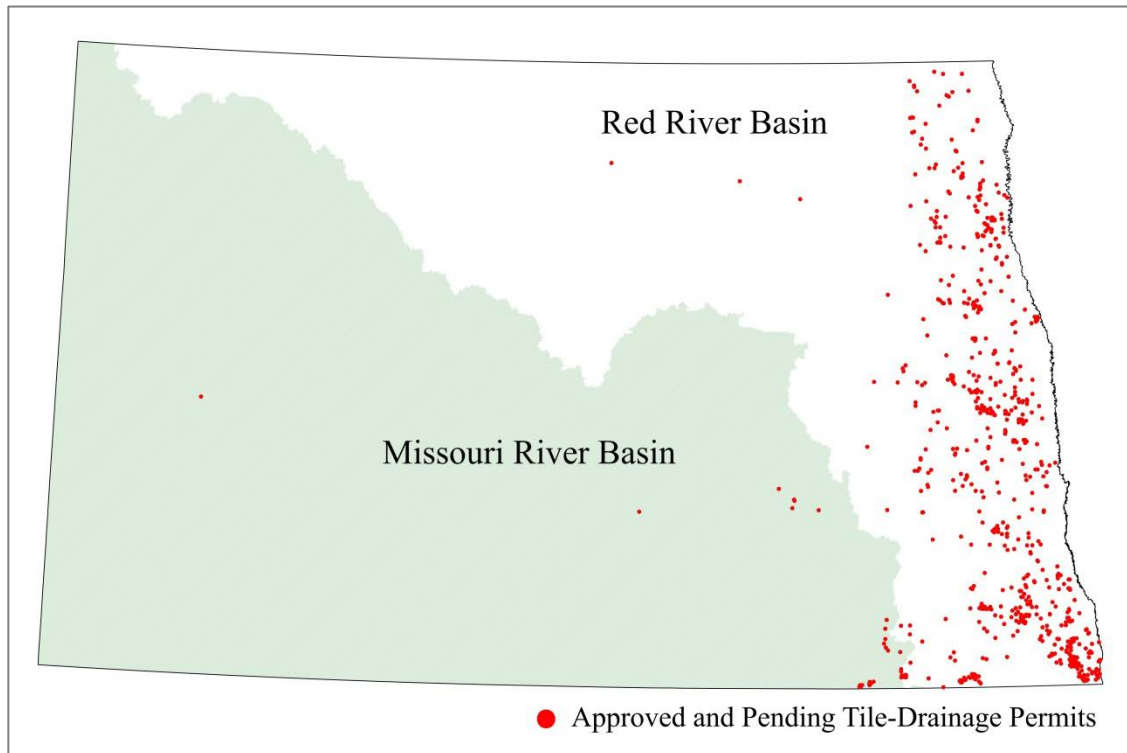


Figure 1. State-wide distribution of approved and pending tile-drainage permits (ND State Water Commission database, December, 2012).

Tile drains skim the NO_3^- from the surface of the aquifer and release it to nearby surface water. It is estimated that the principal contributor of nitrogen inputs to the Gulf of Mexico and the North Atlantic Ocean are agricultural in origin (Randall and Mulla 2001, Howarth et al. 1996). Increased NO_3^- loading in the Mississippi has been directly linked to the spread and increased severity of hypoxia within the Gulf of Mexico (Rabalais et al. 1996). Subsurface drains bypass the reduced zones where denitrification is most likely to occur, contributing to higher NO_3^- yields as they discharge directly to surface water (Dinnes et al. 2002).

In some geologic environments, subsurface drainage may be beneficial to water quality. Draining soils increases their capacity to store moisture, which can reduce surface runoff volumes in certain situations. In comparison with surficial agricultural drainage, decreased surface runoff associated with drain tiles can improve water quality by reducing soil, chemical, and nutrient losses from a field (Fraser and Fleming 2001). Drain tiles have the potential to decrease pesticide loads by orders of magnitude; and phosphorus losses, which are generally associated with erosion, may be reduced (Gilliam et al. 1999, Ayars and Tanji 1999).

In agricultural soils, a high water table can have numerous negative impacts on crops. By removing excess water from the soil and lowering the water table, drain tiles enhance crop yields by allowing proper root-zone aeration and facilitating root proliferation, function, and metabolism (Fraser and Fleming 2001). Hydraulic efficiency in drain tiles is commonly reduced by mineral deposits, silt deposition and roots from nearby vegetation (Grass 1976). Biological clogging from bacteria may also affect hydraulic efficiency in drain tiles. The most prevalent and problematic form of biofilm accumulation is iron ochre, but biofilms may also be composed of manganese deposits, sulfur slimes, and iron-sulfides (Ford 2005).

Remediation of NO_3^- is effectively completed through the process of denitrification. This naturally-occurring process reduces NO_3^- to non-reactive nitrogen gas (Korom 1992). Denitrification requires the following: the availability of electron donors, an anaerobic environment, and the presence of nitrogen digesting bacteria (Korom 1992, Starr and Gillham 1993). The availability of suitable electron donors within aquifer sediments has been shown to be the controlling factor in this reaction

(Korom 1992 and references therein). According to Korom (1992), the most common electron donors are organic carbon, sulfide (typically as pyrite, FeS_2), and ferrous iron minerals, with manganese also possibly contributing. The same species are also cycled in drain tiles and may form biofilms or deposits that reduce hydraulic efficiency in drain tiles (Ford 2005).

Research has suggested that biofilms may be responsible for denitrification within subsurface lines in eastern North Dakota (Casey et al. 2002, Derby et al. 2009, Sawatzky 2009). As noted above, subsurface drainage tiles clogged with biofilm accumulation are potentially capable of the natural attenuation of NO_3^- by denitrification. Species of bacteria capable of denitrification, *Arthrobacter* spp. and *Brevibacter* spp., have been found within biofilm samples taken from subsurface drain tiles (Knighton 1997).

Samples of tile drain discharge from the Oakes Best Management Practices (BMP) research field have shown significantly lower NO_3^- concentrations than the nearby surrounding groundwater. These samples suggest that denitrification may be occurring via the manganese biofilm within the tile drains (Sawatzky 2009). On the other hand, Korom et al. (2005, 2012) showed that significant denitrification occurs by electron donors in aquifer sediments in North Dakota. My hypothesis is that more denitrification at the BMP site is occurring through the consumption of electron donors present within the aquifer sediments at the site, rather than through denitrification occurring within the tile drain system.

SITE DESCRIPTION AND GEOLOGY

The BMP site (Figures 2, 3, and 4) is a 64-ha agricultural field in the NW1/4, Sec. 29, T.130N, R.59W, Dickey County, ND, containing two transects of buried subsurface agricultural drainage. The primary objective for the BMP field site was to develop methods of monitoring leachate losses under irrigated crops (Derby et al. 1997). The BMP site is within a larger site, the OITA, which was constructed by the United States Bureau of Reclamation (USBR) in the 1980s to investigate feasibility of irrigation and artificial recharge in southeastern North Dakota from diverted James River water (Frietag and Esser 1986).

There are two lines of drain tiles that run from the south end of the BMP site to the north (Figure 4) where they intersect a drainage canal, which flows into the nearby James River. The drains at the site consist of corrugated plastic pipe, 6-inches (15 cm) or 8-inches (20 cm) in diameter, and buried approximately 8 feet (2.4 m) below the surface at the site. The BMP site tile drainage system differs from most current designs, in that the drainage is deeper and more widely spaced, six to eight feet (1.9 to 2.5 m) deep and 1,200 feet (366 m) apart. As a comparison, tile drain depths are generally three to four feet (1 to 1.2 m) deep and 40 to 100 feet (12 to 30 m) wide (Schuh 2008). Surrounding the tile drains is a 12-inch (30 cm) gravel envelope, with gravel brought in from off-site. A number of monitoring wells and field lysimeters (Derby and Knighton 2001) are installed in parallel east to west transects across the site. Details of the instrumentation can be found in Derby and Knighton (2001), Derby et al. (1998), and Casey et al. (2002).

At the BMP site, a variety of clay, sand, silt, and gravel deposits cover the present surface. These sediments, the Oahe Formation, were deposited in environments including river, pond, wind-blown, and mass-movement (Bluemle 1979a).

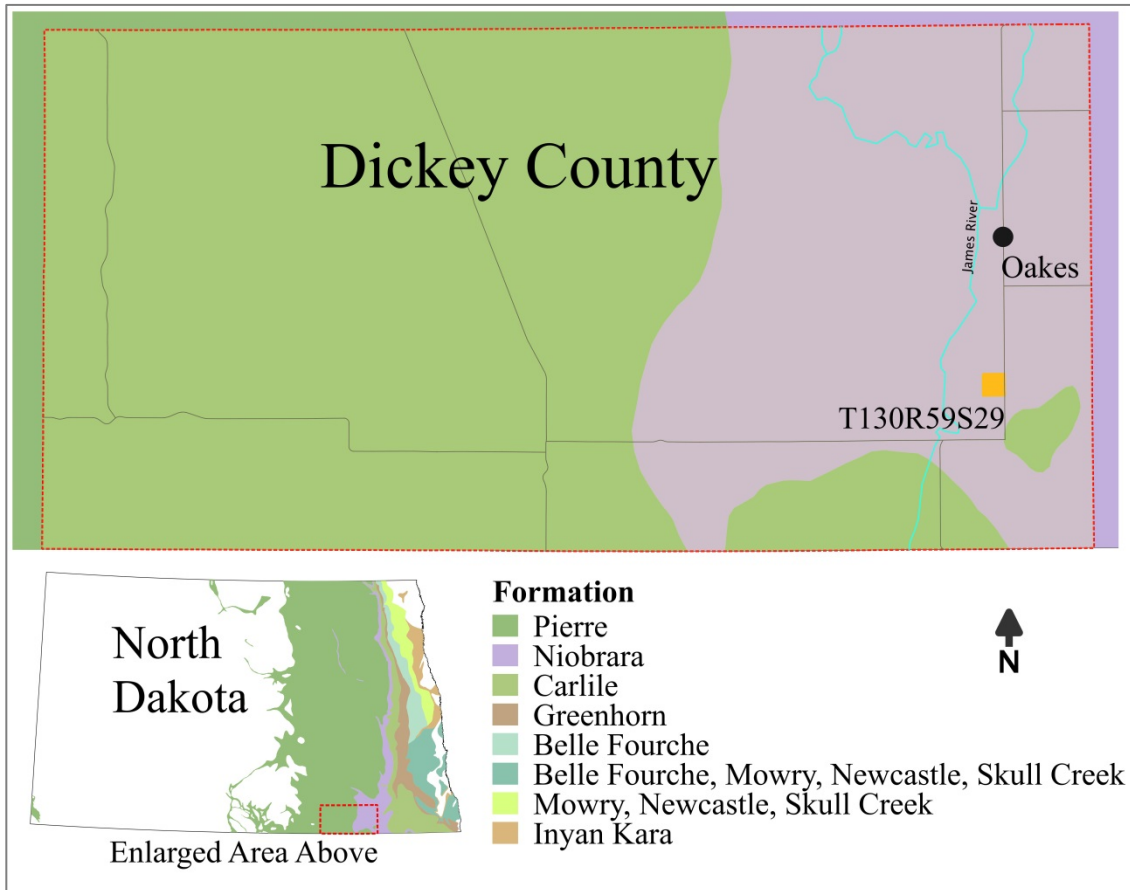


Figure 2. Underlying Bedrock near the Oakes Irrigation Test Area (OITA) (created using data from NDGIS Hub).

Several glacier advances and retreats likely scoured the underlying Niobrara and nearby Pierre formations to derive the facies of the Coleharbor. Till samples from the Coleharbor at various depths exhibit an average of 36% shale composition by weight (Bluemle 1979a).

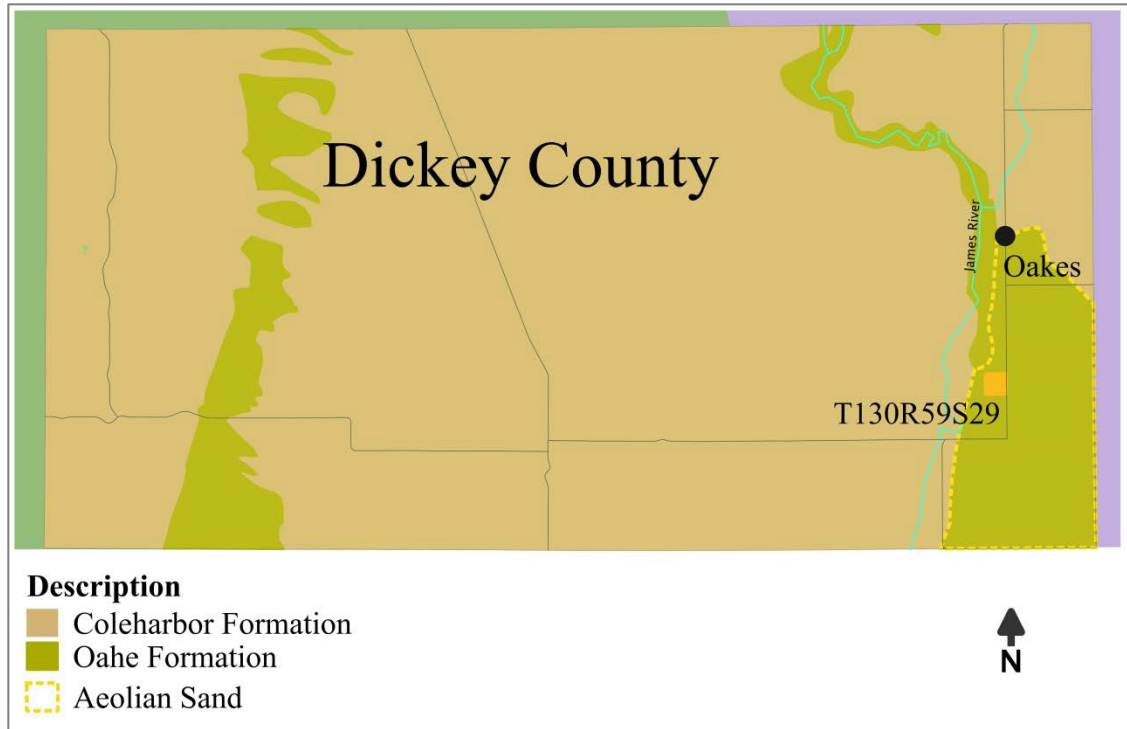


Figure 3. Map of surficial geology of Dickey County, ND (created using data from NDGIS Hub)

The Coleharbor Group overlies the Cretaceous Pierre Formation shale, with the exception of the eastern part of Dickey County where the Cretaceous Niobrara Formation is the underlying calcareous shale formation (Figure 2 and Table 1). The shales of the Pierre Formation are commonly found exposed on the east side of the Missouri Escarpment, where Coleharbor Group sediments become thin. In a similar study involving electron donor potential, the Niobrara Formation was shown to have over twice the amount of available electron donors as the Pierre Formation in east-central North Dakota (Klapperich 2008).

The BMP site sits atop the unconfined Oakes aquifer, underlying an area of about 93 mi² (240 km²), with the James River creating a flow boundary along the western edge. The aquifer was the result of a two separate stages of deposition. The early, lower aquifer materials were deposited as valley fill. These deposits consist of fine to coarse sand and

gravel with interbedded silt and clay deposits. After the valley became blocked in the south, glacial Lake Dakota was formed and covered an area from South Dakota to 3 miles (5 km) north of Oakes. During the Lake Dakota stage, the deposited aquifer materials were of deltaic and lacustrine origins, with fine to medium sand and silt, and silt and silty clay.

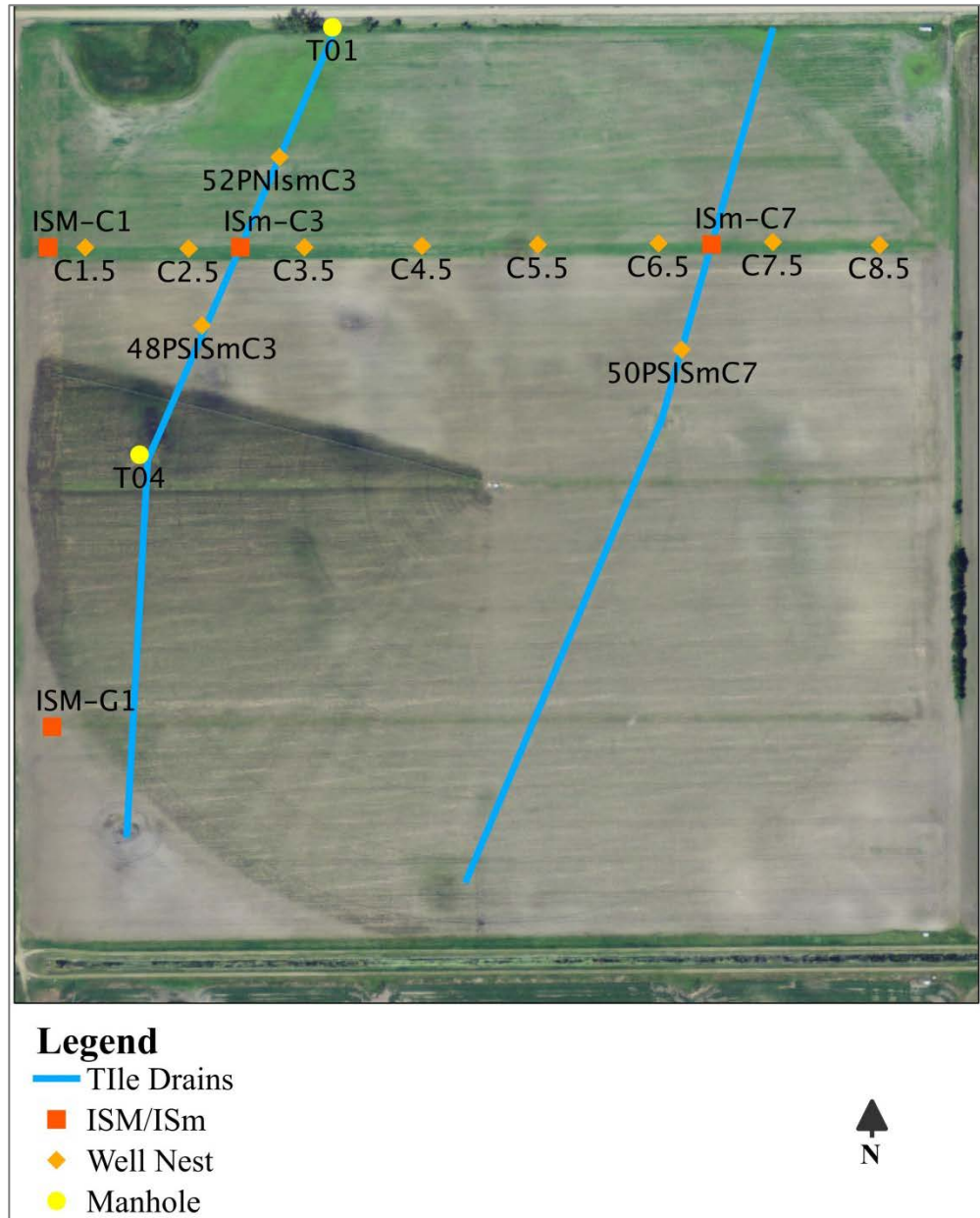


Figure 4. Overview of BMP test site showing sediment sample locations, ISM/ISm locations, and tile drain transects.

These deposits form the majority of the present land surface in the region (Armstrong 1980). Oakes sits near the stratified sand and gravel deposits similar to a deltaic complex. These delta deposits are composed of quartz, shale, lignite, Canadian shield silicate, and carbonate sediments (Bluemle 1979a). Considering the proximity of the Oakes aquifer, the black noncalcareous shales within the delta deposits are likely derived from the Niobrara shale.

Table 1

Simplified Stratigraphic Column of Dickey County, Showing Formations of Interest (adapted from Bluemle 1979a)

AGE	UNIT NAME	DESCRIPTION	THICKNESS (m)
Quaternary	Oahe (Holocene)	Sand, silt, and clay	?
	Coleharbor (Pleistocene)	Till, sand, gravel, silt, and clay	0 – 183
Tertiary			Absent
Cretaceous	Pierre Formation	Shale	366 – 549
	Niobrara Formation	Calcareous shale	

MATERIALS AND METHODS

The overall objective of this research is to quantify, locate, and understand the occurrence of denitrification within an artificially drained agricultural site. It was determined that three possible settings existed within the OITA that may be capable of denitrification: the aquifer sediments, the tile-drain gravel pack, and within the tile drain itself. In order to determine and compare the denitrification potential of these three sources, a two-part study was created. Analysis of aquifer sediments for electron donors, and the measurement of denitrification rates within the sediments and tile drain gravel pack comprise the first part of the study. For the second part of the study, a pair of tracer tests were conducted within a transect of drain tile.

Aquifer Denitrification Research

Subsurface sediment samples were collected in September of 2008 by coring the aquifer sediments at the study site. Eighteen potential sample locations were identified based on previous well logs. Hydraulic soil sampling equipment from the USBR was used to collect the samples. Several samples were collected from each site at varying intervals. Additional samples were collected from the tile drain gravel pack during June and July of 2009. A total of 15 sites yielded 49 samples, the locations of which are marked on Figure 4. Samples were collected in acrylic core sleeves (ID = 2.54 cm, OD = 2.82 cm), labeled, and capped at both ends before being placed in coolers and transported to the University of North Dakota. The samples were later placed in glass jars, labeled, and frozen until needed for analysis.

The samples were analyzed for texture, inorganic carbon (IC) and organic carbon (OC) content, inorganic sulfide (IS) and organic sulfide (OS) contents, ferrous iron

[Fe(II)] content, manganese (Mn) contents, and Munsell color. Only the sediments smaller than gravel (<2.0mm) were analyzed for electron donor contents and IC. Prior to any chemical analysis, each sample was first oven dried overnight at 103°C and ground into a fine powder.

OC was determined by a high temperature combustion method (Churcher and Dickout, 1986). IS was determined by chromium reduction modified slightly by using larger amounts of reagents (Canfield et al. 1986). Fe(II) and Mn were measured through wet chemical extraction (Klapperich 2008) by adapting methods used by Kennedy et al. (1999). The results of total Fe(II) combined the Fe(II) recovered by the wet chemical extraction method and the Fe(II) corresponding to IS, which is assumed to be primarily from pyrite (FeS₂). From the sediment samples, 14 were randomly selected for analysis of OS in a Leco SC-432 DR Sulfur Analyzer. All chemical analyses were completed at UND's Environmental Analytical Research Laboratory (EARL). Duplicate analyses were performed as quality control for the entire OC analyses, and less frequently for other analytical techniques. Appendix A includes detailed methodologies for all analyses.

Statistical analysis was carried out on the electron donor data from the 49 aquifer sediment sample locations. The normality of the individual populations was tested prior to the comparison of electron donor distribution. This was accomplished via the Shapiro and Wilk "W-test" (Gilbert 1987). Each donor was tested for both the lognormal transformed and non-transformed populations. Based on the results from the "W-test" (Appendix B) the non-parametric Spearman Rho test (Conover 1971), which does not assume an underlying distribution, was employed for statistical analysis.

Correlations between the different donors and different sediment facies were tested. The data for the tile drain gravel pack samples were not included in the sediment correlation, as no textural analysis was performed on those samples. The one-tailed version of the Spearman Rho test using critical values corresponding to $\alpha = 0.10$, $\alpha = 0.05$, and $\alpha = 0.01$ was used to determine if positive or negative correlations existed.

In-situ denitrification rates for the aquifer sediments at the OITA were measured using a pair of stainless steel chambers driven into the aquifer sediments, referred to as “in-situ mesocosms” (ISMs). The ISM developed by Schlag (1999) is a larger version, with an aquifer volume of 186 L, of the in-situ microcosms (ISm) used for Gillham et al. (1990) and Bates and Spalding (1998). The ISM, a stainless steel cylindrical chamber measuring 0.39 m in diameter by 1.5 m long, permits sizeable water quality samples (~1L) to be obtained regularly over long periods (>2 years). Since their first use in the Elk Valley Aquifer in northeastern North Dakota, ISMs have successfully monitored the chemical evolution of groundwater at several sites (Korom et al. 2005, Korom et al. 2012).

Suitable ISM locations were determined based on cross sectional maps of the aquifer sediments provided by the USBR. Locations were selected with the goal of measuring the denitrification rates in distinctly different aquifer sediment textures. In-situ denitrification rates were measured using stainless steel chambers at four sites. Two sites employed ISMs, ISM-C1 and ISM-G1 (Figure 4), which enclosed coarse aquifer materials and fine-grained sands, respectively. For the remaining sites, a much smaller chamber was used, an in-situ microcosm (ISm) with a sediment volume of 3.2 L. The

smaller chamber size of the ISm allowed for a water sample from within the gravel pack surrounding the tile drains.

ISM-G1 was installed 4.5-6 meters below the land surface, in fine-grained aquifer sediments near the G1 well nest (Figure 4). ISM-C1 was installed 4-5.6 meters below the land surface, in coarse-grained aquifer sediments near the C1 well nest (Figure 4). Two tracer tests were performed in each ISM to determine in situ denitrification rates. The first gravel pack ISm, ISm-C3, was installed 1.5-2 meters below the land surface, within the tile drain gravel pack next to well nest C3 (Figure 4). The ISm was later reinstalled at the same depth in the gravel pack near well nest C7 (Figure 4). Gravel for the envelope around the tile drains was imported from off-site, denitrification occurring within the envelopes would likely be from the development of manganese bacteria growth within the gravel pack pore spaces.

For the sampling of the ISMs and ISms, Groundwater was pumped from the site into a reservoir, amended with NO_3^- and Br^- , and then siphoned back into sampling devices. The dilution of amended water with native groundwater was measured with Br^- tracer. Any loss of NO_3^- beyond what is explained by the dilution of Br^- was attributed to denitrification. Korom et al. (2005) described in detail ISM installation, amendment, and sampling methodology.

Tile Drain Denitrification Research

On the 3rd and 4th of June 2008, two tracer tests were performed within a transect of drain-tile at the Oakes BMP site. The tests were conducted for the purpose of investigating the possibility of NO_3^- , PO_4^{3-} and NH_4^+ removal and/or uptake by drain tile

biomass. The tracer tests were conducted with the 20-cm (8-inch) diameter tile-drain between manhole T04 and manhole T01 (Figure 4).

The first tracer test, performed on June 3, 2008, involved the injection of NaCl into the drain at manhole T04. The purpose of this test was to establish a sampling schedule for the second tracer test based on the comparison of electrical conductivity (EC) versus time at the downstream manhole T01 (Table 16).

A total volume of 15 L of water was bailed from manhole T04 and transferred into a reservoir. The water in the reservoir was amended with 737 g of food grade NaCl, thoroughly mixed, and then injected directly into the drainage pipe at manhole T04 over two minutes. The EC was recorded within the drainage pipe at manhole T01 for approximately three hours.

The data from the first tracer test showed that the peak EC occurred approximately 100 minutes following the injection, with the beginning pulse arriving in 86 minutes and returning to near-background levels in 200 minutes. Based on this information, monitoring of the second tracer test would begin one hour subsequent to the injection and continued at regular intervals for nearly four hours following the injection.

The second tracer test was performed on June 4, 2008. A total volume of 10 L of water was bailed from manhole T04 and transferred into a reservoir. The water in the reservoir was amended with reagents listed on Table 2. The amended water was injected directly into the drainage pipe at manhole T04 over the course of one minute.

Water samples were collected using an improvised sampling device within the drainpipe at Manhole T01. Following collection, the samples were passed through 0.45 μm disposable filters, then preserved and stored for analysis. Samples to be analyzed for

NO_3^- -N and Br^- were filtered directly into 60 mL plastic bottles. Samples to be analyzed for total phosphorus (TP) and NH_4^+ -N were filtered directly into 250 mL plastic bottles containing 1 mL of concentrated H_2SO_4 for every 50 mL of sample.

Table 2

Reagents Added for 2nd Tile Drain Tracer Test

Reagent	Constituent Monitored	Constituent Amount Added (g)
NaNO_3	NO_3^- -N	39.00
NaBr	Br^-	32.50
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	Total P (TP)	8.03
NH_4Cl	NH_4^+ -N	7.80
Volume:	10 L	
Rate of Injection:	10 L/min	
Duration of Test:	229 min	

Analyses were performed at the University of North Dakota's EARL. Br^- and NO_3^- -N were analyzed with the use of a Dionex DX-120 Ion Chromatograph. TP was analyzed using HACH kit, method #8190. NH_4^+ -N was analyzed as NH_3 using an Accumet ion selective electrode. However, at the pH levels of the water in the tile drain, ammonium is the dominant species. To return the pH of acidified samples to neutral, NaOH was added as required during analysis of TP.

RESULTS AND DISCUSSION

Aquifer Sediments

The textural analysis was modified based on the classification of grain sizes adopted from USGS (2003). All 49 samples were analyzed for gravel, sand (coarse, medium, and fine), silt, and clay contents. Figure 5 illustrates the weight percent of electron donors for each sediment texture classification including the gravel pack for comparison. Detailed results of the sediment texture analysis are reported in Appendix B.

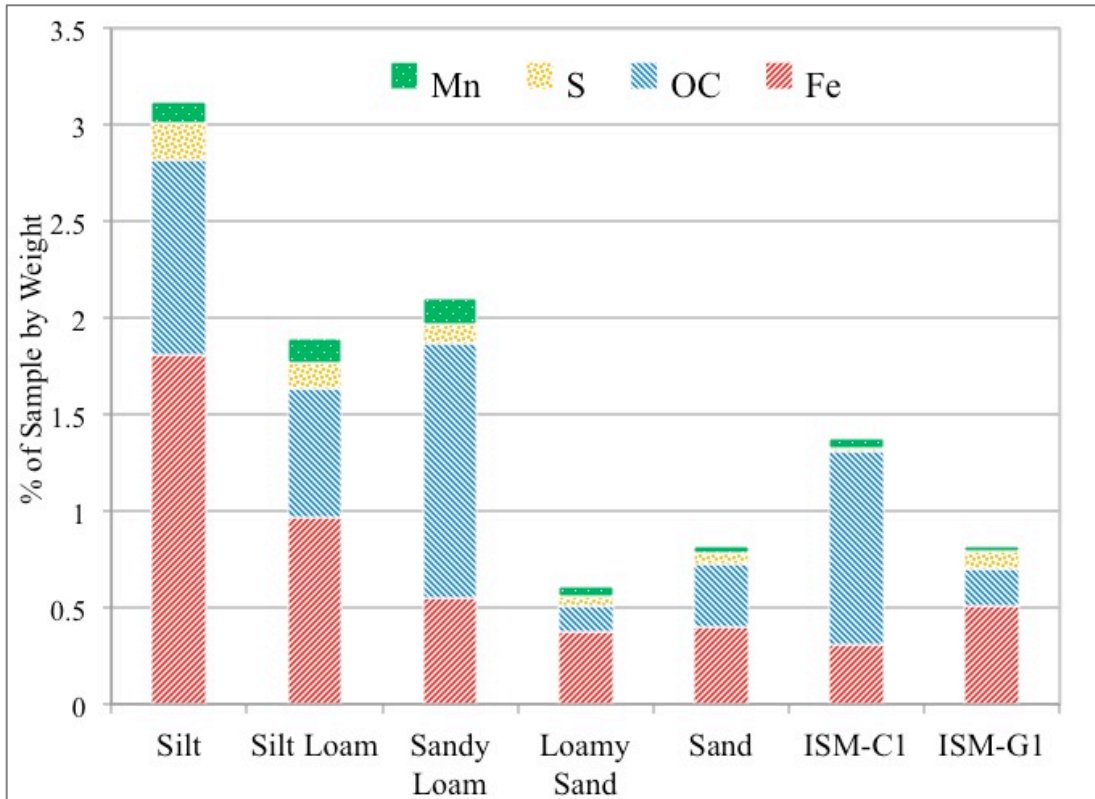


Figure 5. Weight percent of electron donors.

Table 3

Results of Each e⁻ donor Test. All Results are Reported by Weight %. Results for the Organic Donors Represent Values Adjusted for Pre-treatment (PT) Weights

Sample ID	Textural Classification	%S ⁻	OC (PT Eq) (%)	Mn (%)	Fe(II) (%)	Avg Pyrite Fe (%)	Total Fe(II) (%)
ISM-C1 A	Sandy Loam	0.007	0.087	0.299	0.090	0.006	0.096
ISM-C1 B	Loamy Sand	0.011	0.067	0.089	0.030	0.010	0.040
ISM-C1 C	Sand	0.024	0.104	0.012	0.327	0.021	0.348
ISM-C1 D	Sand	0.004	0.073	0.035	0.153	0.004	0.157
ISM-C1 E	Sand	0.009	1.664	0.098	0.302	0.008	0.310
ISM-C1 F	Sand	0.020	1.186	0.019	0.267	0.018	0.285
ISM-C1 G	Sand	0.032	0.150	0.021	0.300	0.029	0.329
ISM-C1 H	Silt Loam	0.014	0.557	0.112	1.591	0.012	1.603
C1.5 A	Loamy Sand	0.000	0.404	0.068	0.324	0.000	0.324
C1.5 B	Loamy Sand	0.102	0.312	0.041	0.455	0.091	0.546
C1.5 C	Sandy Loam	0.169	0.753	0.080	0.566	0.151	0.717
C1.5 D	Silt Loam	0.232	0.739	0.206	0.118	0.207	0.325
C2.5 A	Loamy Sand	0.003	0.067	0.047	0.118	0.003	0.121
C2.5 B	Loamy Sand	0.071	0.136	0.040	0.208	0.063	0.271
C2.5 C	Sandy Loam	0.103	4.410	0.065	0.445	0.092	0.537
C2.5 D	Sandy Loam	0.083	2.101	0.241	0.814	0.074	0.888
C2.5 E	Silt Loam	0.044	0.729	0.073	0.535	0.039	0.574
C3.5 A	Sand	0.013	0.180	0.002	0.422	0.012	0.434
C3.5 B	Sandy Loam	0.157	0.172	0.035	0.296	0.140	0.436
C3.5 C	Silt Loam	0.132	0.444	0.071	0.542	0.118	0.660
C3.5 D	Silt Loam	0.224	0.510	0.160	0.624	0.200	0.824
C4.5 A	Loamy Sand	0.003	0.020	0.115	0.030	0.003	0.033
C4.5 B	Loamy Sand	0.057	0.036	0.047	0.336	0.051	0.387
C4.5 C	Loamy Sand	0.099	0.096	0.118	0.533	0.088	0.621
C4.5 D	Sand	0.091	0.035	0.055	0.472	0.081	0.553
C5.5 A	Sand	0.015	0.023	0.100	0.177	0.013	0.190
C5.5 B	Loamy Sand	0.007	0.084	0.027	0.475	0.006	0.481
C5.5 C	Sandy Loam	0.076	0.357	0.034	0.561	0.068	0.629
C5.5 D	Sand	0.084	0.389	0.028	0.533	0.075	0.608
C5.5 E	Sand	0.119	0.727	0.004	0.534	0.106	0.640
C6.5 A	Sand	0.000	0.036	0.006	0.151	0.000	0.151
C6.5 B	Loamy Sand	0.107	0.091	0.003	0.485	0.096	0.581
C6.5 C	Loamy Sand	0.127	0.056	0.005	0.480	0.113	0.593
C6.5 D	Silt	0.187	1.012	0.110	1.640	0.167	1.807
C7.5 A	Loamy Sand	0.002	0.068	0.018	0.120	0.002	0.122
C7.5 B	Loamy Sand	0.021	0.361	0.052	0.398	0.019	0.417
C7.5 C	Sand	0.136	0.108	0.064	0.417	0.121	0.538
C7.5 D	Sand	0.149	0.169	0.051	0.508	0.133	0.641

Table 3 (continued)

Sample ID	Textural Classification	%S	OC (PT Eq) (%)	Mn (%)	Fe(II) (%)	Avg Pyrite Fe (%)	Total Fe(II) (%)
C8.5 A	Sand	0.001	0.133	0.024	0.177	0.001	0.178
C8.5 B	Sand	0.082	0.065	0.017	0.421	0.073	0.494
C8.5 C	Loamy Sand	0.126	0.106	0.053	0.501	0.112	0.613
ISM-G1 A	Sand	0.093	0.222	0.003	0.449	0.083	0.532
ISM-G1 B	Loamy Sand	0.000	0.166	0.045	0.484	0.000	0.484
ISM-C3GP	Gravel Pack	0.012	0.888	3.233	0.029	0.011	0.040
ISM-C3BGP	Gravel Pack	0.000	0.413	0.415	0.059	0.000	0.059
48PSISmC3	Gravel Pack	0.023	1.193	0.221	0.138	0.021	0.159
52PNISmC3	Gravel Pack	0.005	1.485	0.220	0.179	0.004	0.183
ISM-C7GP	Gravel Pack	0.002	0.723	0.221	0.016	0.002	0.018
50PSISmC7	Gravel Pack	0.001	0.370	0.083	0.045	0.001	0.046

Organic Carbon

From 49 individual samples, 98 OC analyses were performed (Table 3). The highest OC concentrations were measured in silt with 1.01% by weight, and the lowest OC values were 0.02% by weight for loamy sand and sand. OC accounted for approximately 42% of the e^- donors available in the sampled material from the OITA. A few sandy-loam and sand samples contained anomalous percentages of OC. These were assumed to be buried paleosols, and remained included in the analysis. It is also a significant e^- donor within each sediment facies. Duplicates show fair reproducibility well below a percent difference of 25%. The complete OC results and calculations are reported in Appendix B.

Silt loam samples contained the highest amounts of organic carbon, ranging from 0.38% to 0.84% by weight. OC accounted for about 31% of the e^- donors available within the silt loam sediment facie samples. Loamy sand analyses showed an average OC concentration of 0.17% by weight, contributing to 27% of the e^- donors available within

that particular facies. The sand facies also showed significant OC contents, at 0.33% OC by weight, contributing to 40% for e⁻ donors available within the facies.

Inorganic/ Organic Sulfide

Overall, IS accounts for about 5% of the total electron donors present in the sediment samples. Values ranged from 0.003% in sand to 0.232% in silt loam. With pyrite noted as the most commonly occurring sulfide mineral, it was assumed that all of the IS measured in this test was in the form of pyrite (Schoonen 2004). IS was measured below the detection limit in eight of the samples, all of them texturally classified as sand or loamy sand.

Inorganic sulfide within the silt loam samples averaged about 0.14% by weight and account for about 7% of the e⁻ donors present within the silt loam (Figure 5). Within the loamy sand samples, IS averaged nearly 0.06% by weight and accounted for about 8.8% of the e⁻ donors present within the loamy sand samples. The sand samples also averaged 0.06% IS by weight accounting for nearly 10% of the e⁻ donors present within the sand samples. Pyrite recoveries for inorganic sulfur analysis were >95%. The complete results and calculations are shown in Appendix B.

Klapperich (2008) determined that a modified method of inorganic sulfide analysis could be used for organic sulfide (OS) analysis. Based on his methods, testing for IS was repeated on 14 samples. The entire set of 14 samples yielded OS results below detection. The duplicate analyses yielded organic sulfide results below detection. Therefore, OS as an electron donor was not considered further in the present study. Klapperich (2008) noted that OS yielded the lowest values of e⁻ donors tested in his electron donor research within bedrock formations.

Ferrous Iron

Ferrous iron results are the product of two tests: the Fe(II) associated with pyrite as is measured by the Canfield method, and measured as non-pyritic Fe(II) by the modified Kennedy technique using wet chemical extraction. Ferrous iron follows the pattern of the other e^- donors within the facies, being low in sand and higher in silt loam. Ferrous iron is also a dominant e^- donor present in all the facies, averaging near 46% Fe(II) by weight of all samples included in this study. Of the 49 analyses, the highest value came from a silt sample with an average value of 1.81%. The lowest Fe(II) values, 0.03% and 0.02% were from loamy sand and gravel samples, respectively. The complete Fe(II) results and calculations are reported in Appendix B.

Ferrous iron was significantly more abundant in the silt loam facies than the other e^- donors. The overall Fe(II) average for the silt loam facies was 0.97% by weight. The loamy sand and sand facies showed nearly the same overall Fe(II) average with 0.38% and 0.40% concentrations by weight, respectively.

Manganese

A method similar to that used for Fe(II) was applied to determine manganese concentrations in the sediment facies. Rhodochrosite ($MnCO_3$) recovery produced an average manganese recovery of 85%. The complete manganese results and calculations are reported in Appendix B.

Overall, manganese accounted for approximately 6% of the total e^- donors present in all the samples. Values ranged from 0.002% to 0.299% within a sand and sandy loam, respectively. The tile drain gravel pack contained significant amounts of manganese, averaging 0.74% by weight, likely due to the manganese biofilm accumulation associated

with the tile drains. With the exception of the tile-drain gravel pack, the values for manganese also appear to follow the pattern of increasing e^- donor concentration with decreasing sediment size.

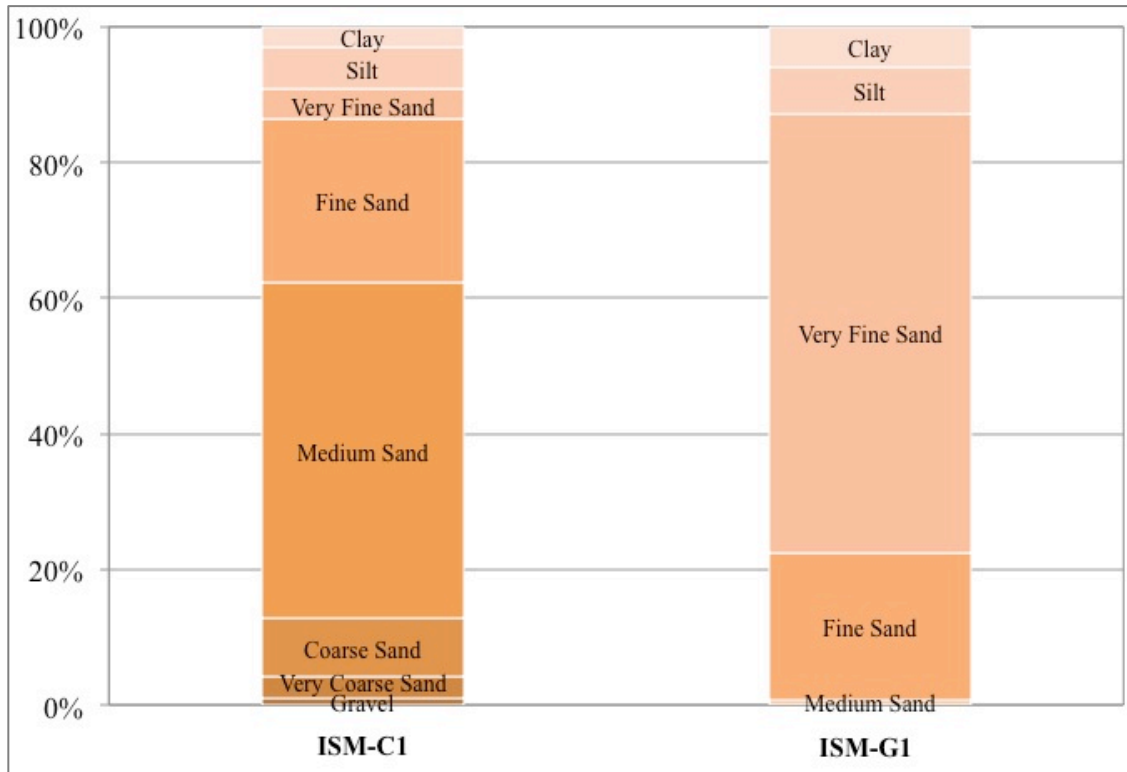


Figure 6. Chart showing textural analysis of ISM-C1 and ISM-G1.

Comparison of electron donors by weight percent with another site of denitrification study within eastern North Dakota shows the OITA having higher OC percentages within the three finer-grained sediment textures. The sandy loam, silt loam, and silt present at the OITA have an average range of 0.665% to 1.319% OC by weight, whereas sediments from the Elk Valley Aquifer in eastern North Dakota had a maximum OC content of 0.43% (Korom et al. 2005). Both of these sites contain relatively high OC when compared with the Karlsruhe site, having 0.017% OC (Korom et al. 2012).

Statistical Correlations

The results from the Shapiro and Wilk “W-test” (Appendix B) showed that the electron donors could not be considered to be normally distributed, regardless of log transformation or not. The results of the Spearman Rho test, presented in Table 4, indicated that a positive correlation at a significance level of $\alpha = 0.01$ was found between inorganic sulfide and ferrous iron, as well as organic carbon and manganese. At a significance level of $\alpha = 0.10$, positive correlations exist between inorganic sulfide and organic carbon, organic carbon and ferrous iron. Organic carbon and manganese were positively correlated with silt at $\alpha = 0.01$, whereas ferrous iron was correlated with silt at $\alpha = 0.05$. Once again, if the significance level is expanded to $\alpha = 0.10$, inorganic sulfide is also positively correlated with silt. All of the electron donors showed a negative correlation with sand textures. Manganese was positively correlated to both silt and clay. Organic carbon was positively correlated with both gravel and silt. The sediment textures failed to show a positive correlation, with gravel and sand negatively correlated as well as sand and silt.

Maharjan (2009) found similar correlations between electron donors and sediment texture at a study site within eastern Iowa. The eastern Iowa site showed a higher correlation of electron donors with clay than silt, whereas the OITA electron donors were correlated with silt. This difference is likely due to the sandy nature of the aquifer at the OITA and its lack of clay textures. Also similar to the eastern Iowa site, the electron donors IS and Fe at the OITA are positively correlated to one another at $\alpha = 0.01$. If we increase the significance level to $\alpha = 0.10$; IC, Fe, and OC are all positively correlated to one another. Manganese as an electron donor was not studied at the eastern Iowa site.

Table 4

Results of Spearman's Rho Test

Spearman Rho for positive correlation								
Ho: There is not a positive correlation of the two donors' average values								
	IS	OC	Fe	Mn	Gravel	Sand	Silt	Clay
IS	X	0.187*	0.748	-0.071	0.178	-0.298	0.206*	0.222*
OC		X	0.234*	0.398	0.405	-0.463	0.424	0.104
Fe			X	-0.160	0.108	-0.390	0.281	0.212*
Mn				X	0.199*	-0.463	0.456	0.295
Gravel					X	-0.269	0.064	0.097
Sand						X	-0.912	-0.108
Silt							X	0.011
Clay								X
	Positively correlated at 0.05 α				Negatively correlated at 0.05 α			
	Positively correlated at 0.01 α				Negatively correlated at 0.01 α			
*. Indicates correlation significant at 0.10 α								

ISM/ISm Results

The first ISM tracer test (TT1) lasted 112 days, starting August 13, 2008 and ending December 2, 2008, the first ISm tracer test was initiated at the same time. The second ISM tracer test (TT2) lasted 129 days, starting June 2, 2009 and ending October 10, 2009. The second ISm tracer test began on day 50, or July 3, 2009, of the second ISM tracer test. During both periods the general aqueous chemistry species were monitored, which included products and reactants associated with denitrification

The relative change of the dilution-tracing Br^- is of importance to our study of denitrification in the aquifer sediments. Tracking Br^- in the ISM/ISm's permits the

evaluation for NO_3^- -N removal via dilution or through denitrification. The normalized concentrations of these anions are displayed in Figure 6 for the tracer tests at the four Oakes sites. This shows the concentration trends and relative changes compared to dilution.

During the first tracer test, the NO_3^- -N concentration in the ISM-G1 began at 76.2 mg/L and was reduced to 6.63 mg/L throughout the 112 day test. The Br^- concentration in ISM-G1 began at 44.4 mg/L and remained at 95.1% of the amended concentration for the course of the experiment. When corrected for dilution, the denitrification rate in ISM-G1 was 0.59 mg/L/day for TT1. In contrast, during the first tracer test for ISM-C1 the Br^- began at 40.7 mg/L and diluted to 18.2 mg/L, retaining 44.7% of its initial concentration. When TT1 for ISM-C1 is corrected for dilution, the denitrification rate becomes 0.06 mg/L/day. It appears as though ISM-C3 also exhibited a similar dilution as shown by Br^- concentrations, with 51.0% of the amended concentration remaining. When corrected for dilution, the denitrification rate within ISM-C3 was 0.11 mg/L/day. Figure 7 illustrates the dilution corrected Br^- and NO_3^- -N zero order denitrification rates.

During the second tracer test (TT2), the NO_3^- -N concentration in the ISM-G1, experienced a less significant loss (Figure 7) beginning at 72.5 mg/L and dropping to 30.5 mg/L throughout the 129 day test. The Br^- concentration in ISM-G1 began at 43.4 mg/L and remained within 91.3% of the initial concentration. When corrected for dilution, TT2 for ISM-G1 indicates a denitrification rate of 0.28 mg/L/day. Once again, during the second tracer test for ISM-C1 the Br^- shows evidence of tracer test dilution, with Br^- concluding TT2 with 46.7% of the initial concentration.

The denitrification rate for TT2 within ISM-C1 is comparable to the first at 0.03 mg/L/day. During the course of TT2, ISm-C7 Br⁻ concentrations remained within 93.1% of their initial concentration. When corrected for dilution, ISm-C7 indicated a denitrification rate of 0.30 mg/L/day; however, fit of the data to zero-order denitrification is not as good as for the other tracer tests (Figure 8). The ISm-C7 tracer test began 48 days after the start of the second tests in ISM-G1 and ISM-C1.

Denitrification rates for the tracer tests conducted at the OITA are expressed as zero-order denitrification reactions. Zero-order reactions are generally the standard for the majority of published aquifer denitrification rates (Korom 1992, Green et al. 2008, Korom 2012). Compared to another eastern North Dakota ISM site, a site whose published zero-order denitrification rate was amongst the highest recorded in the literature, the ISM-G1 rate is 1.9 times faster at 0.59 mg/L/day (Korom et al. 2005, Green et al. 2008).

Comparison of the rate found within ISM-C1 to the same site shows ISM-C1 to be 4.9 times slower at 0.06 mg/L/day. The zero-order denitrification rate for ISM-C1 is comparable to those rates found within the Karlsruhe aquifer of north-central North Dakota. The zero-order denitrification rates found within the ISMs placed in the tile-drain gravel pack at the OITA, an average of 0.20 mg/L/day, were similar to the first tracer test in the Elk Valley Aquifer (Korom et al. 2005).

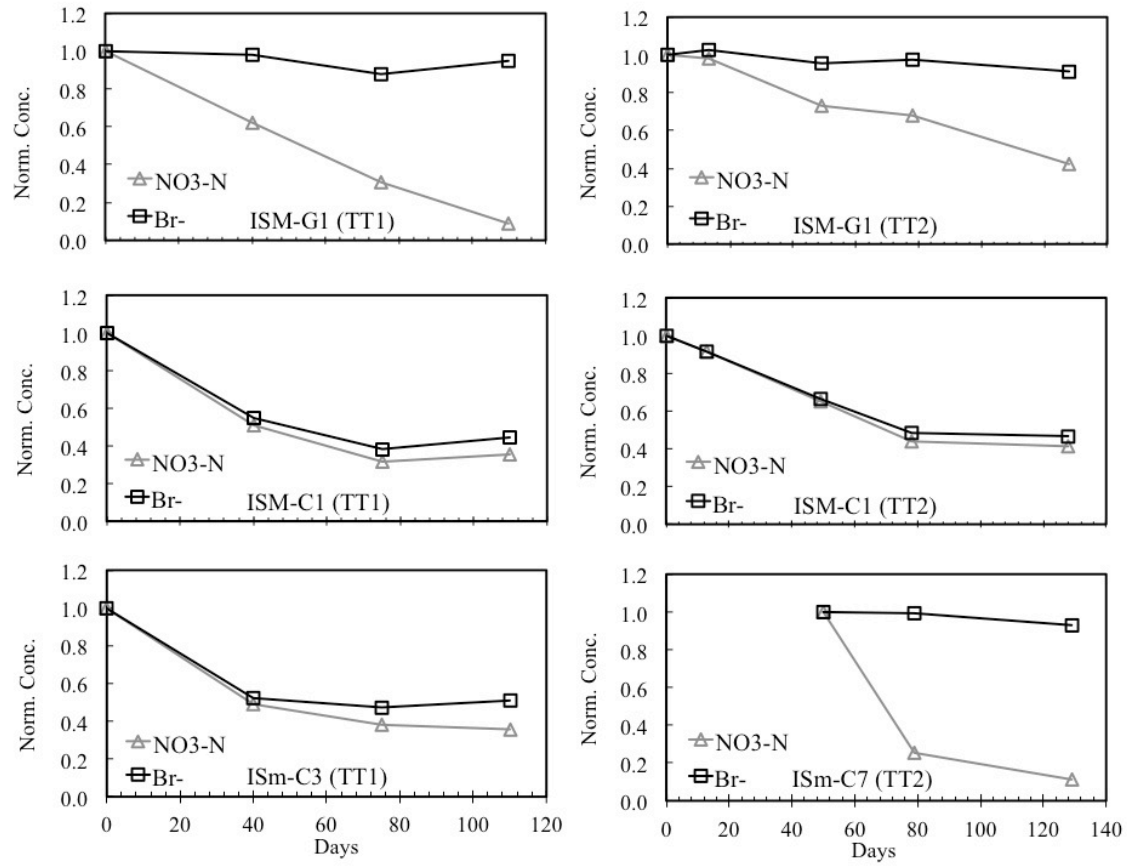


Figure 7. Important anions from ISM/ISm tracer tests.

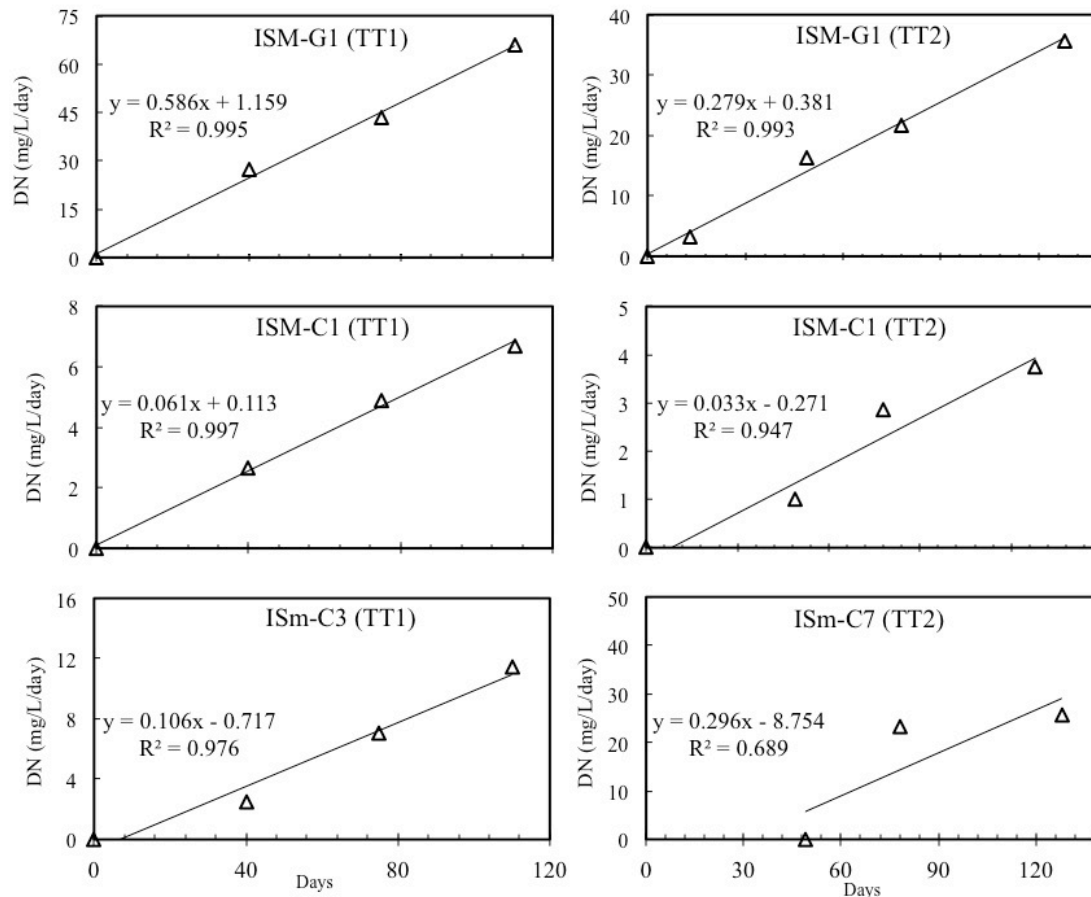


Figure 8. Zero-order denitrification rates observed from ISM/ISm tracer tests.

Drain Tile Tracer Test

For the drain tile test conducted on June 4, 2008, the concentrations for each analyte were plotted versus time (Figure 8). The area under each curve was calculated and background concentrations were removed. Anions, NO_3^- -N and Br^- , were analyzed twice with two injections per analysis. The concentration of each analyte was then plotted with the concentration of bromide over time and the ratio of the two areas calculated (Table 4). The ratios of bromide to each analyte for the amended water and the ratios obtained from the tracer analysis are presented in Figure 9.

The amended water for the tracer test had a Br^- to NH_4^+ -N ratio of 1: 0.24, and the results from the analysis yielded a ratio of 1: 0.30. This increase indicates a production of

NH_4^+ . Being the only cation measured during the tracer test, the increased Na^+ in the amended water was likely exchanged for NH_4^+ on cation exchange sites on minerals and organic matter in the biomass in the tile drain. Without the analysis of all major cations, this hypothesis cannot be further evaluated. The amended water for the tracer test had a Br^- to TP ratio of 1: 0.24, and the results from the tracer analysis yielded a ratio of 1: 0.23. Based on the sensitivity of the TP test, it is unlikely that the small decrease in TP was significant. The amended water for the tracer test had a Br^- to NO_3^- -N ratio of 1: 1.20, and the results from the tracer test yielded a ratio of 1: 1.215 – 1.254. The increase of NO_3^- -N shown in the analysis is not assumed to be production of NO_3^- -N, rather was a result of the sampling methodology. In conclusion, no loss of NO_3^- -N was evident during the tracer test in the tile drain.

The temporal analysis of water quality patterns can be affected by advection, chemical diffusion/dispersion, and chemical reactions. At the scale of the tile drain tracer test, advection response time would be short, with a horizontal scale of 396 meters and a horizontal flow velocity of 0.07 m/sec, yielding a response time of 94 minutes. According to Sawatsky (2009), tracer tests performed near wells at the OITA provided a hydraulic conductivity ranging from 0.44 – 0.95 m/hour. The advection response time from the injection wells to discharge within the subsurface drain would be between 3.2 – 6.9 hours.

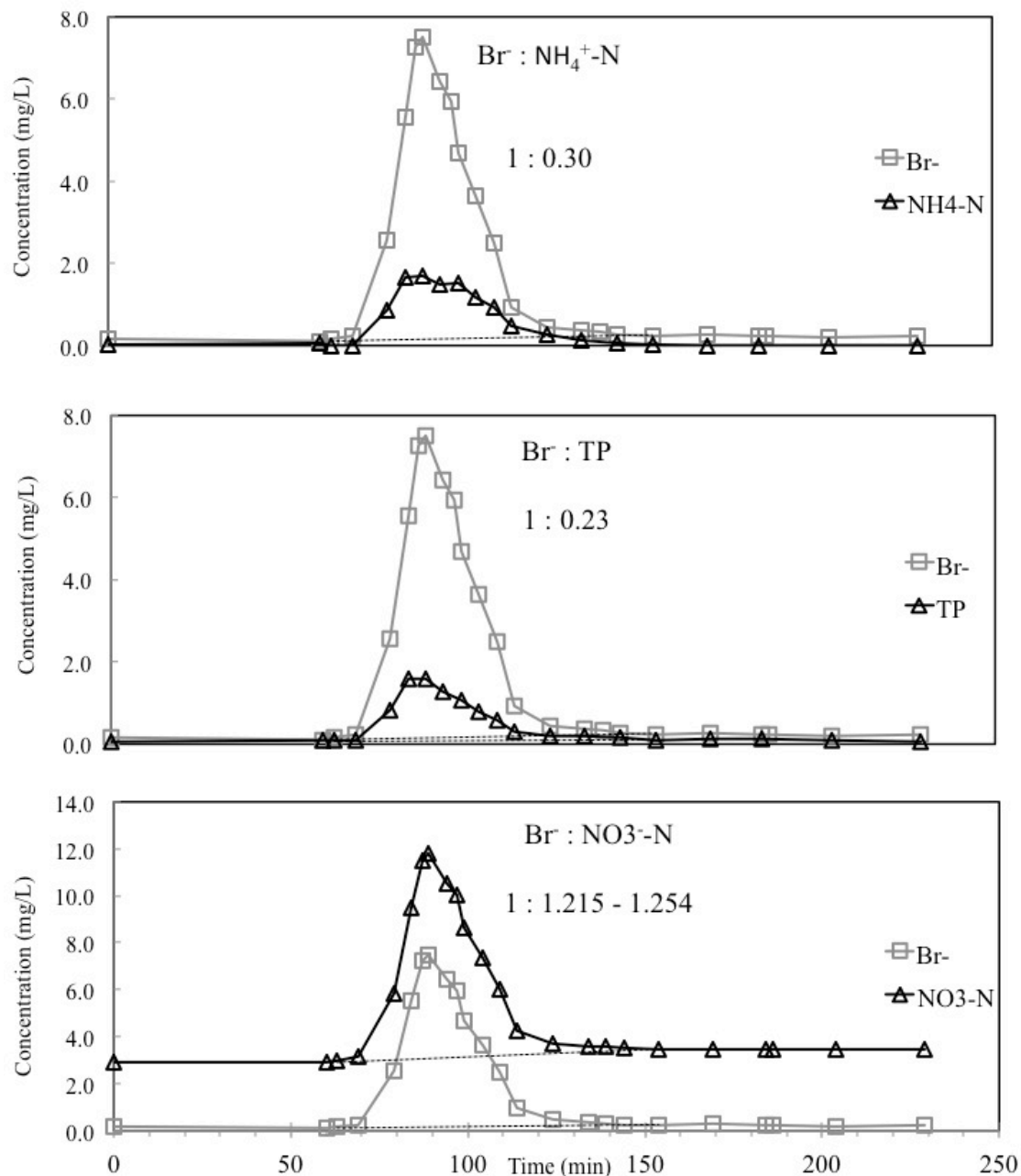


Figure 9. Comparison of analytes from tile drain tracer test.

Based on the data provided from the sediment analyses and the ISm tests in the gravel pack, we know that denitrification occurs within the imported gravel pack. Fetter (2001) lists between 0.36 to 36 m/hour as the range for hydraulic conductivities of well-sorted gravel. Using this range, the travel time within the gravel pack would be between

18 minutes and 11 seconds until groundwater is discharged into the tile drains. Using the maximum zero-order denitrification rate from the ISm gravel pack tests of 0.296 mg/L/day, the gravel pack would reduce the nitrate concentration of groundwater entering the tile-drains by approximately 4×10^{-3} mg/L, which is too low to detect with the methodologies used herein.

CONCLUSIONS

A study of denitrification potential within multiple mediums was conducted in the Oakes Irrigation Test Area of southeastern North Dakota, and showed differences in their possible potential. Aquifer materials containing fine-grained materials had the highest amount of electron donors, and in-situ tracer tests performed in fine-grained aquifer materials exhibited the highest rate of NO_3^- attenuation. Both the electron donor analysis and the ISM tracer tests performed in aquifer sediments showed that finer-grained materials remove NO_3^- more quickly. The tile-drain tracer test indicated that the manganese biofilm present at this site have no significant effect on NO_3^- removal.

Organic carbon, inorganic sulfide, and ferrous iron were the substantial electron donors at the site, with no measureable quantity of organic sulfide present. Manganese was present the sedimentary facies at the site, however it was found to be concentrated within the tile drains and tile drain gravel pack. Organic carbon concentrations in silt-loam ranged from 0.44% to 0.74%, 0.09 % to 4.41% in sandy-loam, 0.06% to 0.40% in loamy-sand, and 0.03 to 1.664% in sand. The percentage of pyrite as inorganic sulfide (IS) was between 0.01% to 0.23% in combined silt-loam and silt. IS concentrations ranged between 0.01% to 0.17% in sandy-loam, 0.003% to 0.13% in loamy-sand, and

0.001% to 0.15% in sand. Ferrous iron concentrations ranged between 0.32% to 1.81% in silt and silt-loam combined, 0.10% to 0.89% in sandy-loam, 0.03% to 0.62% in loamy sand, and 0.15% to 0.64% in sand facies. Manganese was found in higher concentrations within the three finer grained facies with concentrations ranging between 0.03% to 0.30%, whereas loamy-sand ranged between 0.003% to 0.12%, and sand between 0.003% and 0.10%. ISM-G1, which recorded the fastest rates of denitrification had a larger percentage of the e^- donor IS than ISM-C1. ISM-G1 also had larger percentages of e^- donors IS and Fe^{2+} .

Statistically significant correlations exist for various e^- donors, showing a general increase in donor content as sediment size decreases. These results are similar to those of Maharjan's (2009) research involving electron donors and sediment size. The donors are also generally correlated with each other, indicating that if increased concentrations of one donor are found, it is likely that high concentrations of the other important donors will be found.

Results from the ISM/ISm tracer tests help to confirm the correlation between sediment size and denitrification potential. The denitrification rates for the two tracers tests performed in ISM-G1 were 0.59 and 0.28 mg/L/day. ISM-G1 was installed in a fine-grained loamy sand facies (Figure 8). The denitrification rates from the two tests performed in ISM-C1 were 0.061 mg/L/day and 0.033 mg/L/day. ISM-C1 was installed in a sand facies composed primarily of coarse and medium grained sands. The rates found in ISM-G1 were the highest rates measured amongst 25 denitrification tests conducted throughout the Midwest (Korom, personal communication), with ISM-C1 rates comparatively similar to previous tests. The elevated denitrification rates present

within ISM-G1 suggest that any denitrification occurring at the site is occurring rapidly from within the fine-grained sediment facies. The textural analysis from ISM-G1 indicates that the ISM was installed in nearly 65% very fine-grained sand, with less than 1% of the ISM-C1 sediment textures classified as larger than fine-grained sand. ISM-C1 was installed in primarily medium-grained sand (Figure 6). The sediments contained within ISM-C1 contain more electron donors by weight than the very fine-grained sands of ISM-G1 (Figure 5). ISM-C3 was installed in the gravel envelope, next to the tile drain near well nest C3. The denitrification rate measured in ISM-C3 measured was 0.11 mg/L/day. The tracer test within ISM-C3 showed evidence of heavy dilution by native groundwater. The ISM was later reinstalled in the tile drain gravel envelope next to well nest C7, resulting in less dilution from native groundwater. ISM-C7 recorded a zero-order denitrification rate of 0.30 mg/L/day, with a less reliable goodness of fit than that of ISM-C3. The increased size of the gravel in the gravel pack reduces the surface area, thus reducing the reactivity of the drains. The substantial denitrification in ISM-C7 is likely to be the result of manganese bacterial influences.

Within the tile drains, also congested with manganese biofilm, the results from the tracer test show no significant uptake of nutrients. The tracer test does indicate a slight production of NH_4^+ , which was possibly exchanged with Na^+ during the amendment. It is suggested that future tile drain tracer tests provide analysis of all major cations, to further evaluate this hypothesis. Total phosphorus in the tile drains showed a slight decrease in concentration, which was considered insignificant or within analytical error. The amended water for the tracer test had a Br^- to NO_3^- -N ratio of 1: 1.20, with the tracer test

yielding a ratio of 1: 1.215–1.254. The increase of NO_3^- -N shown in the analysis is not assumed to be production of NO_3^- -N, rather inadequacies in the sampling methodology.

The results of the tile drain tracer tests, the ISM tracer tests, and the aquifer sediment analyses support the hypothesis that denitrification at the Oakes BMP site is occurring mainly within the aquifer sediments at the site and not from within the tile drains. It is concluded that the biomass within the drain tile did not react with or store NO_3^- -N. Based on analyses of material from the tile drain gravel pack and from the tile drain biofilm, the tile drains are likely to have the chemical potential to remove NO_3^- via natural attenuation; however, retention times are too low for any denitrification to noticeably decrease nitrate concentrations in the drain effluent. Reducing the hydraulic retention time of the tile drain (and thereby reducing its hydraulic efficiency) may be necessary for it to serve as a functional in-line denitrification bioreactor.

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