Technical Report No: ND09-01

**CORRELATION OF ELECTRON DONOR CONCENTRATIONS IN SEDIMENTS
WITH SEDIMENT PROPERTIES: NEW PROVIDENCE, IOWA**

by

**Brijesh Maharjan
Scott F. Korom
Department of Geology and Geological Engineering
University of North Dakota
Grand Forks, ND 58202**

July 2009

CORRELATION OF ELECTRON DONOR CONCENTRATIONS IN SEDIMENTS WITH SEDIMENT PROPERTIES: NEW PROVIDENCE, IOWA

By

Brijesh Maharjan[1] and Scott F. Korom[2]
Graduate Student[1] and Associate Professor[2]
Department of Geology and Geological Engineering
University of North Dakota
Grand Forks, ND 58202

July 2009

North Dakota Water Resources Research Institute
Director: G. Padmanabhan
North Dakota State University
Fargo, North Dakota 58108-6050

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGMENTS

ABSTRACT

The concentrations of electron donors in aquifer sediments are important in understanding the fate and transport of redox-sensitive constituents in ground water, such as nitrate. In this study, 50 sediment samples were collected from below the water table from 11 boreholes at the US Geological Survey Agricultural Chemicals Transport site near New Providence, Iowa. All samples were analyzed for gravel, sand (coarse, medium, and fine), silt, clay, inorganic carbon contents and for the following electron donors: organic carbon, ferrous iron, and inorganic sulfide. A subset of sediment samples was analyzed for organic sulfur, but all of the 14 samples were below detection; therefore this potential electron donor was not considered further. Nonparametric correlation analysis was done with the data for the other three electron donor concentrations, inorganic carbon concentrations, sediment grain sizes, and sediment depths. The major finding was that electron donor concentrations are positively

correlated to the smaller grain sizes and to each other. These findings suggest that most aquifer denitrification at this site takes place in zones having lower hydraulic conductivities.

INTRODUCTION

Nitrate is the most common groundwater contaminant and because of growing anthropogenic sources, nitrate pollution is increasing (Korom, 1992). In addition to animal and human health concerns, nitrate contributes to environmental problems like eutrophication and a range of associated effects, including damage to fisheries in coastal ecosystems (Davidson and Seitzinger, 2006). The hypoxia in the northern Gulf of Mexico, due to excessive nitrogen (N) and other nutrients loading in the Mississippi River, is the second largest human-caused hypoxia zone in the world's coastal waters (Turner et al., 2005), with a size exceeding 20,000 km^2 (Turner et al., 2008). Nitrogen export from the Mississippi River system has increased two- to seven-fold over the last century (Goolsby et al., 2000).

Our research site is near New Providence in north-central Iowa. The introduction of nutrients from chemical fertilizer, animal manure, wastewater and atmospheric deposition from this area contributes to the N load of the Mississippi River (Becher et al., 2000). This site is one of the Agricultural Contaminant Transport (ACT) study units of the National Water-Quality Assessment Program (NAWQA) of the US Geological Survey (USGS). The ACT Program is assessing the sources, transport and fate of chemicals applied to crops in agricultural basins across the nation. The basins represent a range of agricultural settings as well as a range of landscapes with different geology,

soils, topography, climate and hydrology (Capel et al., 2008). The following two ACT objectives, with respect to nitrate, are addressed by the research herein:

1. Assess transport and transformation of selected chemicals as affected by natural processes.

2. Develop tools and quantitative methods to characterize the transport and fate of chemicals within the watershed, extrapolate the findings to similar, unmonitored agricultural and environmental settings.

With respect to the first ACT objective listed above, the natural process most greatly affecting nitrate transport is denitrification, which is the microbially-mediated reduction of nitrate. Molecular N, N_2, is the terminal product of this oxidation-reduction (redox) reaction; its triple bond makes it relatively non-reactive (Korom, 1992). Once nitrate becomes a groundwater contaminant, there are three requirements for its denitrification: low oxygen concentrations, bacteria capable of mediating the reaction and electron donors for the bacteria to use in the redox reactions (Firestone, 1982). Korom (1992) concluded that the supply of electron donors is the critical factor for groundwater denitrification; without it, bacteria can reduce neither oxygen nor nitrate. Typically, the supply of electron donors associated with subsurface sediments is larger than the supply dissolved in groundwater (Kennedy et al., 1998; Hartog et al., 2005; Everett et al., 2006). Electron donors associated with denitrification include organic carbon (OC) (Korom, 1992; McMahon et al., 1999; Rivett et al., 2008), ferrous iron [Fe(II)] minerals (Postma, 1990; Ernstsen, 1996; Senn and Hemond, 2002) and sulfide, both as organic (OS) (Bohlke et al., 2002) and inorganic (IS) (mainly pyrite) (Korom et al., 2005; Schwientek et al., 2008; Majumder et al., 2008) species.

7

Therefore, with respect to the second ACT objective listed above, tools are required to help characterize electron donors in the sediments in the saturated zones of watersheds and related agricultural and environmental settings. So far, only a few papers have been published on this topic. Hartog et al. (2002) and Helvoort et al. (2007) noted that finer fractions of sediment are more reactive than coarser fractions. However, a tool capable of defining watersheds in terms of electron donors is necessary to assess the fate and transport of the chemicals within these watersheds. Regional differences should also be expected in characterizing aquifers due to differences in local mineralogy and sediment texture (Konen et al., 2003).

The facies concept can be a useful tool, which apparently has not been yet applied in characterizing the electron donors of aquifer sediments. However, Allen-King et al. (1998) used this method to characterize the sorption of organic compounds in sediments. One can make a facies-based approach to sediment textures and model heterogeneous deposits (Miall, 1985; Helvoort et al., 2007) in terms of the availability of electron donors. Certain relationships also exist between hydraulic conductivity and statistical parameters that describe the grain-size distribution (Alyamani and Sen, 1993). Therefore, I intend to do texture analysis of sediments and pursue the following objectives in this project:

1. Measure electron donor contents [OC, IS, OS and Fe(II)] in the sediments at the New Providence (NP) site.

2. Determine the statistical correlation of electron donors, inorganic carbon (IC) and sediment textures.

SITE GEOLOGY

The ACT Eastern Iowa Basins Study Unit includes the Wapsipinicon, the Cedar, the Iowa and the Skunk River Basins and encompasses about 50,500 km^2 (19,500 mi²) in eastern Iowa and southern Minnesota. The glaciated land surface has three distinct regions in the Eastern Iowa Basins Study Unit: the Des Moines Lobe, the Iowan Surface and the Southern Iowa Drift Plain. (Kalkhoff et al., 2000)

The South Fork Iowa River, which is part of the Iowa River watershed, is representative of corn and soybean row cropping in the Midwest (Kalkhoff et al., 2000). Alluvium and till are at the surface throughout the South Fork of the Iowa River watershed. Close to the U.S. Geological Survey gage site, South Fork Iowa River NE of New Providence, IA (USGS 05451210), surficial deposits are dominated by DeForest Formation alluvium and Noah Creek Formation valley train outwash deposits.

At the NP site (Figure 1), which is located southwest of the gage, elevations range from approximately 300 m in the upper part of the watershed to approximately 285 m, measured from North American Vertical Datum of 1988. The watershed consists of a low-relief modern floodplain underlain by alluvial deposits and till, bounded by slightly higher relief ridges.

Underlying the modern floodplain, surficial deposits of the DeForest Formation are dominated by very dark gray to brown, noncalcareous to calcareous, sandy loam alluvium with variable thicknesses between < 1 to 5 m (3 to 16.5 ft). Underlying the DeForest Formation, the Noah Creek Formation consists of dark yellowish brown medium to coarse gravelly sand ranging between 4.5 to 12 m (15 to 40 ft). With some variability, the Noah Creek Formation is underlain by Dows Formation-Morgan Member
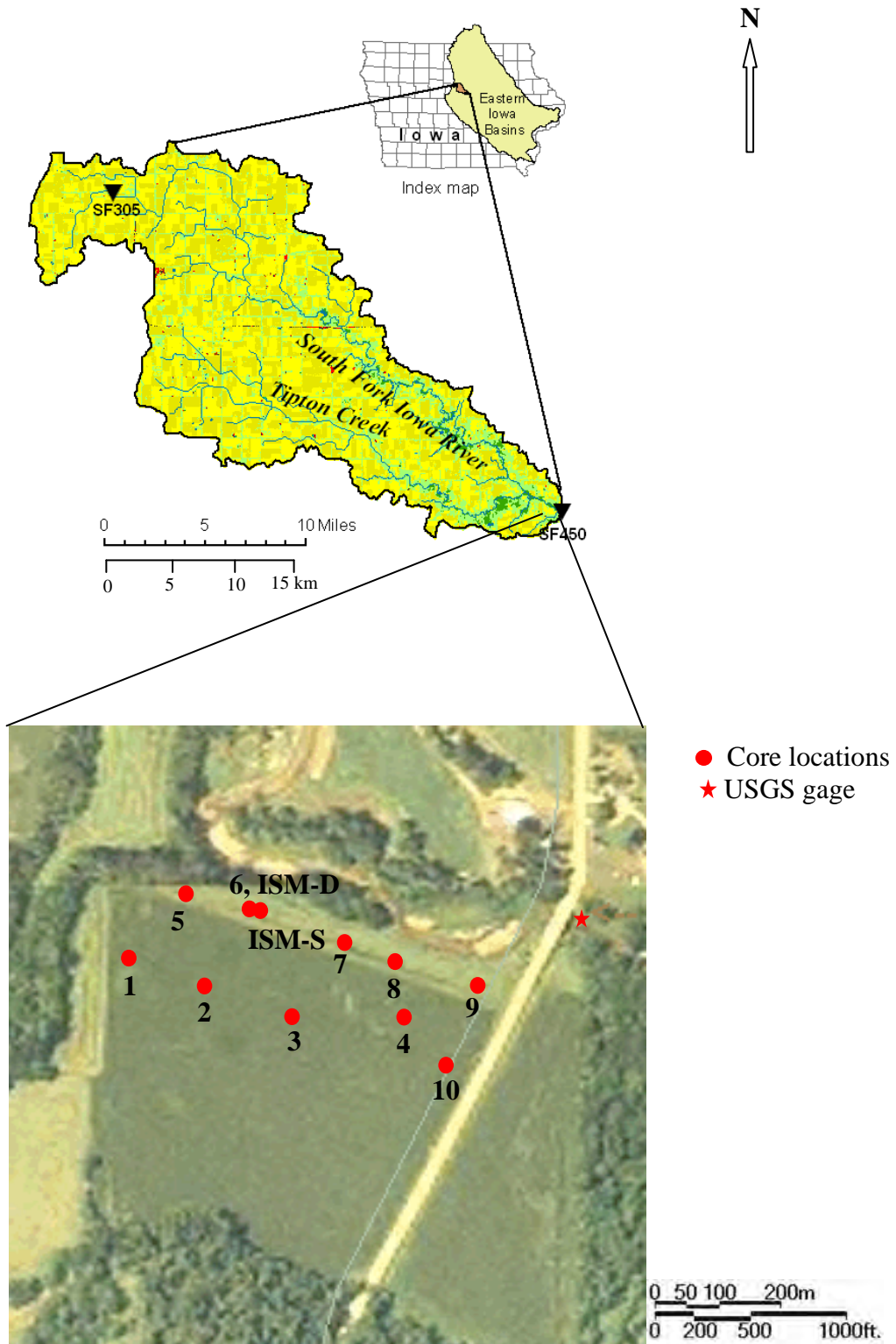
9

Figure 1. New Providence Site (adapted from http://ia.water.usgs.gov/nawqa/eiwa_ACT.html)

till deposits. These till deposits are stratified loam to silt loam, grayish brown and quite variable in thickness, ranging from 3 to 5 m (10 to 16.5 ft). (E. Smith, personal communication)

MATERIALS AND METHODS

50 subsurface sediment samples were collected from below the water table from 11 boreholes at the research site. Borehole locations are recorded in Maharjan (2008, Appendix A). A small drill rig was used to collect the sediment samples in acrylic core sleeves: 14 of them were collected in November, 2006, 30 in March, 2007 and the remainder in December, 2007. The samples were capped at both ends, put in coolers and transported to the University of North Dakota. All cores were later shifted to plastic storage containers, homogenized by gentle mixing, labeled and stored in high density polyethylene containers in a freezer. The samples were analyzed for texture, IC and OC contents, IS contents, Fe(II) contents, mineralogy and Munsell color. OS contents were measured for 14 samples. Only the sediments smaller than gravel (> 2.0 mm) were analyzed for electron donor contents and IC. Each sample was first oven dried over night at 103^oC and grinded into fine powder before any chemical analysis.

Particles sizes smaller than 0.0625 mm were determined by the hydrometer method of sedimentation analysis and sizes larger than 0.0625 mm were determined by wet-sieve analysis (ASTM, 1998). Sediment grains were divided into gravel (> 2.0 mm), sand ($\leq$ 2.0 and > 0.0625 mm), silt ($\leq$ 0.0625 mm and > 0.004 mm) and clay ($\leq$ 0.004 mm). However, sand was further differentiated as fine, medium and coarse (USGS, 2003). Some of the clay contents were found to be below the quantifiable detection limit

11

(1%) and for the purpose of the statistical analysis, 1/2 the detection limit value was assigned to them. Only two samples were below the quantifiable detection limit for silt and one other was below the detection limit for gravel. We reported these quantities as 0%. 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) was measured through wet chemical extraction (Salinas 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 (FeS_2). Some of the sediment samples were chosen for analysis of OS (Salinas Klapperich, 2008) in a Leco SC-432 DR Sulfur Analyzer.

Some of the electron donor contents were found to be below their quantifiable detection limits (Table 1). Generally, we assigned values of 1/2 the detection limit to values, which were below the limit. In the case of OC, duplicate values were available for comparison. These duplicates were tested for their percentage difference using the formula in Maharjan (2008, Appendix F). Duplicates whose percentage difference was within ± 30% were considered reproducible and an average value was used. Duplicates that exceeded this threshold were assigned 1/2 the detection limit.

Table 1. Quantifiable Detection Limits of Electron Donors

Electron Donor	Quantifiable Detection Limit (%)
Organic carbon (OC)	0.02
Inorganic sulfide (IS)	0.003
Ferrous ion (Fe (II))	0.003
Organic sulfur (OS)	0.01

Standards were analyzed for each electron donor test. Dextrose ($C_6H_{12}O_6$) was used as the standard for OC analysis and had average recoveries of 99.8% ± 3.4% (n=3). Pyrite (FeS_2) was the standard for IS analysis and had average recoveries of 90.6% ± 0.3% (n=3). For Fe(II) analysis, siderite ($FeCO_3$) served as the standard and had average recoveries of 88.4% ± 2.3% (n=7).

The X'Pert advanced XRD machine was used to analyze sediment mineralogy. The methodology and complete results are reported in Maharjan (2008, Appendix E). Munsell color classification was done for all the collected sediment samples and they are reported in Maharjan (2008, Appendix B).

RESULTS AND DISCUSSION

The texture analysis was based on the classification of grain sizes adopted from USGS (2003). All the 50 sediment samples were analyzed for gravel, sand (coarse, medium, and fine), silt and clay contents. The result of the texture analysis along with other analysis results is given in Table 2. Detailed results of the sediment texture analysis are also given in Maharjan (2008, Appendix D).

X-ray diffraction showed significant amount of quartz and dolomite and calcite in some sediment samples. We could not find any significant peaks for minerals potentially responsible for electron donors in the samples. We could detect a possible single small peak for each of amphibole and clinochlore in almost all the XRD scans. However, we could not find other related peaks for these Fe(II)-bearing minerals as verification. Commonly, detection limits of XRD for minerals ranges from 1% to 3% by weight depending on background noise, peak resolution of the diffractogram pattern and sample

Table 2. Texture and Electron Donor Analysis of New Providence, Iowa, Sediment Samples.

Samples		Texture analysis				IC (%)	OC (%)	IS (%)	Fe(II) (%)	OS (%)
Core No.	Depth (m)	Gravel (%)	Sand(%)	Silt (%)	Clay (%)	as CO3				
			total							
C 1	2.44 - 3.66	5.18	86.49	4.82	3.51	7.41	0.063	0.026	0.237	
C 1	3.66 - 4.88	41.83	50.08	6.27	1.82	13.25	0.035	0.060	0.662	
C 1	5.79 - 6.10	4.17	30.78	53.15	11.9	17.06	0.359	0.089	0.783	
C 2	3.35	35.35	55.01	7.89	1.75	8.58	0.186	0.033	0.286	
C 2	3.66	47.94	27.16	20.22	4.68	6.98	0.558	0.224	0.577	
C 2	3.66 - 3.96	8.6	35.75	41.31	14.34	15.56	0.294	0.102	0.934	
C 2	5.79 - 6.10	4.75	89.63	3.89	1.72	3.79	0.035	0.027	0.153	
C 2	7.01 - 7.32	1.44	92.27	4.59	1.7	2.25	0.024	0.028	0.170	
C 3	2.44 - 2.59	20.77	73.89	4.48	0.86	5.49	0.044	0.024	0.170	
C 3	3.66 - 3.81	47.26	46.24	6.5	0.5	10.36	0.020	0.016	0.144	
C 3	6.10 - 6.71	40.4	54.31	4.44	0.84	9.00	0.018	0.012	0.211	
C 4	2.44 - 2.74	26.96	68.86	4.17	0.5	2.65	0.051	0.0015	0.113	
C 4	4.57 - 4.88	0.62	92.41	2.56	4.41	8.47	0.040	0.0015	0.221	
C 4	7.01 - 7.32	1.31	92.8	3.26	2.63	10.20	0.058	0.119	0.445	
C 5	2.13 - 2.44	0.78	16.41	70.94	11.88	8.93	2.064	0.0015	0.586	
C 5	2.44 - 3.66	50.2	39.78	10.02	0.5	5.89	0.057	0.0015	0.131	
C 5	3.66 - 4.88	60.61	36.33	3.05	0.5	12.36	0.050	0.0015	0.061	
C 5	5.49 - 6.10	17.46	82.54	0	0.5	9.96	0.010	0.0015	0.128	
C 5	6.10 - 6.86	27.91	70.03	0	2.05	10.16	0.055	0.070	0.335	
C 6	2.13 - 2.44	4.65	77.52	15.69	2.13	1.74	0.215	0.009	0.149	
C 6	2.44 - 3.66	27.21	60.81	11.98	0.5	7.15	0.079	0.010	0.167	
C 6	3.66 - 4.88	41.89	50.27	7.84	0.5	10.03	0.010	0.002	0.149	
C 6	4.88 - 5.18	13.91	81.03	5.06	0.5	9.34	0.010	0.004	0.132	
C 6	6.71 - 7.32	20	72.39	4.89	2.73	10.14	0.020	0.007	0.144	
C 7	2.13 - 2.44	1.21	95.52	3.28	0.5	1.99	0.026	0.002	0.082	
C 7	2.44 - 3.66	1.6	92.12	6.29	0.5	2.18	0.223	0.008	0.199	
C 7	4.88 - 5.18	13.11	80.46	6.43	0.5	8.30	0.021	0.129	0.256	
C 7	7.01 - 7.32	38.44	56	3.76	1.79	9.11	0.010	0.003	0.139	
C 8	2.13 - 2.44	0.46	73.5	19.2	6.85	3.88	0.204	0.005	0.135	
C 8	3.05 - 3.66	47.12	44.75	7.1	1.03	7.51	0.045	0.005	0.108	
C 8	3.66 - 4.27	44.14	47.87	3.83	4.14	10.11	0.068	0.054	0.262	
C 8	5.79 - 6.10	18.11	75.46	2.14	4.29	9.83	0.048	0.041	0.298	
C 8	6.10 - 6.40	15.21	80.85	0.74	3.19	3.22	0.032	0.021	0.155	
C 8	7.01 - 7.32	37.41	54.8	4.17	3.62	10.08	0.050	0.074	0.304	
C 9	2.13 - 2.44	0.37	87.07	11.62	0.93	2.10	0.121	0.003	0.093	
C 9	3.35- 3.66	39.84	49.14	10.16	0.87	7.67	0.167	0.137	0.319	
C 9	4.57 - 4.88	0	84.99	13.17	1.84	9.38	0.142	0.076	0.650	< 0.01
C 9	5.79 - 6.10	32.67	62.76	4.56	0.5	8.26	0.041	0.063	0.383	< 0.01
C 9	6.10 - 6.40	45.56	46.78	5.96	1.71	7.02	0.040	0.026	0.132	< 0.01
C 10	2.13 - 2.44	2.97	79.06	11.47	6.49	3.20	0.032	0.002	0.050	< 0.01
C 10	3.05 - 3.66	38.91	47.78	8.99	4.31	15.15	0.010	0.006	0.156	< 0.01
C 10	4.57 - 4.88	29	50.69	14.23	6.09	18.06	0.710	0.003	0.181	< 0.01
C 10	5.79 - 6.10	17.1	78.1	1.18	3.64	8.48	0.023	0.011	0.127	< 0.01
C 10	7.01 - 7.32	30.25	59.97	5.3	4.48	18.20	0.132	0.015	0.178	< 0.01
ISM - S	2.44 - 3.05	33.6	52.41	10.53	3.45	6.43	0.127	0.017	0.160	< 0.01
ISM - S	3.05 - 3.66	43.8	42.77	7.88	5.57	14.11	0.117	0.015	0.129	< 0.01
ISM - D	3.66 - 4.27	21.32	70.35	4.51	3.81	12.19	0.010	0.011	0.131	< 0.01
ISM - D	4.27 - 4.88	16.92	78.63	1.92	2.52	10.22	0.010	0.018	0.141	< 0.01
ISM - D	4.88 - 5.33	42.04	49.9	4.79	3.27	10.90	0.010	0.017	0.132	< 0.01
ISM - D	5.33 - 5.79	29.28	63.12	4.6	2.99	9.19	0.010	0.013	0.113	< 0.01

preparation (Zachara, et al., 2004). Our chemical analysis showed that all the electron donors present at concentrations less than 1% by weight which suggested that the minerals bearing Fe(II) or IS are not detectable by XRD scans. All XRD scans are in Maharjan (2008, Appendix E).

Under HCl treatment, the sediment samples yielded inorganic carbon with average content of 9% by weight with a few as high as 18% content. XRD scans of these sediments revealed high peaks of dolomite and calcite. The OC content in the sediments was found to be $0.13\% \pm 0.31\%$ by weight, in average. All the samples were run in duplicate for OC analysis. The OC results are in Table 2.

An average of $0.033\% \pm 0.046\%$ for IS content was found in the sediment samples, with a few being below the detection limit of 0.003%. The results of IS analysis are given in Table 2. A subset of sediment samples was analyzed for OS (See Table 2.), but all of the 14 samples were below detection. Therefore, this potential electron donor was not considered further.

Fe(II) content averaged $0.24\% \pm 0.19\%$ by weight. The results are given in Table 2. Three of the samples were run in duplicate for analysis of IS and Fe(II). Table 3 gives the summary of the contents of the electron donors in the sediment samples.

Table 3. Summary Contents of the Electron Donors in the New Providence, Iowa, Sediment Samples (n = 50).

Electron donor	n	Min / Max (%)	Average (%)	Standard Recovery (%)
Organic Carbon	50	< 0.020 / 2.064	0.134 ± 0.311	99.84 ± 3.39 (n = 3)
Inorganic Sulfide	50	< 0.003 / 0.181	0.033 ± 0.046	90.6 ± 0.26 (n = 3)
Ferrous ion	50	0.050 / 0.934	0.242 ± 0.193	88.43 ± 2.23 (n = 7)

The normality test was conducted for the measured data of the electron donor contents in the sediments using the W test as explained in Gilbert (1987). Most of the data sets were found not to be normally distributed (Maharjan, 2009, Table 12); therefore a nonparametric statistical test was used for the data. Spearman rank coefficient nonparametric test was adopted from Gilbert (1987) to correlate the electron donors among themselves and with the sediment textures and depth. The correlation matrix is presented in Table 4.

There was no correlation between the sediment textures and sediment depths except for silt, which was negatively correlated to depth. The lack of correlation is consistent with heterogeneity associated with alluvial systems. Gravel was negatively correlated to sand, while sand was negatively correlated to silt and silt positively correlated to clay. Among electron donors, IS was positively correlated to depth while OC was negatively correlated to depth. Electron donors were positively correlated to each other at significant levels of 0.01 or 0.05. This suggests that if one kind of electron donor is found in the sediment, it is likely that other two electron donors are also available. This may also suggest a common source of the minerals potentially responsible for these electron donors in given depositional environments. Among all three electron donors, Fe(II) was positively correlated to IC. This suggests Fe(II) and IC may exist in their precipitated carbonate forms. Electron donors were also positively correlated to finer textures, silt and clay, except for IS, which was positively correlated only to clay. A general particle size effect on reactivity was already noted in other previous studies, finer-grained materials are more reactive (Hartog et al., 2002; Helvoort et al., 2007). Our results suggest that the finer-grained sediments at the NP site would have more

denitrification capacity both because of their smaller sizes and because of their greater contents of electron donors.

Certain relationships are expected to exist between hydraulic conductivity and statistical parameters that describe the grain-size distribution (Alyamani and Sen, 1993). My data on textures can be useful in modeling hydraulic conductivities at the site and, therefore, the groundwater flow patterns. The reactive properties are difficult to predict in heterogeneous sites like the NP site. However, using the facies concept, it would be possible to model heterogeneous deposits with the help of grain size distributions (Miall, 1985; Helvoort et al., 2007). With the potential electron donors already measured and their positive correlation to finer textures found, one can use these data in modeling the aquifer to predict the reactive potential for denitrification based on reaction rates currently being measured at the NP site (S. Korom, personal communication).

Table 4. Spearman Rank Coefficient Correlation Matrix.

Correlation r	OC	IS	Fe(II)	IC	Gravel	Sand	Silt	Clay	Depth
OC	1.000	0.287	0.579	-0.119	-0.225	-0.156	0.546	0.365	-0.294
IS		1.000	0.584	0.153	-0.067	-0.175	0.013	0.260	0.374
Fe(II)			1.000	0.278	-0.080	-0.175	0.238	0.273	0.206
IC				1.000	-0.012	-0.442	-0.048	0.356	0.420
Gravel					1.000	1.000	-0.724	-0.036	-0.173	0.111
Sand						1.000	-0.438	-0.213	0.127
Silt							1.000	0.259	-0.494
Clay								1.000	0.054

positively correlated at the significance level of 0.05

positively correlated at the significance level of 0.01

negatively correlated at the significance level of 0.01

negatively correlated at the significance level of 0.05

CONCLUSIONS

To understand the denitrification potential of the NP site in north-central Iowa, sediment samples were analyzed. All samples were first analyzed for gravel, sand (coarse, medium, and fine), silt, clay and IC contents and for the electron donors [OC, Fe(II), and IS], which can contribute towards denitrification. A subset of sediment samples was also analyzed for OS, but all of the 14 samples were below detection; therefore this potential electron donor was not considered further. Nonparametric correlation analysis was performed for the data of the other three electron donor concentrations, sediment grain sizes and sediment depths.

XRD scans did not show significant peaks of minerals potentially responsible for electron donors. We could detect a single small peak for each of amphibole and clinochlore, but could not find other related peaks as verification. XRD scans also showed the high contents of IC content in the aquifer sediments.

There is no correlation between the sediment textures and sediment depths except for silt, which is negatively correlated to depth. Gravel is negatively correlated to sand, while sand is negatively correlated to silt and silt positively correlated to clay. Electron donors are positively correlated to each other at significant levels of 0.01 or 0.05. Electron donors, which are vital for denitrification, are positively correlated to finer sediment textures, silt and clay, except for IS, which is positively correlated only to clay. Our findings suggest that most aquifer denitrification at this site takes place in zones having lower hydraulic conductivities. There is no consistent correlation of electron donors with depth. Sediment textures analysis and correlation confirmed the heterogeneity of the site.

To meet the ACT objective of devising a tool to characterize the transport and fate of nitrates in the watershed, one can use our data for modeling purposes. The facies-based approach can be applied using grain size distributions to estimate both hydraulic conductivities of sediments and now their denitrification capacities based on electron donor contents. Our research suggests that sediments with lower hydraulic conductivities will have the greater denitrification rates and greater denitrification capacities. Future work should seek to verify these observations at other agricultural and environmental settings.

REFERENCES

Allen-King, R. M., Halket, R. M., Gaylord, D. R., 1998. Characterizing the heterogeneity and correlation of perchloroethene sorption and hydraulic conductivity using a facies-based approach. Water Resources Research. 34(3), 385-396.

Alyamani, M. S., Sen, Z., 1993. Determination of hydraulic conductivity from complete grain-size distribution curves. Ground Water. 31(4) 551-556.

American Society for Testing and Materials (ASTM), 1998. Standard test method for particle-size analysis of soils. Vol. 04.08.

Becher, K. D., Schnoebelen, D. J., Kimberlee, Akers, K.B., 2000. Nutrients discharged to the Mississippi river from eastern Iowa watersheds, 1996-97.   Journal of the American Water Resources Association. 36(1), 161-173.

Bohlke, J. K., Wanty, R., Tuttle, M., Delin, G., Landon, M., 2002. Denitrification in the recharge area and discharge area of a transient agricultural nitrate plume in a glacial outwash sand aquifer, Minnesota. Water Resources Research. 38(7), 1105-1131.

Capel, P. D., McCarthy, K. A., Barbash, J. E., 2008. National, holistic, watershed-scale approach to understand the sources, transport, and fate of agricultural chemical. Journal of Environmental Quality. 37, 983-993.

Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M., Berner, R. A., 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chemical Geology. 54, 149-155.

Churcher, P. L., Dickout, R. D., 1986. Analysis of ancient sediments for total organic carbon- Some new ideas. Journal of Geochemical Exploration. 29(2), 235-246.

Davidson, E. A., Seitzinger, S., 2006. The enigma of progress in denitrification research. Ecological Applications. 16(6), 2057-2063.

Ernstsen, V., 1996. Reduction of nitrate by Fe^{2+} in clay mineral. Clays and Clay Minerals. 44, 599-608.

Everett, J. W., Kennedy L. G., Gonzales J., 2006. Natural attenuation assessment using mineral data. Practice Periodical of Hazardous Toxic, and Radioactive Waste Management. 10(4), 256-263.

Firestone, M. K., 1982. Biological denitrification in agricultural soils. American Society of Agronomy. 289-326.

Gilbert, R. O., 1987. Statistical Methods for Environmental Pollution Monitoring. John Wiley & Sons, Inc.

Goolsby, D. A., Battaglin, W. A., Aulenbach, B. T., Hooper, R. P., 2000. Nitrogen Flux and Sources in the Mississippi River Basin. Science of the Total Environment. 248, 75-86.

Hartog, N., Griffioen J., Vander Weijden, C. H., 2002. Distribution and reactivity of O2-reducing components in sediments from a layered aquifer. Environmental Science and Technology. 36(11), 2338-2344.

Hartog, N., Griffioen J., Bergen P. F. V., 2005. Depositional and paleohydrogeological controls on the distribution of organic matter and other reactive reductants in aquifer sediments. Chemical Geology. 216, 113-131.

Helvoort, P. V., Griffioen, J., Hartog, N., 2007. Characterization of the reactivity of riverine heterogeneous sediments using a facies-based approach; the Rhine–Meuse delta (The Netherlands). Applied Geochemistry. 22, 2735-2757.

Kalkhoff, S.J., Barnes, K.K., Becher, K.D., Savoca, M.E., Schnoebelen, D.J., Sadorf, E.M., Porter, S.D., and Sullivan, D.J., 2000. Water Quality in the Eastern Iowa Basins, Iowa and Minnesota, 1996–98. U.S. Geological Survey Circular 1210, 37 p., on-line at http://pubs.water.usgs.gov/circ1210/

Kennedy, L. G., Everett J. W., Ware K. J., Parsons R., Green V., 1998. Iron and sulfur mineral analysis methods for natural attenuation assessments. Bioremediation Journal. 2 (3&4), 259-276.

Kennedy, L. G., Everett J. W., Dewers, T., Pickins, W., Edwards, D., 1999. Application of mineral iron and sulfide analysis to evaluate natural attenuation at fuel contaminated site. Journal of Environmental Engineering. 125(1), 47-56.

Konen, M. E., Burras, C. L., Sandor, J. A., 2003. Organic carbon, texture, and quantitative color measurement relationships for cultivated soils in North Central Iowa. Soil Science Society of American Journal. 67(6), 1823-1830

Korom, S F.,1992. Natural denitrification in the saturated zone: A review. Water Resources Research. 28(6), 1657-1668.

Korom, S. F., Schlag, A. J., Schuh, W. M., Schlag, A. K., 2005. In situ mesocosms: Denitrification in the Elk Valley aquifer. Ground Water Monitoring and Remediation. 25(1), 79-89.

Korom, S. F., 2008. (Personal Communication, Nov. 2008).

Majumder, R. K., Hasnat, M. A., Hossain, S., Ikeue, K., Machida, M., 2008. An exploration of nitrate concentrations in groundwater aquifers of central-west region of Bangladesh. Journal of Hazardous Materials. 159(2-3), 536-543.

Maharjan, B., 2008. Correlation of electron donor concentrations in sediments with sediment properties: New Providence, Iowa. MS Thesis. University of North Dakota, 52 pp.

McMahon, P. B., Bohlke, J. K., Bruce, B. W., 1999. Denitrification in marine shales in northeastern Colorado. Water Resources Research. 35(5), 1629-1642.

Miall, A. D., 1985. Architectural-elements analysis: A new method of facies analysis applied to fluvial deposits. Earth Science Review. 22, 261-308.

Poppe, L. J., Paskeich, V. F., Hathaway, J. C., Blackwood, D. S., 2002. A laboratory manual for X-ray powder. U.S. Geological Survey Open-File Report 01-041. http://pubs.usgs.gov/of/2001/of01-041/index.htm

Postma, D., 1990. Kinetics of nitrate reduction in a sandy aquifer. Geochimica et Cosmochimica. 54, 903-908.

Rivett, M, O., Buss, S. R., Morgan, P., Smith, J. W. N., Bemment, C. D., 2008. Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. Water Research, 42, 4215-4232.

Salinas Klapperich, R. J., 2008. Electron donor potential of Eastern North Dakota shale formations. MS Thesis. University of North Dakota, 103 pp.

Schwientek, M., Einsiedl, F., Stichler, W., 2008. Evidence for denitrification regulated by pyrite oxidation in a heterogeneous porous groundwater system. Chemical Geology. 255(1-2) 60-67.

Senn, D. B., Hemond, H. F., 2002. Nitrate controls on iron and arsenic in an urban lake. Science. 296, 2373-2376.

Smith, E., 2008. (Personal Communication, September 27, 2008)

Tesfay, T., 2006. Dissertation: Modeling groundwater denitrification by ferrous iron using PHREEQC. PhD Dissertation. University of North Dakota, 162 pp.

Turner, R. E., Rabalais, N. N., Swenson, E. M., Kasprzak, M., Romaire, T. 2005. Summer hypoxia in the northern Gulf of Mexico and its prediction from 1978 to 1995. Marine Environmental Research. 59(1), 65-77.

Turner, R. E., Rabalais, N. N., Justic, D., 2008. Gulf of Mexico Hypoxia: Alternate States and a Legacy. Environmental Science and Technology. 42, 2323-2327.

USGS website http://pubs.usgs.gov/of/2003/of03-001/htmldocs/images/chart.gif http://ia.water.usgs.gov/nawqa/eiwa_ACT.html

Zachara, J. M., Ainsworth, C. C., Brown, G. E., Catalano, Jr., J. G., McKinley, J. P., Qafoku, O., Smith, S. C., Szecsody, J. E., Traina, S. J, Warner, J. A., 2004. Chromium speciation and mobility in a high level nuclear waste vadose zone plume. Geochimica et Cosmochimica Acta. 68(1), 13-30.