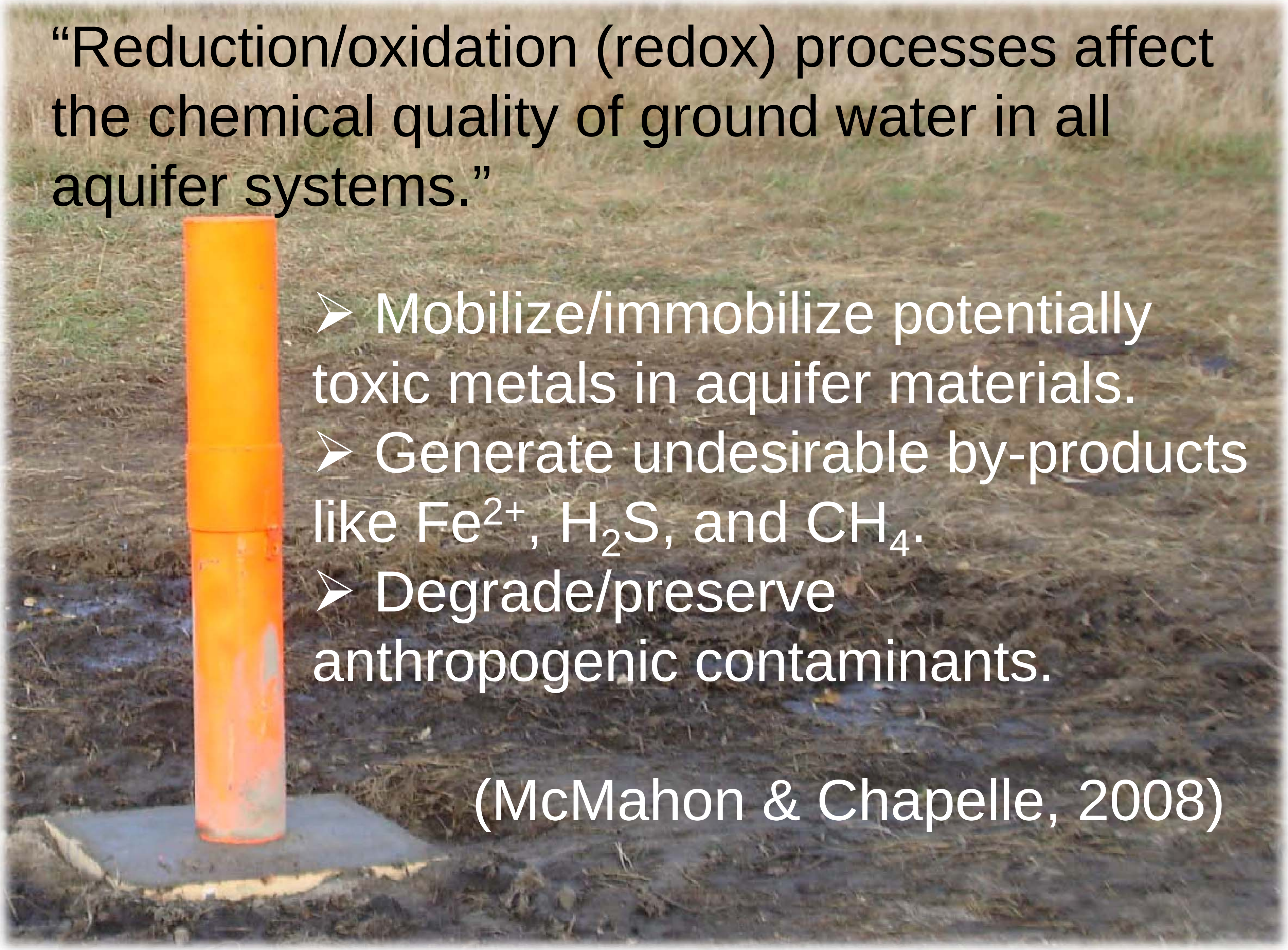
Geologic Processes Linking Electron Donors and Aquifers: Implications for Minnesota

Scott F. Korom

Geology & Geological Engineering

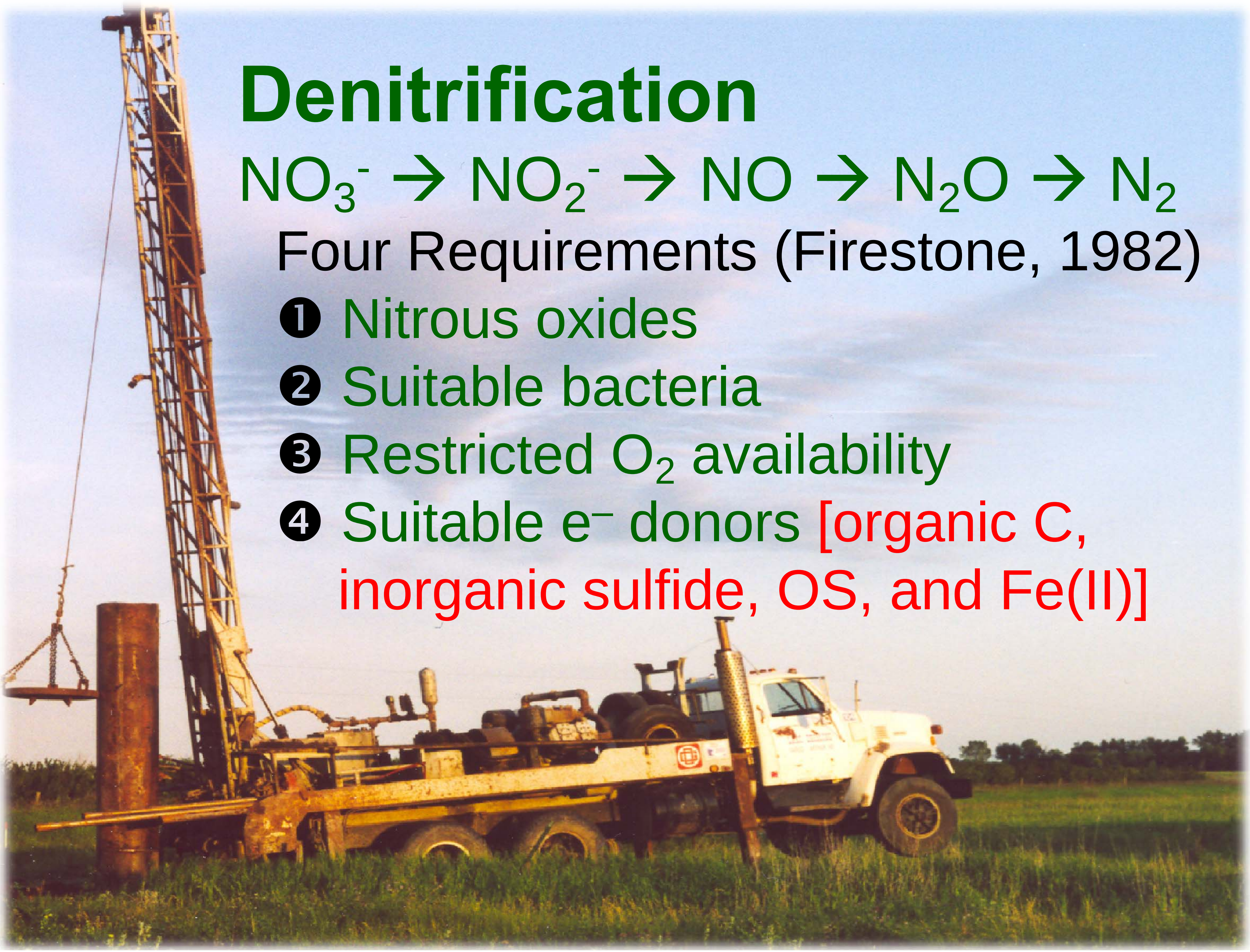
The University of North Dakota



"Reduction/oxidation (redox) processes affect the chemical quality of ground water in all aquifer systems."

- Mobilize/immobilize potentially toxic metals in aquifer materials.
- Generate undesirable by-products like Fe^{2+}, H_2S, and CH_4.
- Degrade/preserve anthropogenic contaminants.

(McMahon & Chapelle, 2008)



Denitrification

$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

Four Requirements (Firestone, 1982)

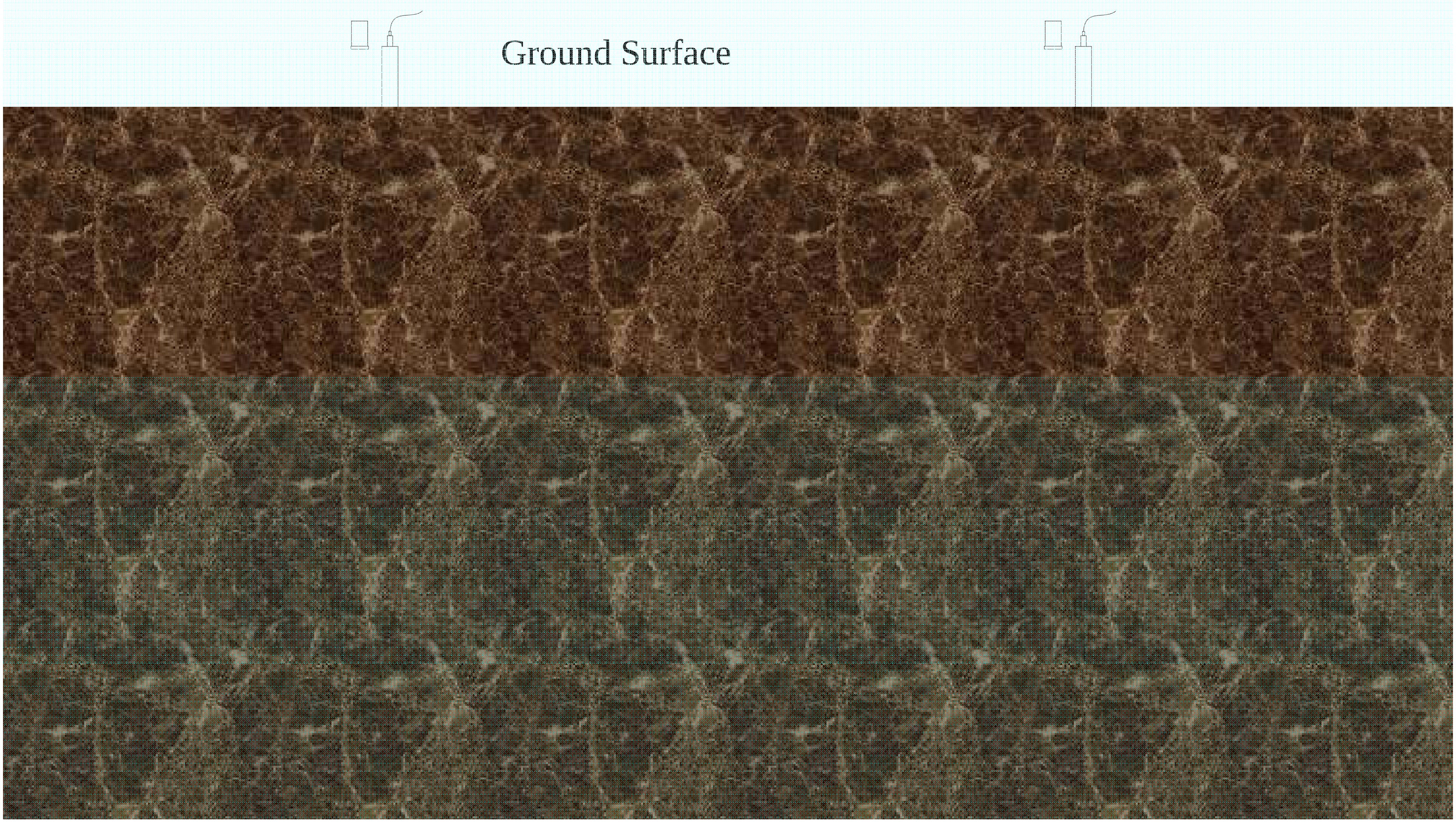
❶ Nitrous oxides

❷ Suitable bacteria

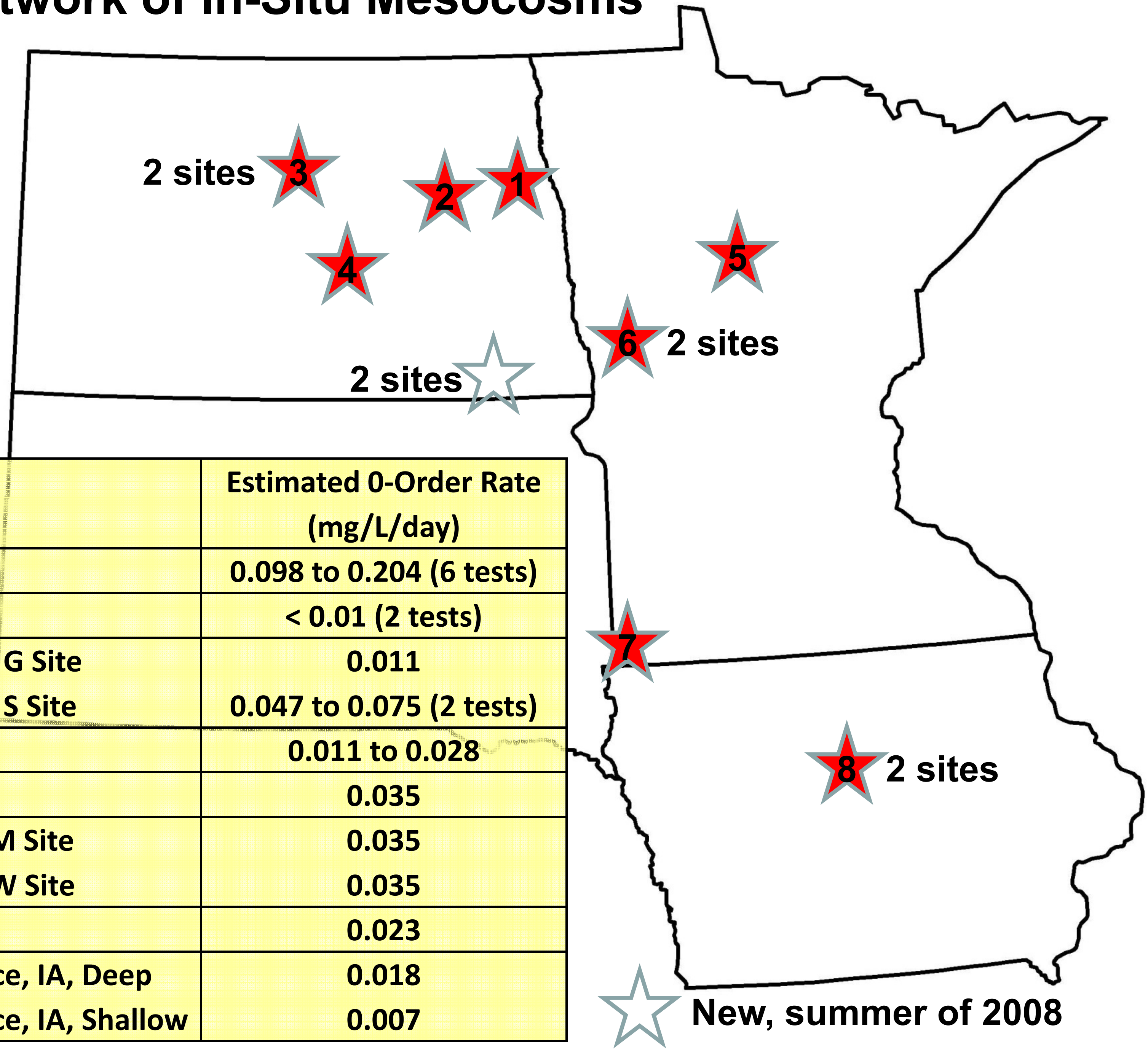
❸ Restricted O_2 availability

❹ Suitable e^- donors [organic C, inorganic sulfide, OS, and Fe(II)]

ISMs: Finished Product



Network of In-Situ Mesocosms



Site	Estimated 0-Order Rate (mg/L/day)
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2. Hamar, ND	< 0.01 (2 tests)
3. Karlsruhe, ND, G Site	0.011
3. Karlsruhe, ND, S Site	0.047 to 0.075 (2 tests)
4. Robinson, ND	0.011 to 0.028
5. Akeley, MN	0.035
6. Perham, MN, M Site	0.035
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Ground Water Monitoring & Remediation

Estimating Aquifer Sensitivity to Nitrate Contamination Using Geochemical Information

by Michael D. Trojan, Moira E. Campion, Jennifer S. Maloney, James M. Stockinger, and Erin P. Eid

(2002)

Abstract

Methods for predicting aquifer sensitivity to contamination typically ignore geochemical factors that affect the occurrence of contaminants such as nitrate. Use of geochemical information offers a simple and accurate method for estimating aquifer sensitivity to nitrate contamination. We developed a classification method in which nitrate-sensitive aquifers have dissolved oxygen concentrations >1.0 mg/L, Eh values >250 mV, and either reduced iron concentrations <0.1 mg/L or total iron concentrations <0.7 mg/L. We tested the method in four Minnesota aquifer systems having different geochemical and hydrologic conditions. A surficial sand aquifer in central Minnesota exhibited geochemical zonation, with a rapid shift from aerobic to anaerobic conditions 5 m below the water table. A fractured bedrock aquifer in east-central Minnesota remained aerobic to depths of 50 m, except in areas where anaerobic ground water discharged upward from an underlying aquifer. A bedrock aquifer in southeast Minnesota exhibited aerobic conditions when overlain by surficial deposits lacking shale, whereas anaerobic conditions occurred under deposits that contained shale. Surficial sand aquifers in northwest Minnesota contained high concentrations of sulfate and were anaerobic throughout their extent. Nitrate-nitrogen was detected at concentrations exceeding 1 mg/L in 135 of 149 samples classified as sensitive. Nitrate was not detected in any of the 109 samples classified as not sensitive. We observed differences between our estimates of sensitivity and existing sensitivity maps, which are based on methods that do not consider aquifer geochemistry. Because dissolved oxygen, reduced iron, and Eh are readily measured in the field, use of geochemistry provides a quick and accurate way of assessing aquifer sensitivity to nitrate contamination.

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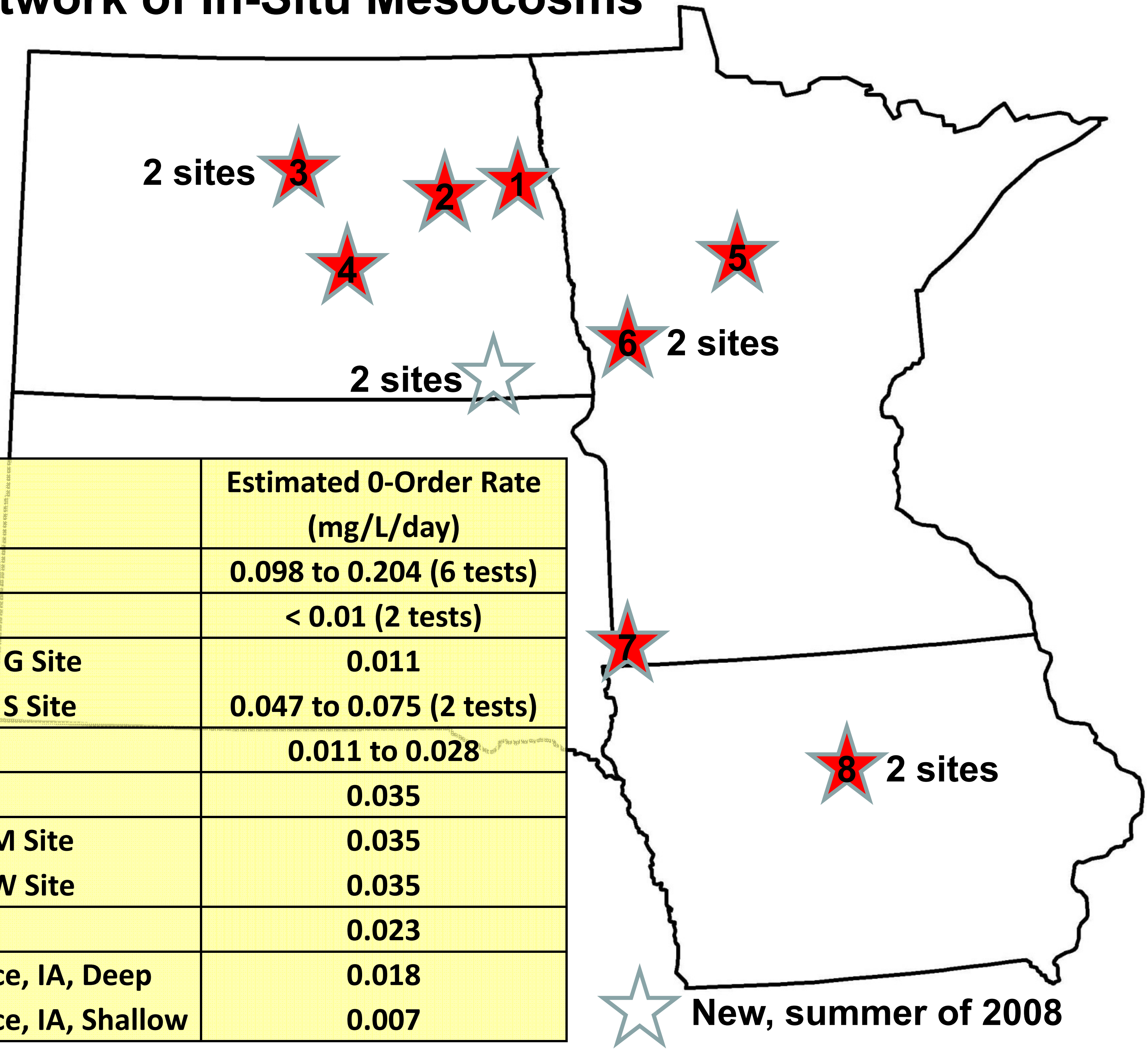

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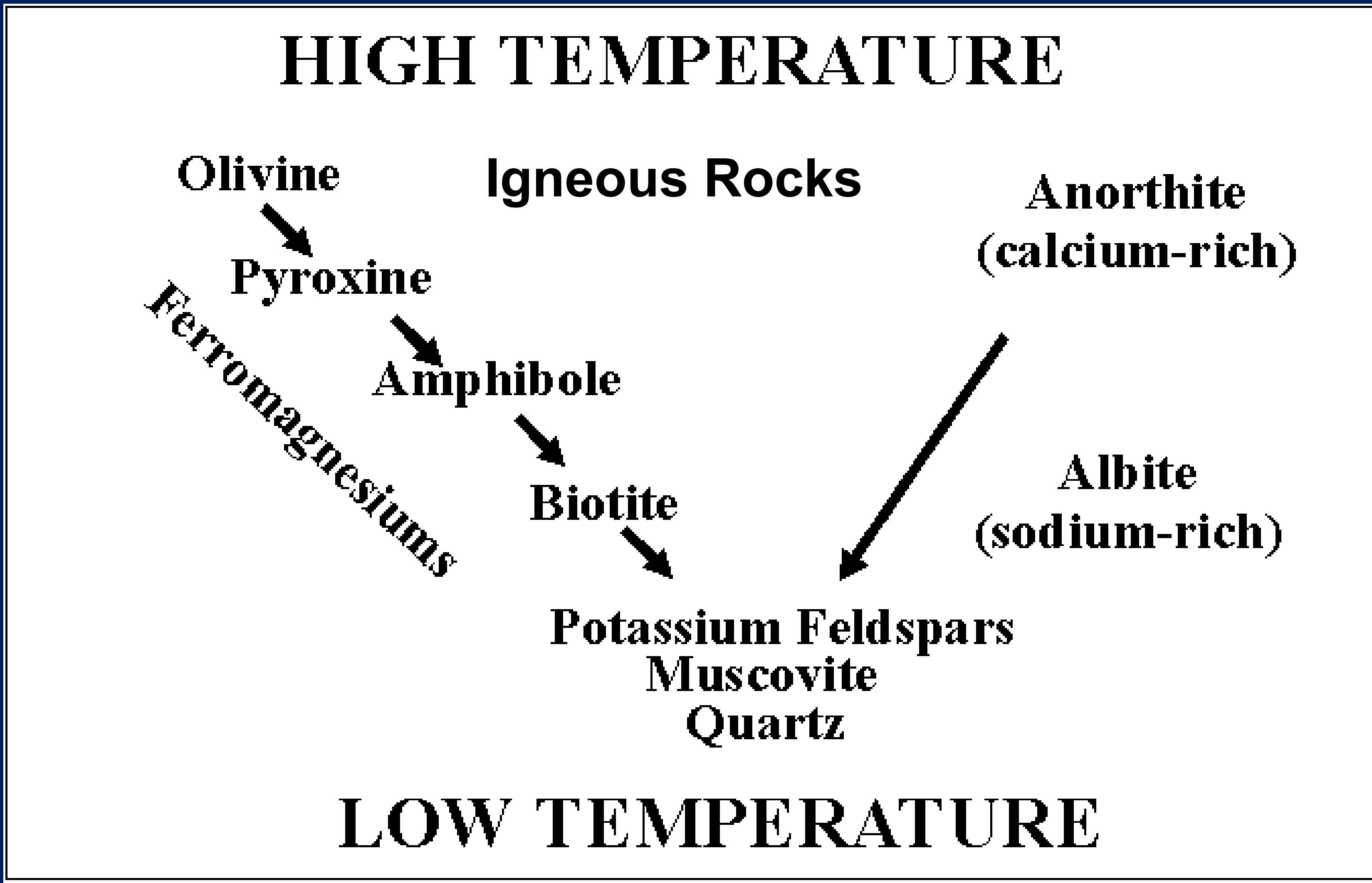
(©2006 McMurdo Dry Valleys LTER)
Photo by Chris Gardner



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Applied Geochemistry
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Oxido-reduction sequence related to flux variations of groundwater from a fractured basement aquifer (Ploemeur area, France)

C. Tarits [a,*], L. Aquilina [b], V. Ayraud [b,c], H. Pauwels [c], P. Davy [b], F. Touchard [b], O. Bour [b]

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[c] *BRGM Water Department, B.P. 6009, 45060 Orléans Cedex, France*

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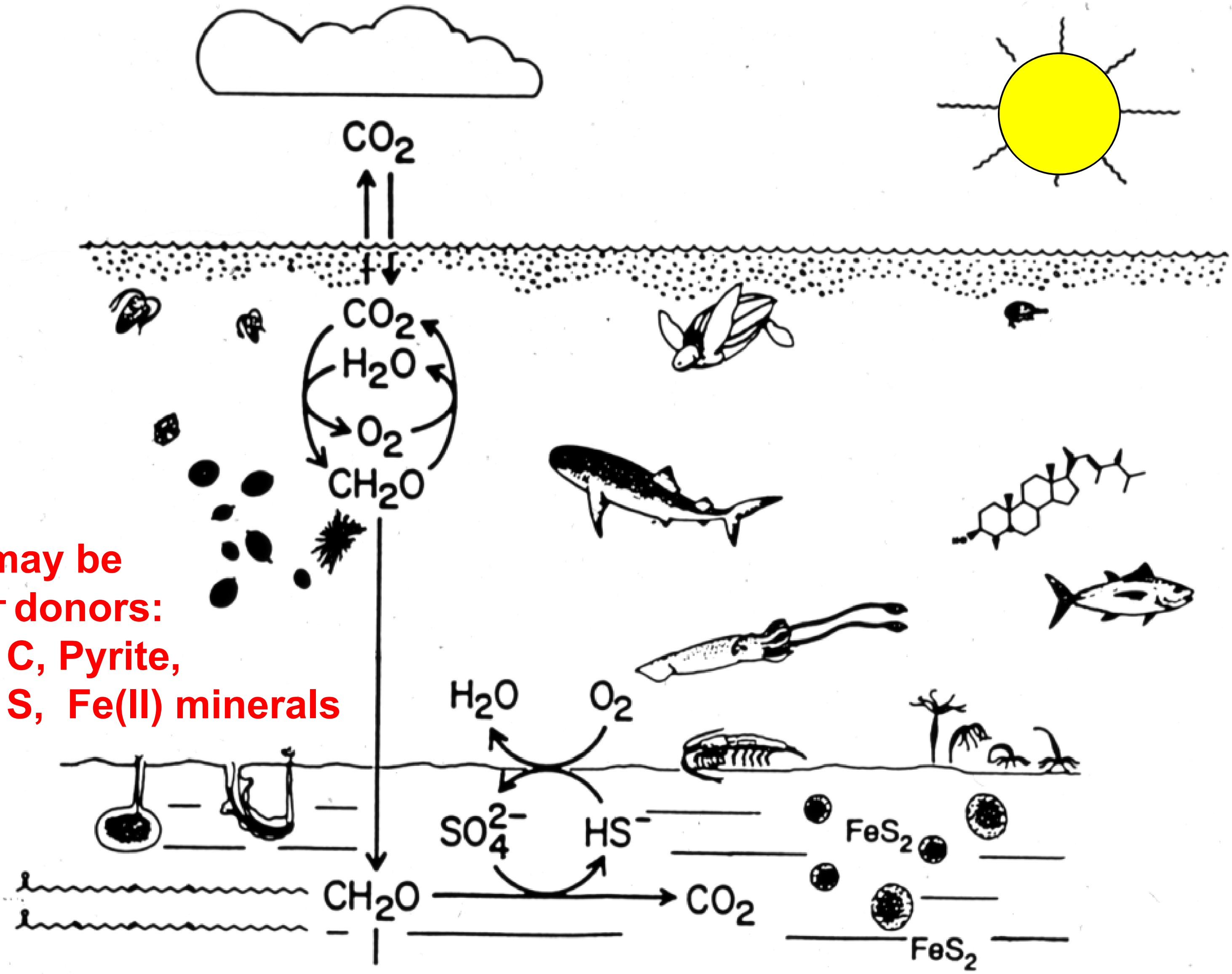
Abstract

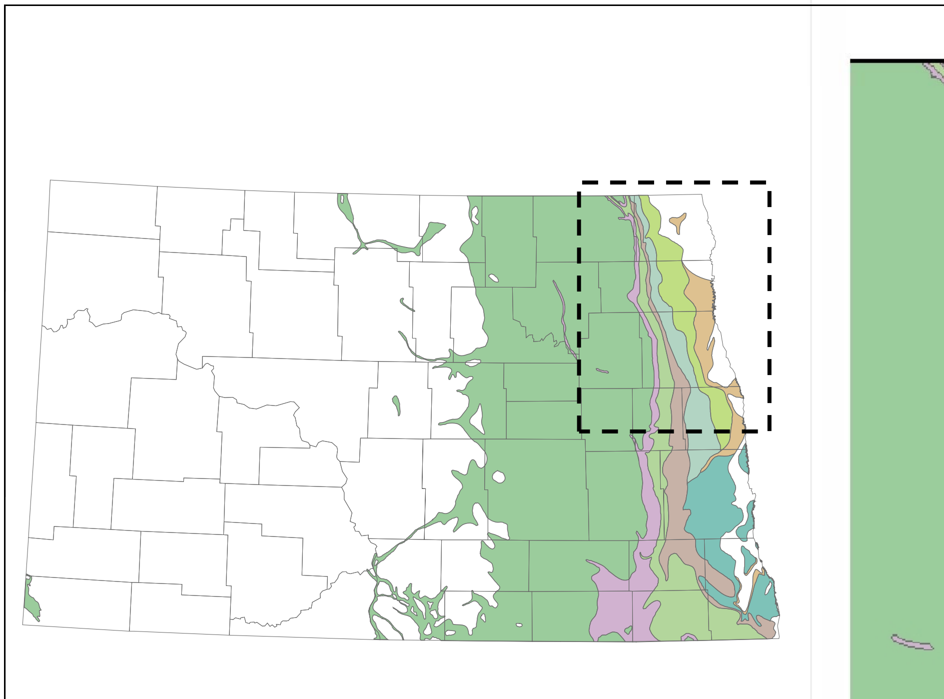
This paper focuses on the chemical evolution of water during the exploitation of a fractured aquifer in a NO_3-rich agricultural environment. During a ten year period, both production rate and chemical parameters were continuously measured in tap water obtained from a deep-water plant in Brittany, France. Changes in SO_4^{2-} and NO_3^- were observed after pumping was initiated. Nitrate concentration decreased during the first 200 days and then stabilized at $\sim 5 \pm 1$ mg/L, while SO_4^{2-} concentration increased rapidly over this period and then showed a steady state increase (0.01 mg/L/day). These changes are attributed to the development of equilibrium between the physical flow parameters and the chemical kinetics of autotrophic denitrification processes that occur in the pyrite-bearing fractures.

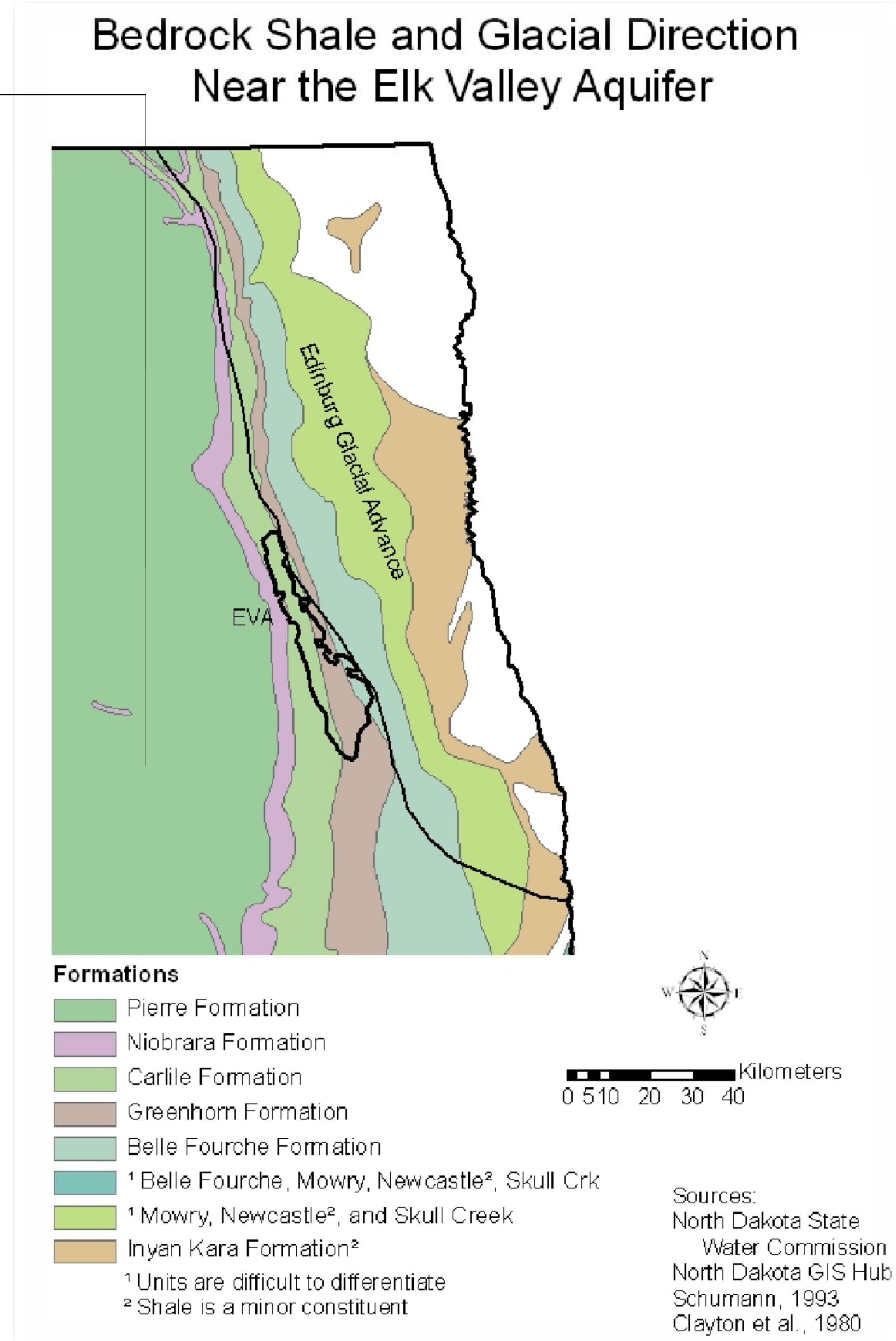
The chemical characteristics of the groundwaters collected in 18 wells located around the site allow identification of two different areas. One is weakly influenced by pumping and is characterized by high NO_3^- concentrations and a short residence time. The second area is directly related to the main pumped well, and characterized by reduced NO_3^- levels combined with an increased SO_4^{2-} production, resulting from the denitrification processes in the pyrite-bearing fractures. Over the last few years, a SO_4^{2-} increase unrelated to denitrification has been recorded in some wells. Based on the NO_3^-, SO_4^{2-} and Fe concentrations, this is attributed to oxidation of S minerals, coupled to Fe^{III} reduction. Exploitation of the aquifer has led to a rapid transfer of the waters within the deep fractures. Their high velocities strongly control the chemical parameters and have led to a redox sequence that has promoted S oxidation, coupled with (1) O_2, (2) NO_3^-, and (3) Fe reduction.



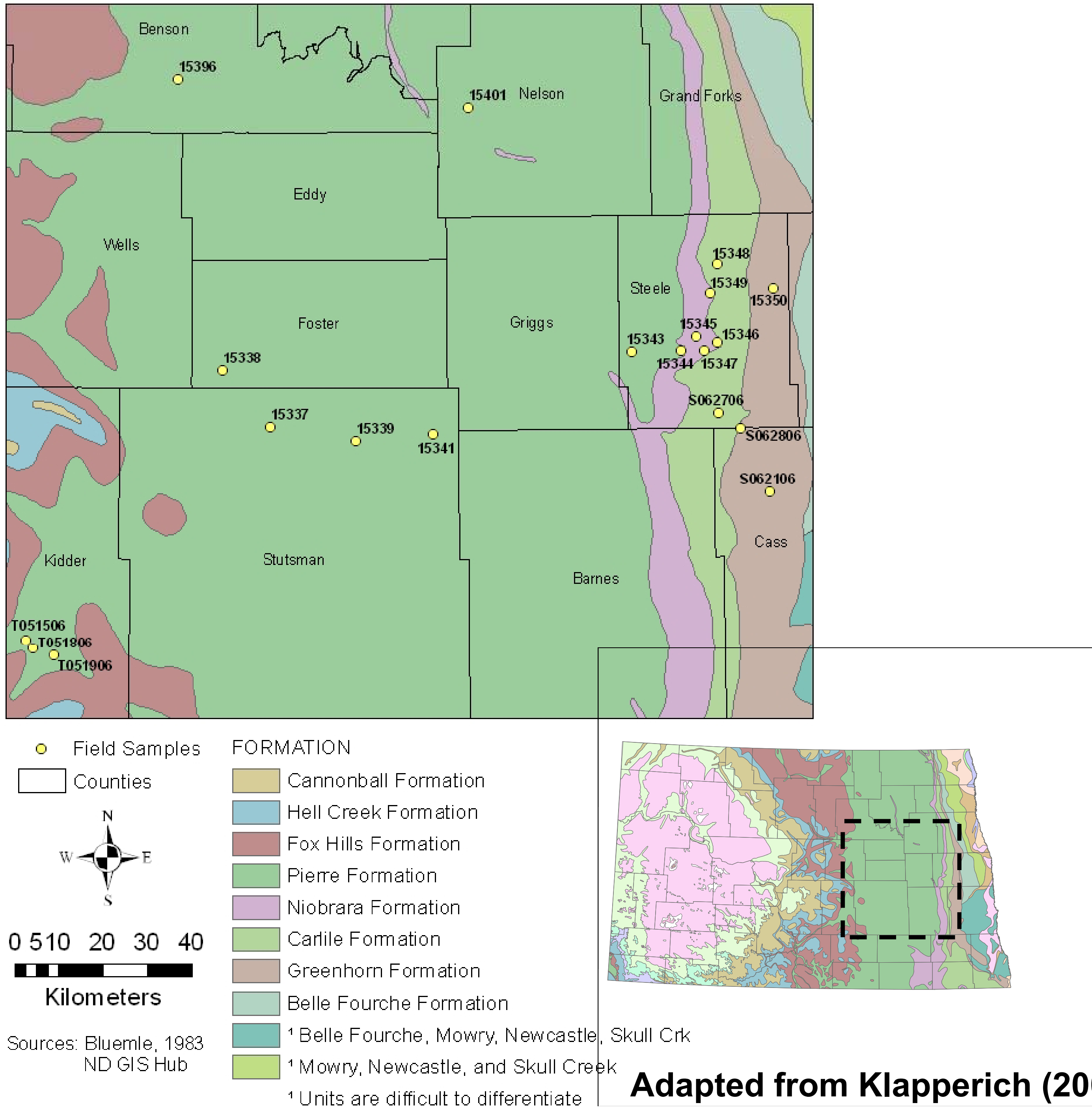
Shales may be rich in e^- donors: Organic C, Pyrite, Organic S, Fe(II) minerals

Adapted from Pratt et al. (1992)





Adapted from Klapperich (2008)



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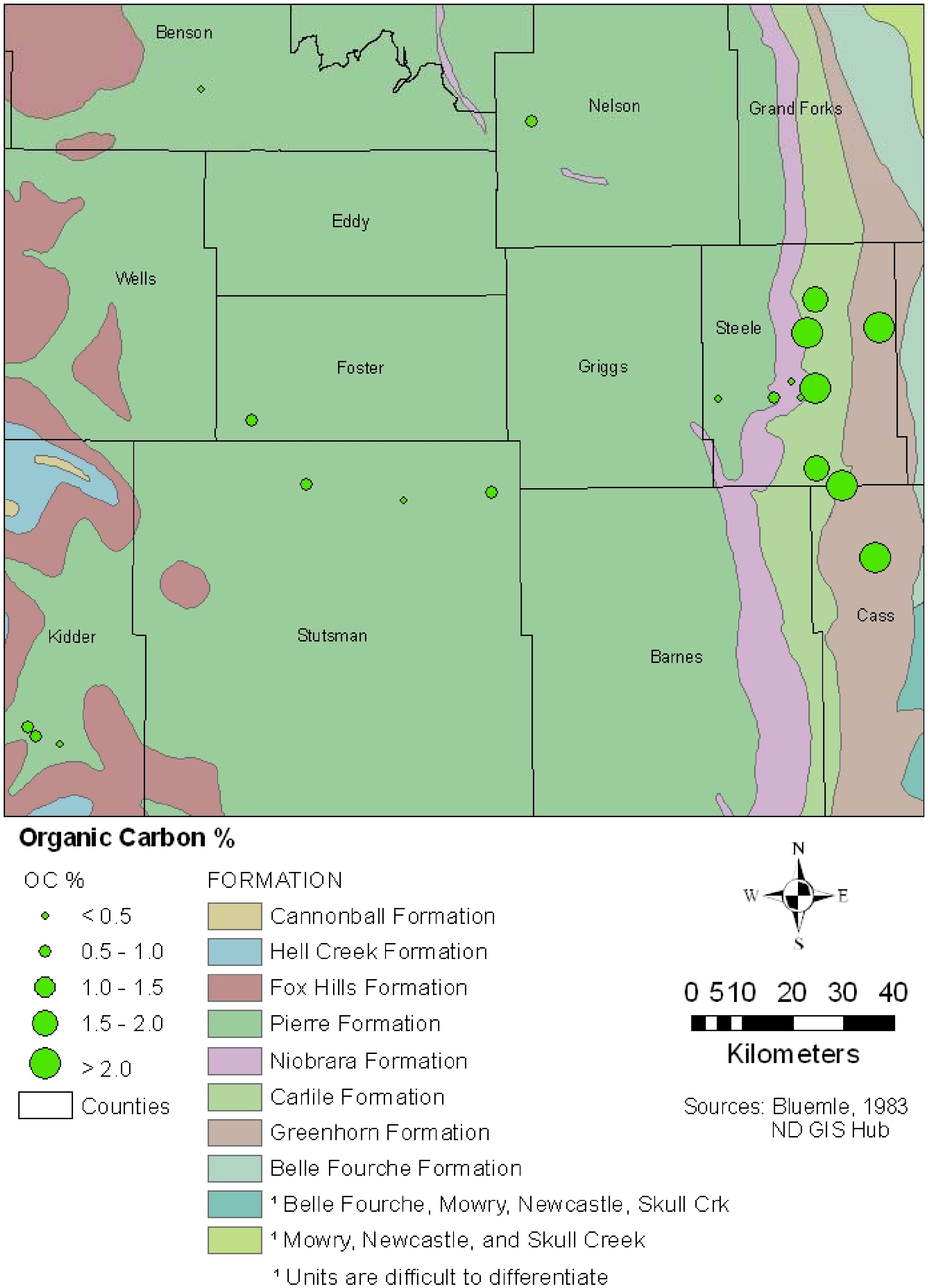

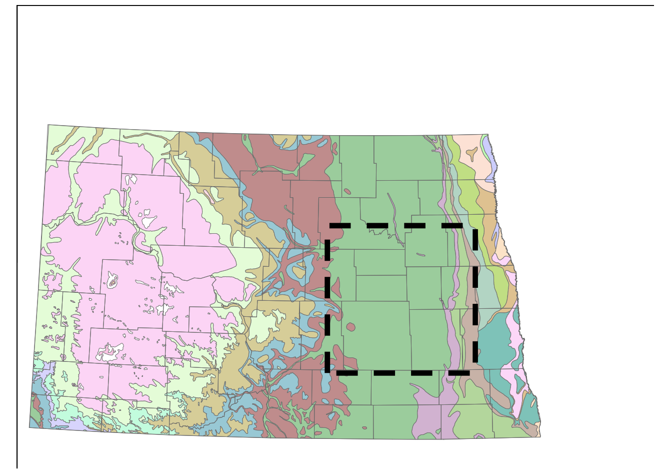

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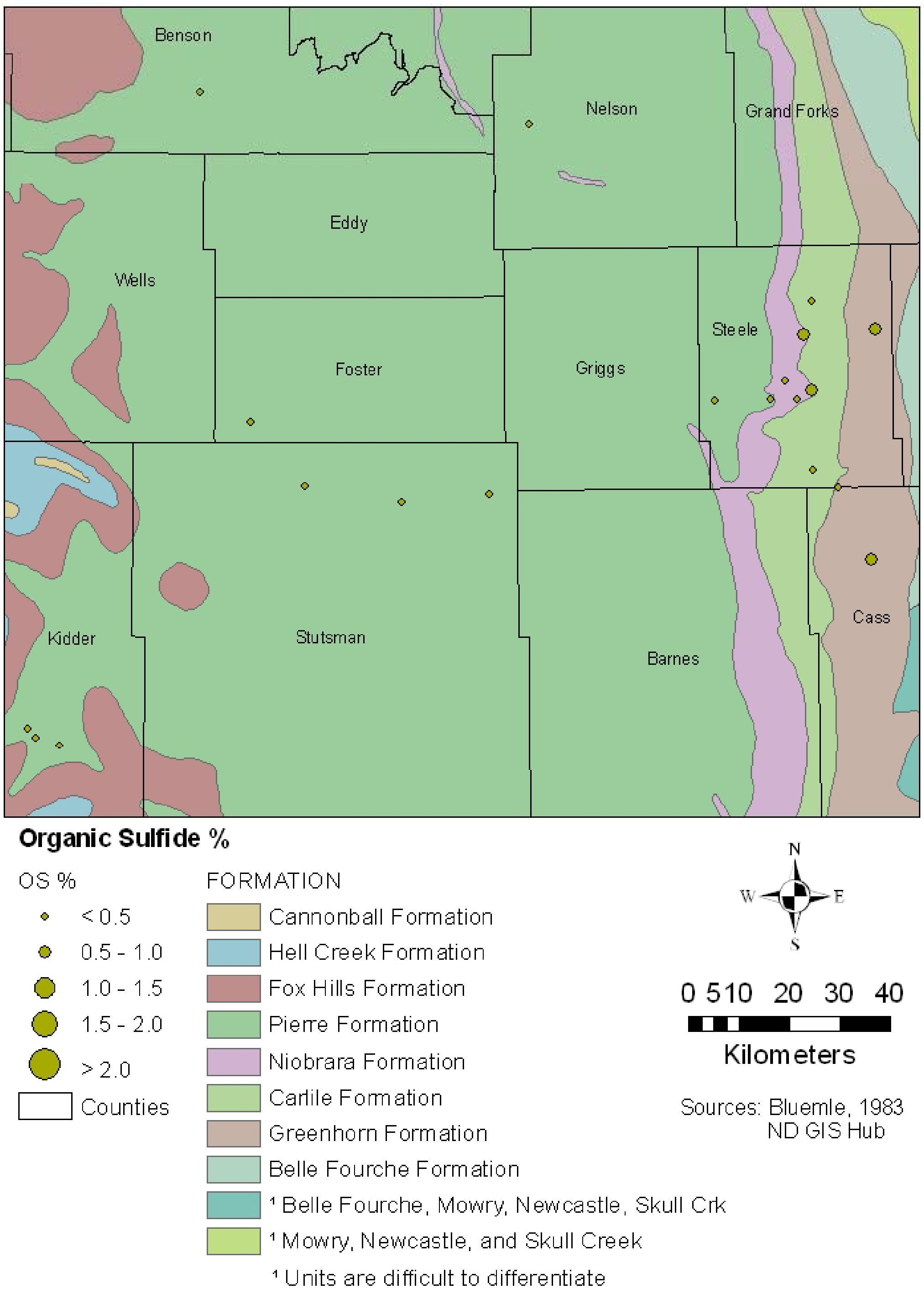

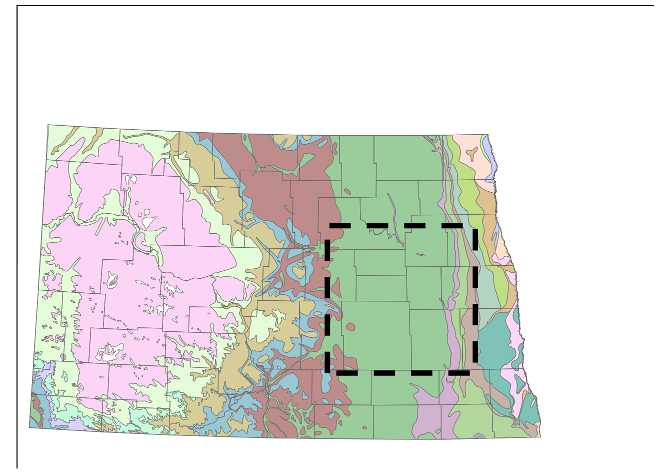

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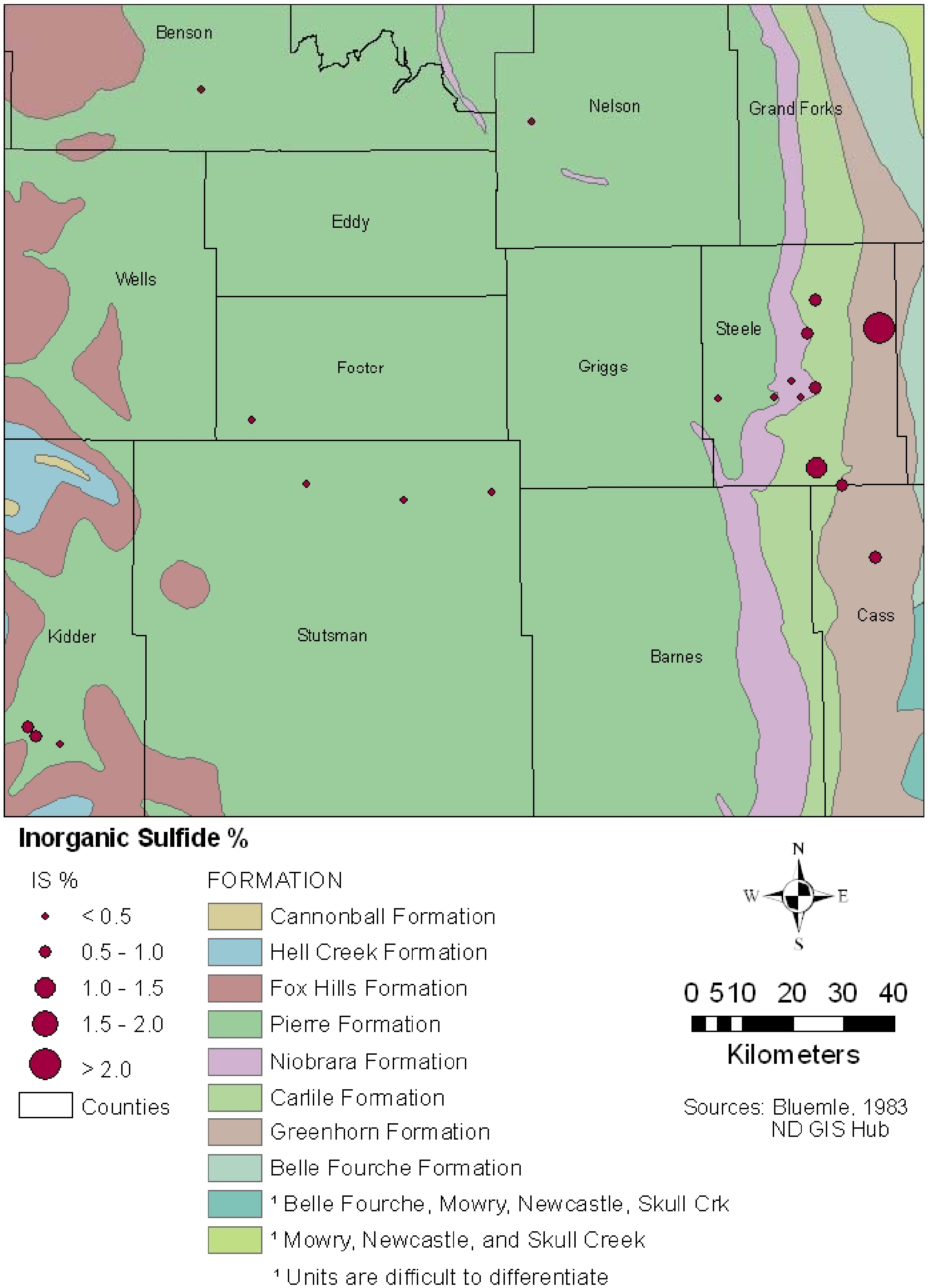

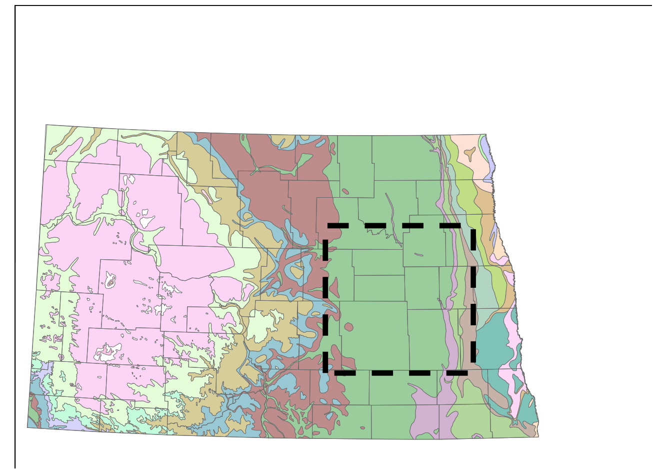

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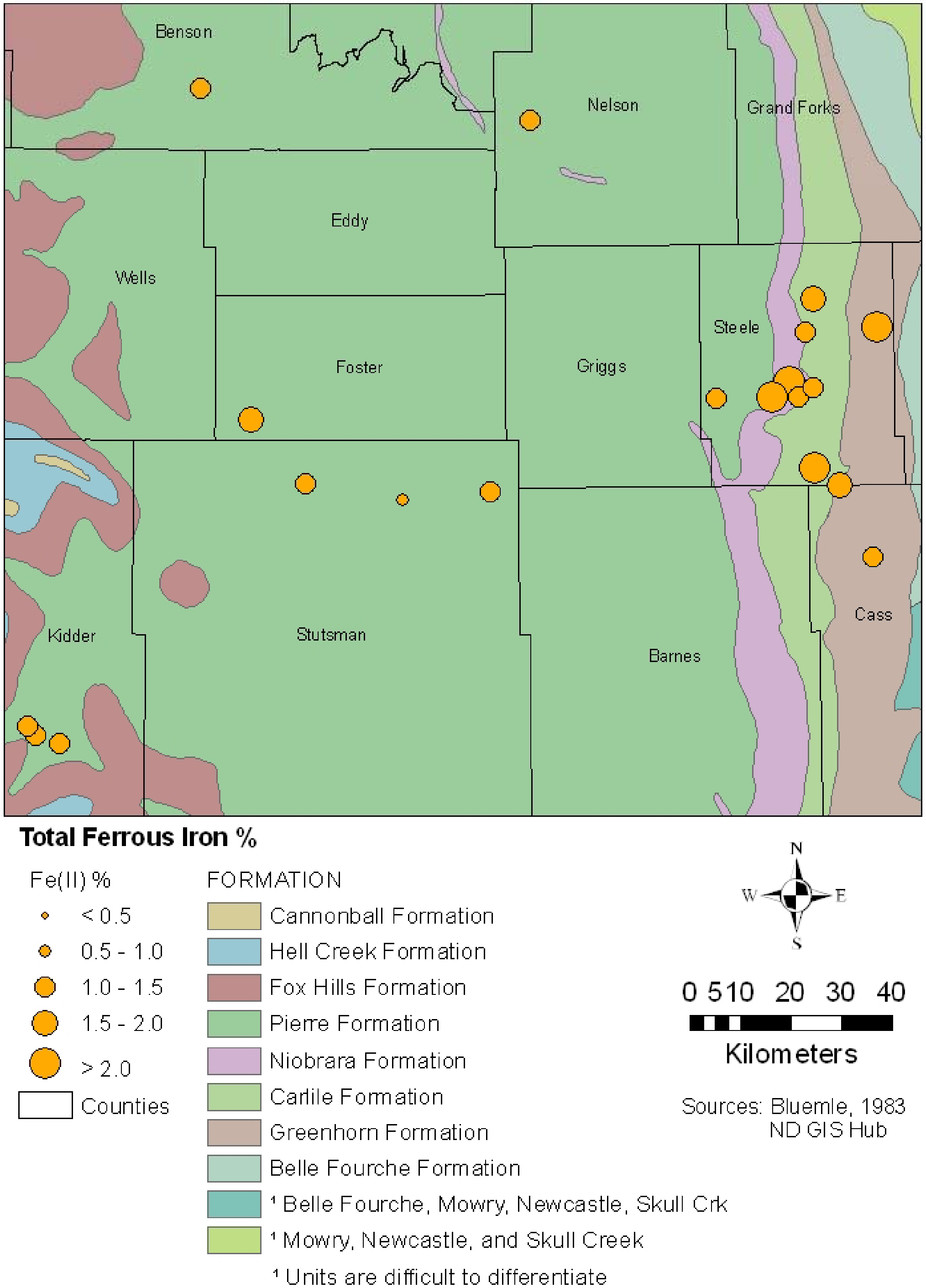

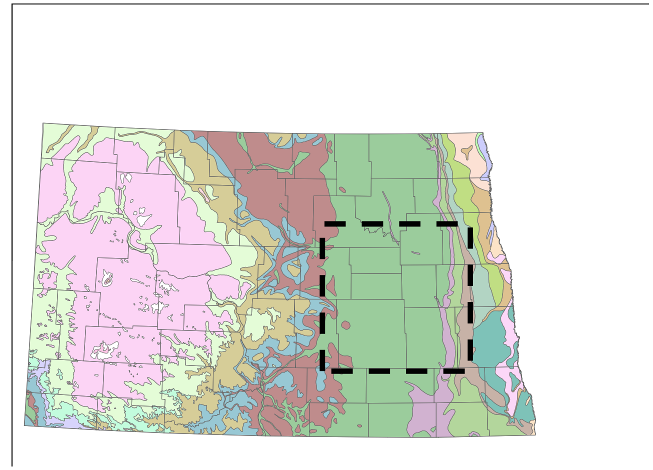

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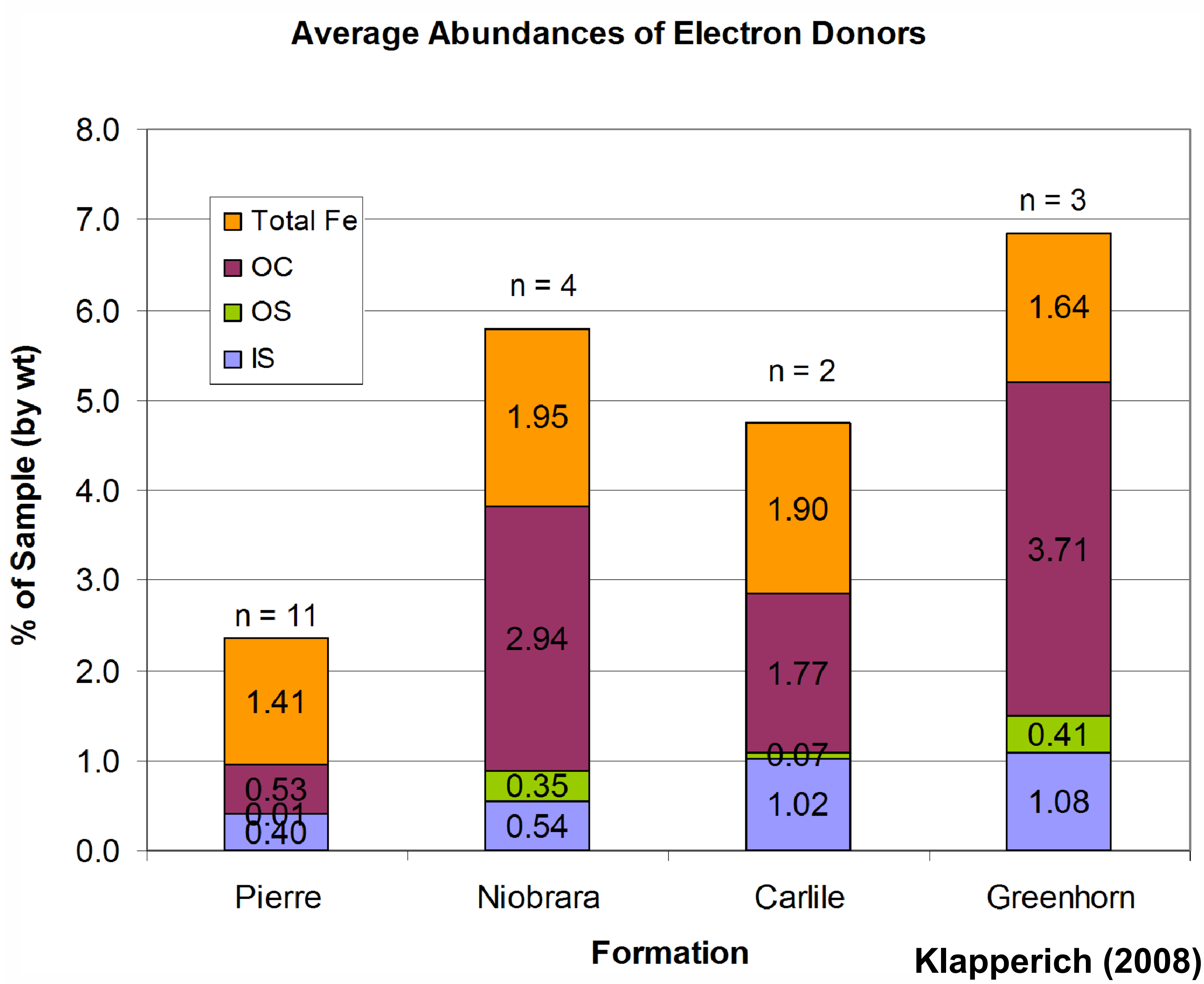
Average Abundances of Electron Donors
% of Sample (by wt)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Total Fe
OC
OS
IS
n = 11
1.41
0.53
0.01
0.40
n = 4
1.95
2.94
0.35
0.54
n = 2
1.90
1.77
0.07
1.02
n = 3
1.64
3.71
0.41
1.08
Pierre
Niobrara
Carlile
Greenhorn
Formation
Klapperich (2008)

Statistical Results

Spearman test (nonparametric) for + correlation				
Ho: No + correlation of the two donors' average values, α = 0.05.				
	IS	OS	OC	Fe
IS	x	Ho rejected	Ho rejected	Ho NOT rejected*
OS		x	Ho rejected	Ho NOT rejected
OC			x	Ho NOT rejected
Fe				x
Longitude	Ho rejected	Ho rejected	Ho rejected	Ho NOT rejected

* Rejected at α = 0.1

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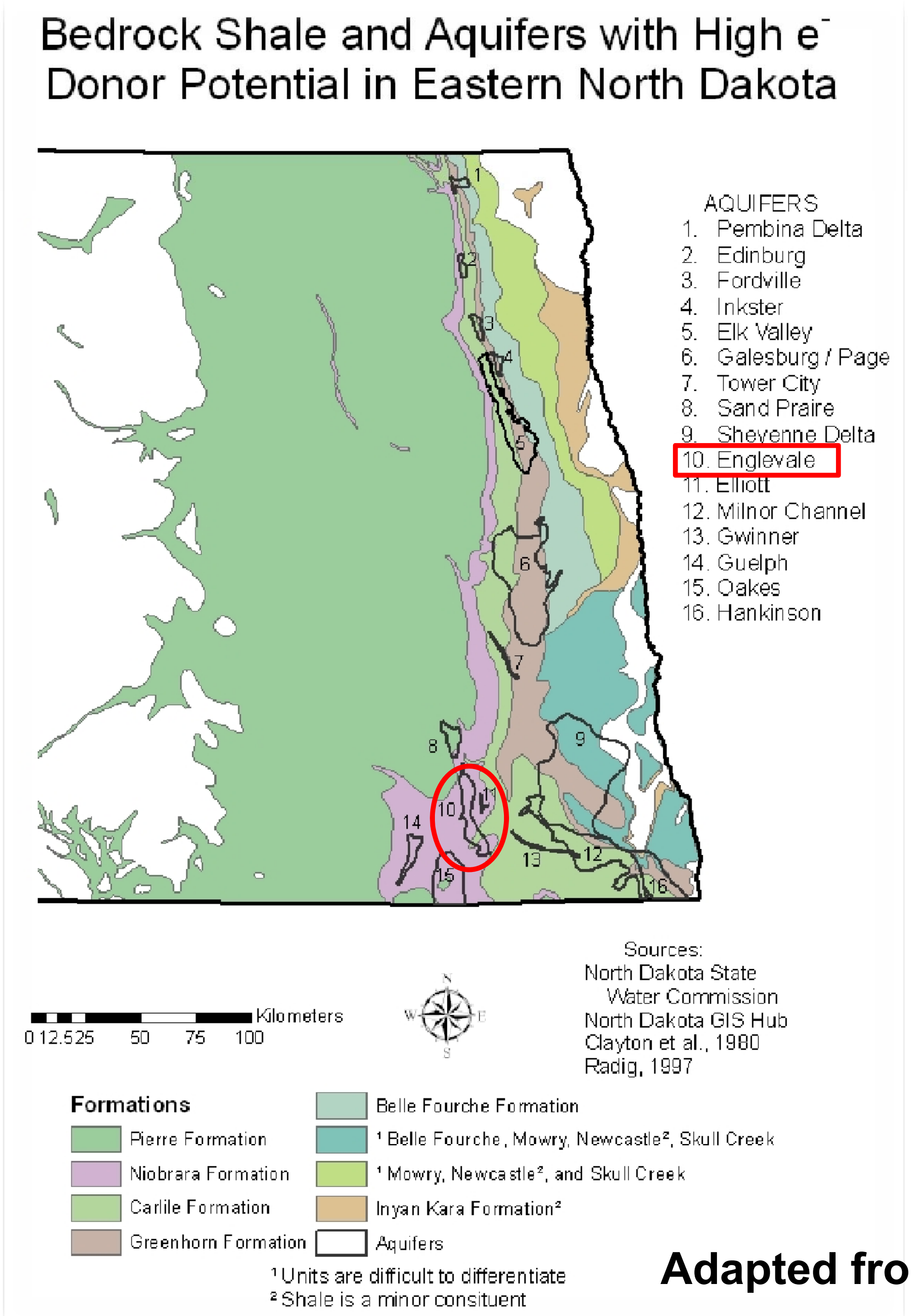
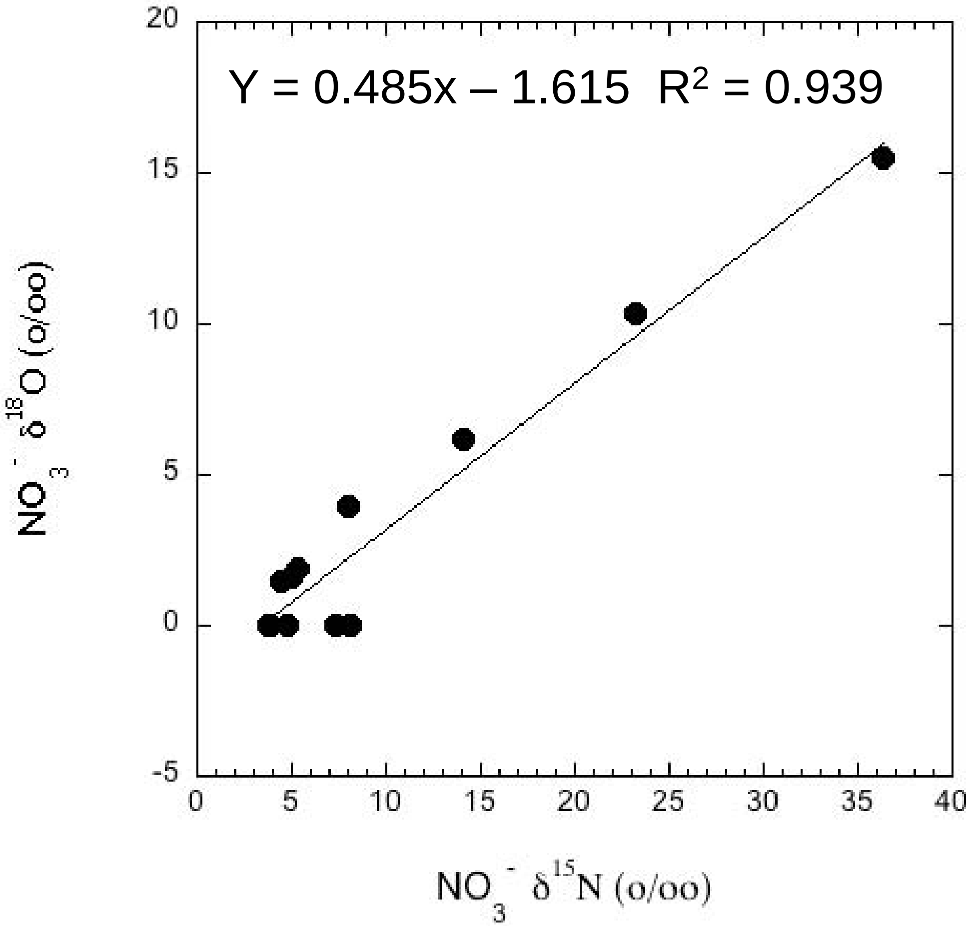


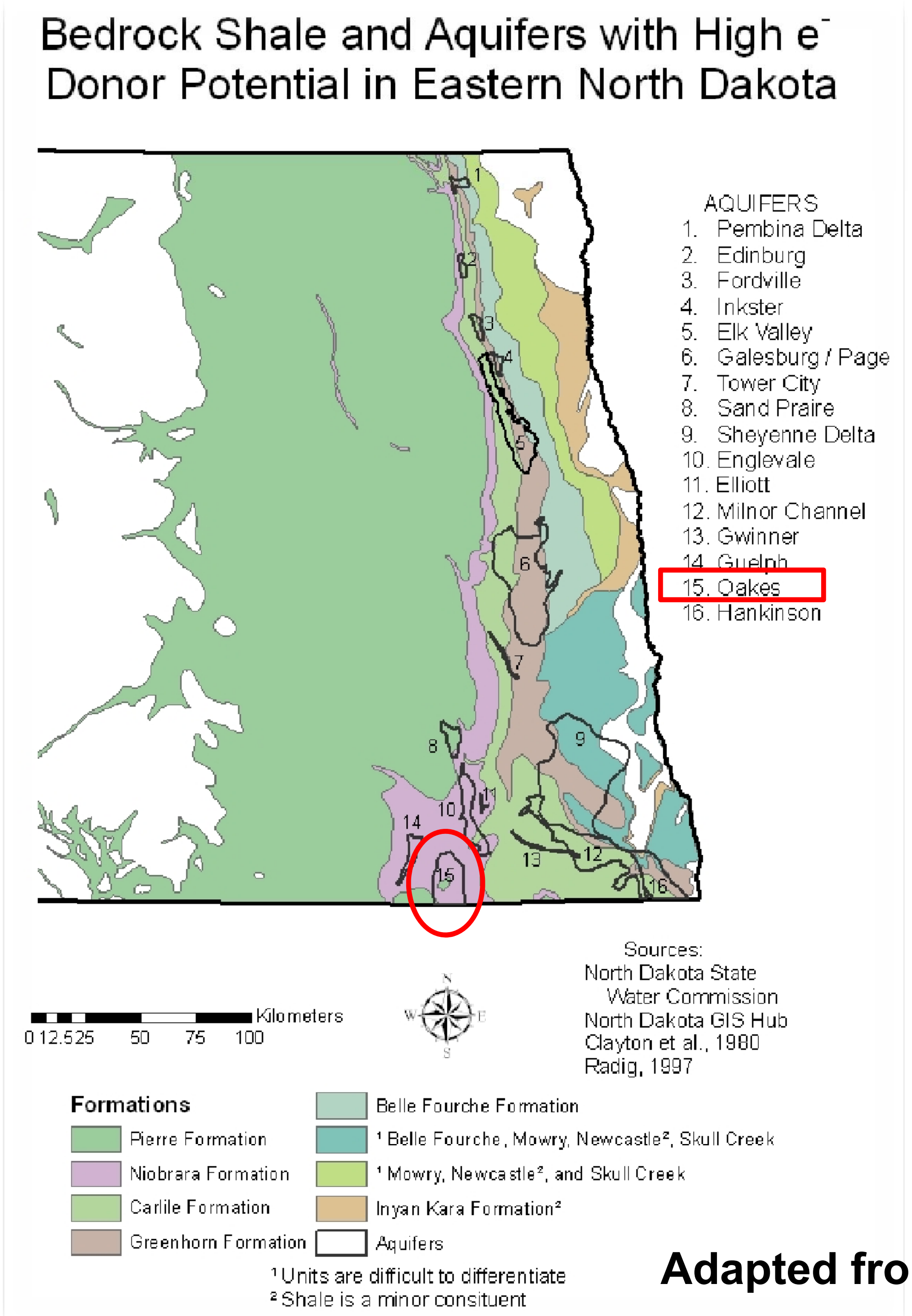
Adapted from Klapperich (2008)

^{18}O vs. ^{15}N of Nitrate in Samples from the Englevale Aquifer



Composite ^{18}O vs. ^{15}N data for Englevale Fall 2006 water samples.

(W. Schuh, ND State Water Commission, personal communication)



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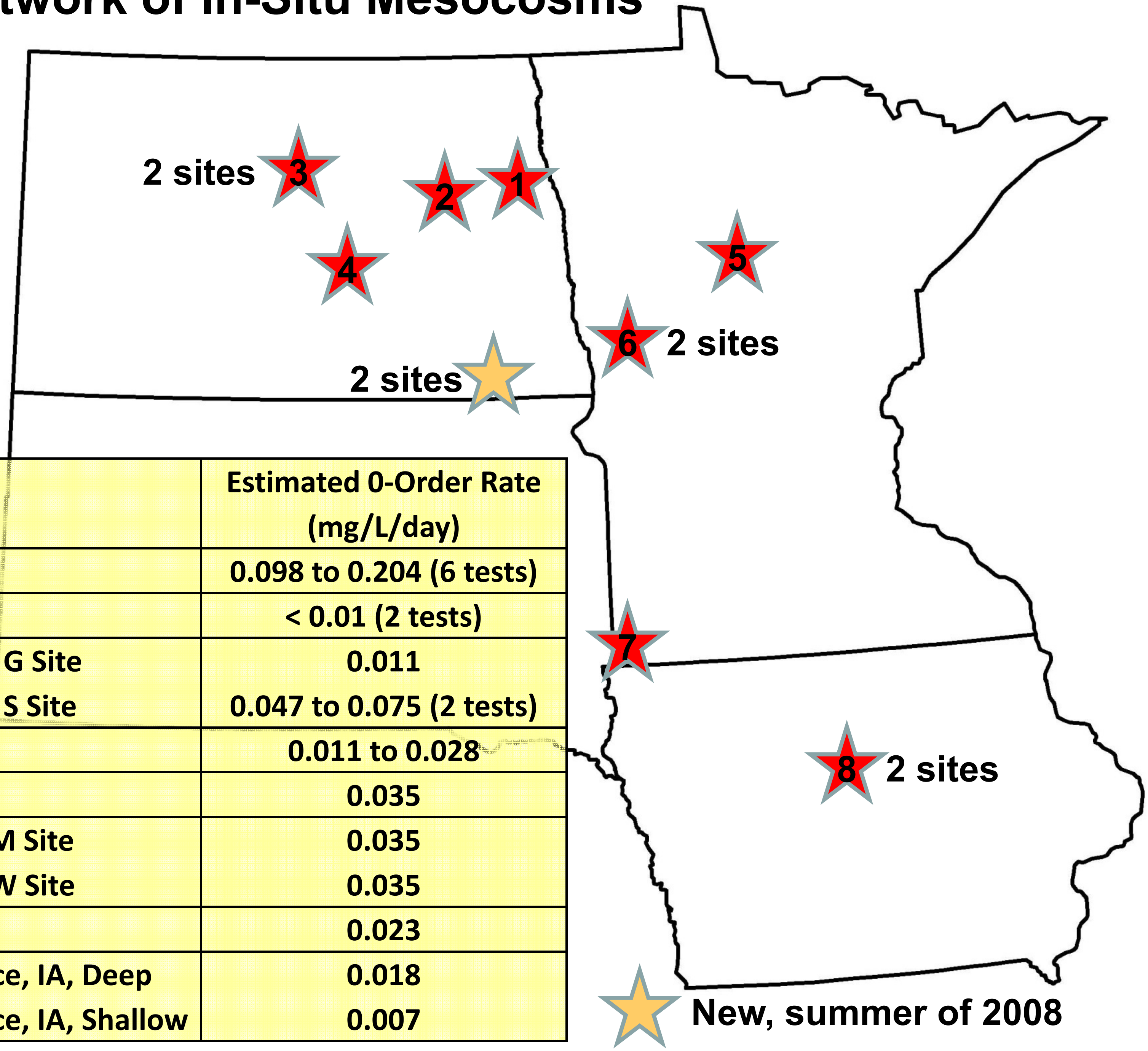

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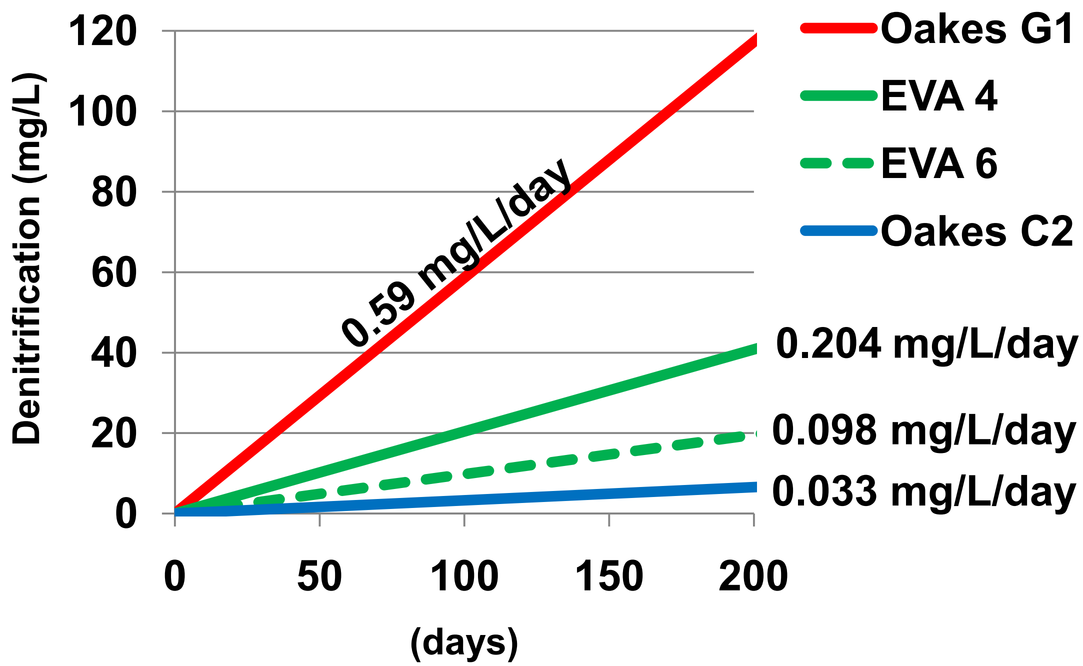
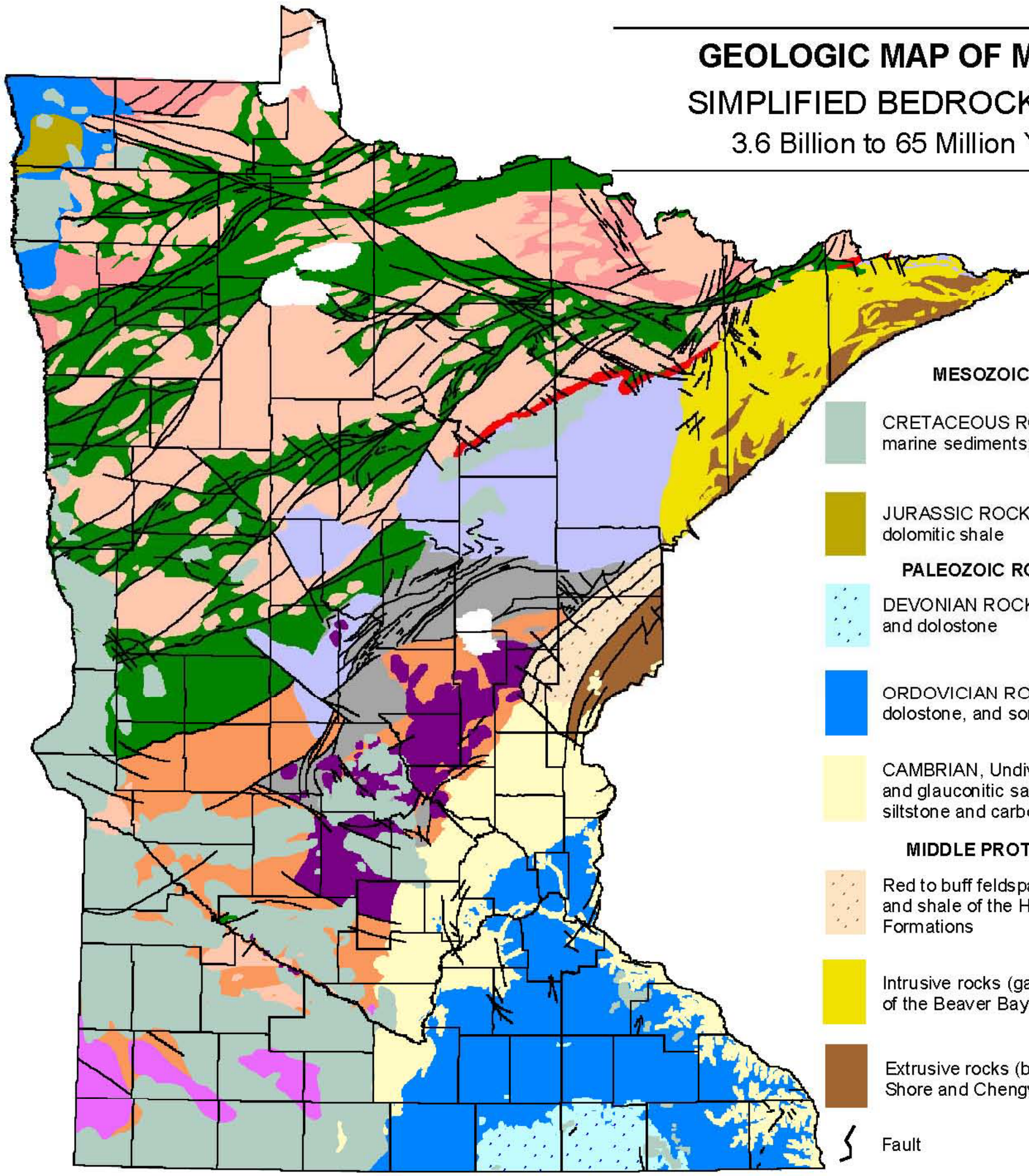
Denitrification: EVA vs. Oakes



GEOLOGIC MAP OF MINNESOTA

SIMPLIFIED BEDROCK GEOLOGY

3.6 Billion to 65 Million Years Ago



DESCRIPTION OF MAP UNITS

(mya = million years ago, bya = billion years ago)

MESOZOIC ROCKS (225 to 65 mya)

CRETACEOUS ROCKS, Undivided - Dominantly marine sediments; shale and sandstone

JURASSIC ROCKS, Undivided - Reddish brown dolomitic shale

PALEOZOIC ROCKS (600 to 225 mya)

DEVONIAN ROCKS, Undivided - Limestone and dolostone

ORDOVICIAN ROCKS, Undivided - Limestone, dolostone, and some sandstone and shale

CAMBRIAN, Undivided - Quartzose and glauconitic sandstone; lesser amounts of siltstone and carbonate

MIDDLE PROTEROZOIC (1.6 to 0.9 bya)

Red to buff feldspathic to quartzose sandstone and shale of the Hinckley and Fond du Lac Formations

Intrusive rocks (gabbro, granite and anorthosite) of the Beaver Bay and Duluth Complexes

Extrusive rocks (basalt and rhyolite) of the North Shore and Chengwatana Volcanic Groups

Fault

EARLY PROTEROZOIC ROCKS (2.5 to 1.6 bya)

Sedimentary and Metamorphic rocks of the Sioux Quartzite formation

Intrusive rocks (granite and granodiorite) of the Penokean orogeny

Meta- and sedimentary rocks (argillite, slate, shale, graywacke) of the Virginia, Thomson and Rove Formations

Iron-Formation (hematite and taconite) of the Biwabik and Gunflint Iron Formations

Metasedimentary rocks (slate, quartzite and metagraywacke) intercalated with volcanic rocks and iron formations

LATE ARCHEAN ROCKS (3 to 2.5 bya)

Intrusive rocks (granite, granodiorite and tonalite) of the Algoman Orogeny

Meta-igneous rocks (granitic gneiss, schist and granite-rich migmatite) grading into granitic rock

Meta-igneous extrusive rocks of mafic to felsic composition (greenstones/amphibolites) and metasedimentary rocks

MIDDLE ARCHEAN ROCKS (3.6 to 3 bya)

Quartzofeldspathic gneiss, amphibolite, and other high-grade metamorphic rocks

Bedrock map based on data from the University of Minnesota - Minnesota Geological Survey, *Bedrock Map of Minnesota, Bedrock Geology, 1993* - Compiled by G.B. Morey.

Simplified description by C.R. Howe, 2000, Mn/DOT

8/15/01

Ground Water Monitoring&Remediation

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by Michael D. Trojan, Moira E. Campion, Jennifer S. Maloney, James M. Stockinger, and Erin P. Eid

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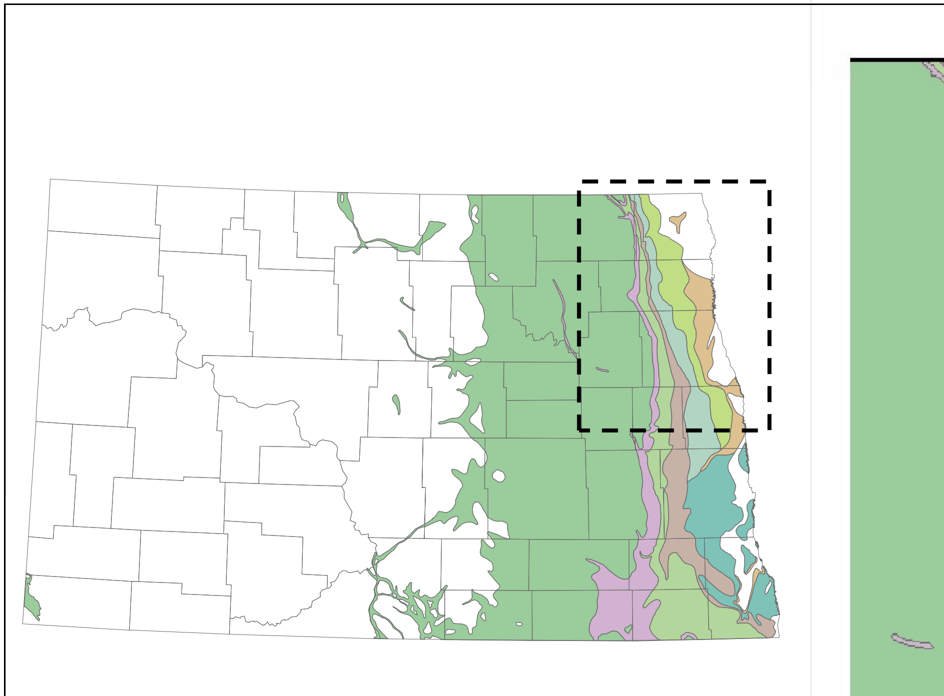

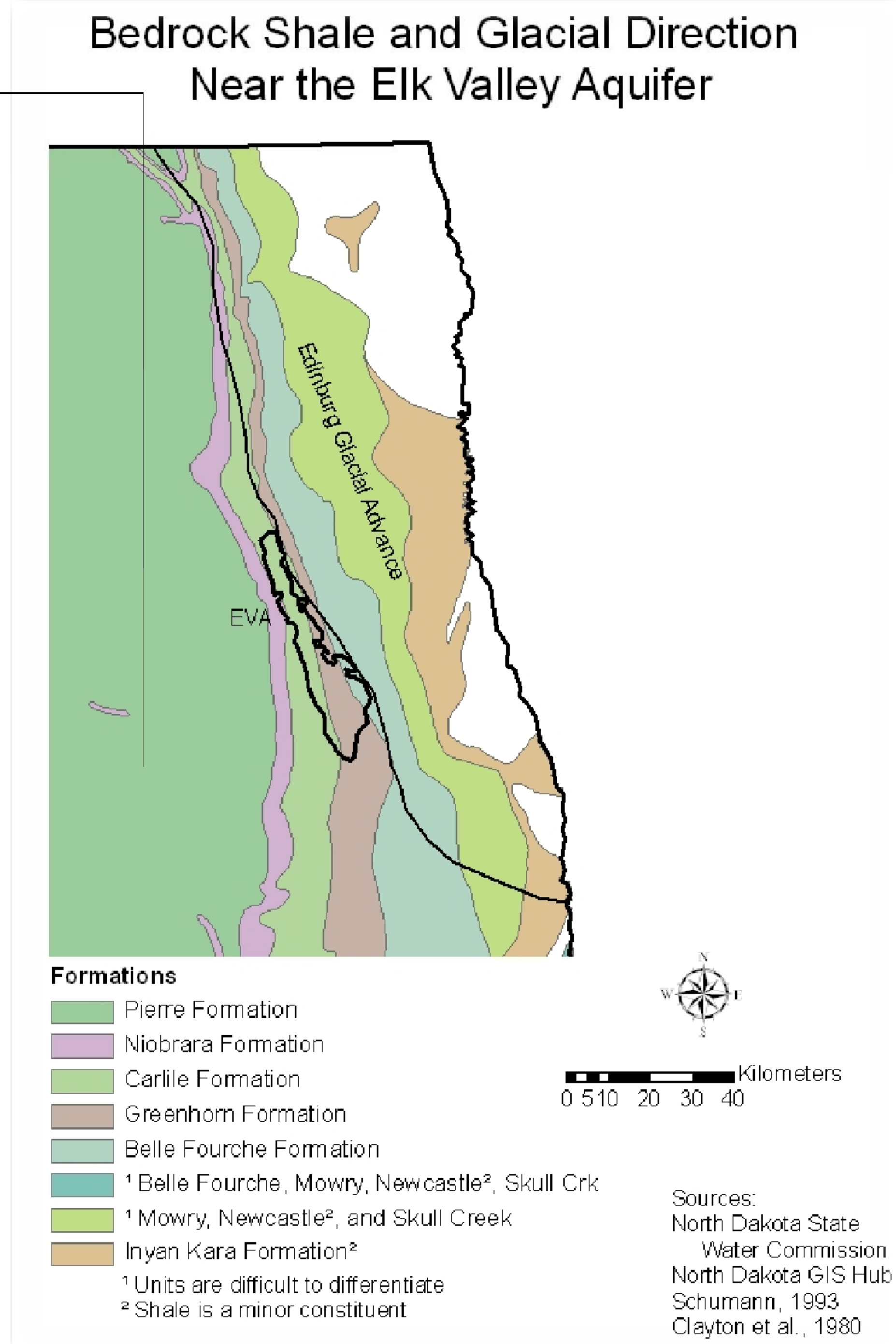

Adapted from Klapperich (2008)

Northern European Plains (Pätsch, 2003)

Ghent, Belgium (237,250)

The Hague, Netherlands (475,904)

Viborg, Denmark (91,405)

La Havre, France (190,905)

(European populations: Wikepedia)

Northern European Plains (Pätsch, 2003)

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Hague, ND (91)

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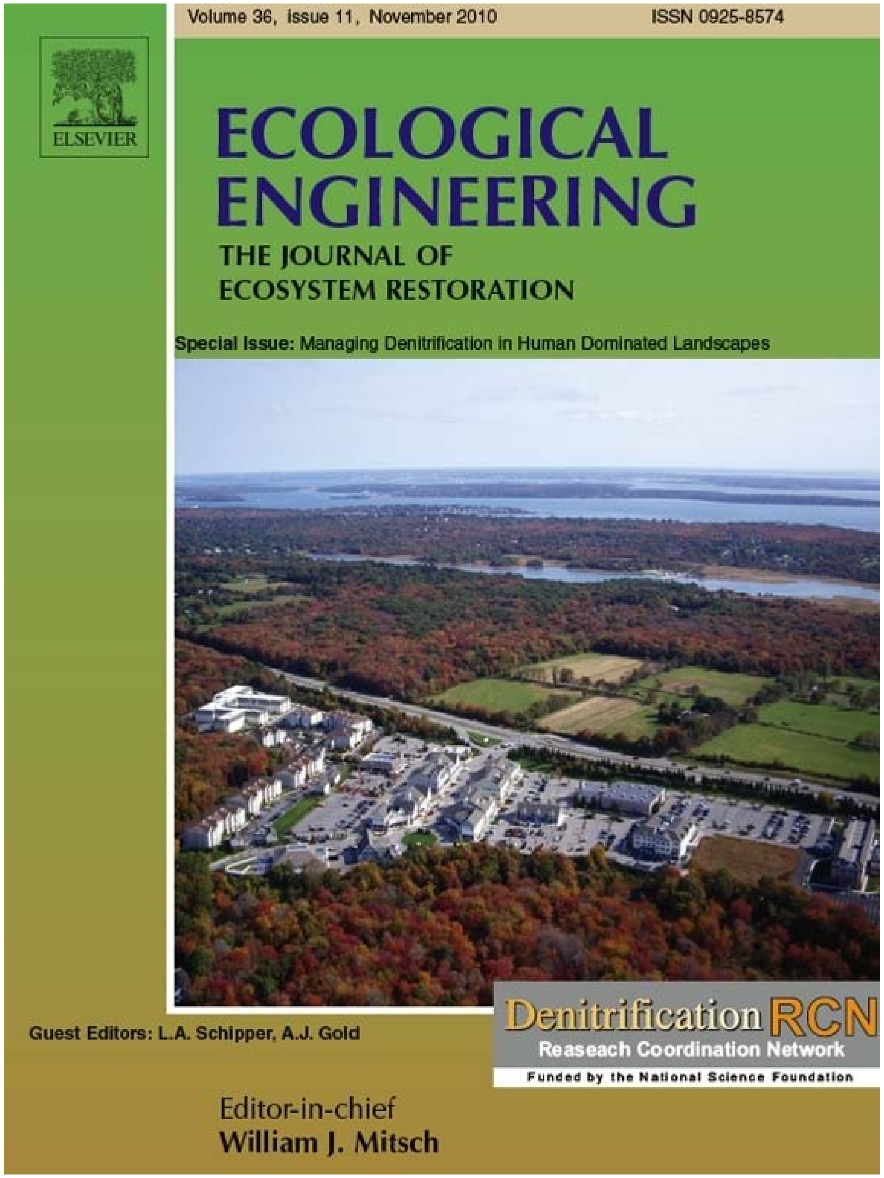
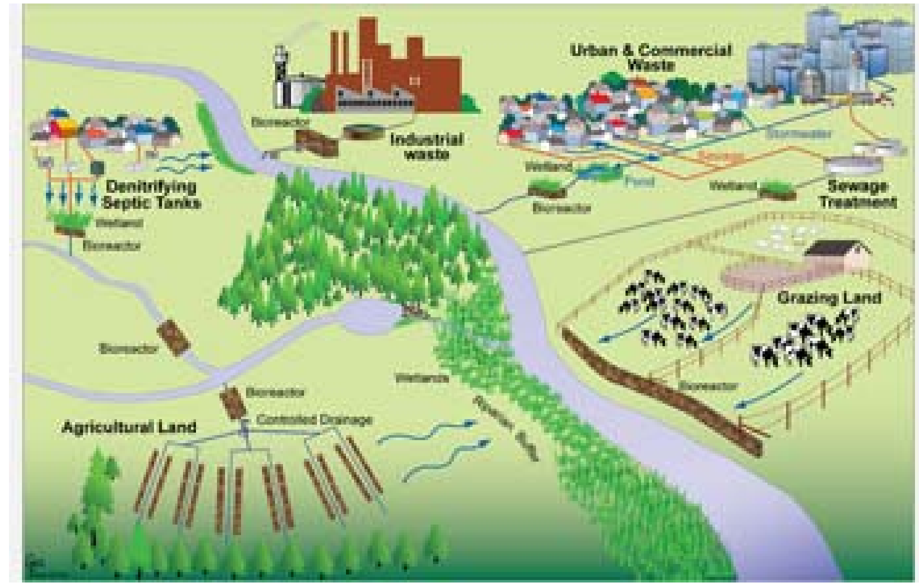
Viborg, SD (832)

La Havre, France (190,905)
Havre, MT (9,621)

(European populations: Wikepedia)

Enhanced Denitrification



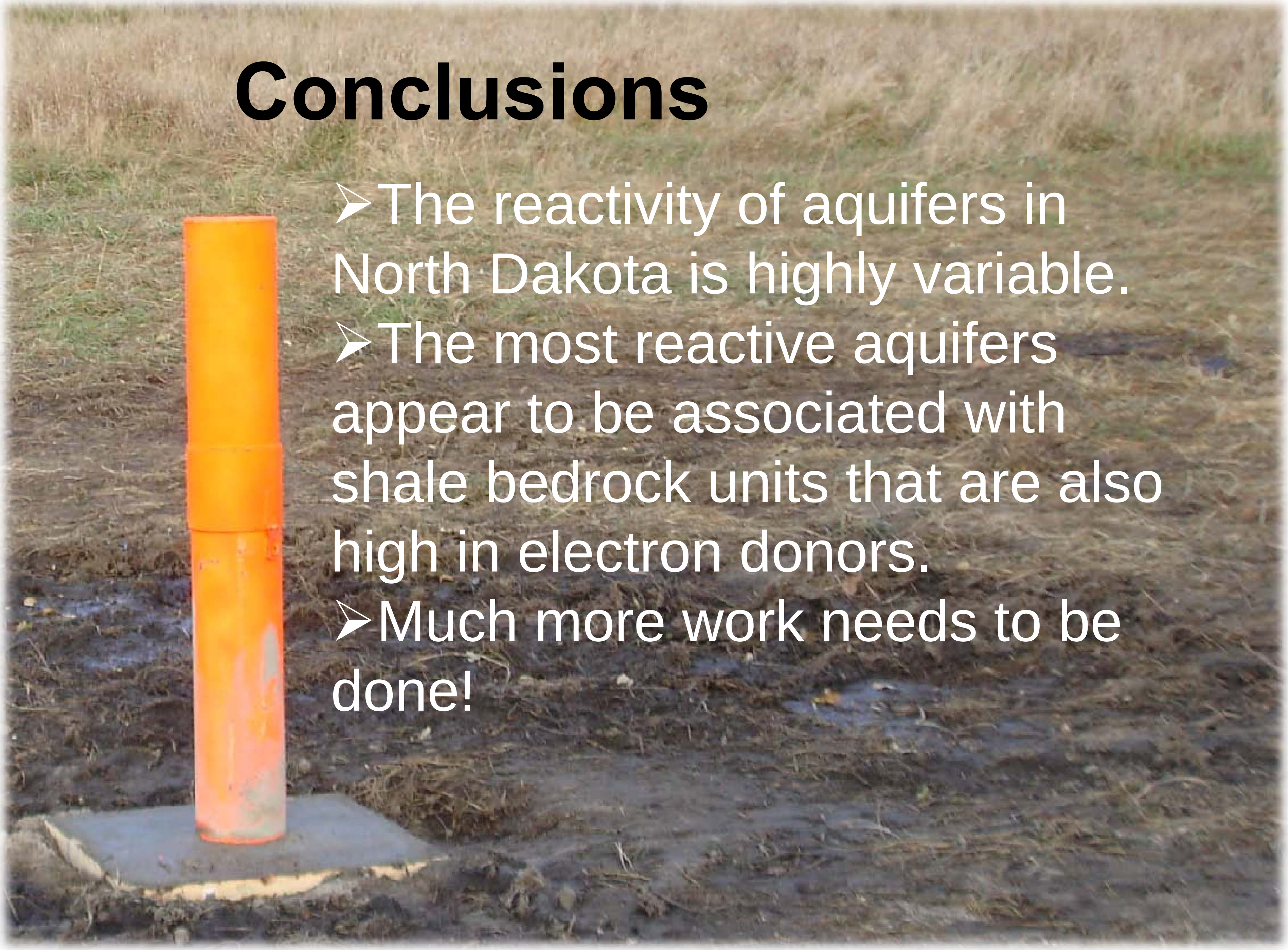


Max Oulton, University of Waterloo

Corey Mitchell, University of Illinois

NSF Press Release 10-206

http://www.nsf.gov/news/news_summ.jsp?cntn_id=117976&org=DEB&from=home



Conclusions

- The reactivity of aquifers in North Dakota is highly variable.
- The most reactive aquifers appear to be associated with shale bedrock units that are also high in electron donors.
- Much more work needs to be done!

Acknowledgments

- Minnesota Department of Agriculture
- Minnesota Department of Health
- Minnesota Pollution Control Agency

Acknowledgments, Part 2

- ND State Water Commission
- ND Department of Health
- ND WRRI (USGS 104B)
- USGS NIWR (USGS 104G, #2006ND126G)
- US BR (Coop. Agreement #08FC602282)
- Ryan Klapperich
- Thank you!