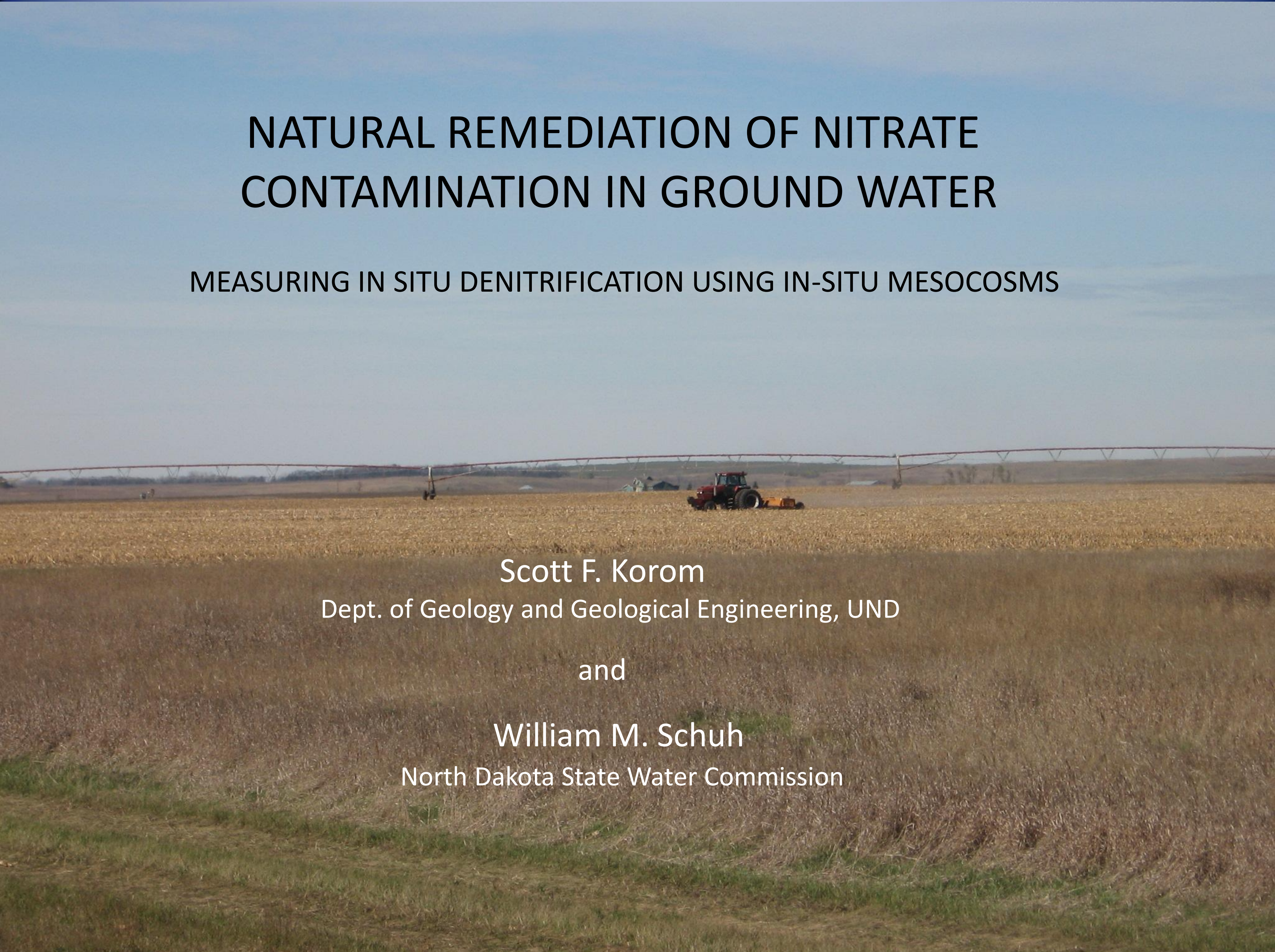

# NATURAL REMEDIATION OF NITRATE CONTAMINATION IN GROUND WATER

## MEASURING IN SITU DENITRIFICATION USING IN-SITU MESOCOSMS

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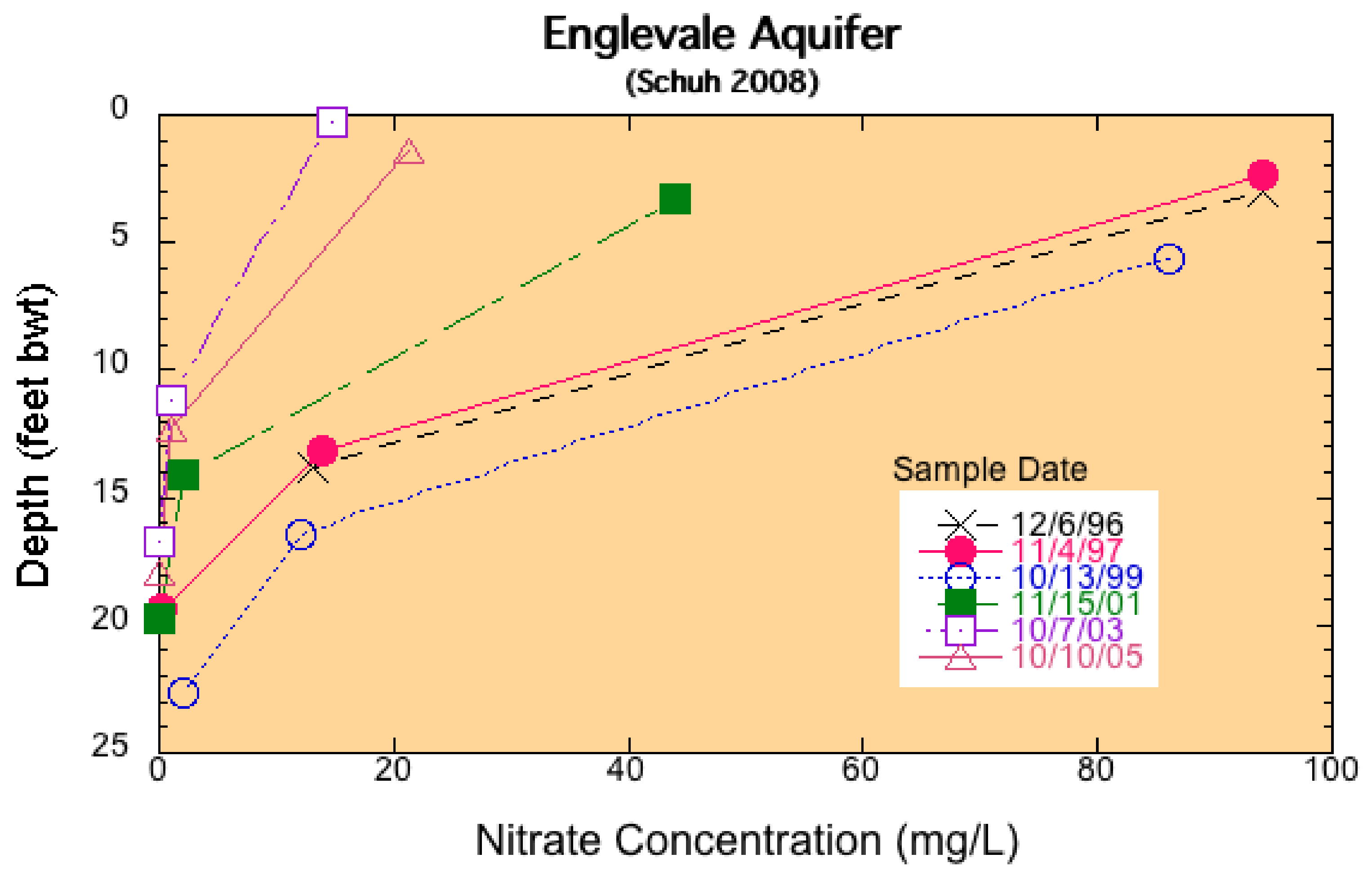
# NITRATE FACTS

- Nitrate - number One Agricultural Contaminant of Ground Water Worldwide (Spalding and Exner 1993) and in the United States and Canada (Burkhart and Kolpin (1993)
- Nitrate can Cause Methemoglobinemia in Humans and Livestock and can potentially be fatal

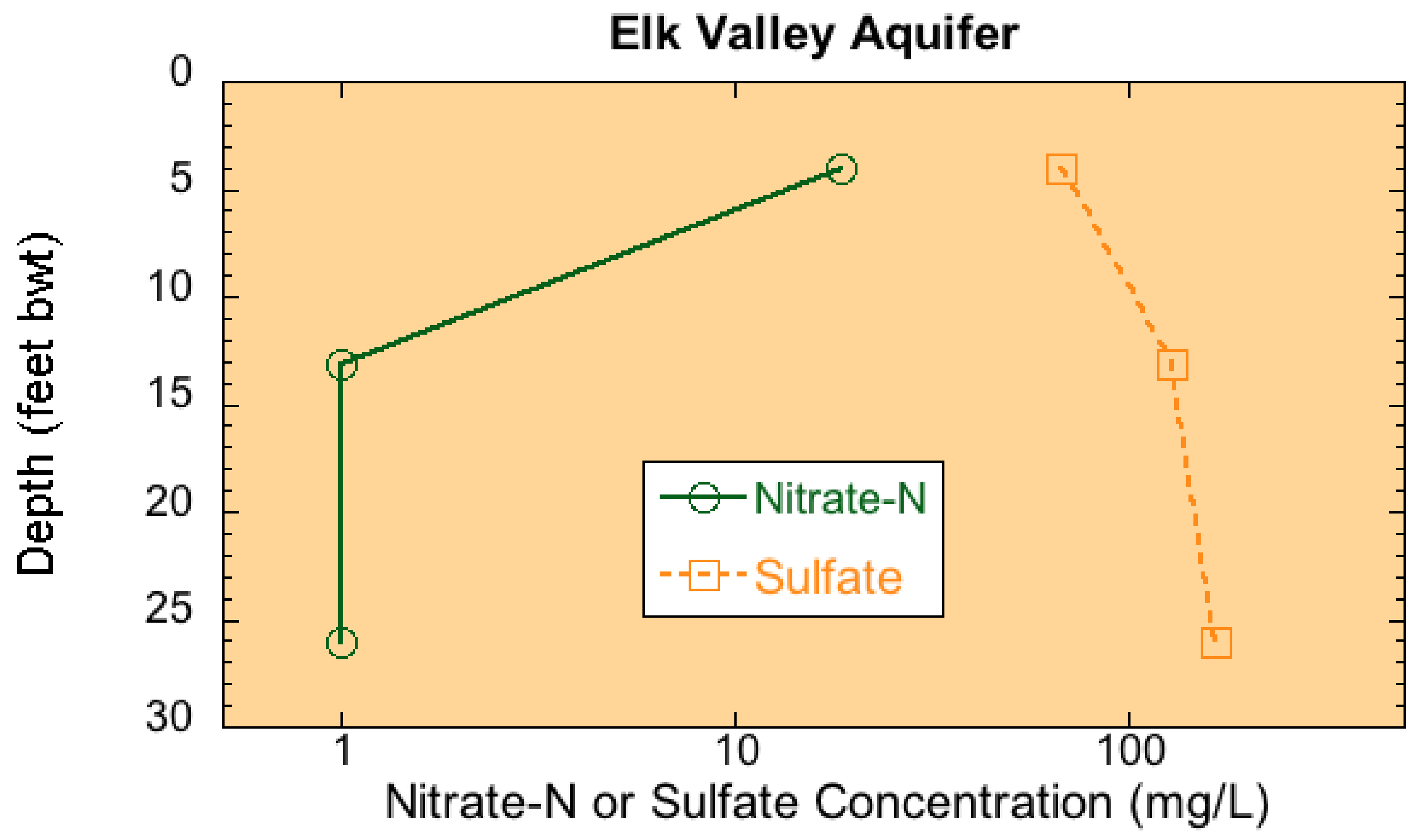
U.S. EPA - 10 mg/L Nitrate-N
WHO - 11.3 mg/L

- Toxicological Interpretation is Complicated by Stratification

# NITRATE STRATIFICATION

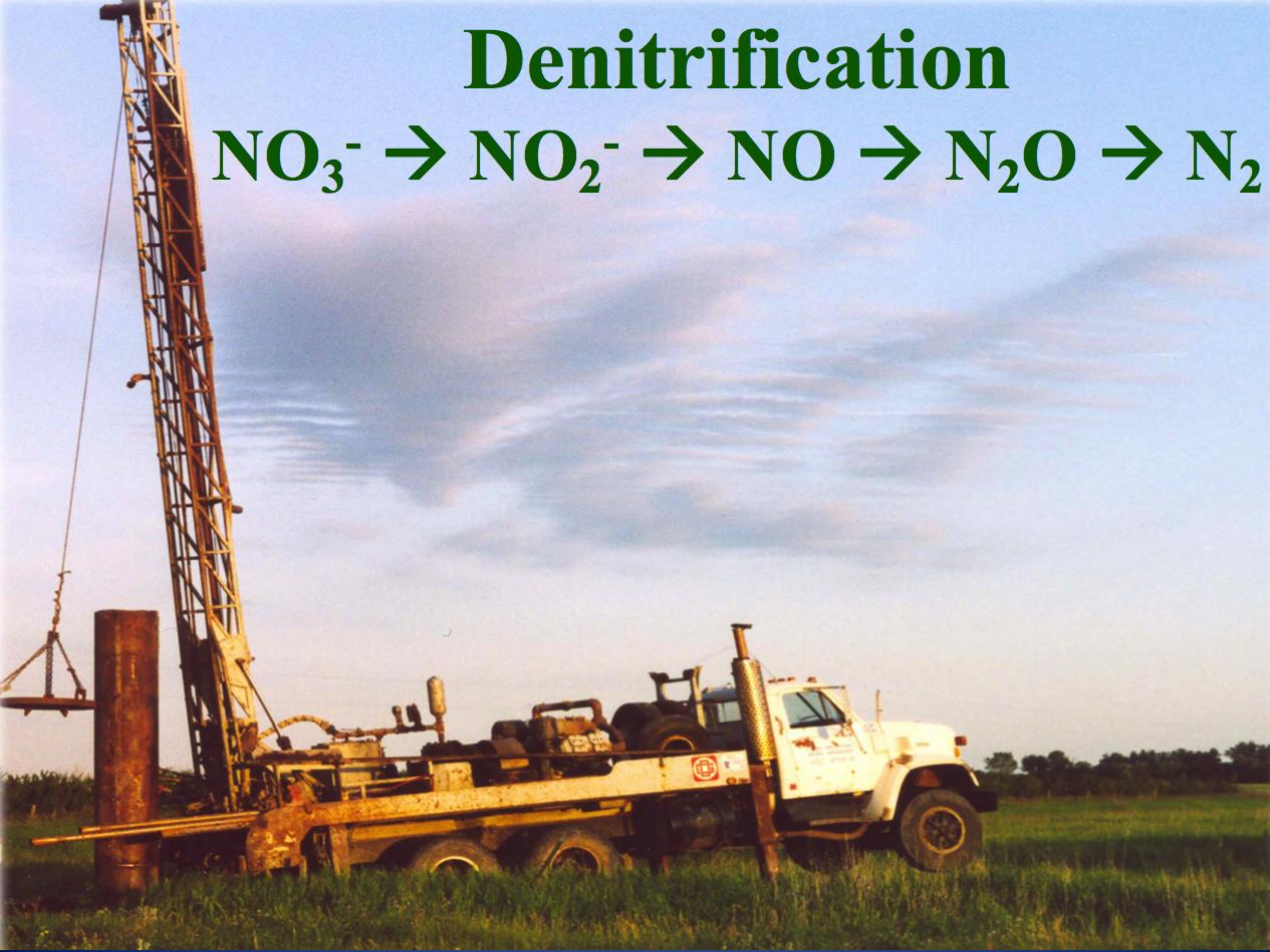


# NITRATE AND SULFATE STRATIFICATION



# Denitrification

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

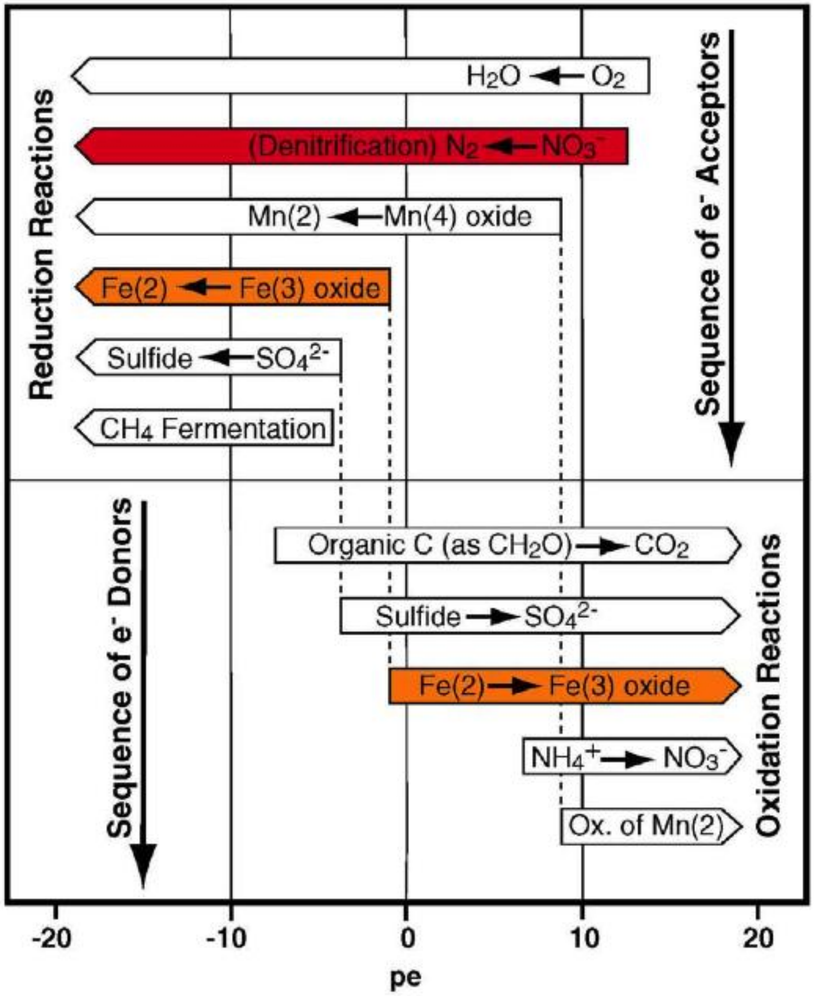


# Denitrification

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

**Four Requirements (Firestone, 1982)**

❶ Nitrous oxides
❷ Suitable bacteria
❸ Restricted $O_2$ availability
❹ Suitable $e^-$ donors

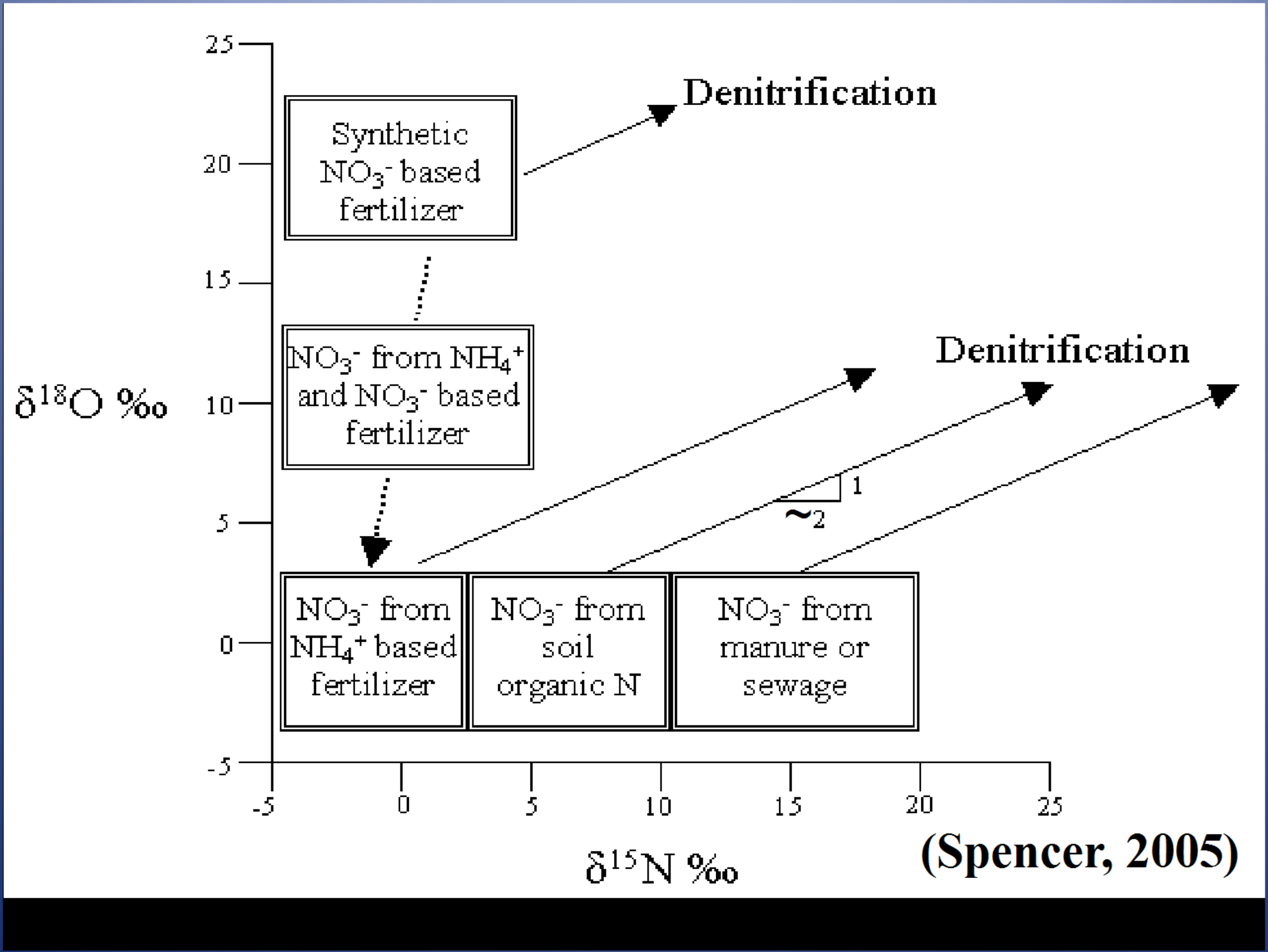


**Adapted from Korom et al. (2009)**

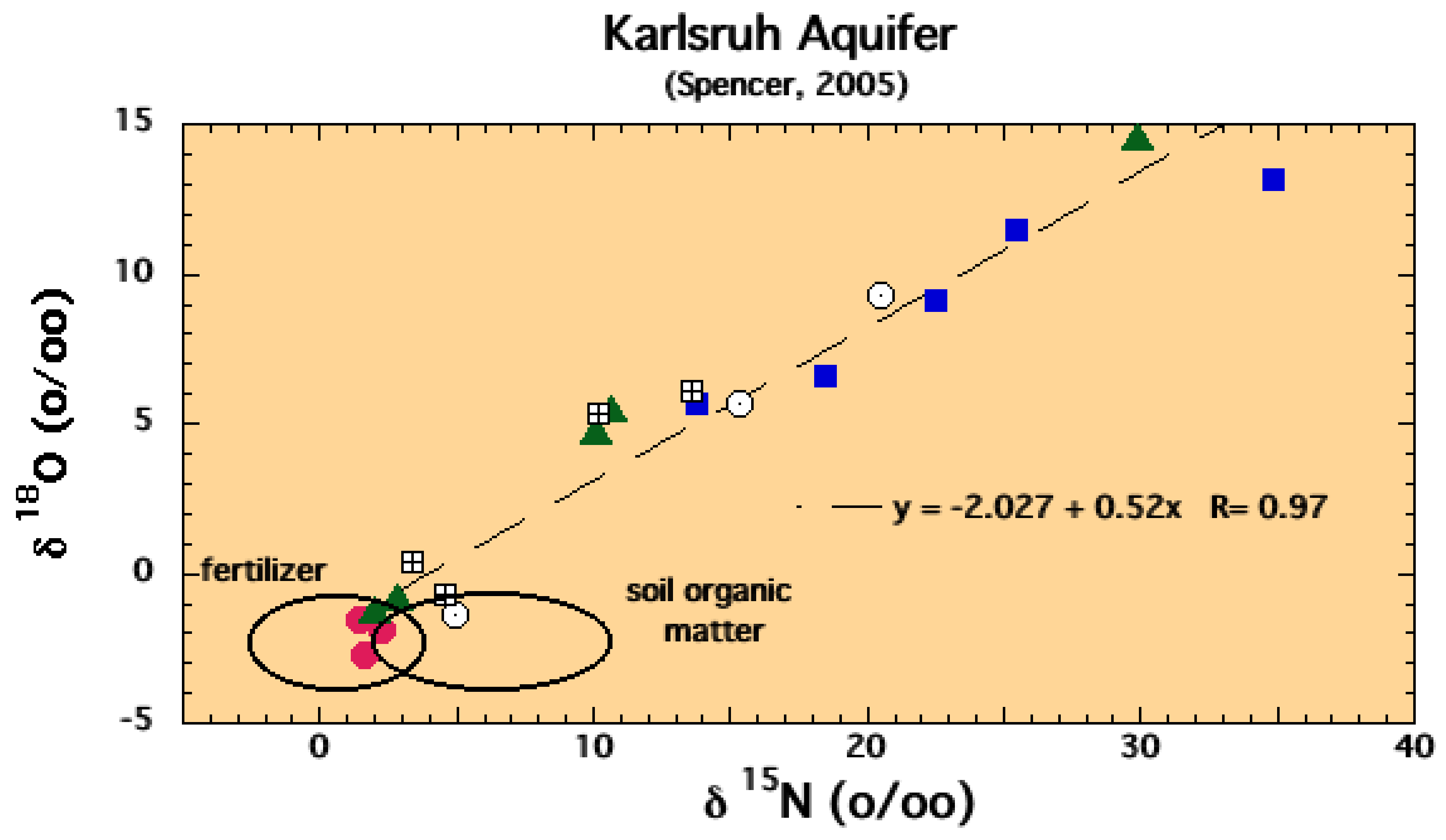
# What Do We Need to Know

1. What Are the Nitrate Sources?
2. Is Denitrification Occurring in ND Aquifers?
3. What Are the Denitrification Rates?
4. What are the Electron Donors?
5. What are the Electron Donor Sources and How Are They Related to Parent Materials?

# IS DENITRIFICATION OCCURRING? ISOTOPE INDICATORS

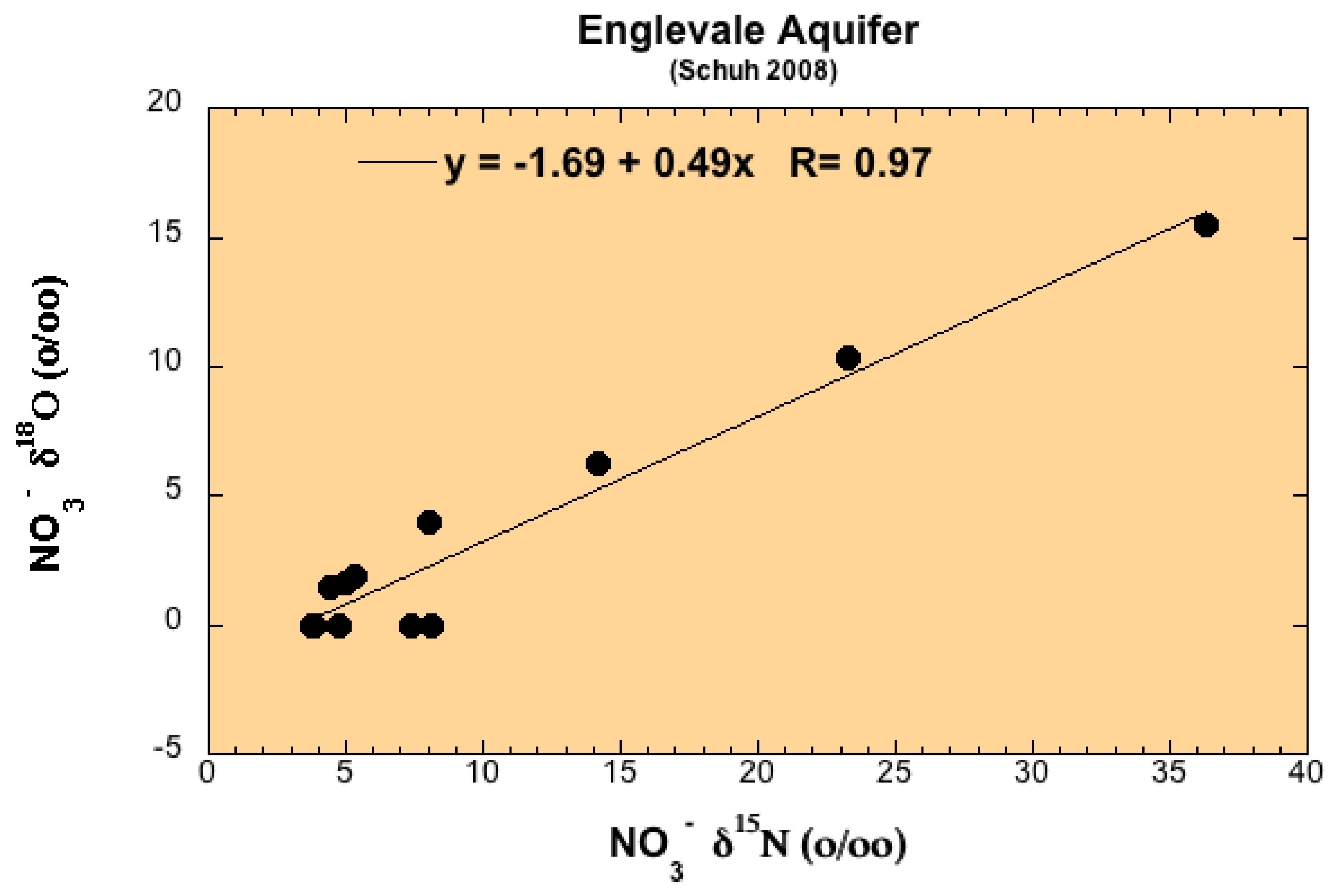


**(Spencer, 2005)**



Karlsruh Aquifer

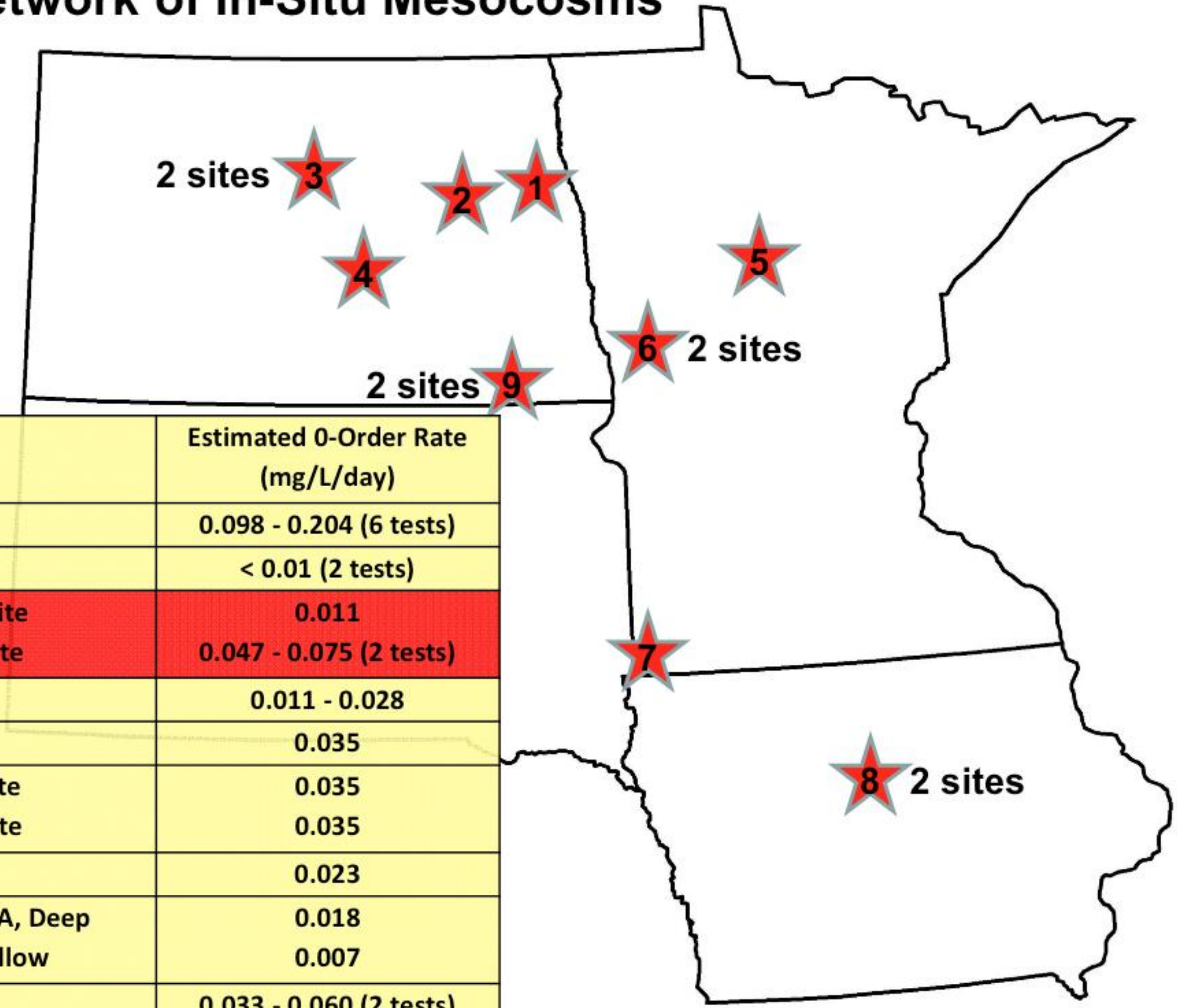
(Spencer, 2005)



## Englevale Aquifer

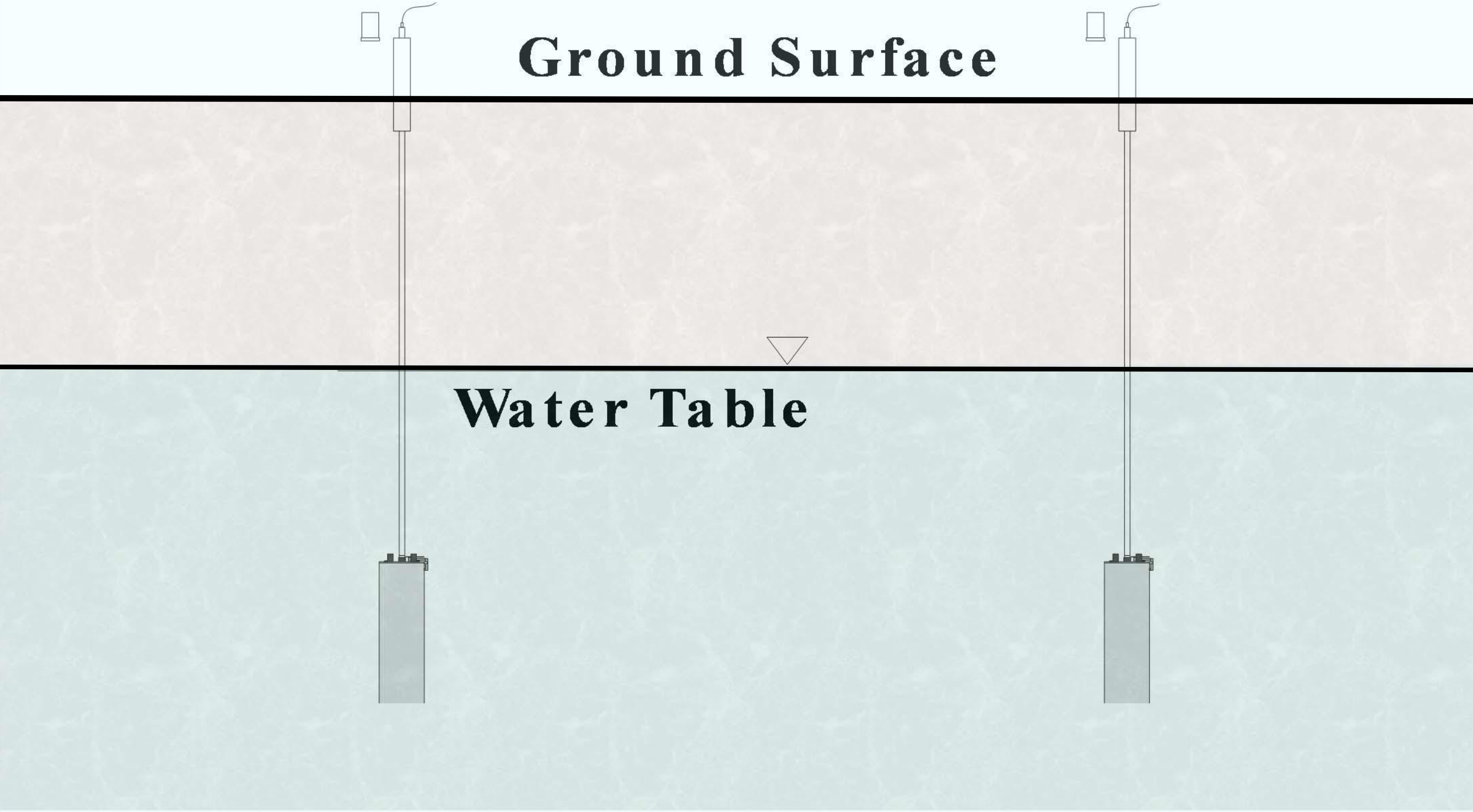
(Schuh 2008)

# Network of In-Situ Mesocosms



| Site | Estimated 0-Order Rate (mg/L/day) |
|---|---|
| 1. Larimore, ND | 0.098 - 0.204 (6 tests) |
| 2. Hamar, ND | < 0.01 (2 tests) |
| 3. Karlsruhe, ND, G Site | 0.011 |
| 3. Karlsruhe, ND, S Site | 0.047 - 0.075 (2 tests) |
| 4. Robinson, ND | 0.011 - 0.028 |
| 5. Akeley, MN | 0.035 |
| 6. Perham, MN, M Site | 0.035 |
| 6. Perham, MN, W Site | 0.035 |
| 7. Luverne, MN | 0.023 |
| 8. New Providence, IA, Deep | 0.018 |
| 8. New Prov., IA, Shallow | 0.007 |
| 9. Oakes C1 | 0.033 - 0.060 (2 tests) |
| 9. Oakes G1 | 0.28 - 0.59 (2 tests) |

# ISMs: Finished Product



Ground Surface

Water Table

# In-Situ

# Mesocosm

# Placement

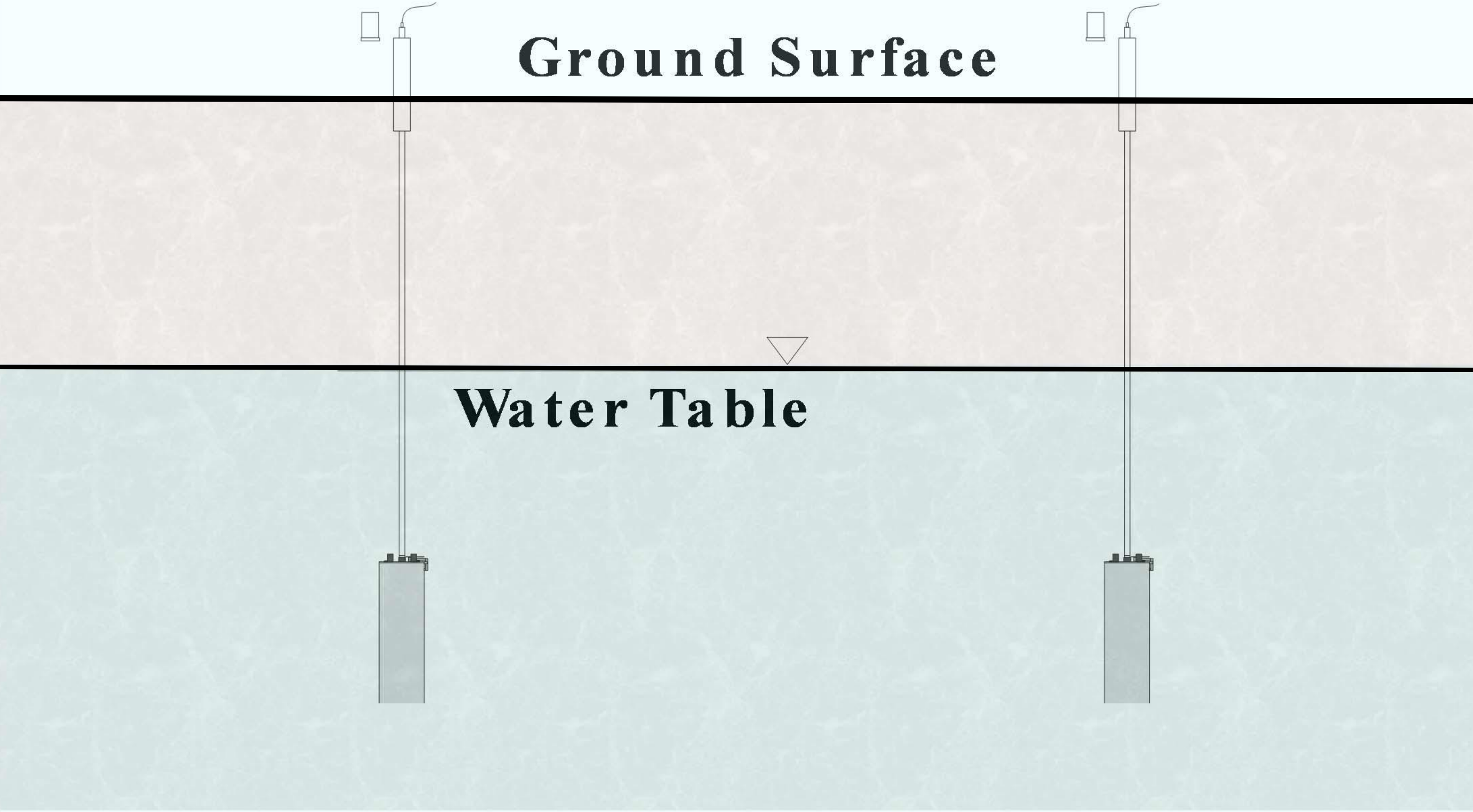
Protective Casing

# In-Situ Mesocosm Placement

## Bailing the Protective Casing

# In-Situ Mesocosm Placement
## “Driving the ISM”

# ISMs: Finished Product

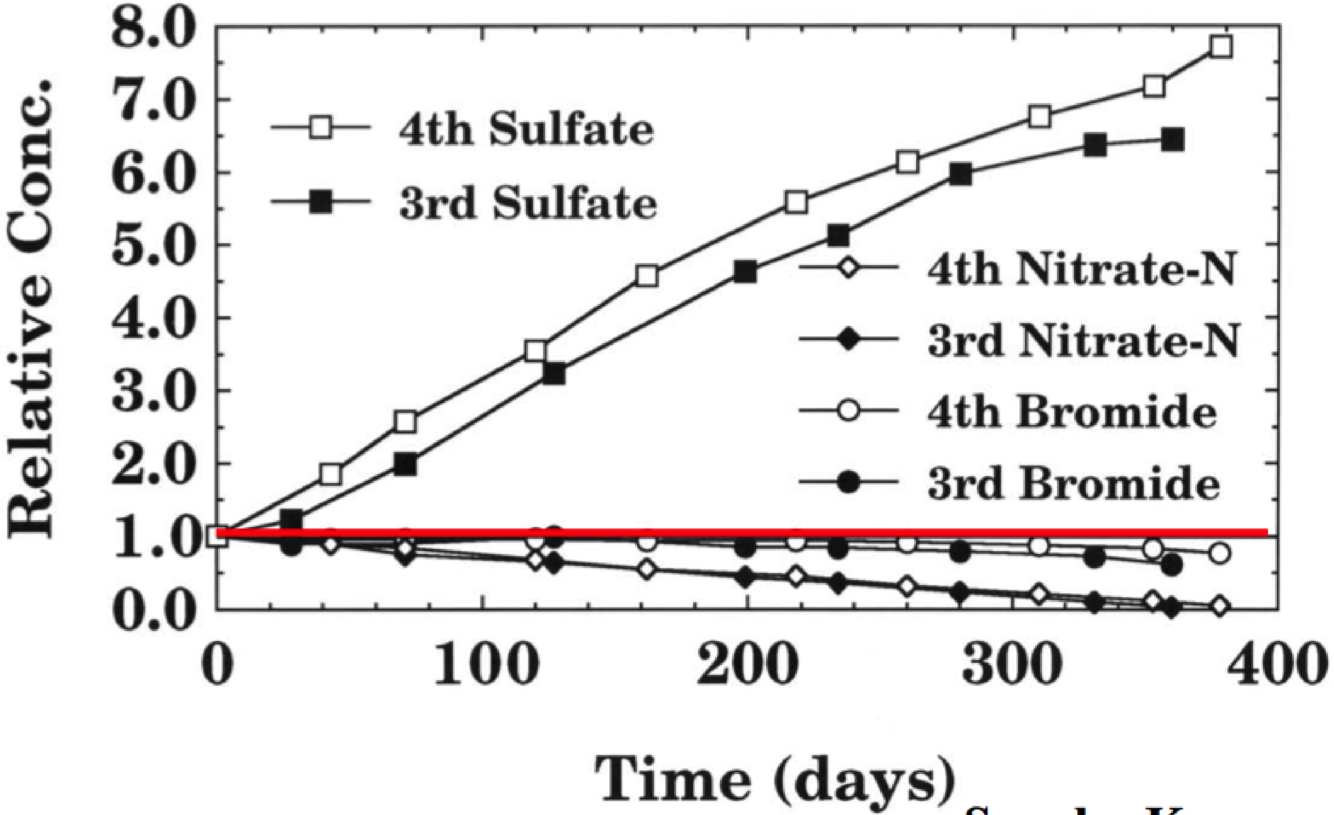


Ground Surface

Water Table


D

# Larimore N-ISM Anions
# 3rd & 4th Tracer Tests



See also Korom et al. (2005)

Test 3 0 - order denitrification rate = 0.19 mg/L-day

Test 4 0 - order denitrification rate = 0.20mg/L-day

# DENITRIFICATION RATES – NITRATE-N

| Location | No. Tests | 0-Order Rate mg/L/d | 0-Order Rate mg/L/year |
|---|---|---|---|
| 1. Larimore ND | 6 | 0.098 - 0.204 | 36 - 75 |
| 2. Hamar, ND | 2 | < 0.01 | 4 |
| 3. Karlsruhe, ND, G Site | 1 | 0.011 | 4 |
| 4. Karlsruhe, ND, S Site | 2 | 0.047 - 0.075 | 17 - 27 |
| 5. Robinson, ND | 1 | 0.011 0.028 | 4 - 10 |
| 6. Akeley, MN | 1 | 0.035 | 13 |
| 7. Merham, MN, M Site | 1 | 0.035 | 13 |
| 8. Perham, MN, W Site | 1 | 0.035 | 13 |
| 9. Luverne, MN | 1 | 0.023 | 8 |
| 10. New Providence, IA, Deep | 1 | 0.018 | 7 |
| 11. New Providence, IA, Shallow | 1 | 0.007 | 3 |
| 12. Oakes, ND, C1 | 2 | 0.033 - 0.060 | 12 - 22 |
| 13. Oakes, ND G1 | 2 | 0.28 - 0.59 | 102 - 215 |

# Parent Material - Sources

- Pyrite sulfur and iron are common in high organic Cretaceous shales – The Pembina Member of the Pierre Formation (Eastern ND), and the Carlile and Greenhorn Formations (Eastern ND)
- Organic Carbon – detrital lignite, buried A horizons, other – Most Common in ND
- Non-pyrite iron (biotite, amphiboles, other) – Fox Hills (East Central ND), Minnesota, Iowa

# CONCLUSIONS

- Glacial aquifers in the upper mid west have substantial denitrification capability
- Local denitrification rates and sources can be measured using ISMs placed within the reducing zone of the aquifer
- 0-order rates vary from 3 mg/L/year to > 200 mg/L/year
- Electron donors vary: Common electron donors include organic carbon, pyrite sulfide and reduced iron, and amorphous reduced iron

# THANK YOU

QUESTIONS?