Network of In-Situ Mesocosms for Monitoring Denitrification in Selected Aquifers of MN and ND

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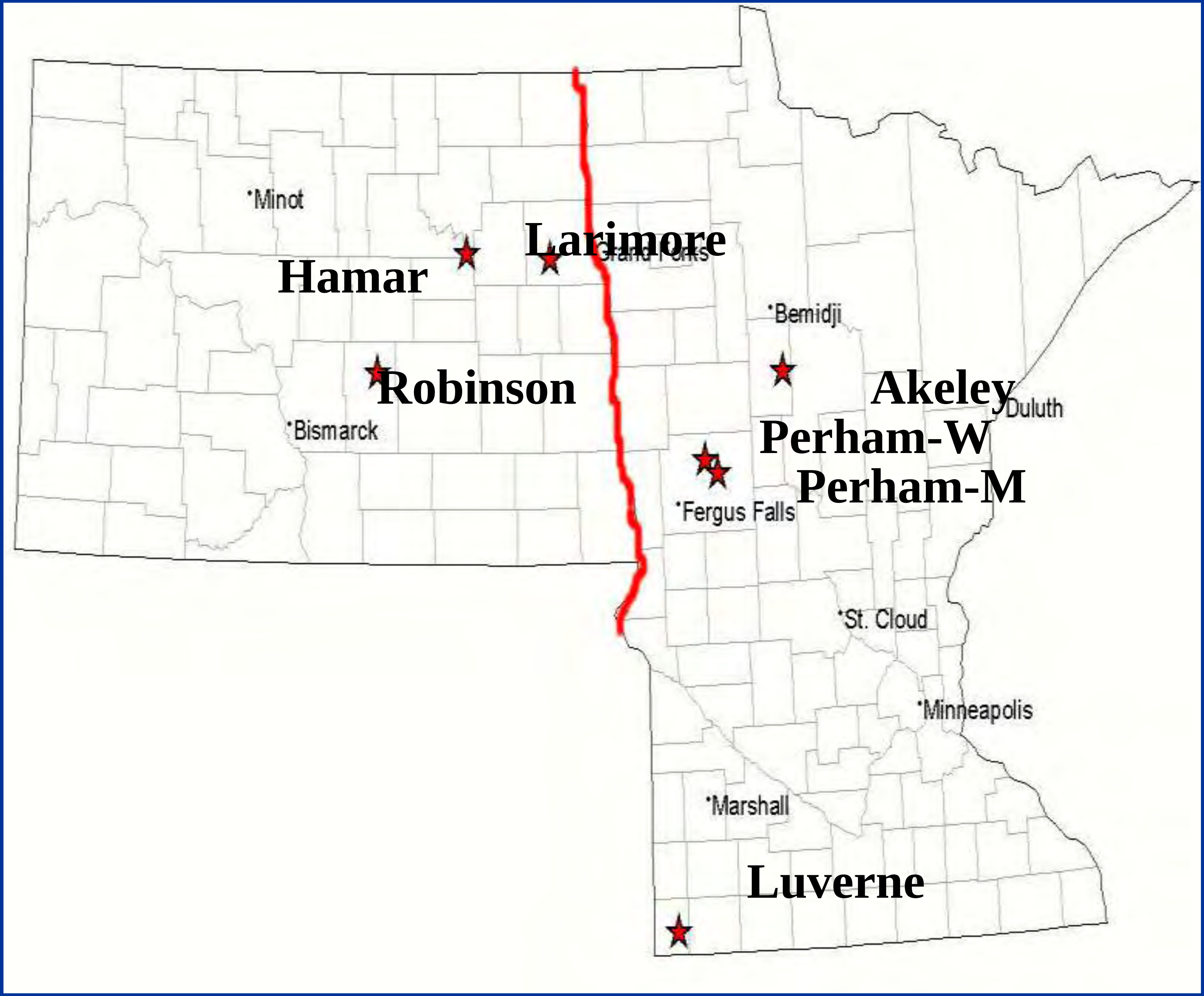
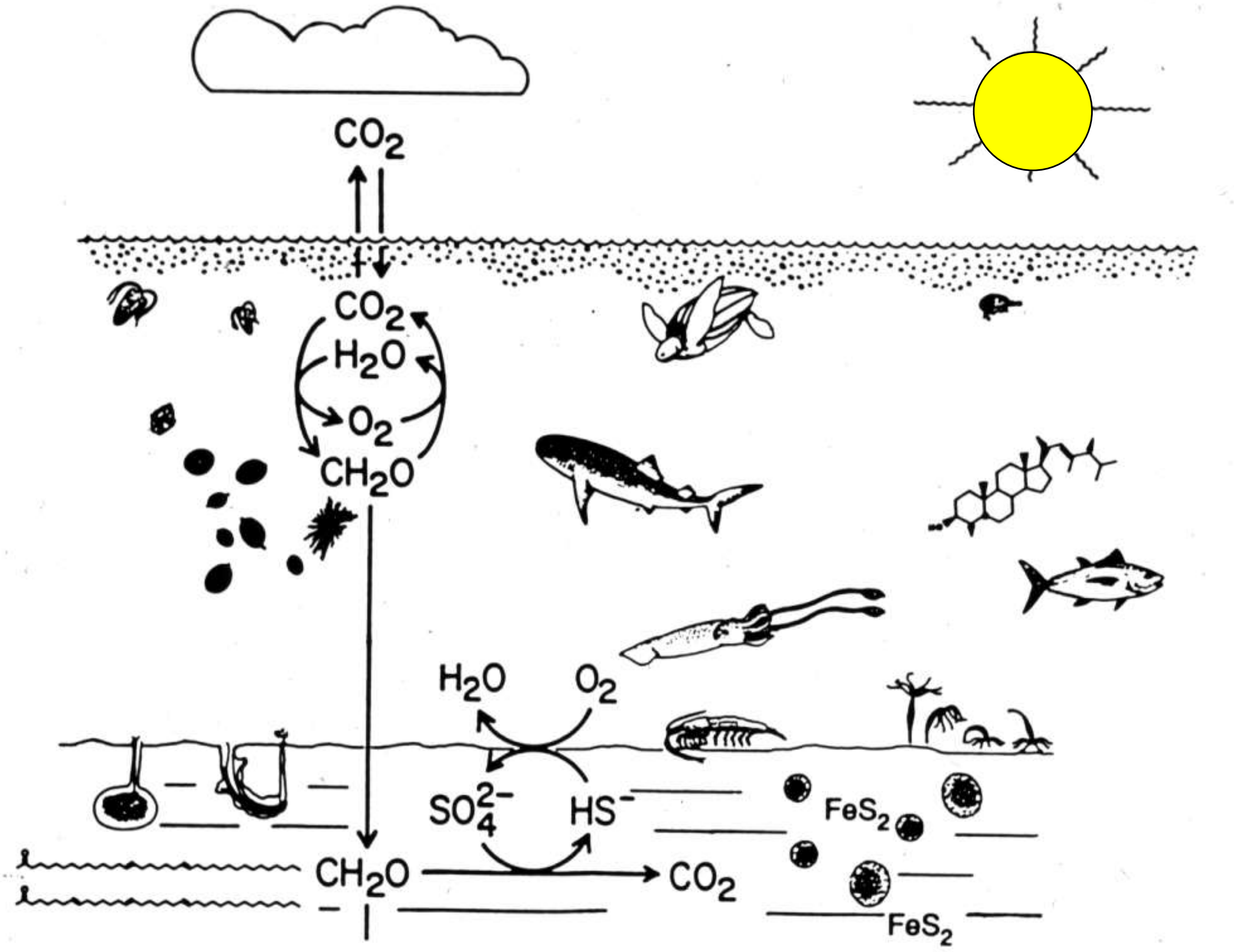
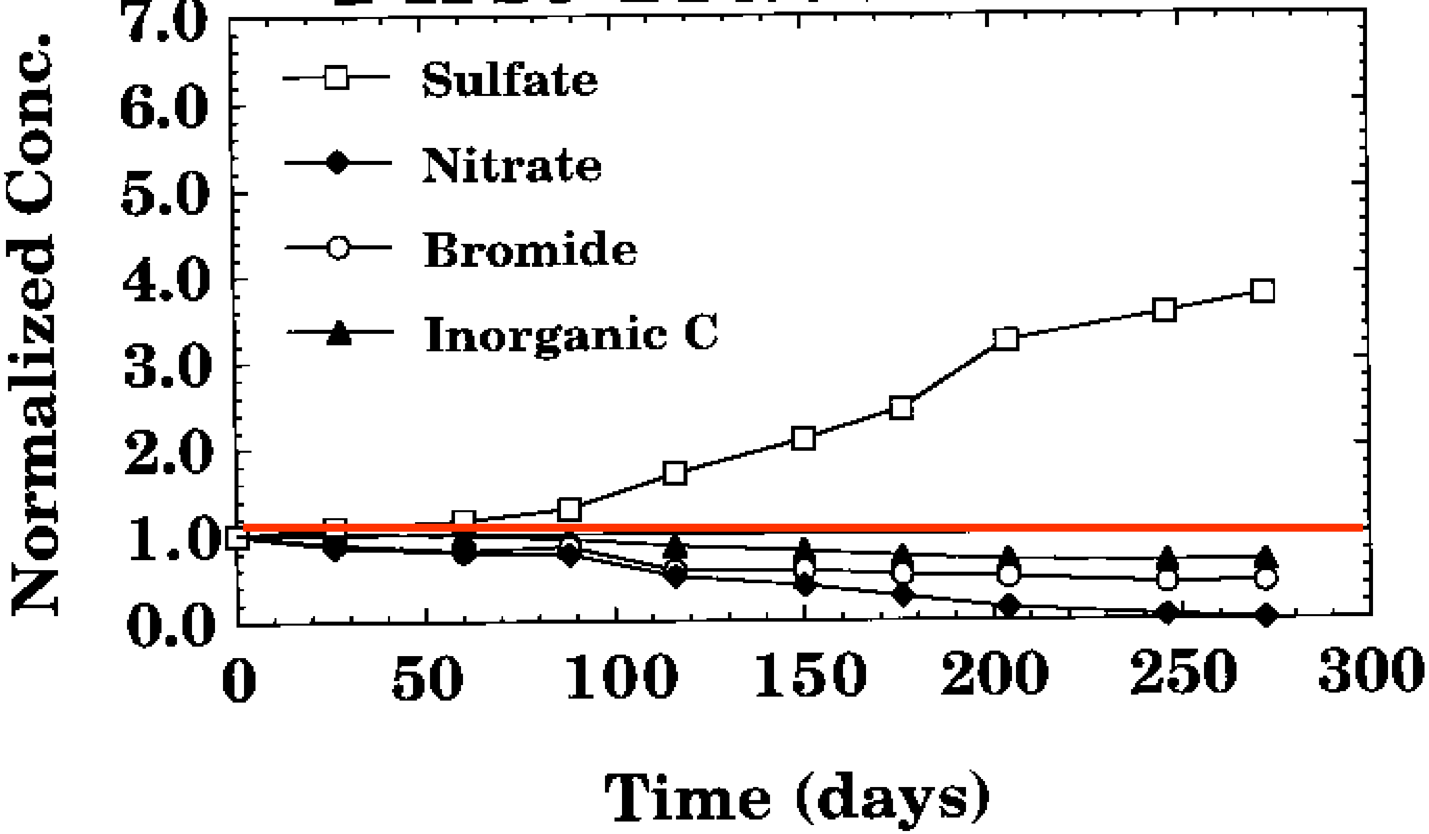

Minot
Larimore
Grand Forks
Hamar
Bemidji
Robinson
Akeley
Duluth
Bismarck
Perham-W
Perham-M
Fergus Falls
St. Cloud
Minneapolis
Marshall
Luverne



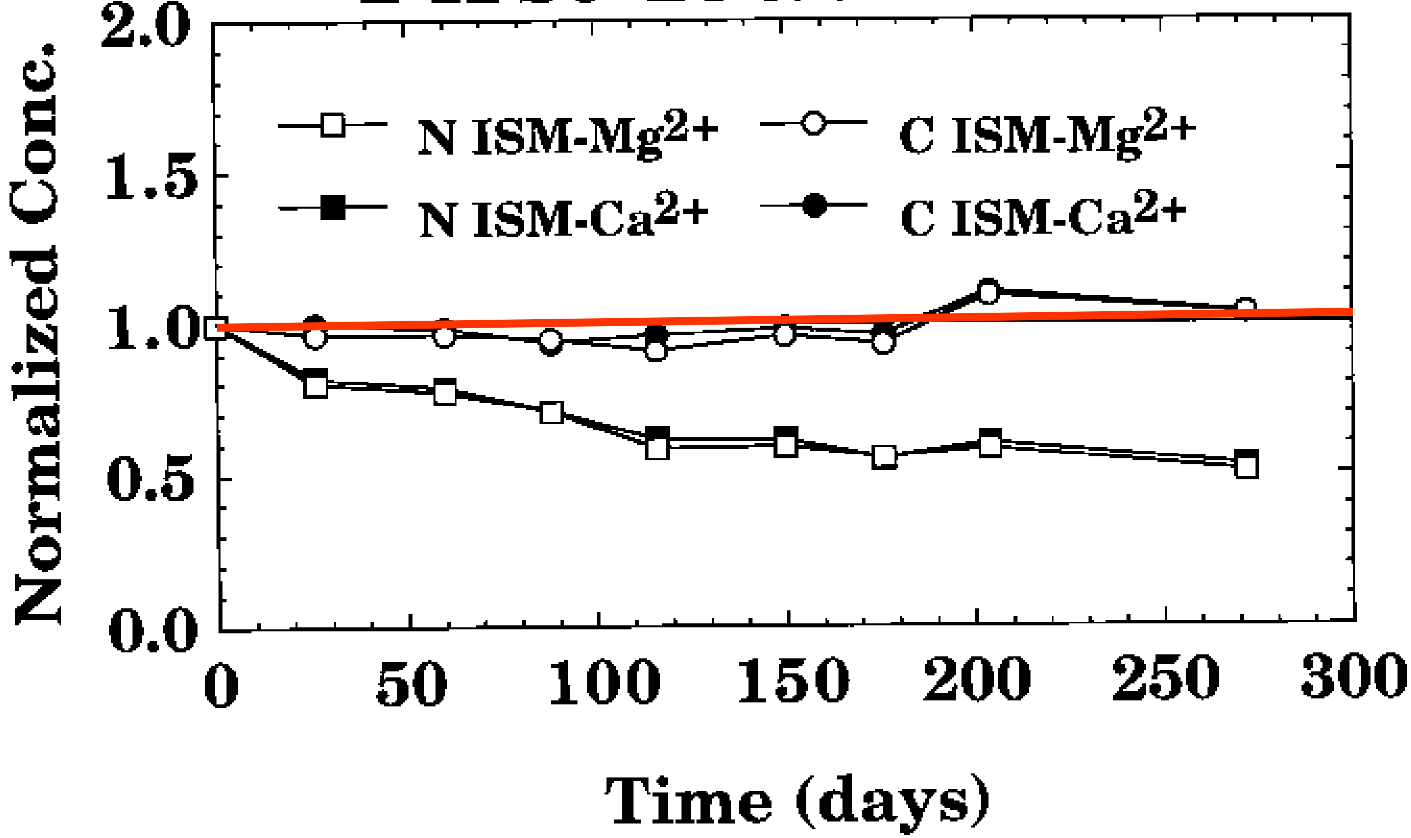
CO_2
CO_2
H_2O
O_2
CH_2O
H_2O
O_2
SO_4^{2-}
HS^-
FeS_2
CH_2O
CO_2
FeS_2

Larimore N-ISM Anions
First Tracer Test

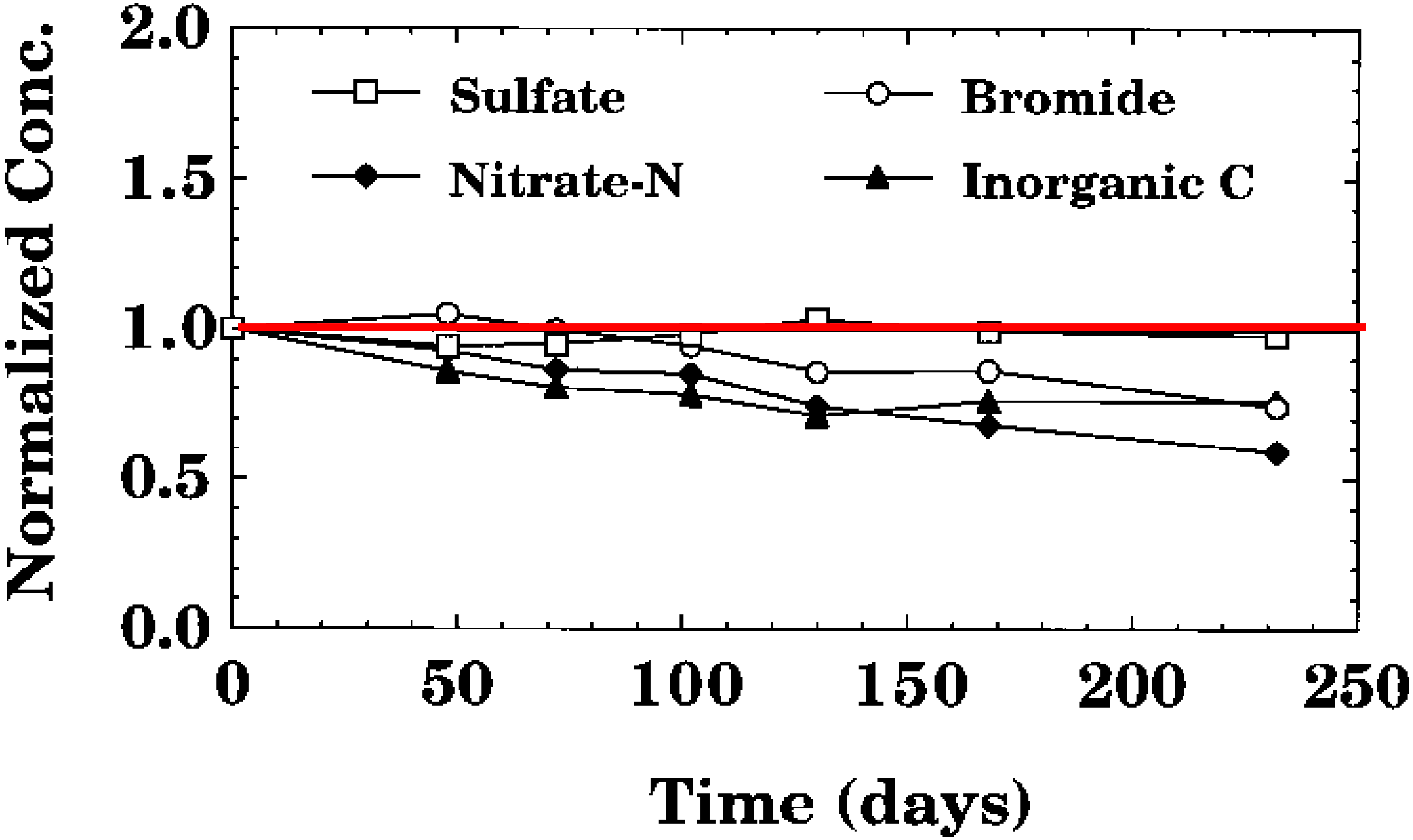


Test 1 denitrification rate = 0.22 mg/L/day

Larimore N&C Cations First Tracer Test

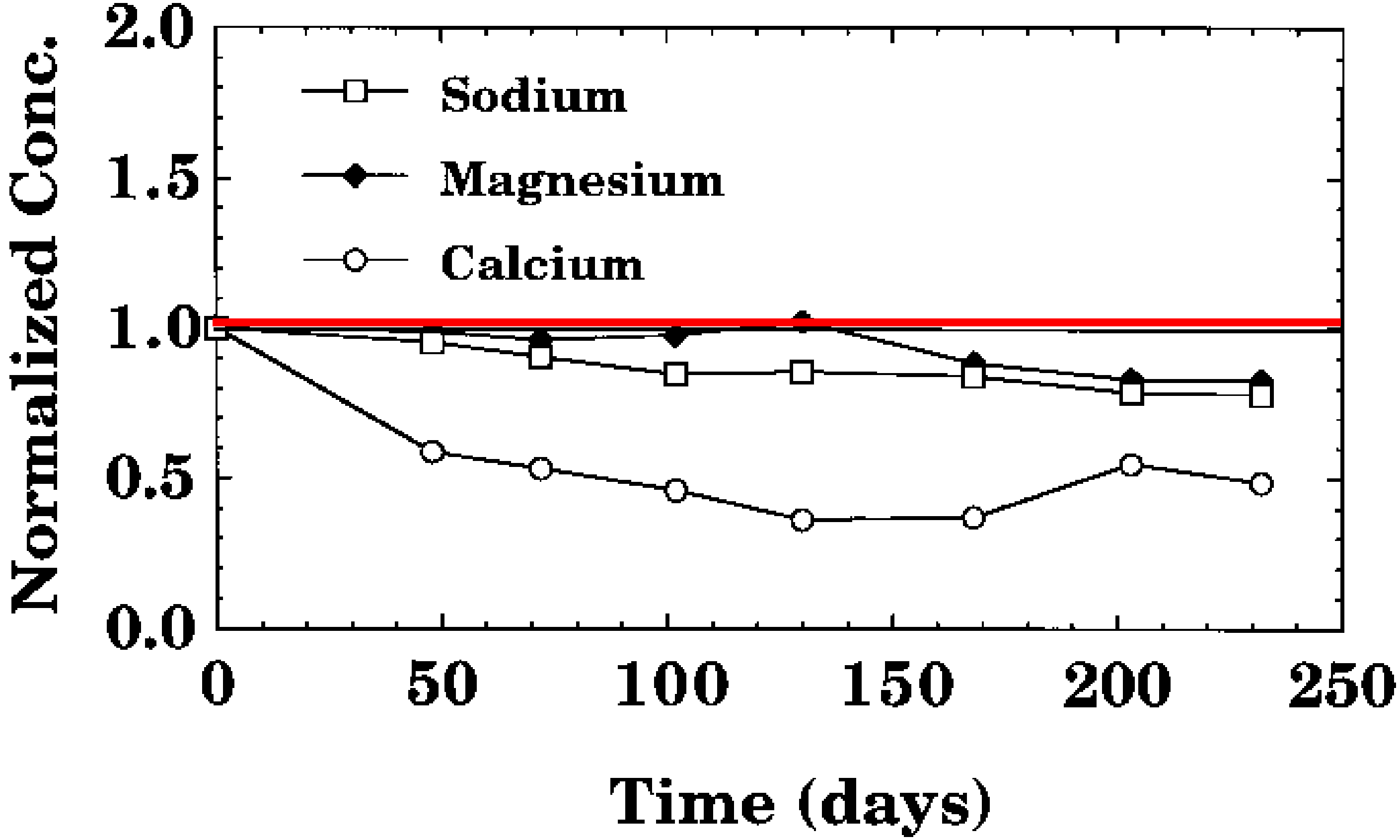


Perham-W N-ISM Anions

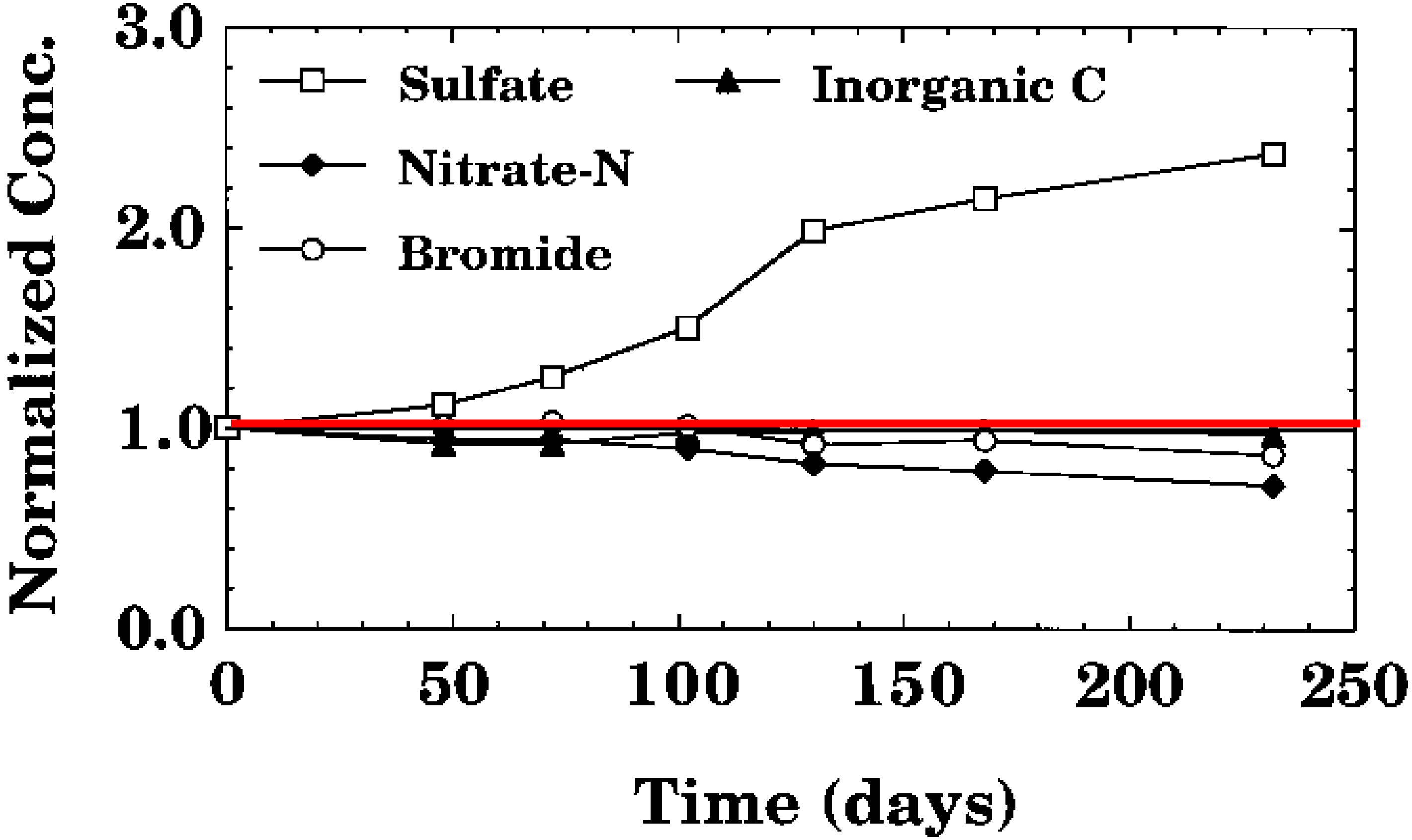


Denitrification rate = 0.06 mg/L/day

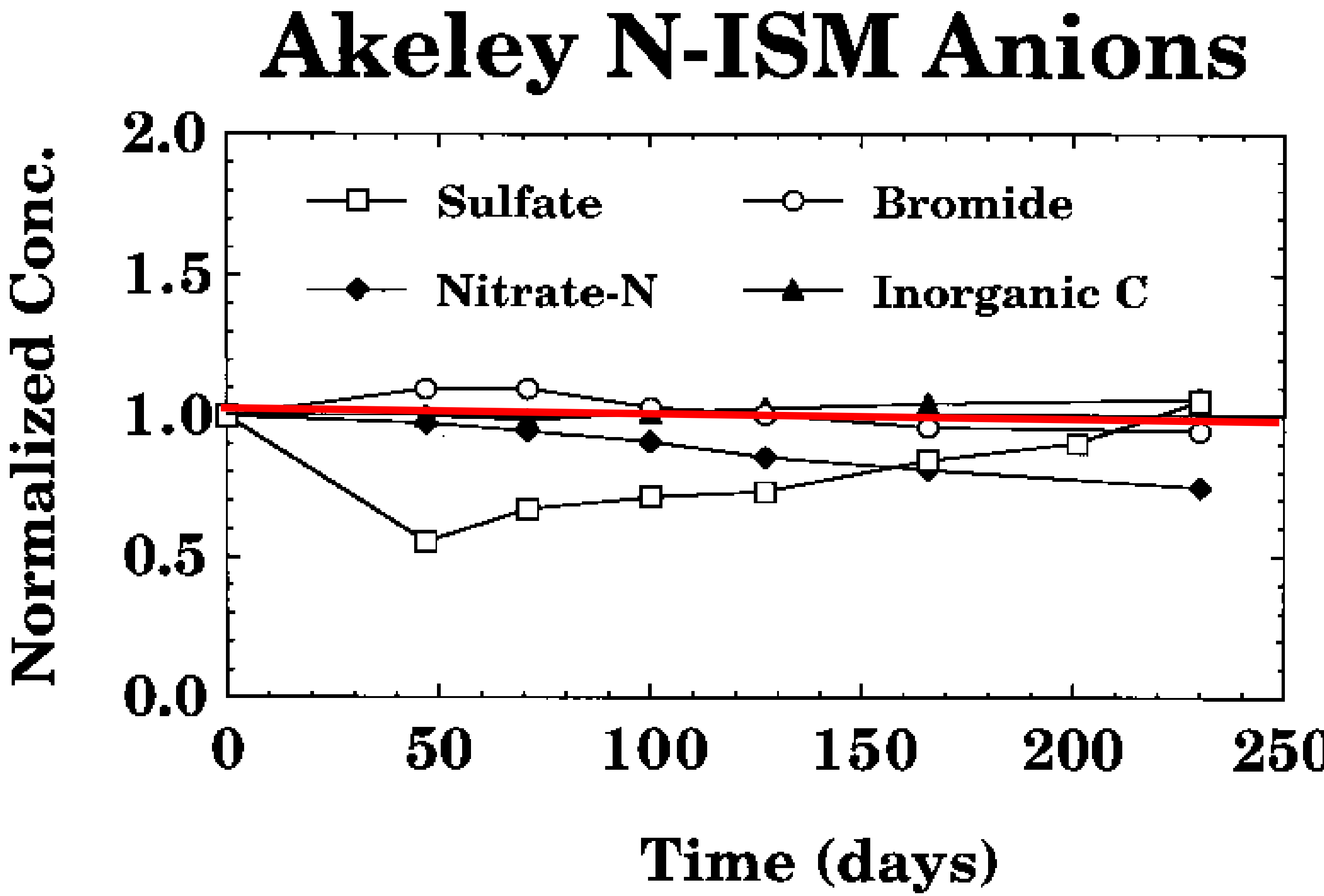
Perham-W N-ISM Cations



Perham-M N-ISM Anions



Denitrification rate = 0.04 mg/L/day



Denitrification rate = 0.04 mg/l/day

Denitrification

- Nitrate is one of the common groundwater contaminants
- Denitrification converts nitrate irreversibly to harmless $N_{2\ (gas)}$.
- One of the limiting factors to the reduction of nitrates is availability of reactive e^- donors
- Commonly denitrification is estimated by reaction products

Denitrification

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

Four Requirements (Firestone, 1982)

➊ Nitrous oxides

➋ Suitable bacteria

➌ Restricted O_2 availability

➍ Suitable e^- donors

Ⅰ. Denitrification by organic carbon:

$$4\,NO_3^- + 5\,CH_2O + 4\,H^+ \Longrightarrow$$

$$2\,N_2 + 5\,CO_2 + 7\,H_2O$$

II . Denitrification by pyrite:

$$5\,FeS_2 + 14\,NO_3^- + 4\,H^+ \Longrightarrow$$

$$7\,N_2 + 10\,SO_4^{2-} + 5\,Fe^{2+} + 2\,H_2O$$

III . Denitrification by ferrous iron:

$$2\,FeS_2 + 6\,NO_3^- + 2\,H_2O \Longrightarrow$$

$$3\,N_2 + 4\,SO_4^{2-} + 2\,FeOOH + 2\,H^+$$

Objectives and Methods

- **Objective:** understanding the denitrification capabilities of aquifers and use them advantageously as a remediation technique
- **Methods:** determining the reduction capacity, texture, mineralogy of aquifer sediments, and analyzing analytical data (from both N and C ISMs) using low temperature hydro-geochemical modeling (PHREEQC)
- **Approach:** Inverse Modeling (Mass Balance) that includes ion-exchange reactions

Summary of Network Results

Site	Rate (mg/L/d)	e^- donor
Akeley, MN	0.04	Fe?
Hamar, ND	< 0.02	?
Larimore, ND	0.11-0.23	S, OC, Fe
Luverne, MN	0.05	S, Fe?
Perham-M, MN	0.04	S, OC, Fe?
Perham-W, MN	0.06	OC
Robinson, ND	0.07	Fe?

Akeley, MN

Research Hypothesis and Progress

- **Hypothesis:** My hypothesis is that ferrous iron is causing reduction of nitrates (reaction III)

- NO_3^- lost unaccounted by the common e-donors, OC and IS, range from ~ 40 to 95 %.

- **Research Progress:** Data collected already
  - Analytical data of all the sites (from previous studies)
  - Texture analyses of some of the samples
  - TOC analyses of some of the samples
  - IS analyses of some of the samples

- **Data to be analyzed in the near future**
  - **- Ferrous and total iron analyses**
  - **- Mineralogy (XRD) and CEC measurements of aquifer sediments**
- **Fe (II) that participates in the reduction of NO_3^- is**
  - **Fe (II) dissolved and ion-exchangeable (*digested in 1 M neutral salt, $CaCl_2$*)**
  - **Fe (II) in amorphous form (*digested in 0.5 M HCl*)**
  - **Fe (II) in crystalline forms (*digested in hot 5 M HCl*)**
- **Fe (II) and total iron will be analyzed in Hach DR2010 spectrophotometer using the required reagents**
- **Finally, modeling output will be compared with the mineralogical data (XRD) and analytical results in order to verify both the numerical procedures as well as the hydrogeochemical reaction schemes.**

Acknowledgments

- *MN Agriculture Department*
- *MN Department of Health*
- *MN Pollution Control Agency*
- *ND Department of Health*
- *ND State Water Commission*
- *ND Rural Water User System Association*
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- *University of North Dakota*
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