Petroleum Microbiology Research Group

University of Calgary

Use of nitrate in souring control of an oil field with low bottom hole temperature

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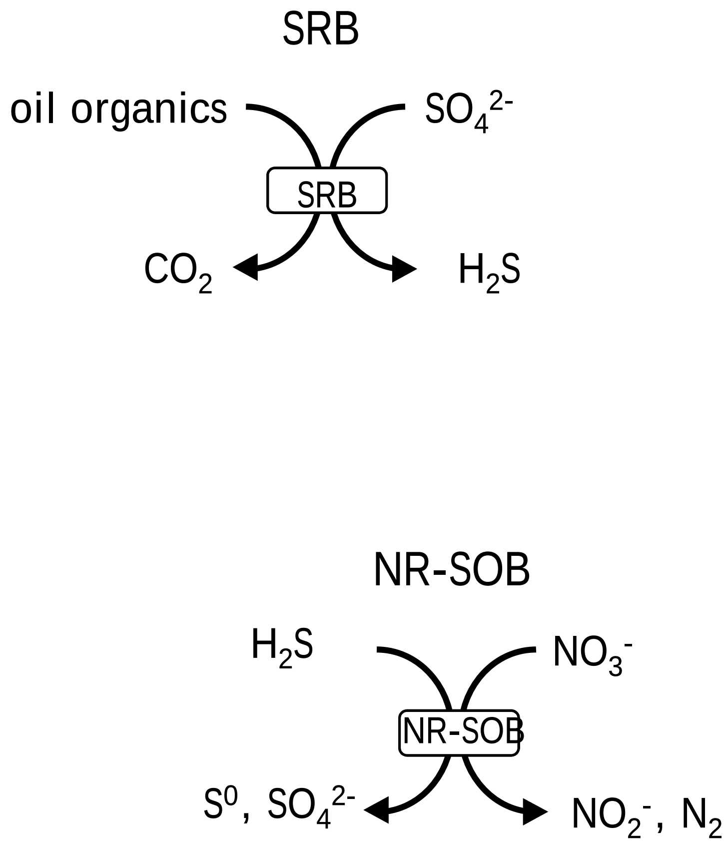
ISMOS2, JUNE 19, 2009

Topics to be covered:

1. Souring control by nitrate injection in low temperature fields
2. What is the electron donor for nitrate reduction in the Enermark field?
3. Can injected nitrate oxidize iron sulfide formed downhole?
4. Microbial community in low temperature oil field under nitrate injection

- **The production of sulfide in oil reservoirs (reservoir souring) can be remediated by injection of nitrate.**
- **Nitrate injection activates 2 new metabolic groups:**



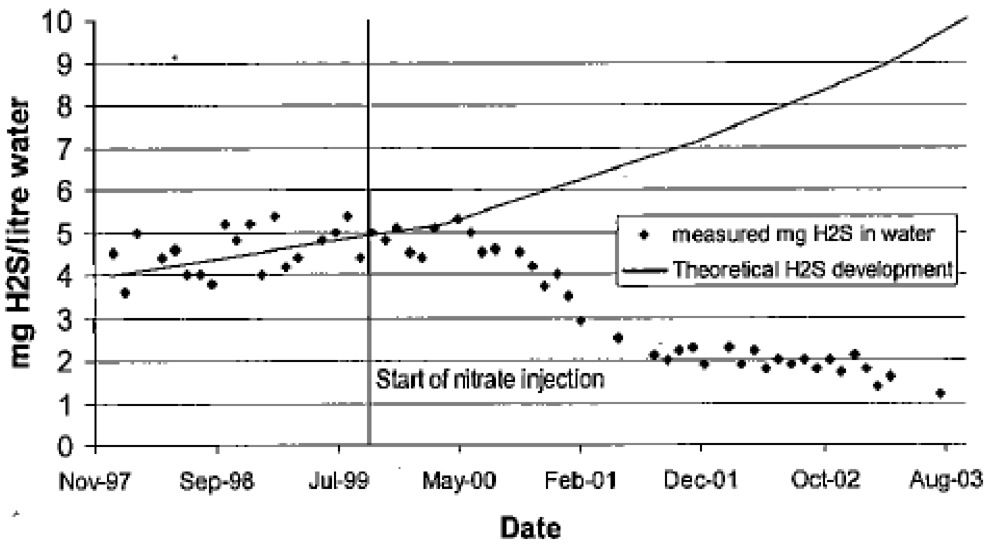
Oil organics: Volatile fatty acids (VFA, a mixture of acetate, propionate and butyrate) used in tests

High-temperature oil fields:

sulfide production limited to injection well bore region because of:

- Cooling of injector well bore region by water injection
- High temperature (60-80 ^{o}C) elsewhere in reservoir
- Nutrient-richness by mixing of injection and reservoir waters

Sulfide production effectively remediated by nitrate because only a limited region of the field needs to be treated.



Gullfaks field
Sunde & Torsvik, 2005

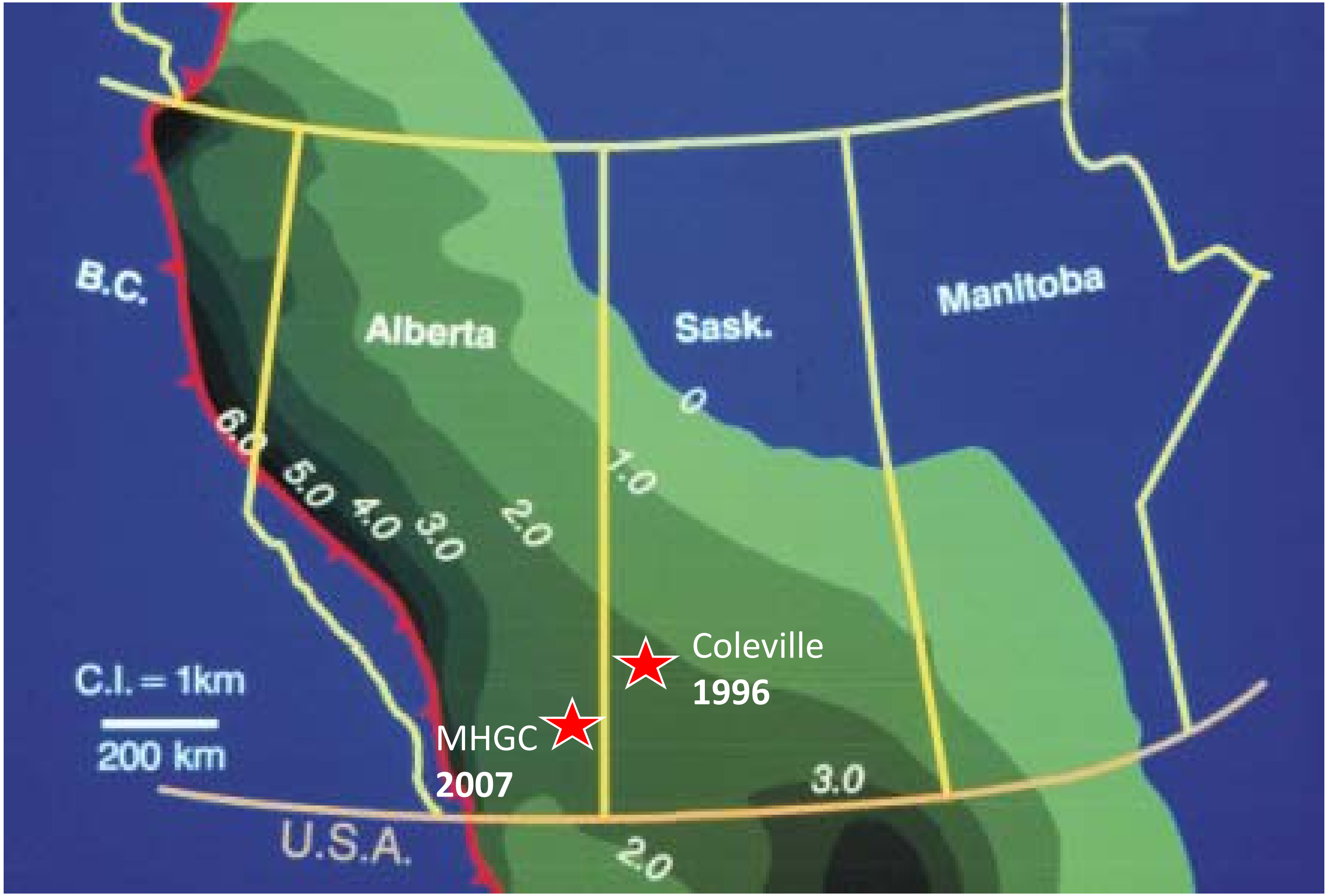
Can fields at:

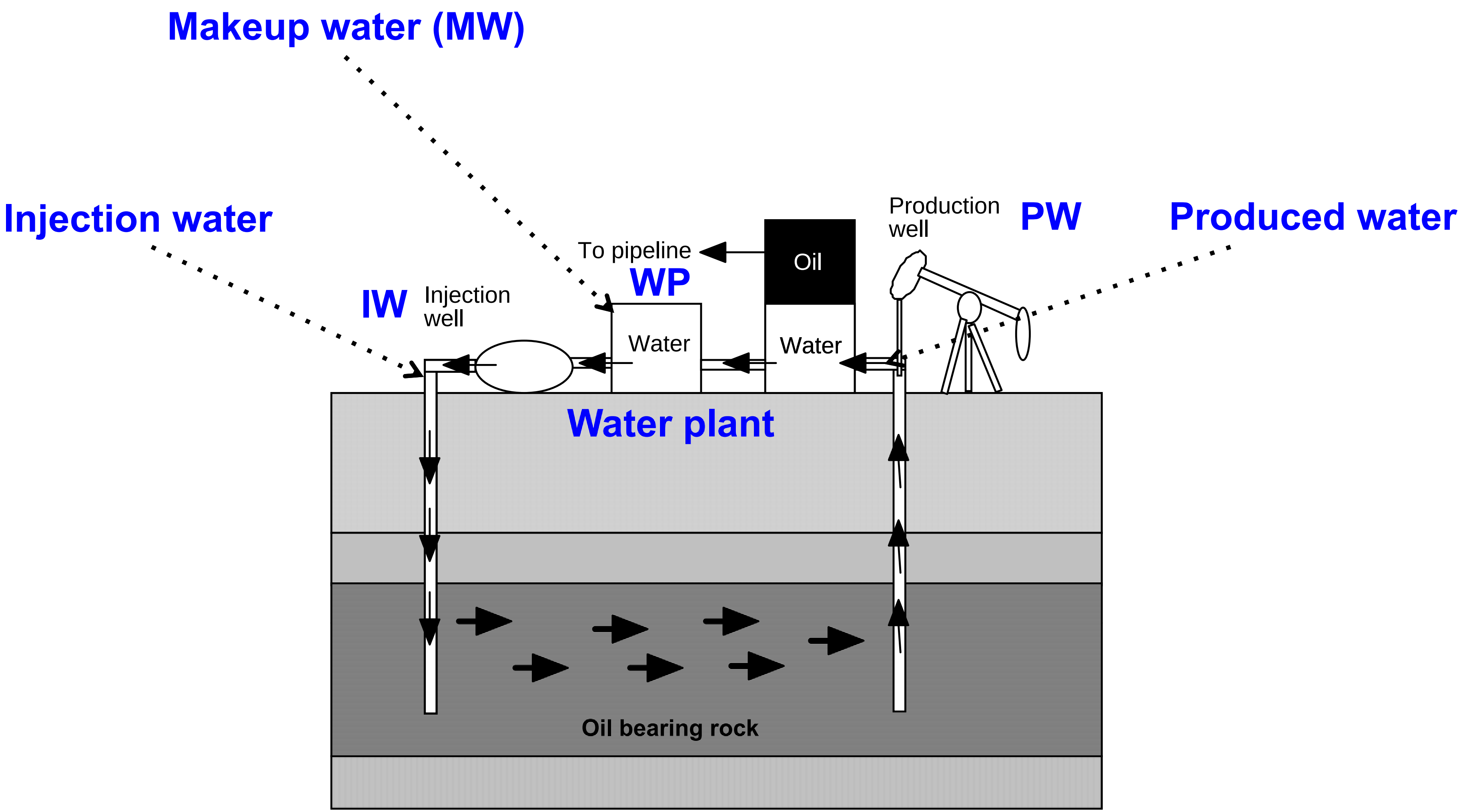
lower depth (1000 m) and, therefore,

lower downhole temperature

be successfully treated with nitrate?

2 Field Sites in the WCSB





- In a water plant produced water and makeup water are mixed to give injection water
- The field is operated by produced water reinjection (PWRI)

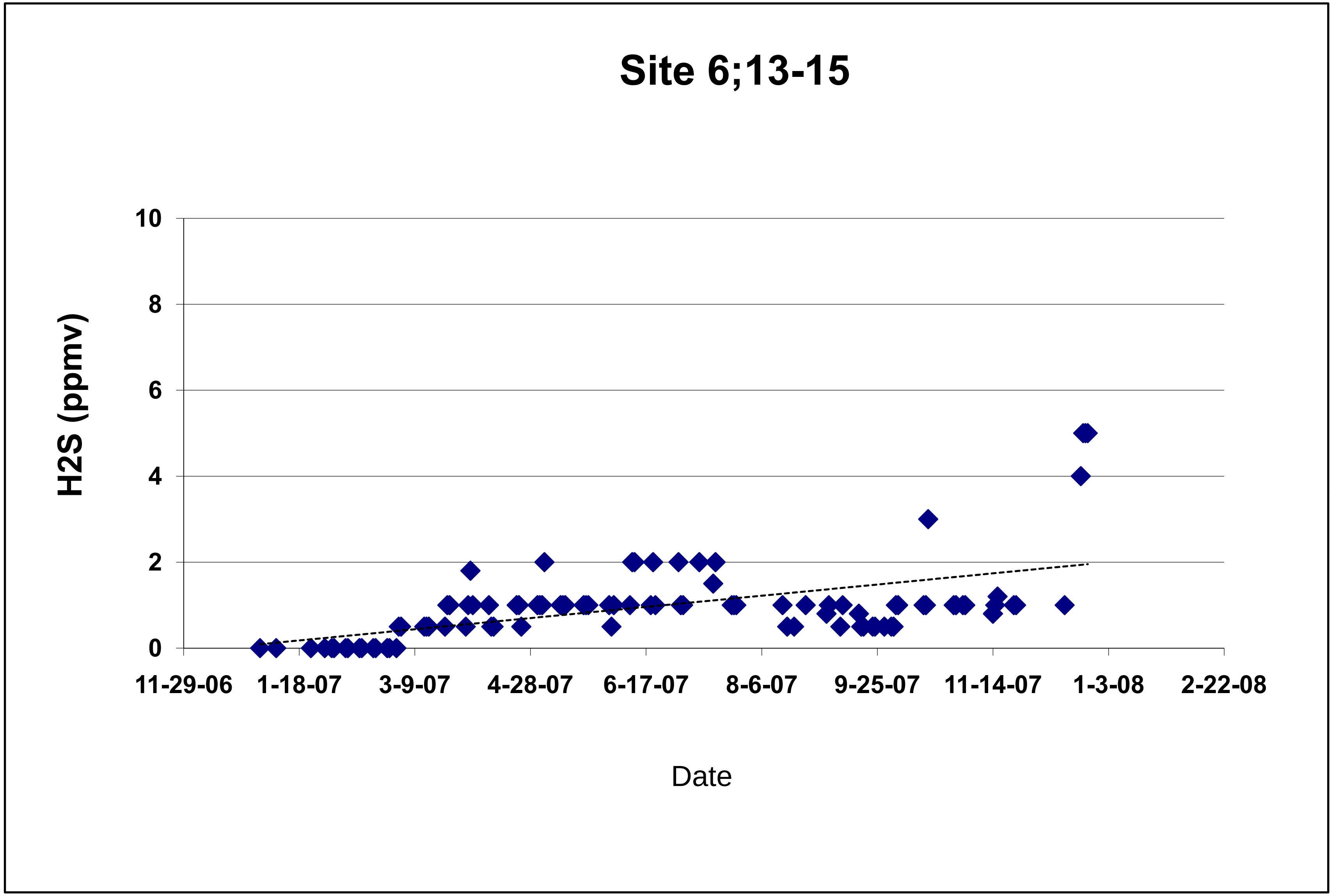
2. Souring control by nitrate injection in onshore fields of low temperature

- **New project MHGC field:**
  - 850 m depth, 30 °C downhole temperature
  - Heavy oil (16 degrees API gravity)
  - 2000: start of water injection
  - Injection water (IW) 3500 m^3/day
  - Oil production 1000 m^3/day
  - Produced water re-injection (PWRI)
  - Makeup water 4 mM (400 ppm) sulfate
  - IW (PW : make-up water = 3 :1) is 1 mM sulfate
  - PW 0 mM sulfate and on average 0.1 mM sulfide

- **Evidence for Souring:**
  - 2006: sulfide (gas phase) increasing
  - Delay caused by sulfide scavenging of reservoir rock

- **Souring could have been prevented by:**
- using make-up water with 0 sulfate

Gas phase sulfide concentrations determined by field personnel



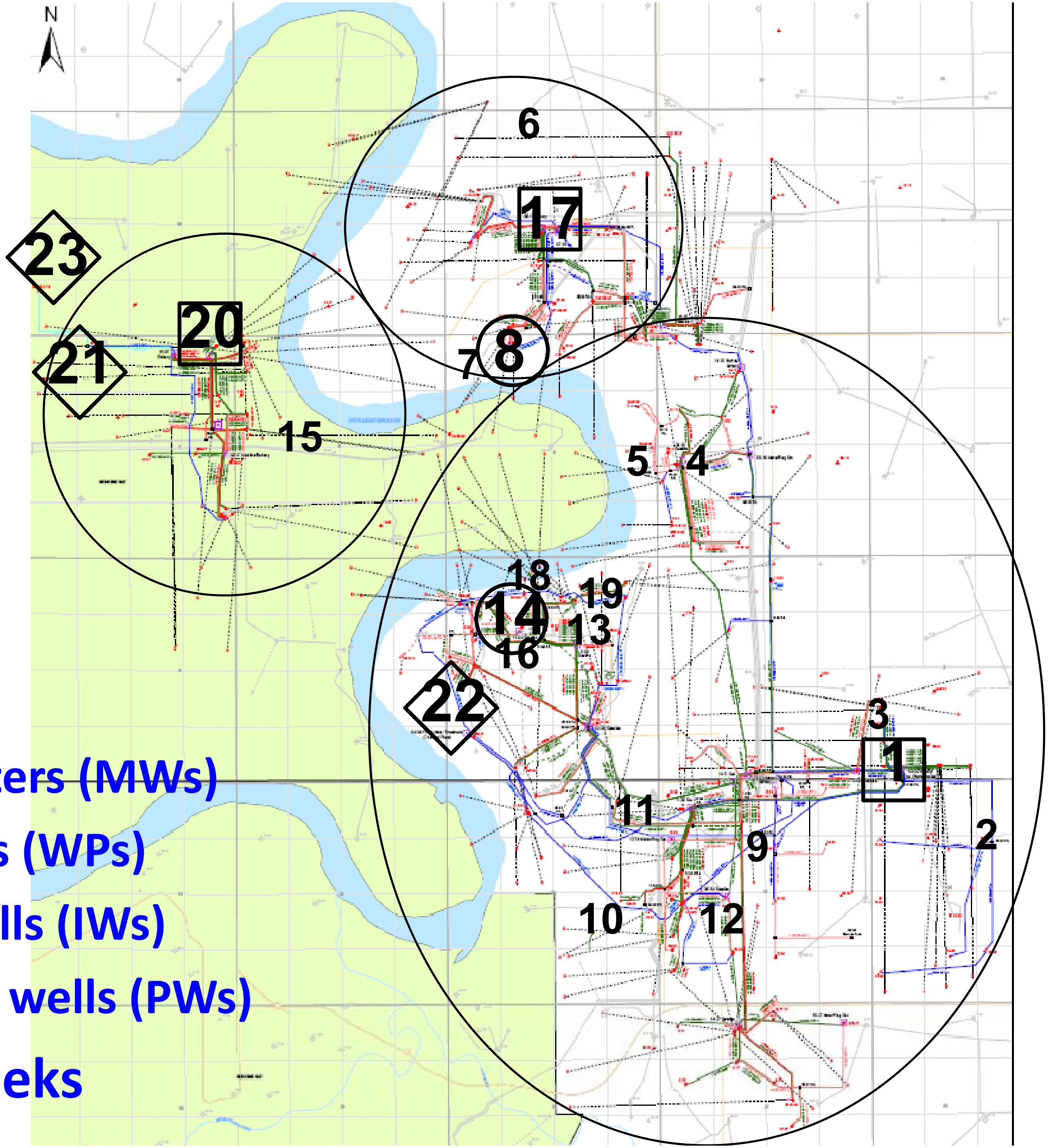
MHGC long-term field-wide nitrate injection:

- **Injected nitrate concentration 2.4 mM field-wide**
  = 150 ppm nitrate = 1.2 mM $Ca(NO_3)_2$ = 200 ppm calcium nitrate

Still going on today

- **Weekly nitrate squeezes at 14-IW from January 2008 – April 2009**

- **Field wide nitrate pulses from July 2008- March 2009 to March 2009.**



23-MW

17-WP

8-IW

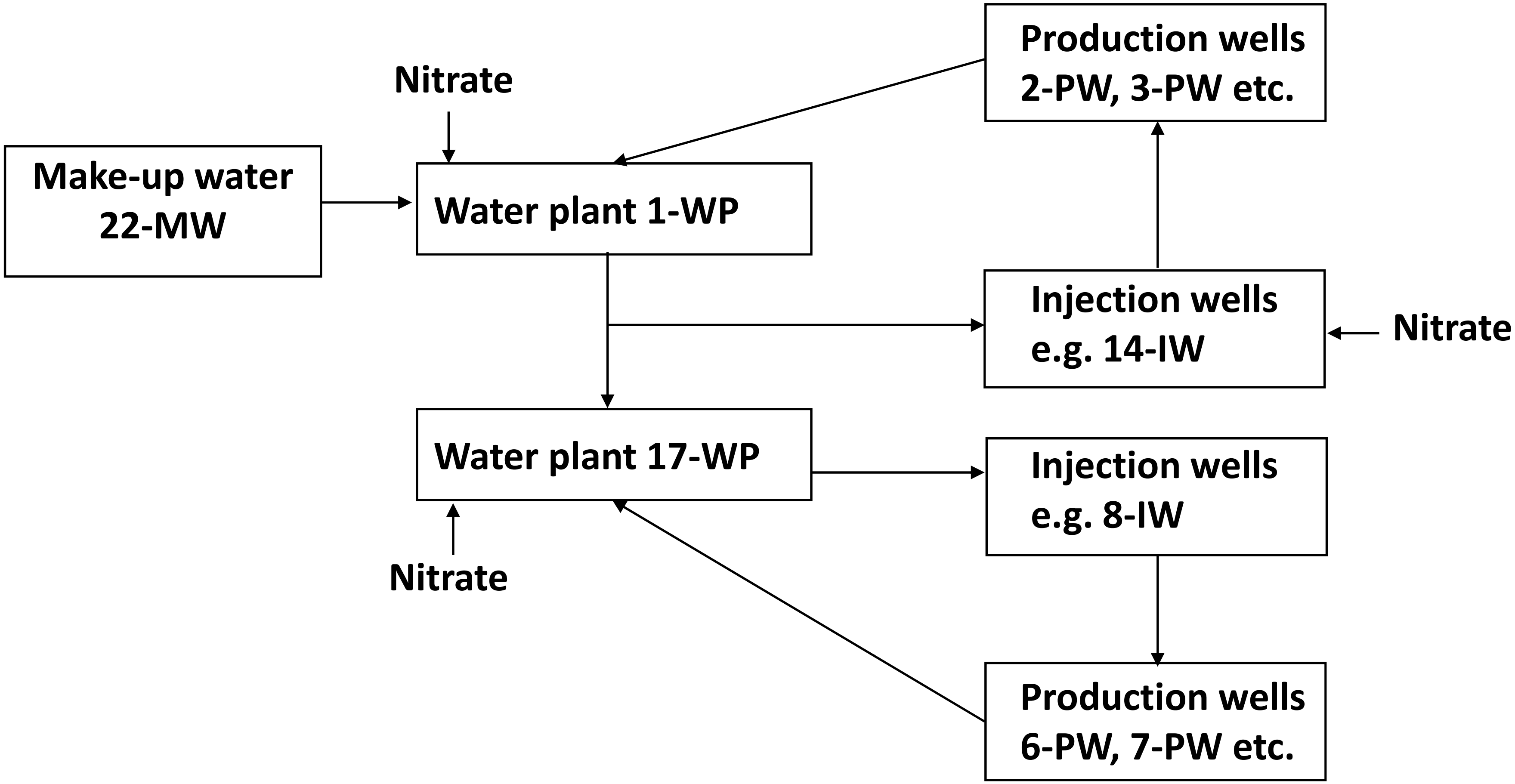
9-PW

We monitor:

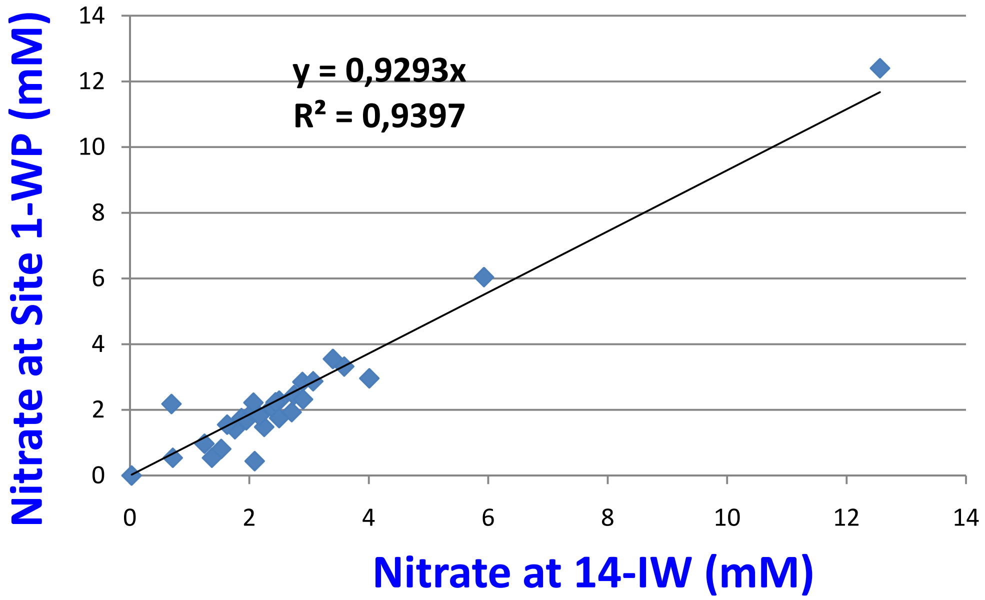
- 3 Makeup waters (MWs)
- 3 Water plants (WPs)
- 2 Injection wells (IWs)
- 15 production wells (PWs)

every 2-3 weeks

Sampling at Waterplant 1-WP

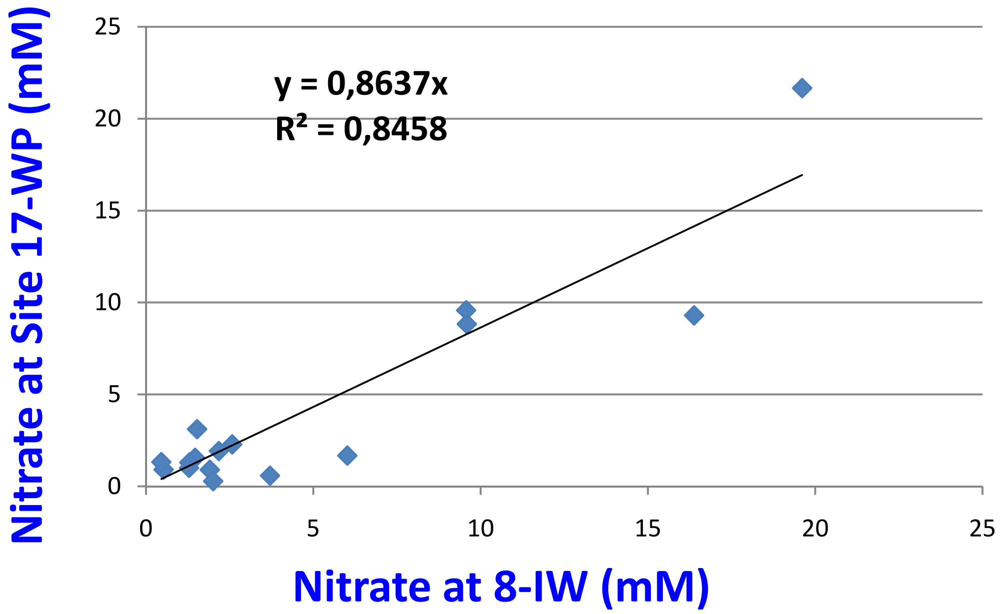


Production wells
2-PW, 3-PW etc.
Nitrate
Make-up water
22-MW
Water plant 1-WP
Injection wells
e.g. 14-IW
Nitrate
Water plant 17-WP
Injection wells
e.g. 8-IW
Nitrate
Production wells
6-PW, 7-PW etc.



1-WP → 14-IW

7% loss of nitrate



17-WP → 8-IW

15% loss of nitrate

Difference is caused by biocide dosing

Overall conclusions:

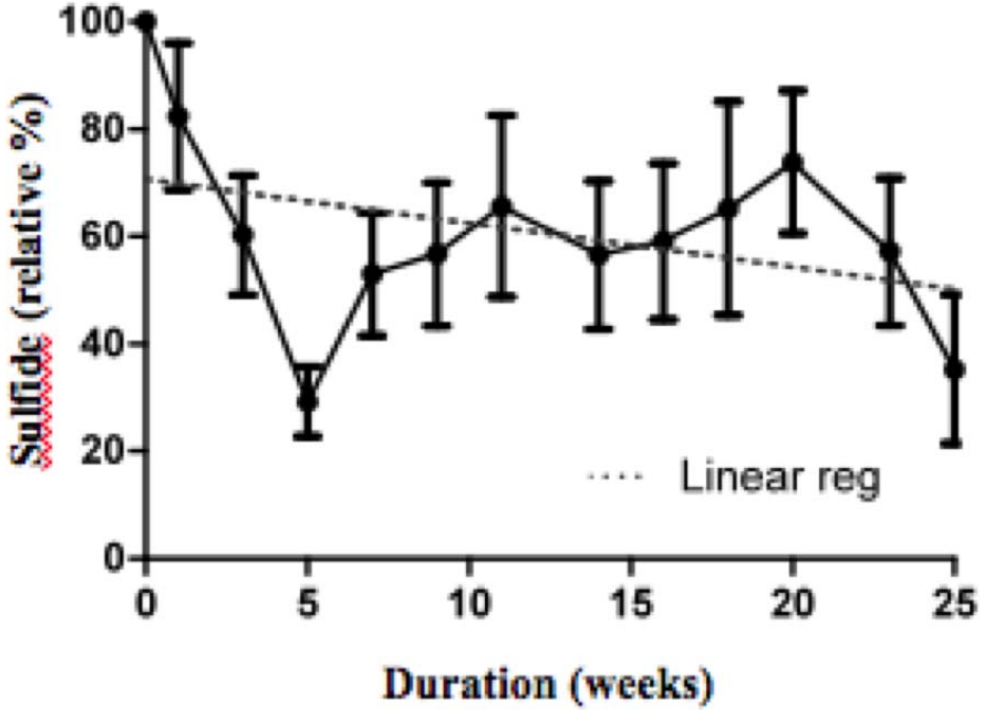
•Nitrate delivered effectively by the injection system to the field
•Losses during transport (due to wall growth of NRB) are 7-15%.

Producing wells – 15 monitored

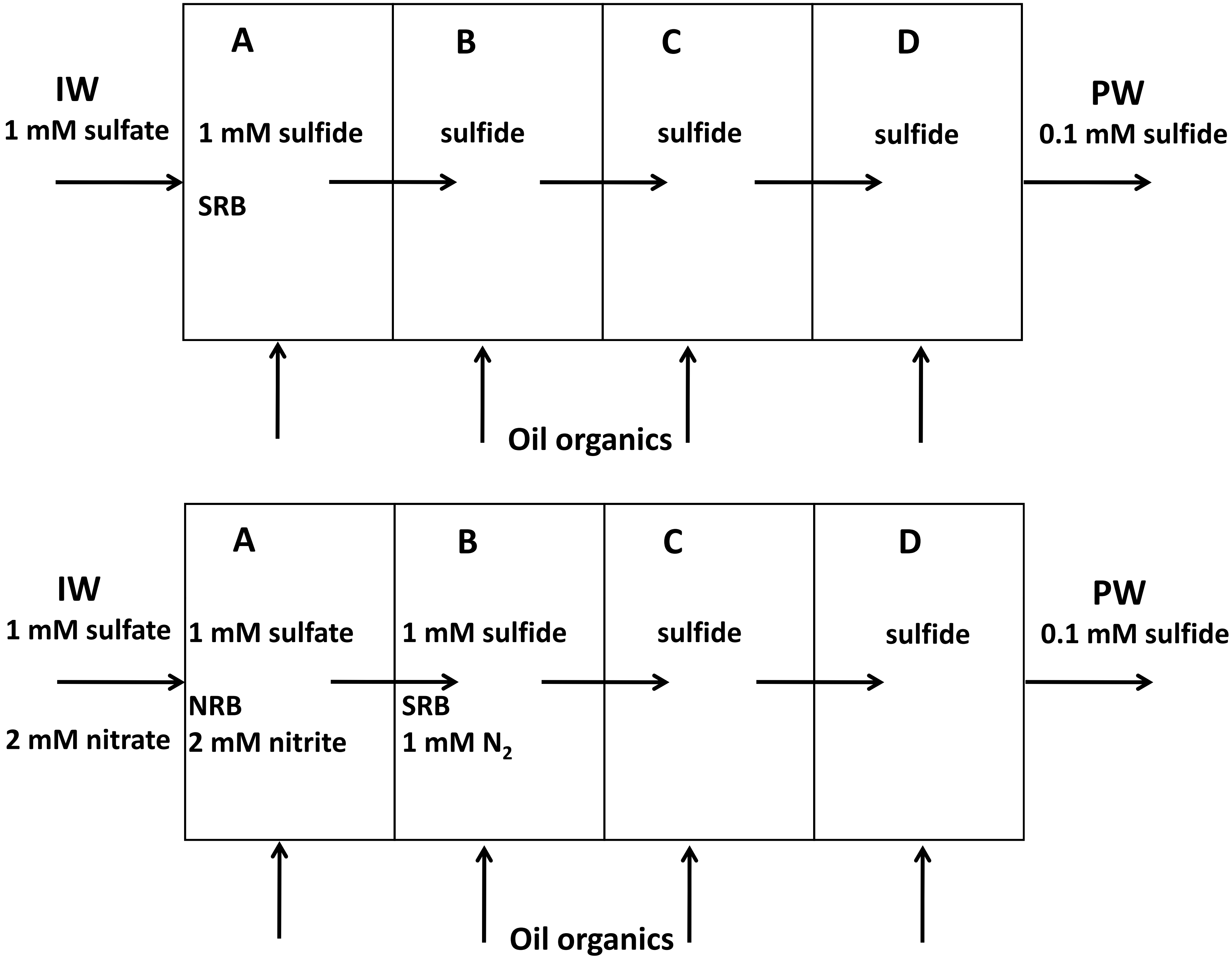
Most are horizontal wells and receive water from more than one injection well

Sampling Point

Average sulfide concentration for 12 PWs

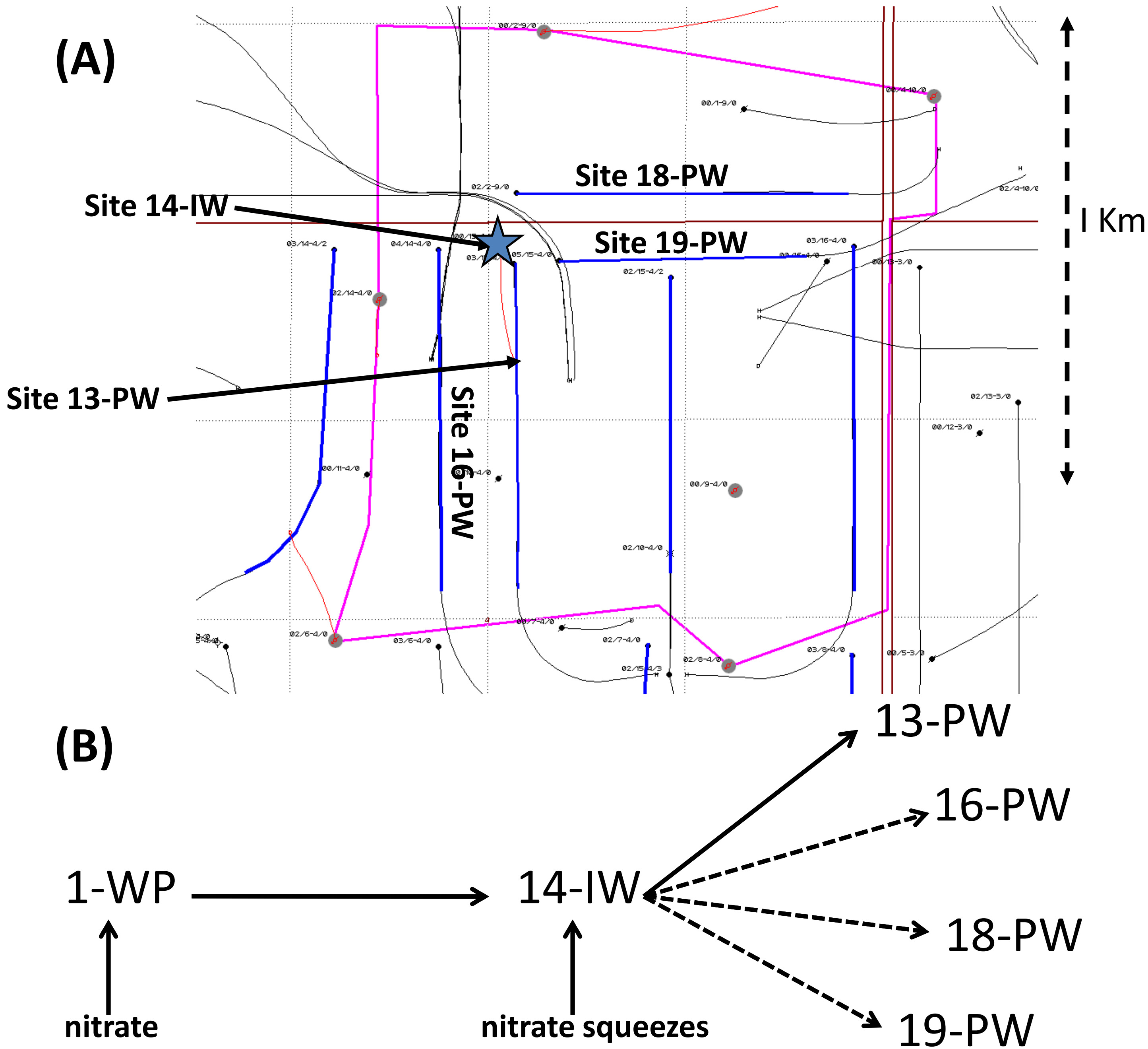


The first 5 weeks look great but why the recovery?


A
B
C
D
IW
1 mM sulfate
1 mM sulfide
SRB
sulfide
sulfide
sulfide
PW
0.1 mM sulfide
Oil organics
A
B
C
D
IW
1 mM sulfate
2 mM nitrate
1 mM sulfate
NRB
2 mM nitrite
1 mM sulfide
SRB
1 mM N_2
sulfide
sulfide
PW
0.1 mM sulfide
Oil organics

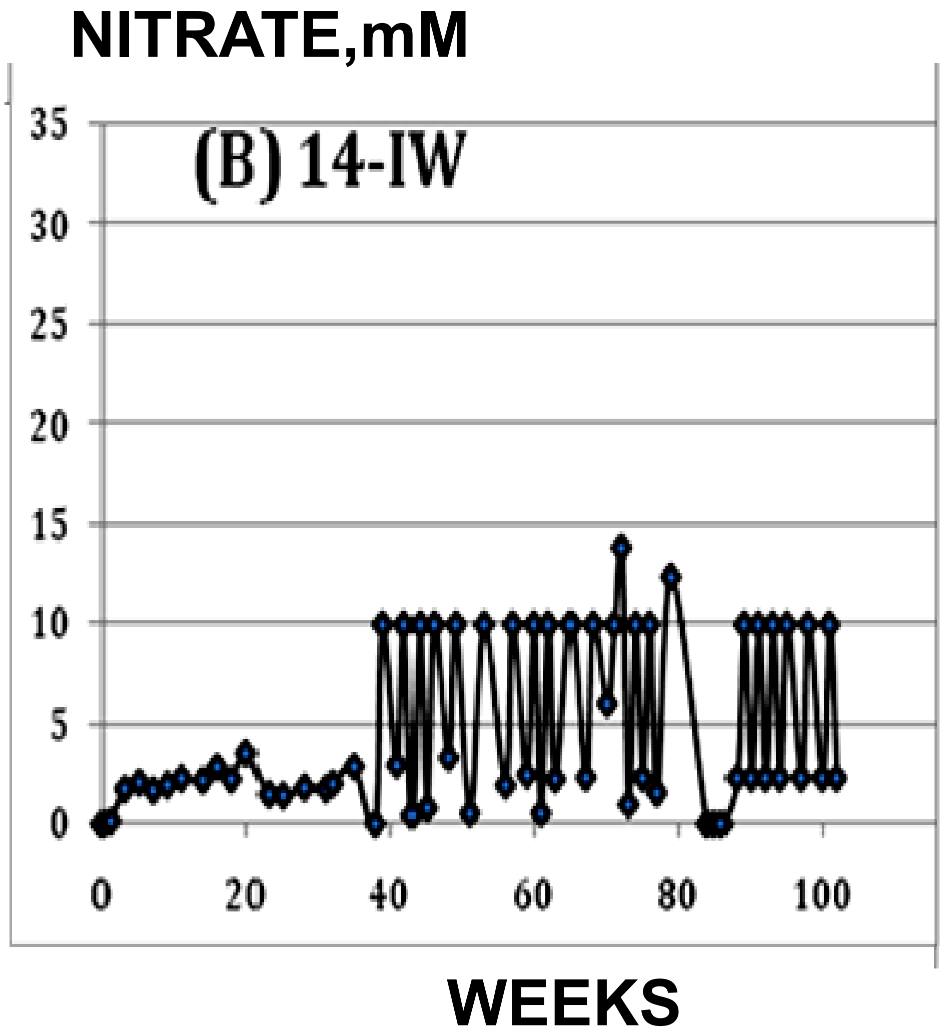
•Injection water contains 1 mM sulfate
•This is reduced to 1 mM sulfide by SRB present as a biofilm close to the injection wellbore
•Nitrate injection gives initially strong inhibition of sulfate reduction in this region
•However, because the field is low temperature bacteria can grow anywhere
•SRB re-grow as a biofilm deeper in the reservoir
•Sulfide concentrations recover to initial levels.

- Hence NRB and SRB grow in different adjacent zones.
- We refer to this as microbial stratification
- Can the stratification be broken by changing the continuous nitrate injection into a pulsing nitrate injection regime?
- Bioreactor studies suggest that this is so (see poster by Cameron Callbeck)

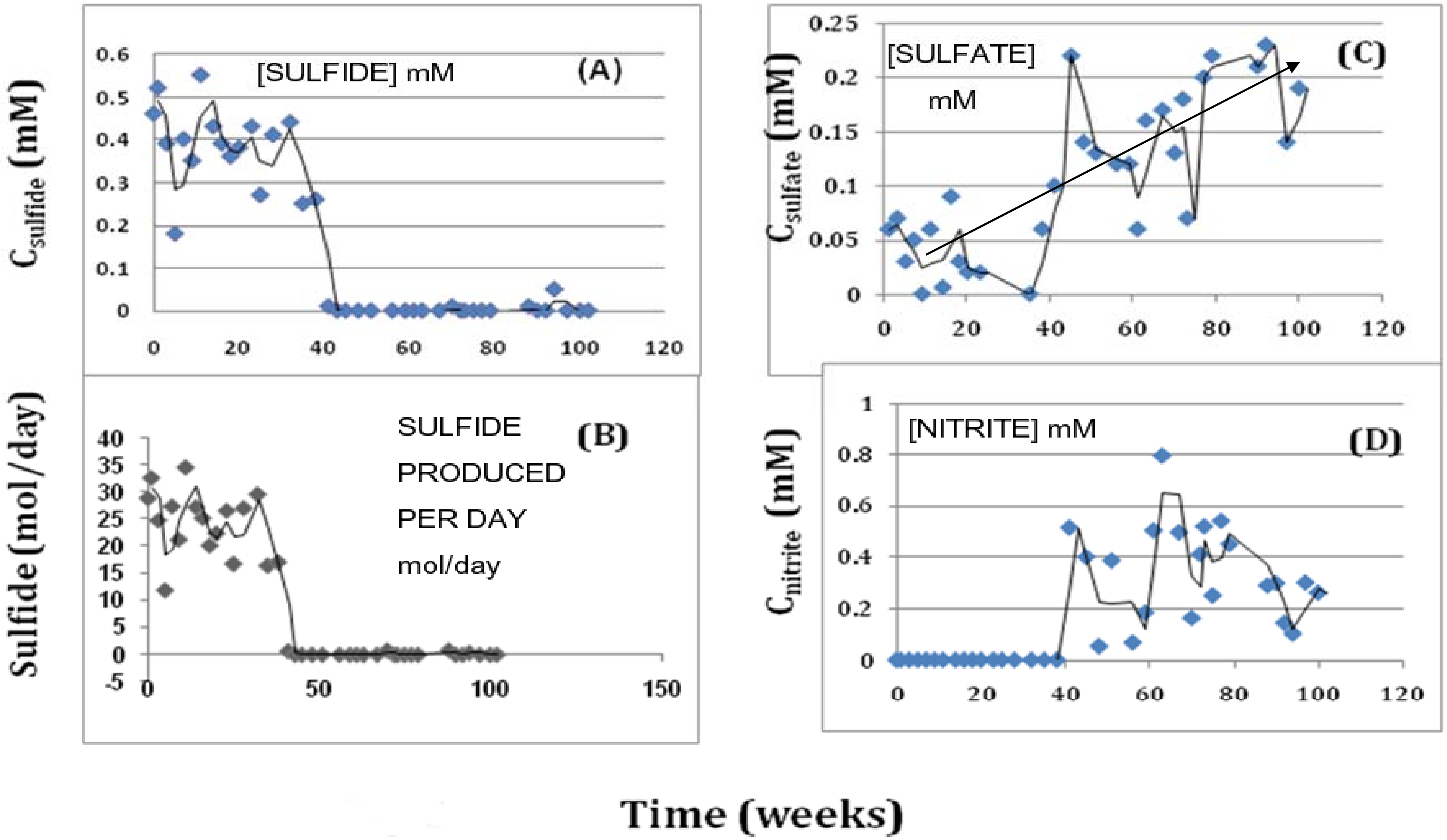

(A)
Site 14-IW
Site 18-PW
Site 19-PW
Site 13-PW
Site 16-PW
I Km
(B)
1-WP
14-IW
13-PW
16-PW
18-PW
19-PW
nitrate
nitrate squeezes

Nitrate Squeezes at 14-IW

- Weekly; 1000 L slug of 45% calcium nitrate injected directly into injection well 14-IW feeding producer 13-PW

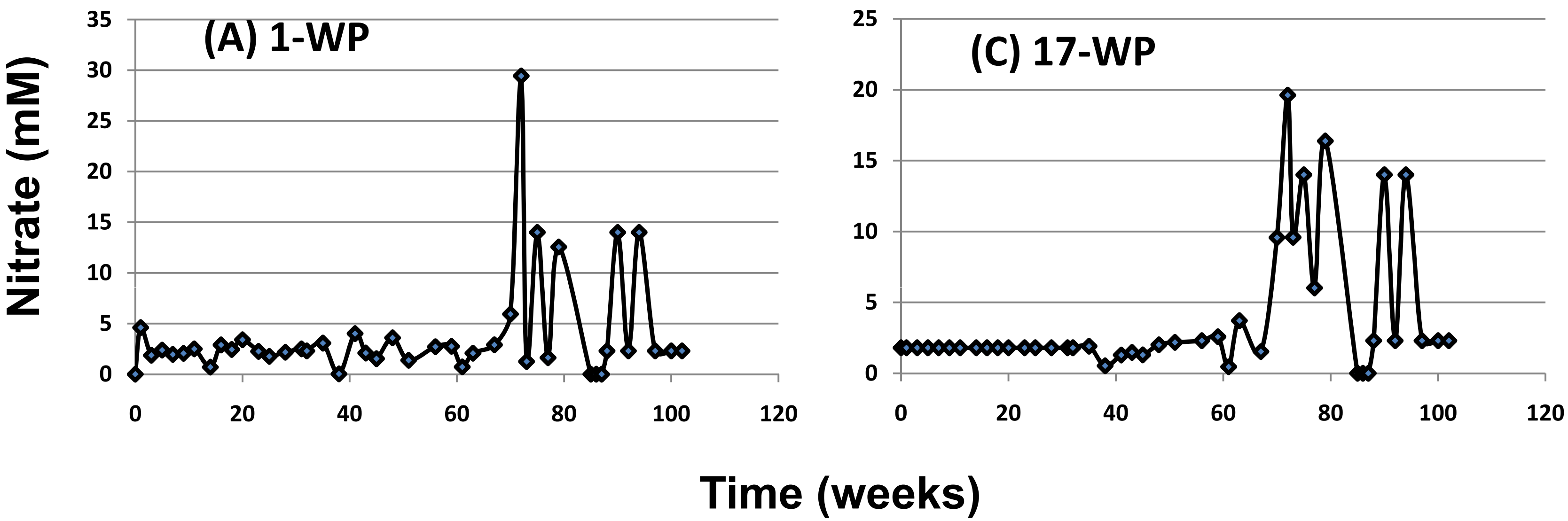


Response at 13-PW



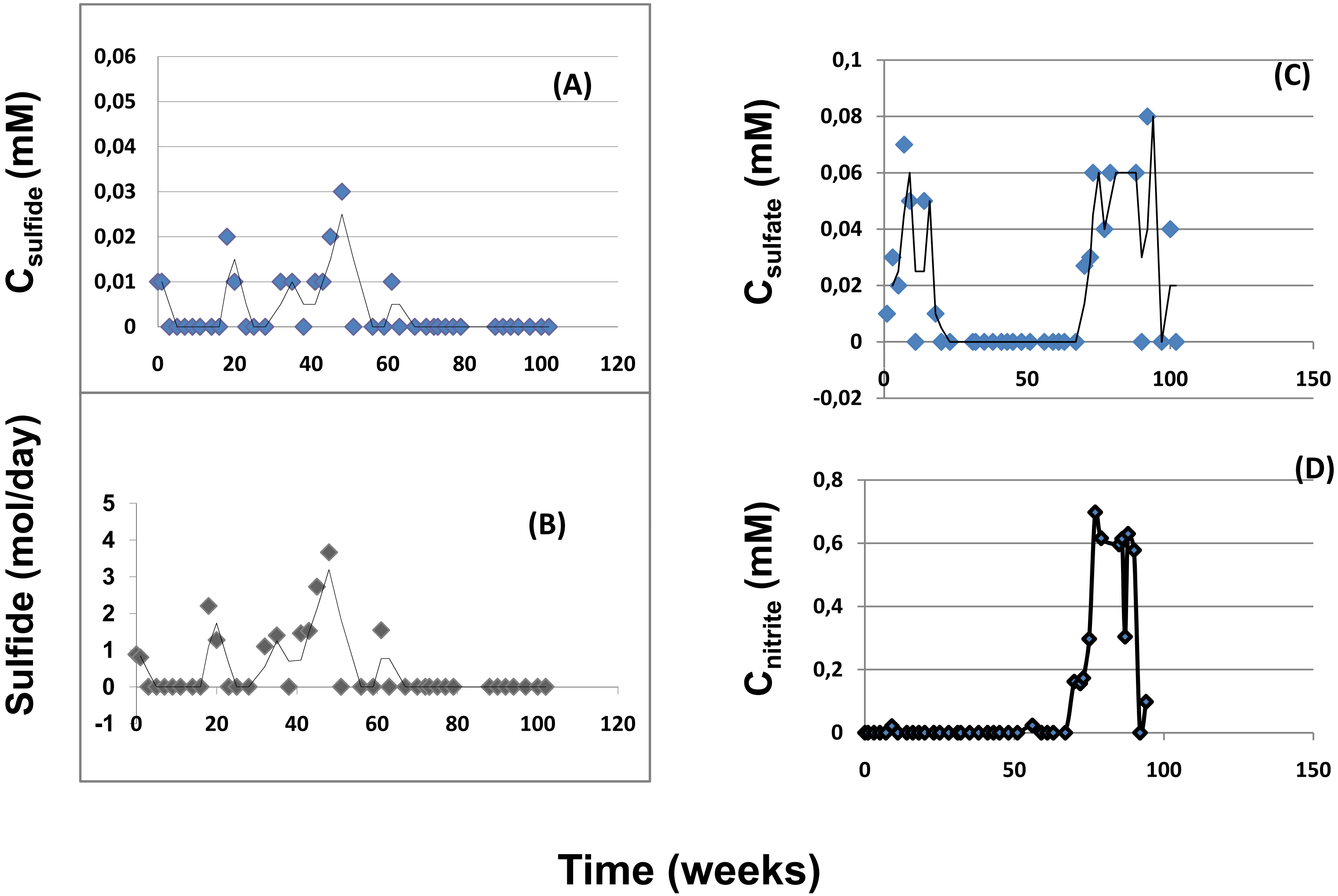
Sulfide production ceased on breakthrough of nitrate/nitrite

Can a pulsing nitrate injection strategy also work field-wide?



High nitrate doses were injected for 1 week at the two main water plants

This gave nitrate/nitrite breakthrough at 7-PW



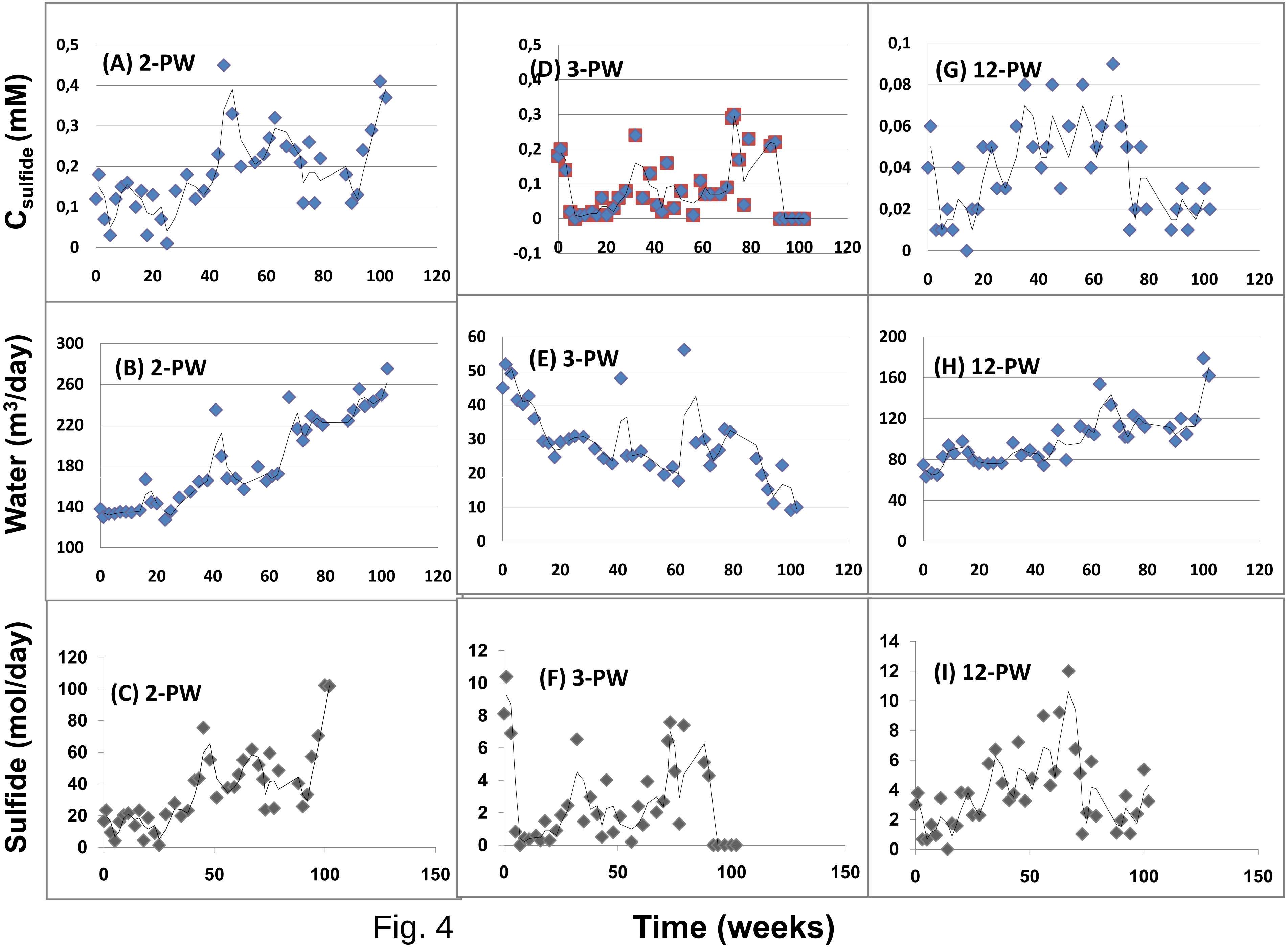
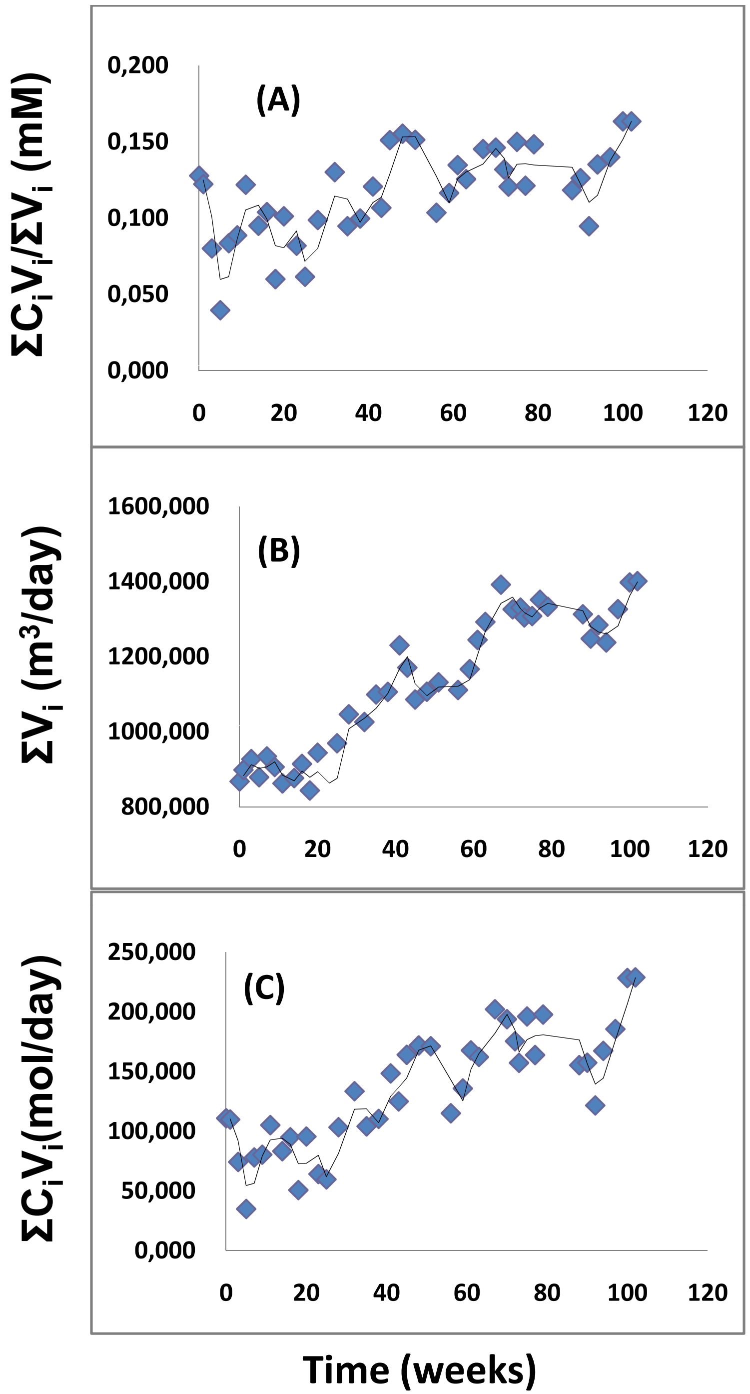

(A) 2-PW
(B) 2-PW
(C) 2-PW
(D) 3-PW
(E) 3-PW
(F) 3-PW
(G) 12-PW
(H) 12-PW
(I) 12-PW
$C_{sulfide}$ (mM)
Water (m^3/day)
Sulfide (mol/day)
Time (weeks)

Fig. 4



Average concentration and total sulfide production for all PWs show:

- **stabilization during pulsing nitrate injection**

- **pattern dominated by 2-PW**

Conclusions:

•Nitrate (2 mM) dosed effectively through the field

•Field-wide sulfide decreased 70% in the first 5 weeks followed by recovery; a model explaining the recovery was presented

•Local increased nitrate dose from weeks 33-101 eliminated production of sulfide at one production well

•Application of field-wide higher doses from weeks 64-96 stabilized sulfide production

•We should concentrate on PWs that contribute most to total sulfide production

Topics to be covered:

1. **Souring control by nitrate injection in low temperature fields**
2. **What is the electron donor for nitrate reduction in the Enermark field?**

Lambo, A. J., Noke, K., Larter, S. R., and Voordouw, G. (2008) Competitive, microbially mediated reduction of nitrate with sulfide and aromatic oil components in a low temperature, western Canadian oil reservoir. Environ. Sci. Technol. 42:8941-8946.

3. **Can injected nitrate oxidize iron sulfide formed downhole?**

Lin, S., Krause, F., and Voordouw, G. (2009) Transformation of iron sulfide to greigite by nitrite produced by oil field bacteria. Appl. Microbiol. Biotechnol. 83:369-376.

4. **Microbial community in low temperature oil field under nitrate injection**

Microbial community composition at 13-PW before and after nitrate breakthrough

Methodology:

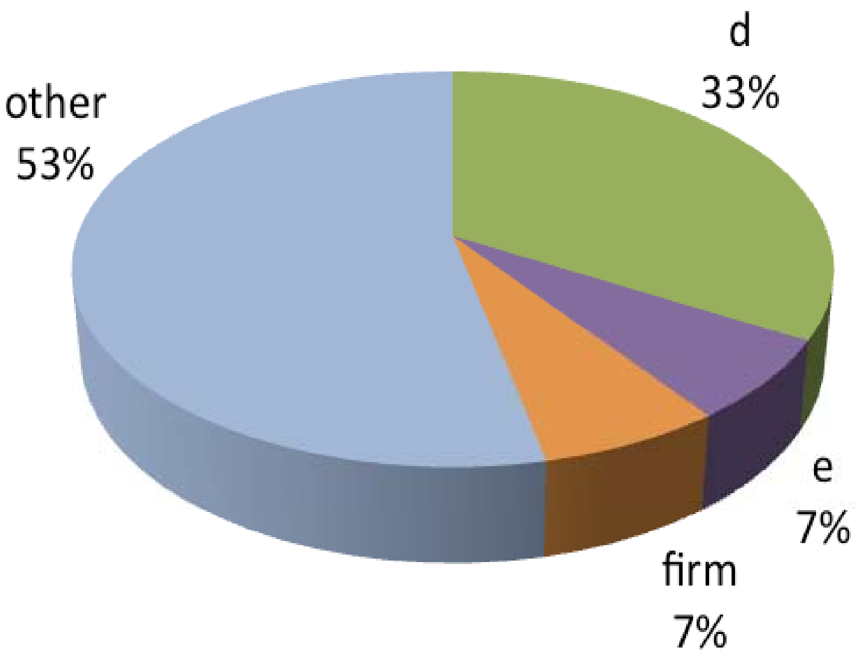
- Isolate DNA directly from produced waters
- PCR amplify using bacterial or archaeal universal 16S primers
- Separate amplicons by DGGE
- Identify by sequencing

- Bacterial component showed increased NRB
- Archaeal (methanogen) component showed decreased diversity

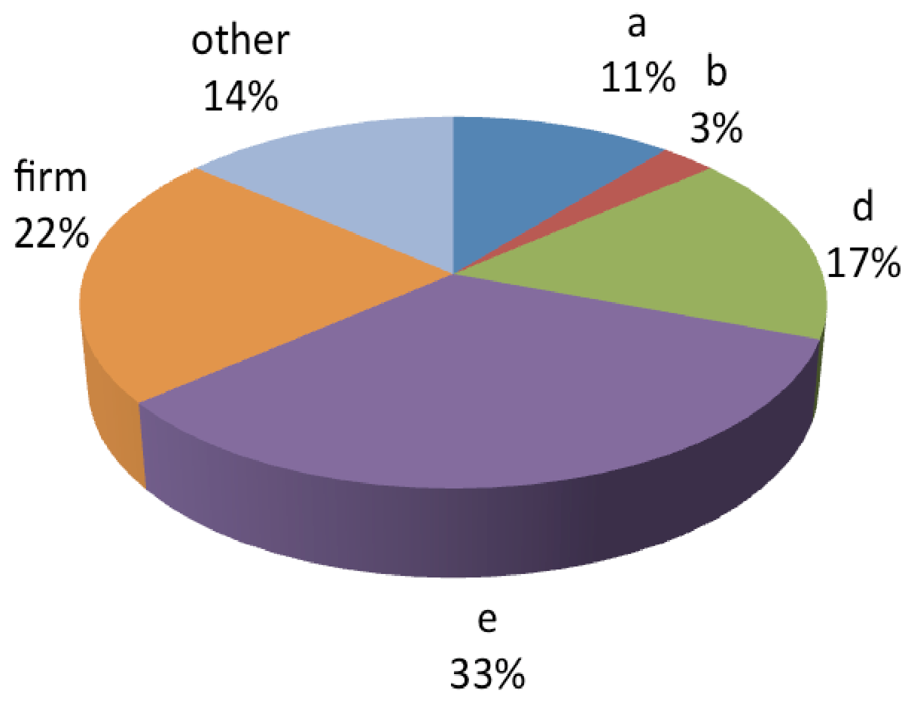
13-PW: Bacteria

α	hNRB
β	hNRB
γ	hNRB
δ	SRB
ε	NR-SOB
Firmicutes	varies
other	varies

Before

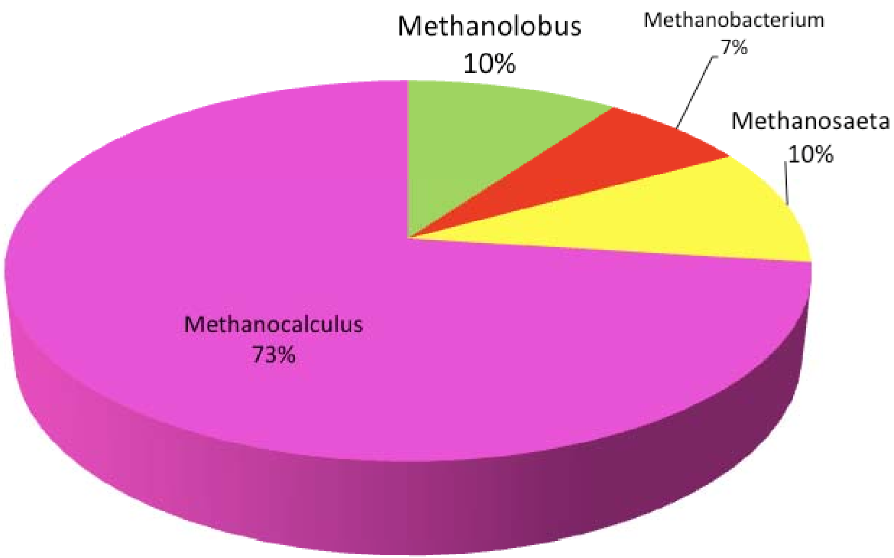


After

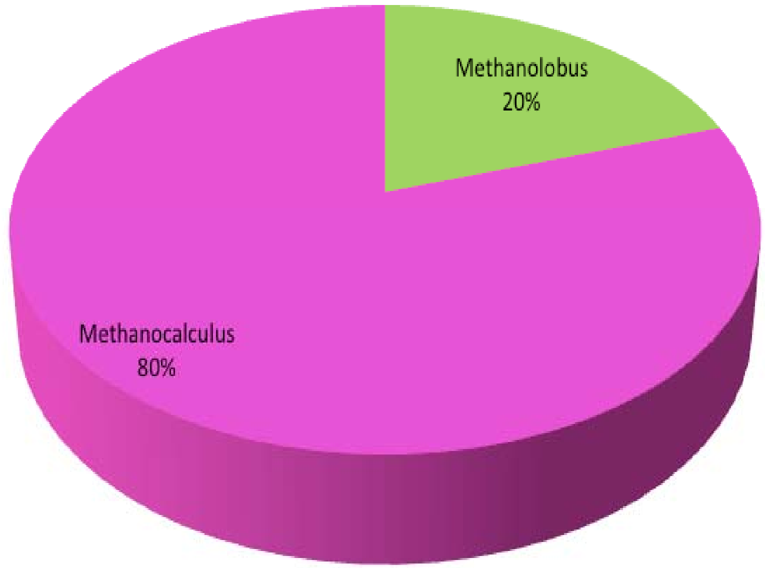


13-PW: Archaea

Before



After



Thanks to “the team” (on first sampling trip to MHGC field)

Tom Jack	Adjunct Professor
Adewale Lambo	PDF
Sasha Grigoryan	PDF
Shiping Lin	Technician
Johanna Voordouw	Technician
Sabrina Cornish	Graduate Student
Rhonda Clark	Project Manager

MHGC oil field study:

Kirk Miner	Baker Petrolite
Ryan Ertmoed	Baker Petrolite
Pat Stadnicki	Enerplus
Bill Clay	Enerplus

Thanks to Institutional and Corporate sponsors

NSERC Industrial Research Chair in Petroleum Microbiology