U.S. Department of Energy — Office of Science

Integrated Field-Scale Subsurface Research Challenge

Environmental Remediation Sciences

Oak Ridge Field Research Center

Oak Ridge *IFRC*

Bioreduction of Uranium with Slow Release Substrates

Presenter: David Watson

ERSP Annual PI Meeting
Lansdowne, Virginia
April 20, 2009

OAK RIDGE National Laboratory

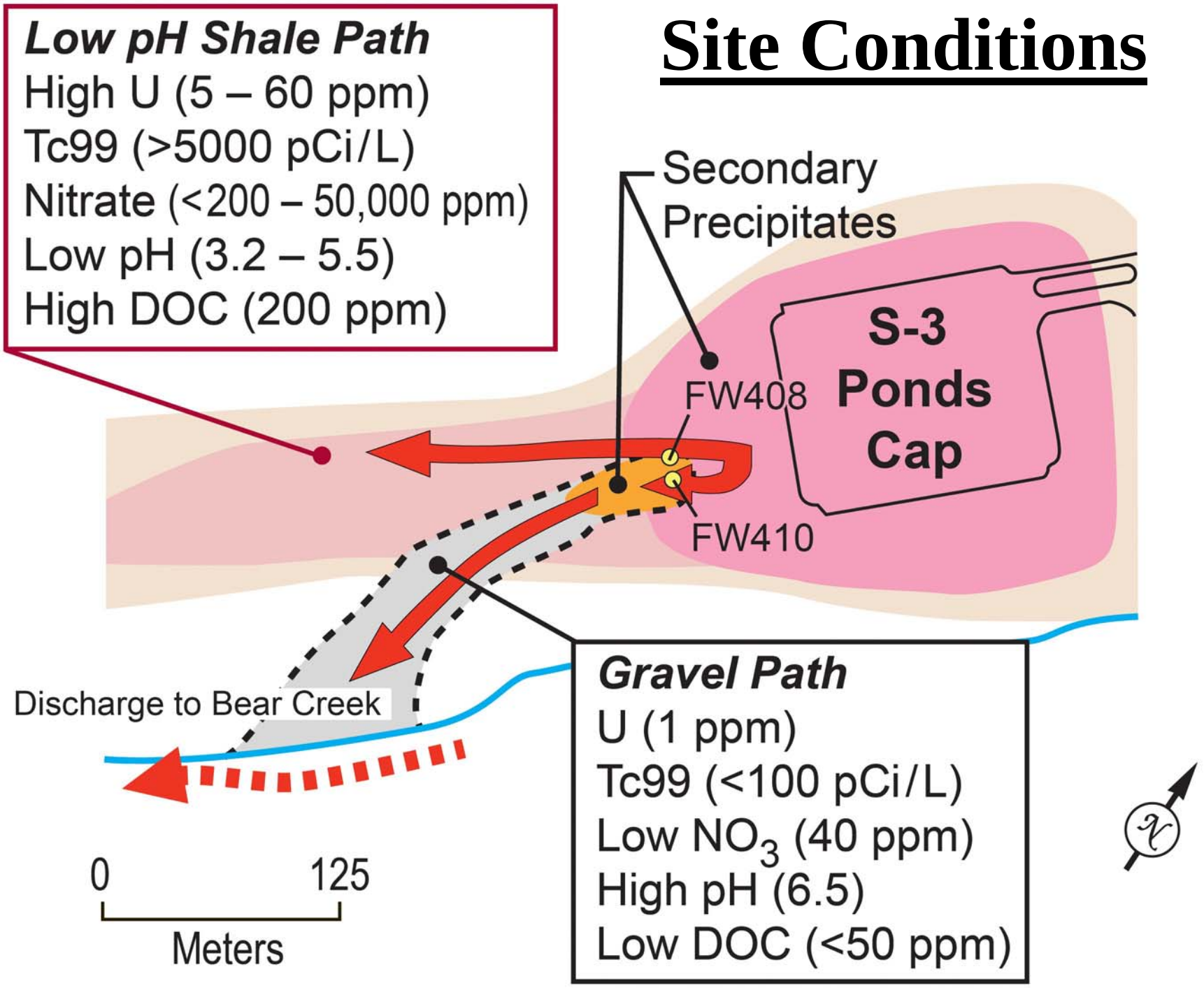
Objectives

- Conduct laboratory and field studies and modeling of slow release substrates:
  - Ca-oleate precipitates and emulsified vegetable oils
  - Is reduction of U(VI) and nitrate possible?
  - Is it sustainable?
- Assess substrate delivery and subsurface distribution issues
- Test direct and remote sensing measurement methods

Tasks and Contributors

- Task leaders – David Watson (ORNL) and Weimin Wu (Stanford)
- Batch rate studies to assess substrates - Weimin Wu (Stanford)
- Column break through and electrical resistivity studies (LBNL) – Yuxin Wu and Susan Hubbard
- Bromide tracer test and injection of emulsified vegetable oil (ORNL) – Field, lab, analytical and data analysis support: Tonia Mehlhorn, Kenneth Lowe, Sally Mueller, Jana Phillips, Kirk Hyder and Jennifer Earles
- Surface ERT geophysics (UT) – Greg Baker et. al.
- PELCAPs and dissolved gases (ORNL) – Brian Spalding and Jennifer Earles
- Microbiology (ORNL) – Chris Schadt and Gengxin Zhang
- Spectrographic (ANL) – Ken Kemner and Max Boyanov
- Modeling (ORNL) – Fan Zhang

Site Conditions



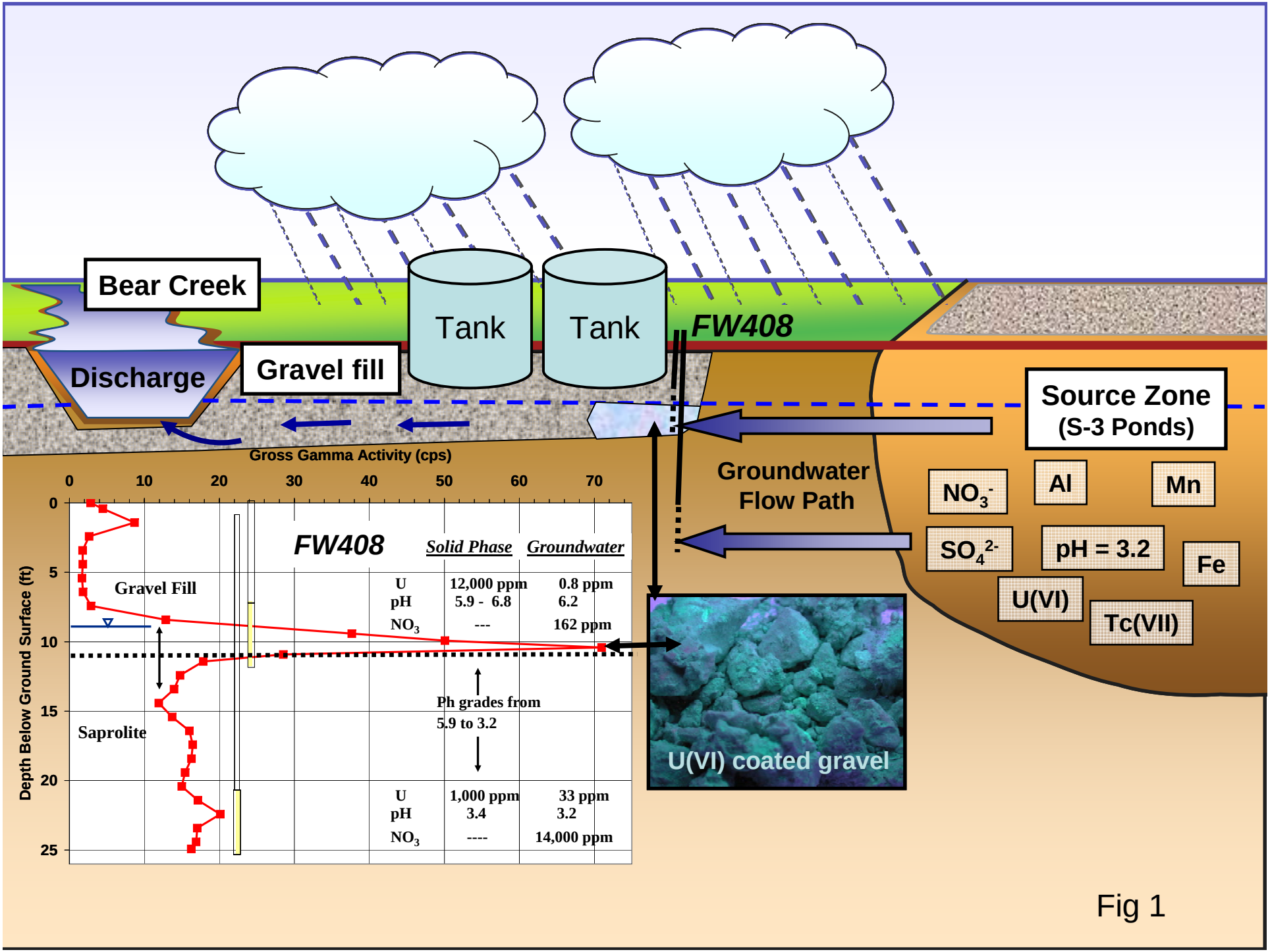

Bear Creek
Discharge
Gravel fill
Tank
Tank
FW408
Source Zone
(S-3 Ponds)
Groundwater
Flow Path
NO_3^-
Al
Mn
SO_4^{2-}
pH = 3.2
Fe
U(VI)
Tc(VII)
Gross Gamma Activity (cps)
0
10
20
30
40
50
60
70
Depth Below Ground Surface (ft)
0
5
10
15
20
25
FW408
Solid Phase
Groundwater
Gravel Fill
U 12,000 ppm 0.8 ppm
pH 5.9 - 6.8 6.2
NO_3 --- 162 ppm
Ph grades from
5.9 to 3.2
Saprolite
U 1,000 ppm 33 ppm
pH 3.4 3.2
NO_3 ---- 14,000 ppm
U(VI) coated gravel

Fig 1

Past studies suggest need to explore substrates that can sustain reducing conditions and decrease costs

Solinst CMT MLS

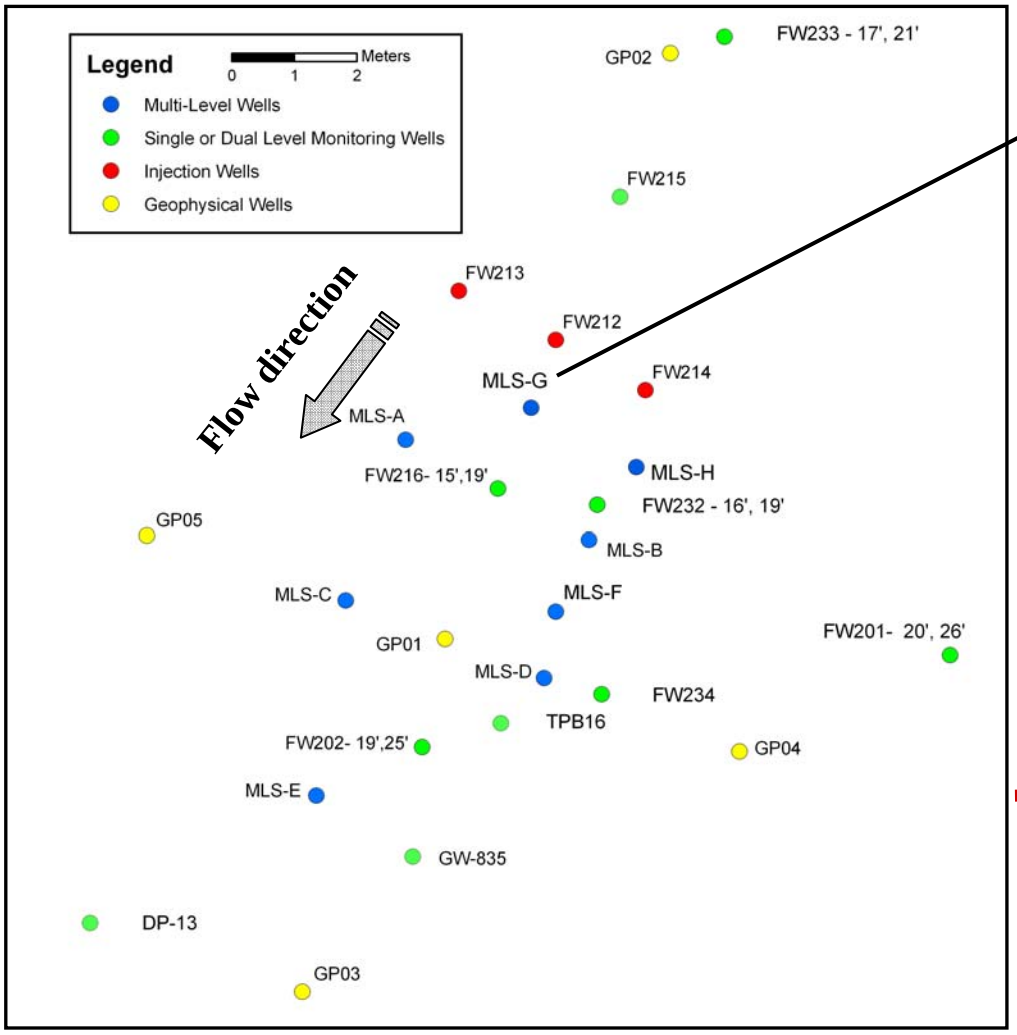
Area 2 Field Plot

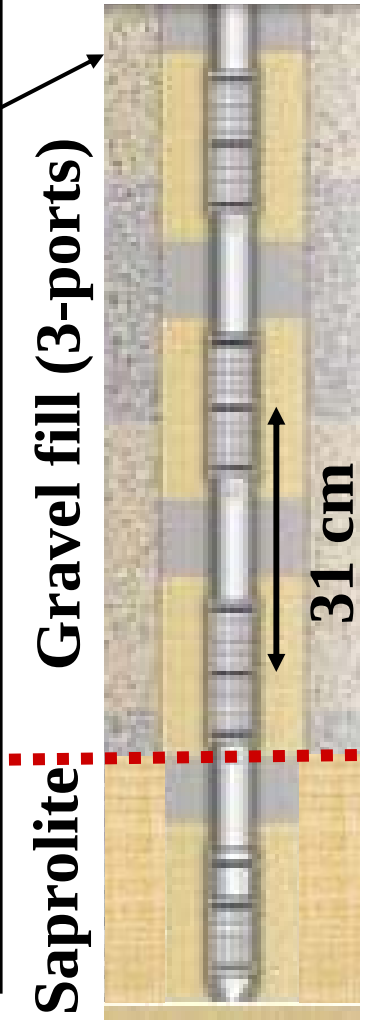
“Scheibe” Site

-Daily injections of ethanol for 1 year

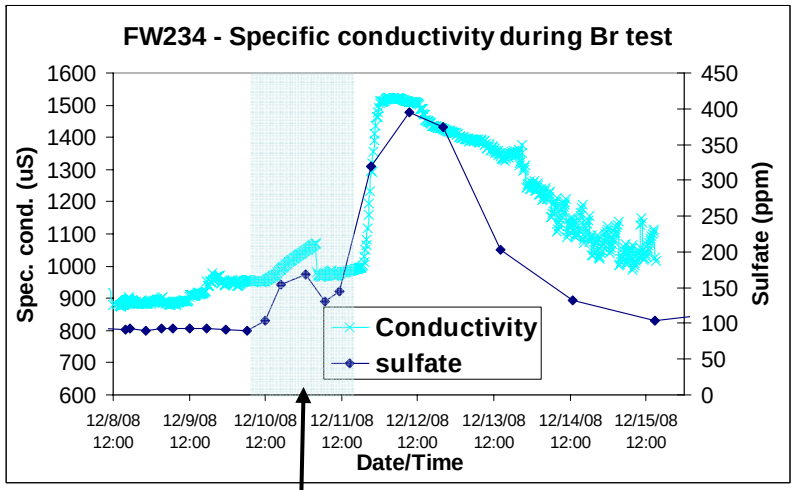
-U conc. below MCL of 0.03 mg/L can be achieved

-Rapid rebound observed when injections stopped in 09/2006

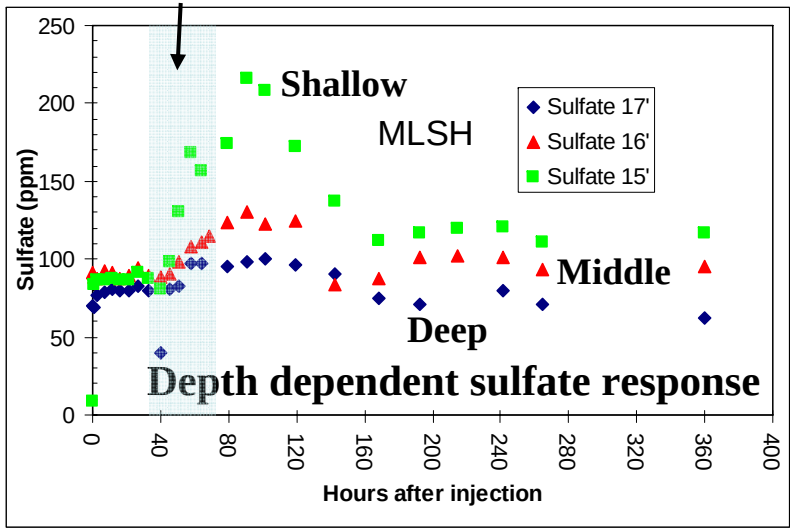


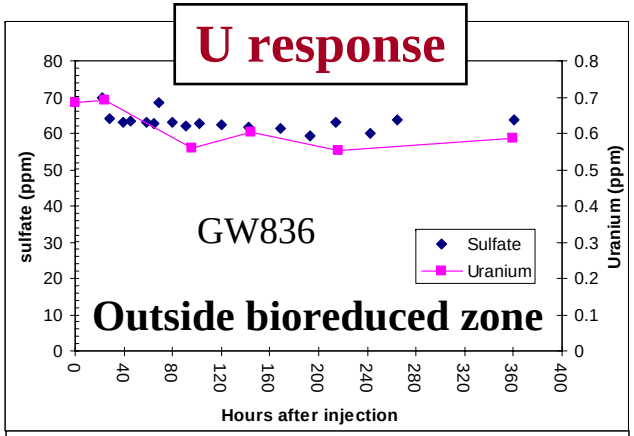


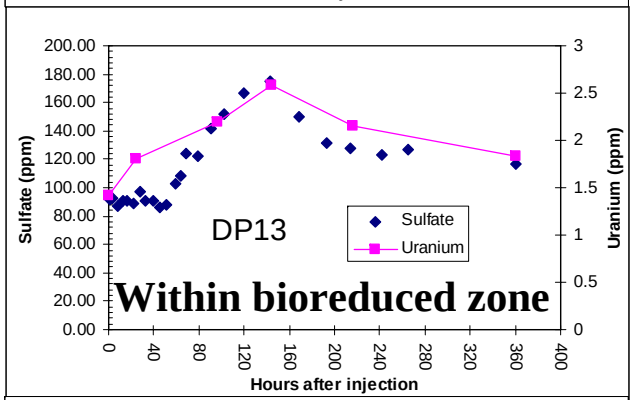
Remobilization of U during storm event within previously bioreduced zone

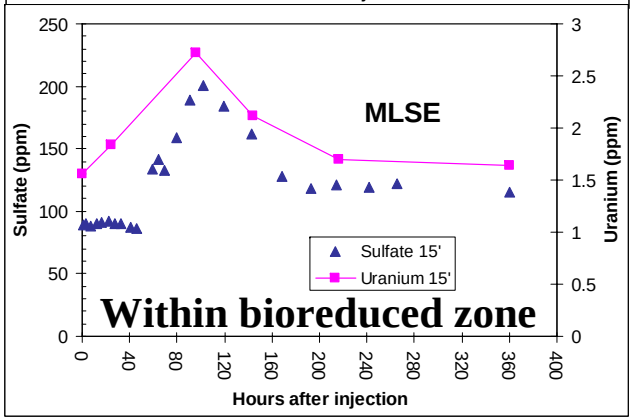


4" rain event from 37-73 hours



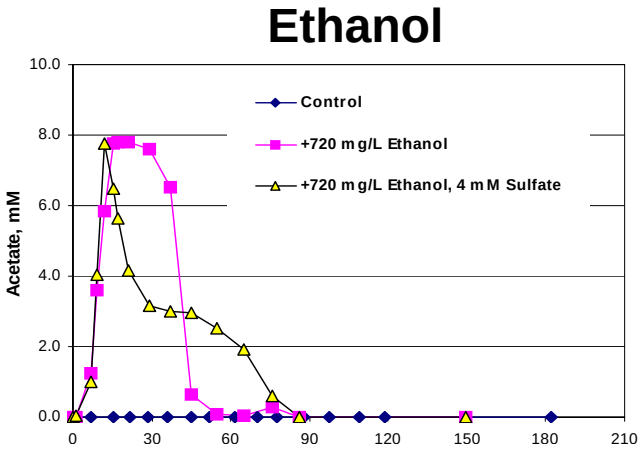


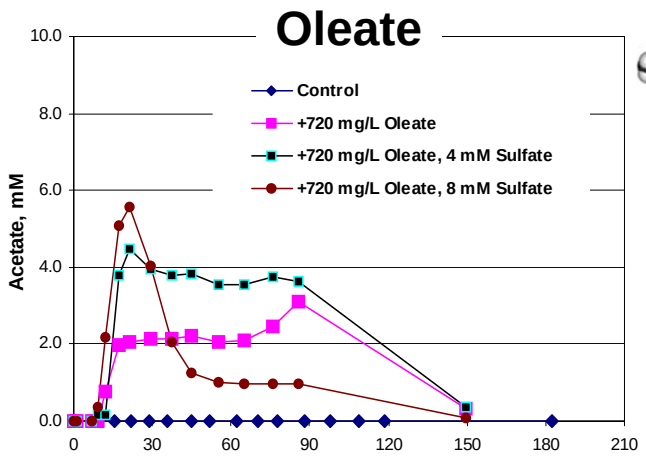




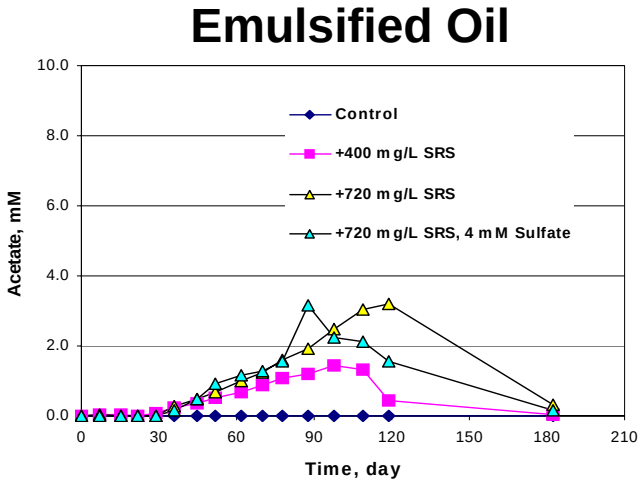
Laboratory Studies
(with site GW and core material)

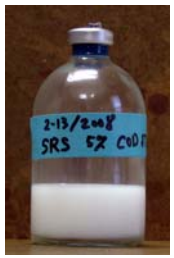
Acetate production from ethanol, Ca-oleate precipitates, and emulsified vegetable oil (EVO)





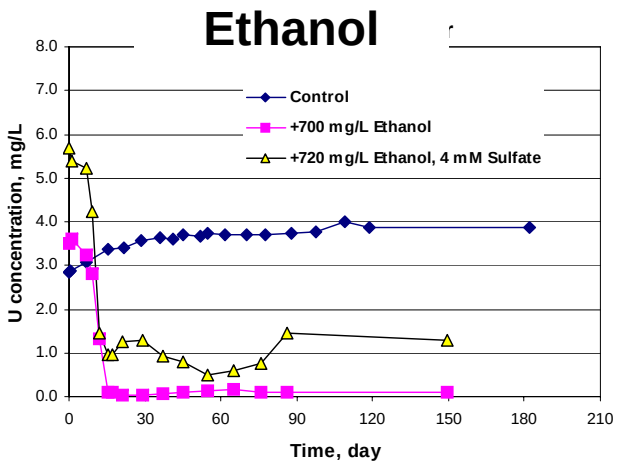
Molecular structure of oleic acid

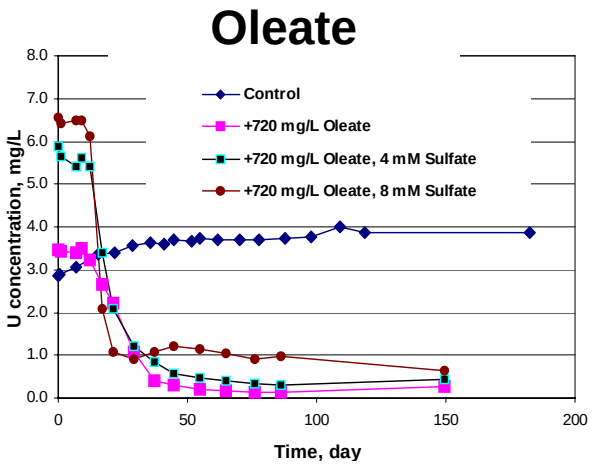


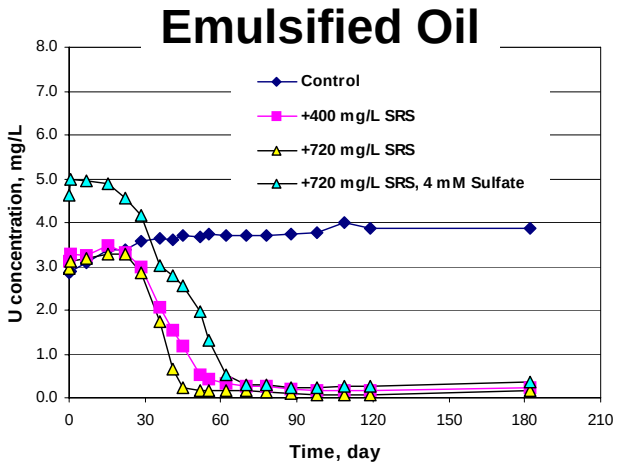


The rate of acetate accumulation suggests that EVO degradation is slow compared to other substrates

The acetate production for all substrates depends on initial sulfate concentration.



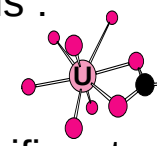




Laboratory Studies

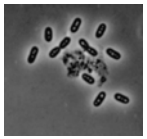
U(VI) reduction by ethanol, oleate, and EVO

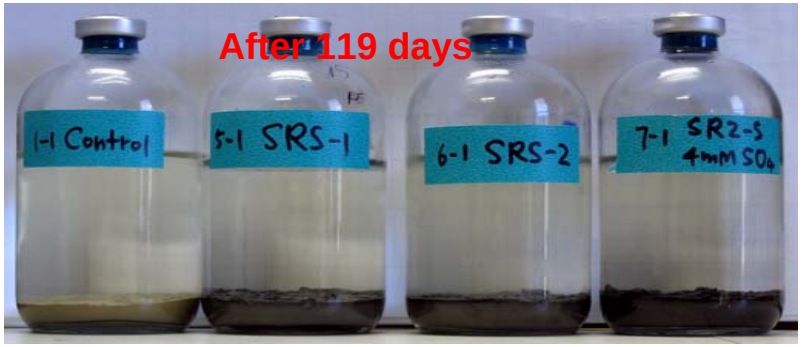
The rate of U(VI) removal in microcosms : ethanol > oleate >> EVO.



U speciation using XANES showed significant (>50%) U(IV)

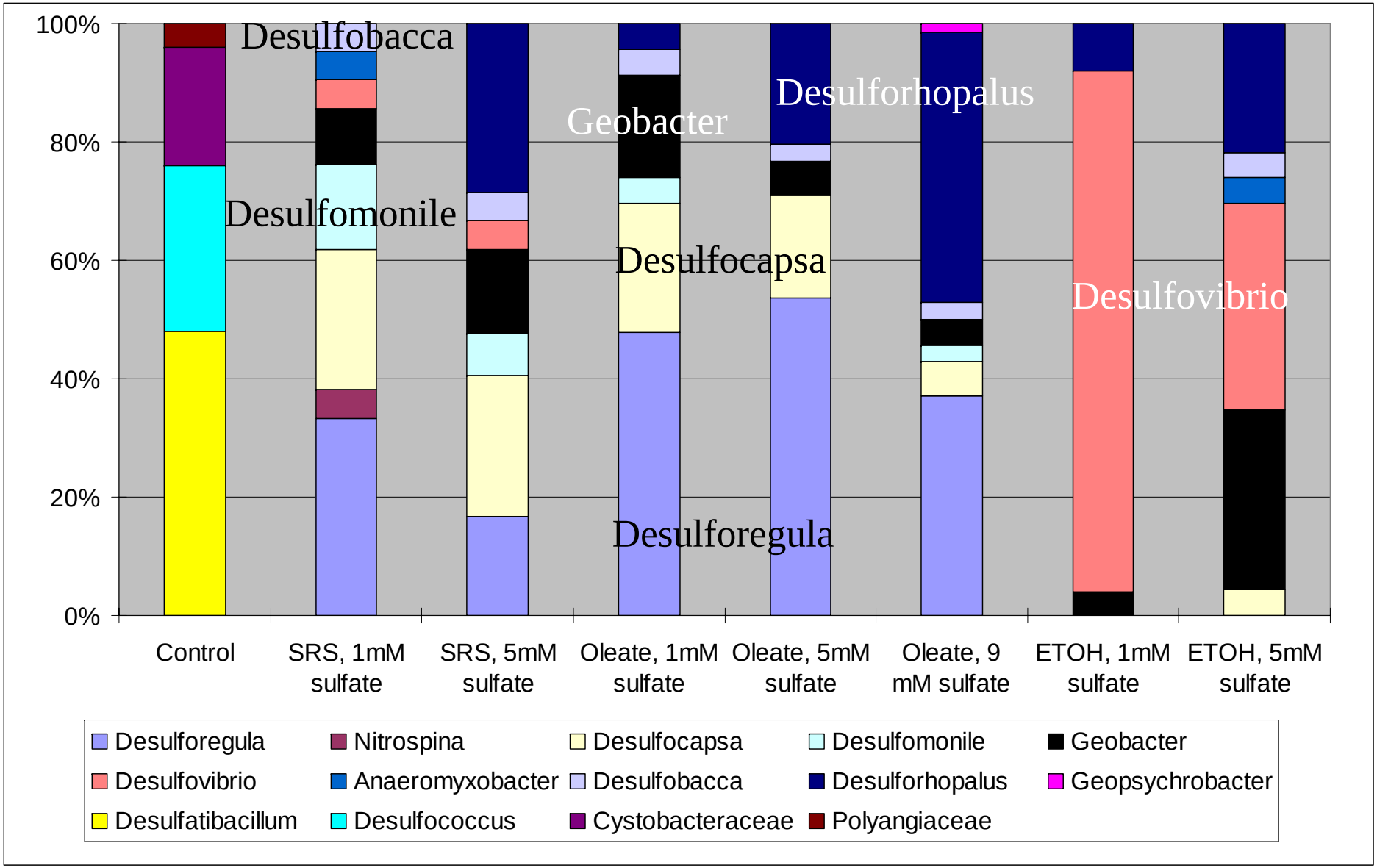
From 16s analysis we infer that *Desulforegula* oxidizes EVO and Ca-oleate and reduces sulfate with by-products of short fatty acids and hydrogen sulfide. The biogenerated hydrogen sulfide of FeS may abiotically reduce U(VI)





Effects of Donor Amendments and Sulfate Conc. on Delta-Proteobacteria

Populations different for SRS and oleate compared to control and ethanol



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Field Experiments

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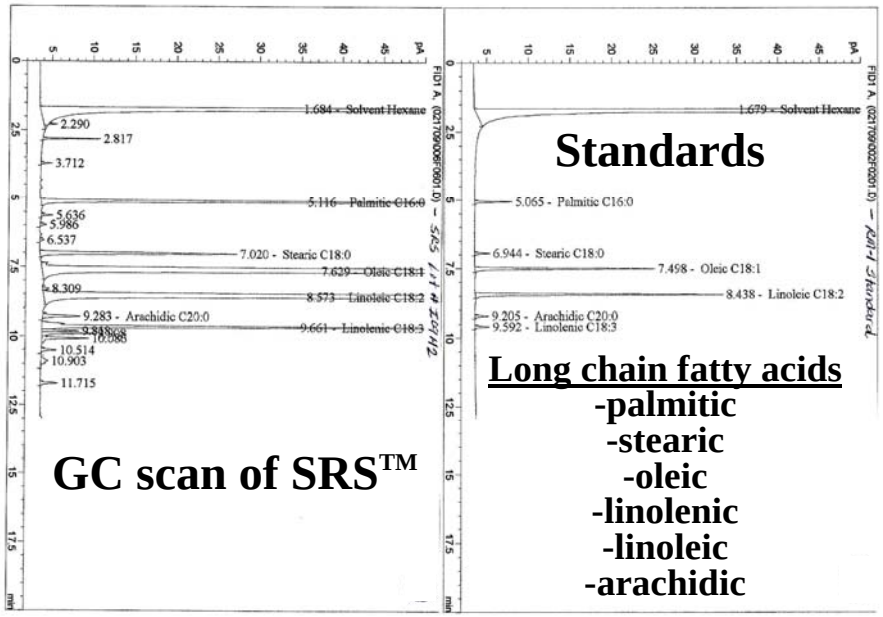

GC scan of SRS™

Standards

Long chain fatty acids
-palmitic
-stearic
-oleic
-linolenic
-linoleic
-arachidic

- 900 gallons of a 20% SRS™ solution (mixed with site GW) injected in 3 wells in @1.5 hours on 2/9/09

-Bromide tracer test (450 ppm) conducted on 12/8/09 in similar manner to SRS injection

SRS™ composition

Soybean oil (%)	60
Yeast extract (%)	0.3
Surfactant (%)	6
$(NH_4)_3PO_4$ (%)	0.05
Remainder water	
Density (kg/L)	0.93
COD (g/L)	1620

5.9 times the amount of COD injected in 2 hours than for the entire year of ethanol injections

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Br and SRS injections

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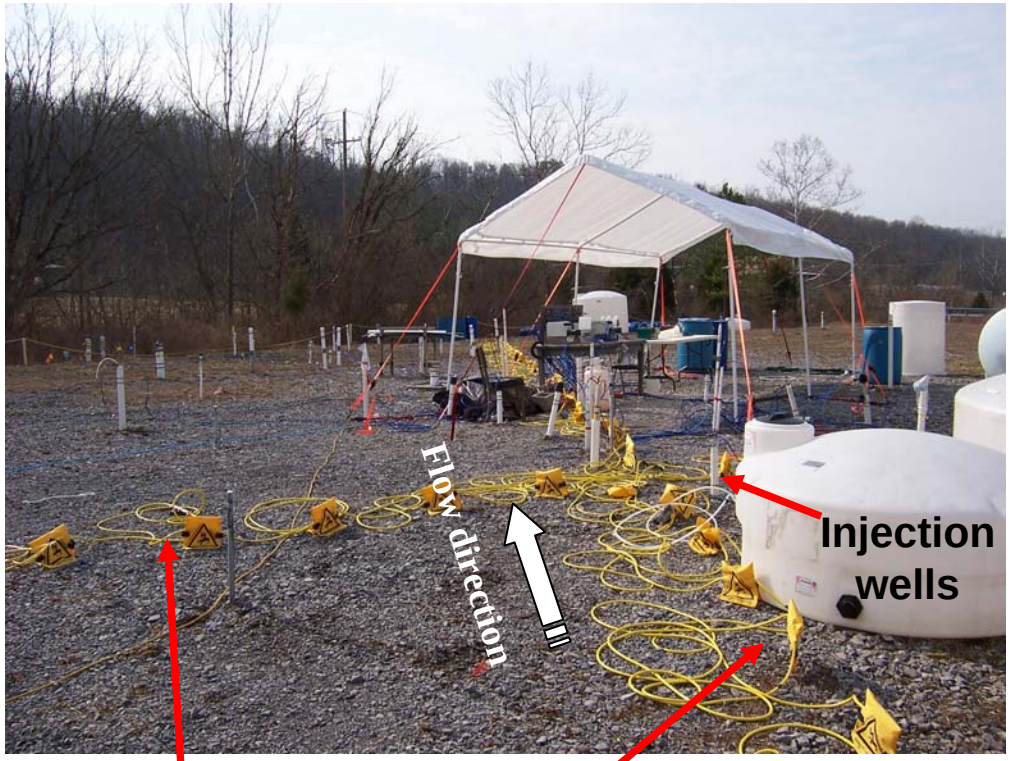

Electrical resistivity surface arrays for tracking SRS plume

Stirring buckets of SRS

Sampling >50 GW wells and seeps

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Analyses

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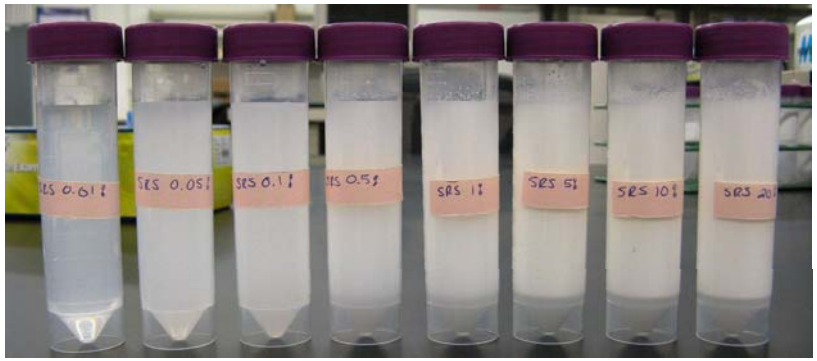
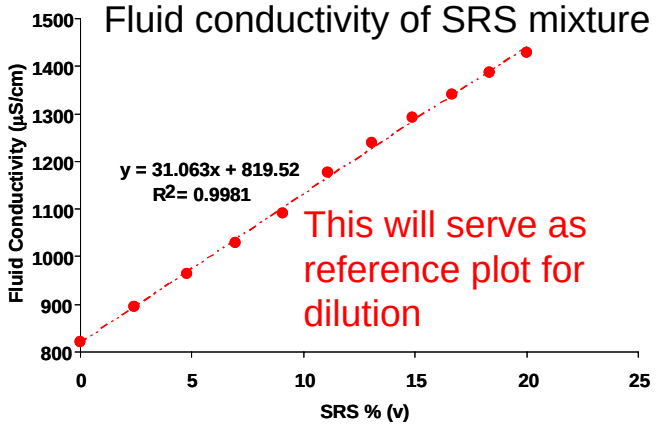
Volatile solid (VS) analysis by oven drying and ashing (Borden, 2007)

- **Visual indicator of % SRS**
- **Specific conductance (both bromide and SRS solutions have a signal), pH, DO**
- **Sulfide odor**
- **Field Hach kit (nitrite, Fe(II), sulfide, COD)**
- **Volatile solids by drying/ashing**
- **IC (anions), ICP/MS (metals), TIC/TOC after SRS lower and indication of bioreduction**





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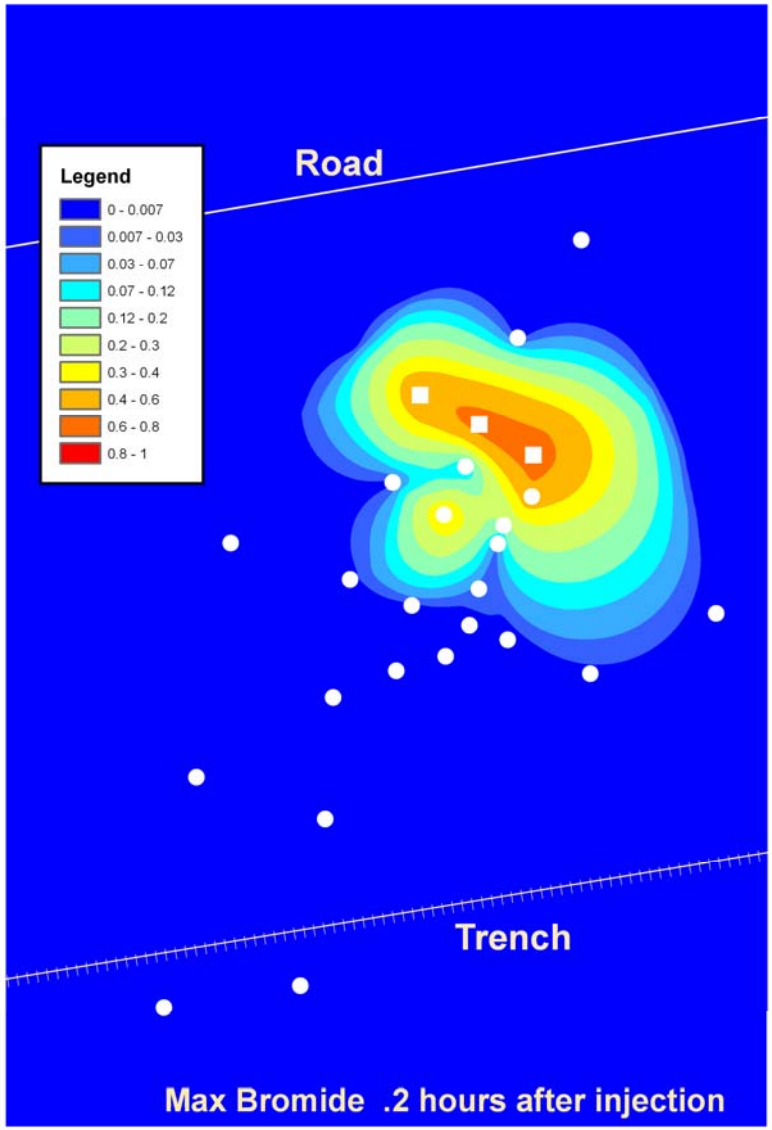
Comparison of Br to SRS C/C_0 concentration contours



- Highest concentration port used for MLS wells
- Fewer time intervals sampled for SRS
- General distribution through center of well field
- SRS slower and more to the left (Impact of SRS floating?)
- Poorly constrained downgradient but reached creek

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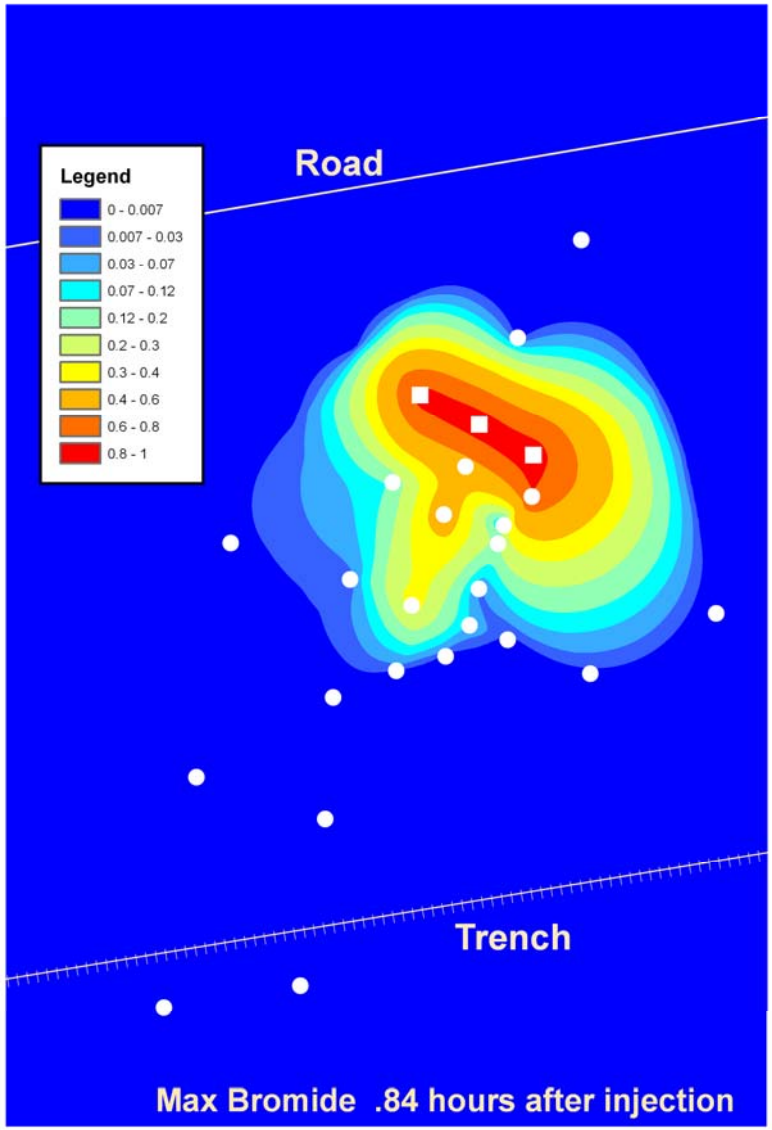

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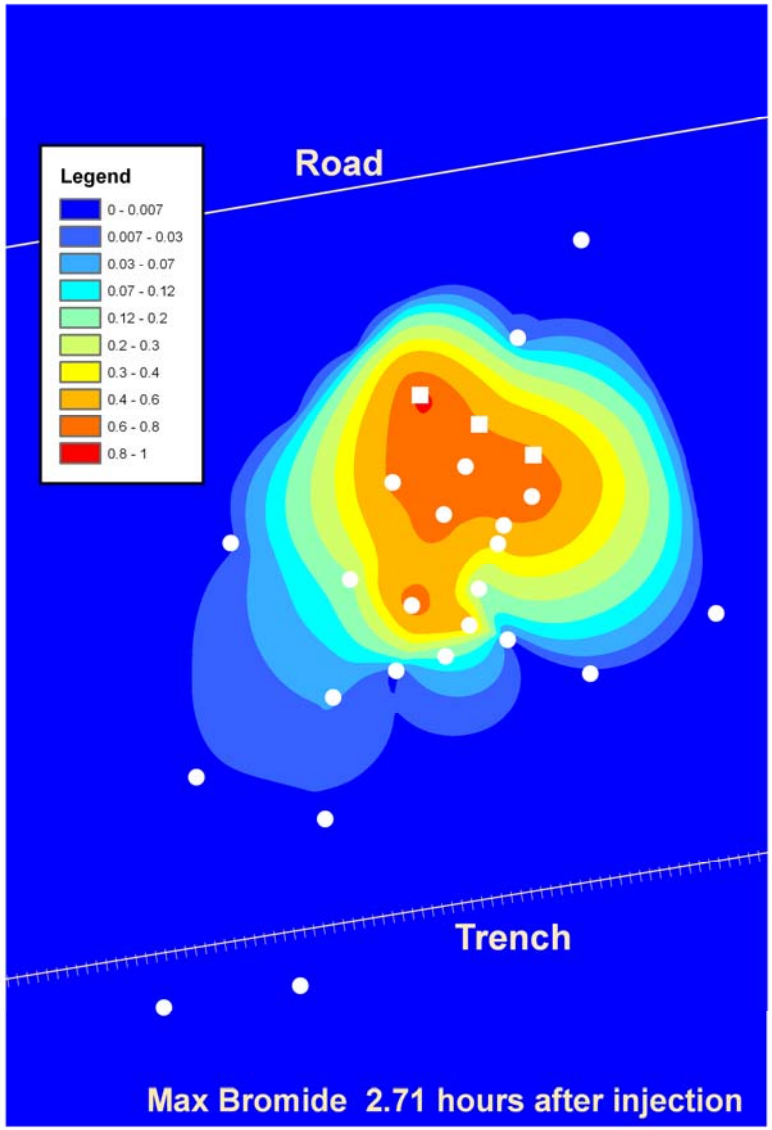

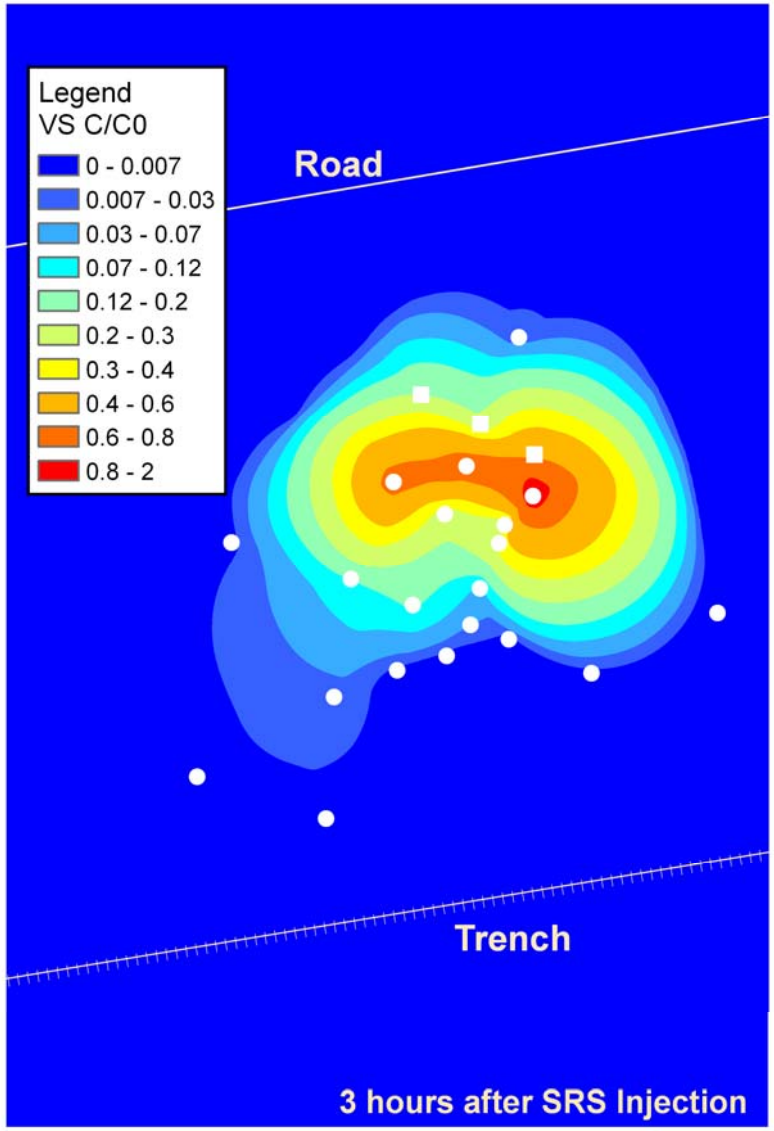

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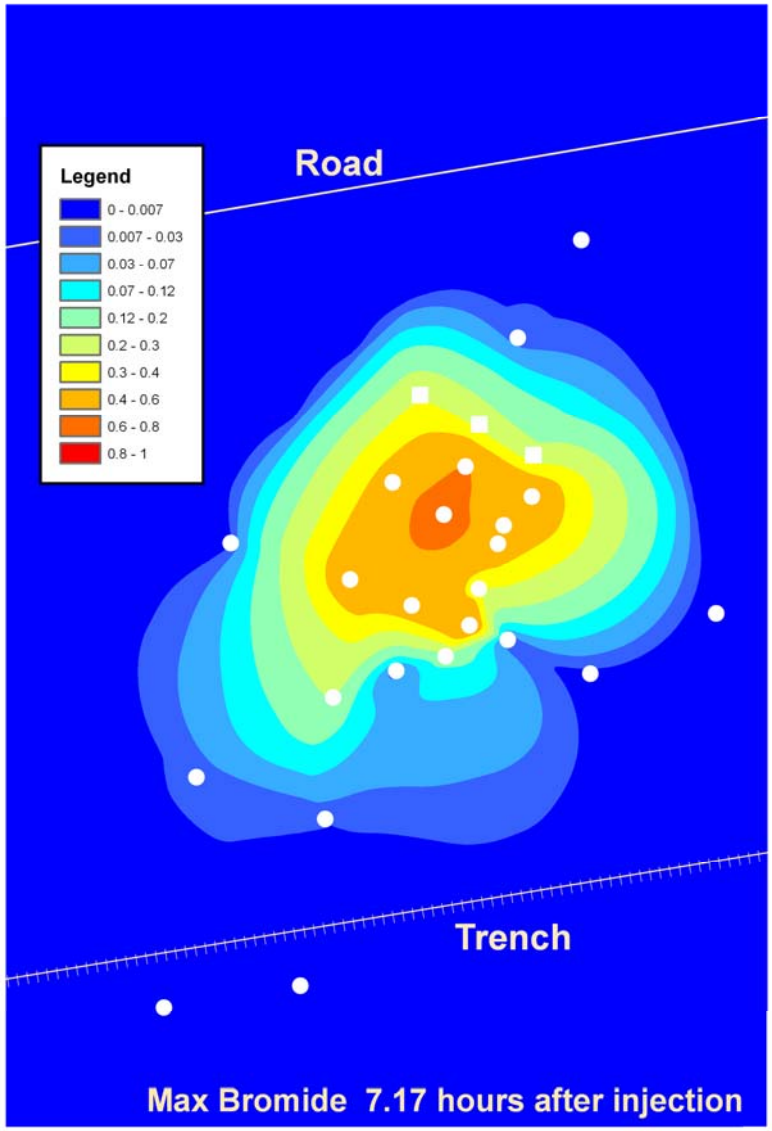

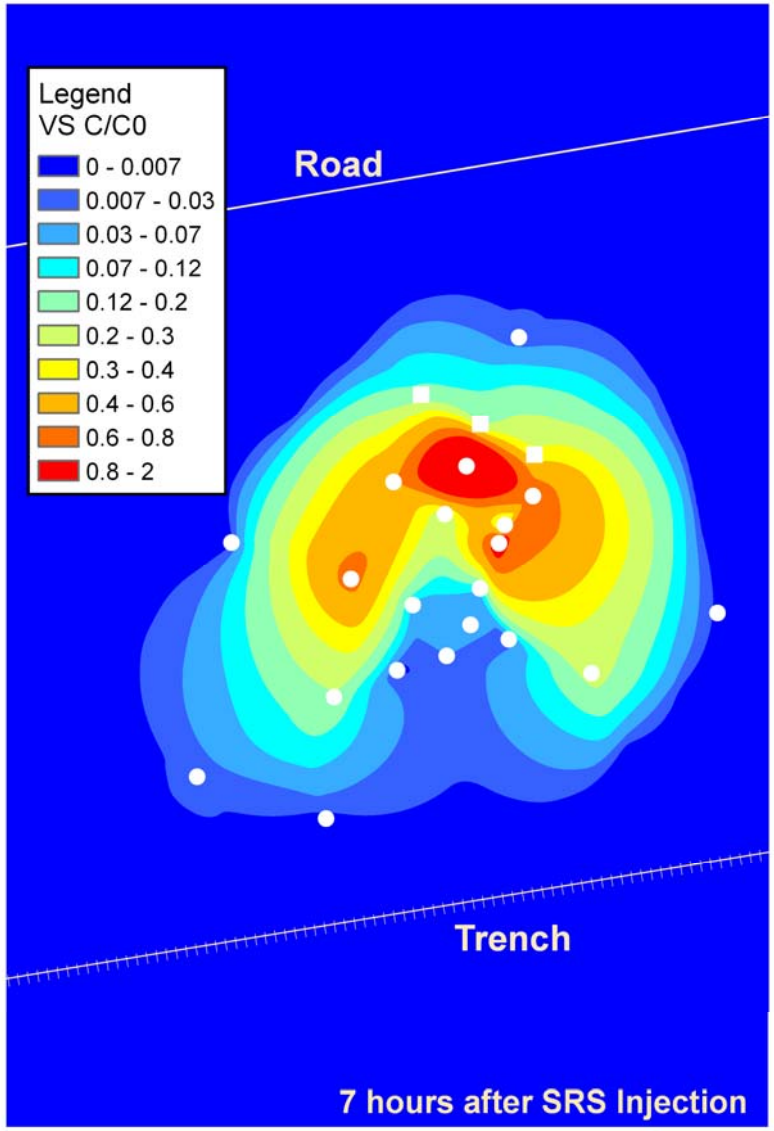

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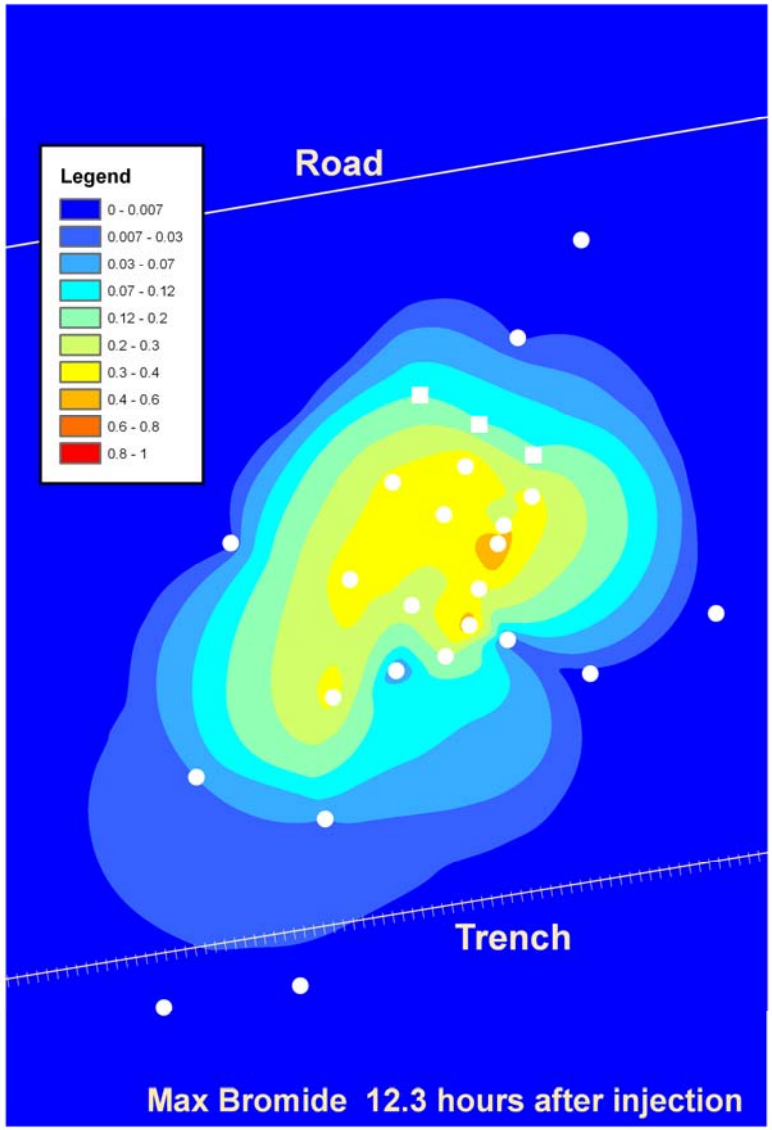

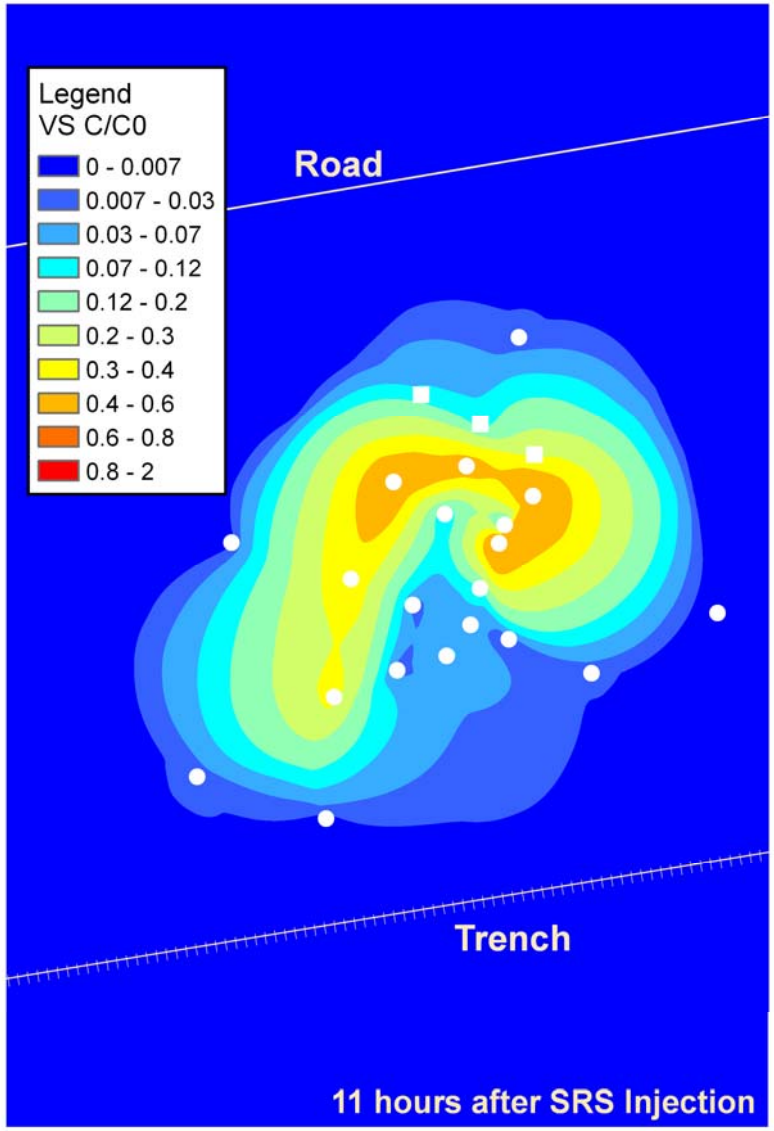

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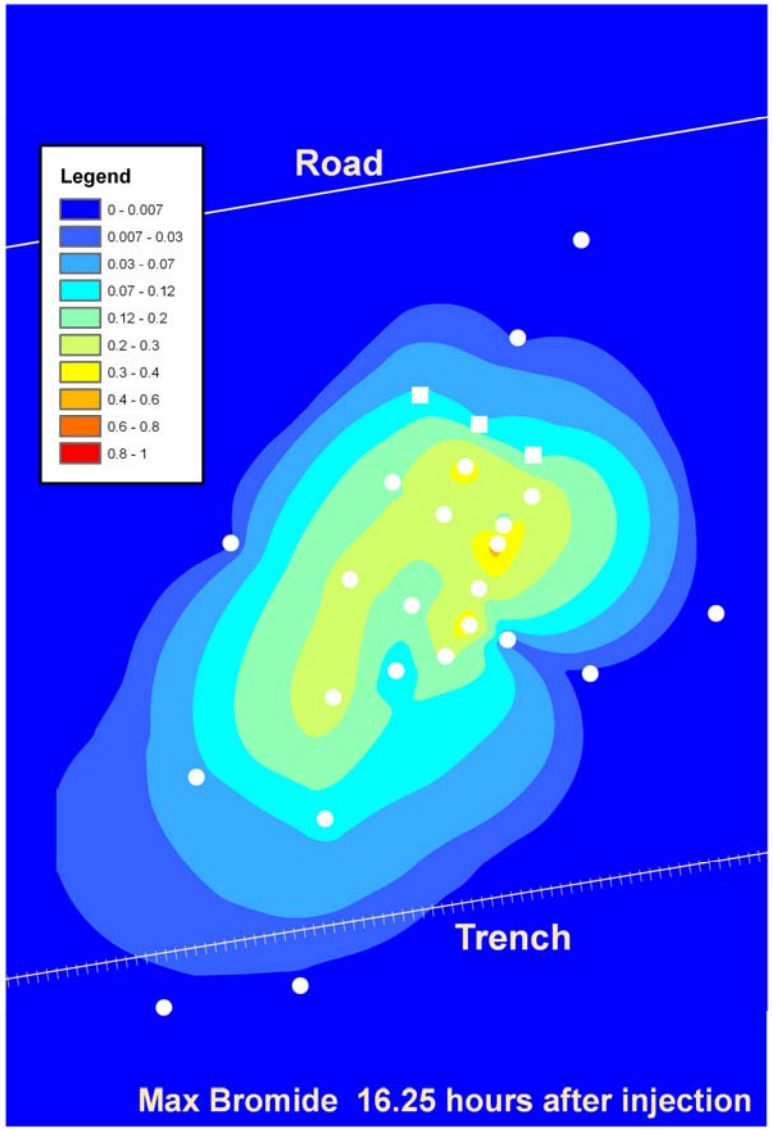

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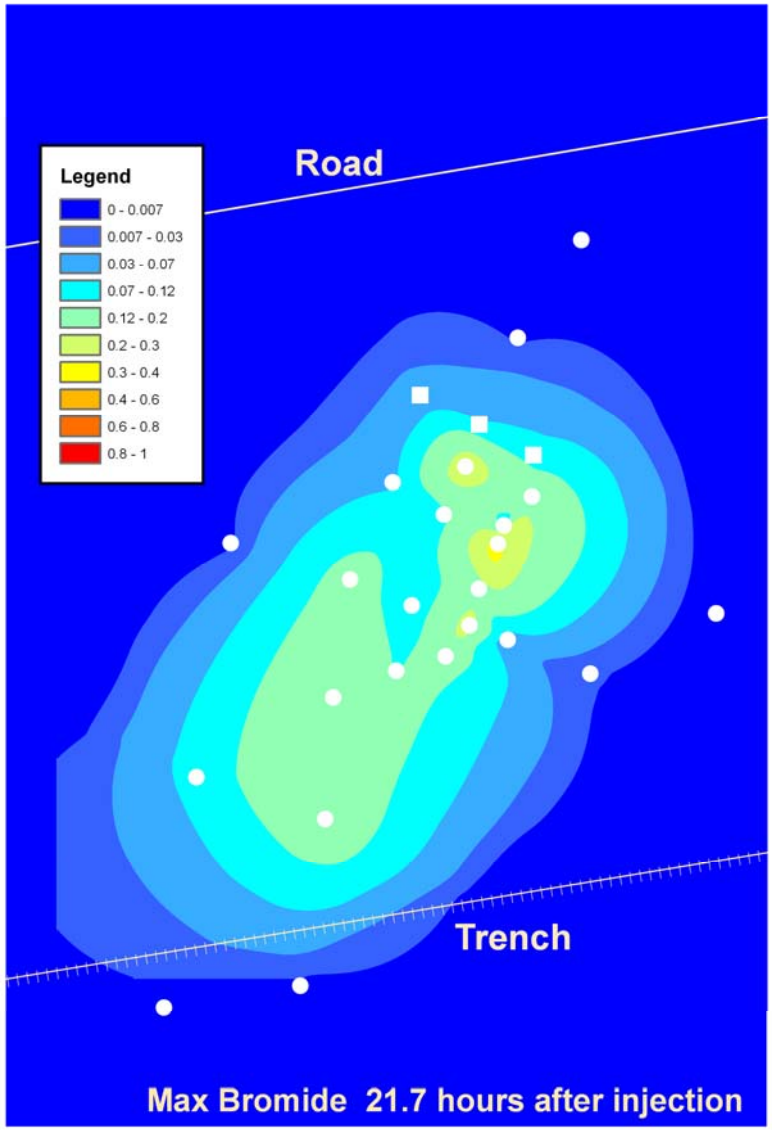

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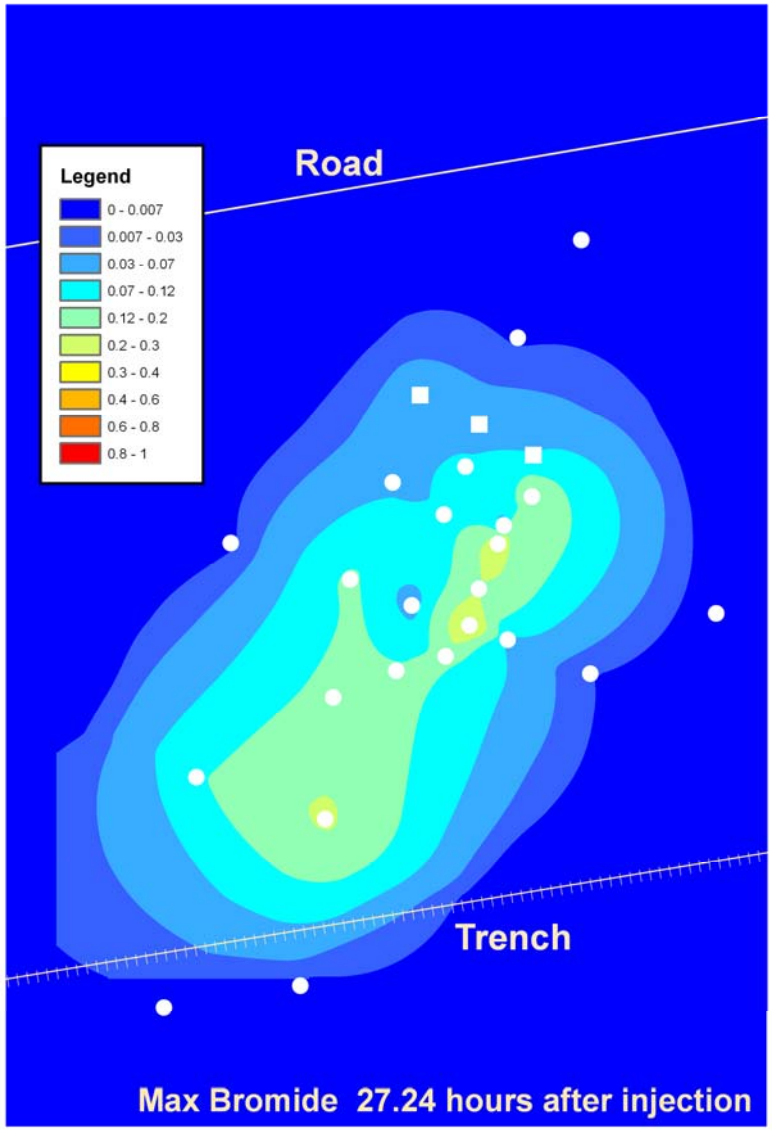

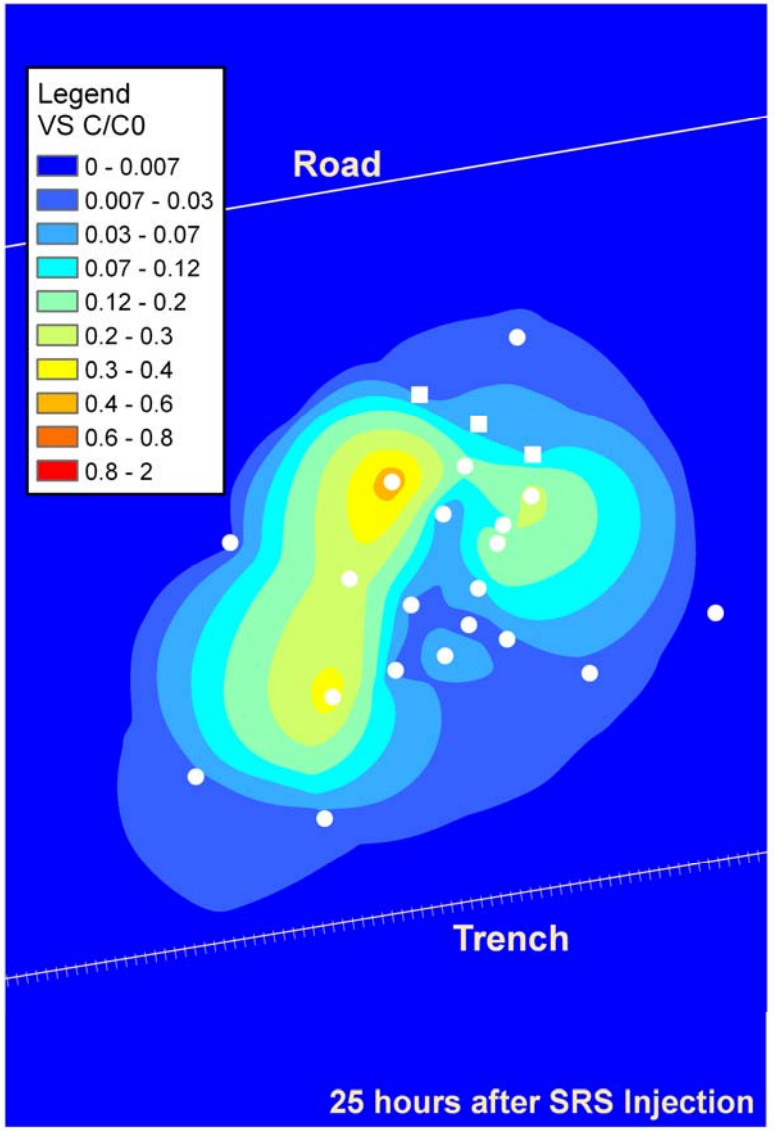

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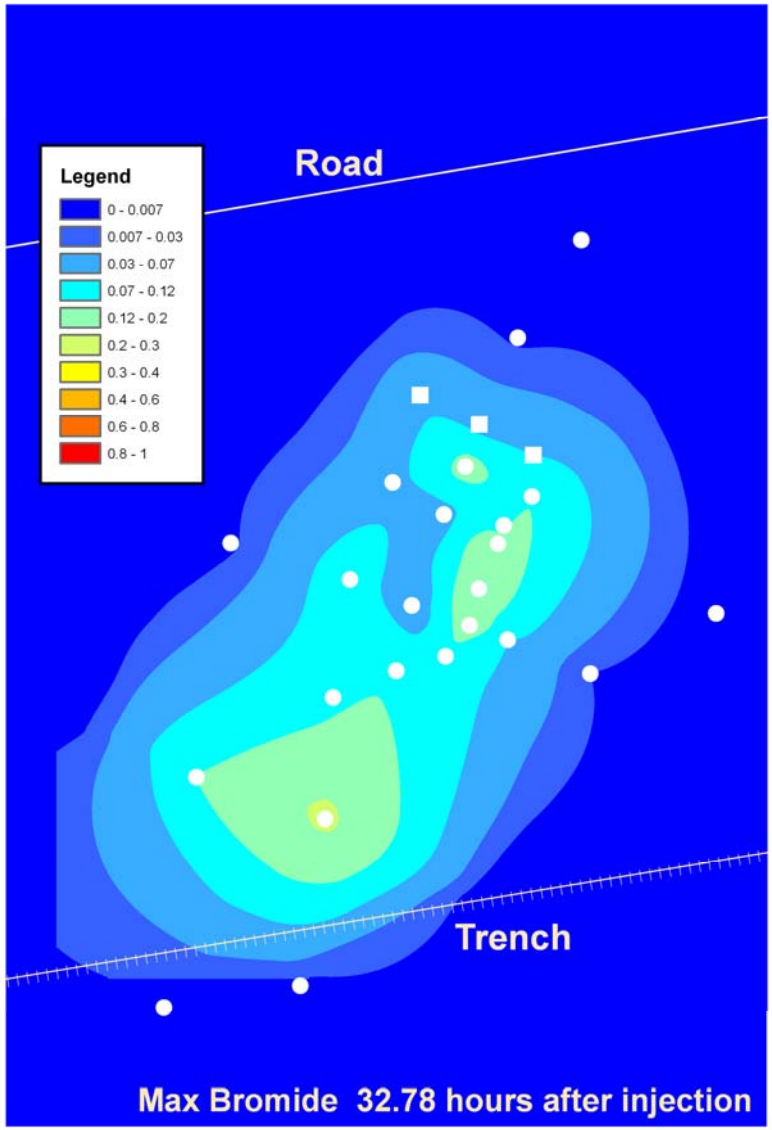

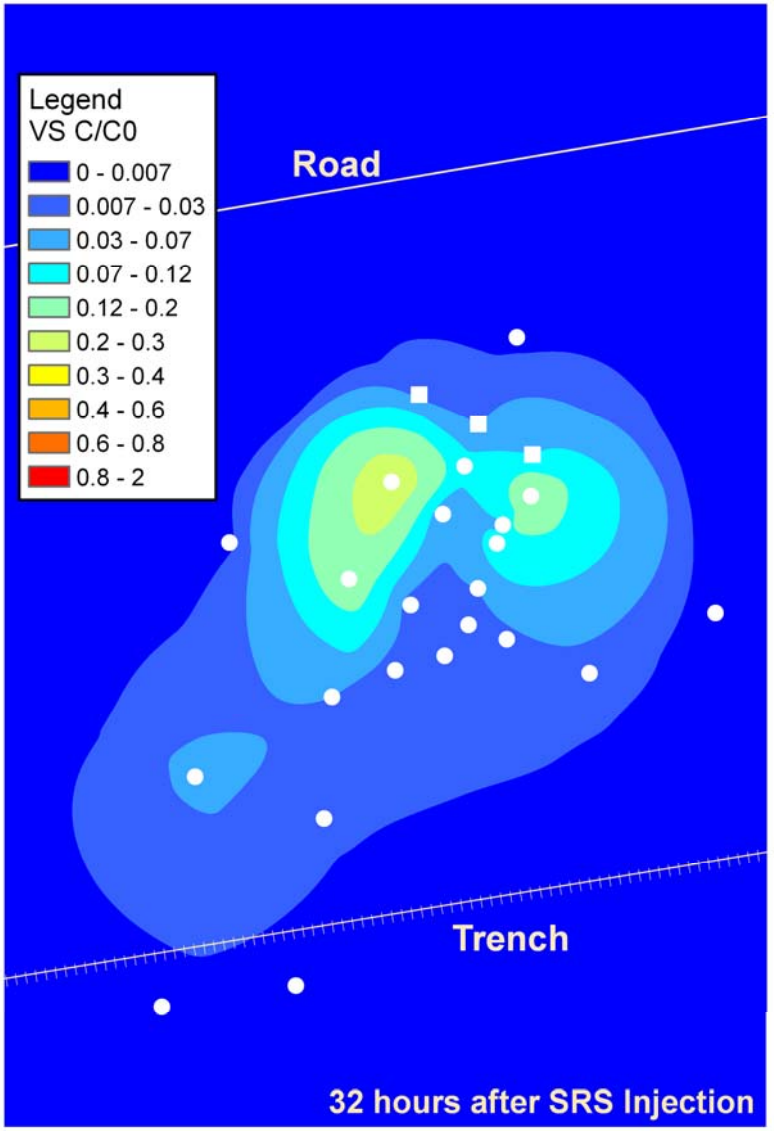

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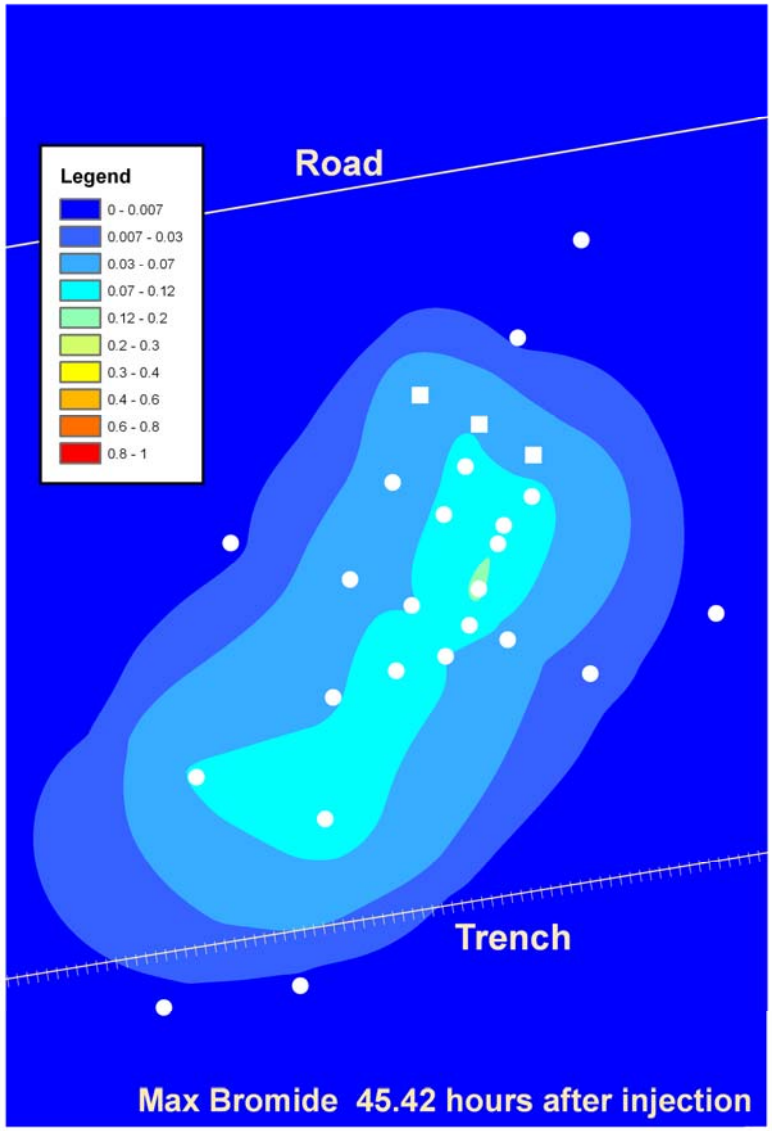

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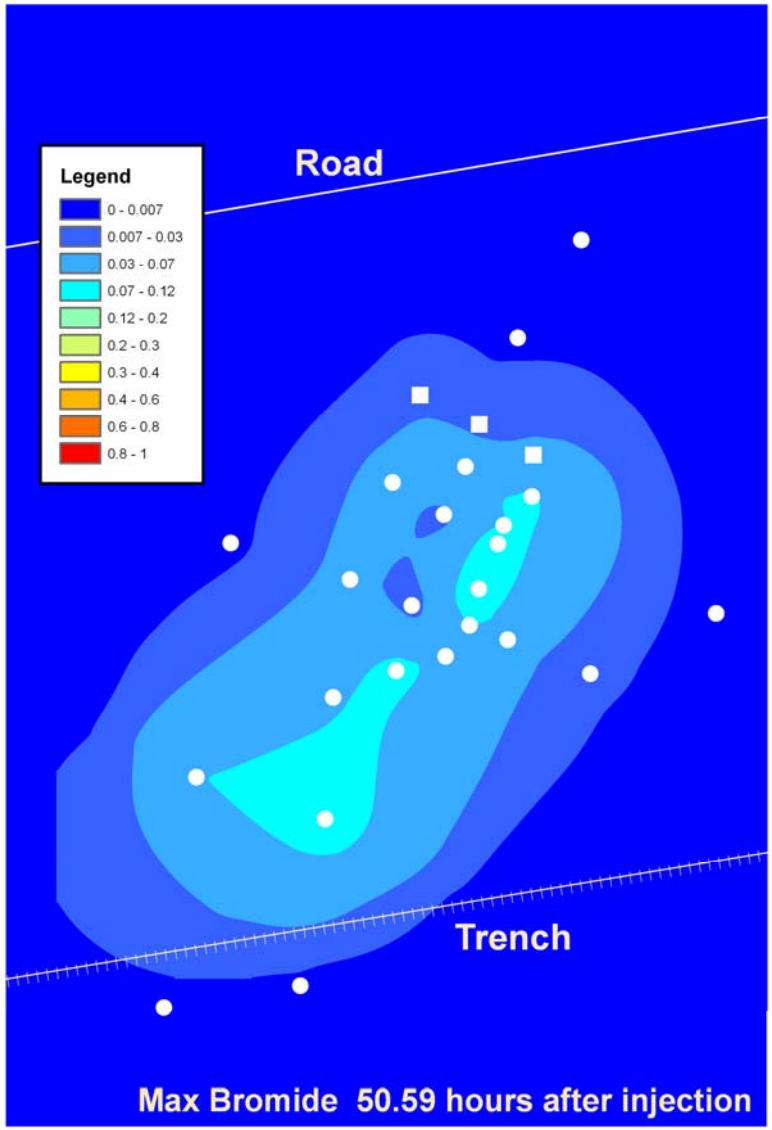

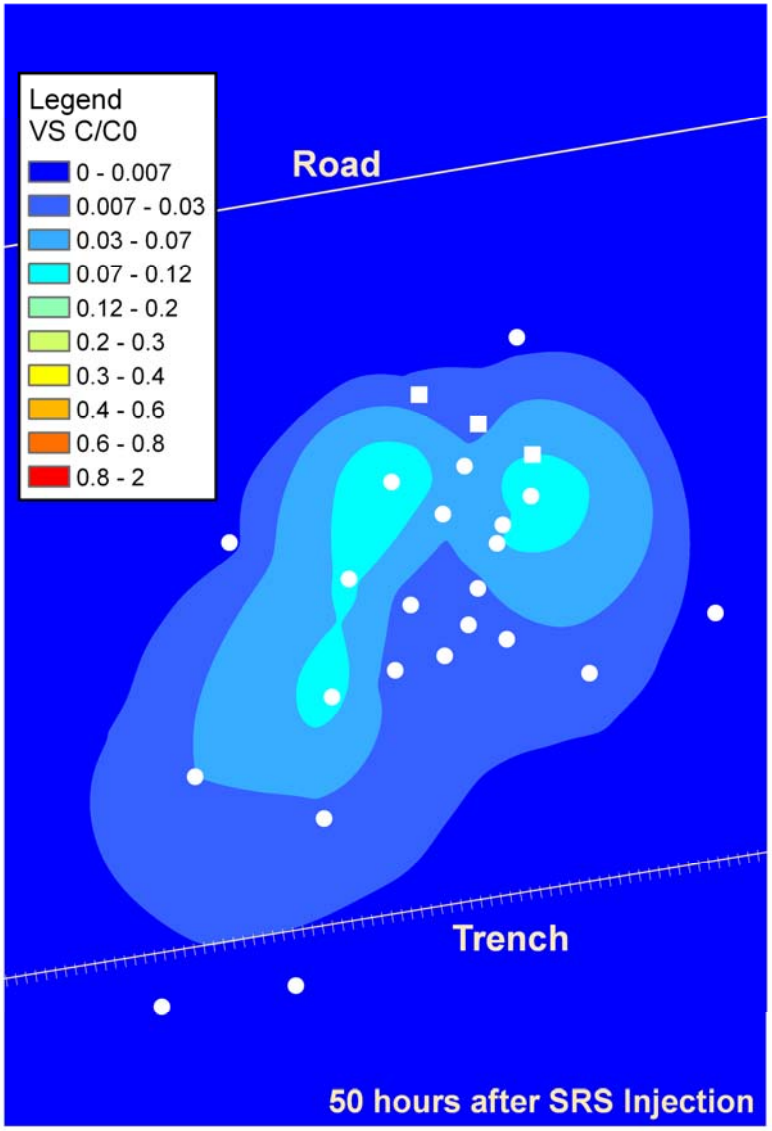

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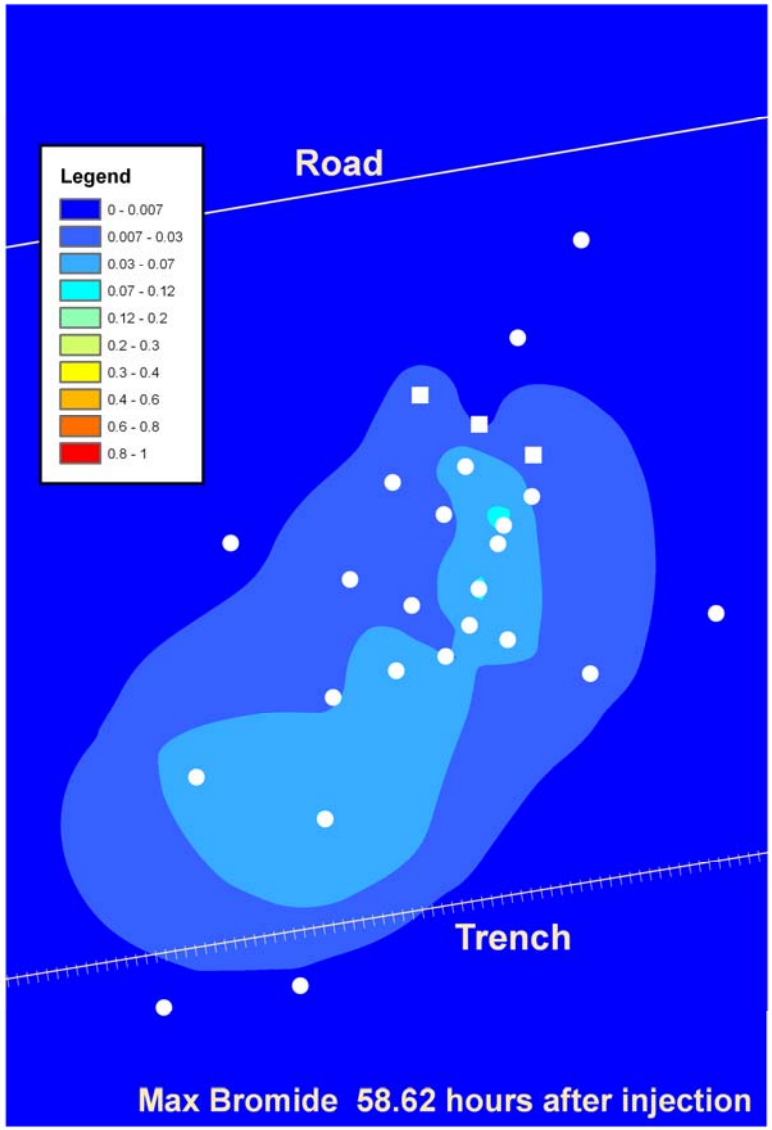

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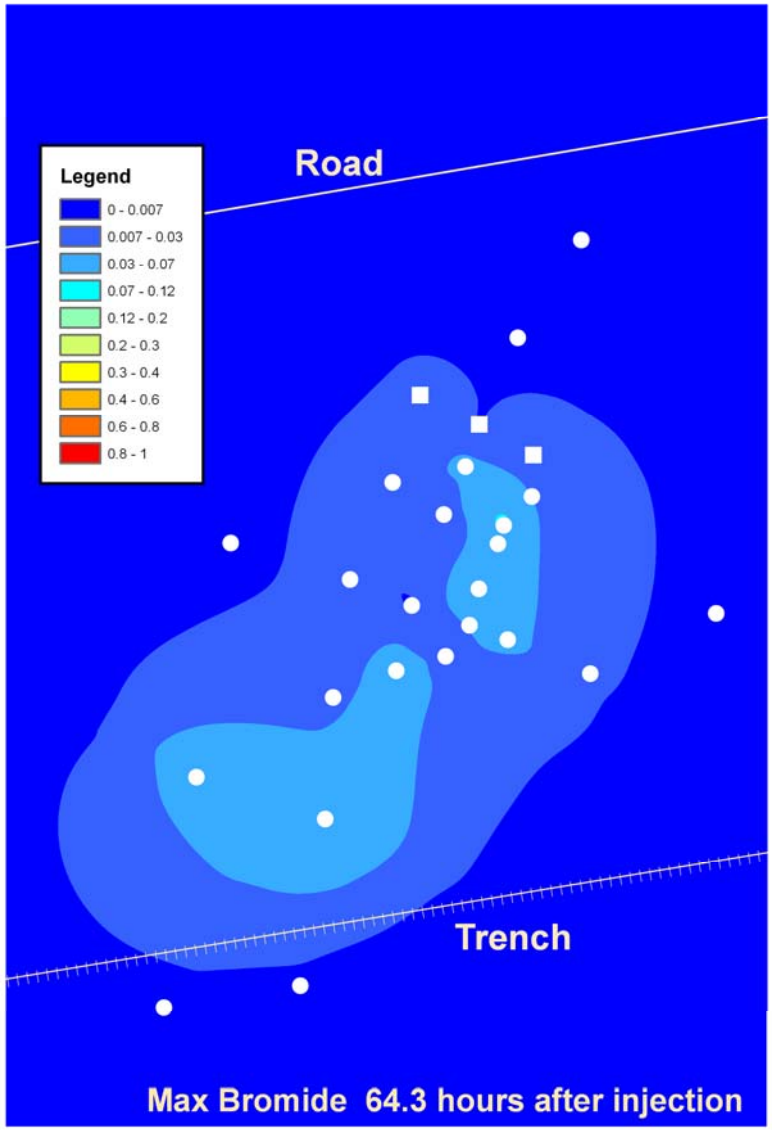

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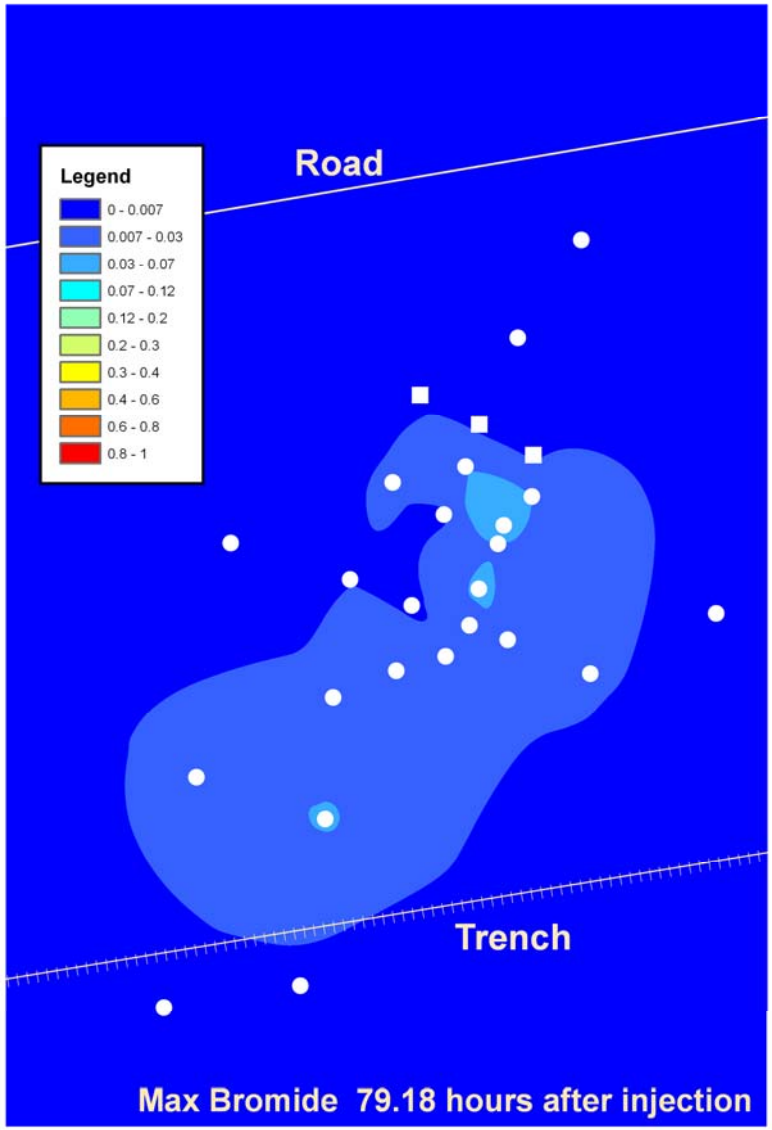

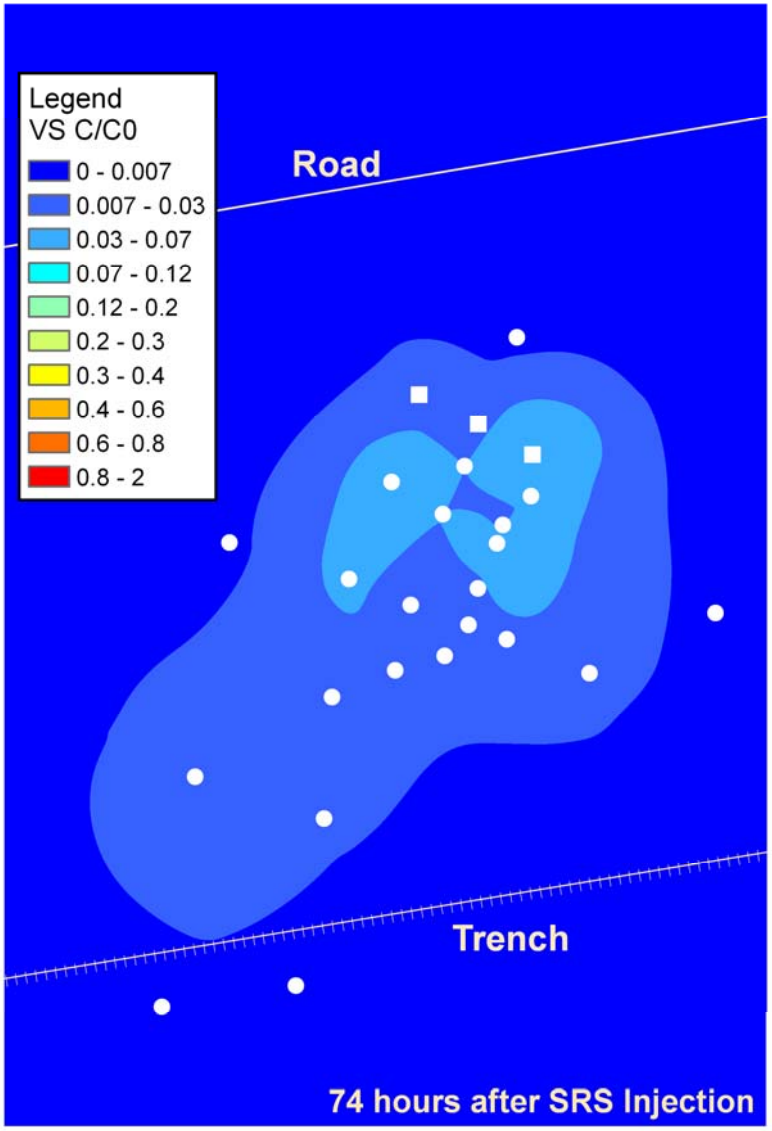

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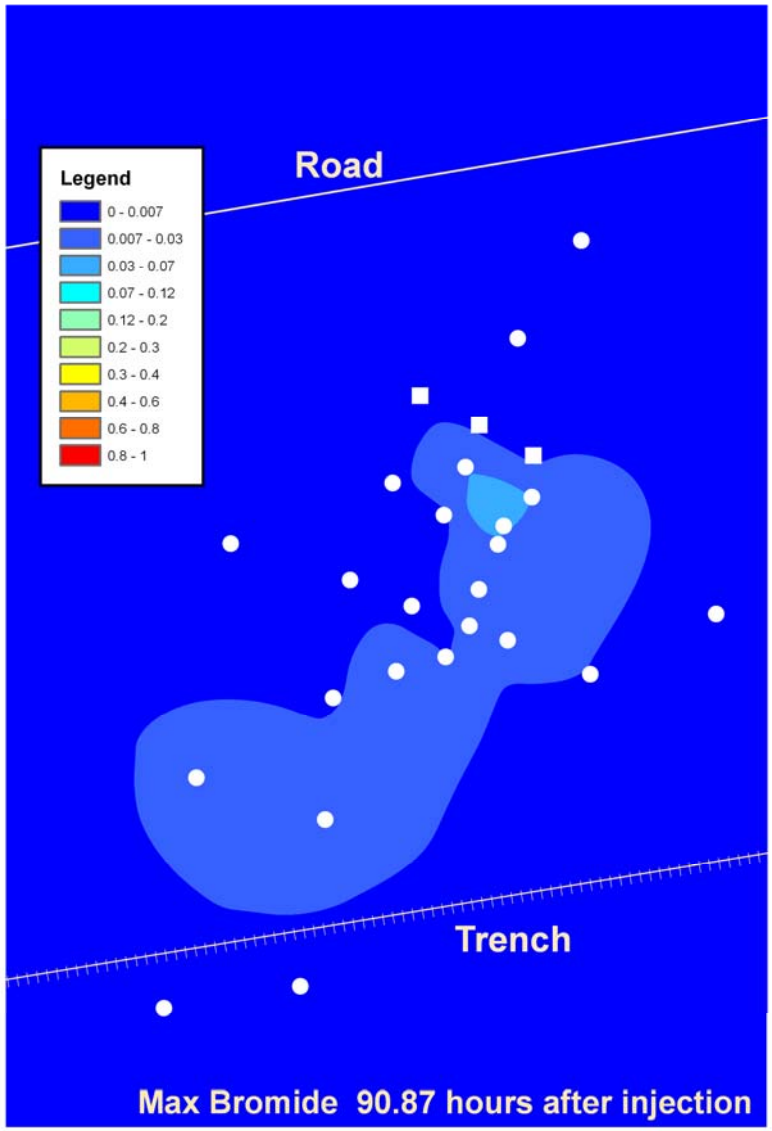

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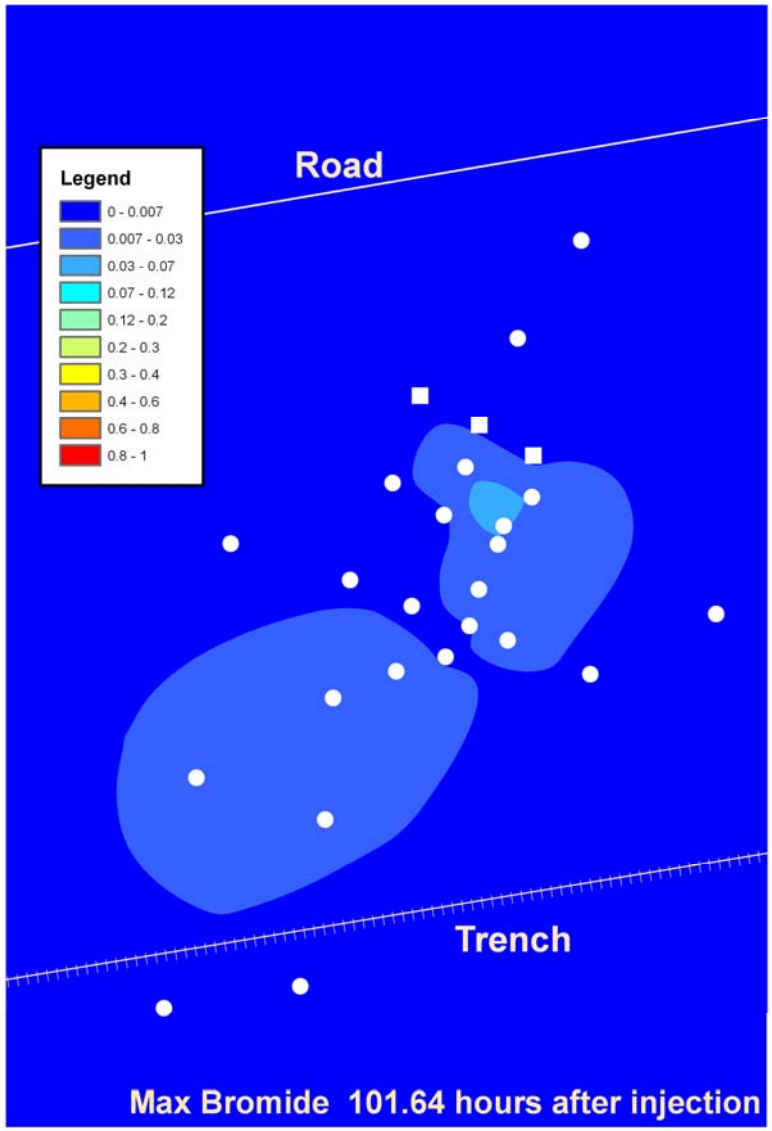

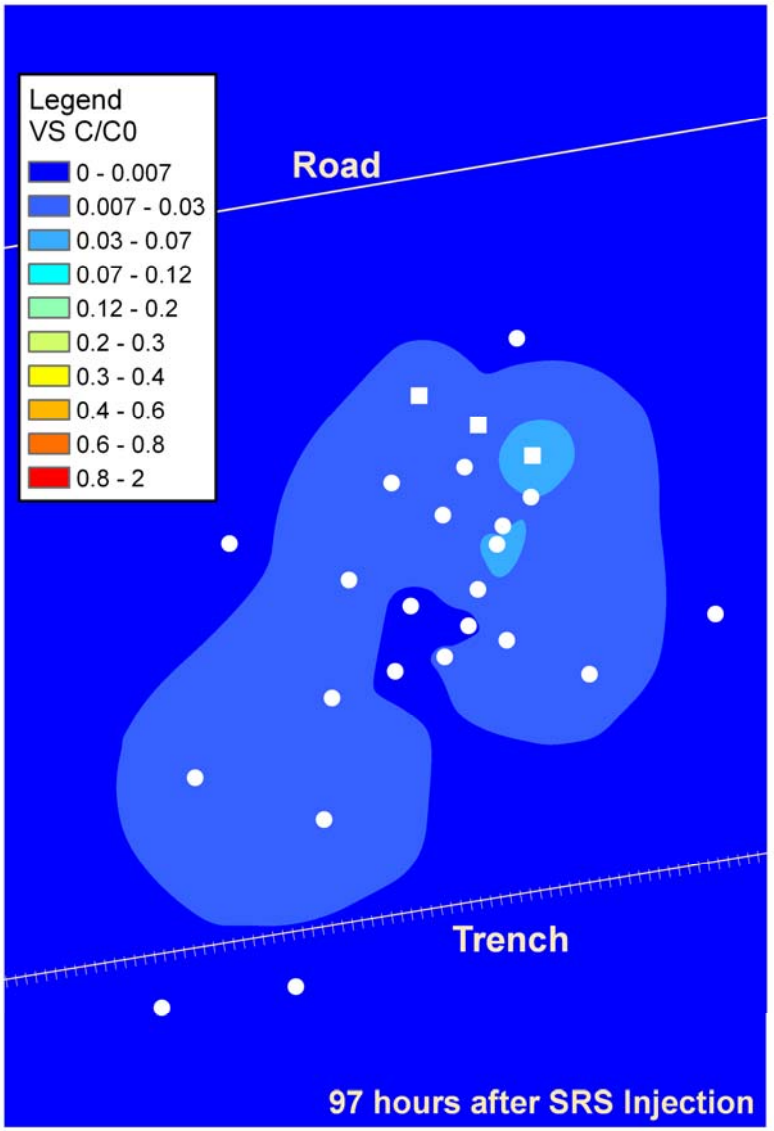

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Comparison of Br to SRS C/C_0 concentration contours

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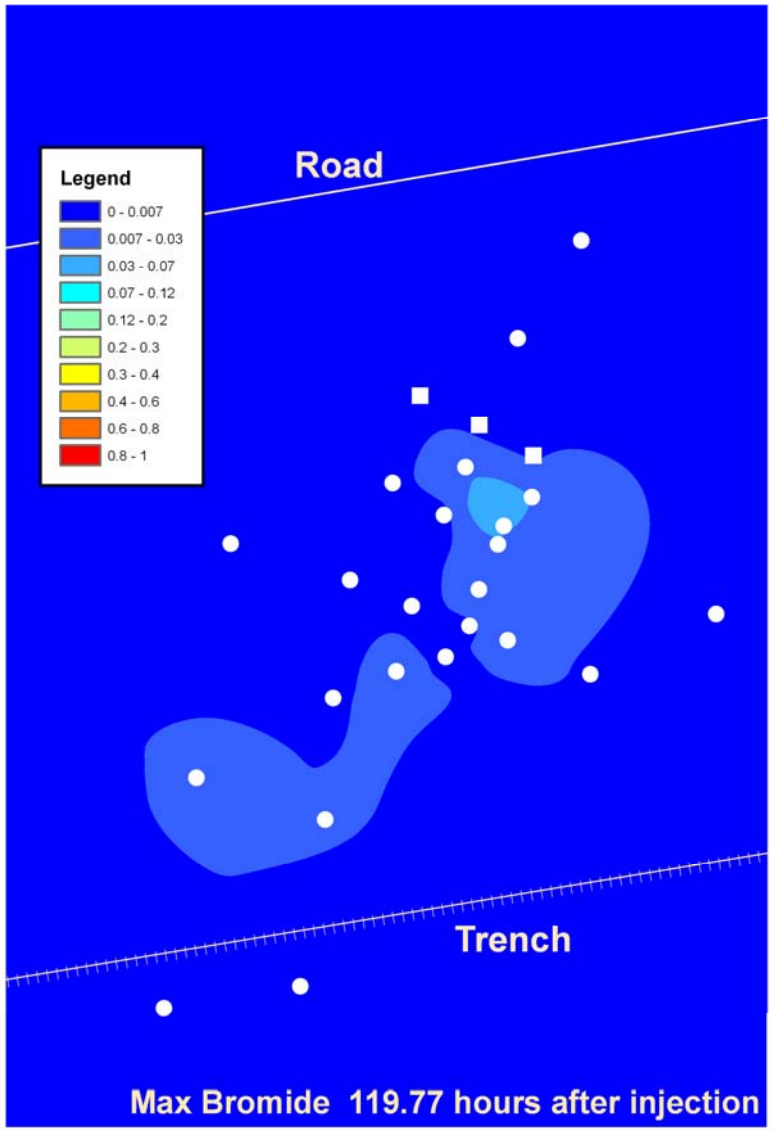

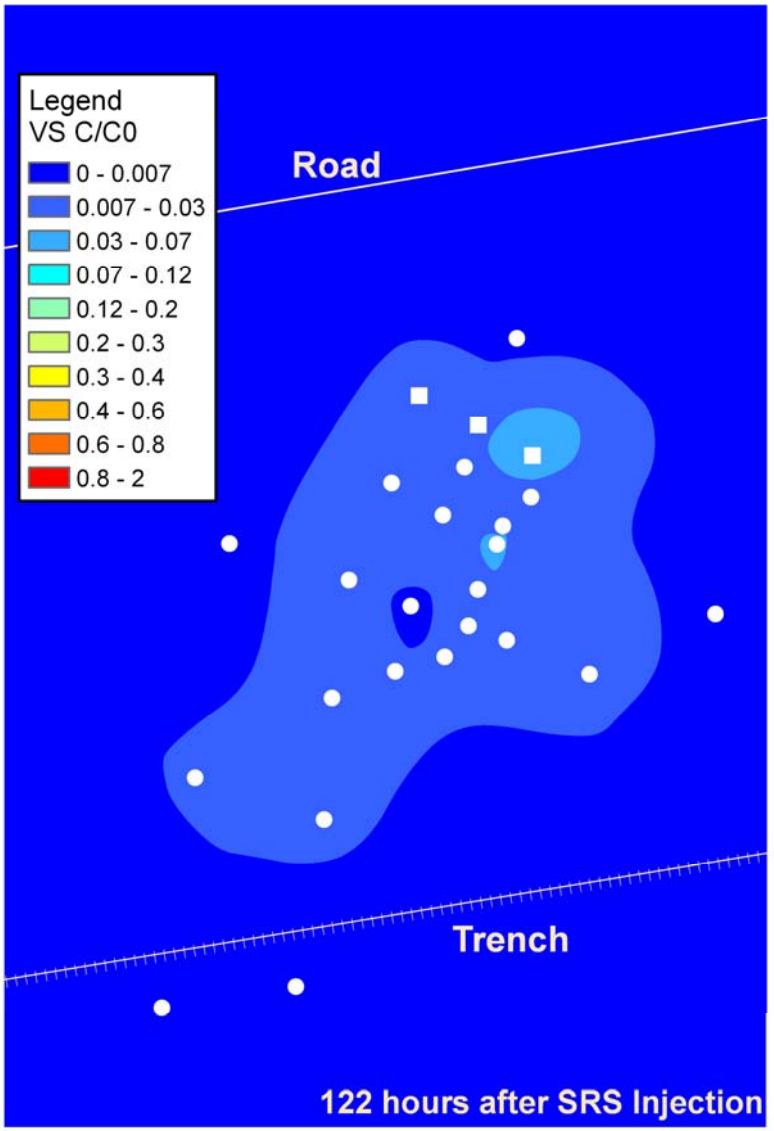

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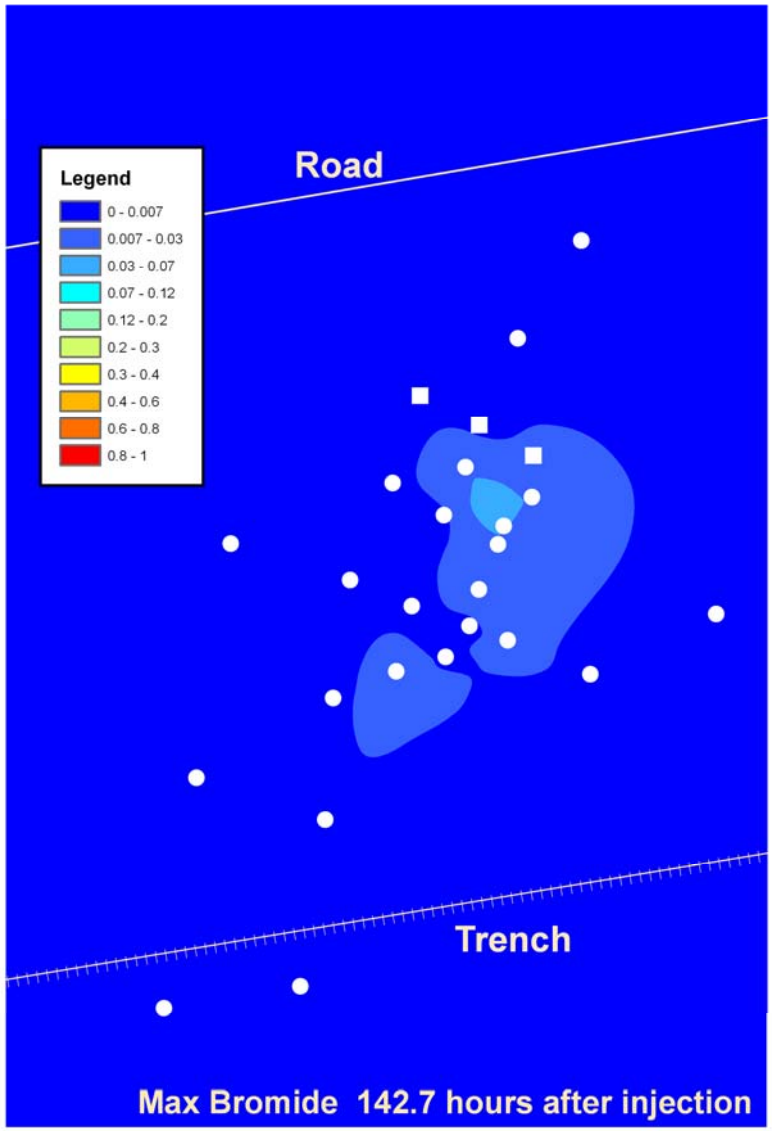
Comparison of Br to SRS C/C_0 concentration contours



No data for this time step

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Comparison of Br to SRS C/C_0 concentration contours

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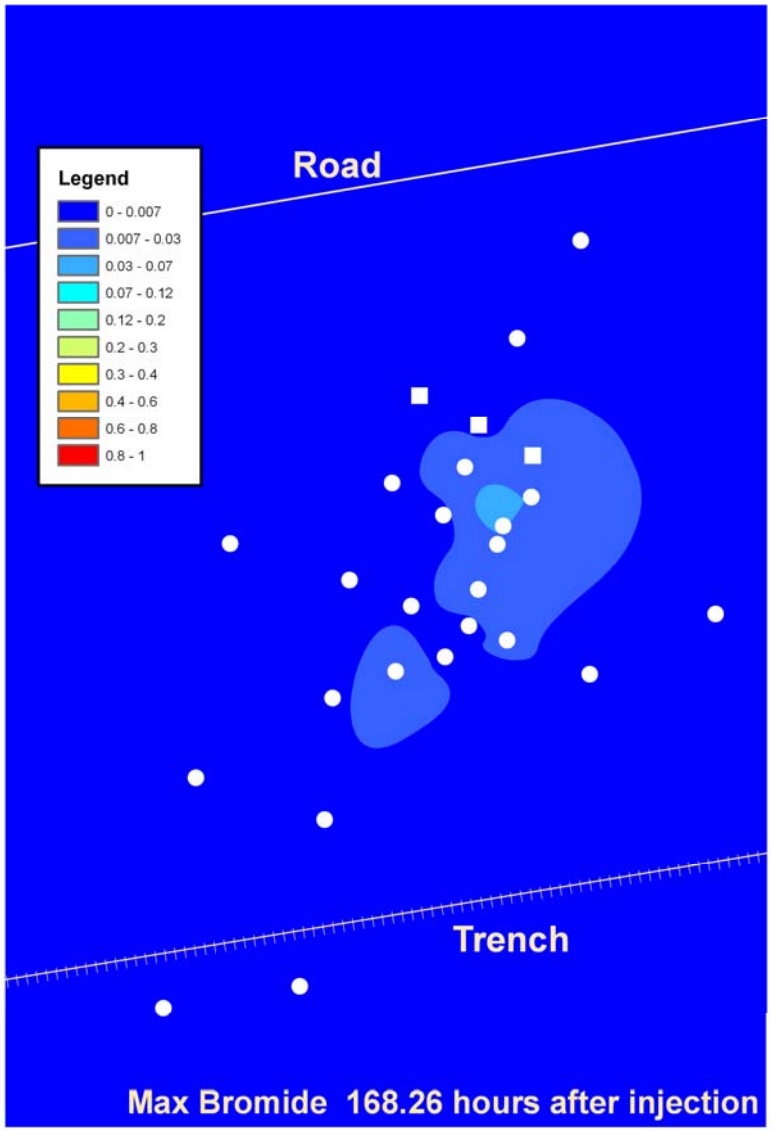
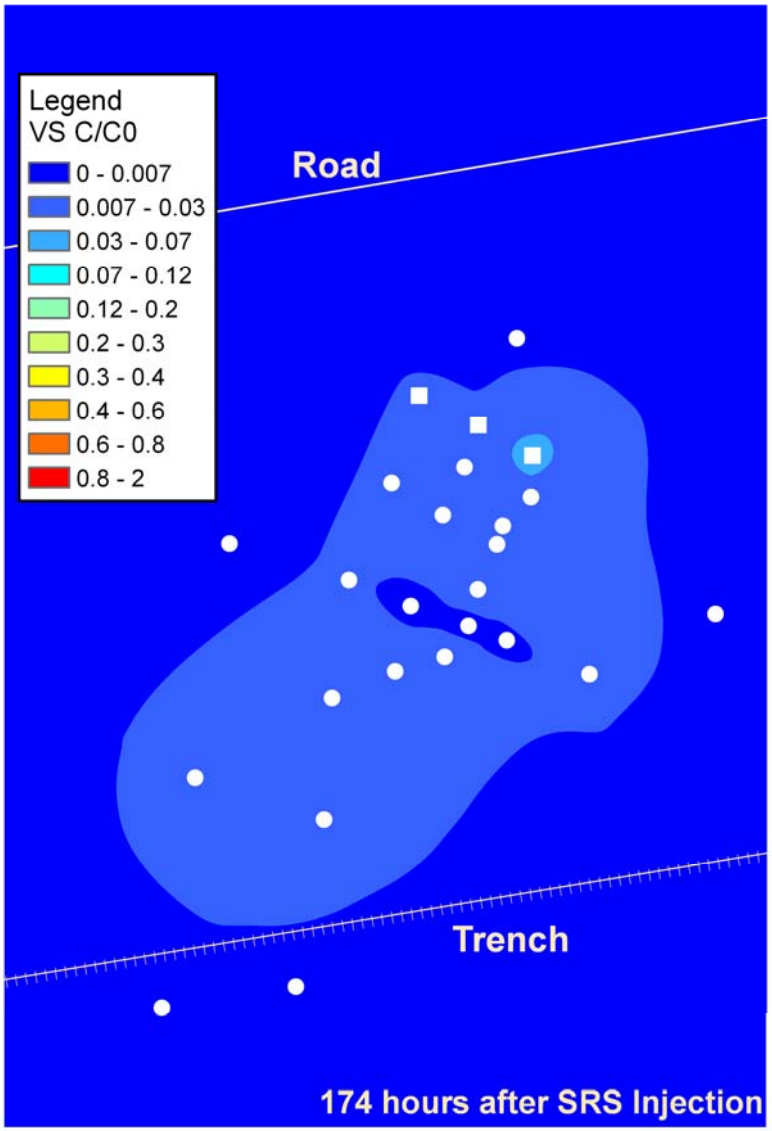
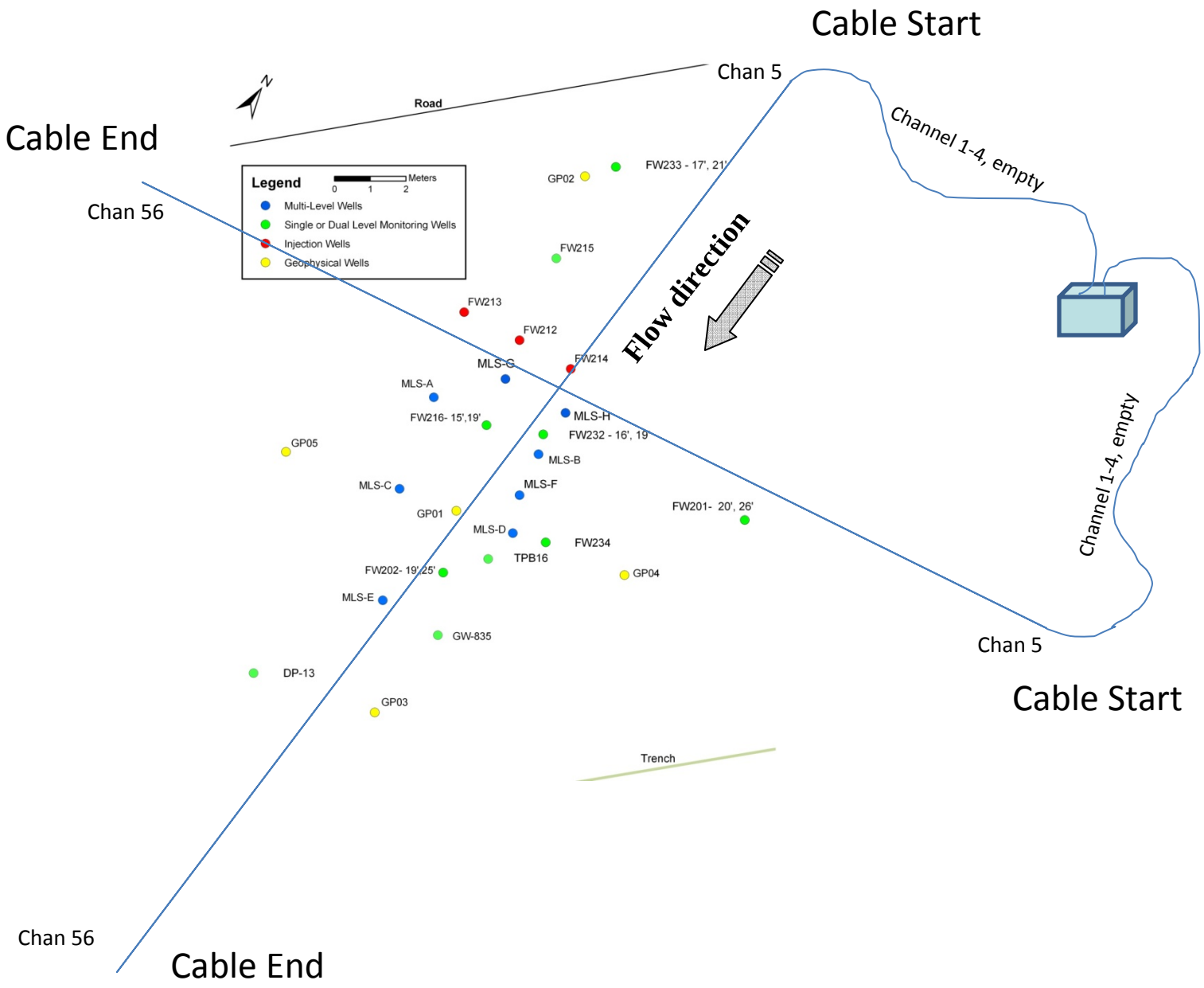




Surface electrical resistivity tomography surveys

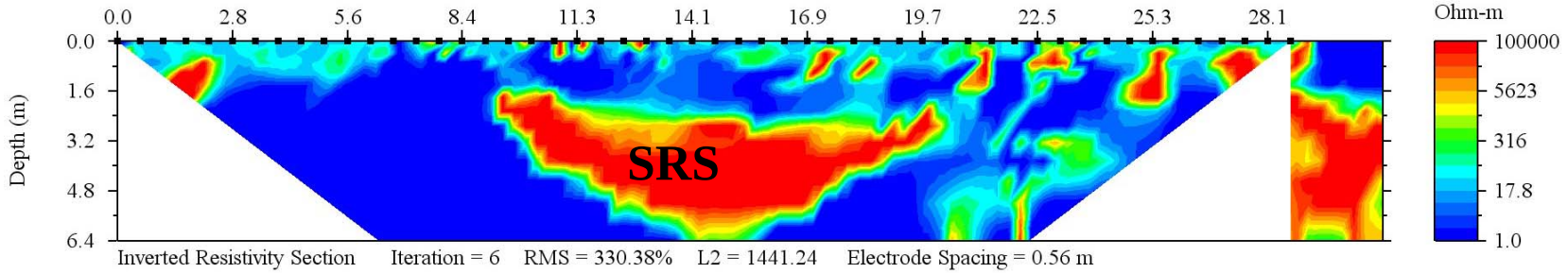


Surface electrical resistivity tomography surveys

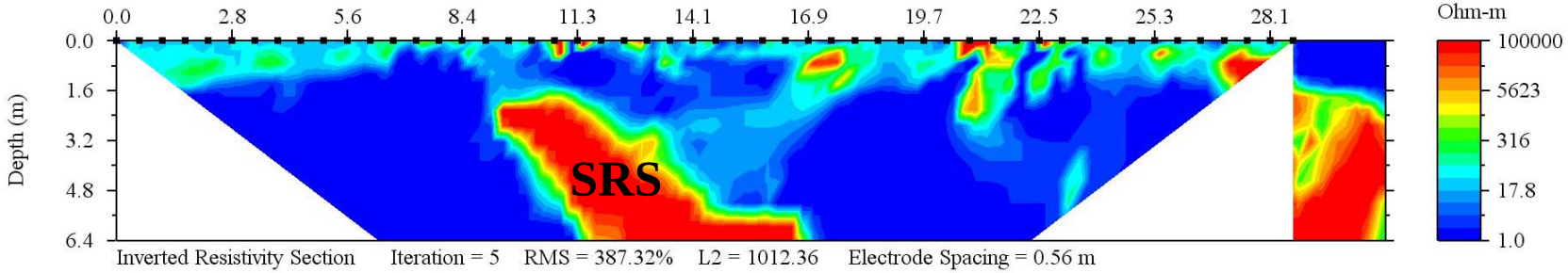
SRS Injection. Injection Began ~8am on 2/9

Shown are TLERT sections, all differenced from a pre-injection ERT section

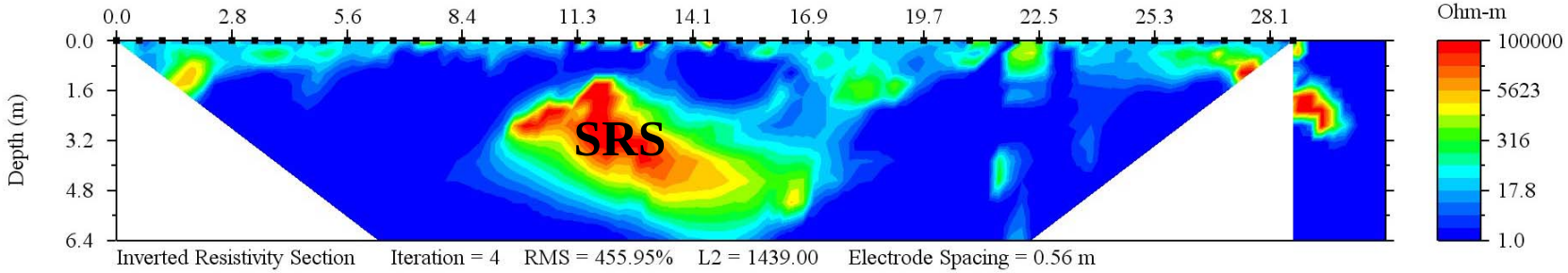
2/9 Evening



2/10 Evening



2/11 Evening



Notes: Survey duration is ~8 hours

Integerated dipole-dipole and Wenner/Schlumberger survery, 0.75 m electrode spacing.

SRS breakthrough compared to Br suggests SRS floating

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Environmental Remediation Sciences

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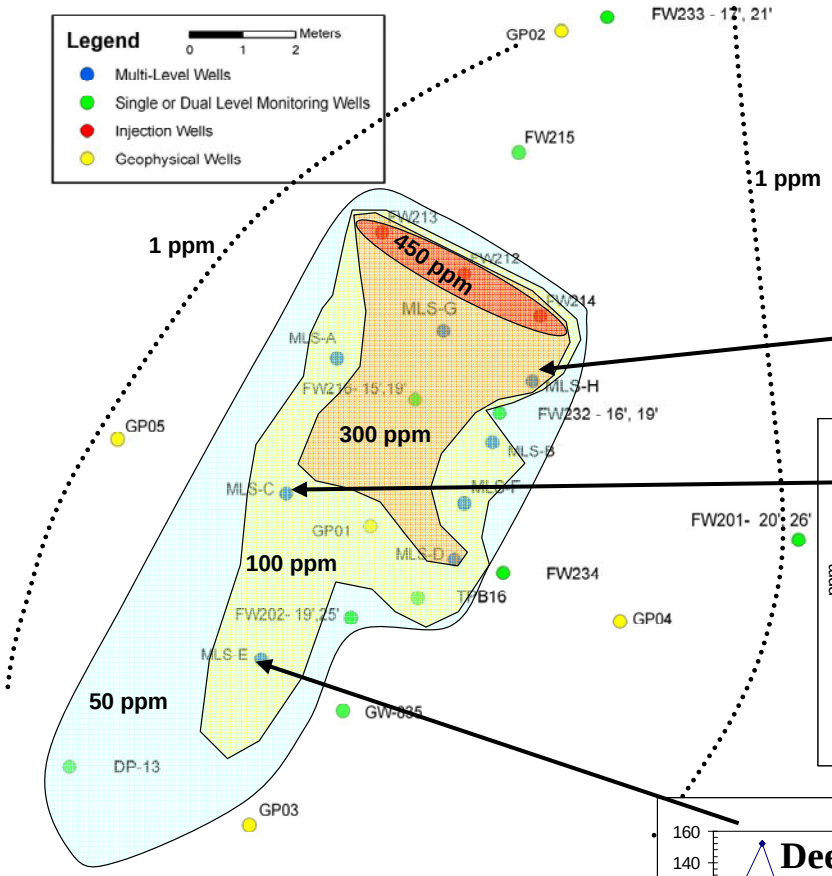
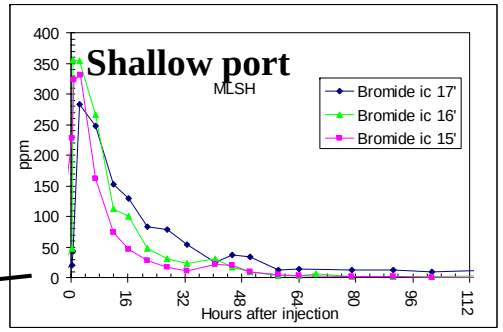
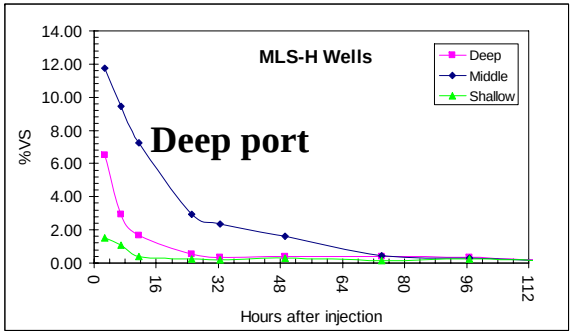
Bromide

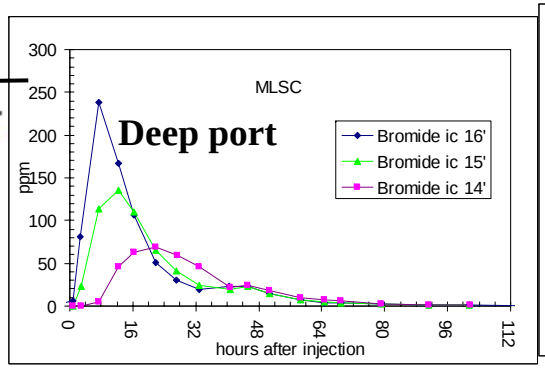
SRS

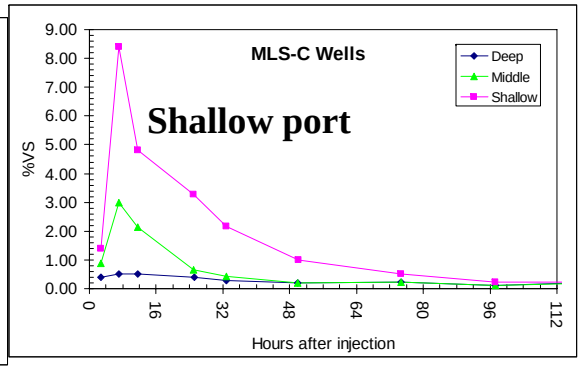


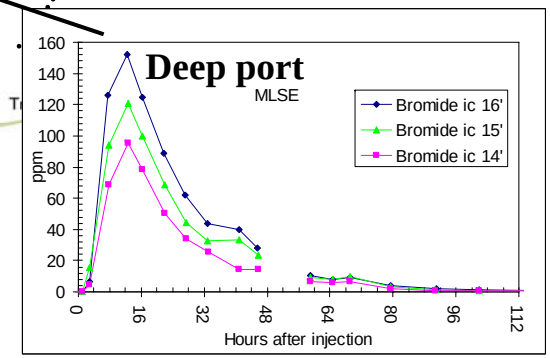
Maximum detected bromide

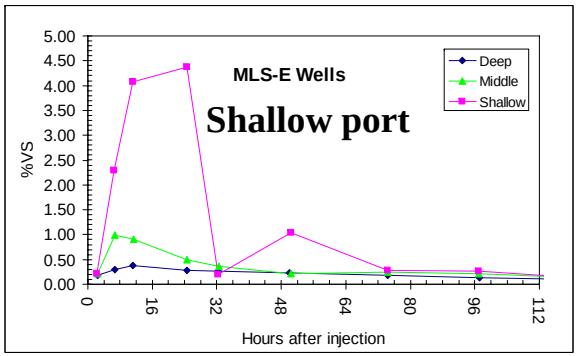




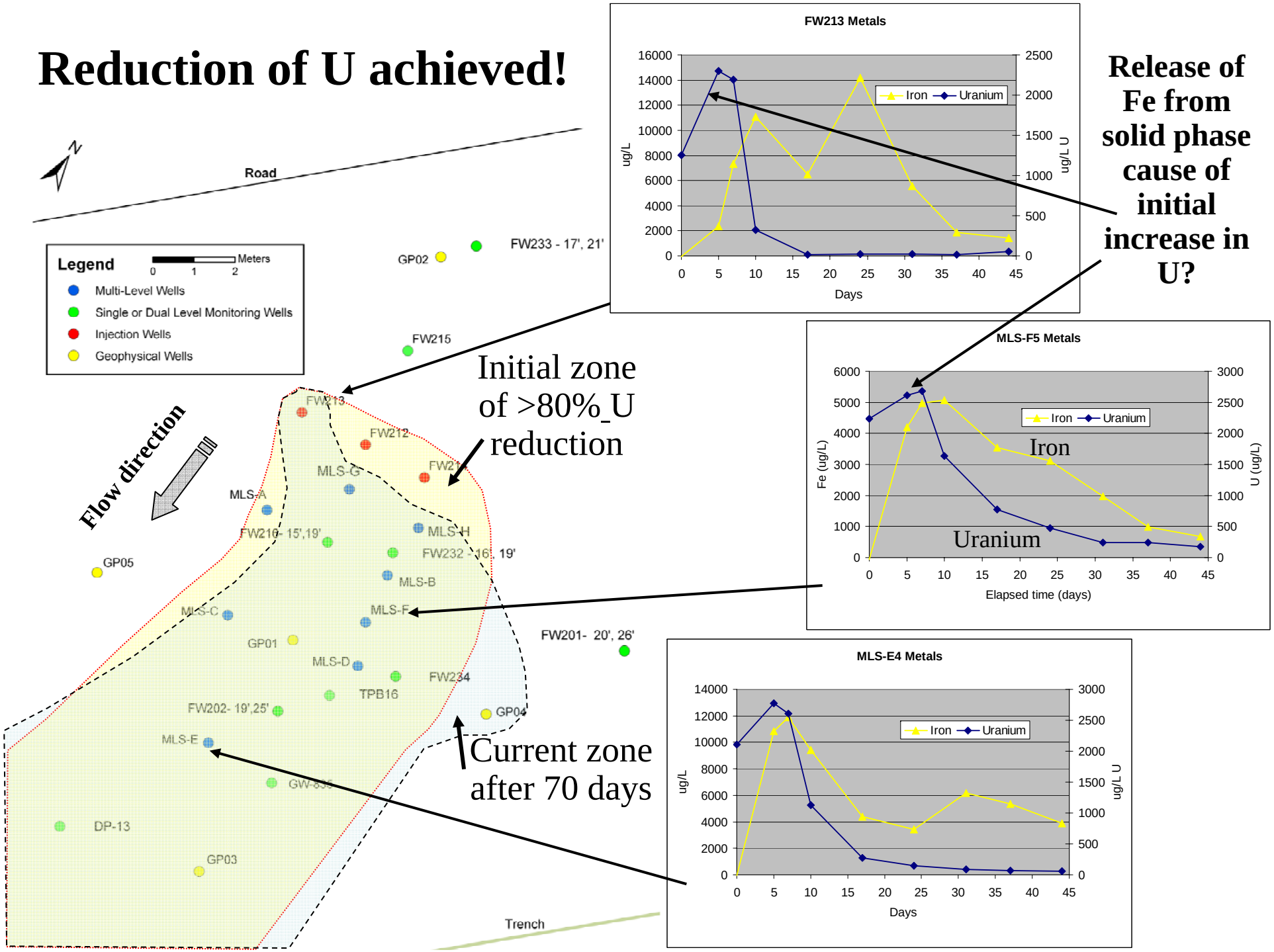




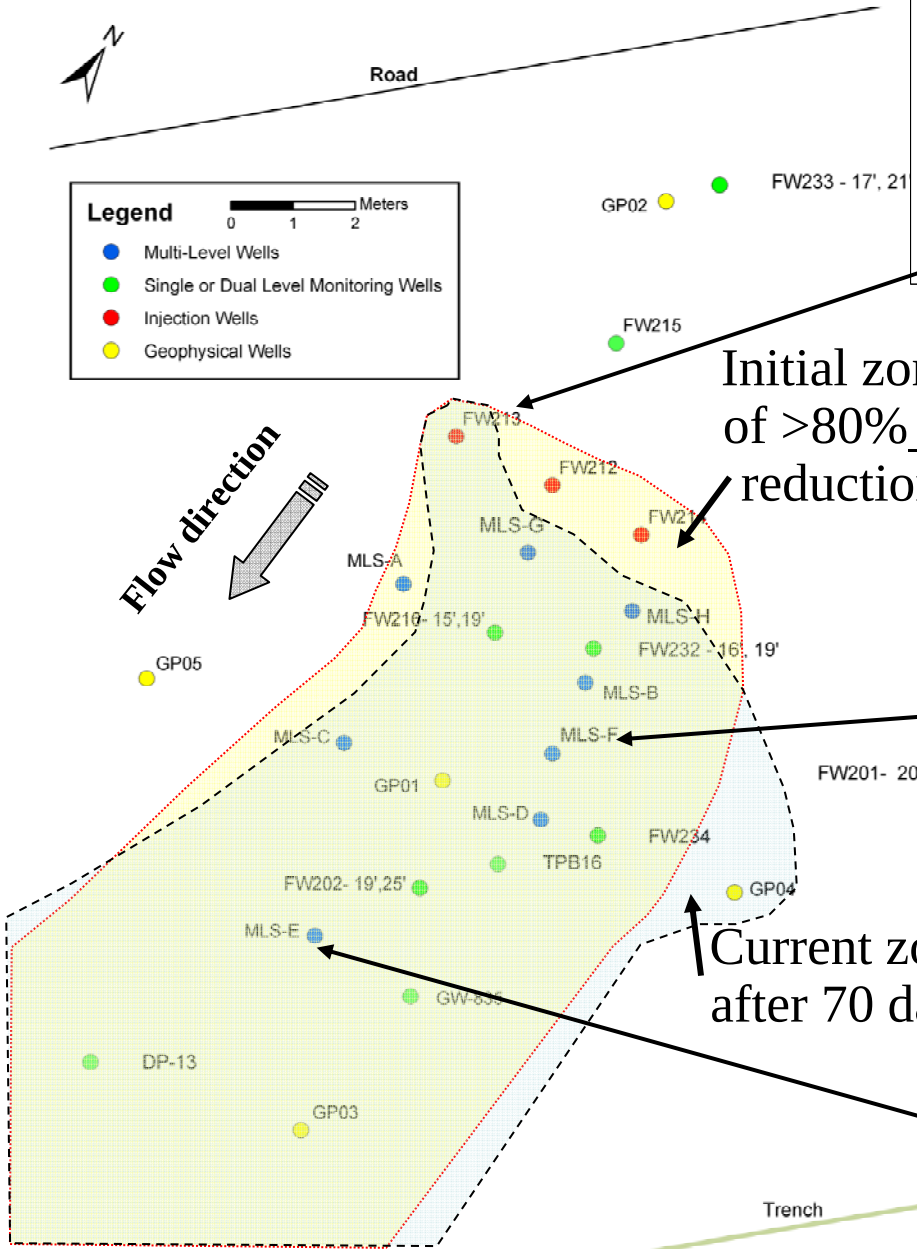


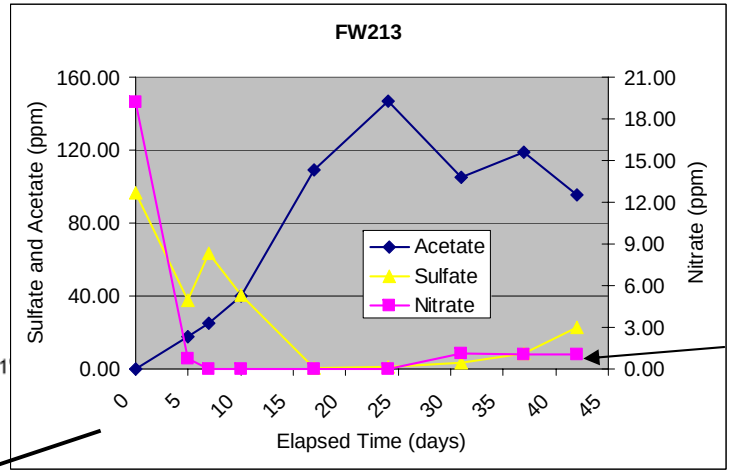


Reduction of U achieved!



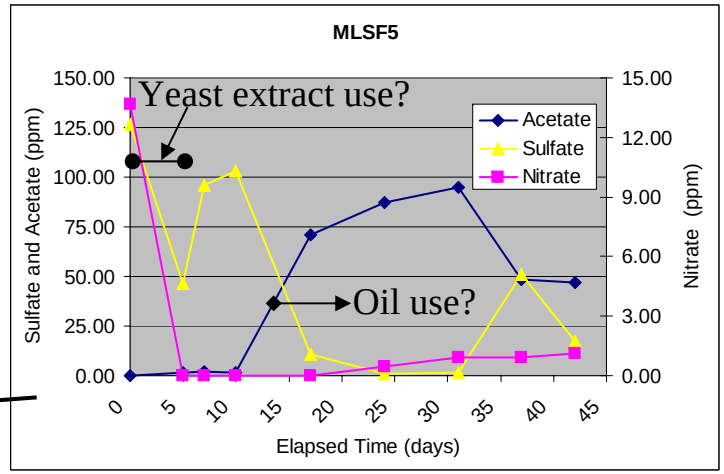
Acetate produced and nitrate removed



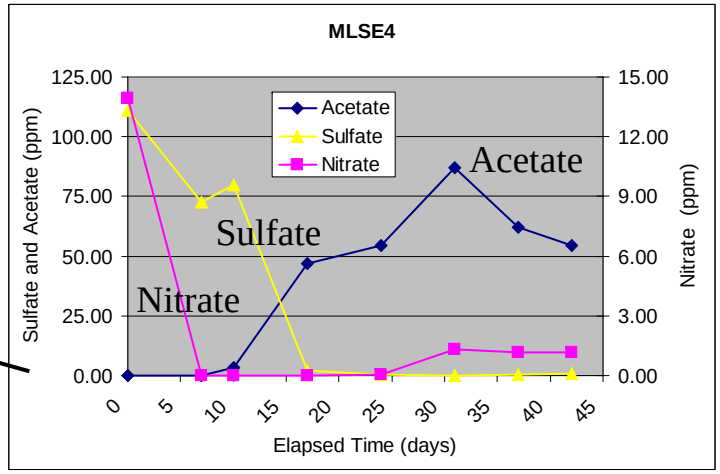


Small rebound in nitrate to 1 ppm

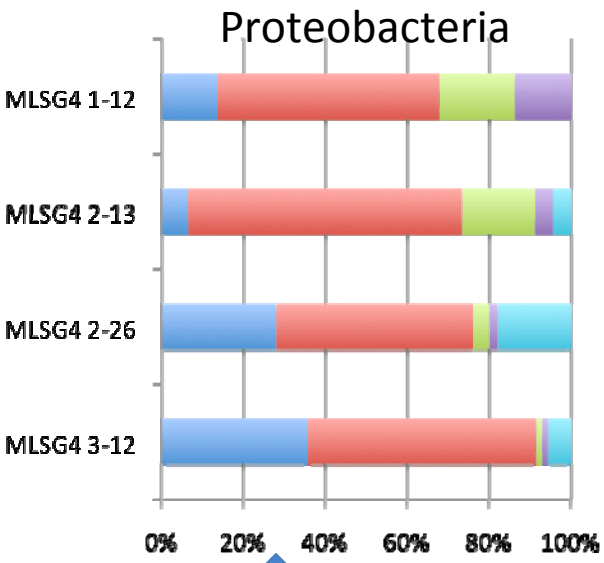
Initial zone of >80% U reduction



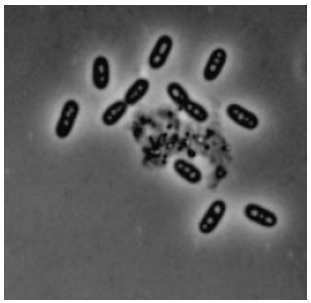
Current zone after 70 days



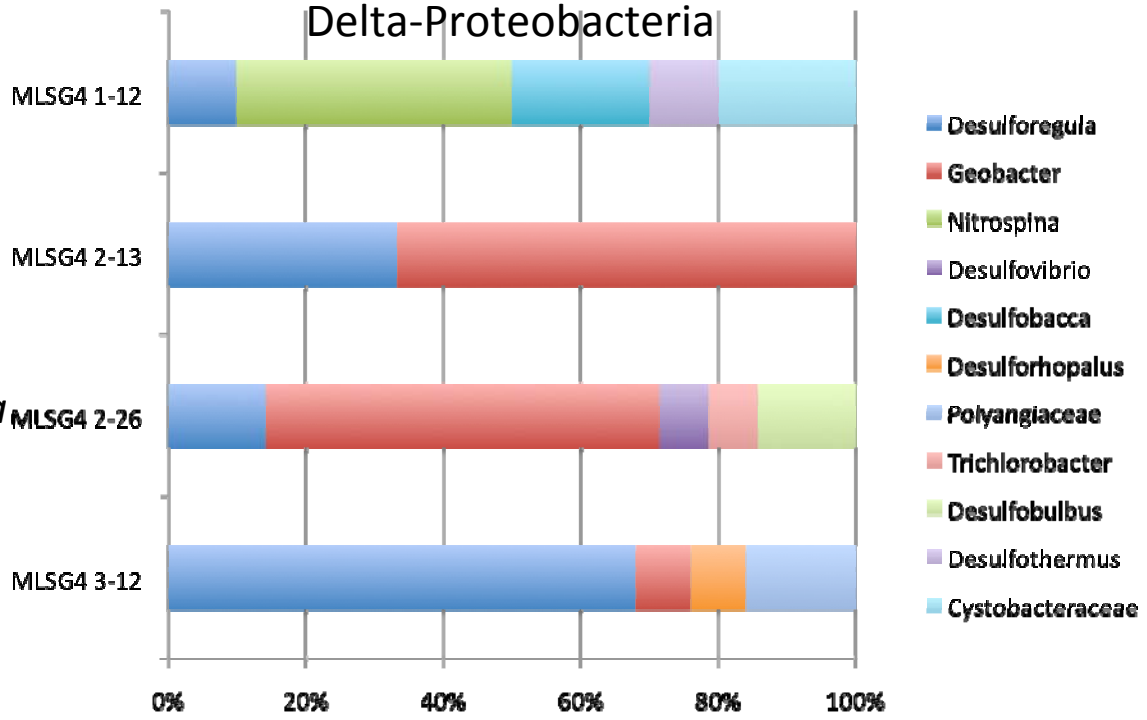
In Situ Groundwater communities during SRS stimulation in our initial analysis using 16S libraries



Delta Proteobacteria increased in abundance through stimulation timecourse



Desulforegula conservatrix (Rees and Patel, IJSEM,2001)



Like the bottle tests Desulforegula and Geobacter are present together. Likely a syntrophic interaction where Desulforegula ferments fatty acids to acetate used by Geobacter

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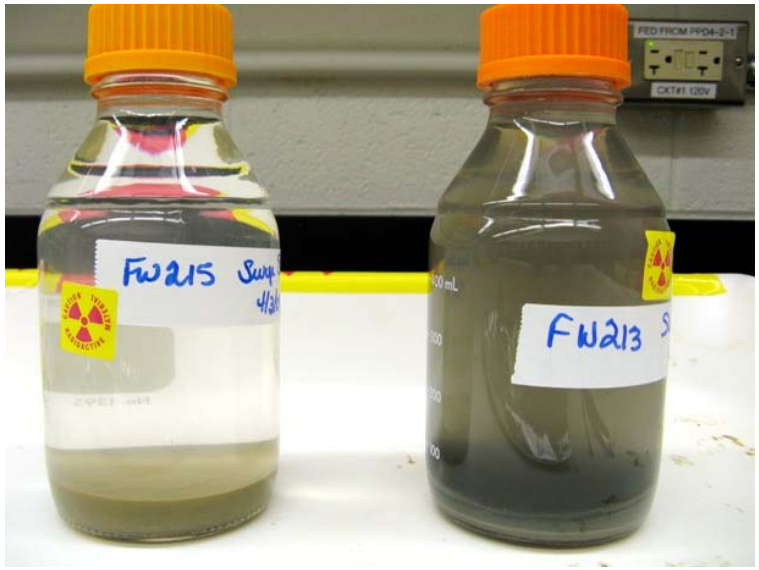
XANES analysis of surge samples

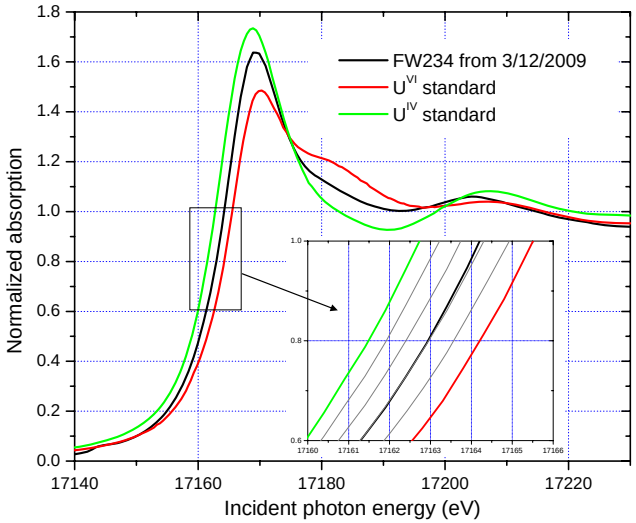


Control Injection well

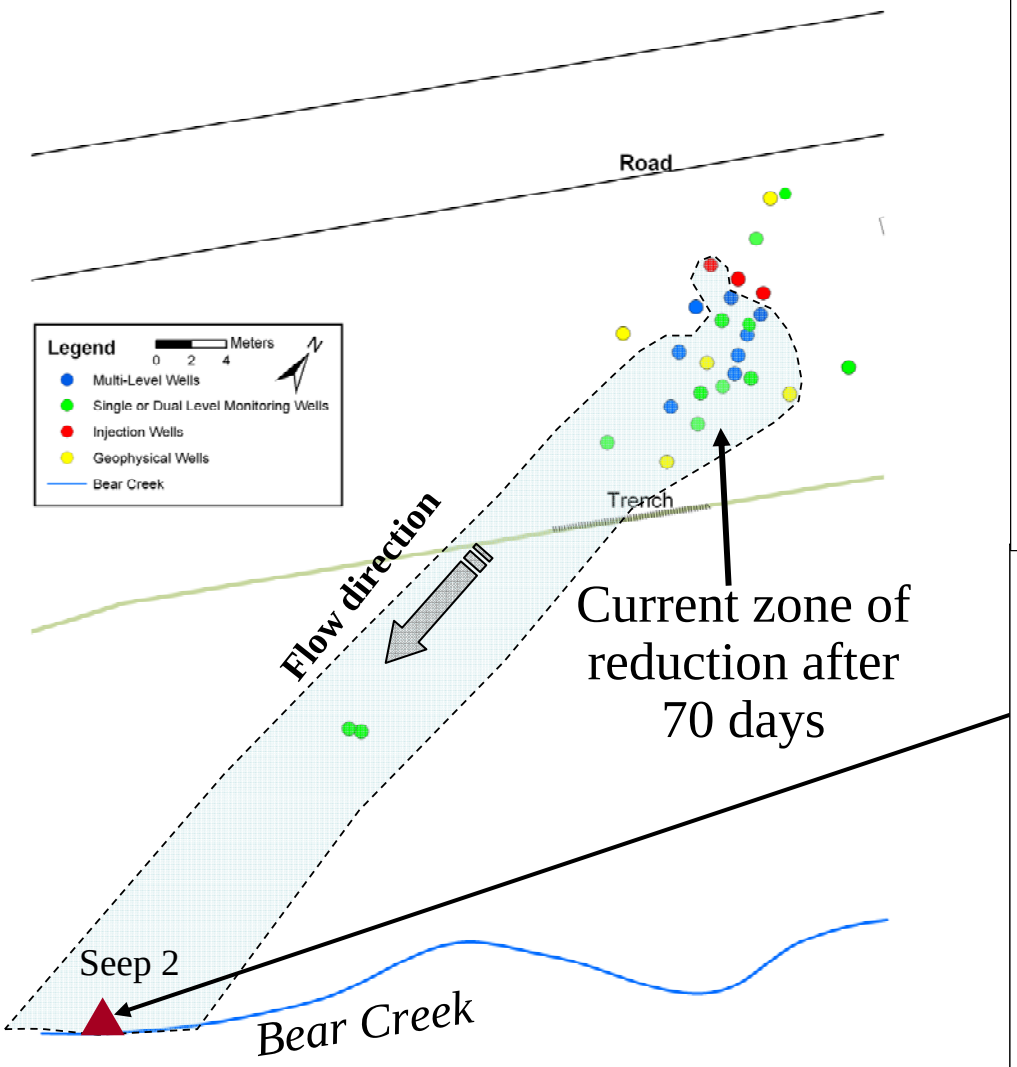
- Up to 85% U(IV) measured in down gradient monitoring wells
- U(VI) observed in control samples

Control 4 m 5 m 10 m

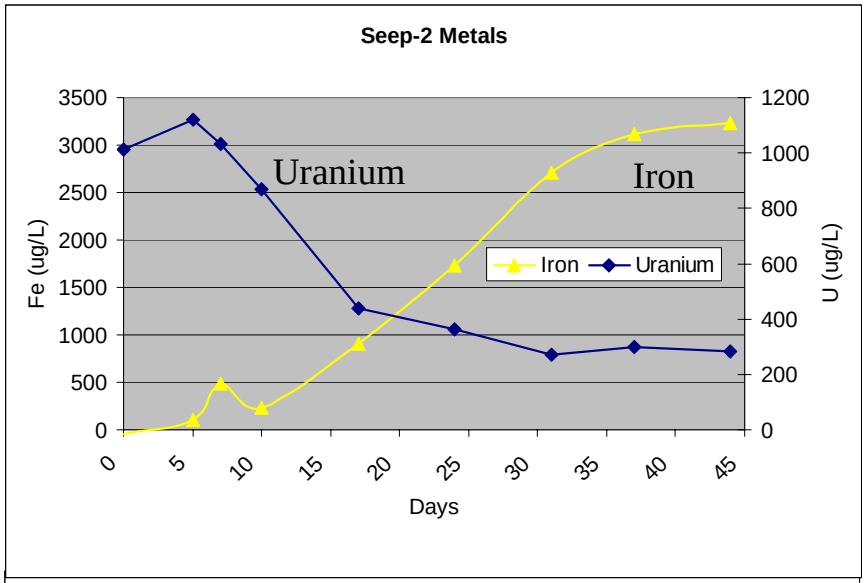
No.	Sample ID	U,mg/kg	U6%	U4%
1	FWB-124 core 17-20 section #1 (before)	nd	90	10
2	FW202 3/17/09 (after)	nd	85	15
3	FW215 1/16/09 Control, before)	nd	95	5
4	FW215 3/17/09 (Control, after)	519.4	95	5
5	FW216 1/27/09 (before)	112.4	100	0
6	FW234 1/16/09 (before)	nd	100	0
7	FW234 from 3/12/09 (after)	441.9	60	40
8	FWB-234 core March 2009(after)	nd	55	45
9	GP01 1/16/09 (before)	nd	90	10
10	GP01 3/17/2009 (after)	96.4	15	85
11	GP03 1/16/09 (before)	nd	85	15
12	GP03 3/17/09 (after)	152.3	15	85

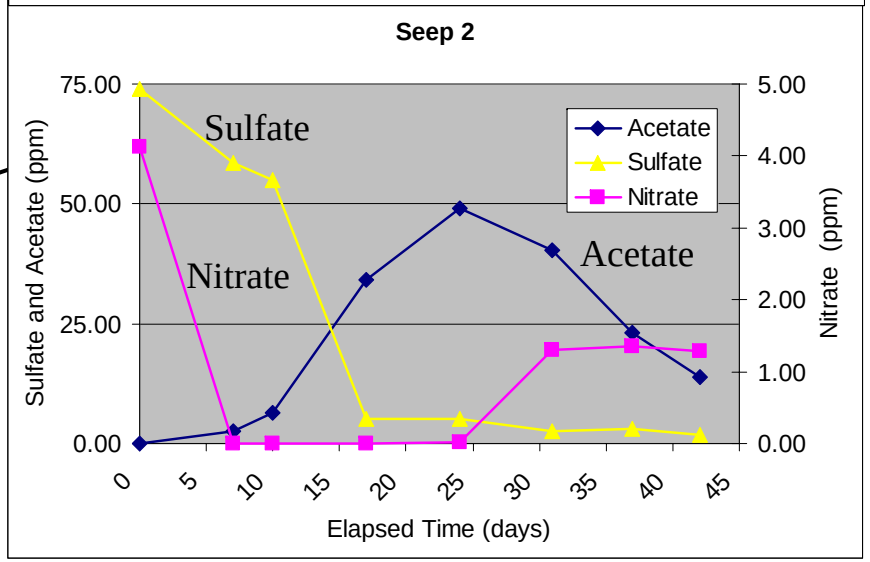


Significant reduction of U concentration in seeps and flux to Bear Creek observed



Seep is 50 meters from injection wells





Conclusions

- **EVO injection achieved sequential reduction of nitrate, Fe(III), sulfate and U(VI) in the subsurface. Acetate was generated after about 2 weeks. U(VI) reduction to U(IV) was confirmed by XANES analysis.**
- **Microbial community depends on electron donor source and sulfate concentration but *Desulforegula* seems to play an important role in oil breakdown.**
- **Comparison of bromide to oil breakthrough curves suggests some floating of the SRS occurs.**
- **Reducing conditions have been sustained for over 70 days and has significantly reduced U flux to Bear Creek the primary exit pathway at the site.**
- **Oil droplet size is important consideration for subsurface delivery.**
- **Identified effective monitoring techniques that we will use to continue to monitor response.**