# Era of the BioGeoPhysioChemoHydrogeologist Is Now: Conceptual Models for LNAPL Remediation

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# Overview

- Development of CSMs for identifying risks, concerns, etc is fairly mature
- CSMs are also sufficient to identify completion of remediation (i.e., there are no more concerns, risk etc)
- Refinement of CSMs for technology Selection, Optimization & Confirmation represent the highest potential for improvement
  - "Unless you align your aspirations with laws of the universe you will fail" Dr. Woodie Flowers
    - Umm ….. Recovery has failed, OFTEN
  - Its not Recovery's fault it's the minions who selected it
  - Recovery is effective at mobility reduction not elimination

- This talk aims to inspire continuation of improvements to CSMs for LNAPL remedy selection

# Looking Back Can be Painful

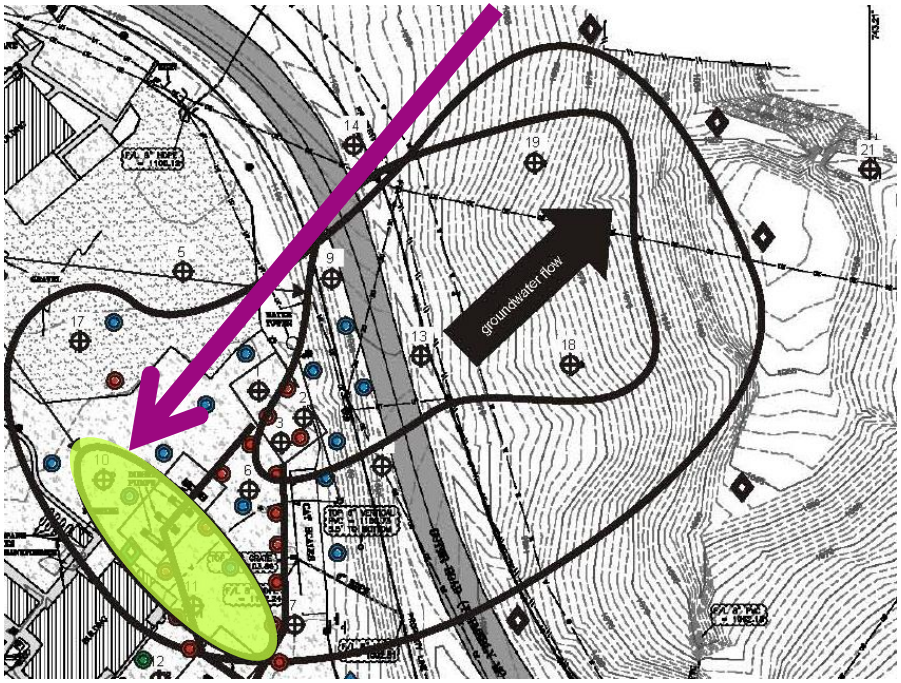
## LCSM from 2010

| | Field Data | Laboratory Analyses | Data Analysis |
|---|---|---|---|
| Tier 1 | •Gauging data<br>•Slug Test<br>•Baildown Testing (one test per well)<br>•Continuous Soil Boring Logs | •LNAPL and water density | •Vertical Distribution of LNAPL<br>•LNAPL Transmissivity<br>•Estimate initial technology LNAPL recovery rates<br>•Evaluate historical recovery data If system exists |
| Tier 2 | •Baildown Testing (multiple tests per well)<br>•Direct Push Borings | •LNAPL and water viscosity<br>•Grain size analyses<br>•Intrinsic permeability<br>•Soil core photography<br>•Soil core analyses<br>•Site Specific fluid interfacial/ & surface tensions<br>•Gas chromatogram of LNAPL | •Recovery modeling based on site specific and published values<br>•Identification of LNAPL type(s) based on LIF data<br>•Recovery modeling to site specific soil core data<br>•Estimation of Recoverable Volumes<br>•Identification of LNAPL type(s) based on GC data |
| Tier 3 | •Baildown/ Manual Skimming Testing (multiple tests over time)<br>•Soil Core Borings<br>•Pilot Testing / Aquifer Pump Tests | | |

Tiered Approach to LNAPL Characterization with LNAPL Transmissivity
MAY 27, 2010

# Tier 1 Initial Site Assessment –
## So what are we going to do if remediation is needed (e.g, Site Sale, Risk, MEP)

- Eight wells exhibiting detections of LNAPL, ranging from 1.4 to 0.1 feet of gauged thickness
- LNAPL baildown testing completed
  - 2 month recovery period for wells to recover 1.3 and 0.85 feet of LNAPL
  - Resulting LNAPL transmissivities ~ 0.002 $ft^2$/day
- Initial and long term recovery performance estimates generated for various technologies

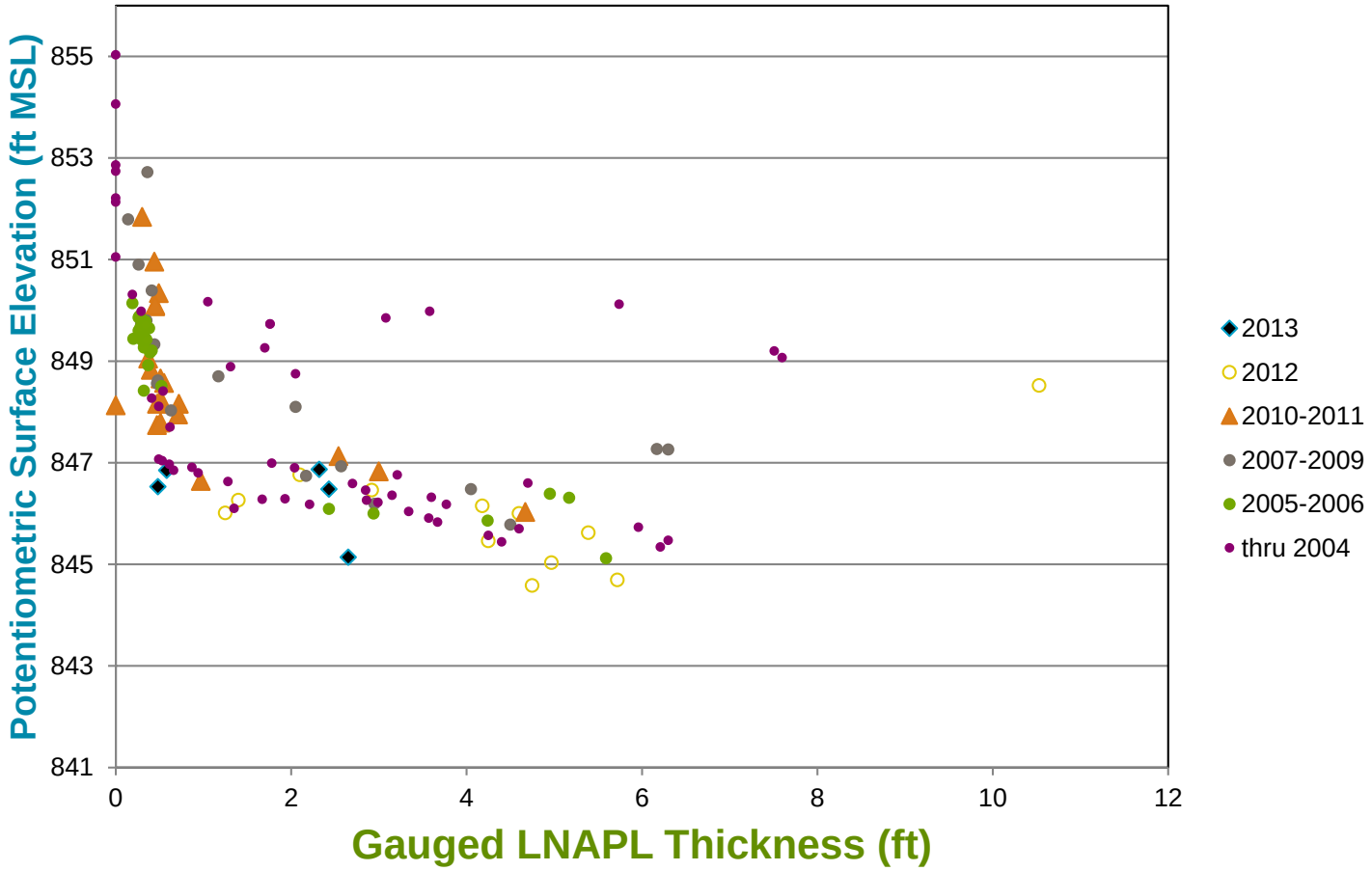



| Time (years) | Skimming (gallons) | Water Enhanced LNAPL Extraction (gallons) | Vacuum Enhanced Skimming (gallons) |
|---|---|---|---|
| *1* | *0.3* | *12* | *2.5* |
| *5* | *1.3* | *52* | *12* |
| *10* | *1.4* | *86* | *23* |
| *50* | *13* | *150* | *85* |

# Example of Ineffective Remedy Selection

## One could argue poor metric too

- Socks in wells do little to ensure closure and inhibit the conceptual model
- Vacuum Truck Recovery does little to affect long-term LNAPL thicknesses

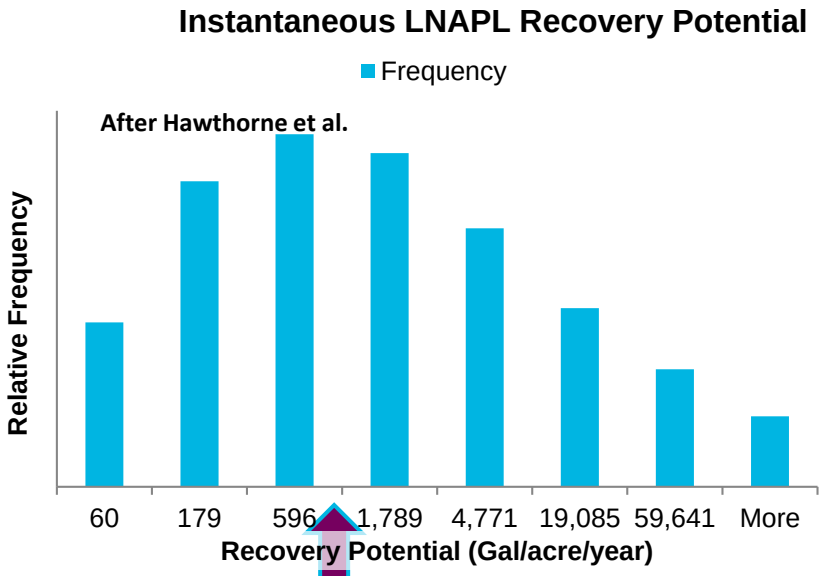


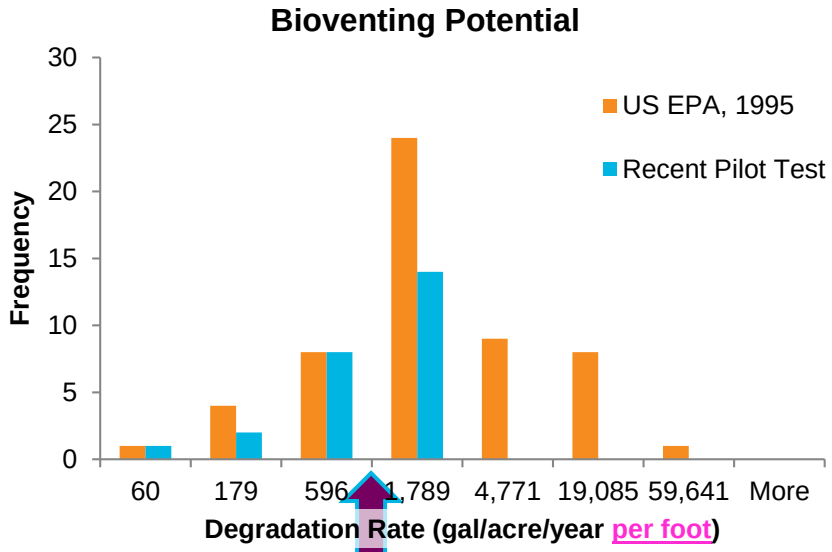
# Basic Conceptual Site Model

| LNAPL Conceptual Site Model (LCSM) Data Collection Parameter | Is a Basic understanding of the Component needed for given LCSM Type | | |
|---|---|---|---|
| Can be Considered Sections in a Report | Initial | Active | Passive |
| Site setting / Land Use / Receptors | Yes | Yes | Yes |
| Geology/ Hydrogeology | Yes | Yes | Yes |
| Source Delineation / Composition / Stability | Yes | Yes | Yes |
| Dissolved-phase / Vapor-phase | Yes | Yes | Yes |
| LNAPL Recoverability | | Yes | Yes |
| Natural Degradation Processes | | | Yes |

# Why don't our CSMs include Biodegradation Potential Beyond NSZD

## API Tn Database versus AFCEE Bioventing Database



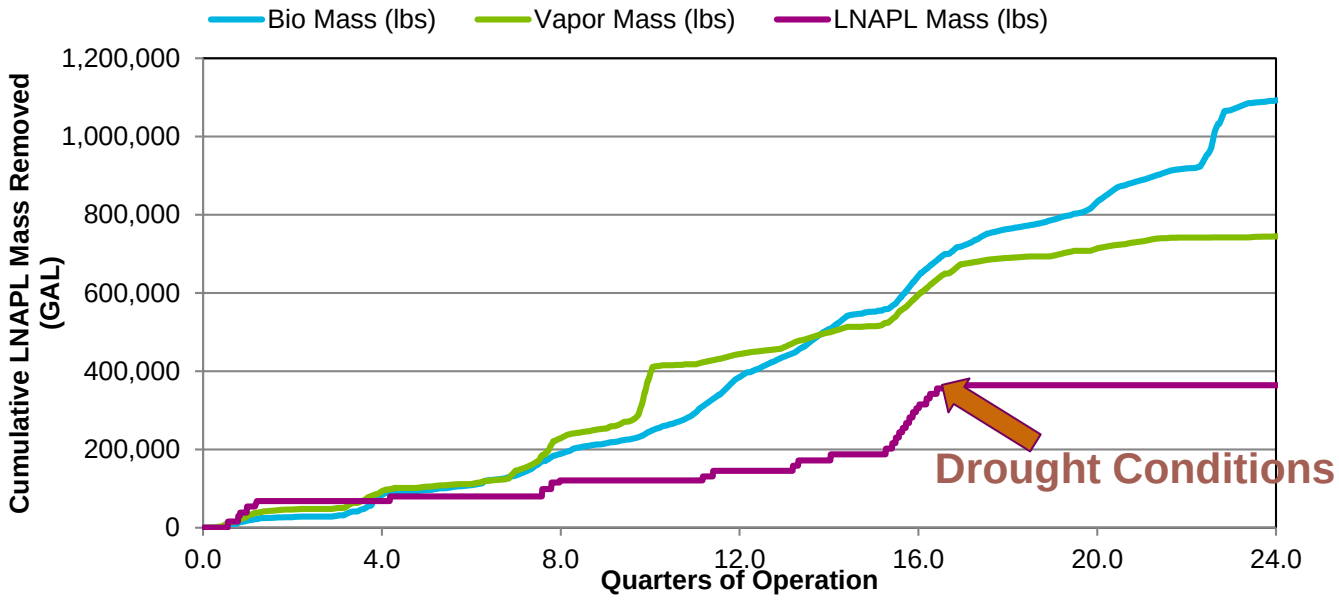

**Average Removal Rates**

- Average INITIAL LNAPL recovery rate ~ Average Bioventing rate FOR 1 FOOT OF SOIL TREATMENT

- Perhaps we should be doing push-pull respiration tests with air and helium rather than or in addition to baildown tests

# Biodegradation Out Competes Vapor and Liquid Recovery for Gasoline Range LNAPL

- Note Initial LNAPL recovery rate higher than both, Long-term this rate decreased the most.
- What Mechanisms will prevail beyond Instantaneous Rates?




- Good Conceptual Models are Needed to Forecast Performance

# Knowledge Development – Improved Respiration Testing Guidance

- Could improve guidance for these measurements to provide three values, Tn, Bioventing potential and NSZD combined
  - Guidance for both helium testing for diffusion constants and guidance for respiration testing are available
  - Similar to baildown tests prior to the ASTM LNAPL Transmissivity Standard
    - Few people conduct these tests for quantitative characterization
    - Learning curve on procedures and repetition may be needed to collect higher quality data
    - Requires some in field problem solving
- In addition where LNAPL exists above and below water-table in similar soil and composition, respiration test could provide insight to biosparge based degradation rates for saturated zone

# We already have data from SVE and Bioventing to start working on Rate metrics

- Use of Monod Kinetics has already been described in literature (Leeson and Hinchee, 1993)

$$\frac{dS}{dt} = \mu_{max} M_t \frac{S}{K_s + S}$$

$$\frac{dS}{dt} = \mu_{max} \alpha S_o$$

Where

S – Molar Substrate Concentration

$M_t$ - Population Concentration

$\alpha$ – Ratio of Population to Initial Substrate Concentration

$\mu_{max}$ – Maximum utilization rate per unit population

  - Temperature as a metric described in 1993 – but that is more performance monitoring
  - Summaries of first order rates for soil gas have previously been documented (DeVaull, 2011)
  - Biosparge estimates could utilize respiration rate constant and potentially account for
    - Saturation differences
    - 1st order loses due to volatilization
    - But not significant soil or LNAPL compositional variability

# Empirical Data has identified Constant Rate relationship for Degradation of Alkanes

- Biodegradation of middle distillates often represents zero order rates (Christensen-Larsen, 1993 )
  - Rather than age dating, simply utilize rate relationship
  - Independent of how much was released rather the concentration because of Monod Kinetics (Galperin & Kaplan, 2008)
  - The microbial population will quickly grow to the maximum and remain constant, with Constant rate based on initial concentration

$$\frac{dS}{dt} = \mu_{max} \alpha S_o$$

$$\frac{d(\boldsymbol{nC_{17}})}{dt} = -\mathbf{4.39}\frac{(\boldsymbol{nC_{17o}})}{(\boldsymbol{Pr_o})}(\boldsymbol{Pr})$$

After Christensen-Larsen, 1993 and Galperin & Kaplan, 2008

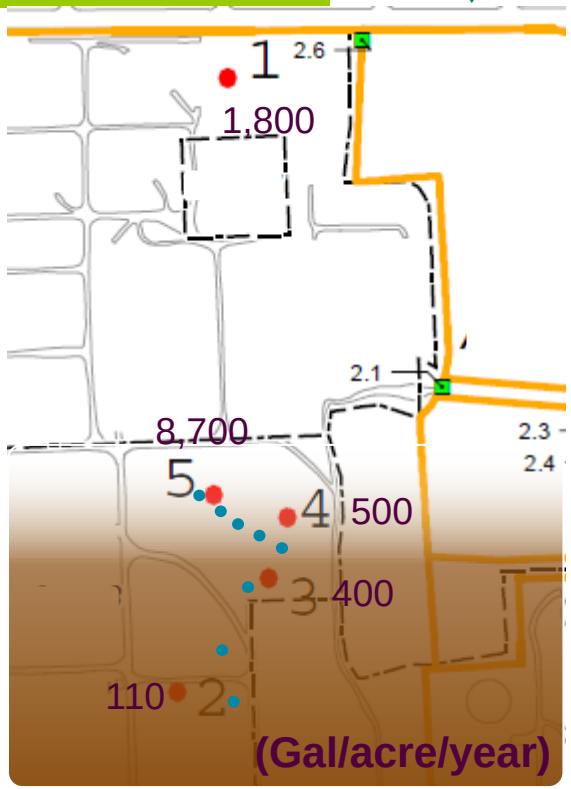
  - 75 % of diesel represented by alkanes

Possible Applications:

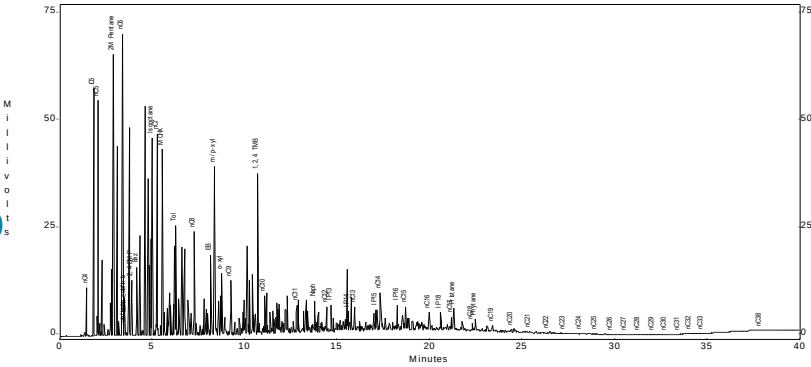
1. NSZD rates from GC/FID data … less costly and independent from CO2 efflux and temperature
2. Consider collecting GC/FID samples over the profile to provide an indication of weathering above, near and below the water-table
3. Biodegradation component represents one mechanism affect ng LNAPL weathering. Similar approaches could potentially be further developed with dissolution and volatilization representing first order.

# NSZD Rates are Great; But What Does An Individual Location Tell Us

- 5 Efflux Traps (Red Dots) Placed based on Shallow (~3 ft) Soil Gas probes (Blue dots)
- Clay Overlies sand in southern portion of Site
- Northern most point exhibits no detected vadose zone impacts with LIF detected submerged smear zone
  - >15% oxygen near water-table
- Remainder of points identify a reverse water fall effect at edge of clay for $CO_2$ efflux
  - Supported based on VMP's beneath clay exhibiting positive and negative pressures corresponding to water-table changes.




- CO2 efflux from NSZD is not consistently 1-Dimensional – Look for alternate methods to rely on

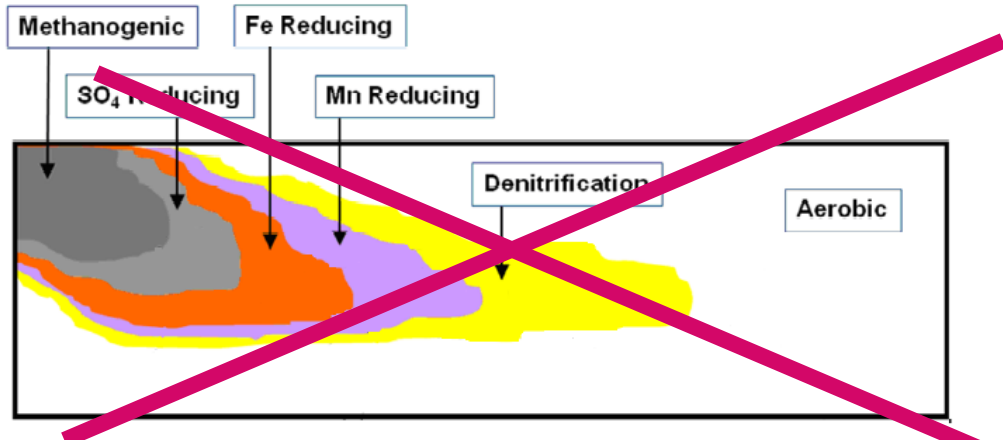


# Monitored Natural Attenuation in Remedy Selection

- The concept of exclusive redox zonation within plumes can inhibit proper remedy selection
- Overlapping Redox zonation well documented in literature
  - Sulfate & Fe reduction
  - Fe Reduction & Methanogenesis &
  - Methanogenesis & Sulfate reduction

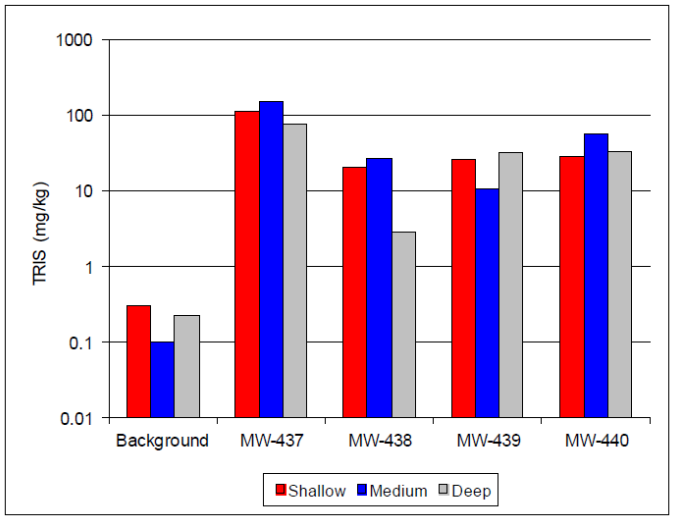
(Jakobsen & Postma, 1999 &
See references within this publication)

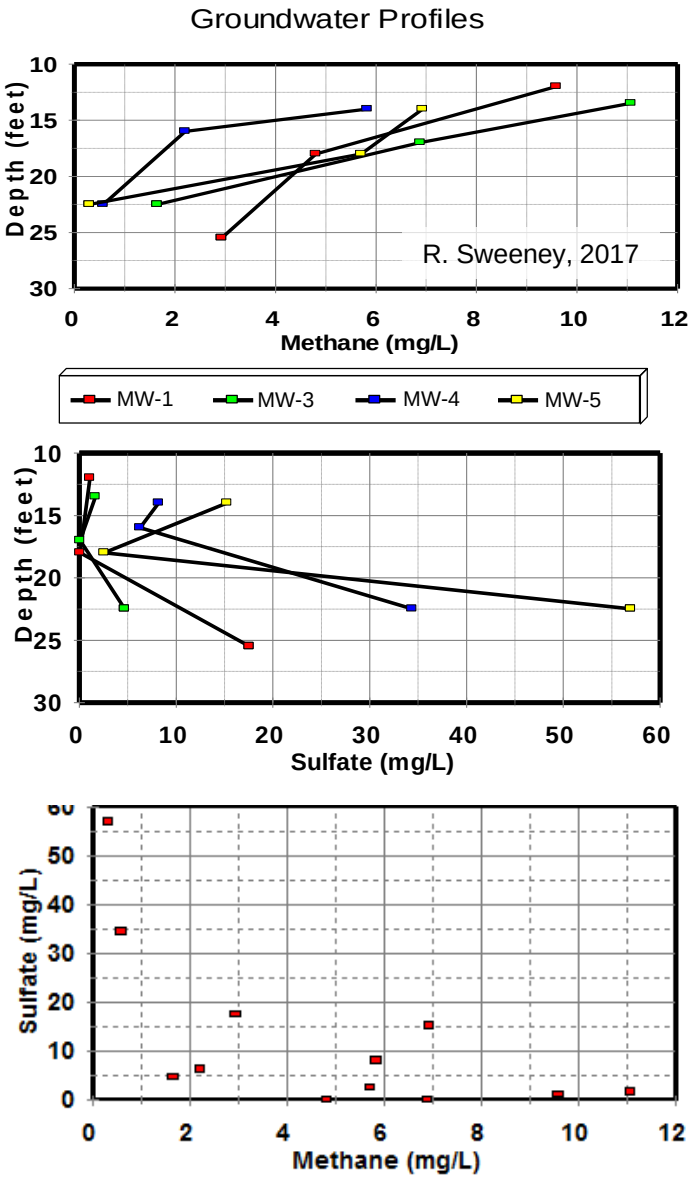
- Electron acceptor availability may not be dominated by groundwater transport
  - 90% of reduced Fe remains in source zone (Ng et al., 2015 )
  - Sulfides readily mineralize
  - 70% of $CH_4$ was show to enter gas phase and oxidize in vadose zone (Cozzarelli et al., 2015)
  - Additionally, electron cycling is often not accounted for where the mechanisms have been identified (Borden et al. 2015)



# Groundwater Profile Data from LNAPL Source Area

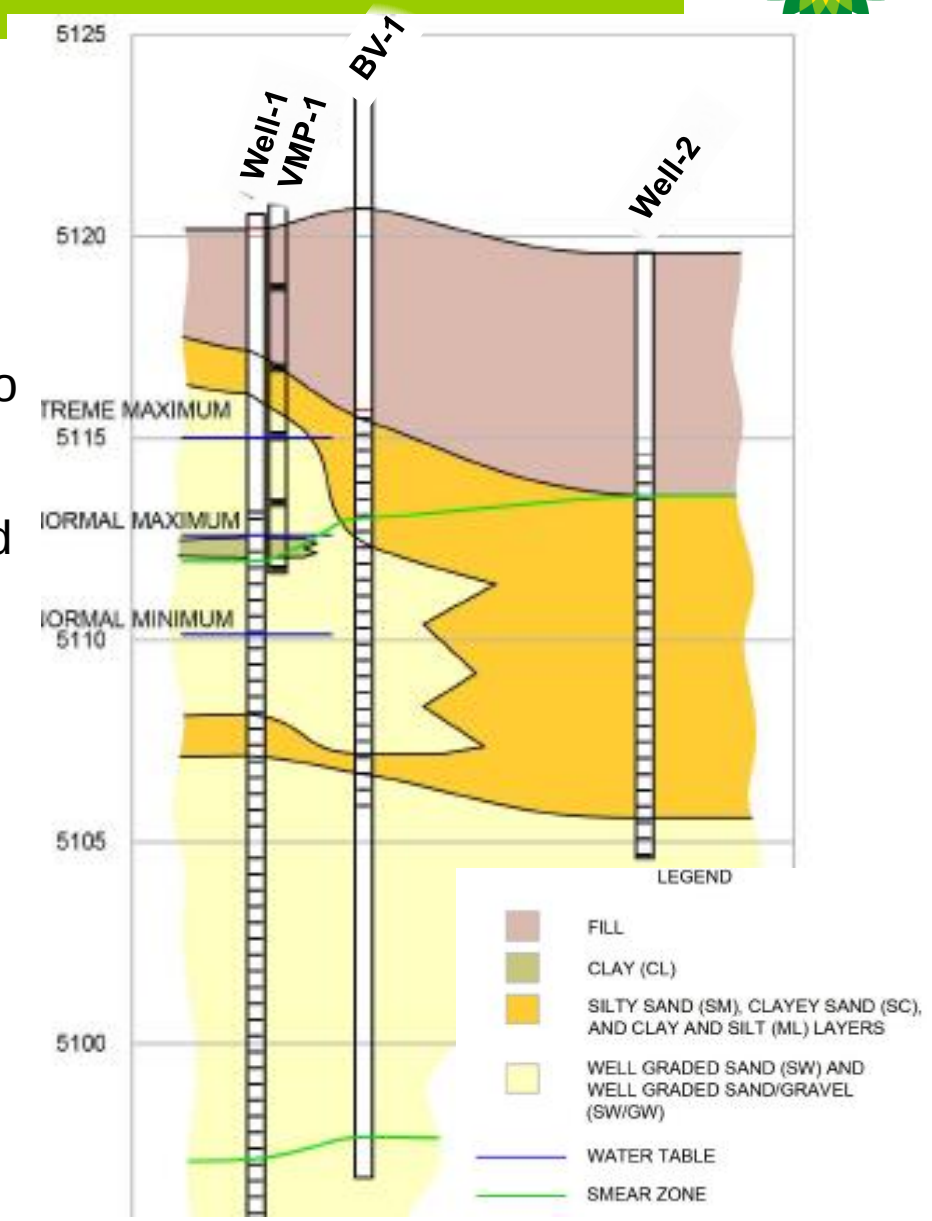
- Site data identify coexistence of Methanogenesis and Sulfate reduction
- Lack of sulfide with low Fe+2 detection could be due to mineralization similar to Bemidji
- Mineralization is often not accounted for in MNA evaluations
- Additionally, electron cycling is often not accounted for where the mechanisms have been identified (Borden et al. 2015)



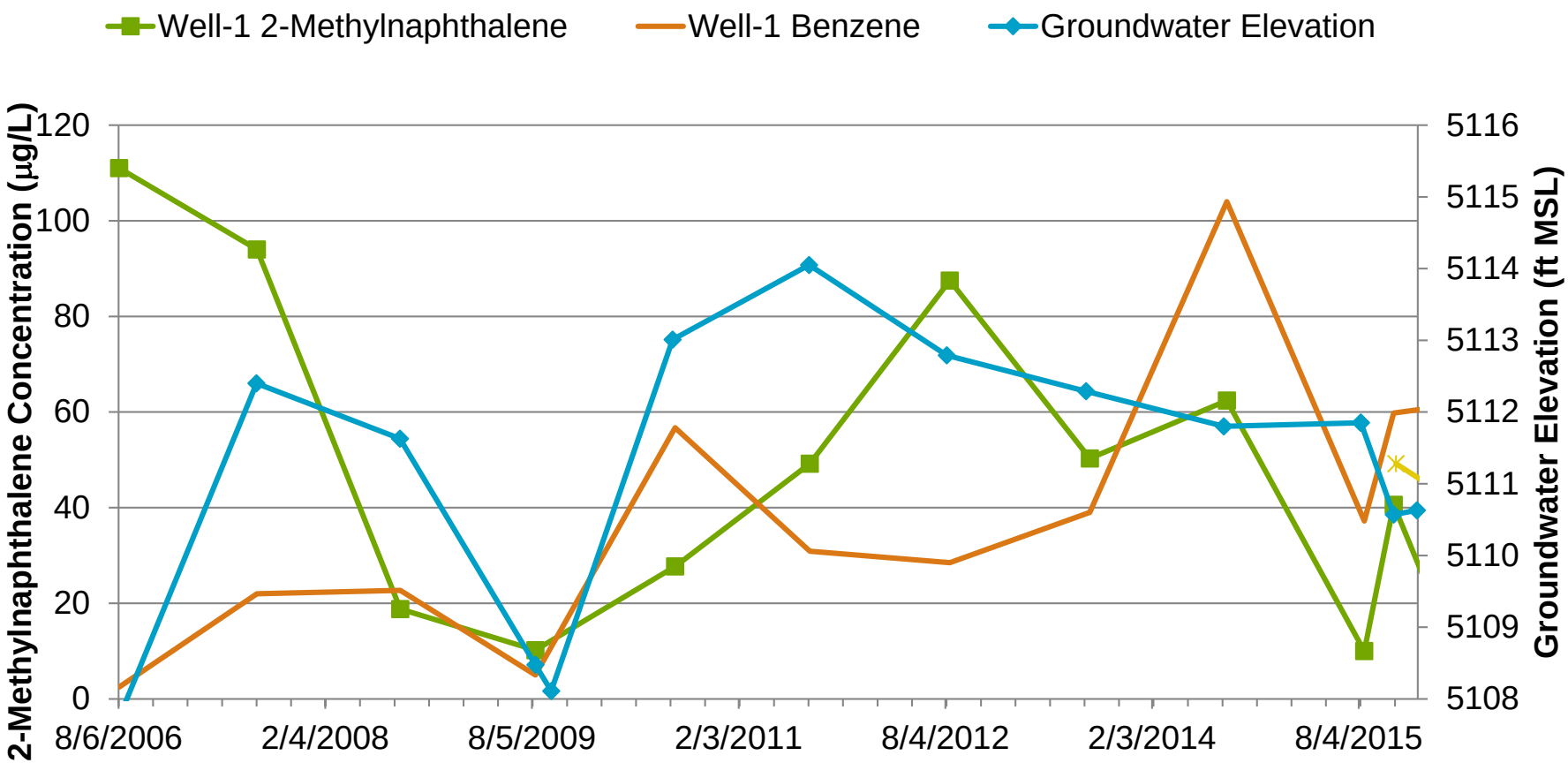
# Dissolved Phase in Source Area

- Adjacent to a river
- Monitored Natural Attenuation was the remedy
- Dissolved concentrations appeared to be increasing over time
- Conducted an evaluation of MNA and pilot of bioventing effect on MNA



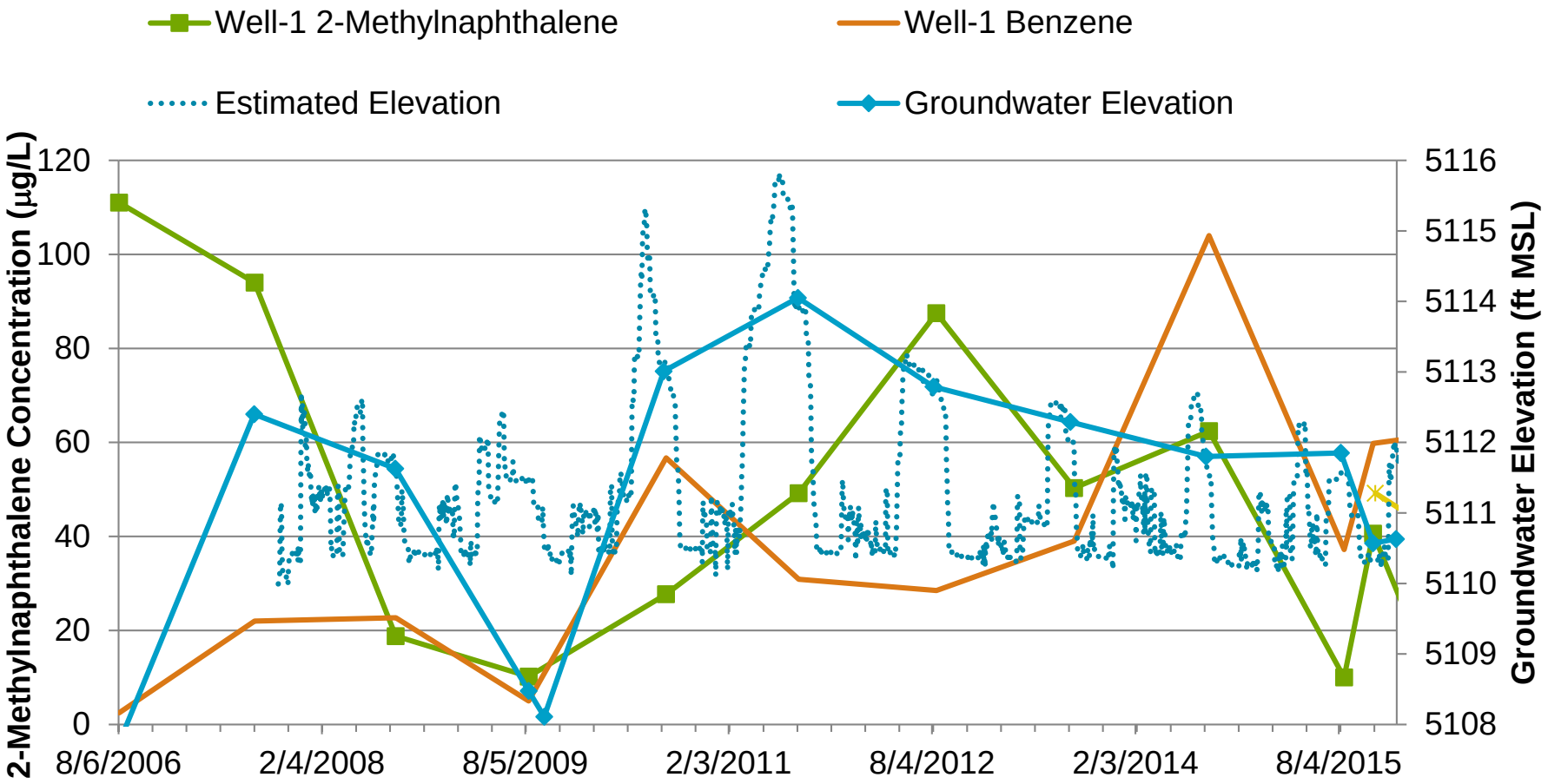
# River Stage versus Dissolved Phase

- Sulfate Reduction estimated to be only significant MNA process
- Is anaerobic degradation addressing these constituents?



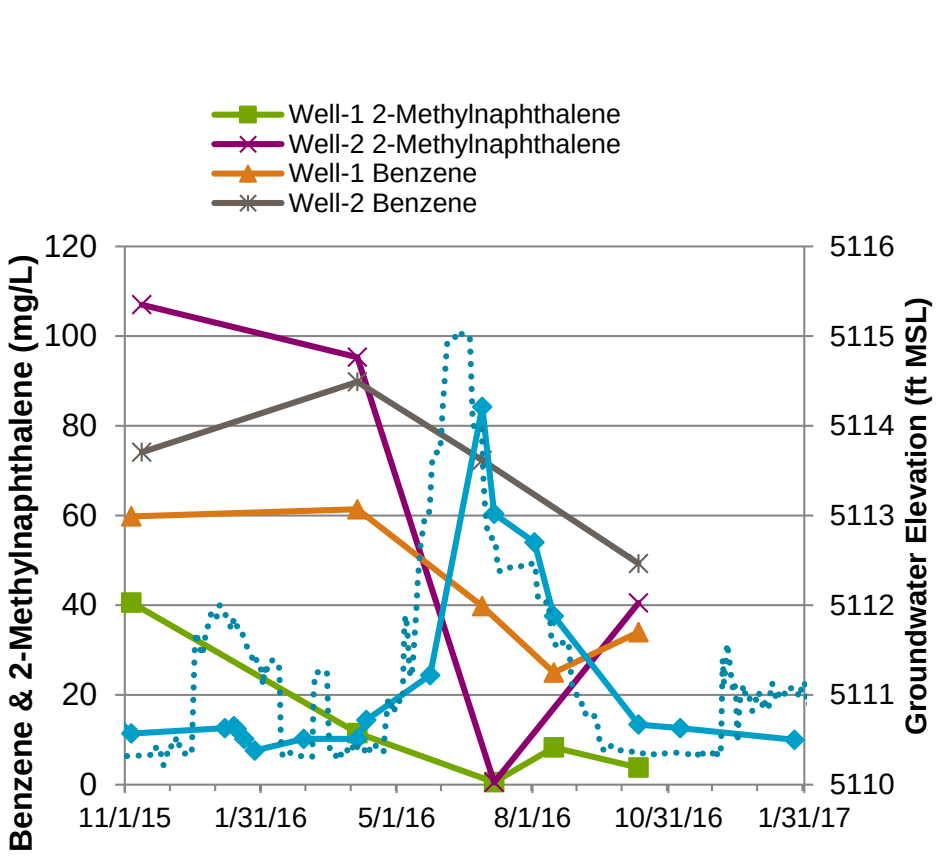
# River Stage versus Dissolved Phase

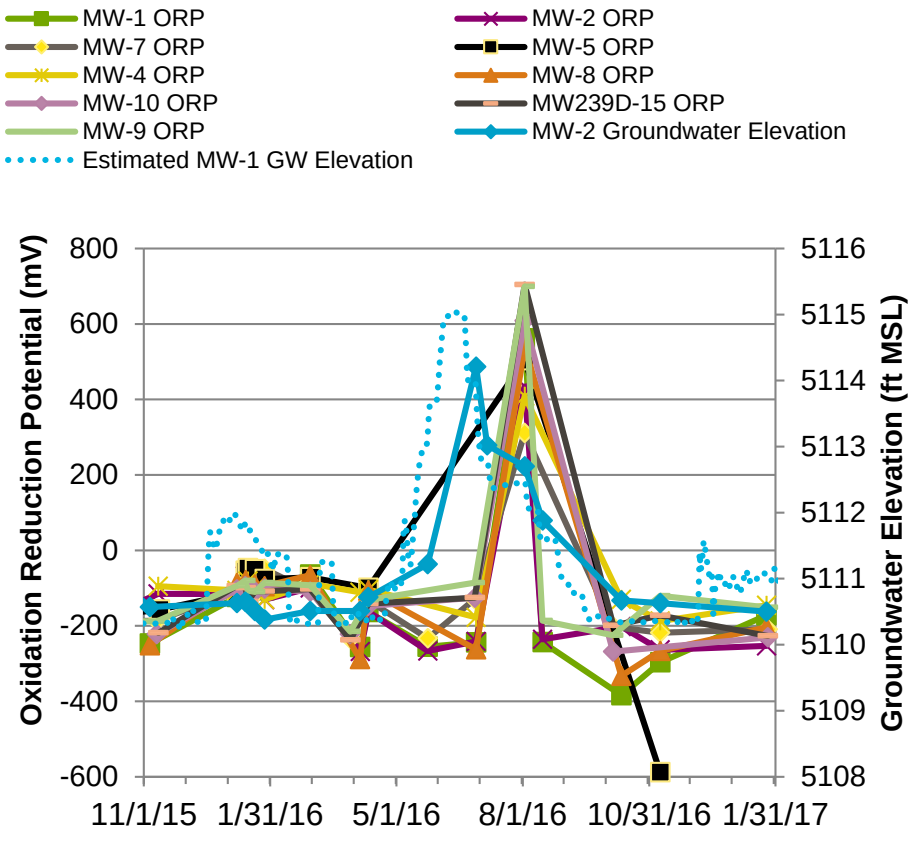
- Annual Sampling Frequency doesn't provide understanding of dissolved dynamics in a hypopheric zone



# Seasonal River flows bring changing conditions

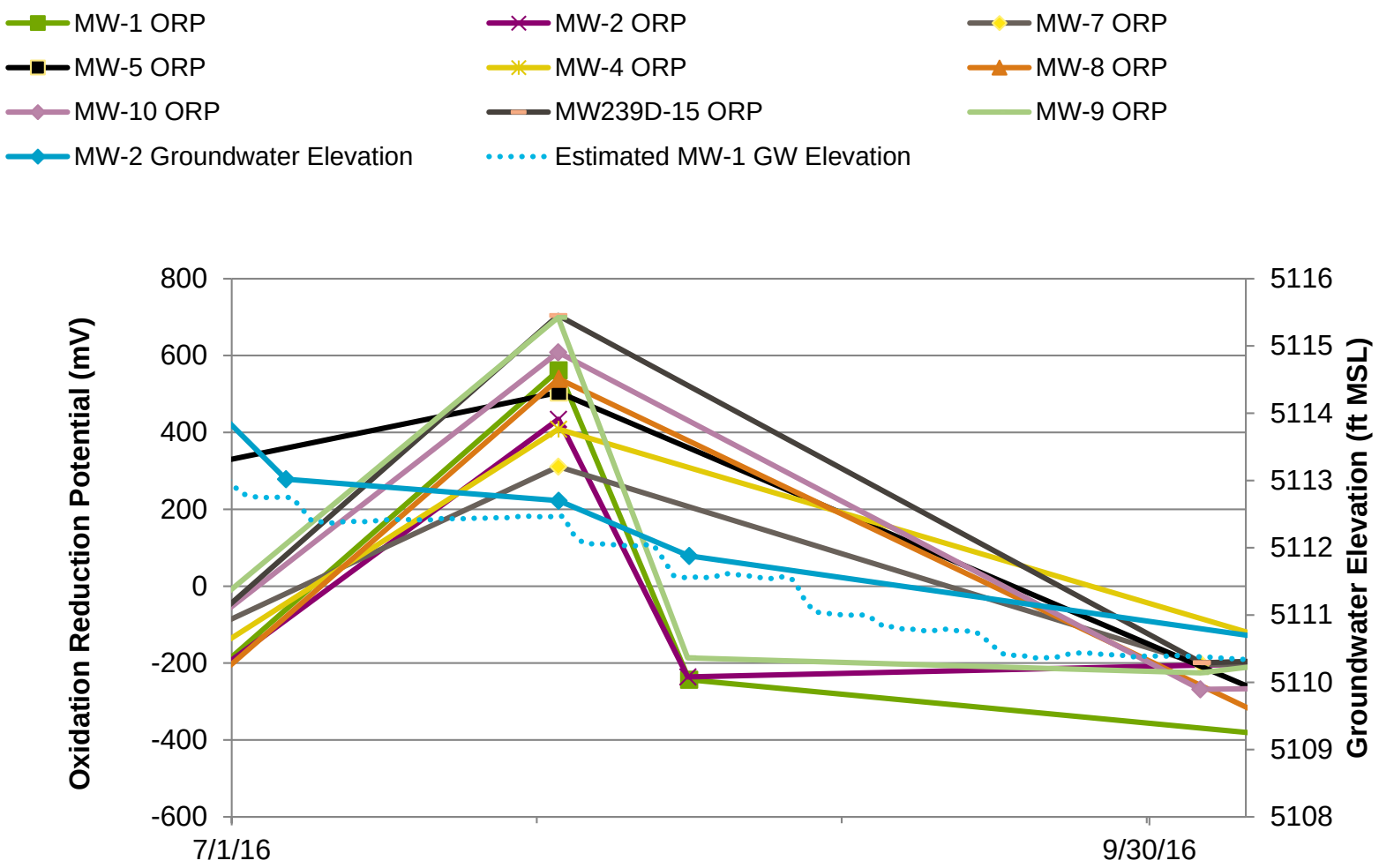
- Increased sampling frequency gives some insights, Improved recommendations made based on these results
- Aeration of vadose zone may affect cycling electron acceptor valence state
- Current dissolved sampling intervals are spatially and temporally arbitrary



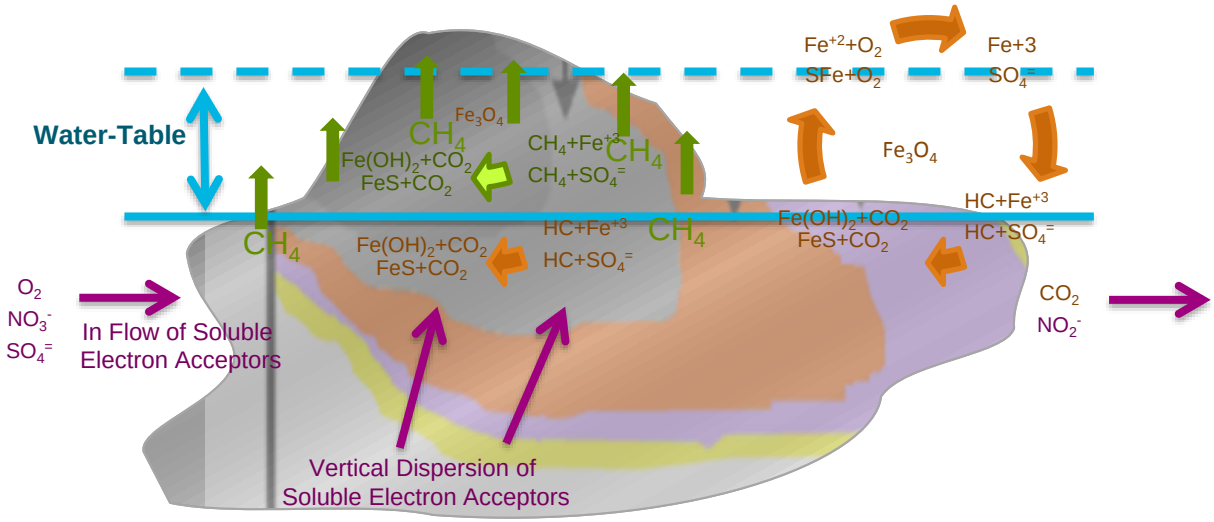
# Take a closer look at ORP

- Note, natural surface water routinely exhibit ORP on the order of 600 mV



# MNA is More Complex

- There is not just one process
  - REDOX Zones Overlap on large scale, discretized at pore scale
    - Sulfate & Fe reduction
    - Fe reduction & methanogenesis &
    - Methanogenesis & sulfate reduction
  - Temporal and vertical distributions exist
    - Take all sampling events over three years and direct them towards temporal and/or temporal discretization
  - Look beyond dissolved samples for bi-products but also to recycling potential



# Remedy Selection
## Between The CSM and Pilot Testing

- LNAPL Tn – provide quantified estimates of LNAPL Recovery
- There is much more to remediation
  - Push Pull Respiration Tests could indicate bioventing
  - GC/FID alternative to $CO_2$ efflux for natural degradation, $CO_2$ Efflux not always indicative of
  - Conduct high temporal or spatial resolution sampling of geochemistry at a minimum and possibly COCs to understand enhancement of MNA
  - Mineralization and cycling of electron acceptors could lead to improved insights
  - Respiration Test initial indicator of biodegradation rates for Sparge?
  - Forecasting of remediation performance beyond instantaneous requires good understanding of
    - LNAPL Distribution
    - Composition
    - Soil properties
    - Multi-phase dynamics
  - Hydrogeology still needs to be combined with dissolved trends
- Knowledge, Tools or even Data already exist to improve selection/optimization of remediation, it's a conceptual barrier preventing the correct choices

# Thank you

## References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