

## CREATIVE THINKING EXCEPTIONAL SOLUTIONS

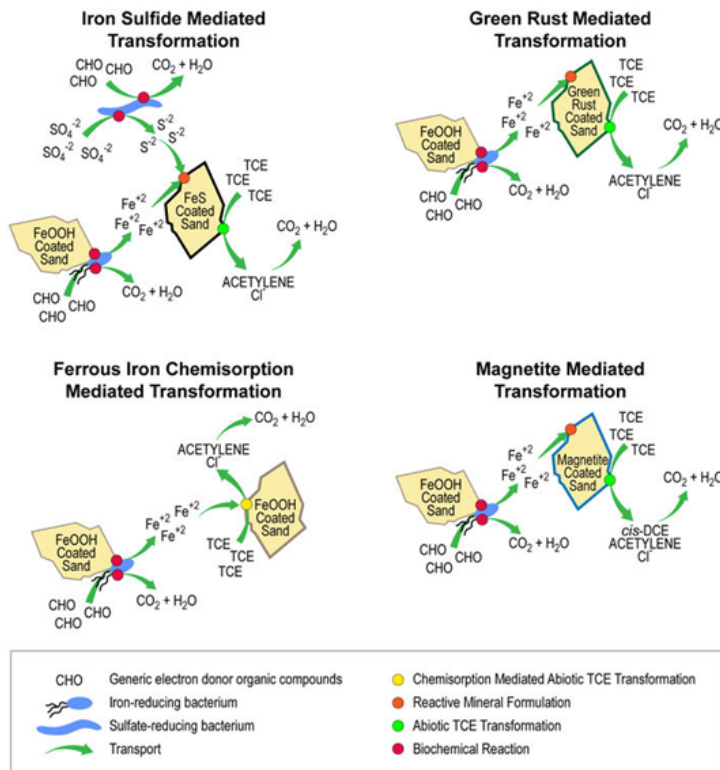
# Developing A Field Deployable ORP Kit to Measure Redox Potential of Aquifer Reactive Solids for Assessment of Abiotic Natural Attenuation

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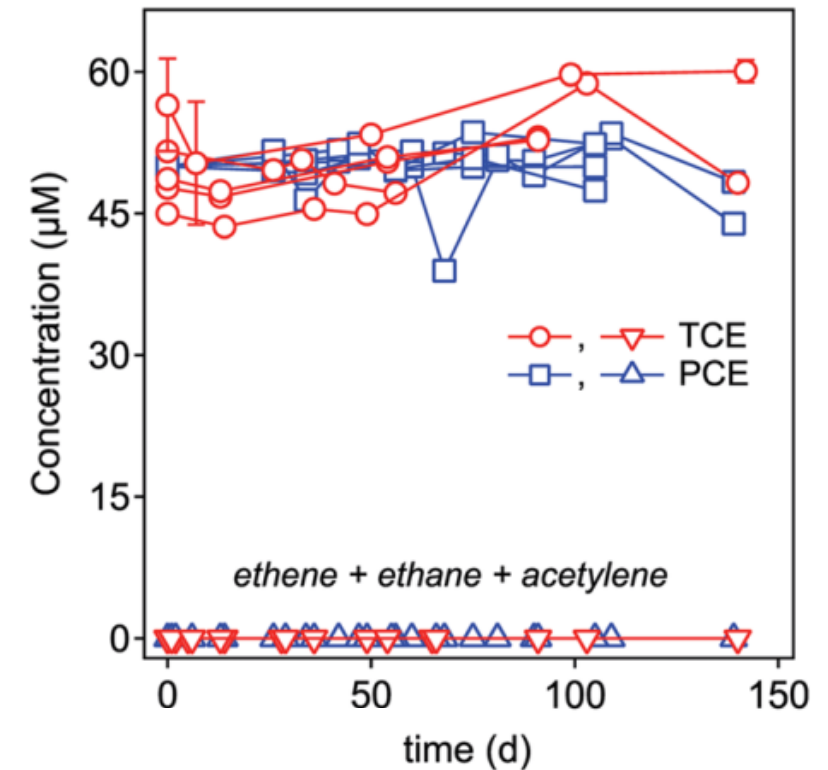
# Motivation: Better Tools to Help Transition Assessment

## Abiotic Natural Attenuation (ANA) Driven by Reactive Iron Minerals



How to quantify and predict ANA rates for chlorinated ethenes?

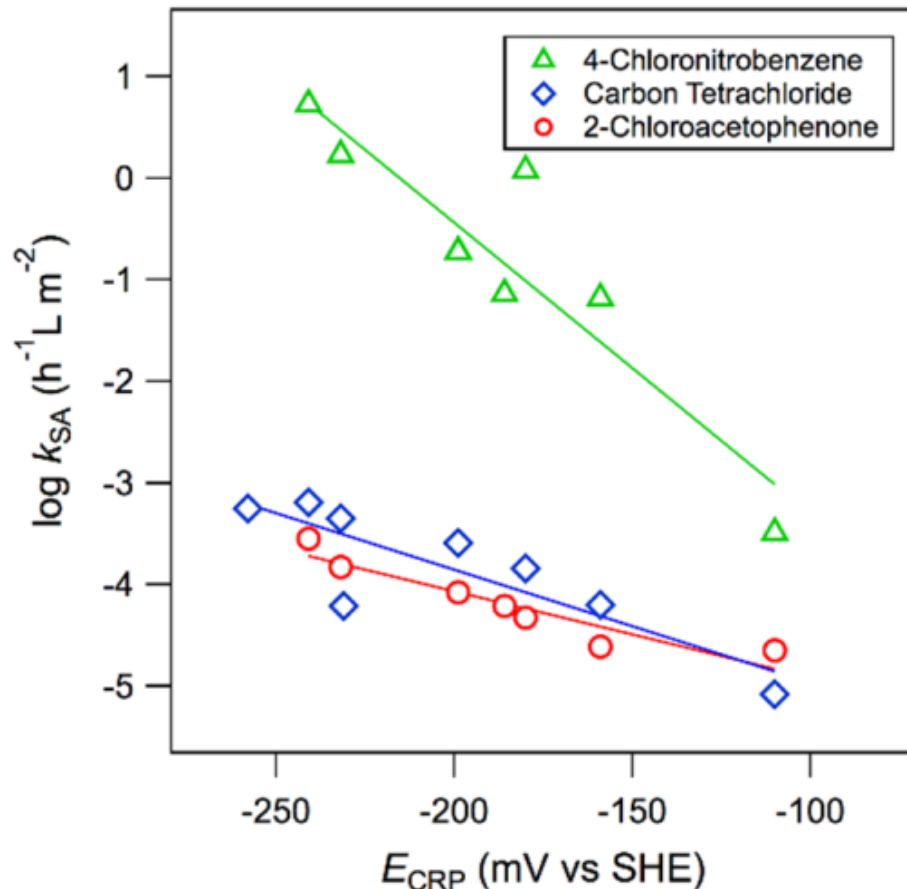
ANA Rates: often too slow to measure within laboratory timescale



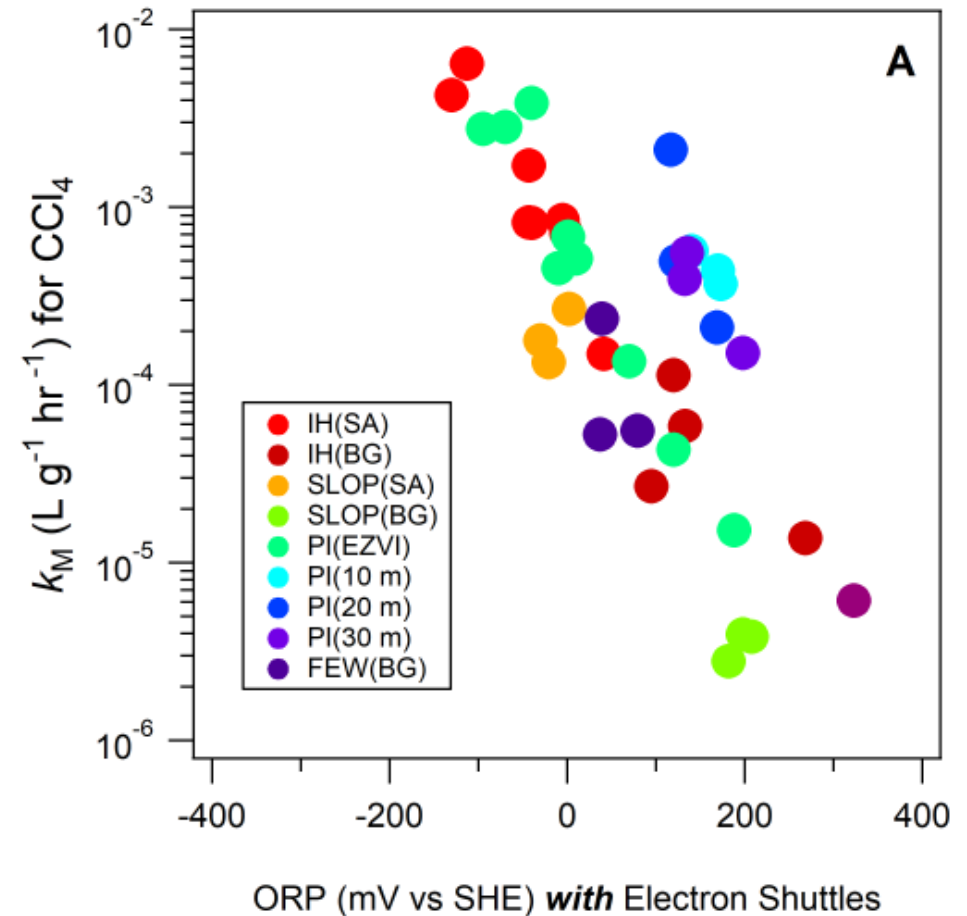
Robinson et al., 2018

# Oxidation-Reduction Potential (ORP) as a Predictor

Model Iron Oxide + Fe(II)  
(Fan et al., 2016, ES&T)

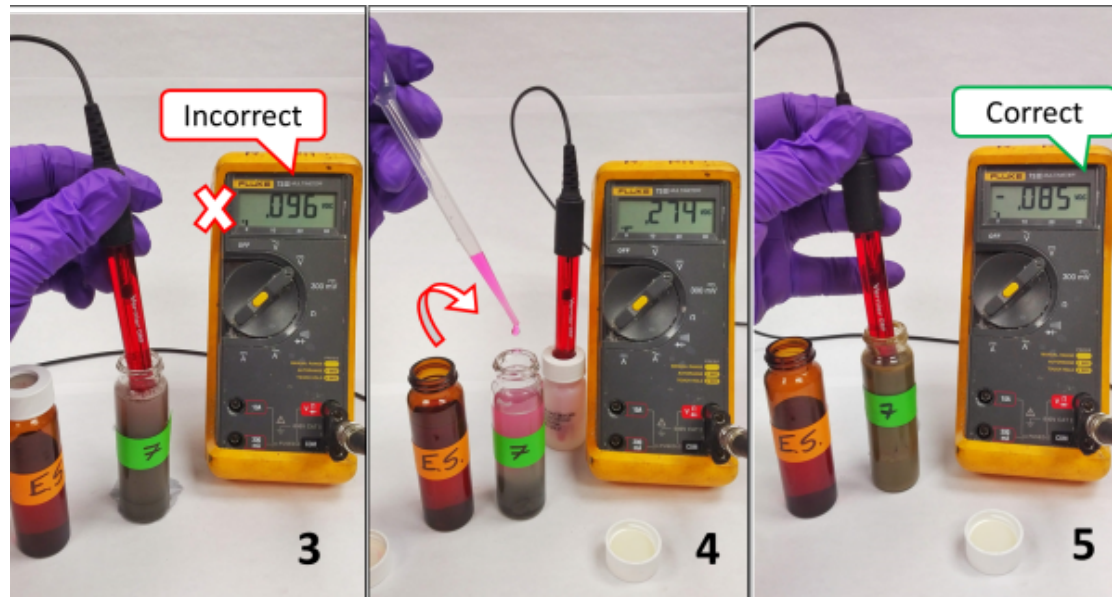


DoD Site materials  
(Kocur et al., 2019, ES&TL)

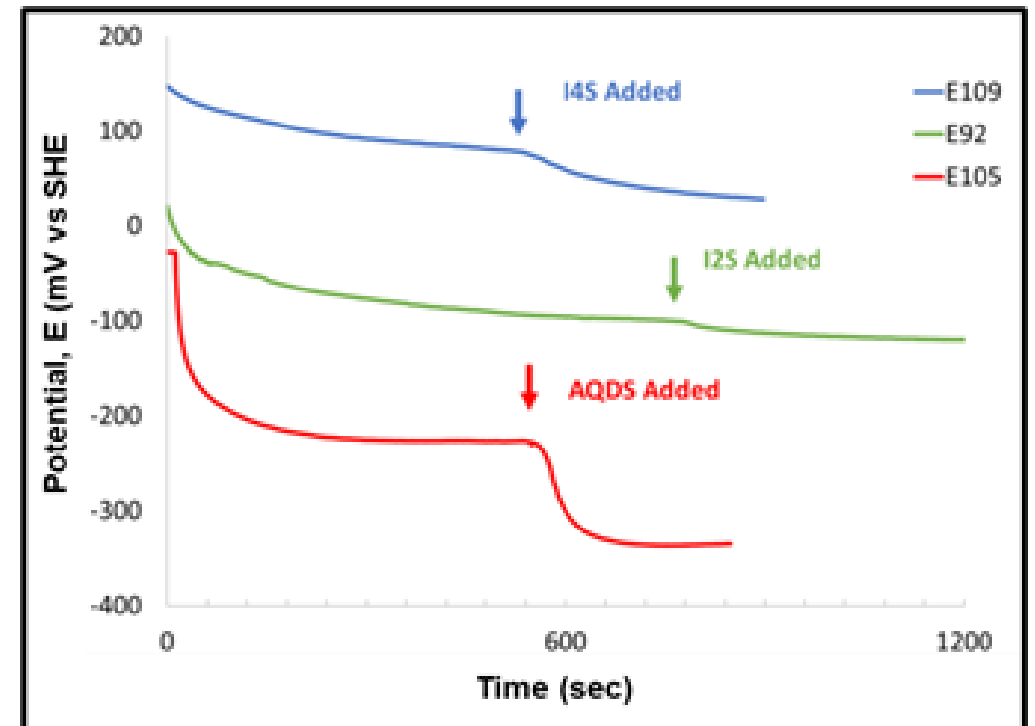




# How to Measure ORP for Reactive Minerals

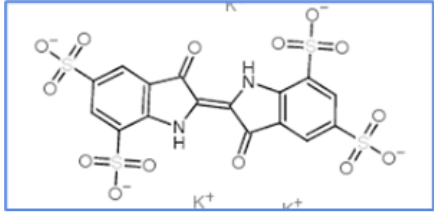


Electron shuttle (ES) improved electrode response to reactive minerals

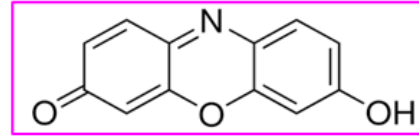


Mediation Effects – Diagnostic Decrease in ORP

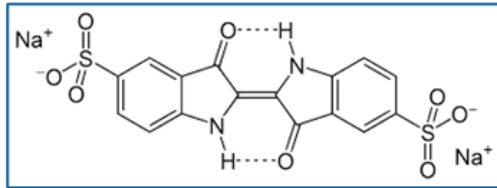
# ORP Kit: Improve Efficiency by Reducing Iterations



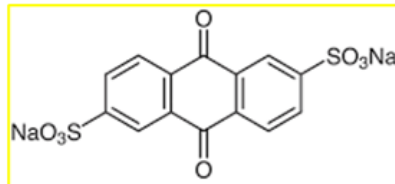
**Indigo tetrasulfonate (I4S)**  
 $E_m^7 = -246 \text{ mV vs. Ag/AgCl}$



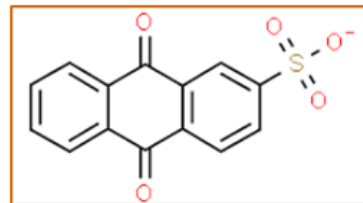
**Resorufin (RSF)**  
 $E_m^7 = -251 \text{ mV vs. Ag/AgCl}$



**Indigo Disulfonate (I2S)**  
 $E_m^7 = -325 \text{ mV vs. Ag/AgCl}$



**Anthraquinone-2, 6- Disulfonate (AQDS)**  
 $E_m^7 = -384 \text{ mV vs. Ag/AgCl}$



**Anthraquinone Sulfonate (AQS)**  
 $E_m^7 = -425 \text{ mV vs. Ag/AgCl}$

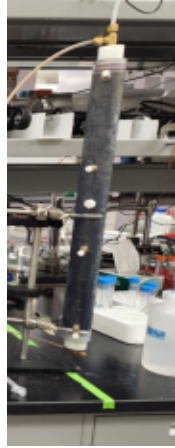


# ORP Kit Development and Refinement

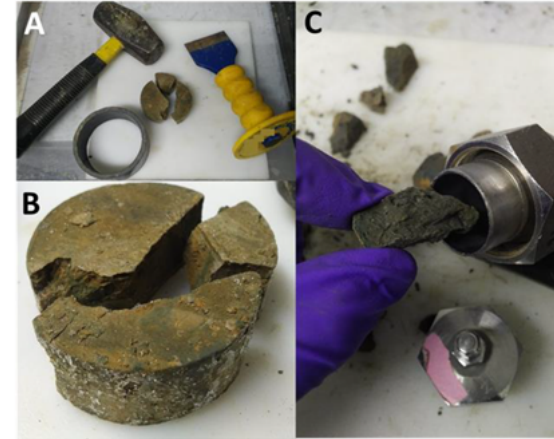
## Assay Validation



Model Minerals  
iron oxides

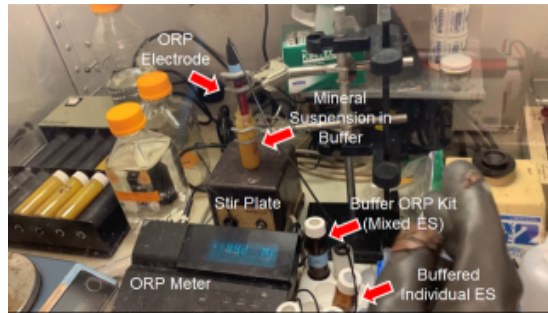


Controlled Site Material  
Amended with ZVI

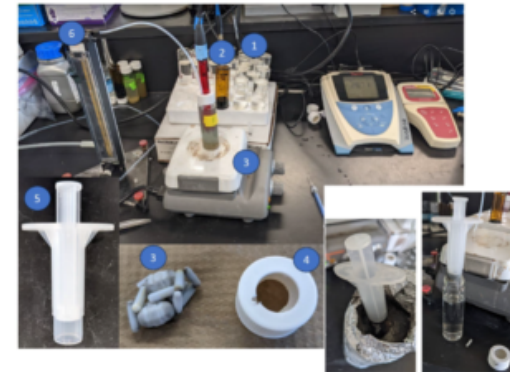


DoD site Materials

## Protocol Development



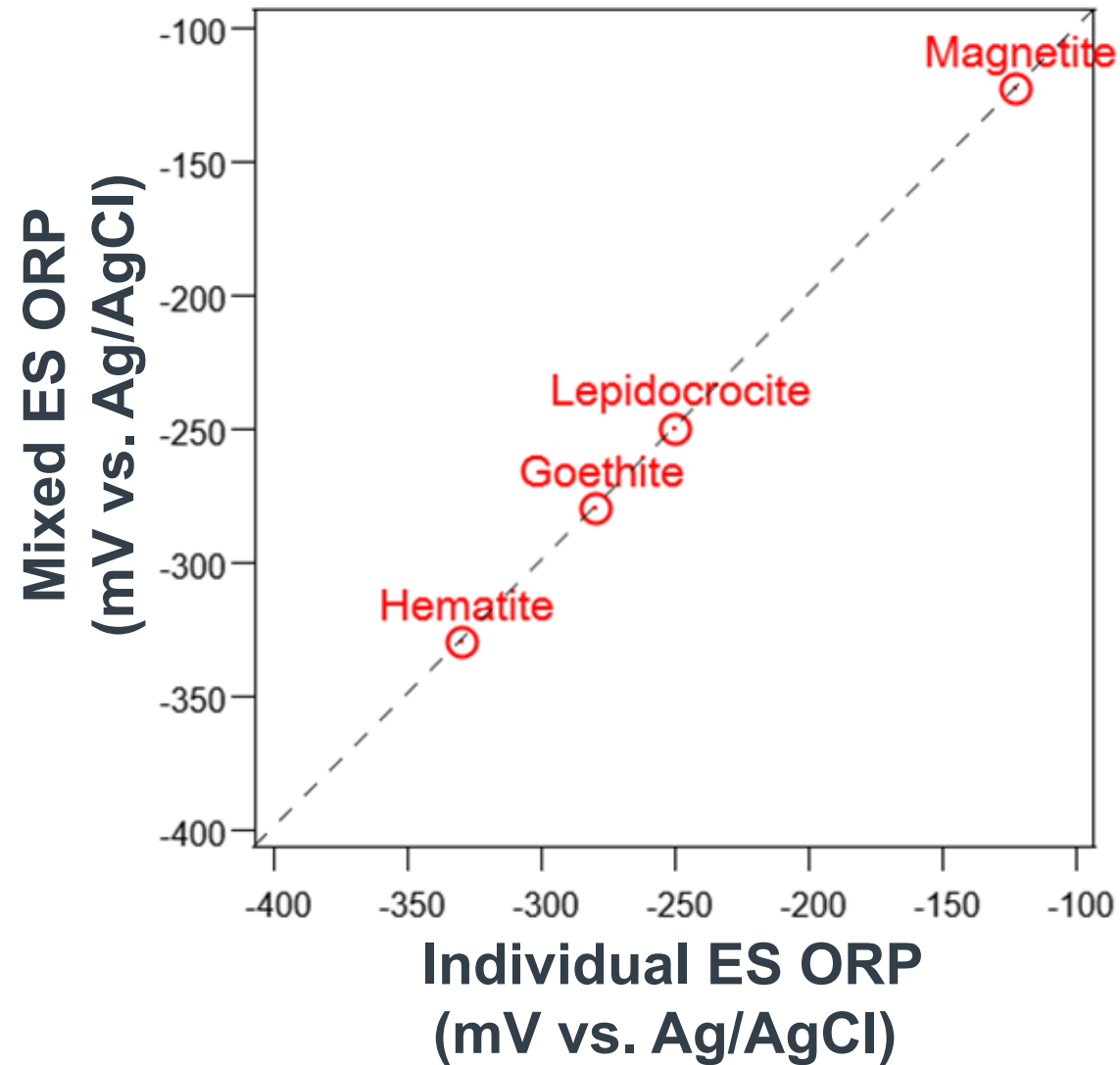
Well Controlled Anaerobic Chamber



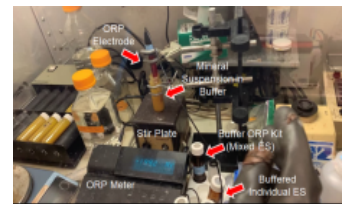
Field deployable



# Proof of Concept – Consistent ORP between Mixed and individual ES

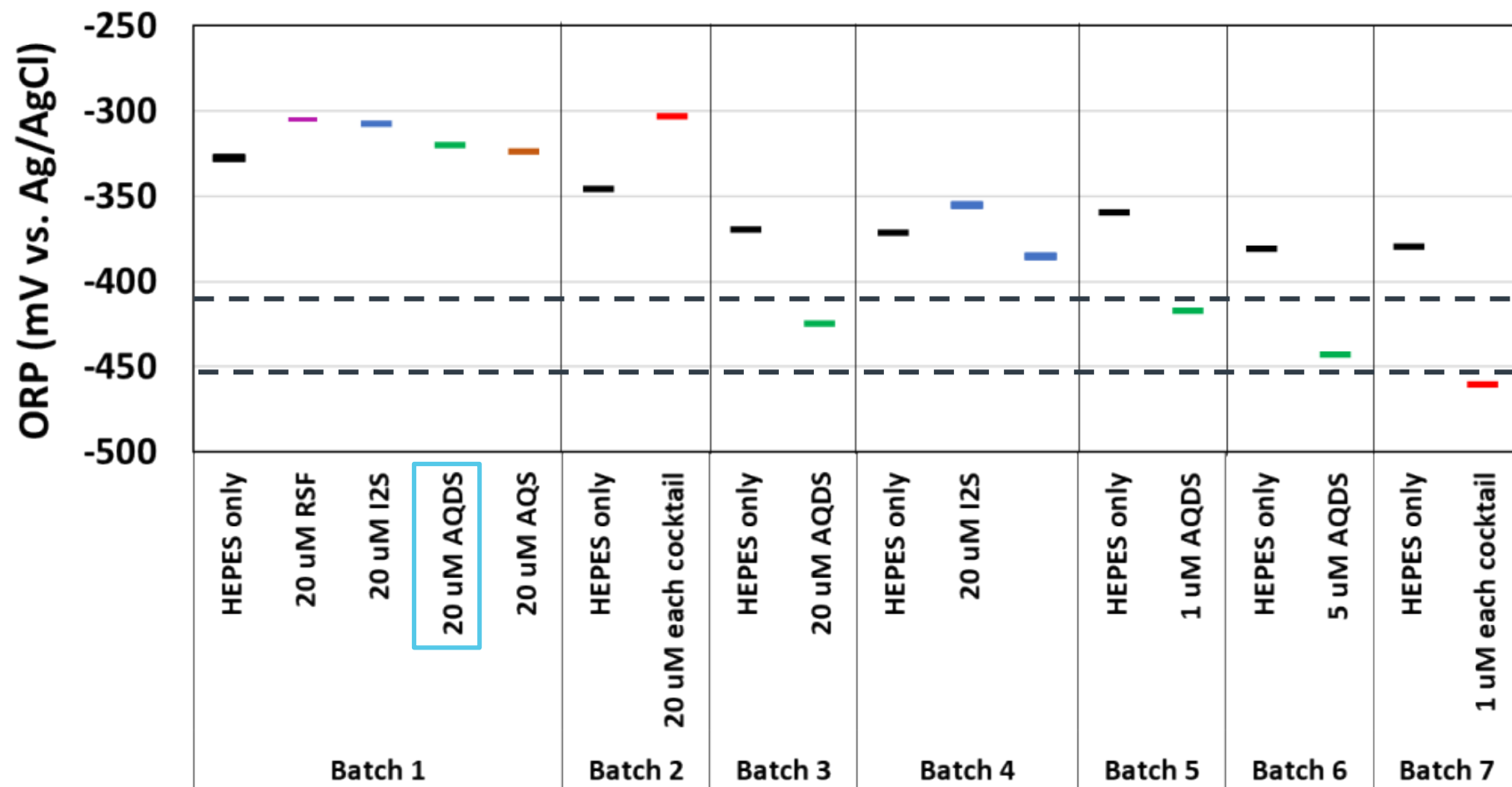


0.5 g/L iron oxide  
0.1 mM Fe(II)

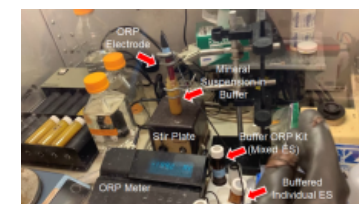


Anaerobic  
Chamber

# Non-Mediating ES May Interfere ORP measurement



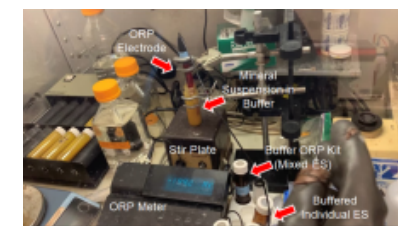
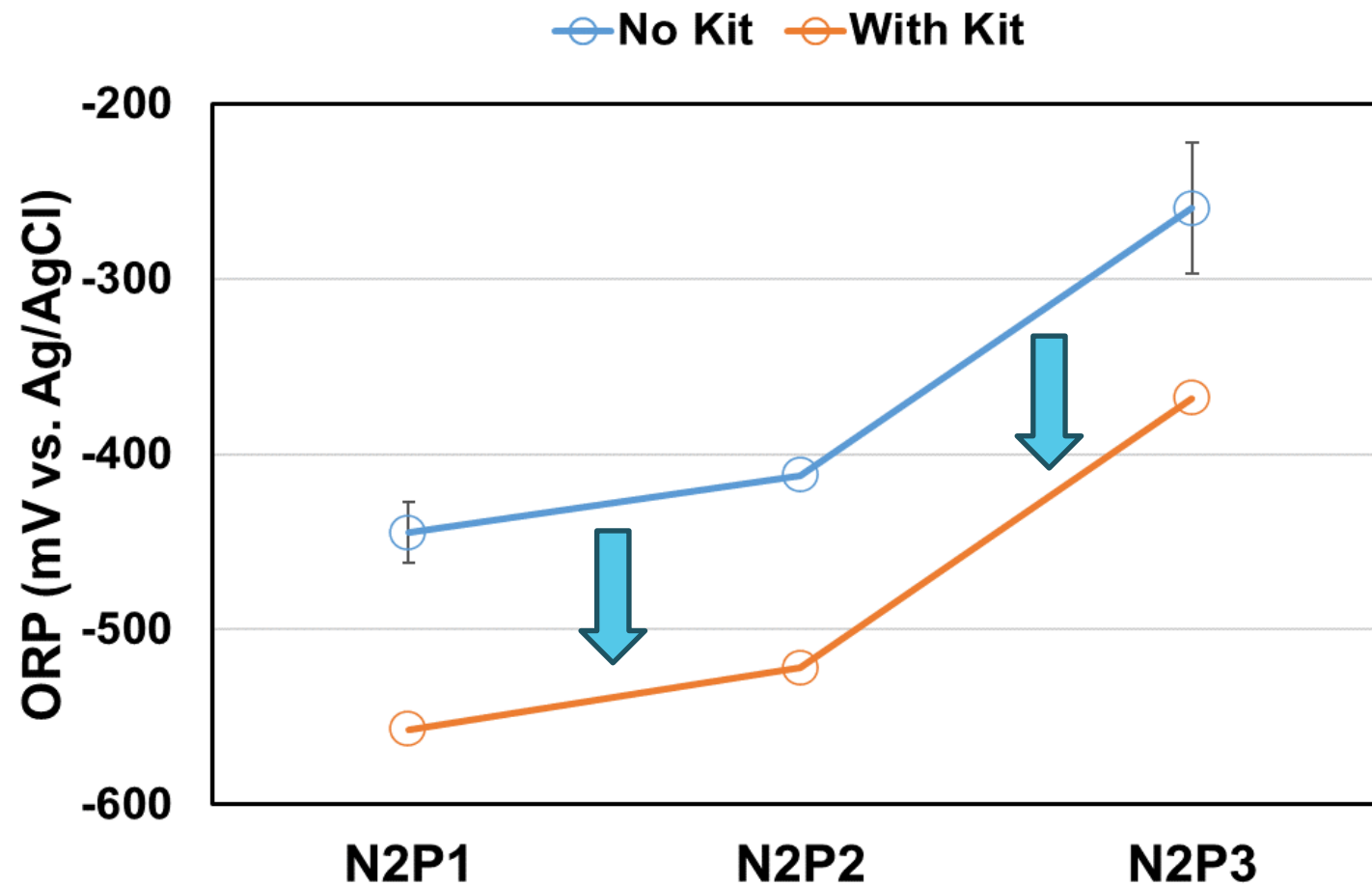
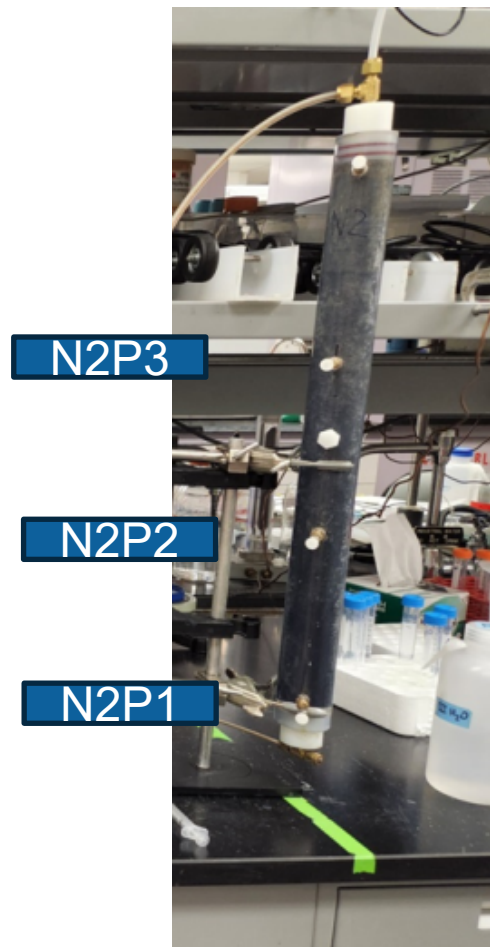
3 g/L goethite  
1 mM Fe(II)



Anaerobic  
Chamber

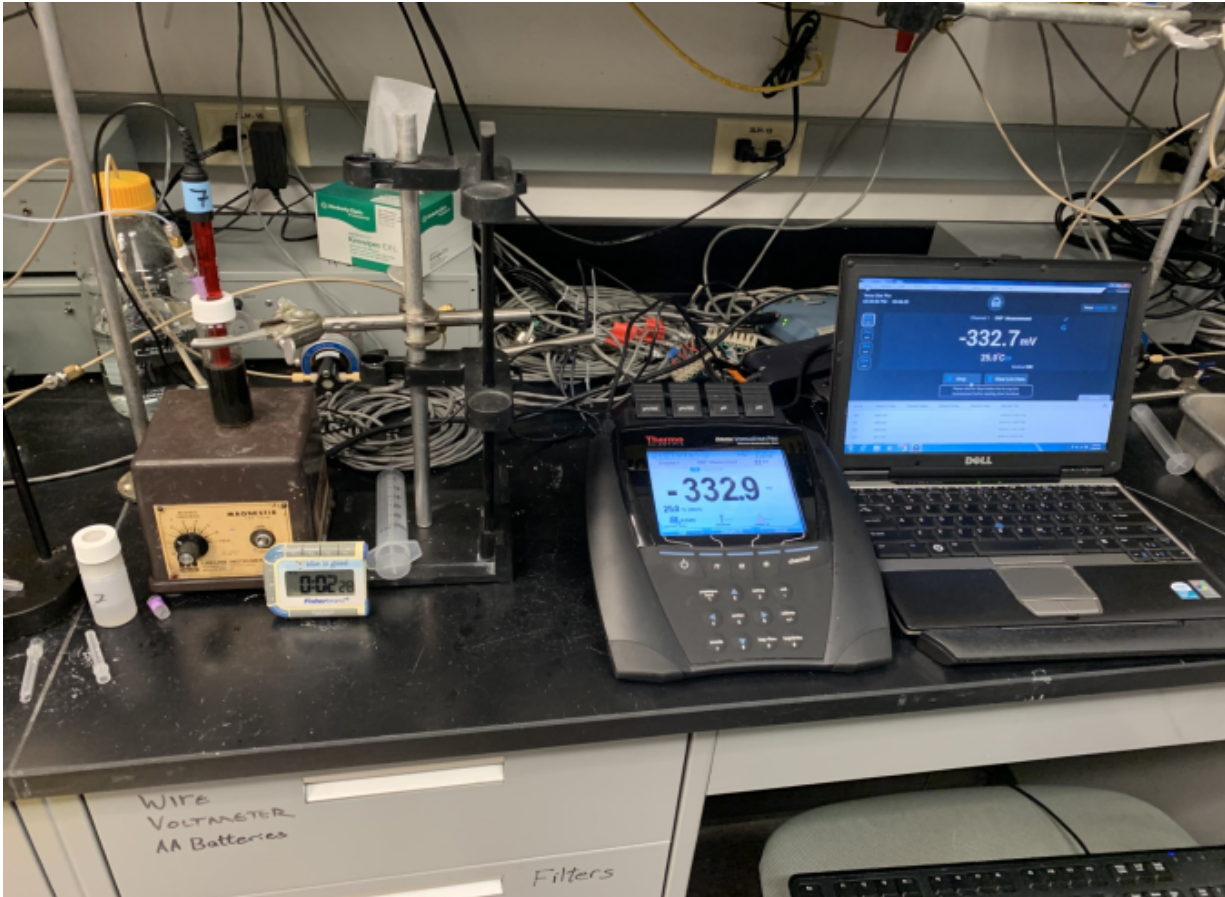


# ORP Kit Validation: Site Material with S-nZVI

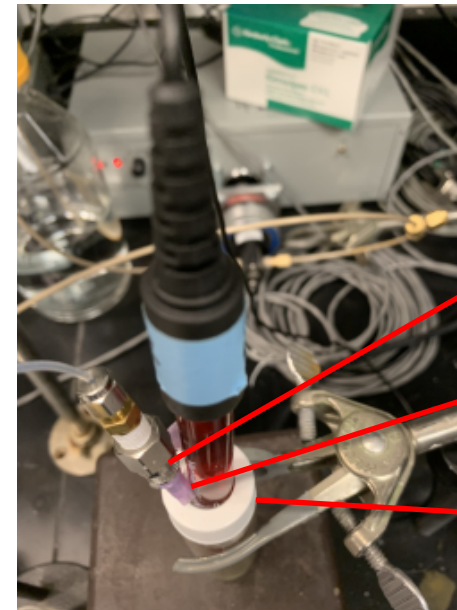


Anaerobic Chamber

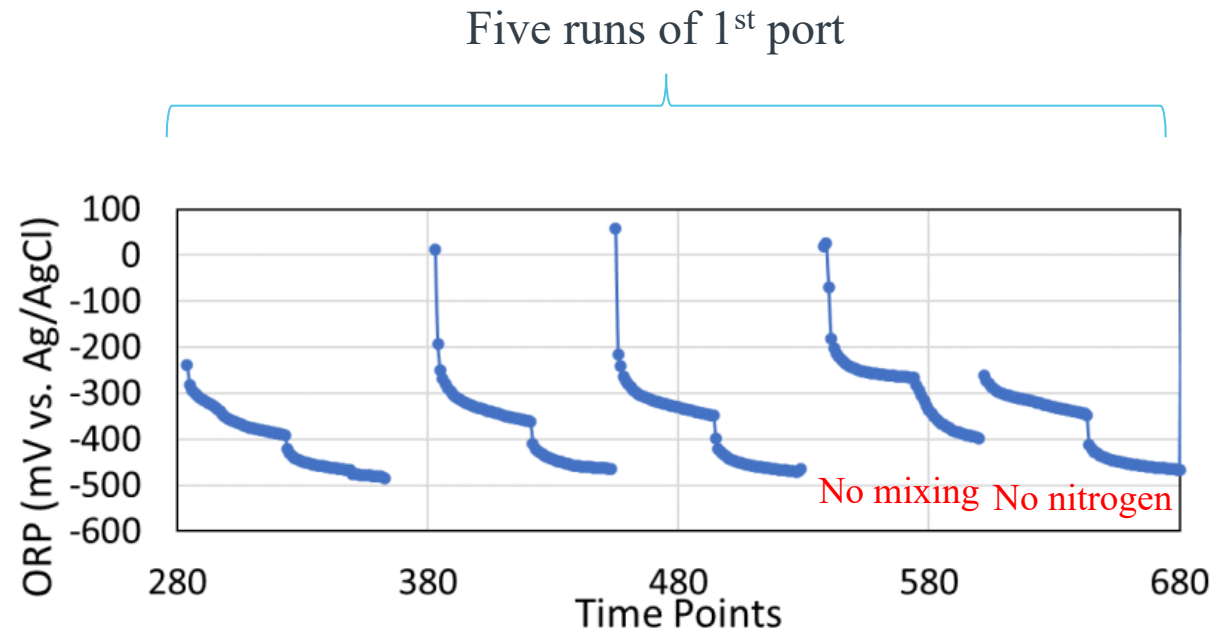
# Develop a Field Protocol: Test Outside the Anaerobic Chamber



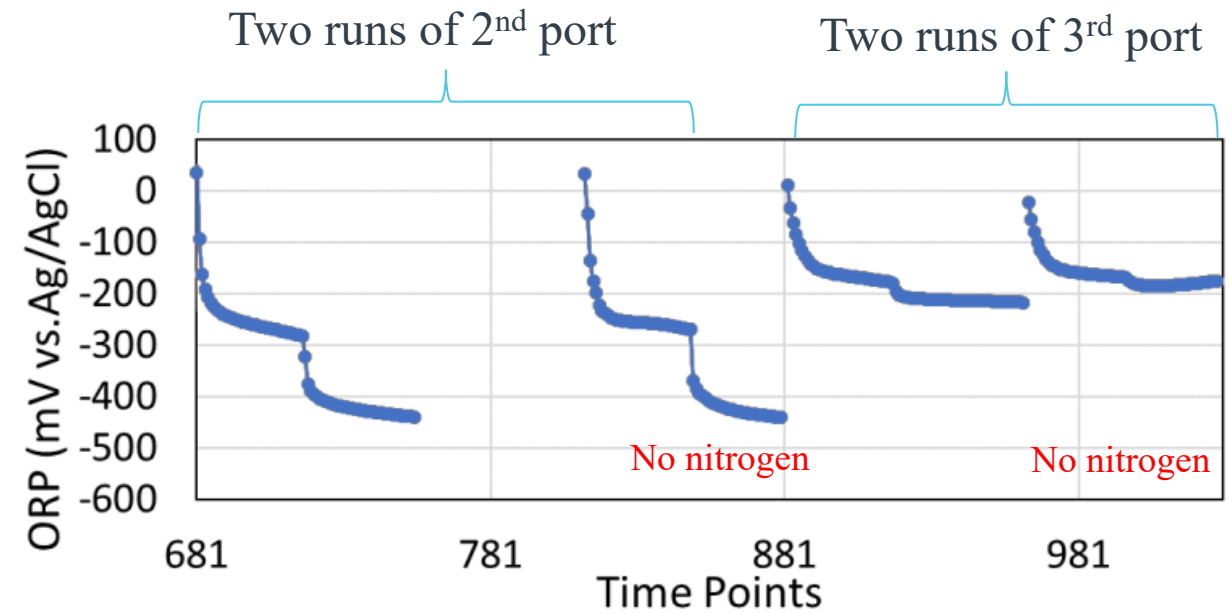
- **SAME** setup as inside glovebox
- Solid in sealed vial under  $N_2$
- $N_2$  headspace sparging
- Continuous data collection



# Measurement Reproducibility

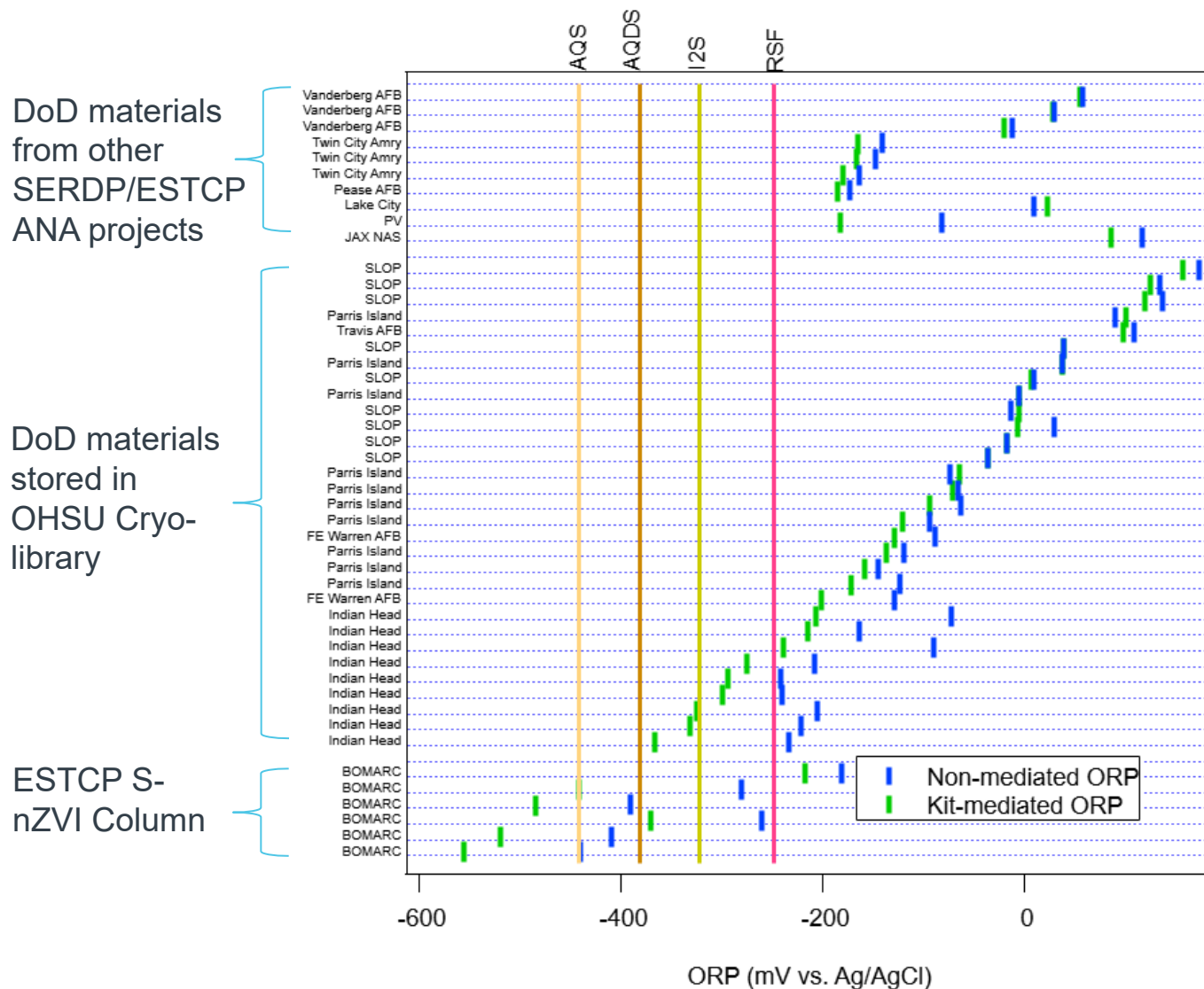


- Excellent reproducibility
- Mixing is needed
- Nitrogen purging is recommended





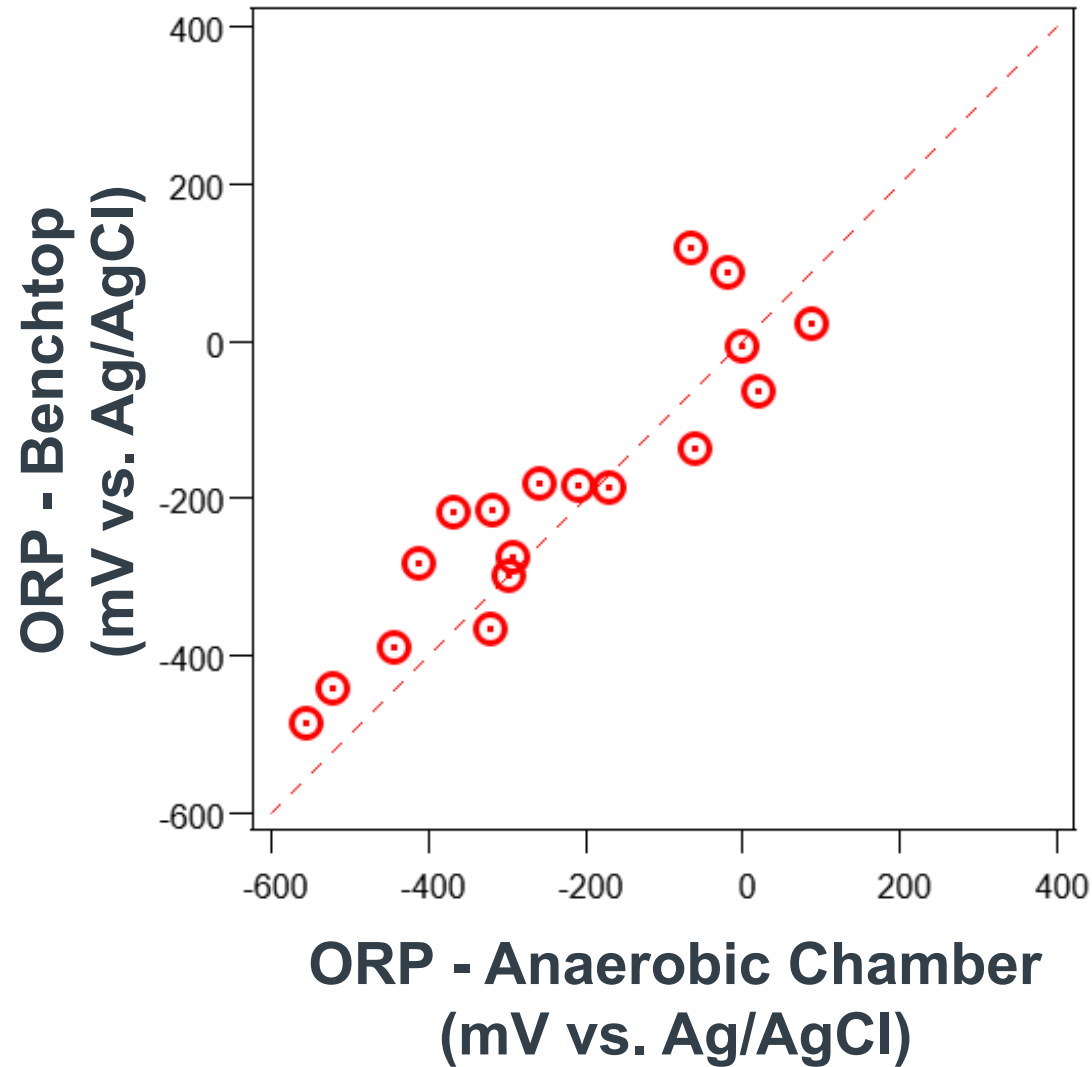
# ORP Kit Validation with DoD Site Materials



- DoD site materials from three sources
- Aged ZVI samples from the field, reactive clays, and min-trap samples
- Mediating effects observed when  $< -100$  mV vs. Ag/AgCl

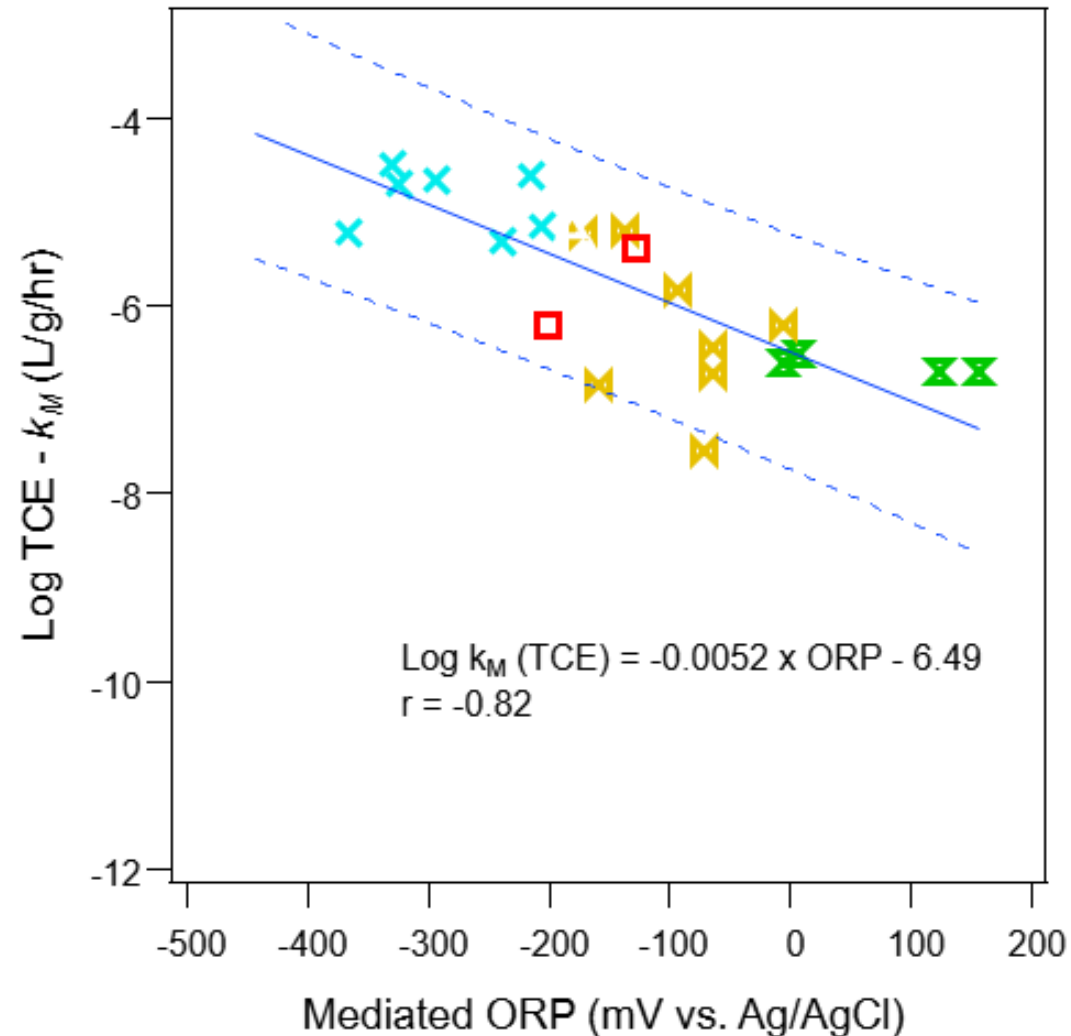


# Similar ORP between benchtop and glovebox



- DoD site materials
- General good agreement between the two
- Benchtop ORP slightly more positive than the anaerobic chamber ORP for most of the samples

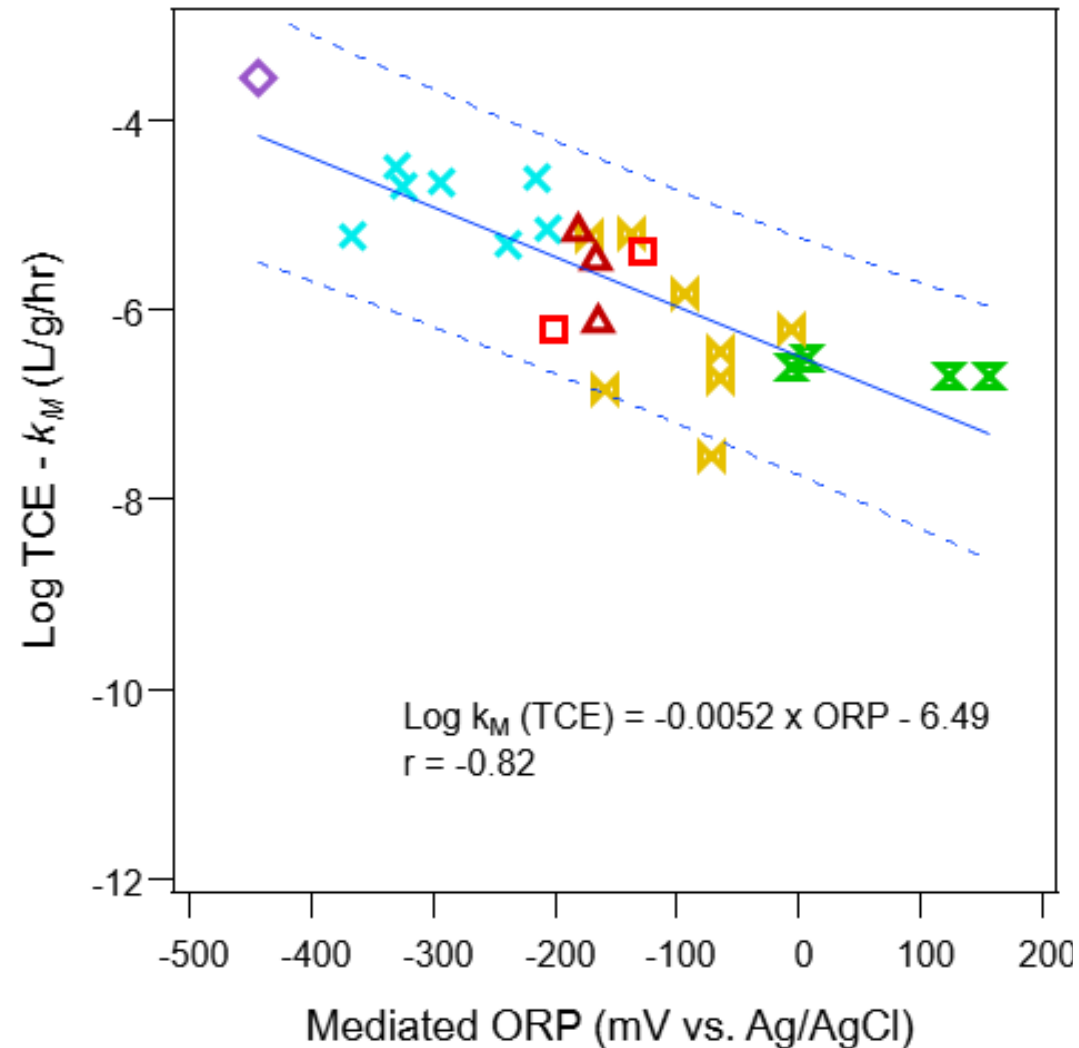
# Correlation with TCE Dechlorination



- 2019 TCE vs. 2023 ORP for OHSU Cryo-library samples observed negative linear correlation



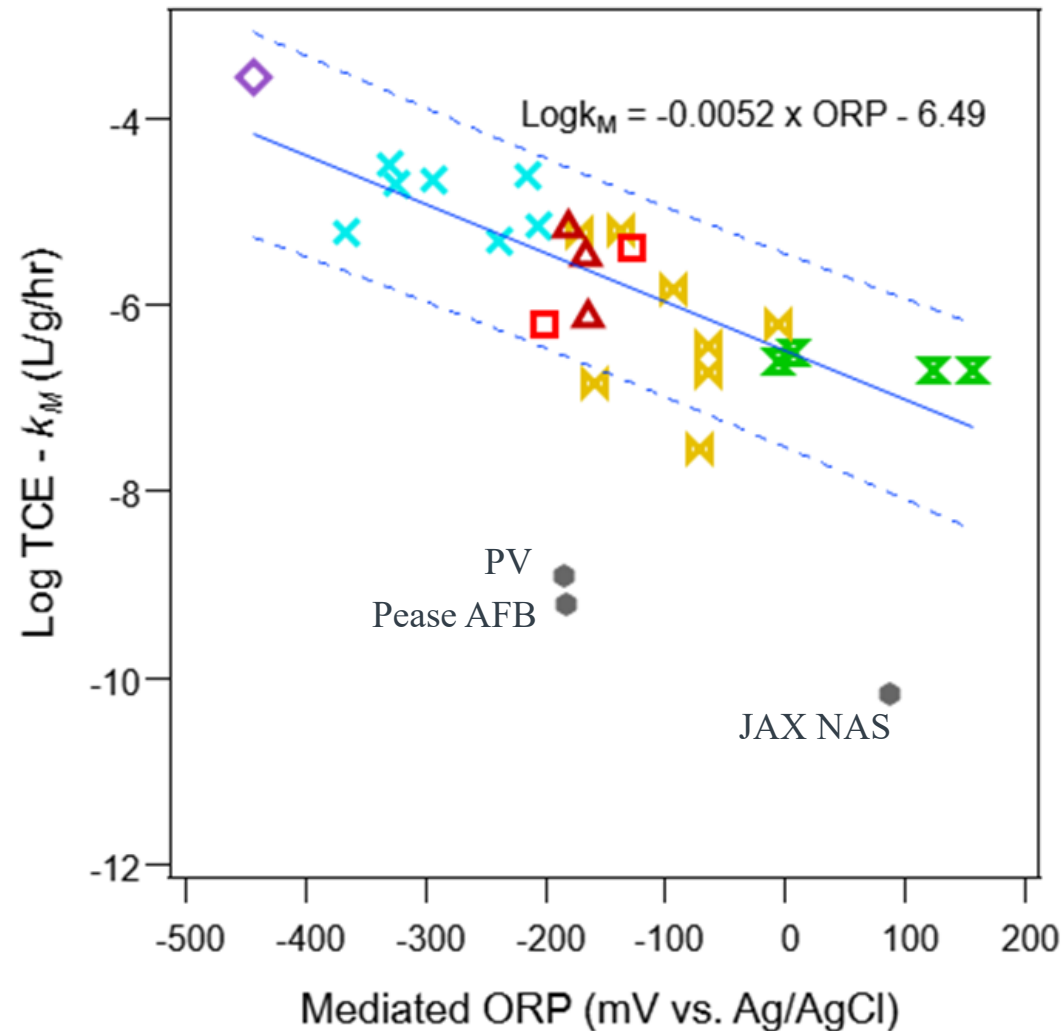
# Correlation with TCE Dechlorination



- 2019 TCE vs. 2023 ORP for OHSU Cryo-library samples observed negative linear correlation
- ESTCP S-ZVI sample and TCCAP sample (Clemson) align with the identified correlation



# Correlation with TCE Dechlorination



- 2019 TCE vs. 2023 ORP for OHSU Cryo-library samples observed negative linear correlation
- ESTCP S-ZVI sample and TCCAP sample (C14 assay) align with the identified correlation
- Outliers seem to follow a similar slope



# Conclusion and Future Work

- Developed and tested a robust and field deployable ORP Kit method
- Mediated ORP as a potentially promising and quantitative indicator for dechlorination kinetics of TCE
- Further refinement to limit  $O_2$  effects and field testing
- Expand our library on ORP-CE degradation rate constants

# Acknowledgements



**ER20-1374**

Field Deployable ORP Kit for Quantitative Assessment of  
Abiotic Monitored Natural Attenuation Rates

## **Other SERDP/ESTCP Colleagues:**

David Freedman, John Wilson, Charlie Werth, Charles  
Schaefer, Craig Divine





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EXCEPTIONAL SOLUTIONS

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