

A Comparative Analysis at Low and High pH Activation of Sodium Persulfate in a Fractured Carbonate Aquifer



- **Jeff Catanzarita**, U.S. EPA, ERT, Edison, NJ,
USA
- **Pamela Tames**, US EPA, Region II
- **Will Caldicott**, ISOTEC Remediation
Technologies, Inc., Newton, MA
- **Ravikumar Srirangam**, PeroxyChem LLC.
Philadelphia, PA

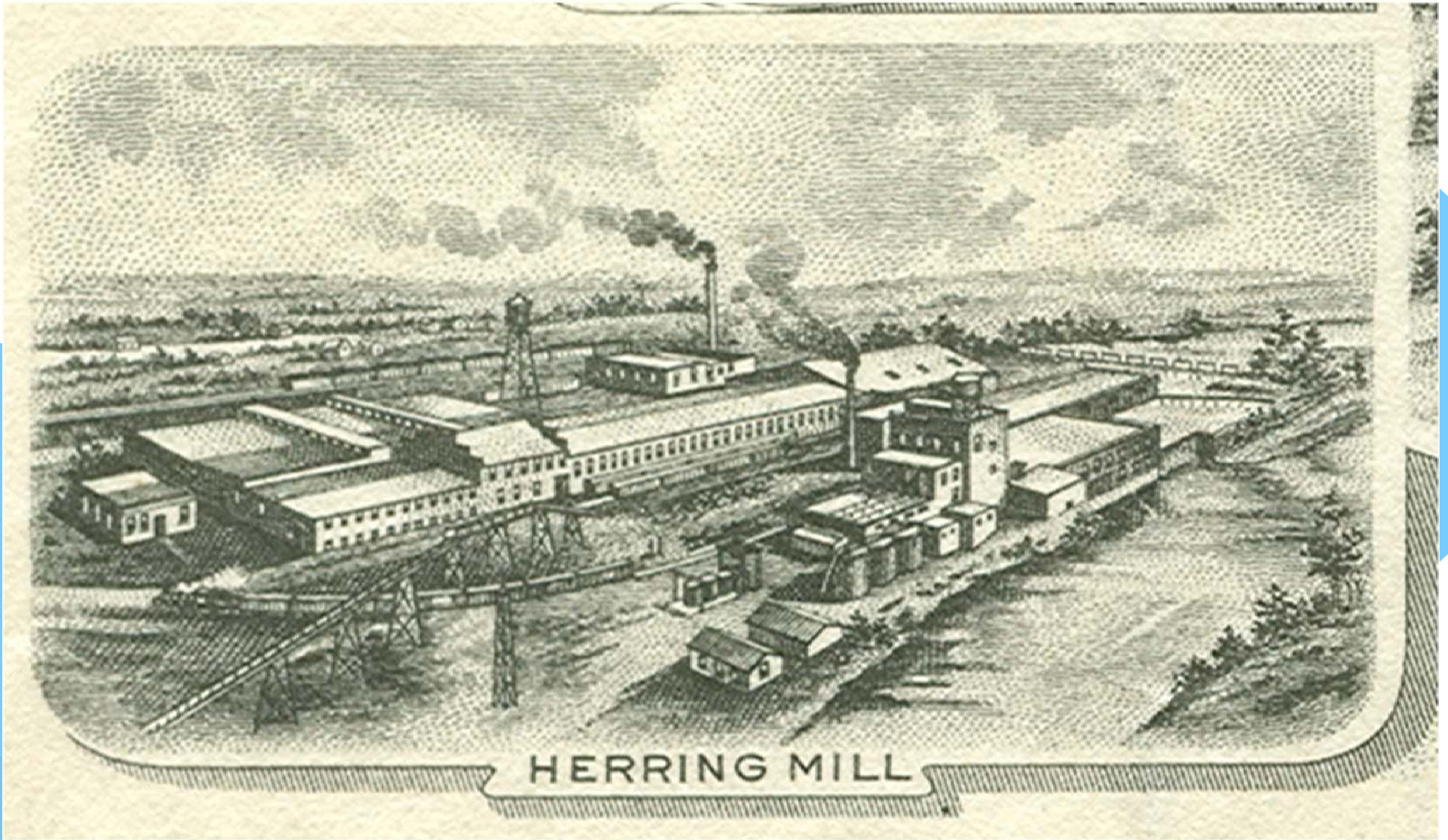


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The Crown Cleaners Site

- Watertown, NY
- 1890's paper Mill
- 1970's textile manufacturing
- 1991 dry cleaning
- Contaminant of concern: Tetrachloroethene (PCE)
- 2012 Record of Decision (ROD)
- Fund lead site
- ROD called for demolition, soil excavation and oxidation of **PCE** in groundwater and fracture rock
- ERT designed demolition, soil excavation and oxidation schemata
- **50-ppb** is GW cleanup target then MNA to 5-ppb MCLs







Scrub/Shrub

Road



Wetland

Developed, Low Intensity

Scrub/Shrub

Scrub/Shrub

Open Water

Wetland

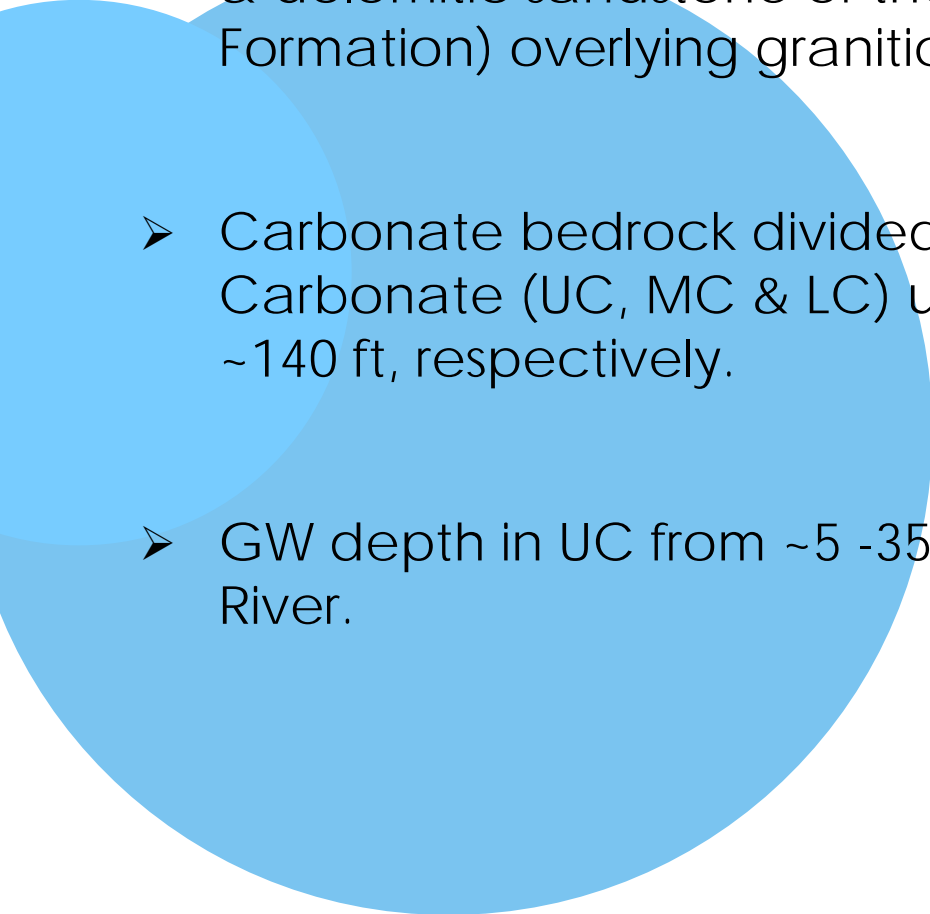

Wetland

Deciduous Forest

Deciduous


SITE HYDROSTRATIGRAPHY

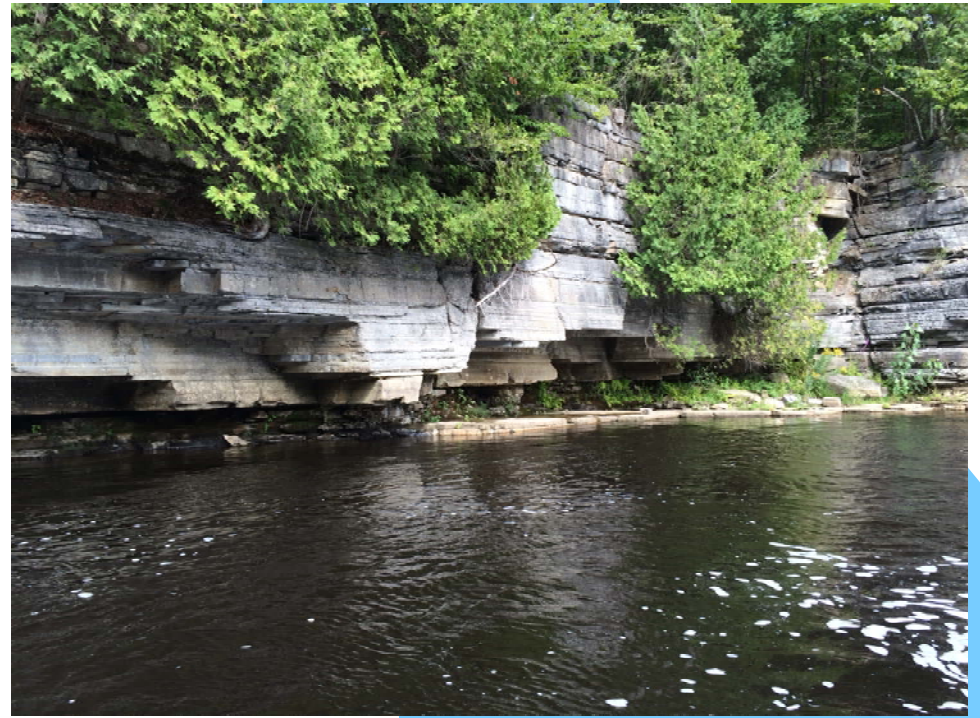


- Glacial till & floodplain deposits (primarily silts & sands) 4 to 5-ft thick in AOC.
 - Bedrock is interbedded & fractured limestone, dolomitic limestone & dolomitic sandstone of the Pamelian Group (Black River Formation) overlying granitic gneiss at ~140 feet bgs.
 - Carbonate bedrock divided into Upper, Middle & Lower Carbonate (UC, MC & LC) units to depths of 50-60 ft, 80-90 ft, and ~140 ft, respectively.
 - GW depth in UC from ~5 -35 ft bgs & GW flow is south towards Black River.
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SITE GEOLOGY



- Substantial geo-physics show predominantly low angle ($<10^\circ$) bedding planes marking changes in lithology, minimal apertures, most frequently dip away from the Black River.
 - Minor near vertical hair line/discontinuous fracture sets striking NW-SE and NE-SW.
 - Consistently no flow or very little vertical groundwater flow (upward) within the carbonate bedrock boreholes.
 - *N.B., bedding plane fractures slightly dip away from the river, but vertical fractures strike toward river.*
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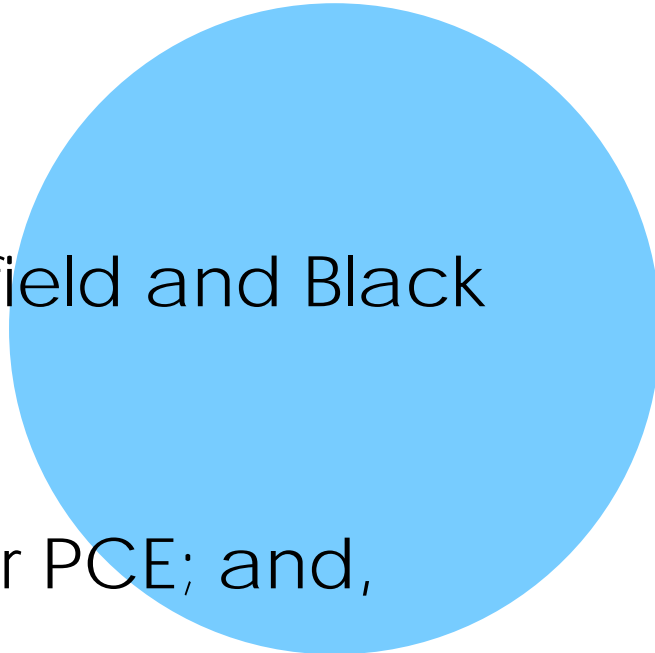
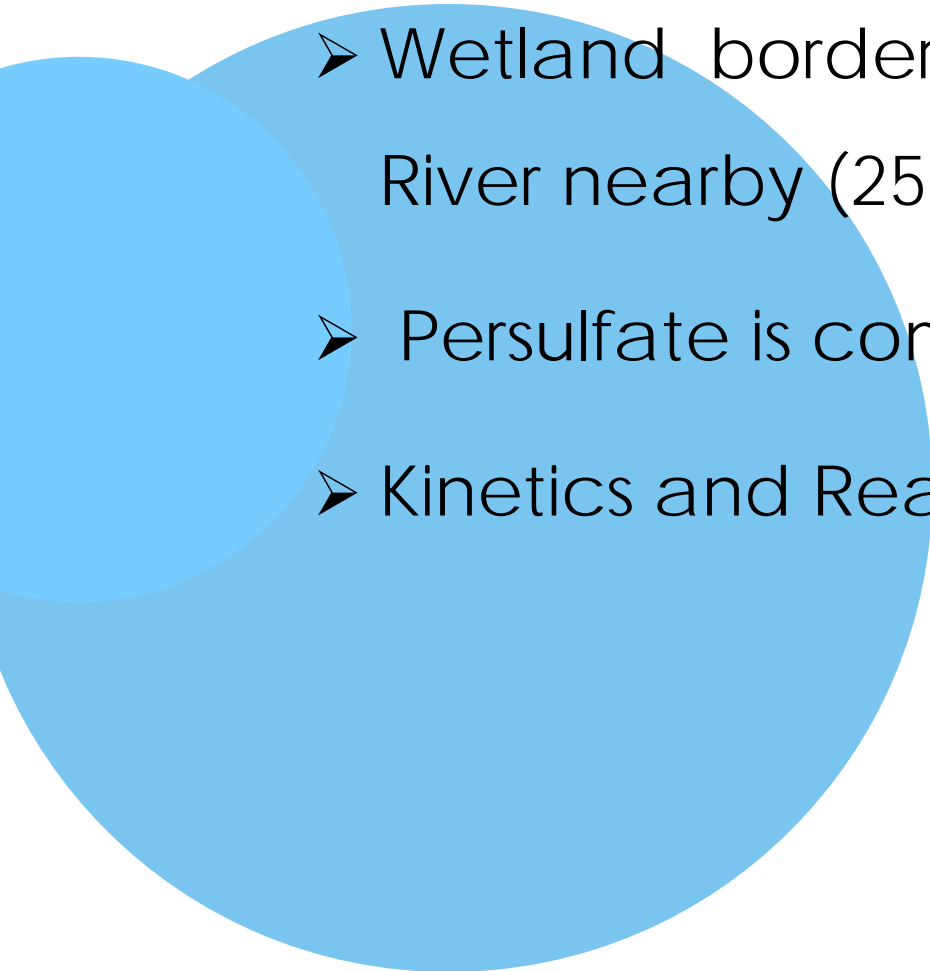

Objectives

- **Objective:** outline two rounds of **Klozur Sodium Persulfate** (Klozur SP) in-situ oxidation injection events (2016 & 2017) utilizing different pH conditions, *i.e.*, low/near-neutral and high/alkaline;
- Alkaline Activated Sodium Persulfate (**SP**) is the oxidant of choice;
- Different theories exist as to PS and the most efficient pH range;
- These (2) rounds of SP oxidation attempt to investigate these theories; and,
- Lessons learned

Oxidant Selection



➤ Why Sodium Persulfate?

- Wetland borders the injection field and Black River nearby (250-ft);
 - Persulfate is commonly used for PCE; and,
 - Kinetics and Reactivity.
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Tetrachloroethene (PCE) Contamination at the Site

- PCE concentrations range from ~ **180-ppm to ND**
 - Only 6 localized wells are highly contaminated
 - Majority of contamination is in shallow MWs
- PCE reductions are evident in some MWs outside AOC
- Recalcitrant or rising PCE/DNAPL concentrations exist within the AOC
- N.B., Solubility of PCE ~200-ppm; **1% rule** 2-ppm potential DNAPL

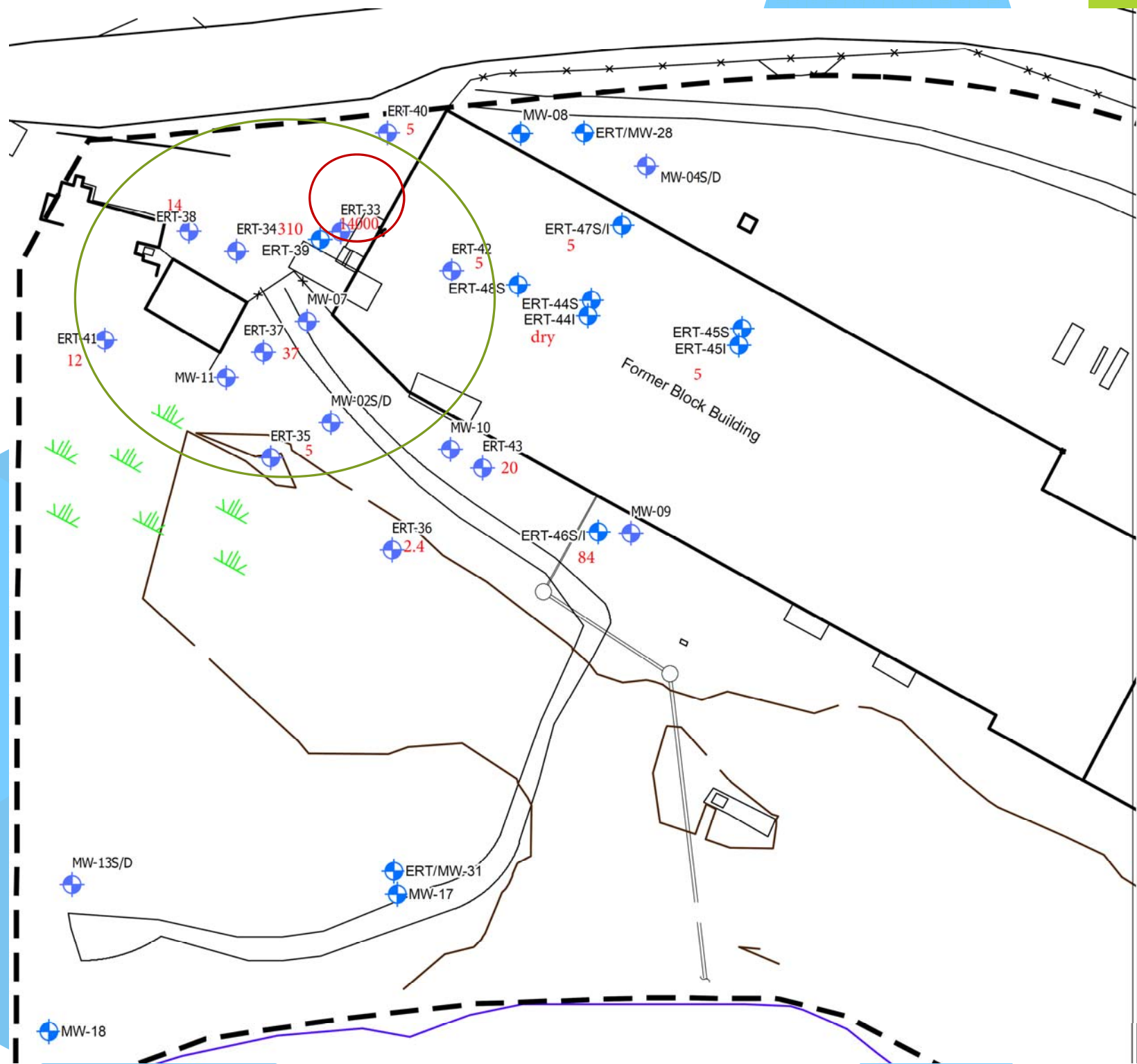
2016

vs.

2017

- The 2016 OX injection utilized PS with a **lower volume of base activator** in rock & overburden
- Molar ratio of base to persulfate used was unknown (vendor proprietary) but assumed to be less than 0.5 to 1
- DPT overburden injection
- Higher Injection rates (typical ~5-10 gpm)
- **23.6K & 9K Gals of 26% PS** in rock and overburden
- Significant daylighting
- Lower pH typically in the near-neutral range post-one month
- ERT-33s increased in PCE

- The 2017 OX injection utilized PS with a **higher volume of base activator** & Modified Fenton's Reagent (MFR) in overburden
- Molar ratio of base to persulfate used was approximately 2:1 following performance of a base buffering capacity test and standard industry practice
- DPT overburden injection *n.b., MFR*
- More pumps & lower injection rates (typical ~0.5-1.5 gpm)
- **23K Gals of 26% PerS** in Rock and **3K Gals of 10% H-Peroxide** & **1.8K Gals of iron catalyst** in overburden
- Less daylighting
- Higher pH typically in the alkaline range post-one month
- GW PCE concentrations increased in ERT-33s



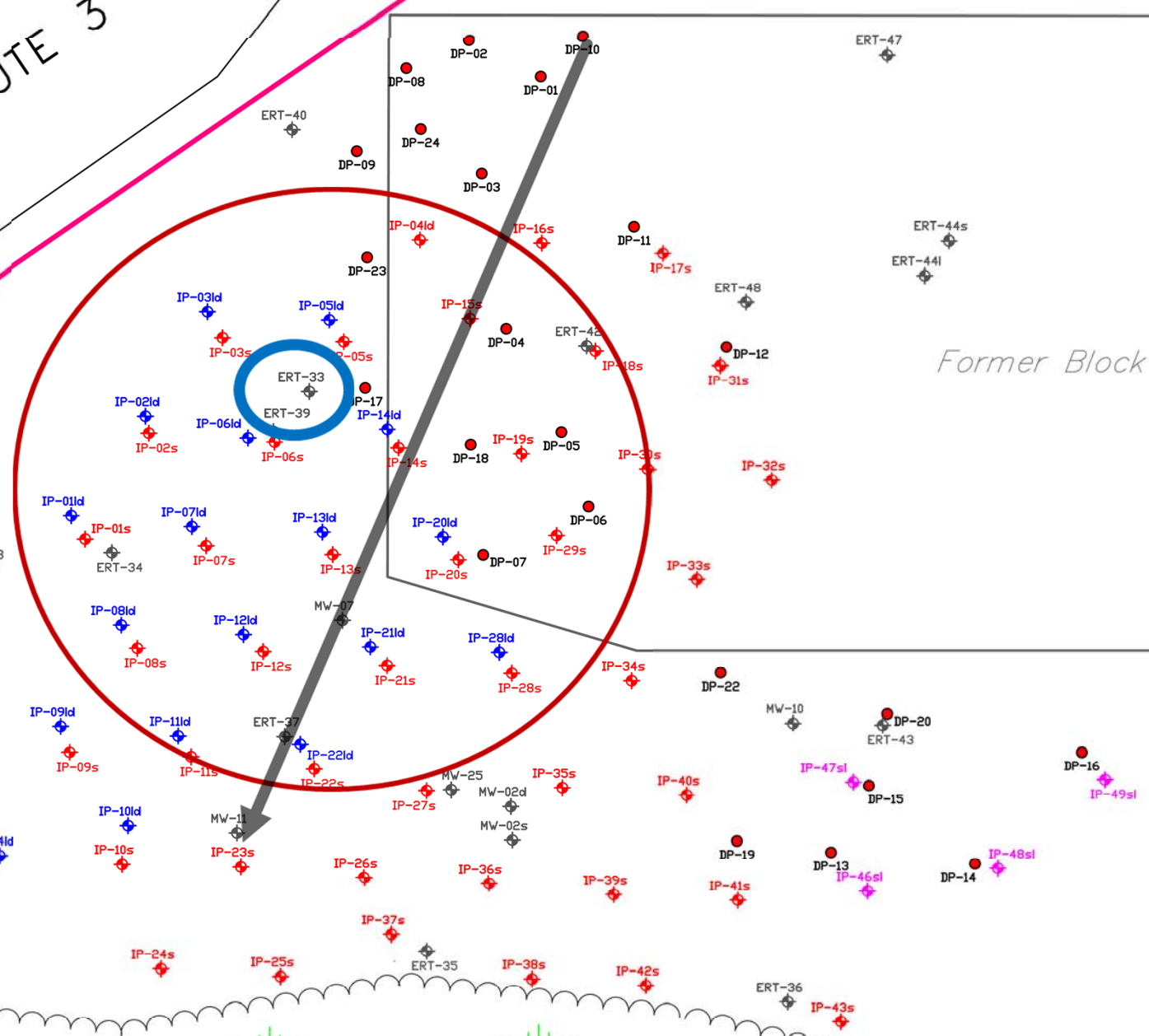
Construction of the Injection Well field

- (4) air hammer drill rigs installed (66) Injection Wells(IWs) within three weeks:
 - **(43)** 30-ft bgs, 2-in dia, 20-ft screens
 - **(19)** nested 2-in, dia, 20-ft screens (@ 55 & 75-ft bgs)
 - **(4)** nested 2-in, dia, 20-ft screens (@ 30 & 55-ft bgs)
- The injection field already maintained sufficient MWs to evaluate injection.

Injection Well Field

NY STATE ROUTE 3

MW-04d
MW-04s
DP-21

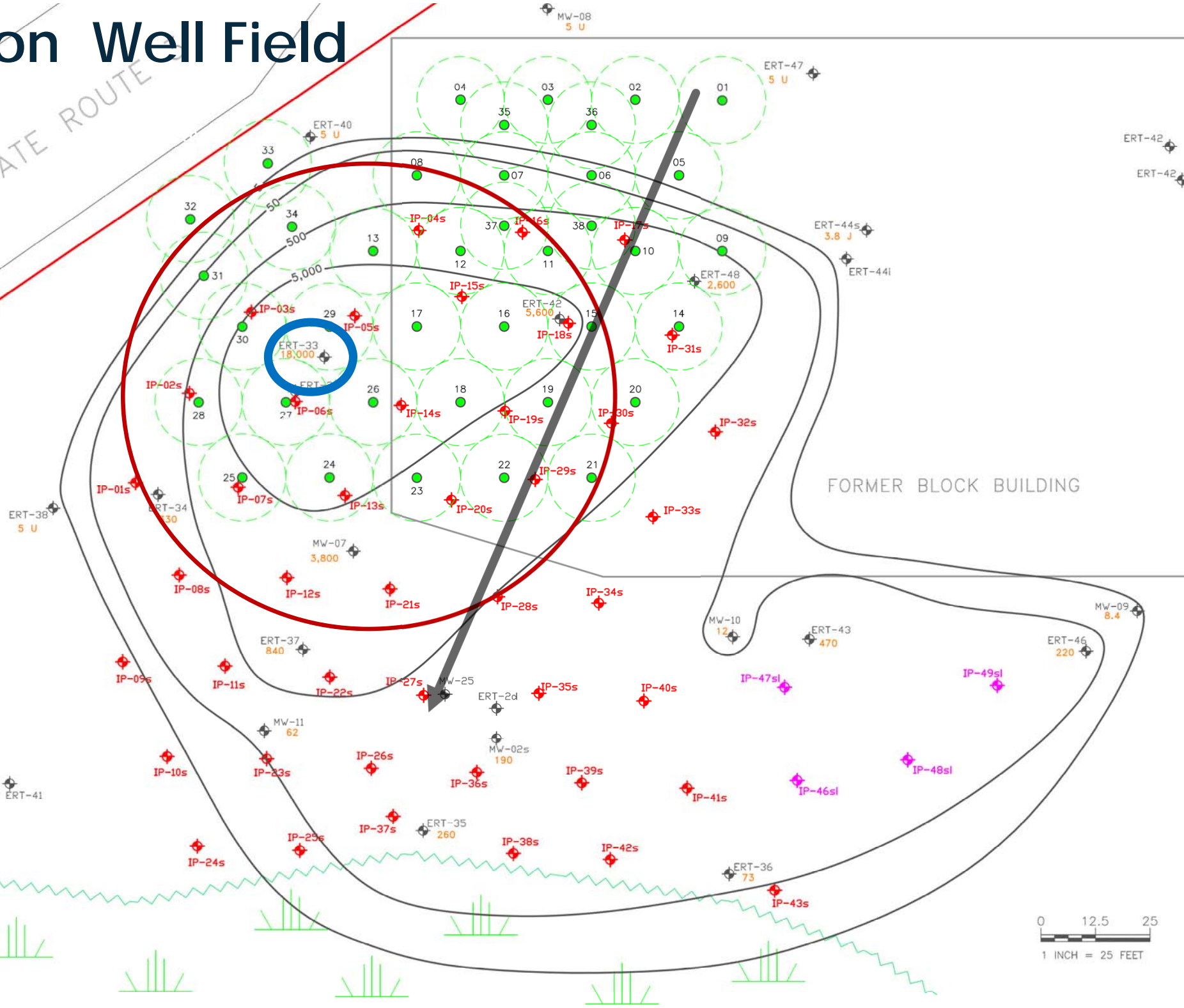


Former Block



Injection Well Field

NY STATE ROUTE



FORMER BLOCK BUILDING



Sampling & Analytical Methods

➤ Sampling

➤ Passive Diffusion Sampler Bags (PDB's)

- PDBs seemingly do not allow SP to cross membrane (further study)

➤ Purged wells with pumps

➤ Analytical (VOCs, Metals, Persulfate, MNA)

➤ Fixed Lab GCMS VOC

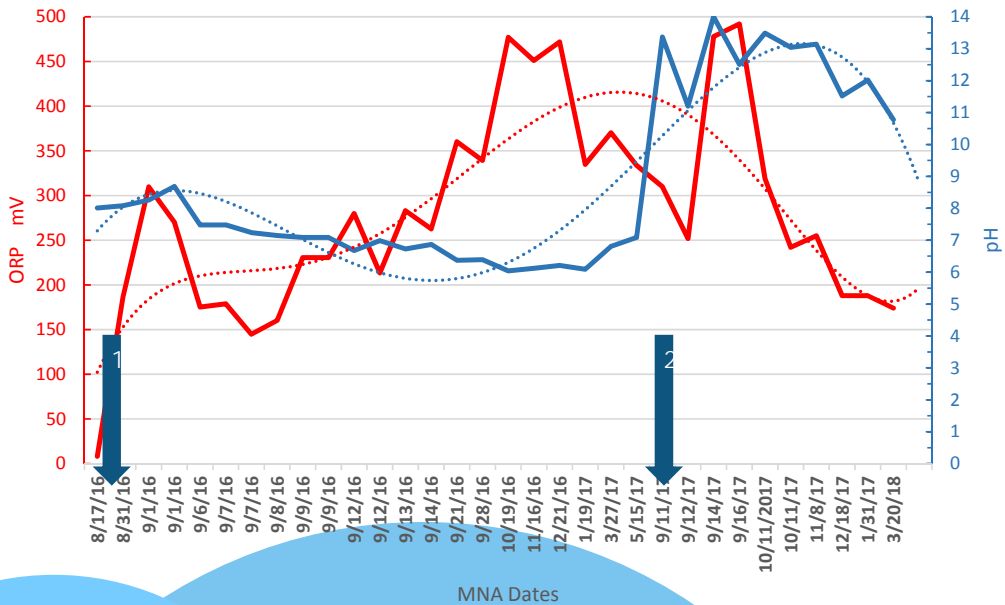
➤ Field test Kit for PS: **CHEMetrics Method 7870**

➤ Both YSI and field MNA instruments

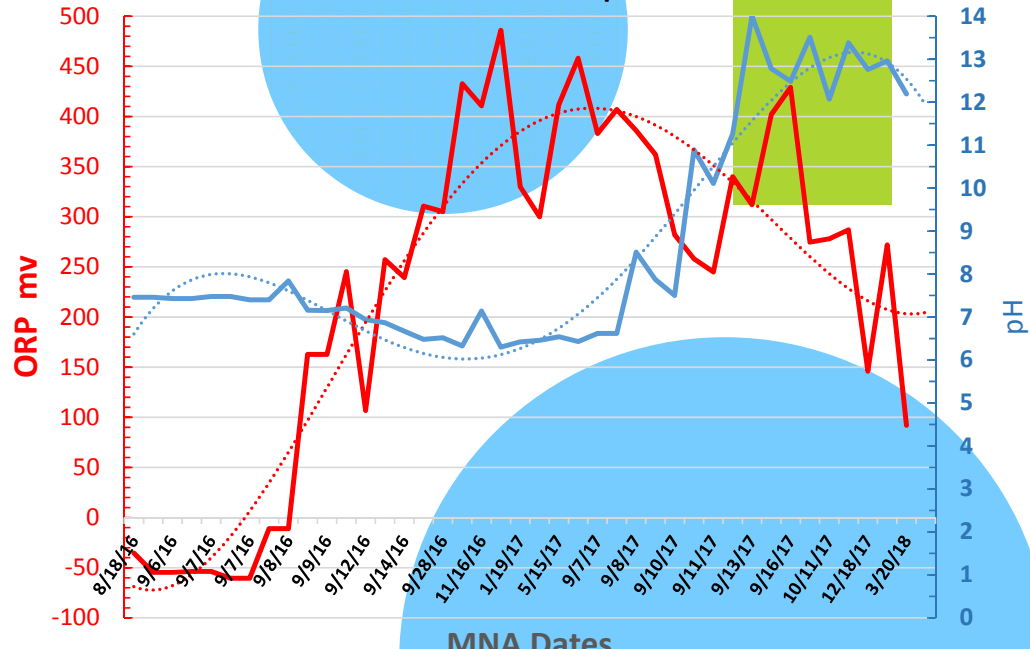
➤ VOC field instrument: **AQR Color-Tec---CVOCs**



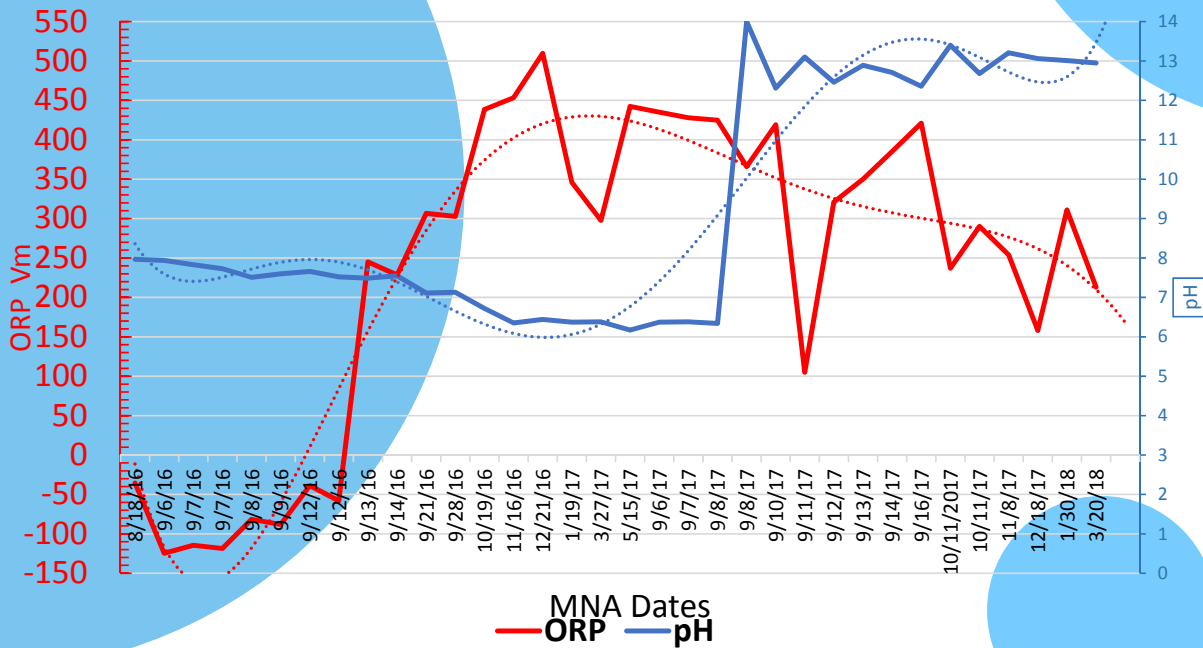
ERT-33s ORP & pH



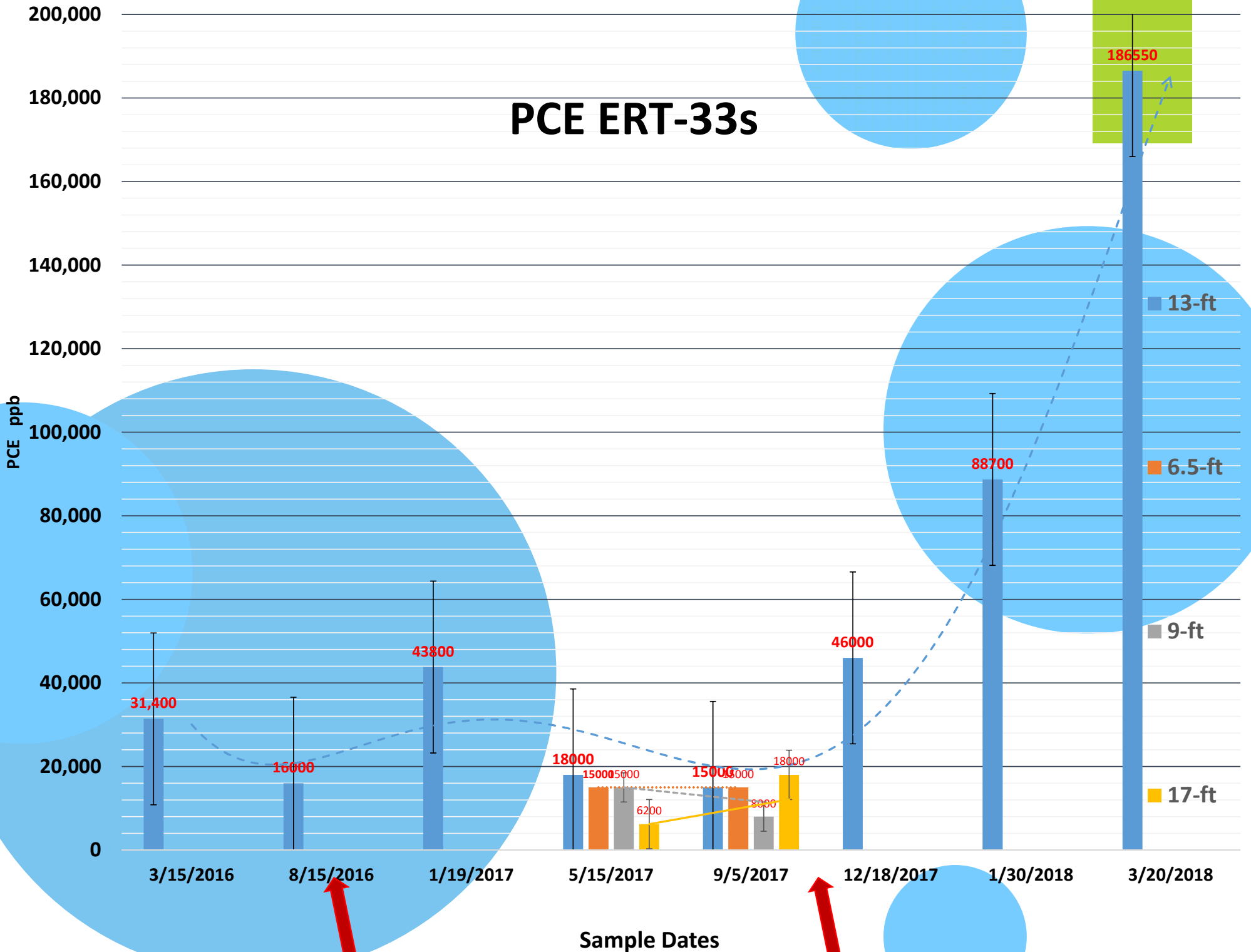
ERT-33i ORP & pH



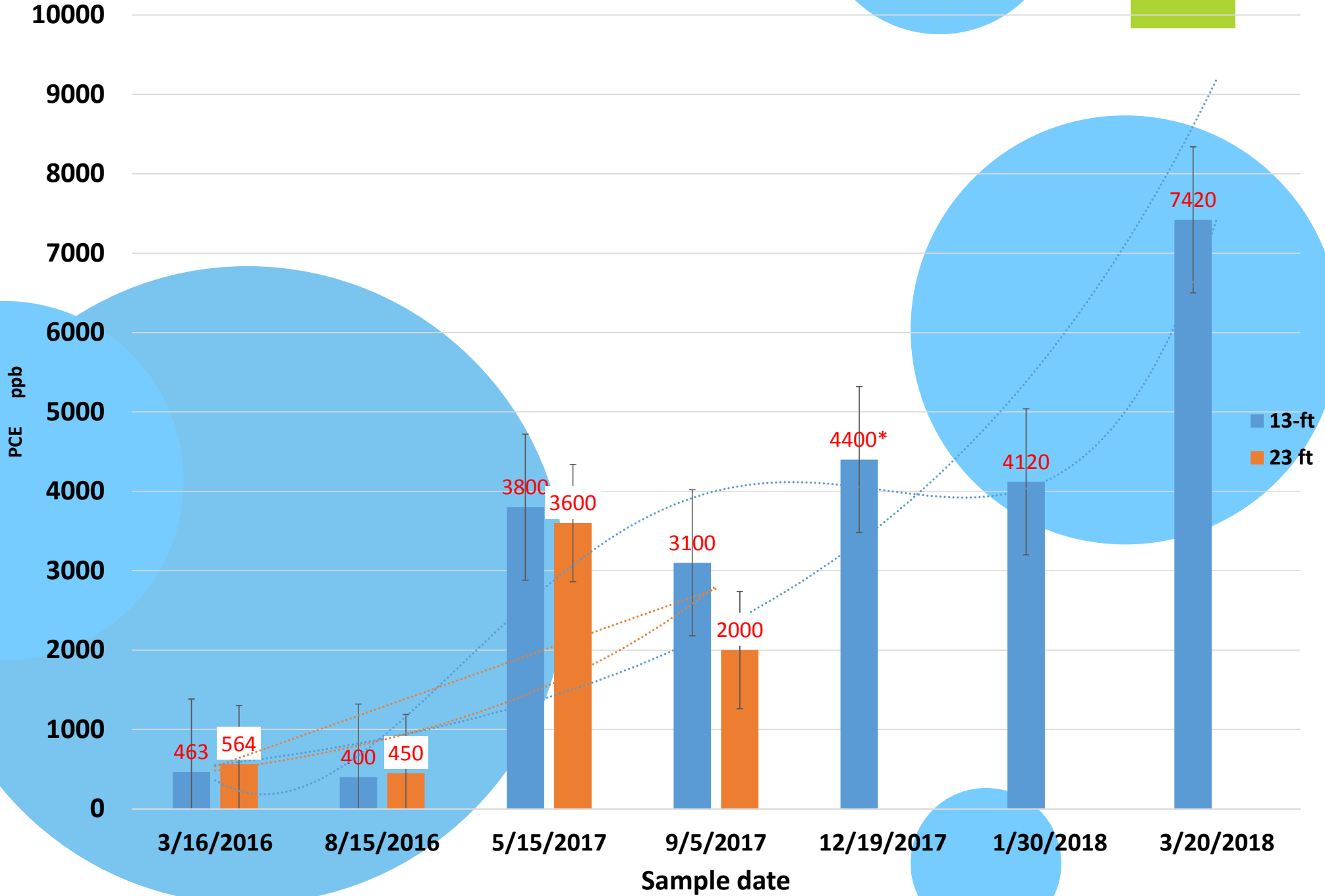
ERT-33d ORP & pH



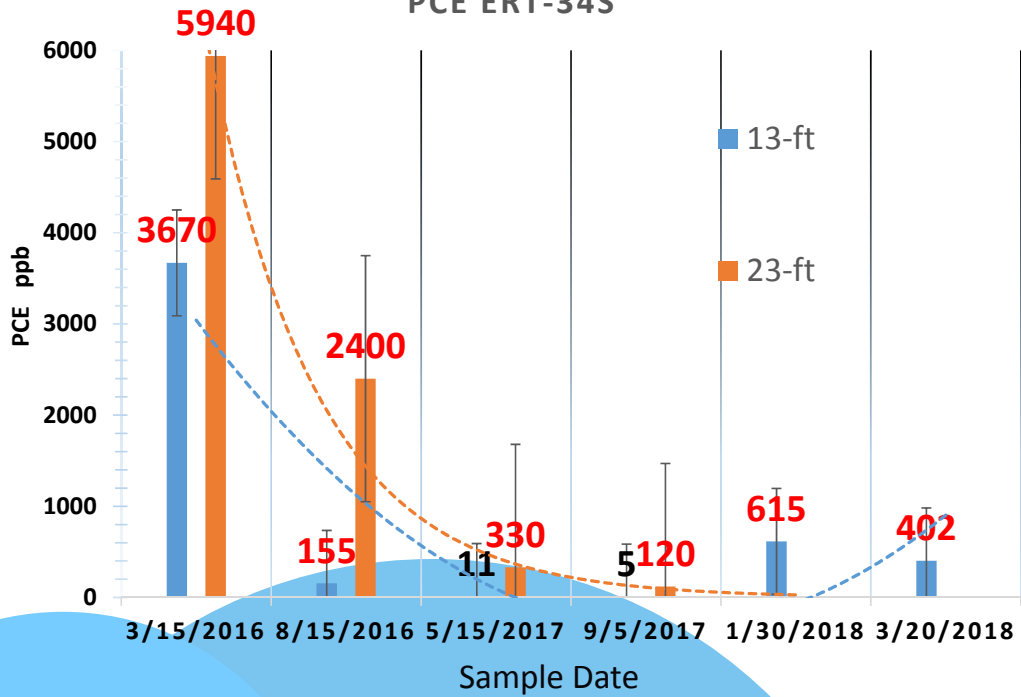
PCE ERT-33s



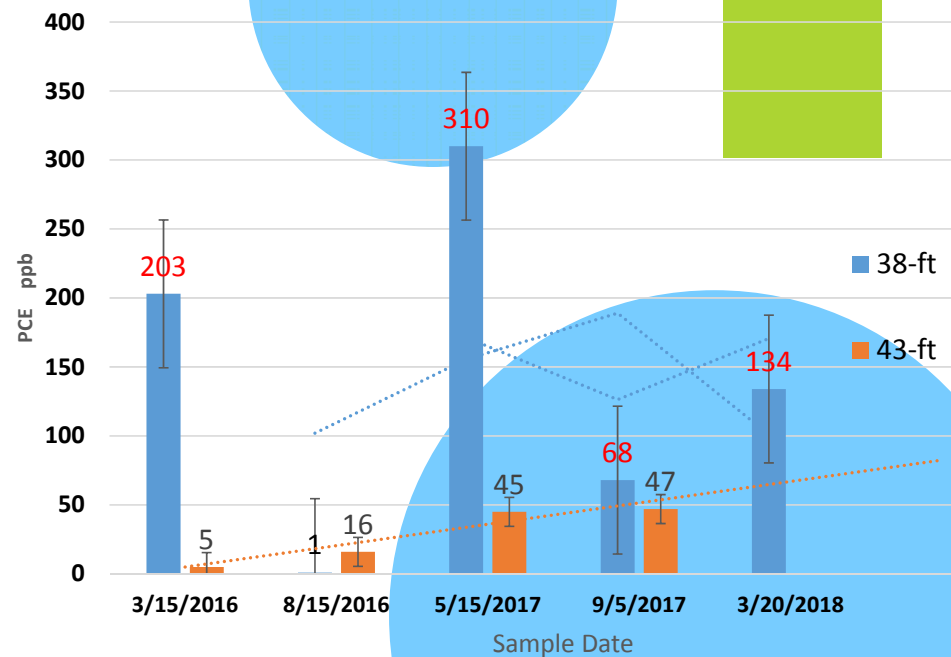
MW-07 13' & 23'



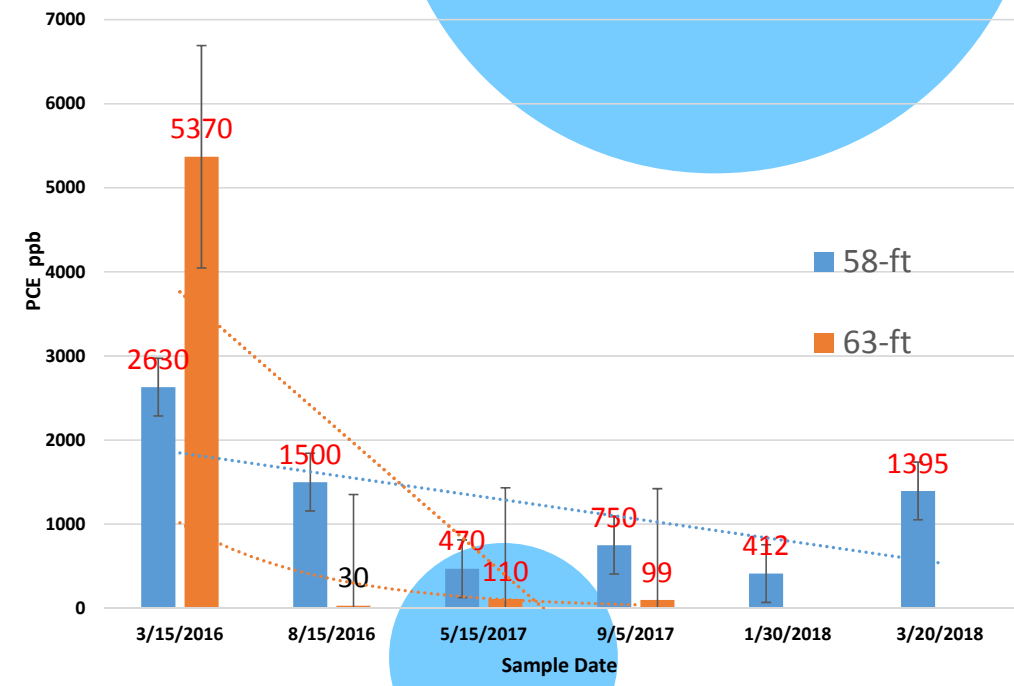
PCE ERT-34S



ERT-34i 38-ft & 43-ft



ERT-34d 58-ft & 63-ft



Findings

- pH increased in second round;
- Since mass was not added, the second injection must have mobilized much more PCE probably due to MFR and pH;
- Lower pumping rates caused less daylighting;
- SP concentrations increased in second round;
- Some PCE reductions occurred outside DNAPL area
- PCE in MWs within DNAPL area increased likely due to DNAPL globule breakdown and dissolution;
- Metals did not significantly increase;
- Chloride data provided no insight
- Could not determine the effect of different pH
- **PCE mass in the 2nd injection is likely due to DNAPL globule breakdown, dissolution phase change enhanced by increased superoxide radical production via higher pH**

Future Actions



- Increase injection well density in DNAPL area;
 - Design injection wells to limit daylighting without blocking Ox to shallow fractures **OR** packer inject;
 - Inject Fenton's into rock to more aggressively address DNAPL; and,
 - Follow up injection with more Sodium Persulfate (possible potassium persulfate) for residual PCE.
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