F-031, in K.A. Fields and G.B. Wickramanayake (Chairs), *Remediation of Chlorinated and Recalcitrant Compounds—2010.* Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2010). ISBN 978-0-9819730-2-9, Battelle Memorial Institute, Columbus, OH, **www.battelle.org/chlorcon**.

Buffering Acidic Aquifers with Soluble Buffer to Promote Reductive Dechlorination

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For many acidic aquifers, pH buffering will be required to bring the pH into a range of 6 to 8, which is favorable for reductive dechlorination. Various pH adjustment agents have been used including soluble materials like sodium or potassium bicarbonate, sodium carbonate, sodium hydroxide, calcium hydroxide (slaked lime) or less soluble materials like calcium carbonate, magnesium oxide, dolomitic hydrated lime, and limestone. Bicarbonates have the lowest pH for saturated solutions of these buffers, but also have the least buffering capacity and the potential for carbon dioxide production. Calcium carbonate or limestone is practically insoluble, but has an equilibrium pH of 9.4. The other soluble reagents including sodium hydroxide, sodium carbonate, and calcium hydroxide have higher pH equilibrium levels and could therefore overshoot the desired pH range. The less soluble buffers are more difficult to deliver and generally have high equilibrium pHs.

A treatability study was conducted for a site where chlorinated solvents and acids were co-disposed. leading to acidic pH levels of 4.0 in the groundwater and 3.4 in the 50 g soil and 100 mL distilled water. Titrations to pH 8.0 were conducted with selected reagents for both soil and groundwater which lead to the following estimated quantities (kg) of the buffers per cubic meter of aquifer assuming 25% porosity: 8.2 sodium hydroxide, 9.2 dolomitic lime, 10 hydrated limestone, 63 magnesium oxide, 153 sodium bicarbonate, 2,281 calcium carbonate, and >3,806 pounds for pulverized limestone. The sodium hydroxide, dolomitic lime, and hydrated limestone, were possible reagents, but the requirements for magnesium oxide, sodium bicarbonate, and either of the limestone products were too high to be practical.

At a New Jersey site with somewhat less acidic groundwater (pH 4.8) and soil (pH 4.2 to 5.0 for 10 g soil in 50 mL distilled water), the buffer requirements to reach pH 8.0 were correspondingly less, ranging from 0.8 kg per cubic meter aquifer (30% porosity) for sodium carbonate to 8.2 kg/m^3 for sodium bicarbonate to 10 kg per cubic meter for calcium carbonate. Sodium carbonate was chosen as the buffering agent. A small field pilot demonstrated that the 68 kg pounds of sodium carbonate in 11,300 L groundwater could be used to raise the pH of the injection well above 6.0 with increased pH levels up to 6.1 m away after 2.5 months.

Full scale injections of 18,450 kg of emulsified vegetable oil (EVO), 4,000 kg sodium carbonate buffer, and 500,000 L groundwater were injected into 44 injection wells within the 55 x 117 x 7.6 m treatment zone. The pH of injection wells increased to >6.0 in all but one injection well after two months. Insufficient chase water was injected with the EVO and sodium carbonate to reach the 22 extraction wells. Additional EVO and sodium carbonate were later injected into the extraction wells.

By injecting a soluble pH buffer with the dilution/chase water, the quantity of buffer can be targeted to meet the buffer demands for the aquifer.

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Overview

- Introduction
- Site Description
- pH Buffering Study
- Pilots
- Full Scale EVO Application, pH Adjustment, and Bioaugmentation
- Results
- Conclusions

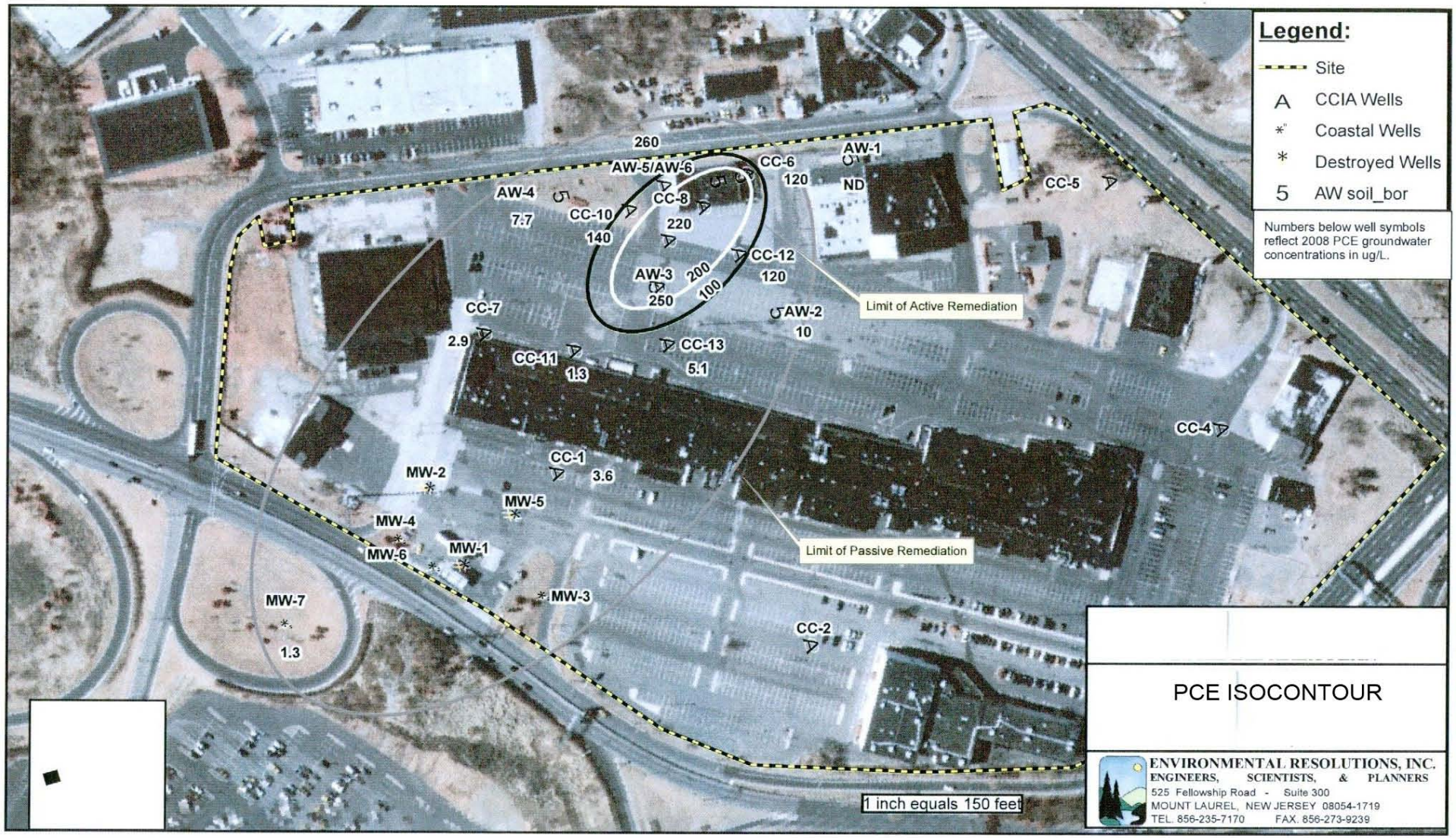
Reductive Dechlorination
Requirements

- Presence of microbial populations (i.e. *Dehalococcoides*) capable of complete dechlorination
- Availability of substrate and nutrients and control of electron acceptors
- Favorable environmental conditions
  - A pH between 6.0 and 8.5 is critical for complete dechlorination

Site Overview

- Brownfield site in Southern New Jersey
- Former Dry Cleaner source of PCE (maximum of 420 μg/L) and CT (maximum of 19 μg/L) with minor daughter products
- High contamination area (>100 μg/L PCE) approximately 183 x 383 x 25 ft
- 60 feet to groundwater table
- Groundwater aerobic
- Aquifer fine to medium sand and silt
- pH 3.9 to 5.3
- No detectable *Dehalococcoides*

PCE Isocontour



pH Buffering Study

Reagent	Sodium Bicarbonate	Calcium Carbonate	Sodium Carbonate
Formula	$NaHCO_3$	$CaCO_3$	Na_2CO_3
Water Solubility (g/L)	91	practically insoluble	33.2
pH Saturated Solution	8.6	9.4	11.4
g to adjust 1 L gw to pH 8.0	0.5	7.5	0.325
g to adjust 1 kg soil to pH 8.0	5.0	5.0	0.43
Lb/ft^3 aquifer with 30% porosity*	0.51	0.64	0.049
Cost ($/lb)	0.27	0.30	0.29

based upon a cubic foot of aquifer with a density of 100 lb/ft^3 (1602 kg/m^3) and a porosity of 0.30 or 8.5 L (2.2 gallons) groundwater per cubic foot of aquifer

Pilot

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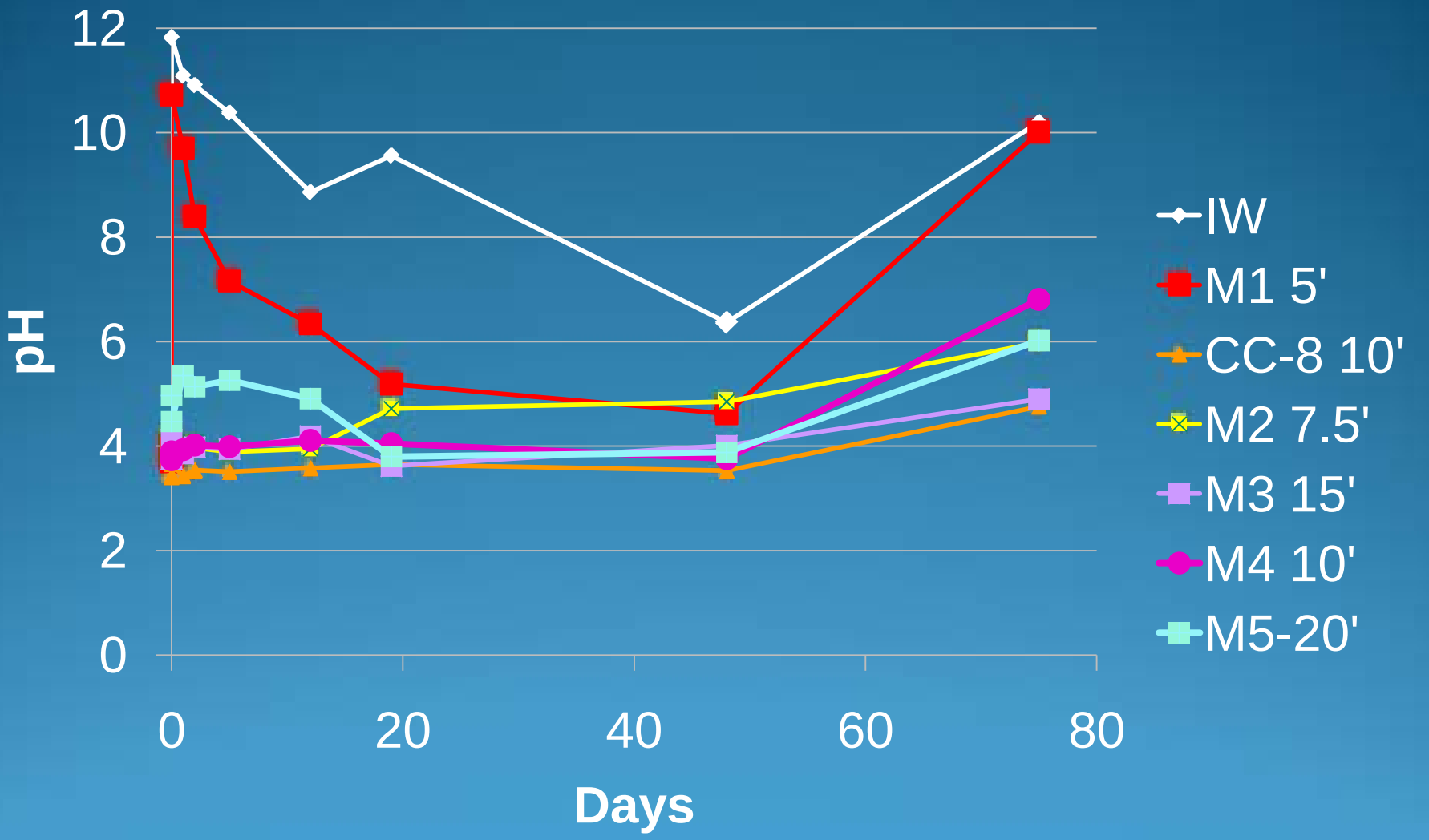
Pilot

- 165 gallons of EVO (SRS) and 330 gallons of water into IW
- Chase with 3,000 gallons water with 150 pounds of sodium carbonate
- Increases in the groundwater head during injection were noted in M1, M2, CC8, M4, M3, and M5 up to 20 feet away

Pilot pH



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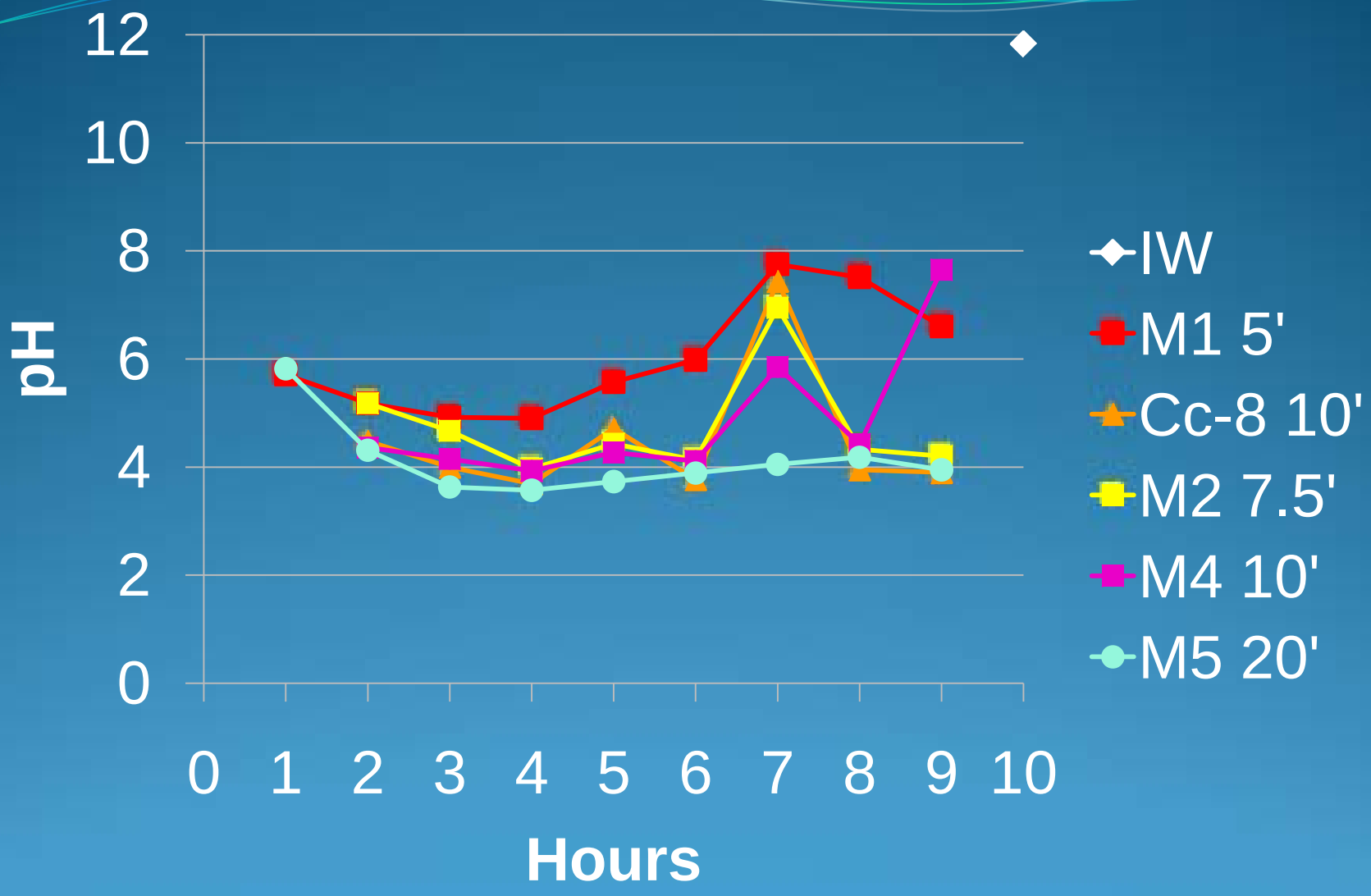
Push (IW) Pull (M5) Test

- Inject 150 pounds sodium carbonate in 200 gallons of groundwater at about 1-2 gallons per minute
- Groundwater recirculated from M5 to IW1 at about 5 to 7 gallons per minute for 8 hours
- Monitored field parameters and depth to water in wells IW, M1 (5’), M2 (7.5’), M4 (10’), and M5 (20’) for 9 hours
- Head increase ranged from 2.1 ft in M1 5 feet away to 0.5 ft in CC-8 and 0.3 ft in M4

Push Pull pH Results



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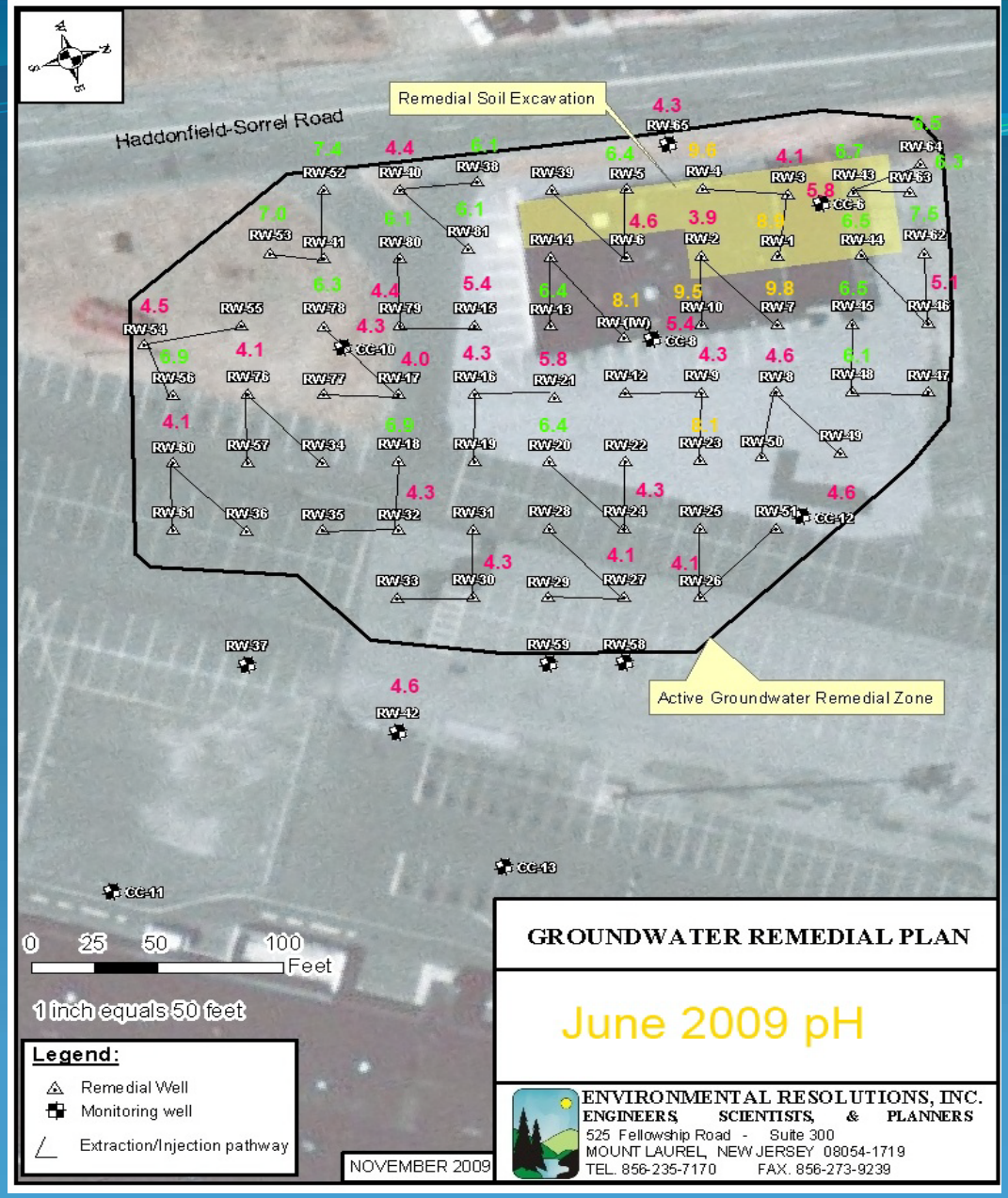
SRS and Sodium Carbonate Injections

- 40,600 pounds of EVO (SRS™)
- 8,800 pounds sodium carbonate buffer
- About 290,000 gallons chase water (about 0.1 pore volume) throughout the 183 x 383 treatment area into 44 injection wells and 22 extraction wells screened 60 to 85’



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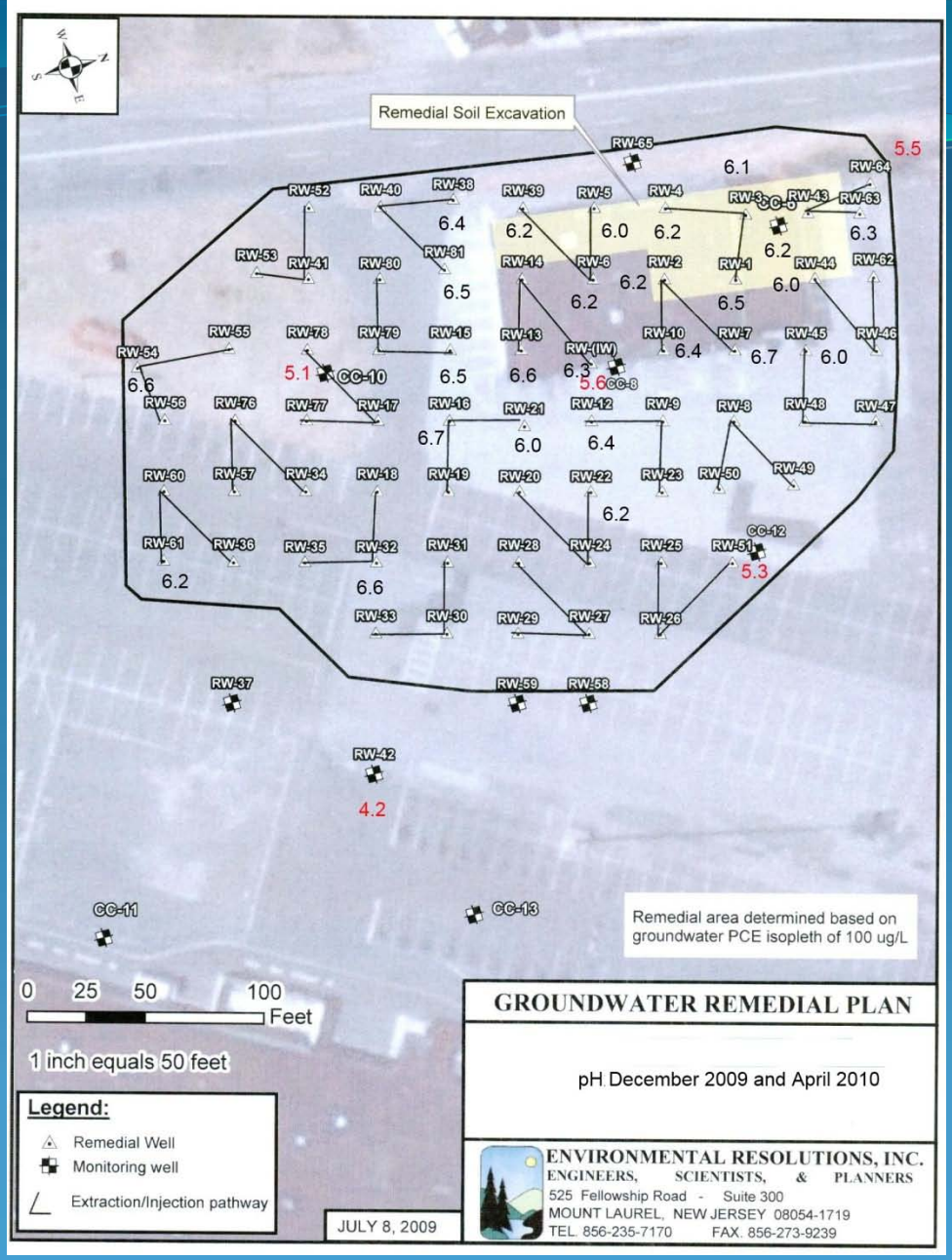
SRS and Buffer Injection Into Extraction Wells and Bioaugmentation

- Inject 6,480 pounds of SRS™, 1,100 pounds of sodium carbonate, and 32,600 gallons groundwater into 22 former extraction wells
- Bioaugment 44 former injection wells with 168 L TSI-DC, 220 pounds of sodium bicarbonate, 100 pounds sodium sulfite, and 12,000 gallons of SRS-amended groundwater



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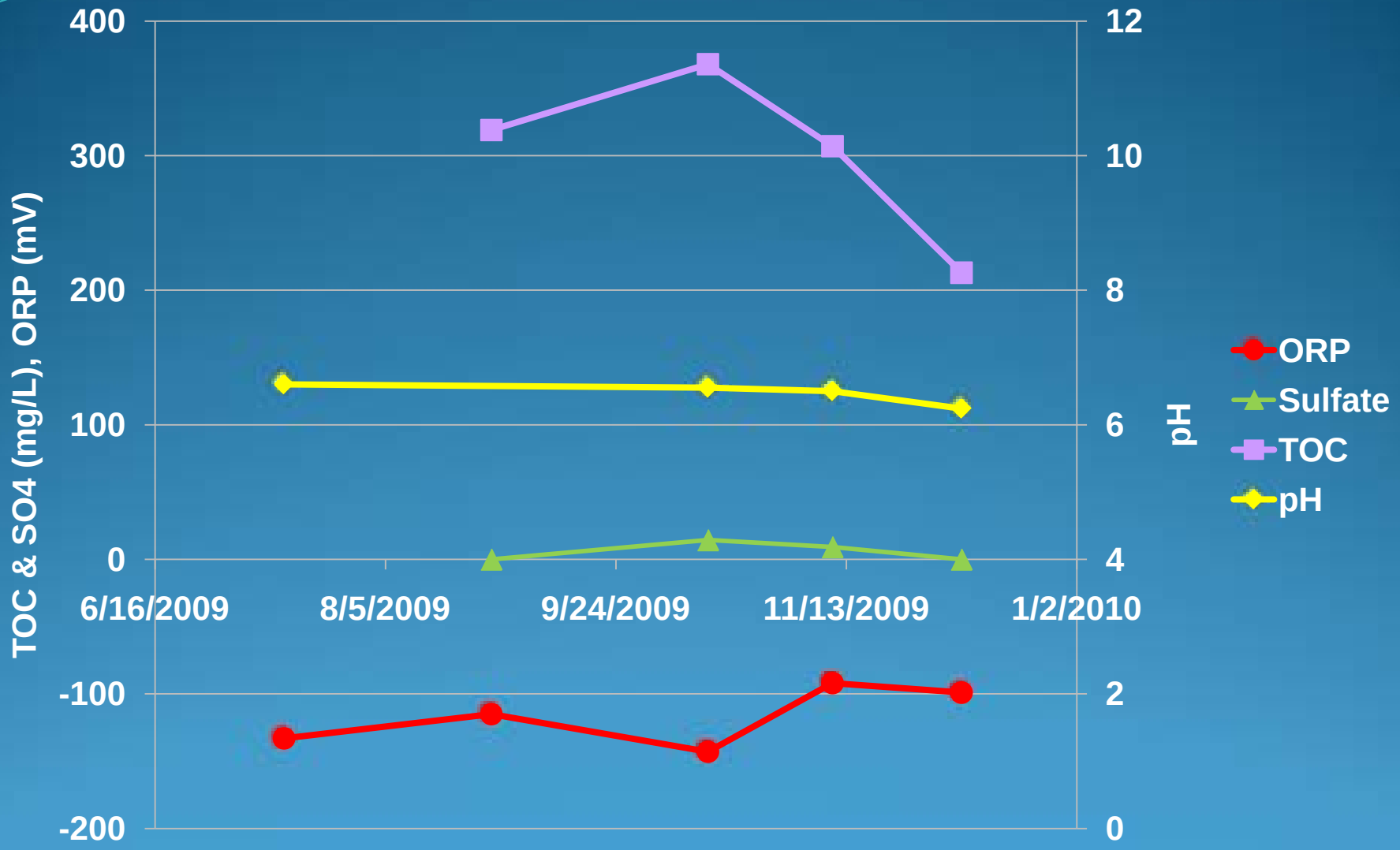
RW-22 pH, ORP, TOC, & Sulfate



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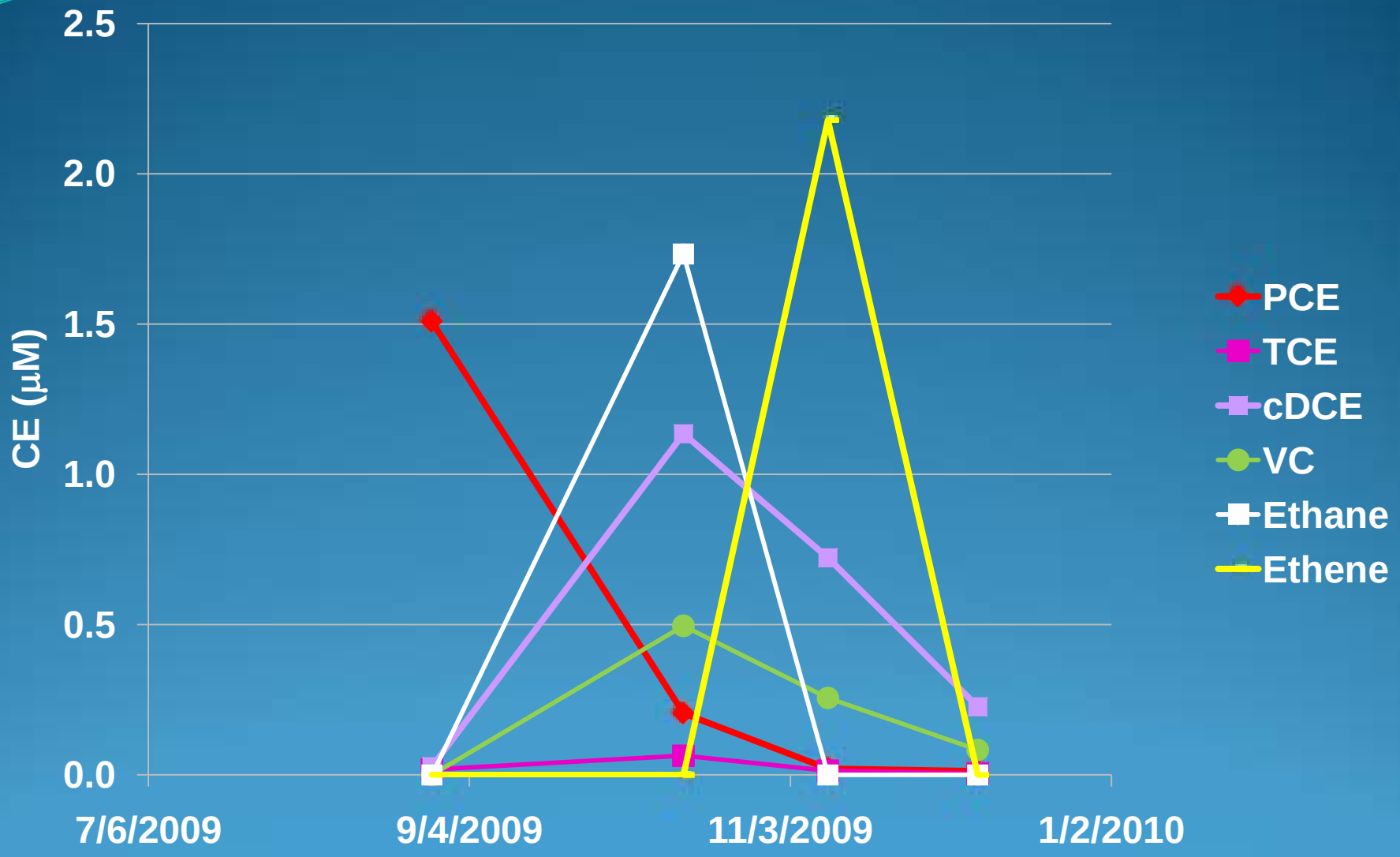
RW-22 CE



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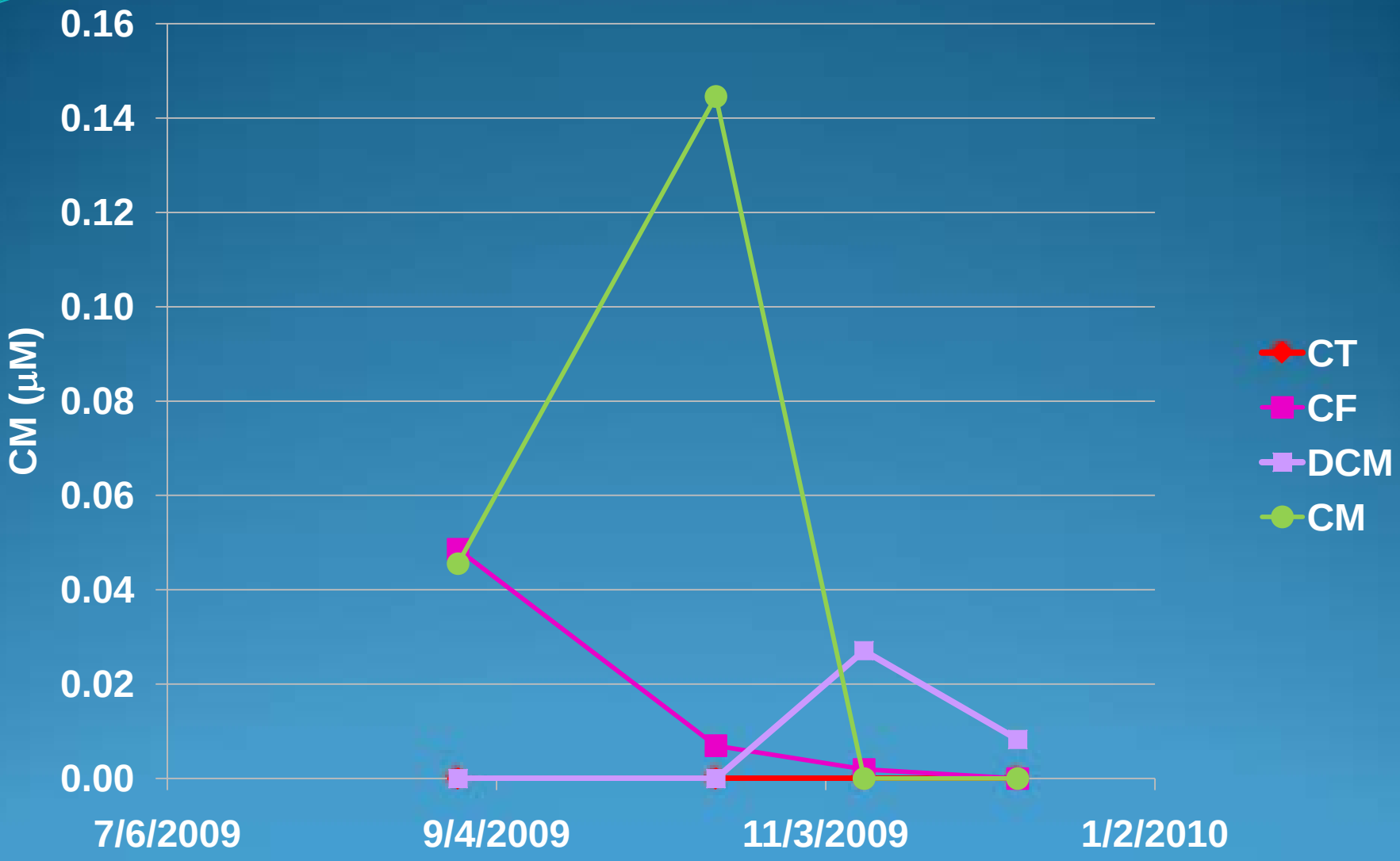
RW-22 CM



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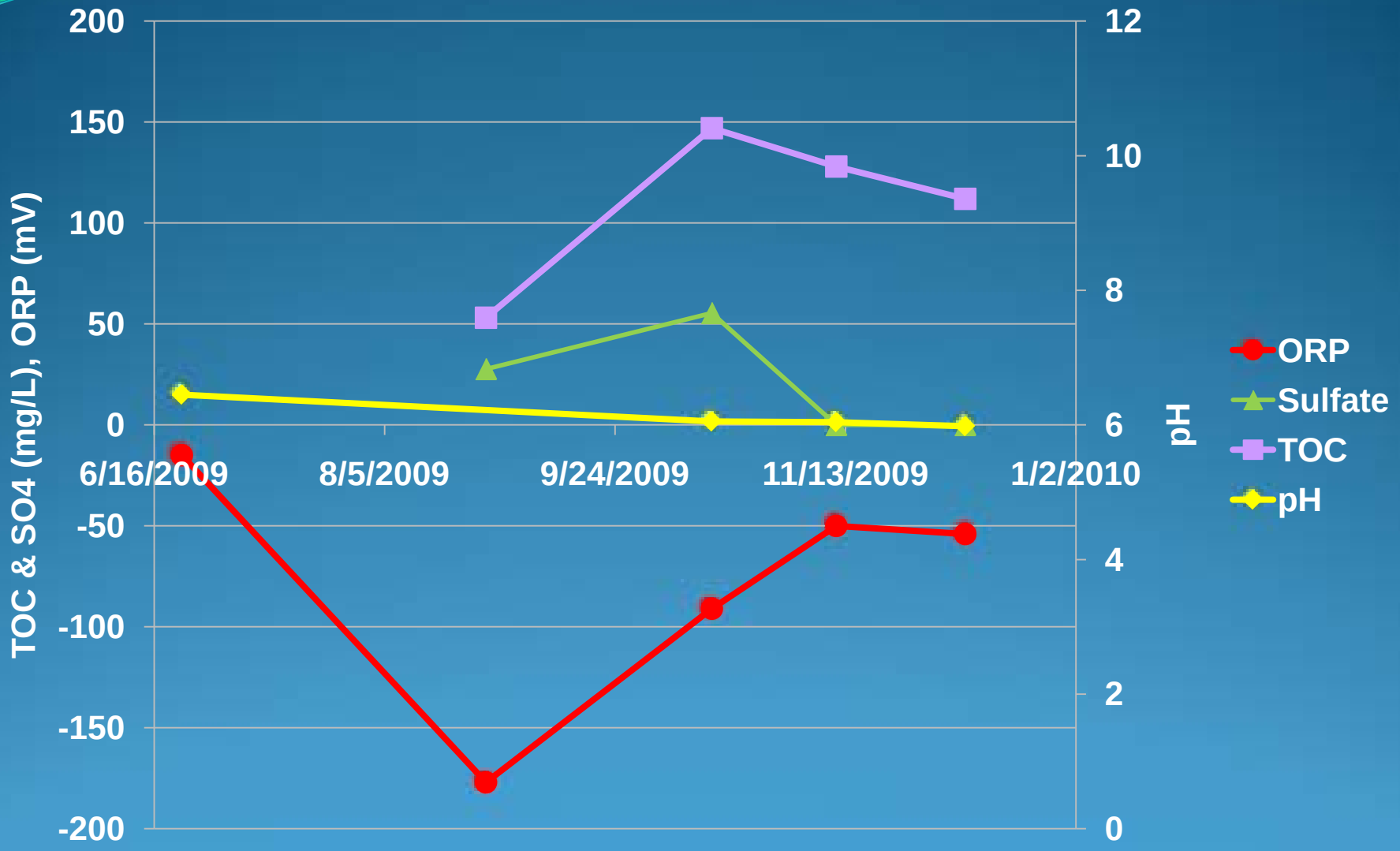
RW-5 pH, ORP, TOC, & Sulfate



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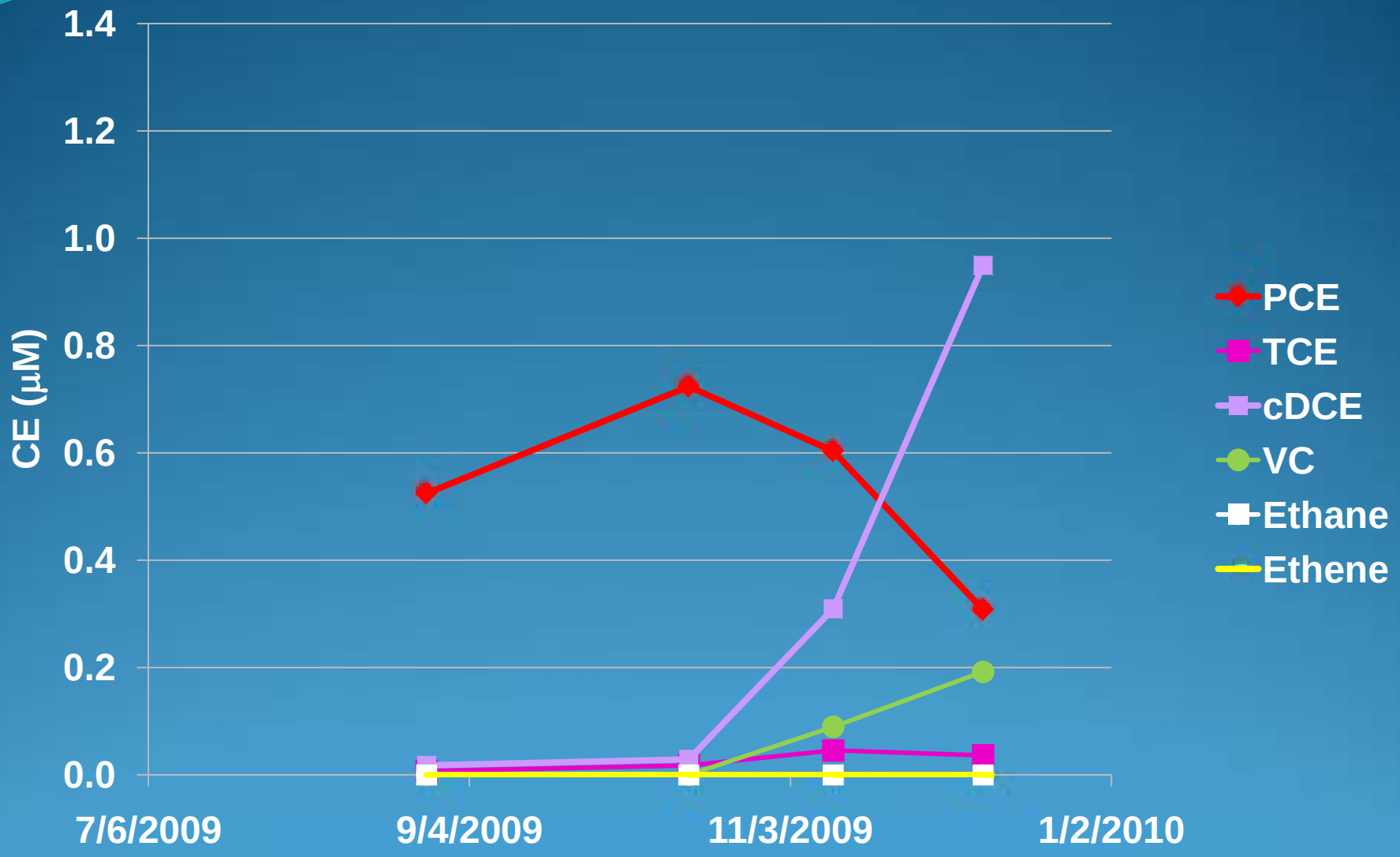
RW-5 CE



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RW-5 CM

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CC-6 pH, ORP, TOC, & Sulfate

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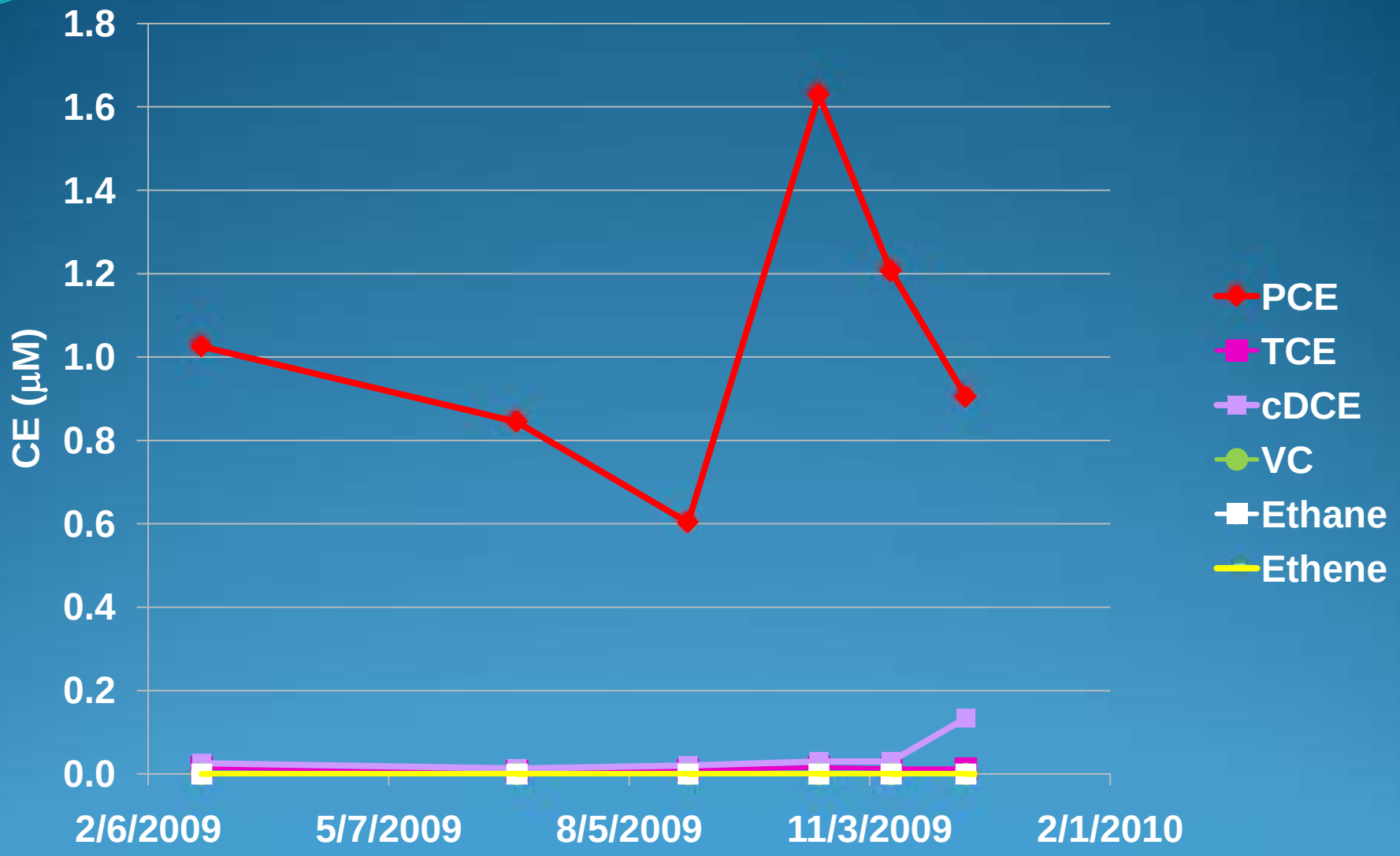
CC-6 CE



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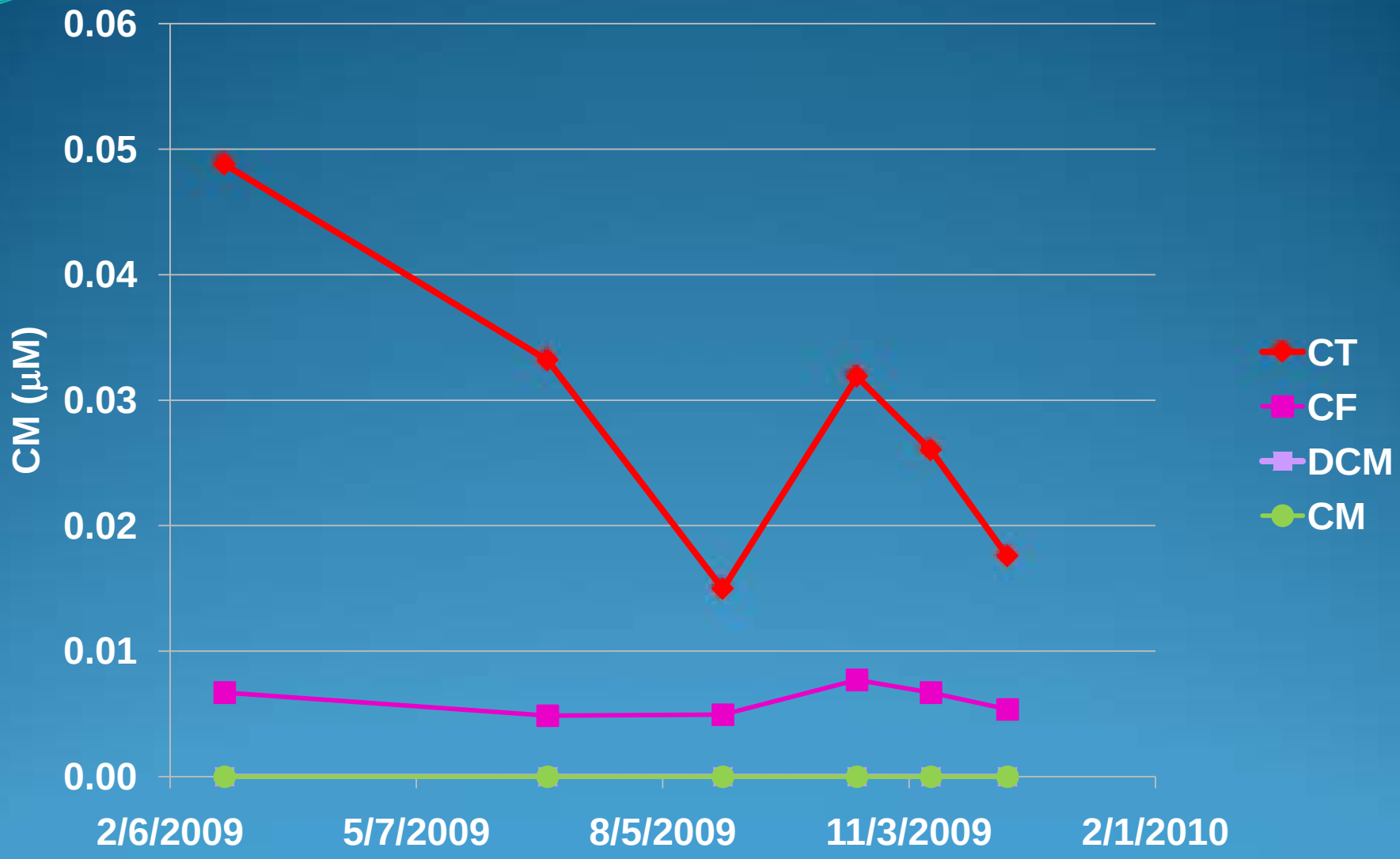
CC-6 CM



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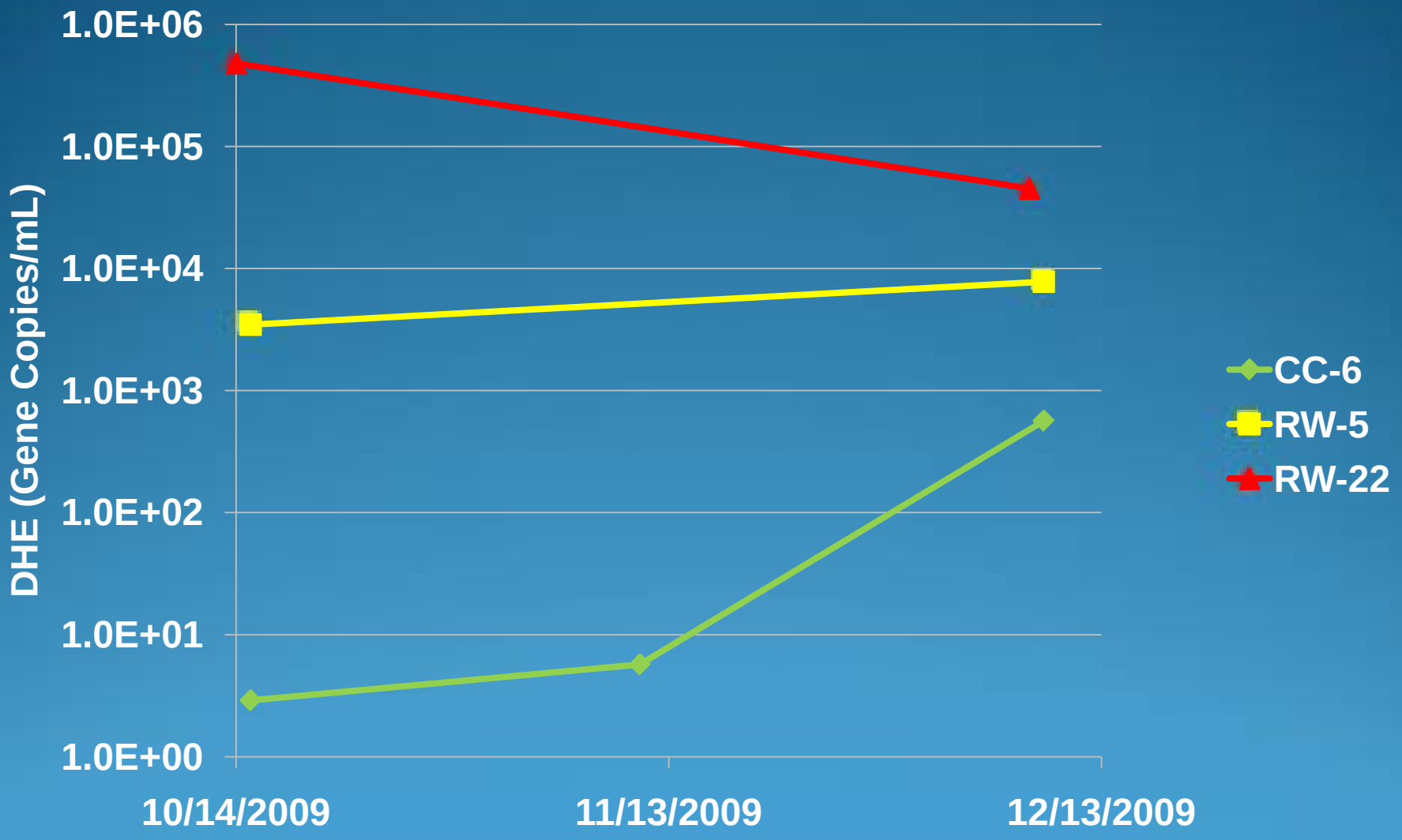
DHE Counts



5/25/2010

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Conclusions

pH adjustment with soluble buffers

- **Can be effective in raising and maintaining neutral pH to promote reductive dechlorination**
- **Buffer concentration can be adjusted to reach pH target**