In-Situ Chemical Precipitation of Cobalt for Long Term Groundwater Remediation

Presenter: Dean Williamson, P.E./Jacobs

Co-authors: Dr. Brian Schroth/Jacobs, Geoff Kiffe/Jacobs

Date: April 17, 2019

JACOBS®

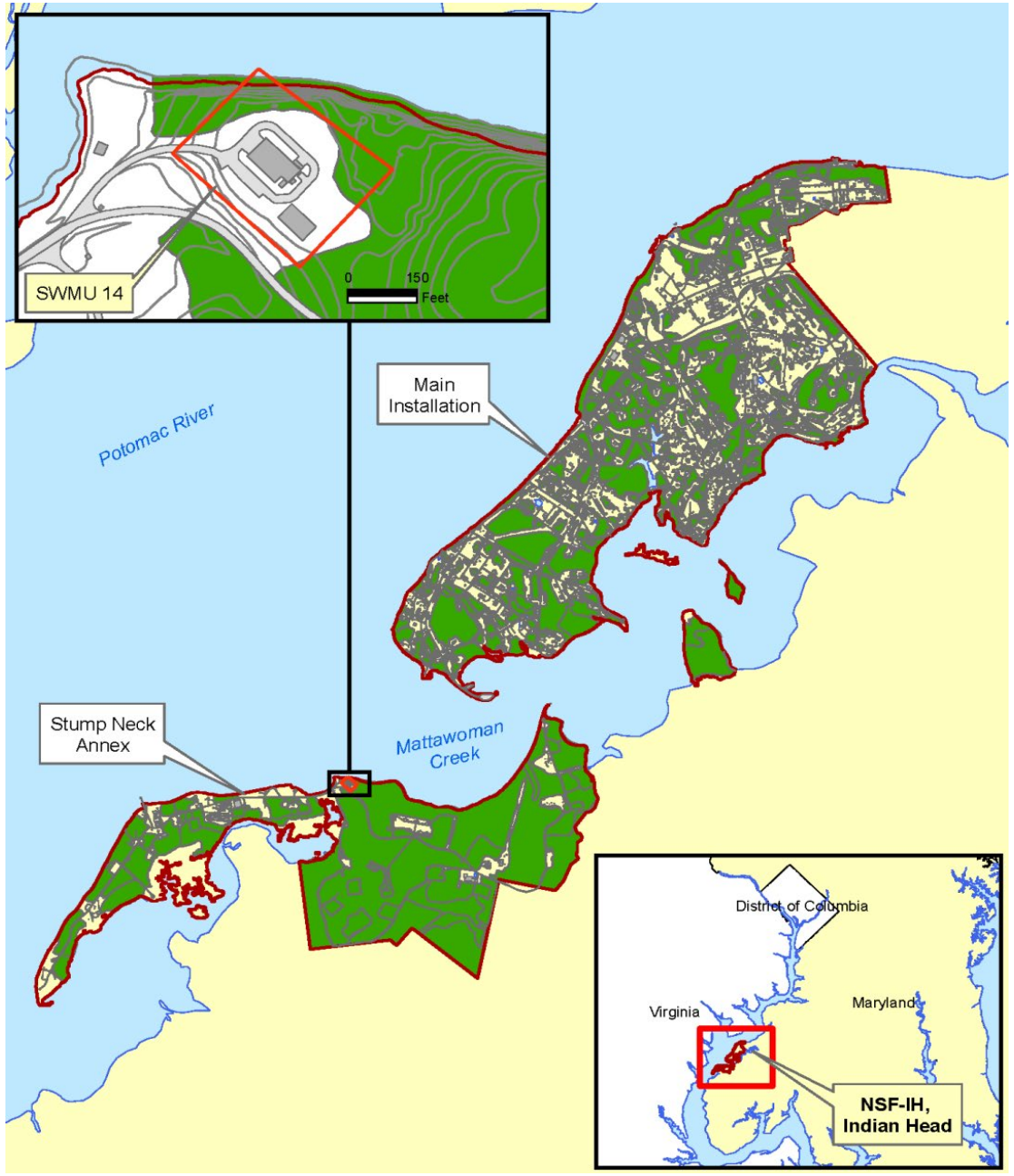
www.jacobs.com | worldwide

Agenda

- Site Description and Remedial Objectives
- Summary of Cobalt Geochemistry
- Pilot Test Approach
- Pilot Test Results
- Pathway Forward

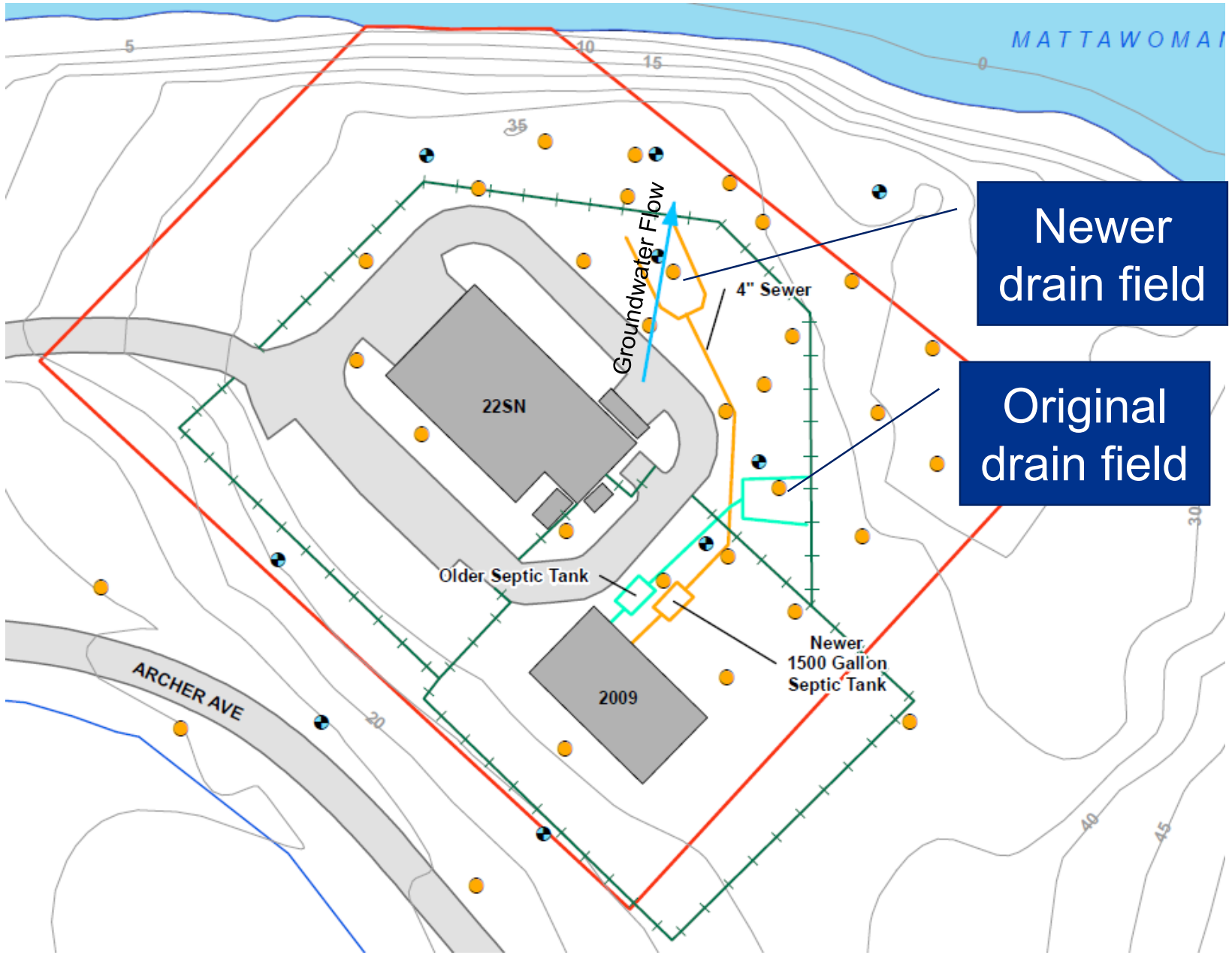
SWMU 14, Naval Support Facility Indian Head, MD

- Approximately 2.4 acres in area
- Photographic laboratory, x-ray facility, and two abandoned-in-place septic tanks with discharge lines and drain fields
- Waste developer and fixer were discharged to the septic systems between about 1968 and 2002
- Photographic chemicals no longer discharged to septic system; building effluent piped to base treatment plant
- Specific use of cobalt has not been documented but cobalt-containing compounds were commonly used in imaging



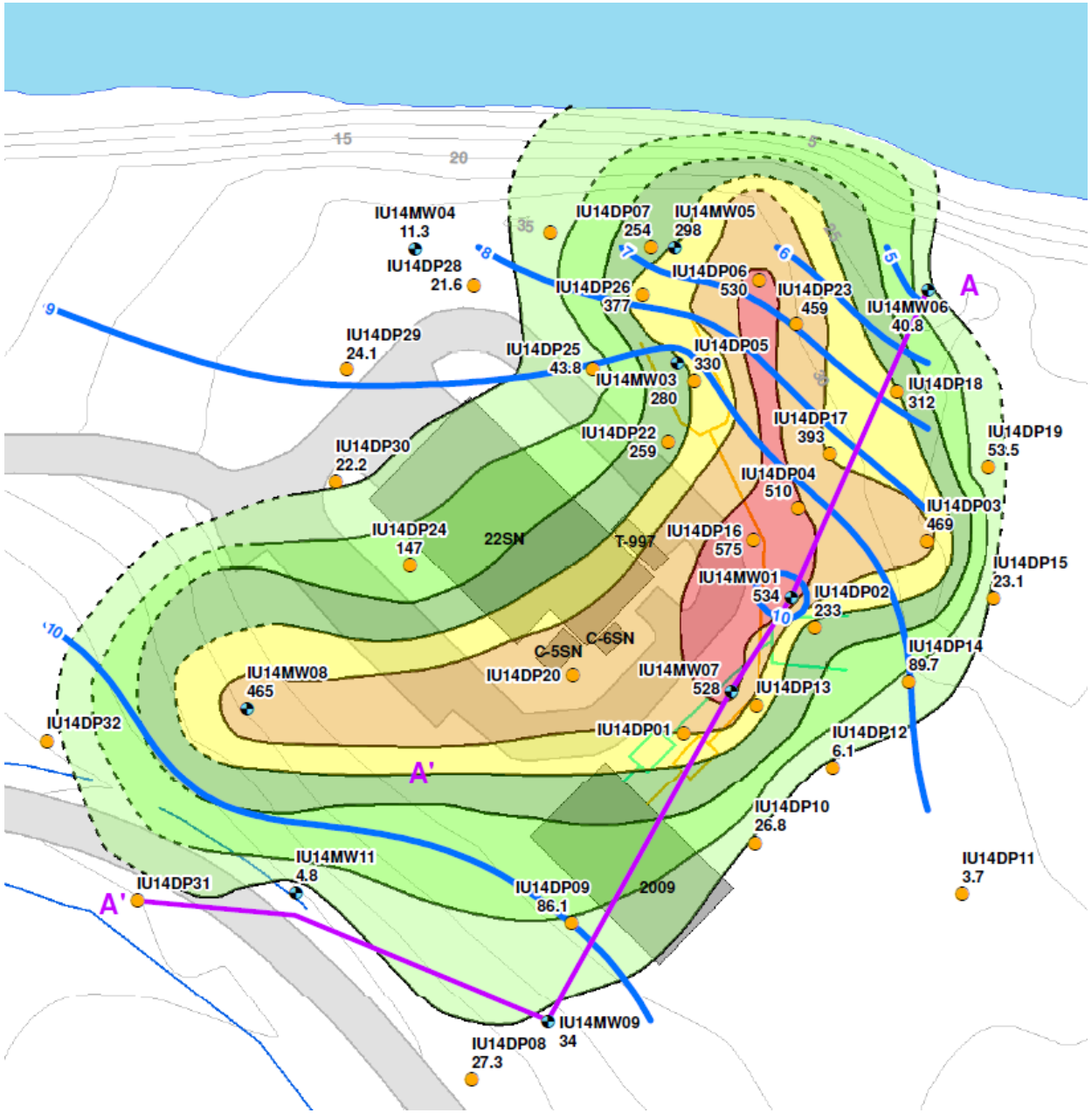
Site Layout

- Only the shallow perched aquifer is impacted
- Groundwater recharge occurs only from incidental precipitation



Cobalt Plume - 2012

- High concentrations generally correspond to drain field locations
- Groundwater flow towards creek; some radial flow occurs
- Natural groundwater conditions are generally aerobic
- DO = <1 to 5 mg/L; nitrate = 4 to 30 mg/L; ORP = 60 to >350 mV; pH = 4.4 to 5.4; low dissolved iron; low TOC

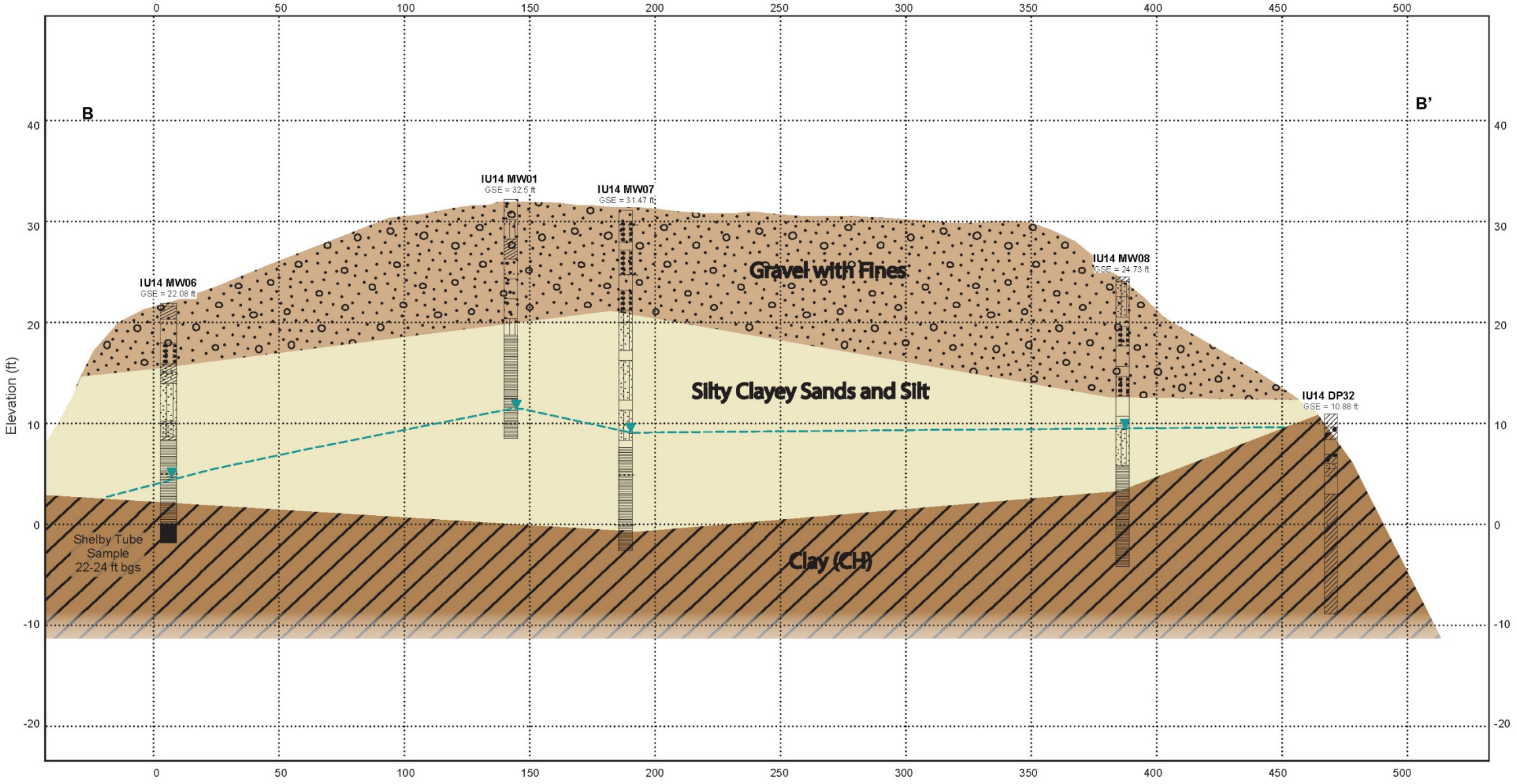


Cobalt Isoconcentrations (ug/L)

- 39.7 - 100
- 100.1 - 200
- 200.1 - 300
- 300.1 - 400
- 400.1 - 500
- > 500.1

JACOBS

SWMU 14 Geologic Cross Section A –A’



JACOBS®

Substantial Reductions in Cobalt Concentrations Have Occurred Naturally Over Time

Well	7/1/2012	8/1/2015	7/27/2016	Percent Reduction
IU14MW01	535	347	352	34%
IU14MW07	529	278	53.4	90%
IU14MW03	280	215	215	23%

Cobalt concentrations in µg/L
Target Cleanup goal = 17.6 µg/L

JACOBS

Remedial Action Objectives and Site Rehabilitation Goals

- Remedial Action Objectives
  - Prevent unacceptable risks to human receptors from exposure to cobalt in the shallow groundwater
  - Reduce cobalt concentrations to meet Site Rehabilitation Goals (SRGs) in the shallow groundwater,
  - Return the shallow groundwater to its beneficial use to the extent practicable.
- Site Remediation Goals
  - Cobalt concentration in groundwater less than or equal to 17.6 ug/L
  - Background groundwater cobalt concentration = 17.6 ug/L

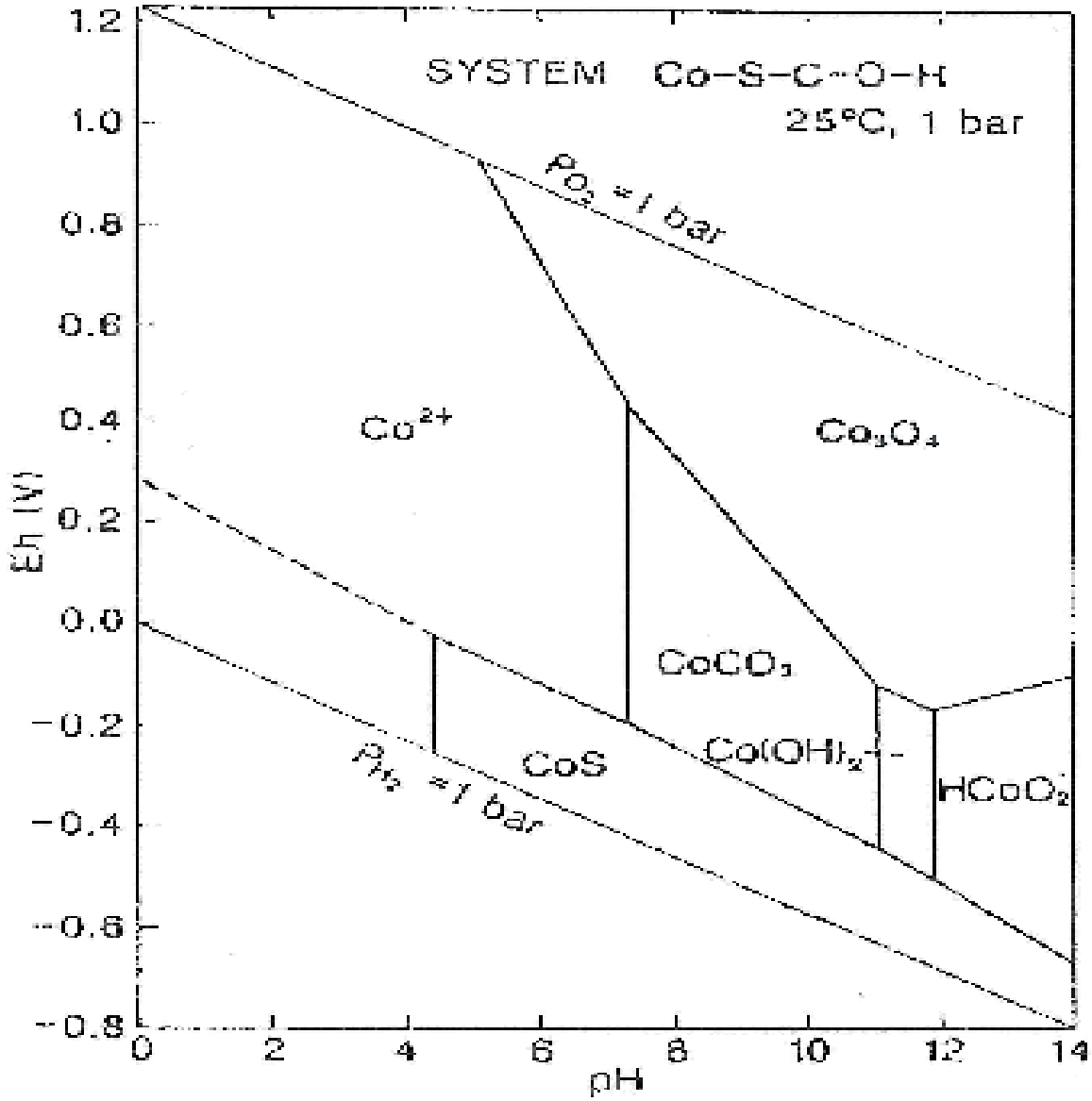
JACOBS

Cobalt Geochemistry

- Oxidation States: +2 and +3
- Cobalt (II):
  - stable valence state in water
  - Most common form in natural water systems
- Cobalt (III):
  - strong oxidizing agent; not thermodynamically stable
  - decomposes under Eh-pH conditions for most natural water
- Cobalt concentration (soil and sediment systems) controlled by adsorption and co-precipitation with manganese and iron oxide minerals
- Cobalt minerals include sulfides, arsenides, sulfo-arsenides, arsenates, selenides, oxides and carbonates

Groundwater Conditions and and Cobalt Phase Diagram

- Cobalt sulfide (CoS) solubility product on the order of 2 x 10^{-21} to 4 x 10^{-25}
- Cobalt carbonate ($CoCO_3$) solubility product ~ 1x 10^{-10}
- In-situ precipitation of cobalt selected for pilot test

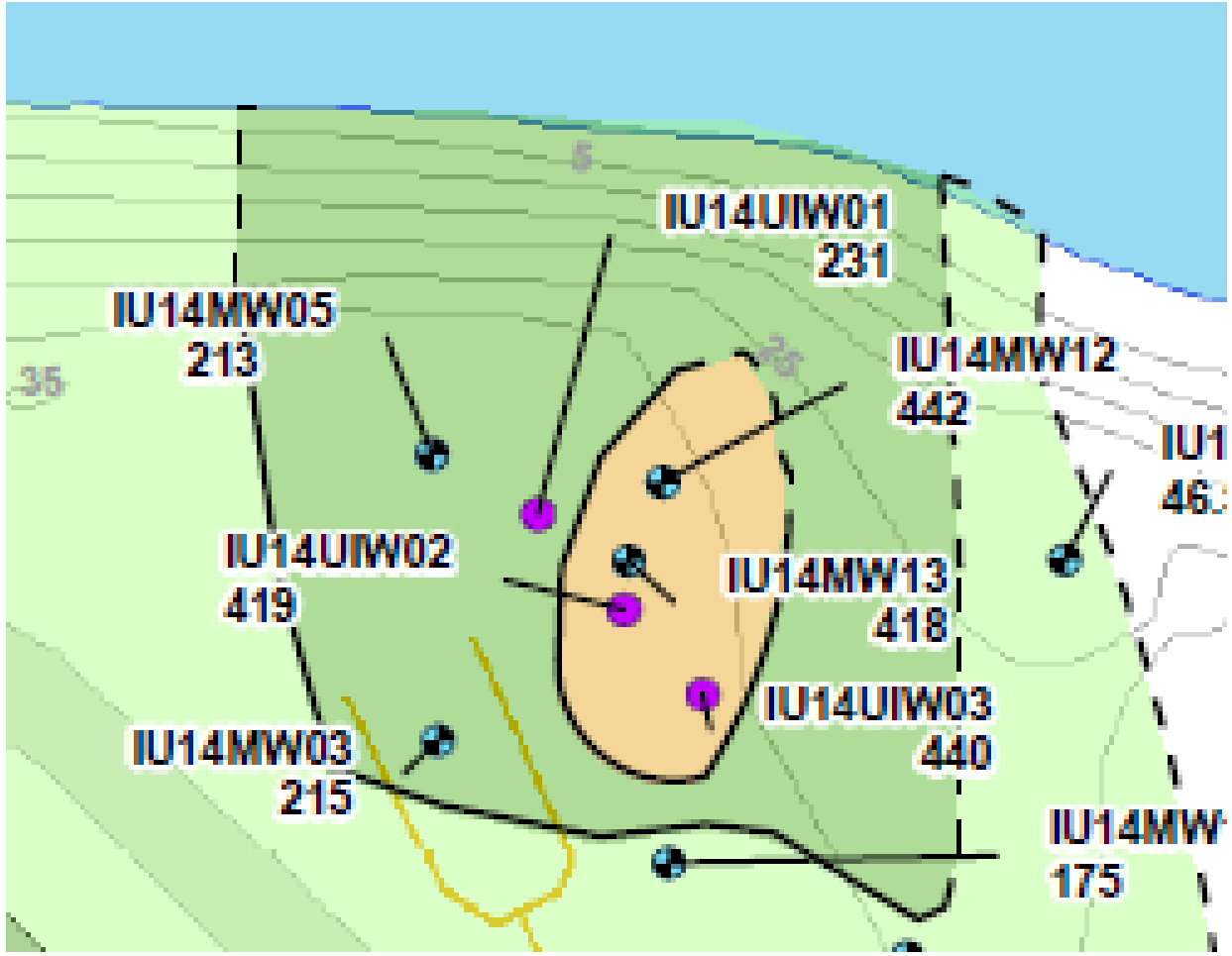


Eh-pH diagram for the system Co-O_2-CO_2-S-H_2O, assuming that ∑Co = 10^{-6} mol/kg, ∑C = 10^{-3} mol/kg, and ∑S=10^{-3} ml/kg

JACOBS

Pilot Test Design

- Target Treatment Area (TTA) selected with elevated cobalt (IU14MW12 and IU14MW13)
- Three injection wells installed upgradient of TTA
- Reagents selected:
  - Emulsified vegetable oil
  - Magnesium sulfate
  - Sodium carbonate



JACOBS

Injection Dosing and Volumes

- Injection wells – 10 ft screened intervals set 20 ft apart
- Target injection volume per well – 1400 gallons, 41 gallons of Emulsified Vegetable Oil
- Injectate reagent concentrations
  - Emulsified Vegetable Oil - 2.7% (27,000 mg/L)
  - Magnesium Sulfate – 1000 mg/L
  - Sodium carbonate – 200 mg/L
- Injections completed in 3 days
- No daylighting or other issues noted during injections

JACOBS

Expected Changes in Geochemistry After Injections

- Dissolved oxygen (DO), nitrate, and oxidation reduction potential (ORP) – decrease
- TOC and Sulfate concentrations – initial increase then decrease
- Dissolved iron and manganese – likely increase
- Methane – potential increase
- Sulfide – possible detections, FeS formation may maintain low sulfide levels
- Alkalinity and pH –increase, possibly attenuated by volatile fatty acid formation
- Cobalt - decrease
- Sodium – increase then decrease (conservative tracer)

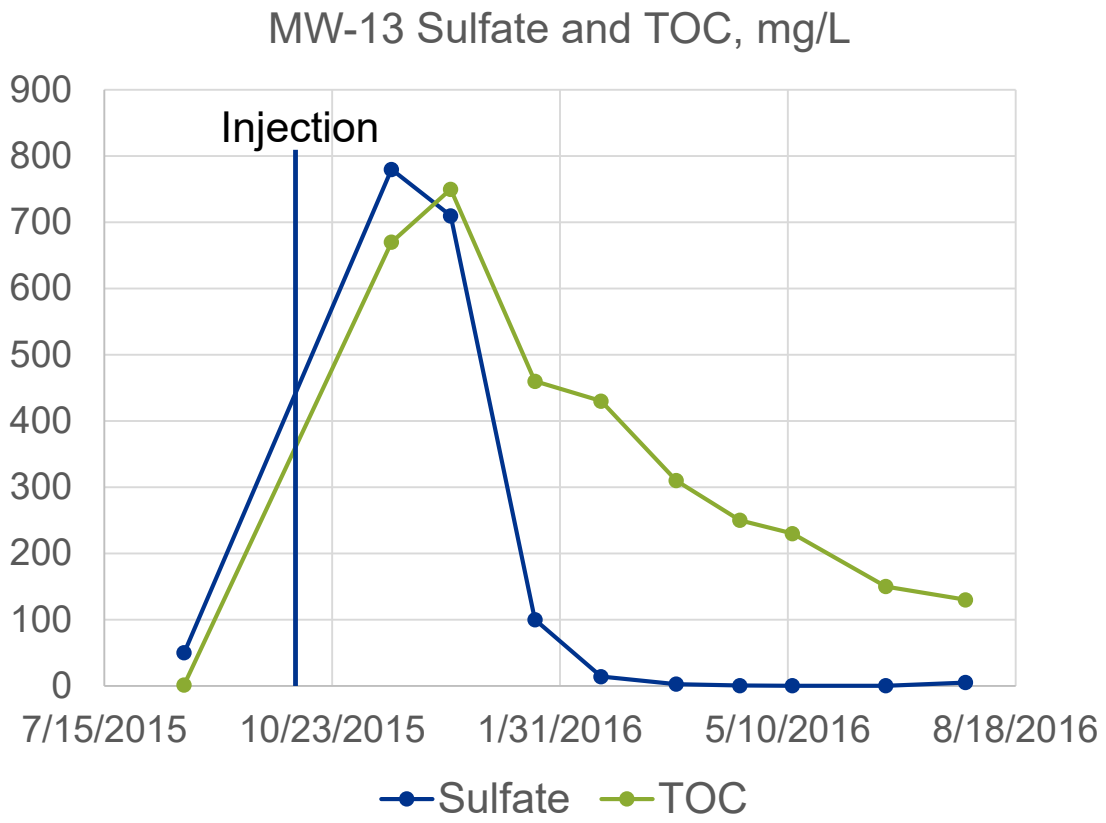
JACOBS

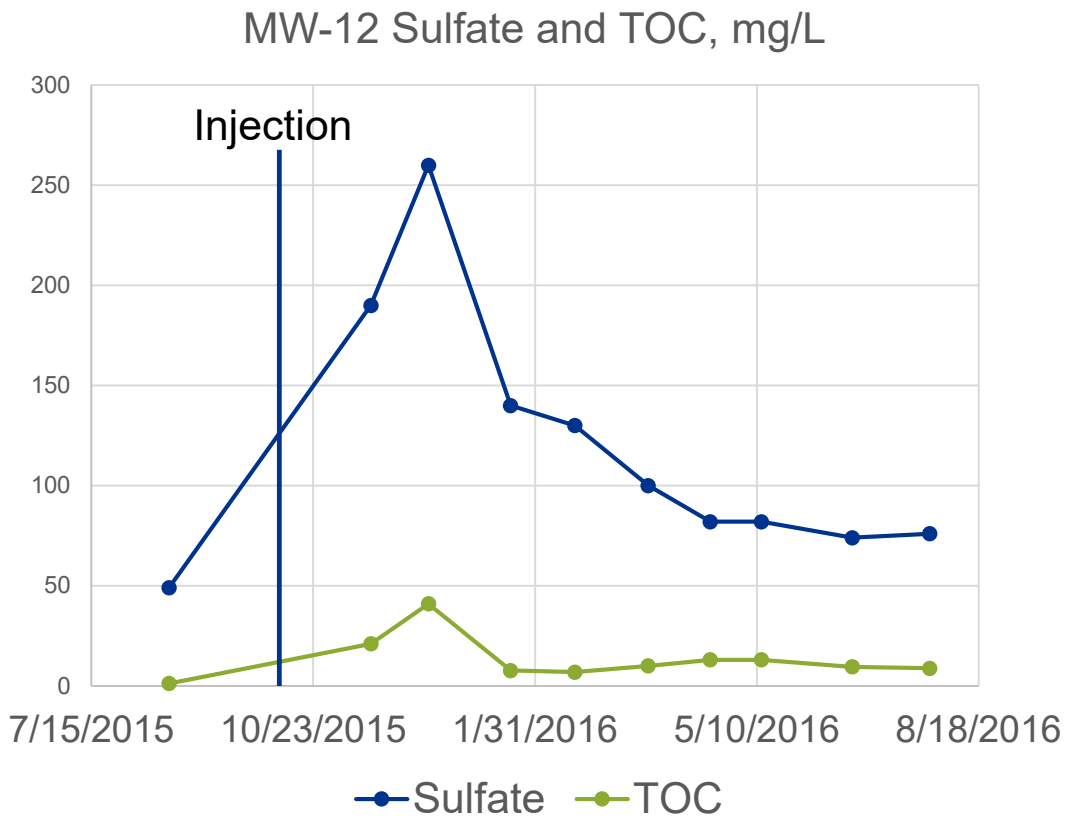
Injection System Set up

Post injection Monitoring Program

Analyte	Baseline Number of Wells	Monthly Post-Injection Number of Wells	9-Month Post-Injection Number of Wells
Total TAL Metals and Mercury	20	3	17
Dissolved TAL Metals and Mercury	20	3	17
TOC	12	3	9
Sulfate	12	3	9
Sulfide	12	3	9
Nitrate	12	3	9
Methane, Ethane, Ethene	12	3	9
Alkalinty	12	3	9

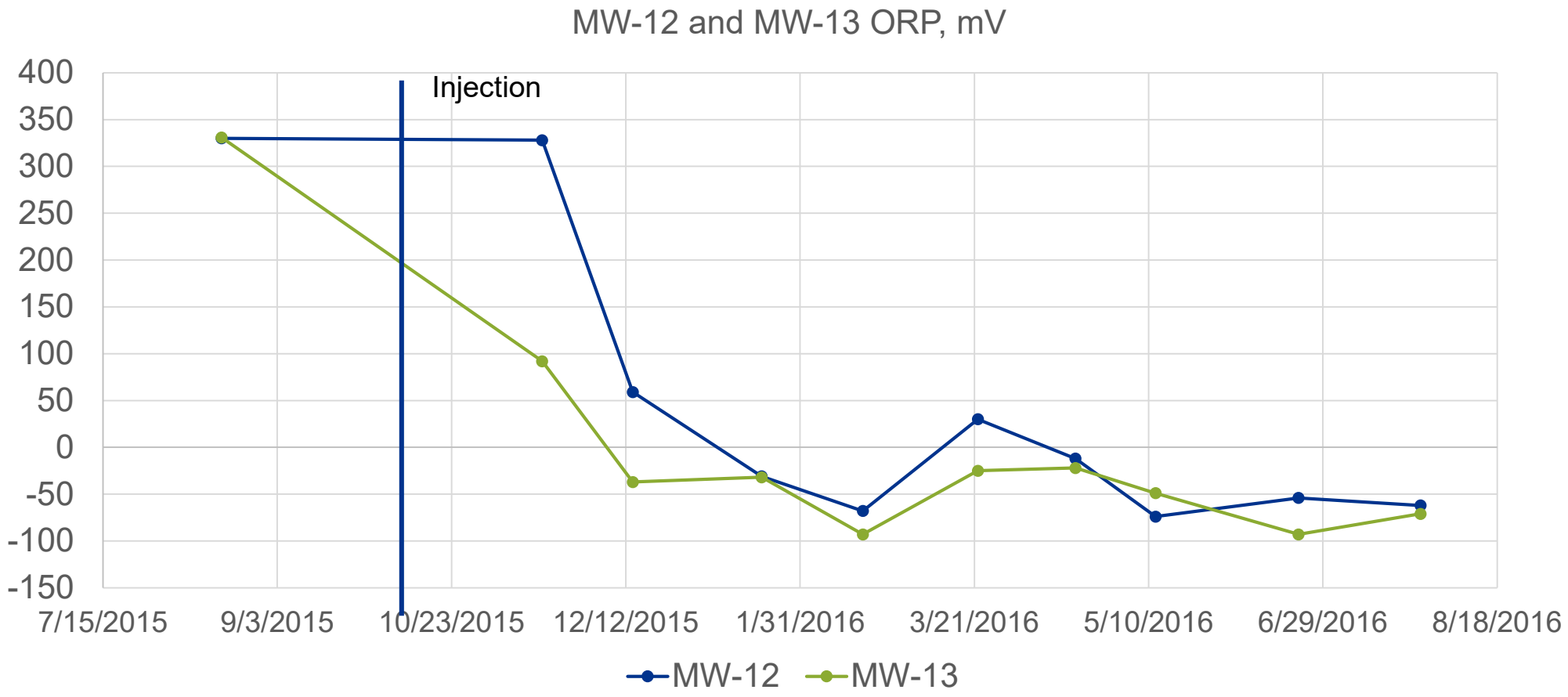
Sulfate and TOC Increase After Injection Indicates Successful Reagent Delivery





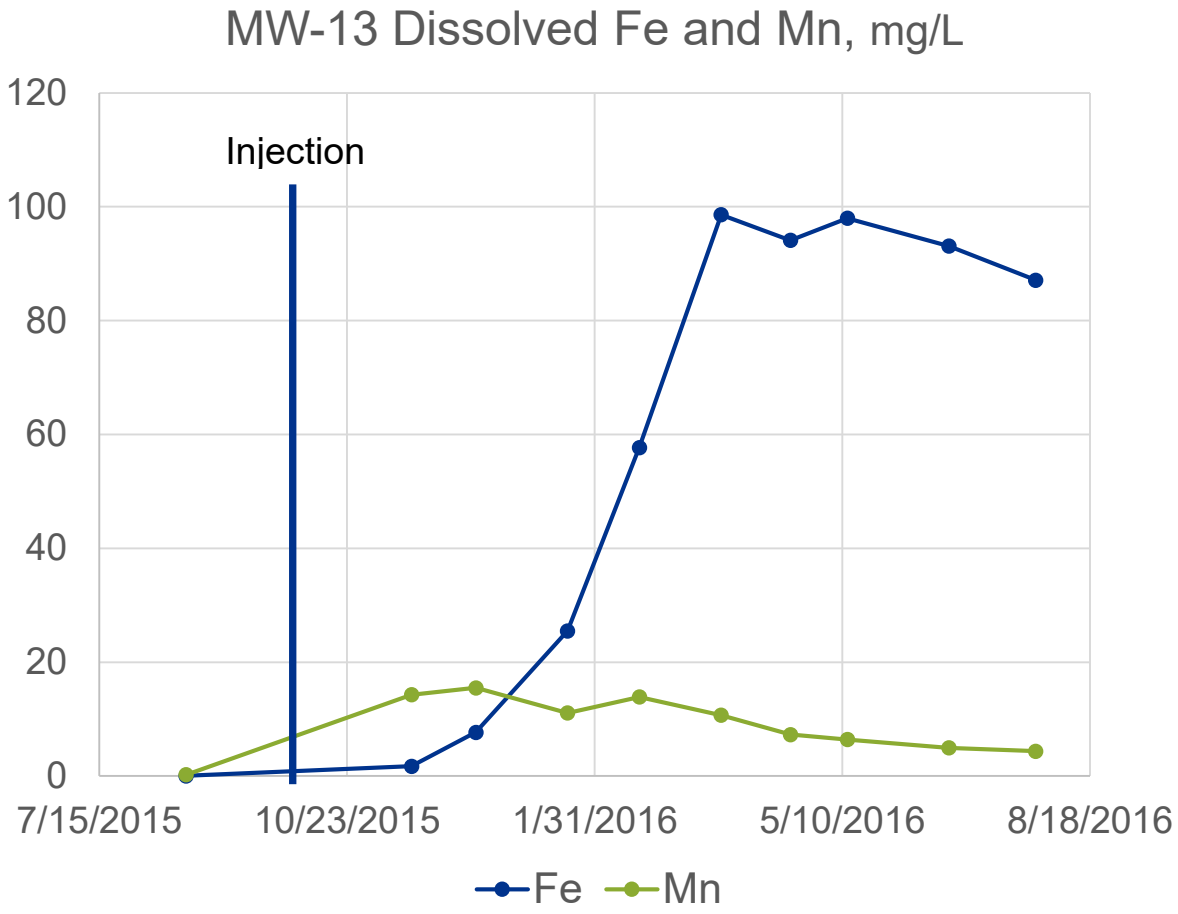
JACOBS

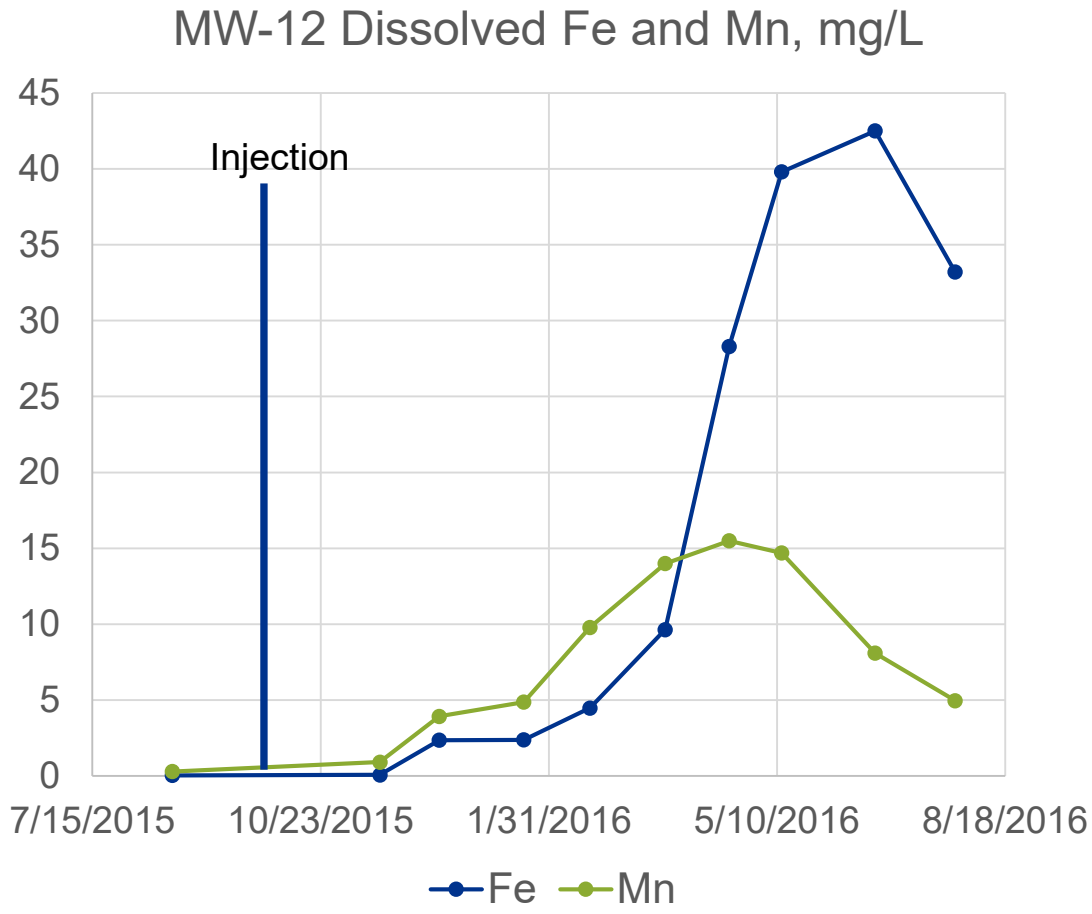
ORP In MW-13 and MW-12 Declined After Reagent Injections



JACOBS

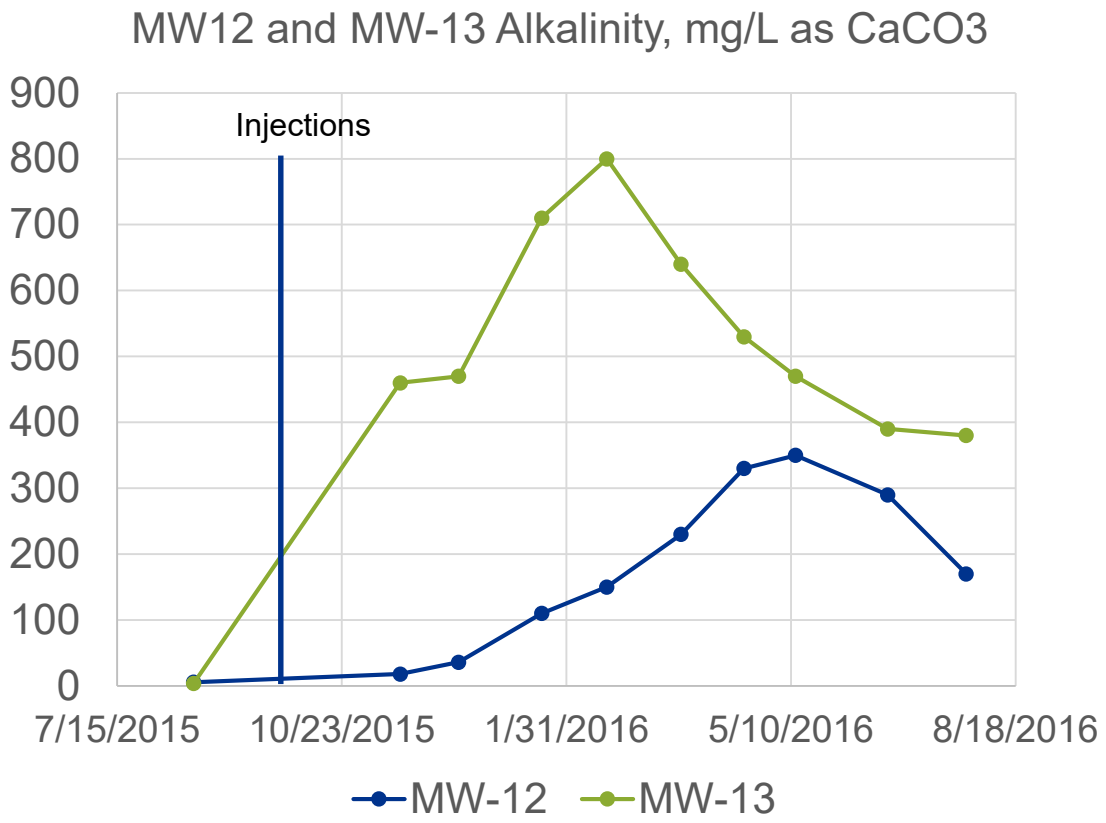
Dissolved Iron and Manganese Increased After Reagent Injections

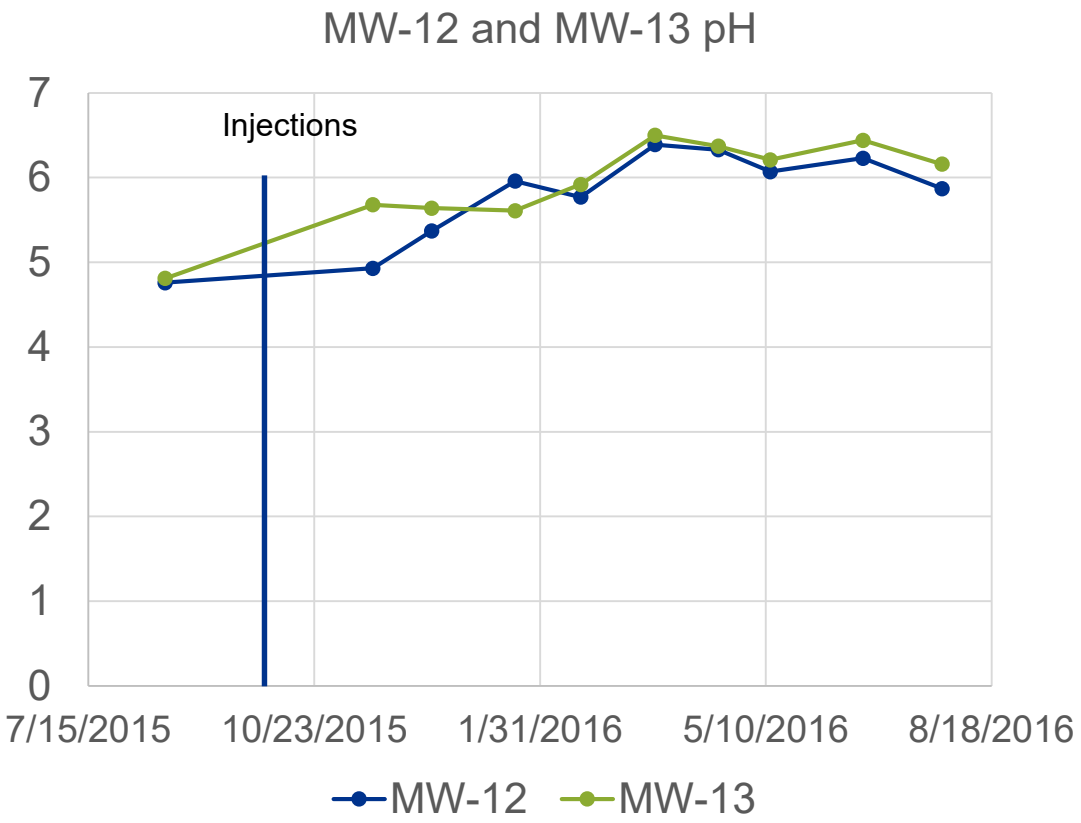




JACOBS

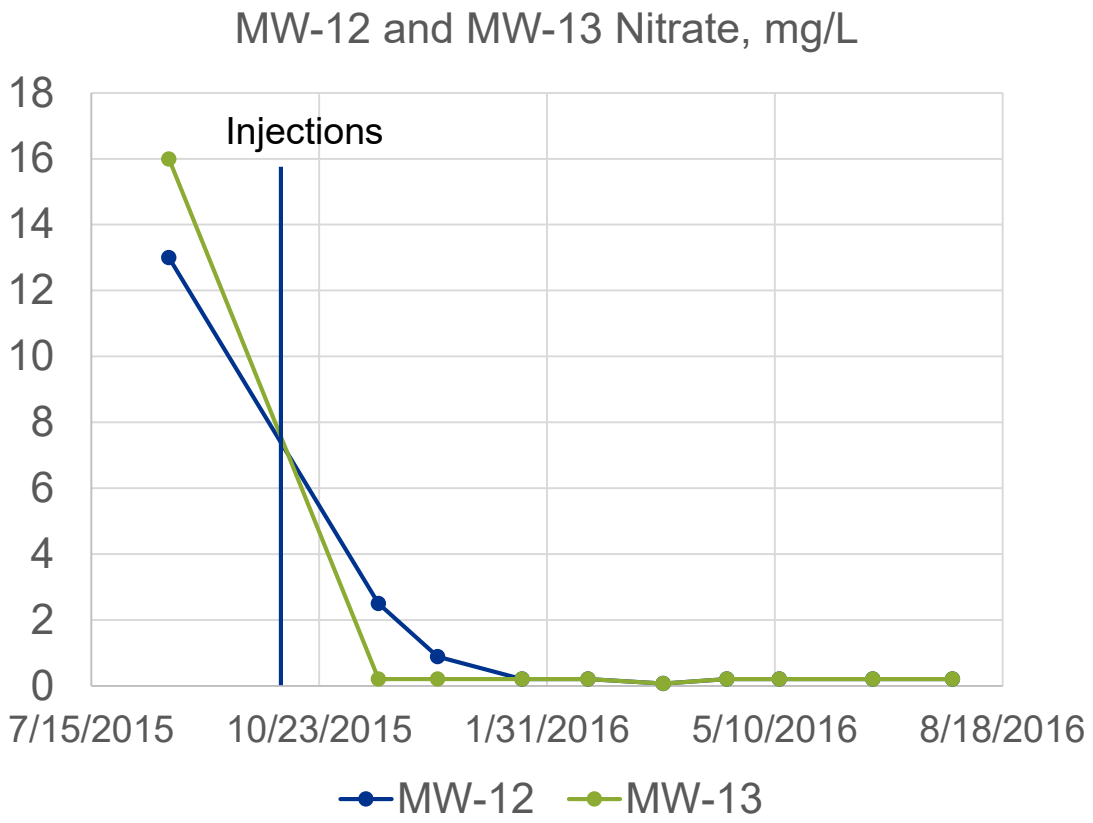
Alkalinity and pH Increased After Reagent Injections

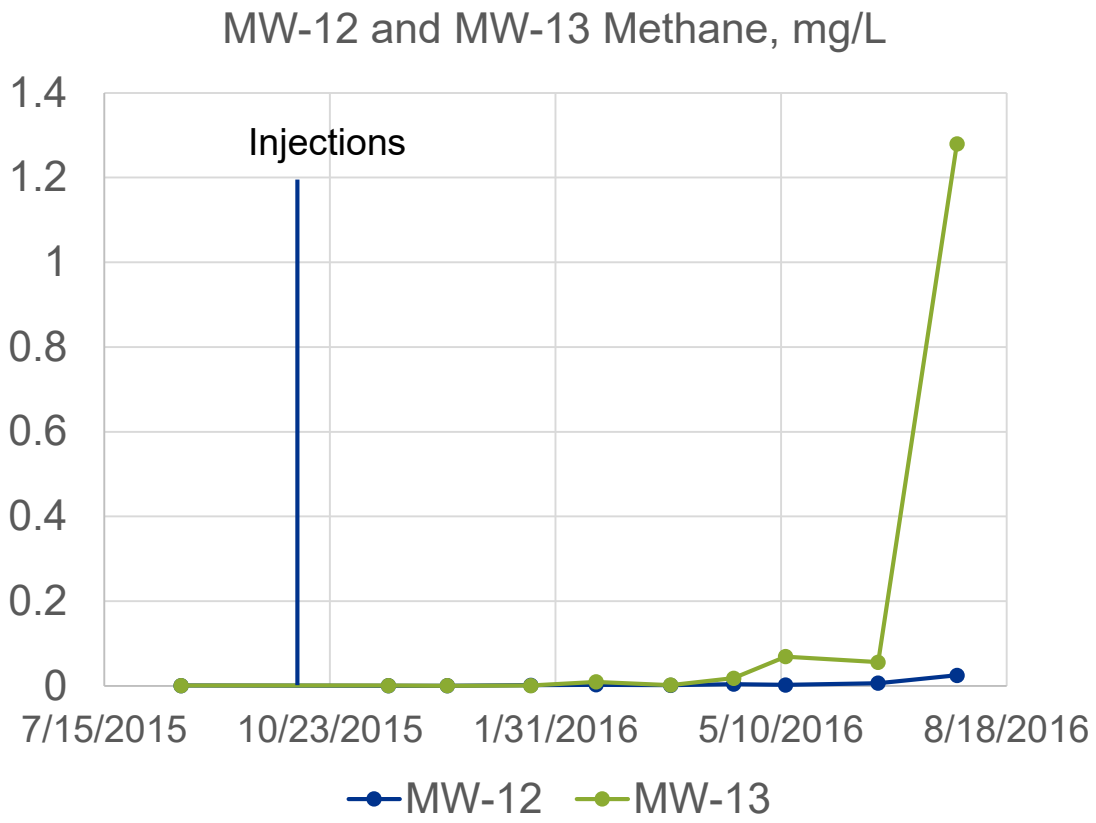




JACOBS

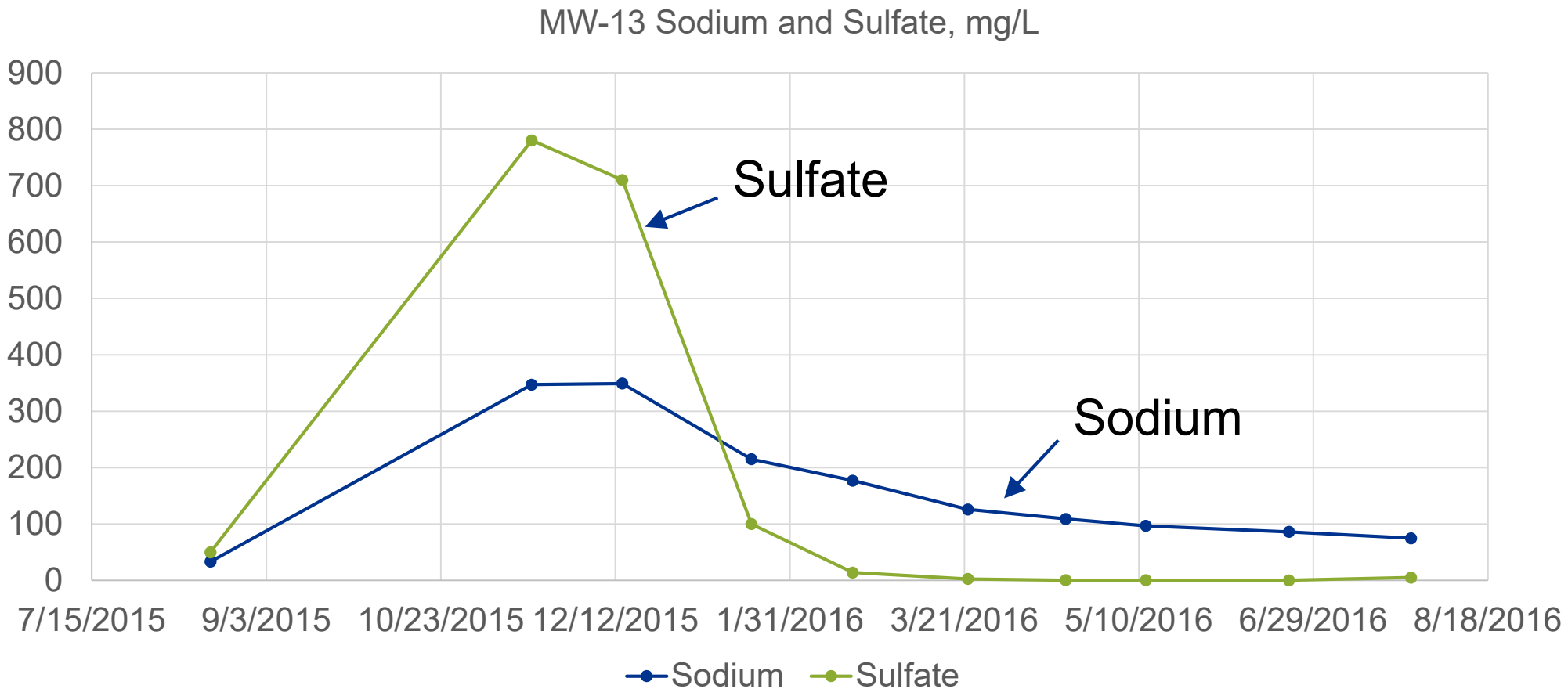
Nitrate decreased; Methane Production Near End of Pilot Test





JACOBS

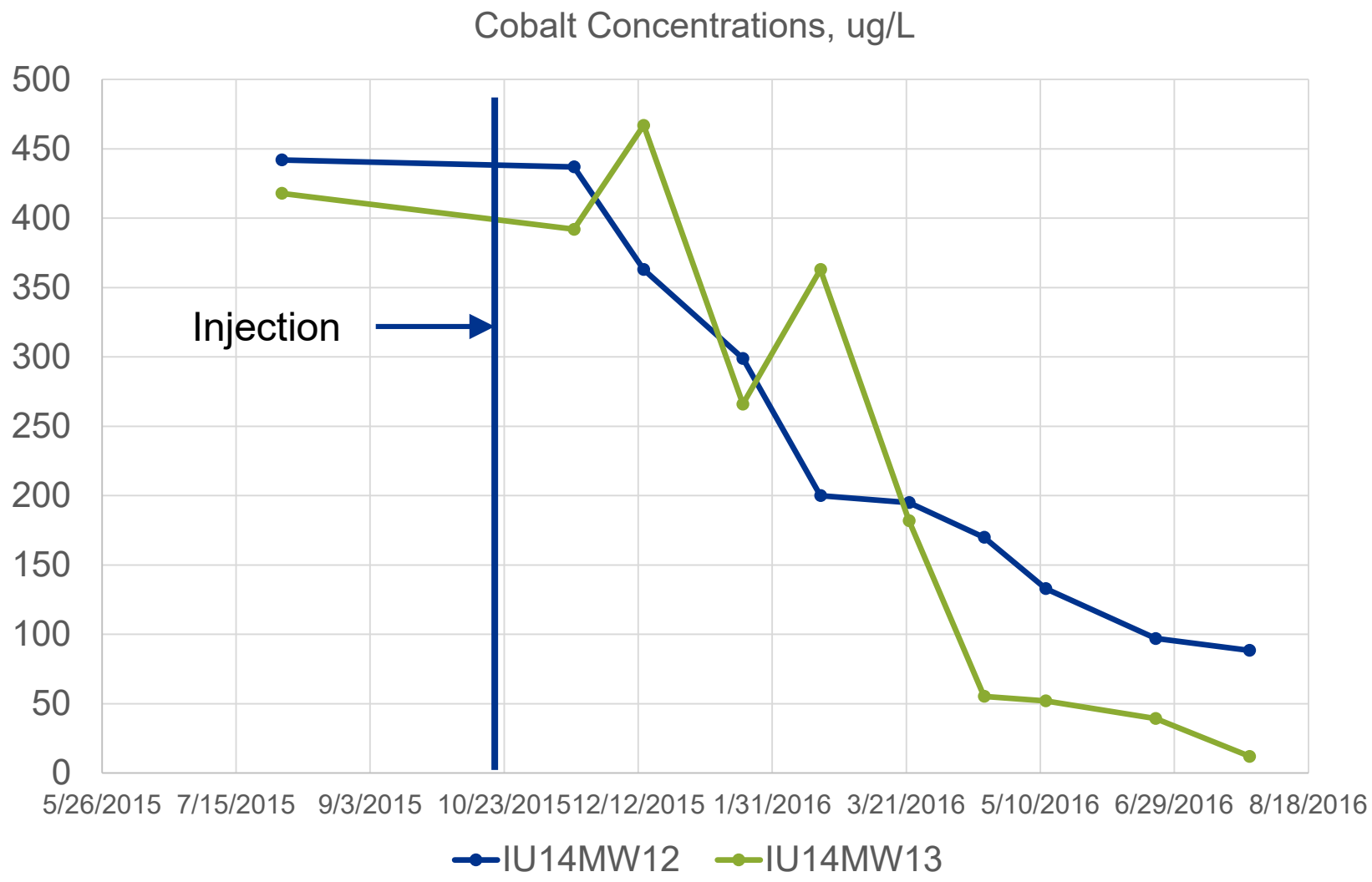
Sodium and Sulfate Responses Suggest Sulfate Consumption Relative to Non-reactive Tracer



Sulfide concentrations all < 1 mg/L

JACOBS

Cobalt Concentration Reductions 9 Months After Injections
IU14MW13 – 97%; IU14MW12 - 80%



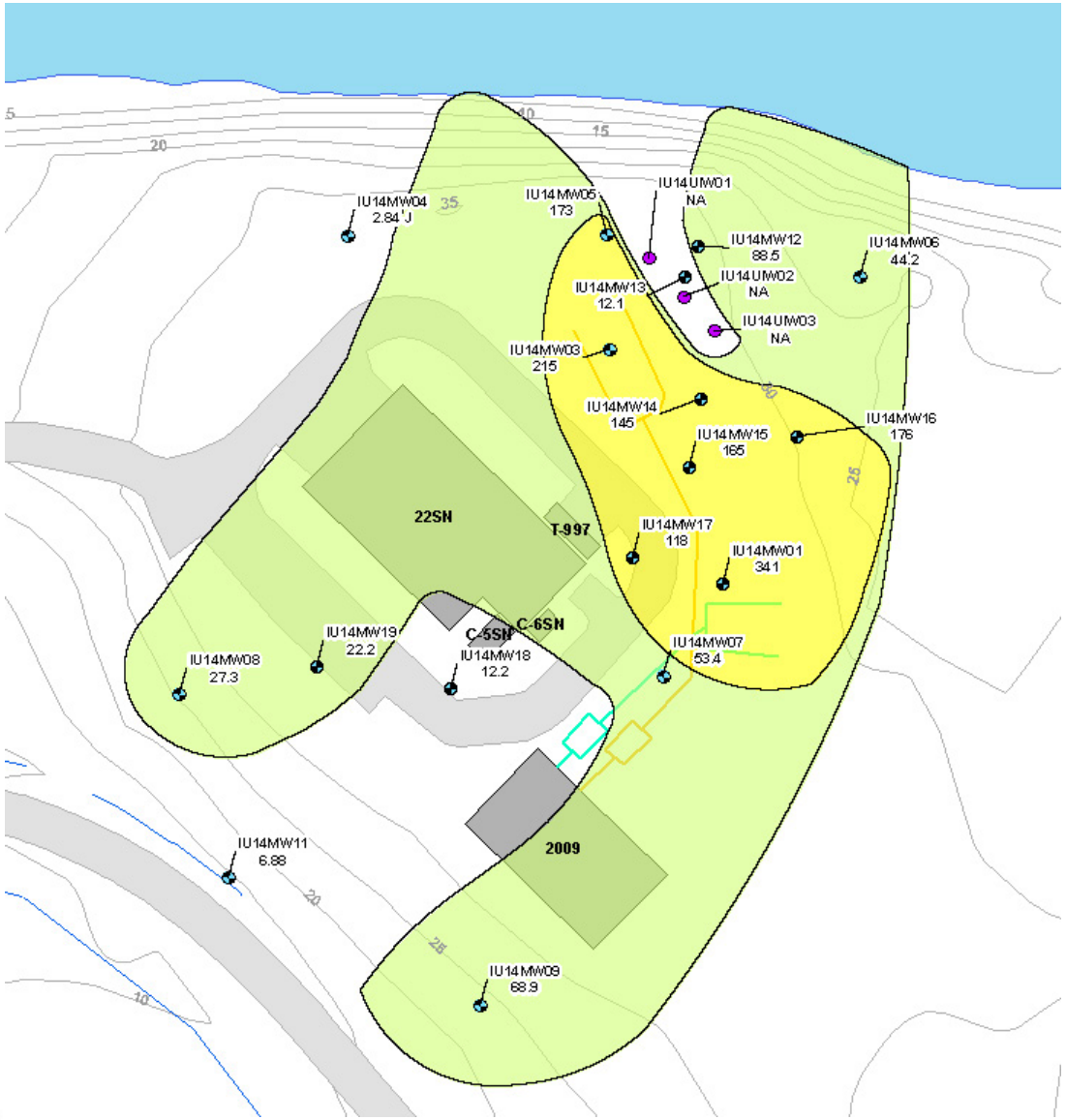
Conclusions From Pilot Test

- TOC, sulfate, and sodium carbonate were successfully delivered into the aquifer and achieved an adequate radius of influence for the pilot test
- Data provides strong evidence supporting the achievement of iron-, manganese- and sulfate-reducing conditions
- Up to 97% reduction in cobalt concentrations in groundwater
- Cobalt reductions likely due to formation of CoS, $CoCO_3$, or co-precipitation with FeS minerals
- Process did not cause mobilization of metals other than iron and manganese
- Data indicate that treatment process is viable and could be considered for full-scale remedy

JACOBS

Pathway Forward

- Feasibility Study and Proposed Plan Completed in 2018
- In-situ precipitation recommended for groundwater with cobalt concentrations >= 100 ug/L
- MNA recommended for areas where cobalt < 100 ug/L
- Time to achieve site closure ~ 21 years
- Full-scale implementation may occur within next 12 to 24 months



2016 Cobalt Concentrations

JACOBS

Thank You!

In-Situ Chemical Precipitation of Cobalt for Long Term Groundwater Remediation

dean.williamson@Jacobs.com

JACOBS®