Treatment of Heavy Metals in Groundwater and Soil with MetaFix® and EHC® Reagents

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PeroxyChem is a company of Evonik Industries AG

Agenda

- MetaFix® reagents: characteristics, dosage, application methods
- Metals Treatment Chemistry: compare & contrast chemical fixation with alkaline precipitation methods
- Bench-scale Optimization Testing: Why, where, how, time & cost
- Example Results from Bench-scale Testing
- Case Studies: Soil and Groundwater Treatment
- Questions & Answers

MetaFix® Reagents

- MetaFix® Reagents are fine-grained, injectable, and neutral pH
- Designed to remove soluble heavy metals using chemical reduction, precipitation, coprecipitation, and adsorption
- Not dependent on biological sulfate reduction or carbon metabolism
  - ✓ performance is not inhibited by high microbial toxicity (e.g., alkalinity, acidity, salts, high COC concentrations)
- Contain iron oxides, iron sulfides, ZVI, ±carbonate, ±phosphate, and ±activated carbon

METAFIX® REAGENTS

MetaFix® Mechanisims

- Primary treatment mechanism is conversion of aqueous heavy metals to low solubility and pH stable mineral precipitates and coprecipitates
- Secondary mechanism is adsorption of soluble heavy metals on iron oxides, iron sulfides, ZVI corrosion products, and activated carbon
- Subject to the metals needing treatment we also use carbonate and phosphate precipitation
- Powdered activated carbon may be added to ensure removal of organically-complexed heavy metals (i.e., methyl mercury and organo-arsenic compounds)

MetaFix® Mechanisms

Metal	Precipitation as Iron-Metal-Oxyhydroxides	Precipitation as Metal Sulfides/Iron Metal Sulfides	Adsorption on and Co-precipitation with Iron Corrosion Products	Precipitation as Metal Carbonates and Phosphates	Adsorption of organo-metal species
As (III, V)		•	•		•
Cr(VI)	•		•		
Pb, Cd, Ni, Zn	•	•	•	•	•
Cu	•	•	•		
Se	•	•	•		
Hg		•	•		•

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MetaFix® Reagents I-7A, I-6A, and I-3

Application of MetaFix® Reagents

Low Dosage Rates

- 0.25% - 4.0% (w/w) for soil
- 0.1% - 1.0% (w/w) for groundwater

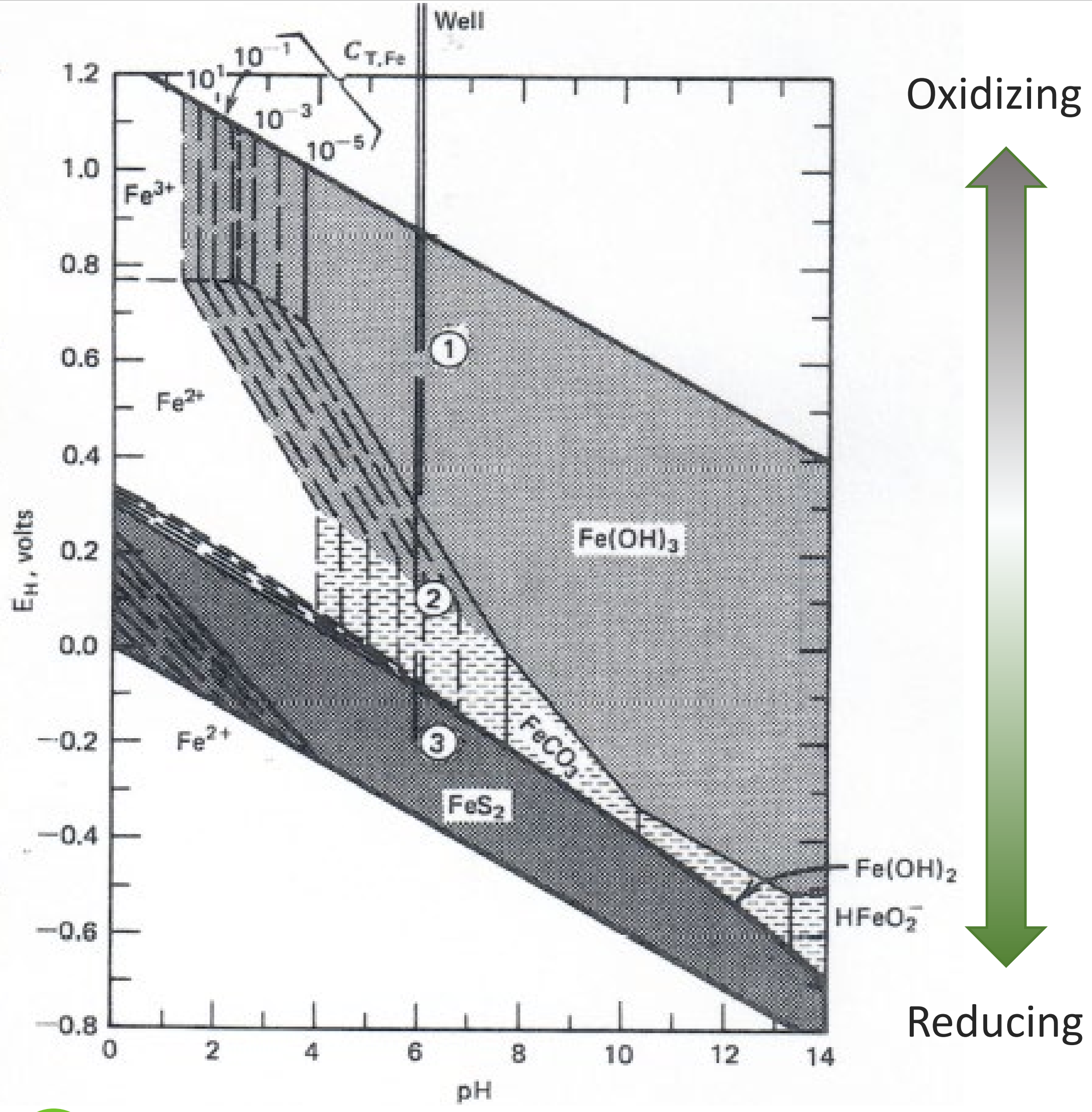
✓ **Application by soil mixing, trenching, or injection (25% – 40% solids) aqueous suspension**

✓ **Low cost treatability testing to determine dosage and enable custom formulation ($2,500)**

Chemistry of Heavy Metal Precipitation

- Mechanisms of heavy metal precipitation are influenced by aqueous chemistry
- MetaFix® reagents are designed to alter aqueous chemistry in ways that will promote the best precipitation reactions
- Combining good understanding of precipitation chemistry for a given metal with knowledge of site geochemistry enables selection of the most appropriate MetaFix® formulation
- Eh-pH Diagrams (Pourbaix) can help identify the mineral forms in which heavy metals can best be precipitated
- Also help to reveal when a custom formulation may be needed.

Understanding Eh/pH Phase Diagrams



Aqueous Iron/Sulfur System as Influenced by pH and Eh

- Each region shows the most thermodynamically stable and therefore likely most abundant species
- Provides no information about kinetics of formation/dissolution
- Horizontal lines indicate electron transfer
- Vertical lines indicate an acid acid-base equilibrium
- Broad Eh-pH zone where iron will precipitate with sulfur to form FeS_2 (ferrous sulfide) in the form of Pyrite or Marcasite
- Note that total iron concentration influences the pH at which iron will begin to precipitate as $Fe(OH)_3$, $Fe(OH)_2$, or $FeCO_3$
- More soluble iron →→ precipitation begins at a lower pH

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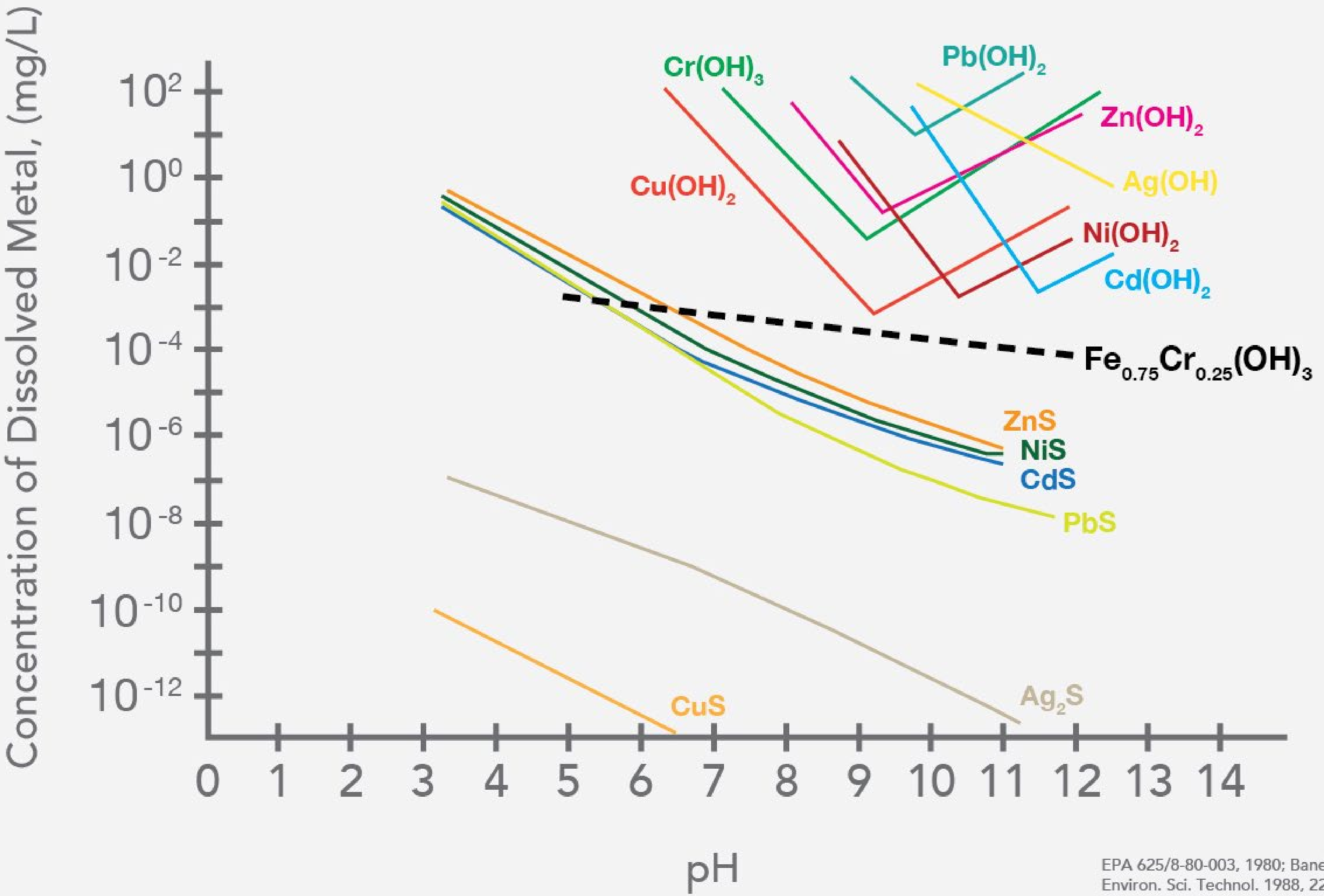
Snoeyink, V.L. and Jenkins, D. 1980. Water Chemistry. John Wiley & Sons. New York

Aqueous Solubility and pH Stability of Heavy Metal Hydroxides, Iron Oxyhydroxides, and Sulfides



EPA 625/8-80-003, 1980; Banerjee et al., 2013. Veolia Water Inc.
Environ. Sci. Technol. 1988, 22, 972-977

Heavy Metal Precipitate Solubilities as Sulfides, Carbonates, & Hydroxides

Table 2-1
Theoretical Solubilities of Hydroxides, Sulfides, and Carbonates of Selected Metals in Pure Water at 25°C (All Units are mg/L)

Metal	*As Hydroxide*	*As Sulfide*	*As Carbonate*
Cadmium (Cd^{2+})	2.3×10^{-5}	6.7×10^{-10}	1.0×10^{-4}
Chromium (Cr^{+3})	8.4×10^{-4}	No precipitate	—
Cobalt (Co^{2+})	2.2×10^{-1}	1.0×10^{-8}	—
Copper (Cu^{2+})	2.2×10^{-2}	5.8×10^{-18}	—
Iron (Fe^{2+})	8.9×10^{-1}	3.4×10^{-5}	—
Lead (Pb^{2+})	2.1	3.8×10^{-9}	7.0×10^{-3}
Manganese (Mn^{2+})	1.2	2.1×10^{-3}	—
Mercury (Hg^{2+})	3.9×10^{-4}	9.0×10^{-20}	3.9×10^{-2}
Nickel (Ni^{2+})	6.9×10^{-3}	6.9×10^{-8}	1.9×10^{-1}
Silver (Ag^{+})	13.3	7.4×10^{-12}	2.1×10^{-1}
Tin (Sn^{2+})	$1.1. \times 10^{-4}$	3.8×10^{-8}	—
Zinc (Zn^{2+})	1.1	2.3×10^{-7}	7.0×10^{-4}

Note Pb and Zn hydroxides versus sulfides. **EPA 625/8-80-003, 1980**

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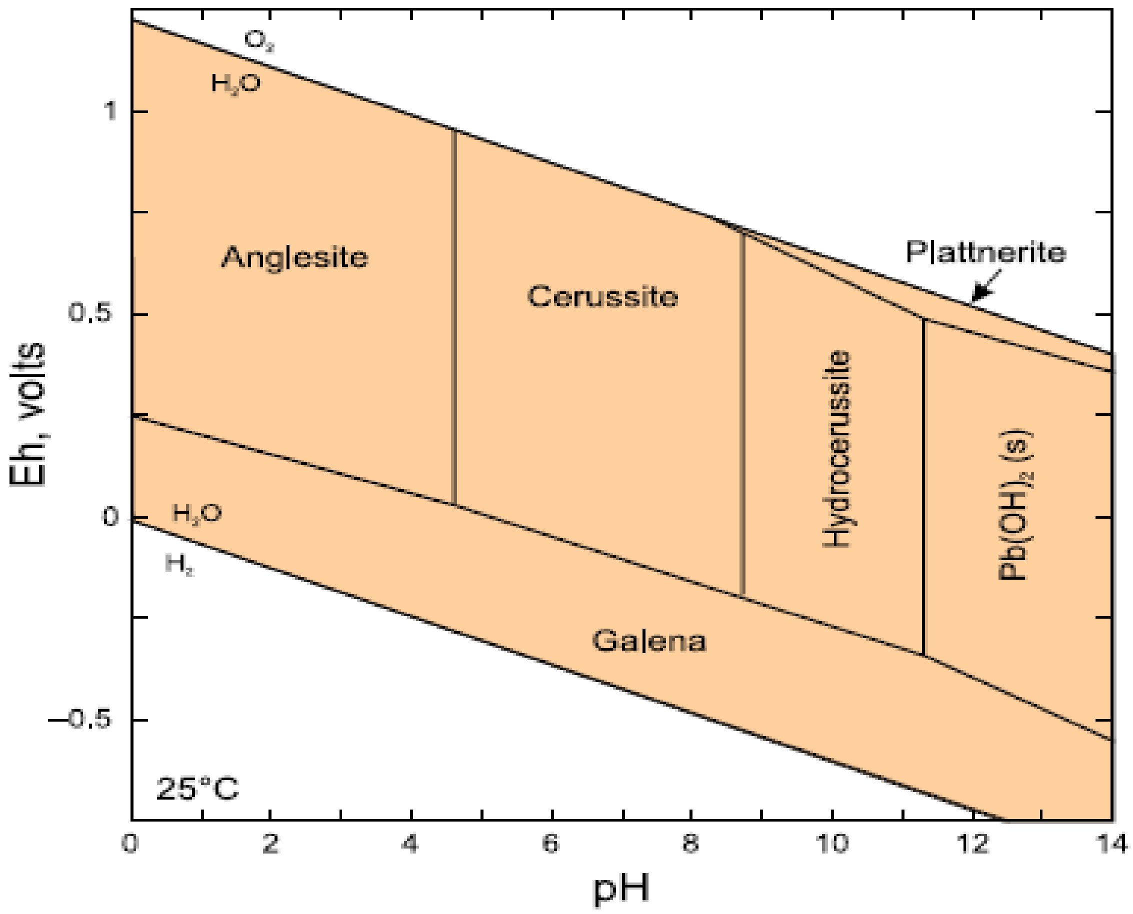
Eh-pH Diagram for Pb in Groundwater with Sulfate



US EPA, 2007. Monitored Natural Attenuation of Inorganic Contaminants in Ground Water. Volume 2. Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium. EPA/600/R-07/140.

Mineral Precipitate	Solubility (µg/L)
Lead Hydroxide $Pb(OH)_2$	2,100
Anglesite $PbSO_4$	30,260
Cerussite $PbCO_3$	7.0
Galena PbS	3.8×10^{-6}
Hydroxypyromorphite $Pb_5(PO4)_3OH$	37 (est.)
MCL	50

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Iron-based Treatment of Cr^{+6}

- Reduction of Cr^{+6} to Cr^{+3} by ZVI is followed by its precipitation as mainly mixed Fe-Cr oxyhydroxides with a mineral structure near goethite (α-FeOOH) with some Cr^{+3} also deposited into a hematite-like structure (Fe_2O_3).[1,2]
- Solubility of Fe-Cr-oxyhydroxides is less than 0.05 µg/L over a broad pH range of 5.0 to 12.0[3]

$$Fe^0_{[solid]} + CrO_4^{2-} + 8\,H^+ \longrightarrow Cr^{+3} + Fe^{3+} + 4\,H_2O \qquad (1)$$

$$(1-x)\,Fe^{3+} + (x)\,Cr^{3+} + 4\,H_2O \longrightarrow Fe_{(1-x)}Cr_{(x)}OOH_{[solid]} + 3\,H^+ \qquad (2)$$

- The Fe-Cr oxide which has the form of hematite (Fe_2O_3) is primarily deposited on the surface of precipitates[2]

1. Blowes et al., 2000. J. Contam. Hydrol. 45: 123-137
2. Tratnyek et al., 2003. In: Tarr, M. Chemical Degradation Methods for Wastes and Pollutants
3. Eary and Rai. 1988. Env. Sci. Technol. 22:972-977.

Solubility of Mixed Fe-Cr Oxyhydroxides

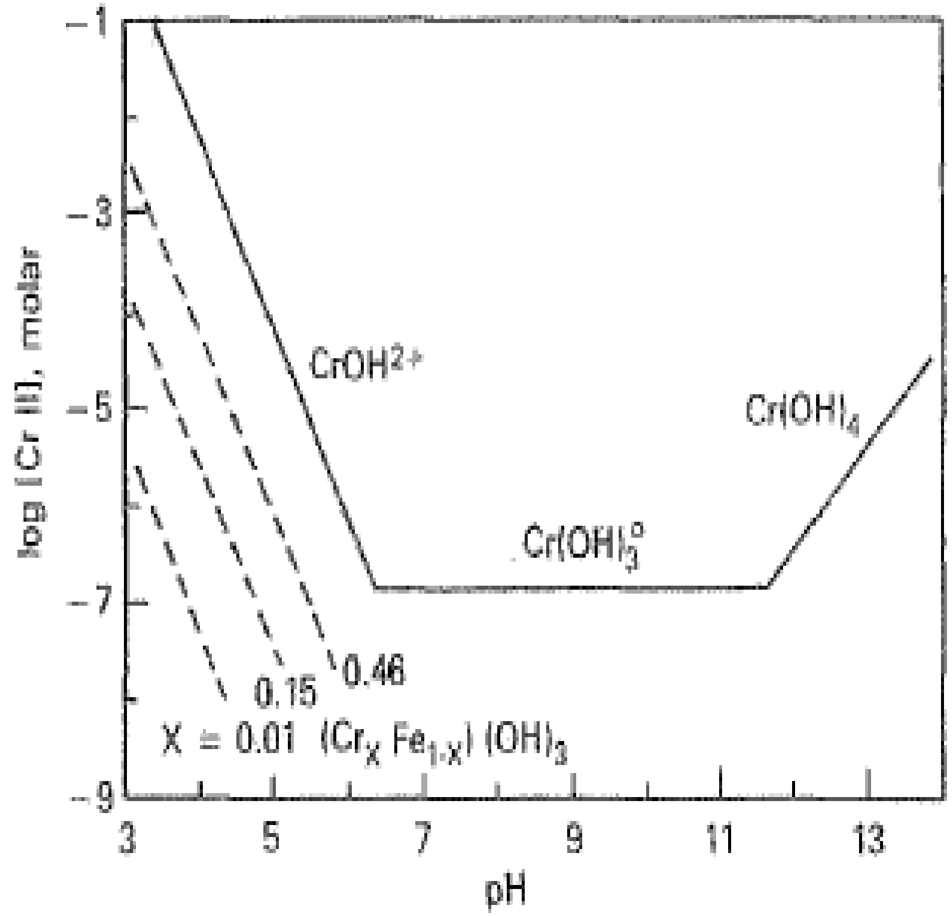


Fig. 3. Solubility-controlling solids of Cr(III). Solid line represents $Cr(OH)_3$. Dashed lines represent $(Cr,Fe)(OH)_3$ at different values of $Cr(OH)_3$ mole fractions (x).

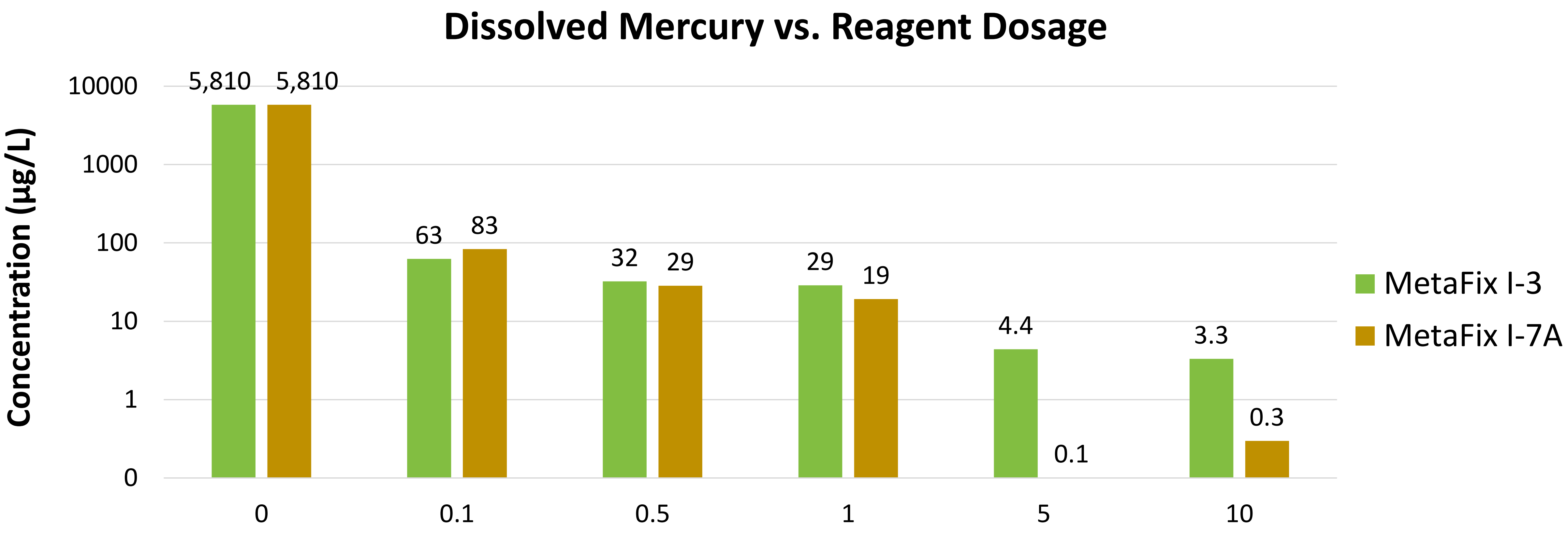
- ✓ Reduction of Cr(VI) to Cr(III) by Fe^{+2} is rapid (minutes)
- ✓ The main product is a mixed Fe-Cr oxyhydroxide
- ✓ Precipitates with more Fe/less Cr have lower solubilities
- ✓ All are much less soluble than $Cr(OH)_3$ and have solubility well below most remedial standards for groundwater
- ✓ The free energy of formation for Fe-Cr oxyhydroxide is lower than that for $Cr(OH)_3$, so it will be preferentially formed when free Fe^{+2} is available

Rai et al., 1989. Sci. Tot. Env. 86:15-23.

MetaFix® Treatability Testing

- Cost-effective way to optimize treatment before starting larger scale treatment
- Completed quickly: usually in 2 -3 weeks after receipt of groundwater and/or soil samples
- Identify most effective reagent
- Provide estimate of required dosage
- Determine need for supplemental pH adjustment
- Potential need for custom formulation

MetaFix® Treatability Testing



- Positive dosage response for both MetaFix® reagents
- Excellent removal of Hg even at dosage as low as 0.1% w/w
- Higher removal efficiency for I-7A formulation: → Better removal of organic forms of Hg?

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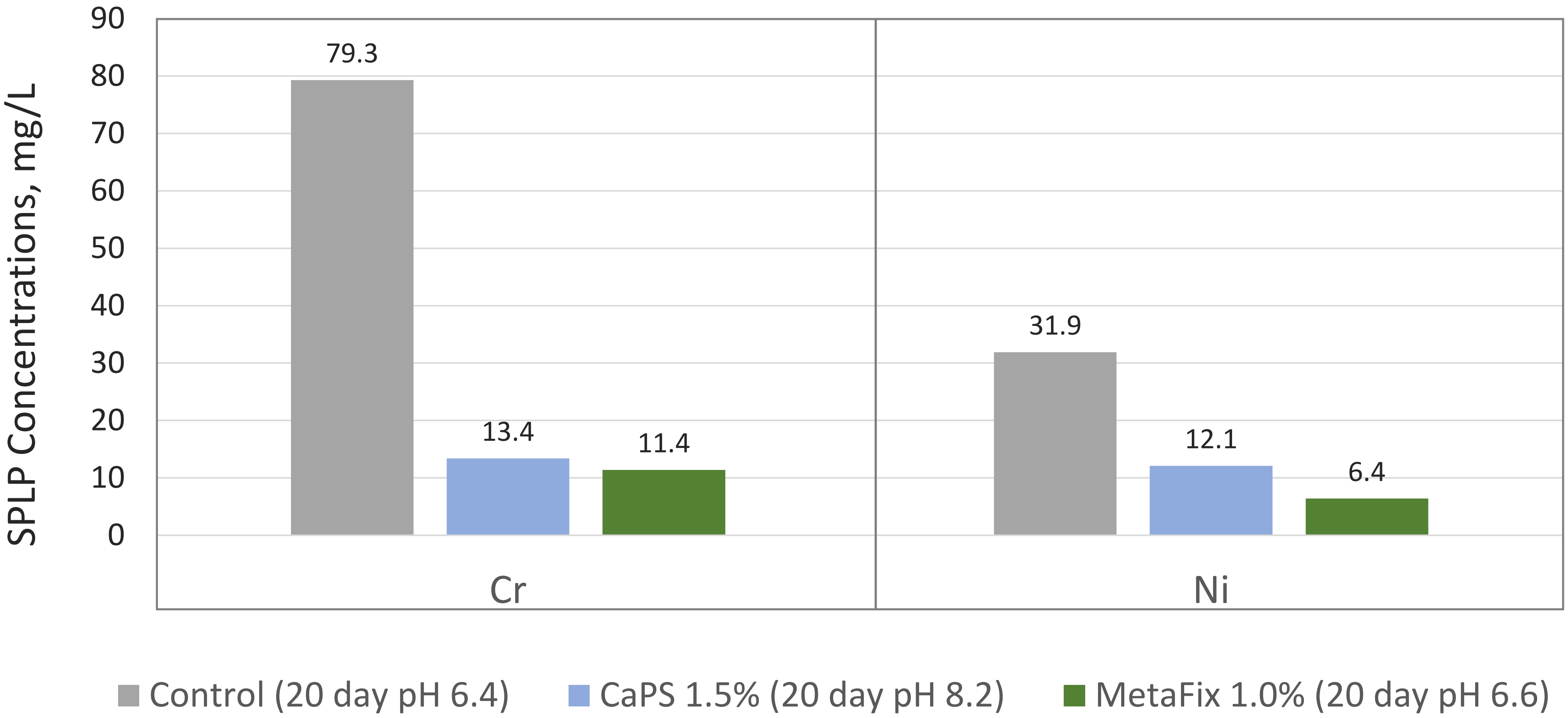
Comparative Performance of MetaFix® and CaSx
(SPLP chromium and nickel in soil/groundwater slurry)



Reagent Dosing, wt/wt% and pH after 20 Days of Treatment

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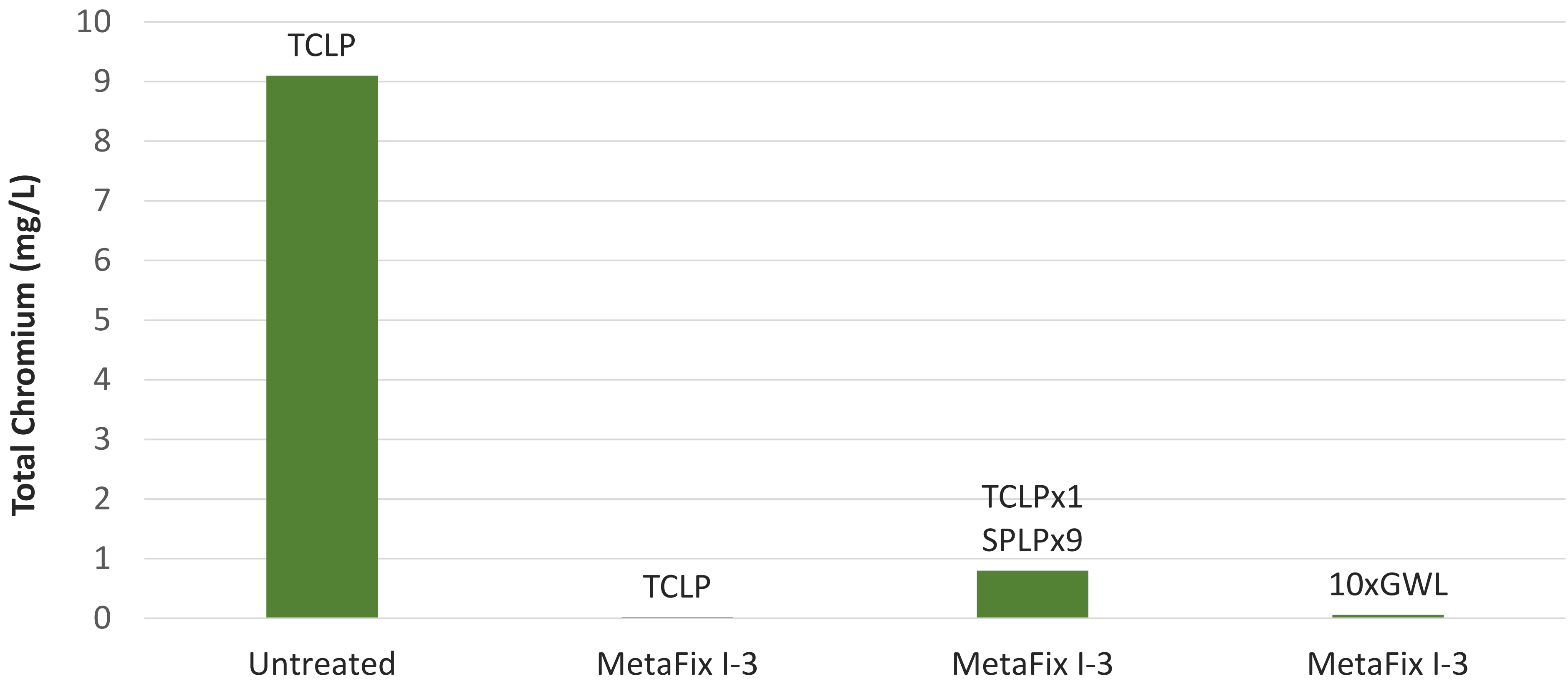
Independent Test Results from Professor D. Cassidy, WMU., D. Gray AECOM. 2014

Stability of MetaFix® Mineral Precipitates



Independent Laboratory US EPA Multiple Extraction Protocol
Values are 9.02, 0.02, 0.80, and 0.06 mg/L

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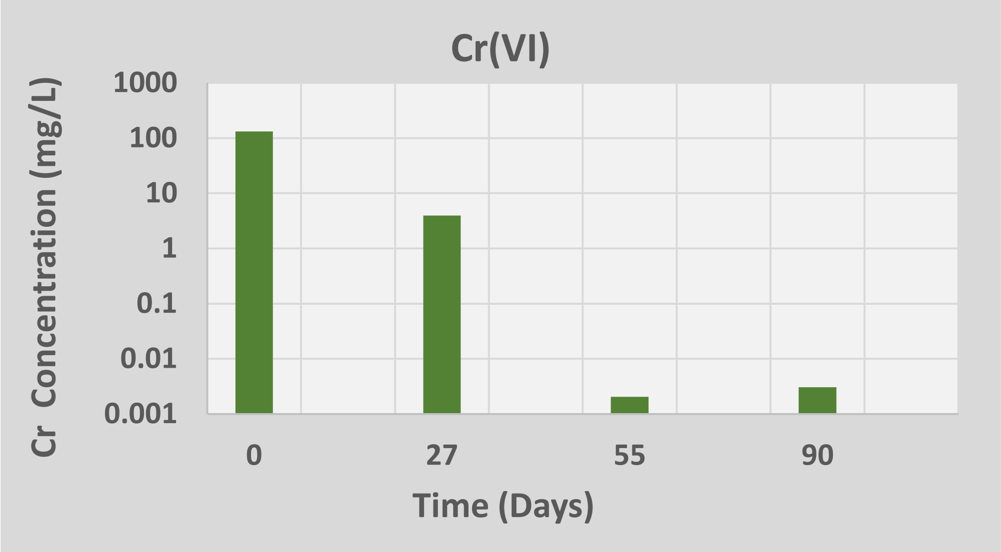
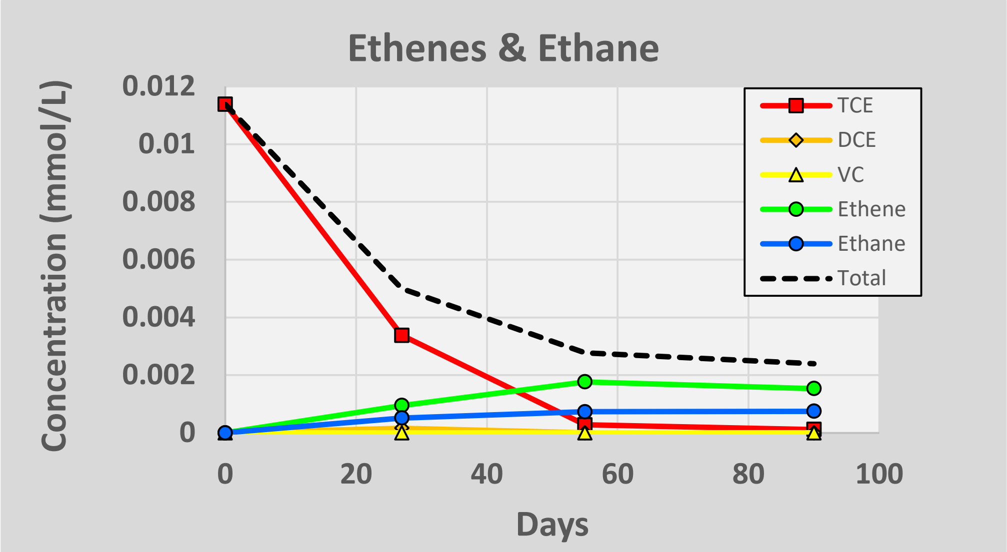
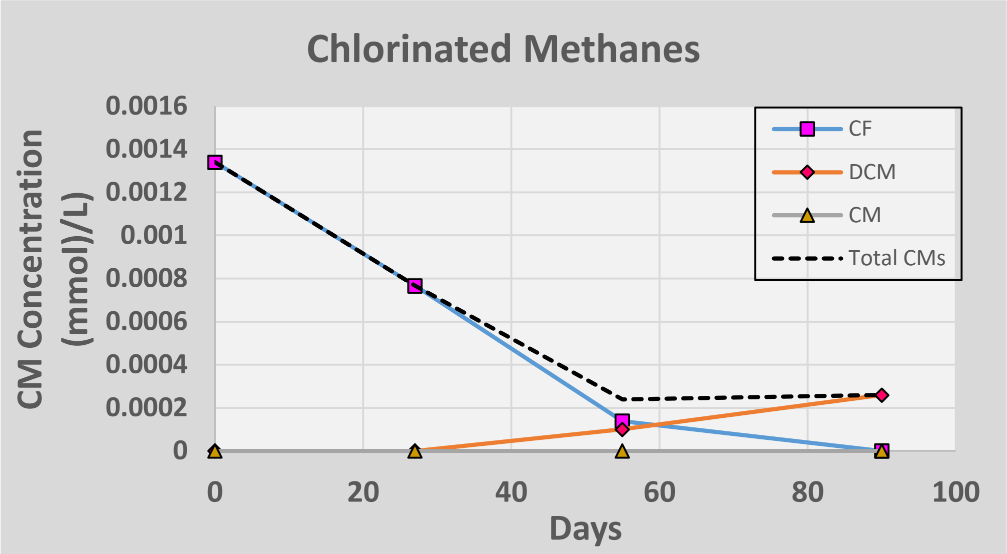
MetaFix® Treatment of Chromium, TCE, and CF in Groundwater





- Effective treatment of heavy metals and chlorinated solvents can be challenging
- MetaFix® reagents allow simultaneous treatment of both metals and cVOCs
- ✓ Cr^{+6} reduced from 132 mg/L to 0.003 mg/L
- ✓ TCE and CF removed with very little accumulation of breakdown products
- ✓ Note production of ethene and ethane



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MetaFix® + EHC® Plus Treatment of Heavy Metals, Cyanide, cVOCs, and Fluorinated Organics

Influence of MetaFix® + EHC® Plus treatment on concentrations of Cr^{+6}, As, Se, TCE, Cyanide, PFOA, and PFOS in groundwater (14 days treatment).

Analyte	Treatment Control	MetaFix® I-3 + EHC® Plus (2.0% w/w)	MetaFix® I-3 + EHC® Plus (5.0 % w/w)	Remediation Goal
pH (SU)	8.36	7.01	6.98	---
ORP (mV)	110	100	51	---
Chromium, Hexavalent (µg/L)	268,000	91,000	<10	11
Arsenic (µg/L)	96.1 (J)	1.8 (J)	1.7 (J)	10
Selenium (µg/L)	124 (J)	6.8	<0.79	5
Cyanide, Free (µg/L)	29.6	1.9 (J)	1.4 (J)	5.2
Trichloroethene (µg/L)	221	1.9	0.37 (J)	200
cis-1,2-Dichloroethene (µg/L)	46.7	1.4	0.36 (J)	620
trans-1,2-Dichloroethene (µg/L)	3.2 (J)	<1.1	<1.1	1,500
Chloroethene (µg/L)	13.8	3.3	0.90 (J)	13
Perfluorooctanoic acid (µg/L)	0.0827 (J)	0.0218 (J) / 0.0200 (J)	0.0218 (J)	12
Perfluorooctane sulfonate (µg/L)	3.47 (J)	0.617 (J) / 0.558 (J)	0.467 (J)	0.012
Notes:				
J. Estimated concentration above the adjusted method detection limit and below the adjusted reporting limit				

MetaFix® Case Study #1
PRB Treatment of Mixed Heavy Metals

- Site: Manufacturing facility in Pacific Northwest
- Consultant: Maul Foster & Alongi
- COCs: Mixed heavy metals (aluminum, arsenic, copper) and high alkalinity
- Treatment: Excavation of source area soil combined with MetaFix® permeable reactive barrier(PRB) designed to prevent migration of residual metals into adjacent river
- Application: MetaFix® mixed into to backfill to cover downgradient wall of excavation to form PRB



Case Study #1
PRB Design and Implementation

- Impacted soil was excavated down to 18 ft bgs and removed
- MetaFix® PRB was installed along sheet piling at the downgradient wall of excavation in conjunction with backfilling the excavation with clean soil
- PRB Dimensions: 80 ft long x 3 ft wide x 15 ft thick (from 5 to 20 ft bgs)
- Target Dosage in Soil: 6% by soil mass
- Mass: 24,000 lbs (12 x 1-ton supersacks)

Case Study #1 Site Map

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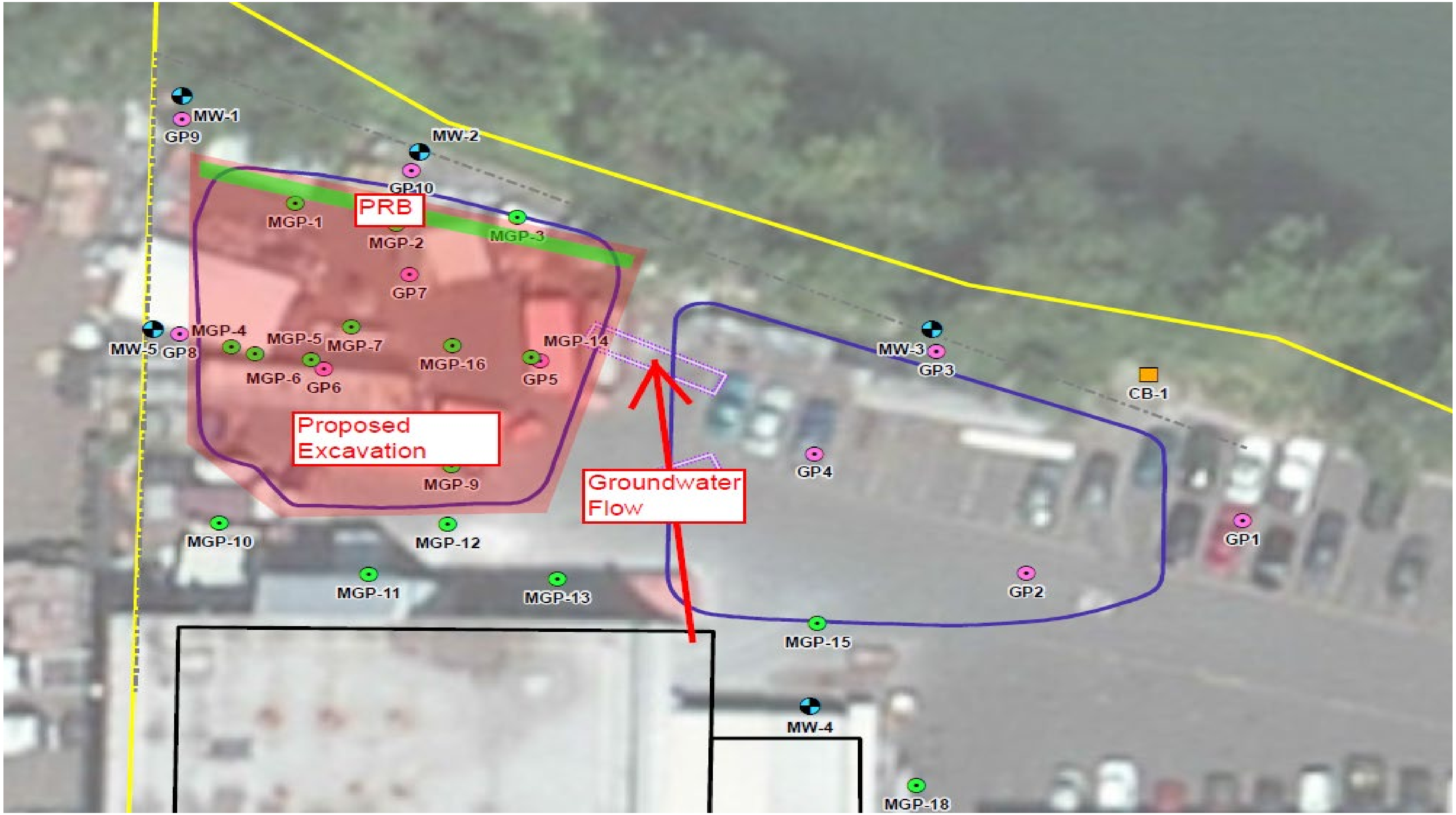
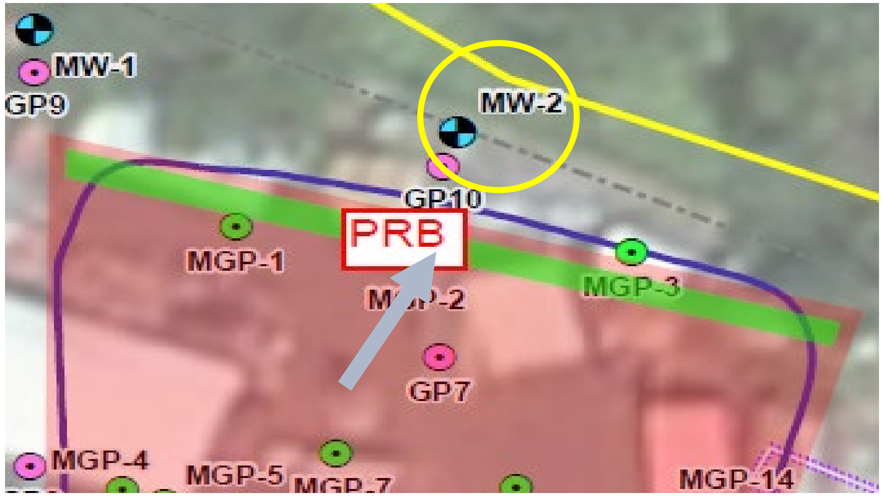


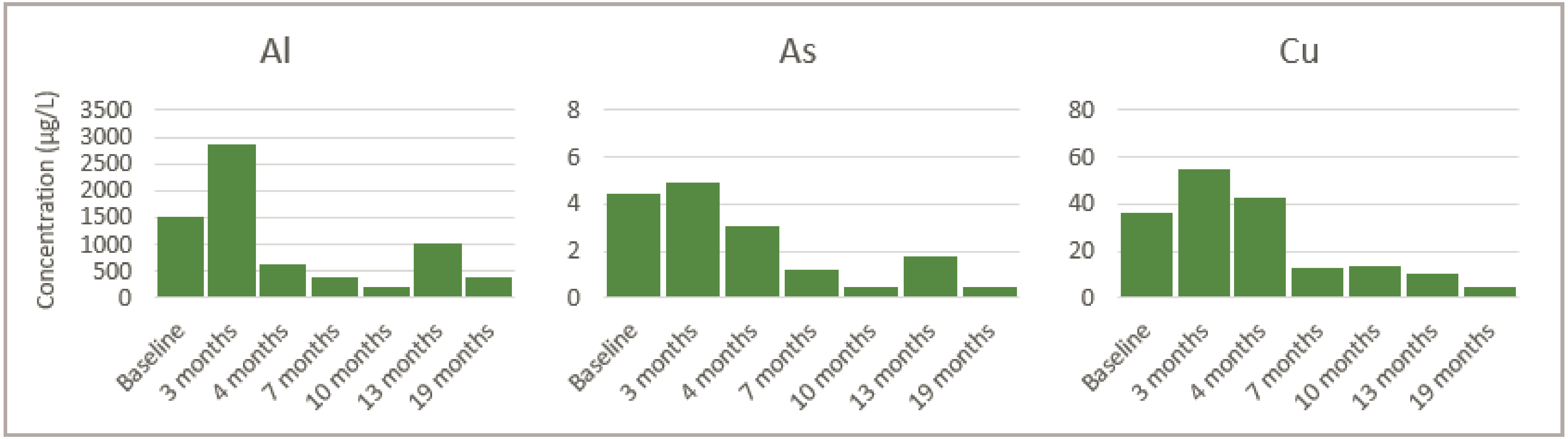
Case Study #1
MetaFix® Installation Simple Soil Mixing with Backhoe

MetaFix® reagent applied in 1.25 ft lifts with 1 supersack per lift and then blended into soil using backhoe

Case Study #1
MetaFix® Performance



- Monitoring data at 3, 4, 7, 13, and 19 months post installation
- Transient post-installation increase presumably due to physical mobilization of metals
- All RGs achieved: Al (750 µg/L), As (2.1 µg/L), and Cu (12 µg/L)



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MetaFix® Case Study #2

- Industrial site in eastern Italy
- Impacts included mercury at up to 400 µg/L and 1,2-dichloropropane at up to 1.0 µg/L
- Bench-scale testing was conducted to determine the most effective MetaFix® reagent
- Also estimate of the required dosage

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Case Study #2
Bench-scale Optimization for Soluble Mercury in Groundwater

Influence of MetaFix® reagent and dosage on leachable mercury.

Soil (g)	Groundwater (mL)	MetaFix® Reagent	Dose (%w/w)	Final ORP (mV)	Final pH (SU)	Leachable Hg (µg/L)	Reduction[1,2] (%)
10.0	200	Control	-	+273	7.32	1.5	-
10.0	200	I-6A Low	1.0	-226	8.00	0.730	57
10.0	200	I-6A High	2.0	-282	8.20	<0.200	94
10.0	200	I-7A Low	1.0	-233	7.61	<0.200	94
10.0	200	I-7A High	2.0	-277	7.81	<0.200	94

1. Half the method detection limit (MDL) was used to calculate % reduction for results below the MDL.
2. Reduction percentages are in comparison to the Control.

- Testing conducted by Resolution Partners, Madison WI.
- Batch tests using a groundwater to soil ratio of 20:1.
- Reaction time was of 7 days
- Leaching solution was site groundwater
- Complete removal of soluble Hg achieved at lower dosage with I-7A
- Little change in pH
- Substantial drop in ORP

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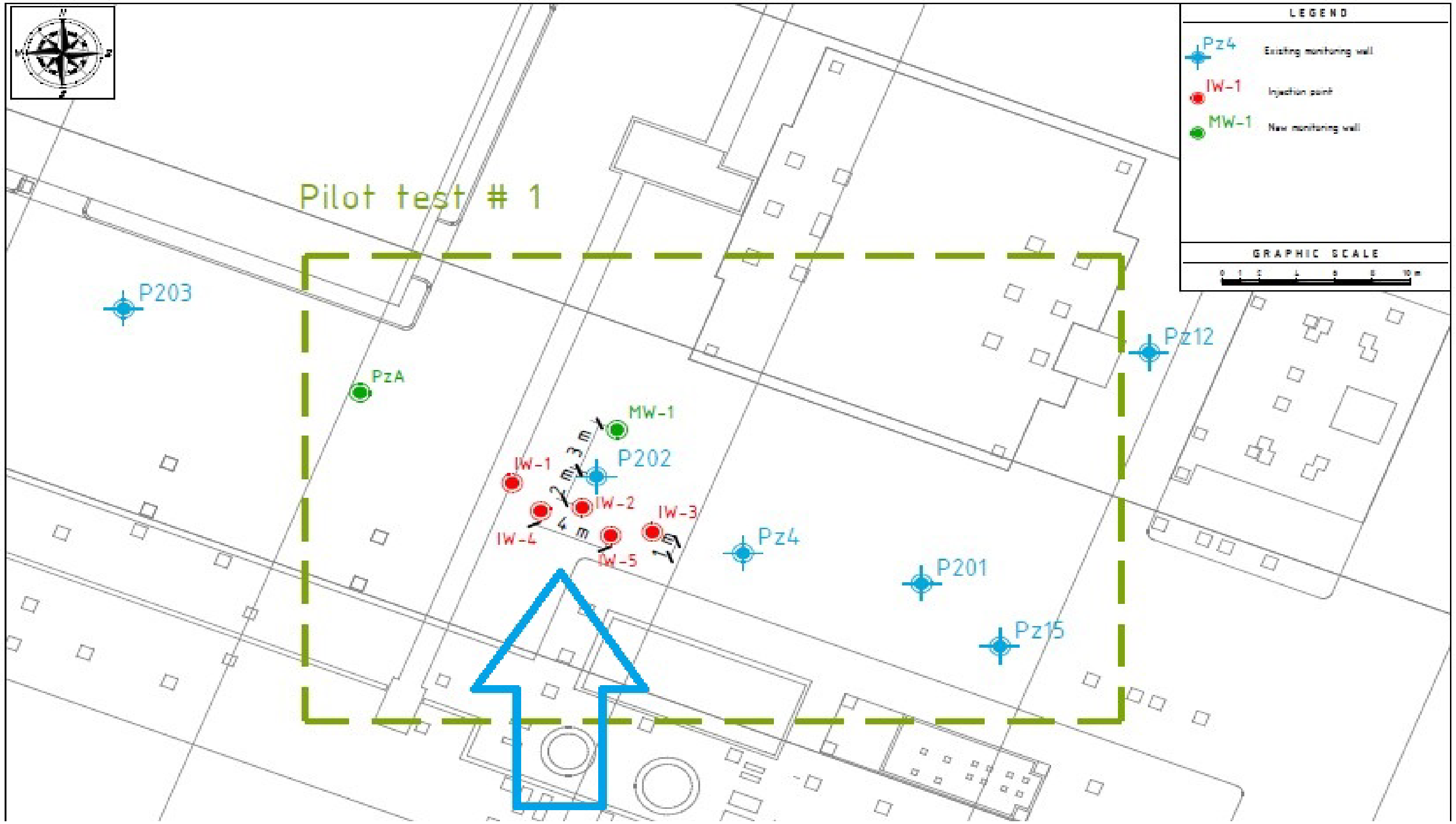
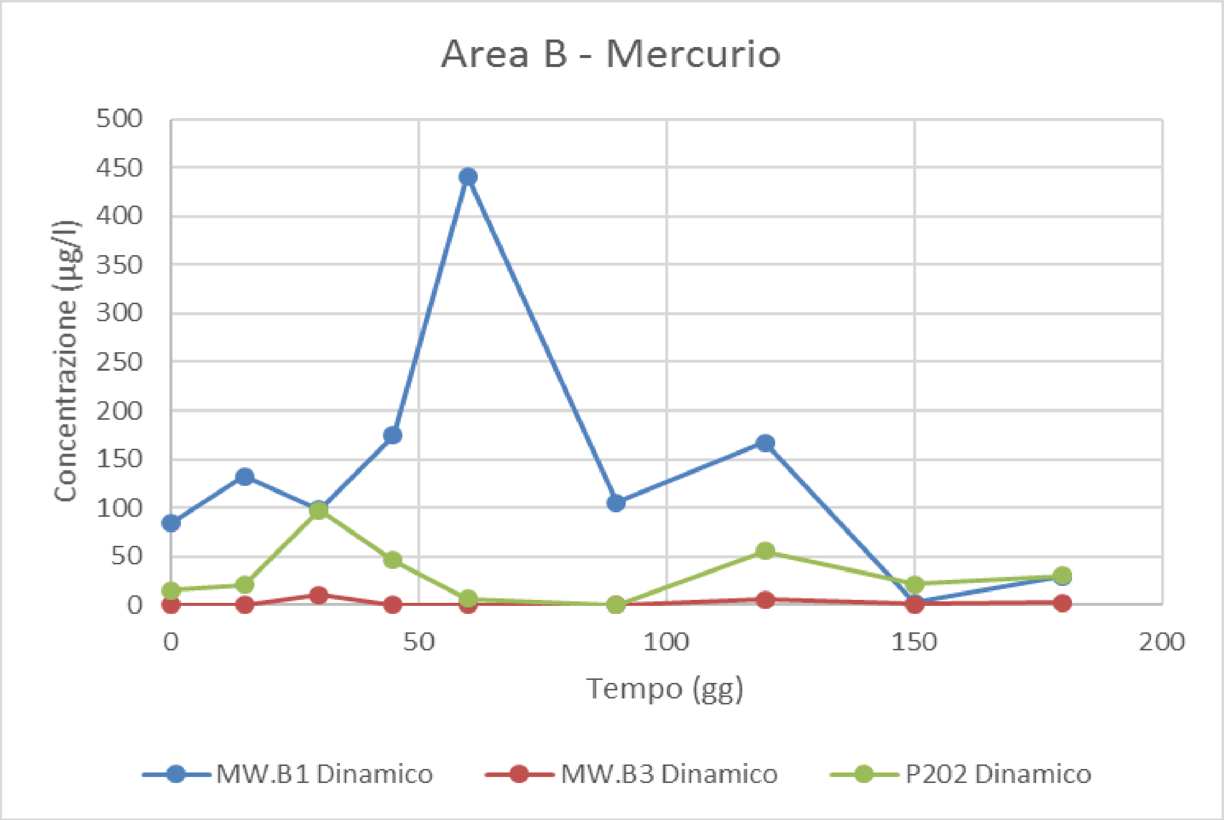
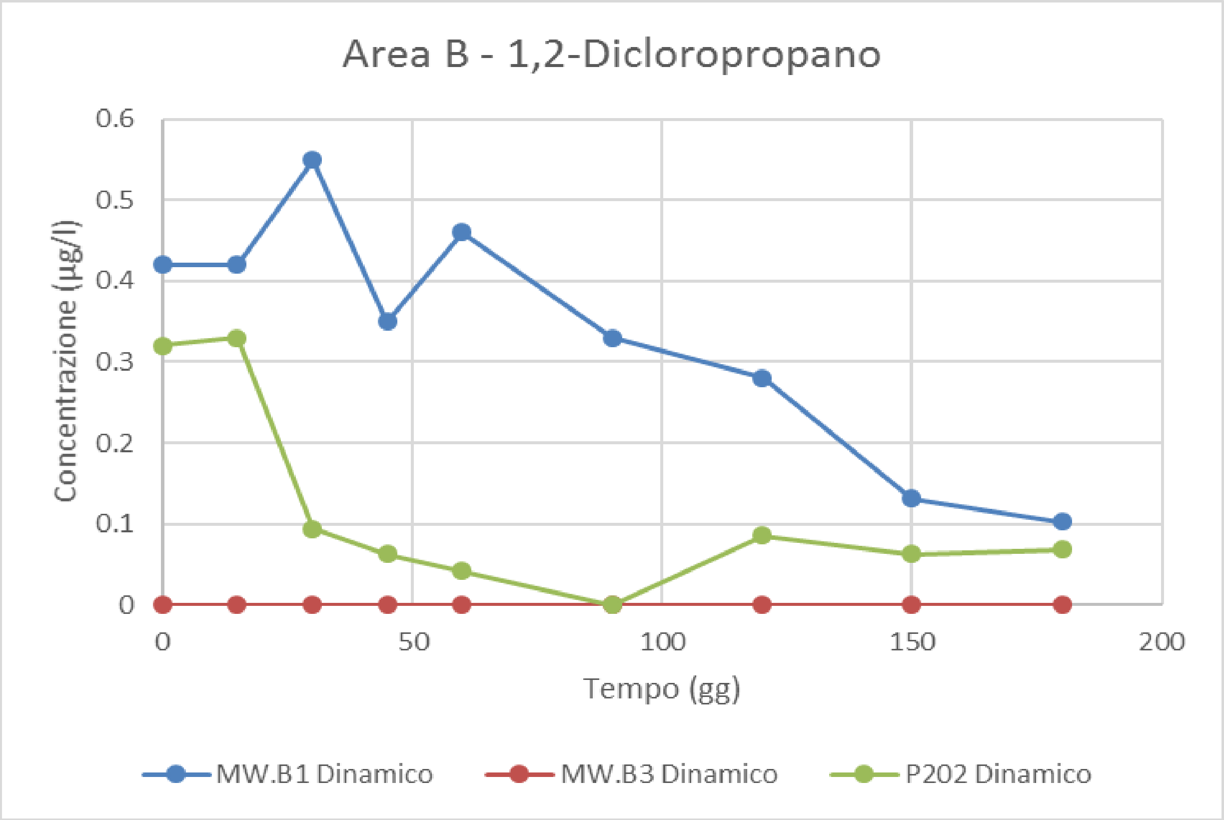
Case Study #2
MetaFix® Treatment of Mercury and 1,2-Dichloropropane



- Reactive zone created with direct push injection
- Low permeability silty sand aquifer at about 12 m bgs
- Targeted zone about 2.0 m thick
- MW1 and P202 re down gradient while MWB3 is cross gradient (and off the map)

Case Study #2
MetaFix® Treatment of Mercury and 1,2-Dichloropropane





- Transient post-injection increase may have been caused by physical release of occluded COI

- Soluble Hg reduced to 2 µg/L at day 150
- RG for Hg is 1 g/L
- 1,2-DCP reduced to below the RG of 0.15 g/L by day 150

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Summary

- Heavy metals are converted into low solubility mineral precipitates, including sulfides, iron sulfides, phosphates, and carbonates
- Simultaneous treatment of heavy metals and chlorinated solvents
- Heavy metal sulfides and iron sulfides have very low solubility and are stable over a broad pH range (reduced susceptibility to rebound)
- Custom-formulations enable successful treatment of even complicated sites
- Low cost treatability screening optimize formulation and confirm required dosage ($2,500)

Thank-you! Questions & Comments?

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