Combining Microbiological, Chemical, and Abiotic Processes for Simultaneous Treatment of cVOCs and Heavy Metals

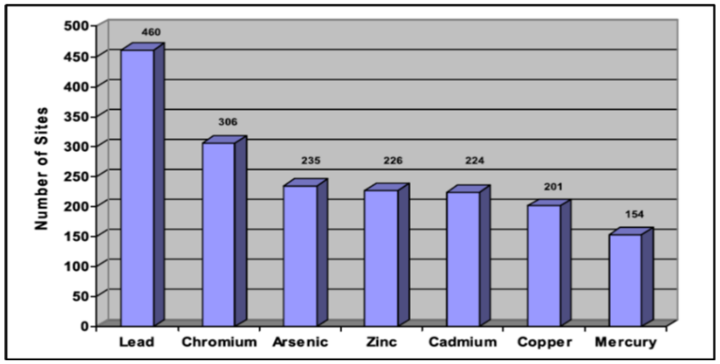
Fayaz Lakhwala and Alan Seech
Evonik Corporation, Piscataway, New Jersey

AEHS Foundation, Inc.
41st Annual International Conference on Soils, Sediments, Water, and Energy
20 – 23 October 2025
Amherst, Massachusetts

EVONIK
Leading Beyond Chemistry

Challenges for In-Situ Remediation of Metals

- Unlike organic contaminants, metals cannot be destroyed.
- Metals exist in a variety of valence states which creates complexity.
- Di-valent metals (Cd, Ni, Pb, Hg etc.) behave differently from metaloids such as As, Cr, Se etc.
- Most metals can be stabilized by chemical reduction; however, the process can also mobilize metals such as Fe, Mn and As.
- Additional analytical tests are needed to understand the geochemistry.
- Groundwater is often contaminated with both heavy metals and chlorinated solvents (CVOCs). Traditional treatments that perform well on metals may not be effective for degradation of CVOCs and vice versa.



Metals most commonly present in all matrices at Superfund Sites (from USEPA, 1996). Approximately 75% of Superfund Sites have some form of metal contamination.

The Opportunity

- Develop an understanding of the mechanisms involved in immobilization of heavy metals, while simultaneously realizing the degradation of chlorinated solvents.
- Understand the limitations of these mechanisms.
- Thereby promote informed decision-making in selecting reagents and treatment methods.

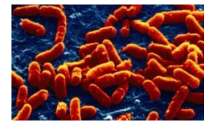
In-Situ treatment of Cr, Ni and Pb at an active industrial facility. Courtesy, TetraTech

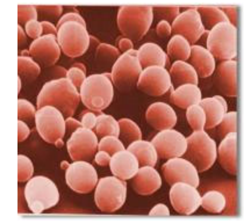
EVONIK Leading Beyond Chemistry

Processes & Mechanisms in Remediation of Dissolved Metals and CVOCs

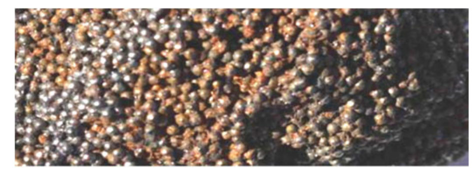
Reductive Biological, Chemical and Biogeochemical Degradation Processes for CVOCs

Reductive Biological Degradation: *Any process that uses fungi and microorganisms with an electron donor to transfer electrons from the relatively reduced reagent to a relatively oxidized contaminant to degrade the contaminant.*





Reductive Chemical Degradation: *Processes where contaminants are treated by transferring electrons from reduced metals (e.g., Zero Valent Iron; ZVI) to relatively oxidized contaminants (e.g., chlorinated organics) to degrade the contaminant.*



Reductive Biogeochemical Degradation: *Processes where CVOCs are treated by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface.*

Pyrite (FeS_2)

Mackinawite ($Fe_{(1+x)}S$

EVONIK Leading Beyond Chemistry

Processes & Mechanisms in Removal of Dissolved Metals

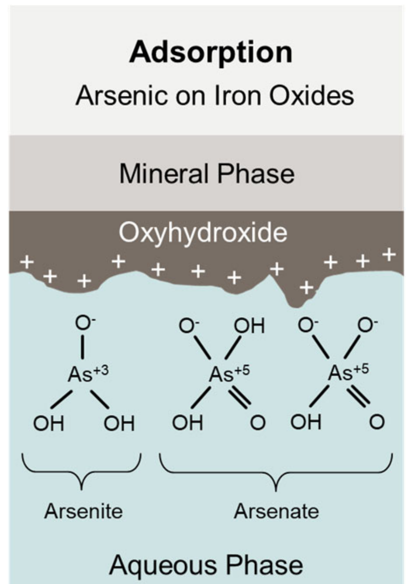
- **Precipitation:** Conversion of a soluble metal into an insoluble form.
- **Co-precipitation:** A form of adsorption in which soluble species are incorporated within a precipitating solid phase.
- **Adsorption:** Binding of a soluble species on the surface of a solid, driven by surface forces/charges.
- **Occlusion:** Encasement of insoluble metals formed by the deposition of insoluble/low solubility layers of other mineral precipitates.
  - physical protection of newly precipitated Cr(III) through precipitation/coprecipitation of iron sulfides and iron corrosion products.
- **Biogeochemical Remediation:** A process that combines physical, chemical, and microbiological mechanisms to remove dissolved metals with biogenically formed minerals.

Reductive Precipitation as Metal Sulfides

$$FeS_{(s)} \rightarrow Fe^{2+}_{(aq)} + S^{2-}_{(aq)}$$

Removal of Arsenic as Arsenopyrite

$$Fe^{2+} + As(OH)_4^- + HS^- \rightarrow \mathbf{FeAsS} + 2.5H_2O + 0.75\ O_{2(aq)}$$



Reduction & Coprecipitation

Removal of Cr(VI) as Iron Chromium Oxyhydroxide

Reduction by ZVI or Ferrous Iron

$$Fe^0_{(s)} + HCrO_4^{2-} + 8H^+ \rightarrow Cr^{3+} + Fe^{3+} + 4H_2O$$

$$3Fe^{2+} + CrO_4^- + 7H^+ \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O$$

Coprecipitation

$$_{(1-x)}Fe^{3+} + {}_{(x)}Cr^{3+} + 4H_2O \rightarrow \mathbf{Fe_{(1-x)}Cr_{(x)}OOH_{(s)}} + 3H^+$$

Eh Range for Reduction of Various Electron Acceptors

Decreasing Amount of Energy Released During Electron Transfer

Aerobic

Oxygen $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \; (Eh^0 = +820)$

Anaerobic

Nitrate $2NO_3^- + 12H^+ + 10e^- \longrightarrow N_{2(g)} + 6H_2O \; (Eh^0 = +740)$

Arsenic (V) $H_3AsO_4 + 2H^+ + 2e^- \longrightarrow H_3AsO_3 + H_2O \; (Eh^0 = +559)$

500

Manganese (IV) $MnO_2(s) + HCO_3 + 3H^+ + 2e^- \longrightarrow MnCO_3\,(s) + 2H_20 \; (Eh^0 = {}^+520)$

Redox Potential (Eh^0)
in Millivolts @ pH = 7 and T = 25^0C

0

Iron [III]FeOOH(s) +HCO$_3$ + 2H+ e$^-$ $\longrightarrow$ *FeCO$_3$ + 2H$_2$0 (Eh^0 = $^-$50)* **Fe[II] in Solution**

PCE ⇨ TCE

TCE ⇨ DCE

DCE ⇨ VC

VC ⇨ Ethene

Sulfate $SO_4^{2-} + 9H^+ + 8e^- \longrightarrow HS^- + 4H_2O \; (Eh^0 = {}^-220)$ **HS$^-$ in Solution**

Optimal range for Dechlorination

Methanogenesis $CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_20 \; (Eh^0 = {}^-240)$

-250

AFCEE, NAVFAC, ESTCP, Principals and Practices, 2004`

EVONIK Leading Beyond Chemistry

Iron-sulfide minerals form, and are stable under ERD/ISCR conditions

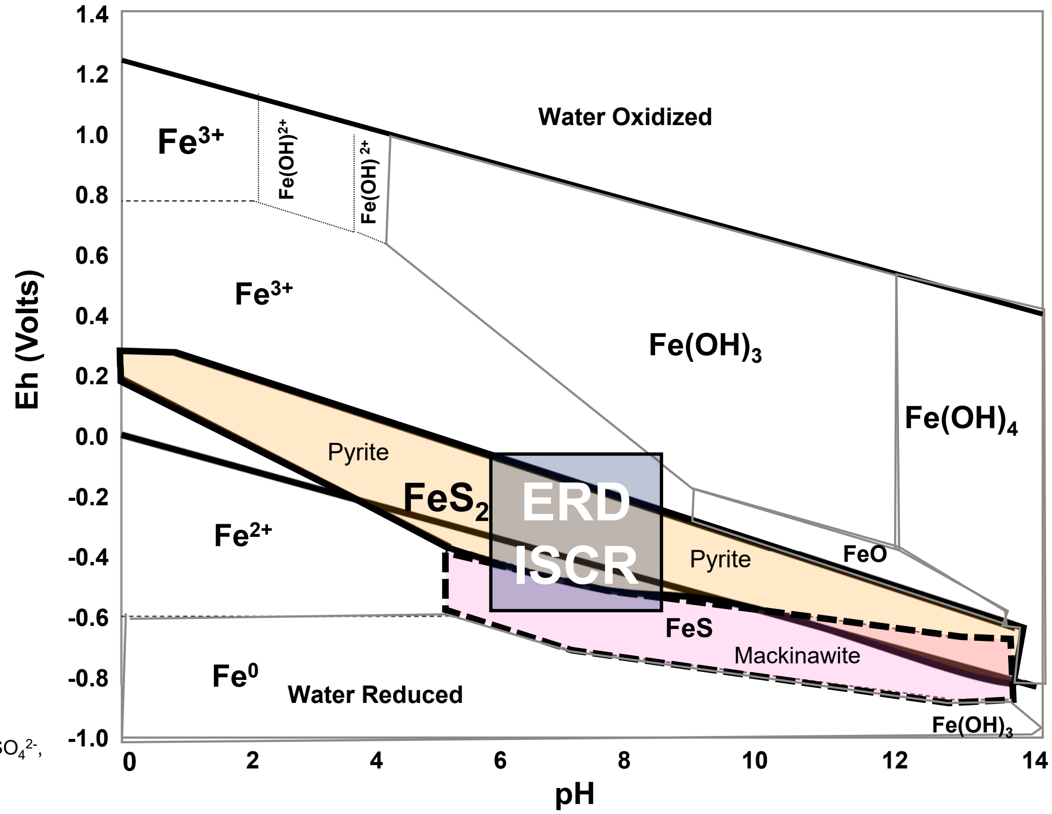
FeS minerals conveniently form, and are stable in the same Eh, pH range as biological reductive dechlorination (ERD) and In Situ Chemical Reduction (ISCR)

Pyrite (FeS_2)

Mackinawite ($Fe_{(1+x)}S$)

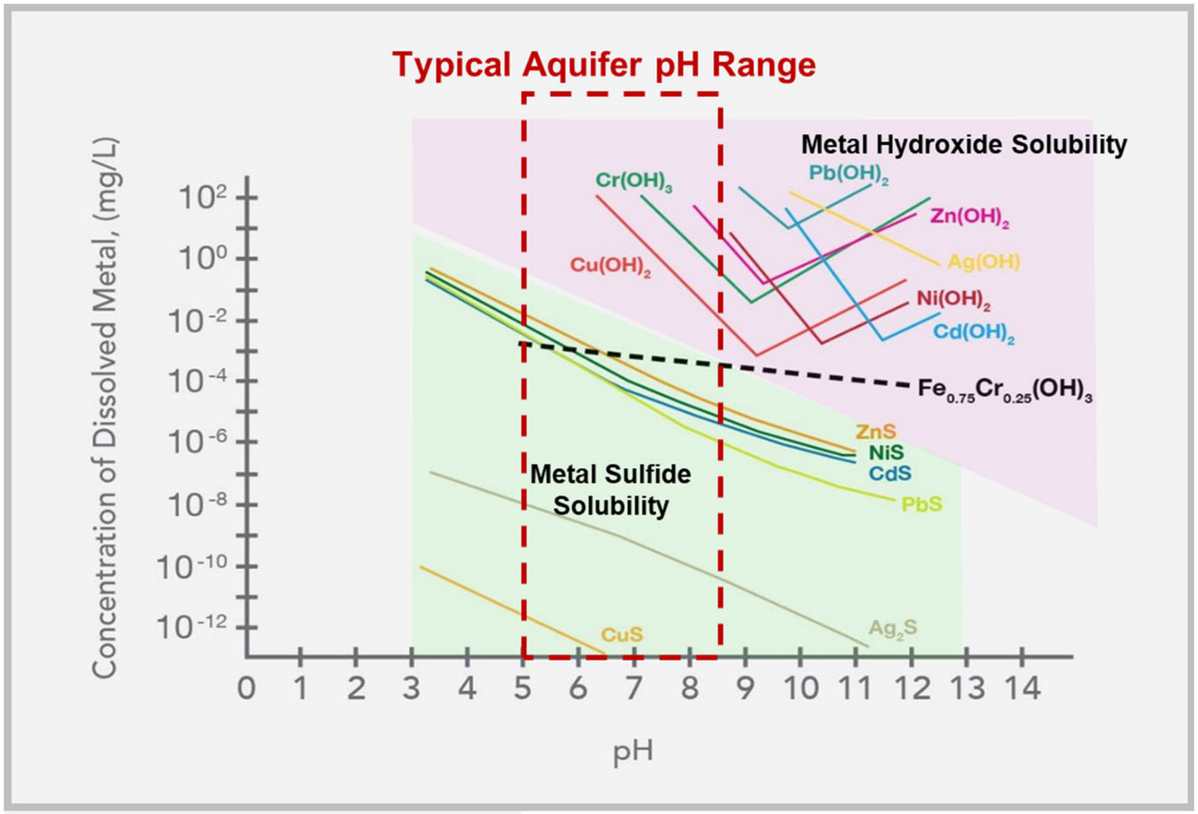
From USGS Water Supply Paper 2254
Fields of stability for solid and dissolved forms of pressure. Activity of sulfur species 96mg/L as SO_4^{2-}, carbon dioxide species 61 mg/L as HCO_3^-, and dissolved iron 56 µg/L

Iron – Sulfur Eh/pH Phase Diagram



Removal of Dissolved Metals

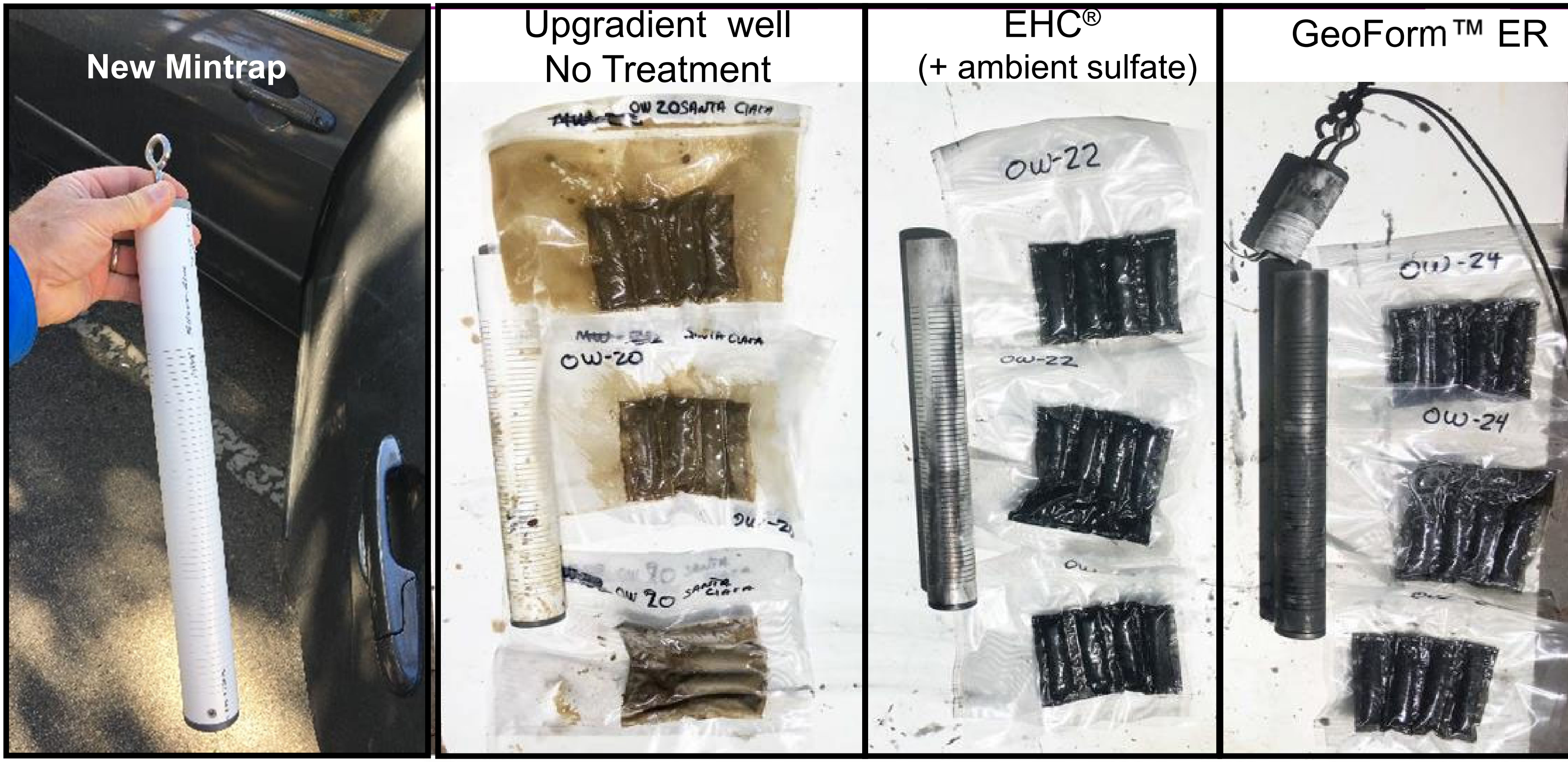
Metal Sulfides *vs* Metal Hydroxides (Lower Solubility & Broader pH Range Stability)



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

Mineral Precipitate	Solubility (µg/L)
Anglesite $PbSO_4$	30,260
Lead Hydroxide $Pb(OH)_2$	2,100
Hydroxypyromorphite $Pb_5(PO4)_3OH$	37 (est.)
Cerussite $PbCO_3$	7
Galena PbS	3.8×10^{-6}
MCL	50

Mintrap™ samples from
EHC® and GeoForm™ ER Application

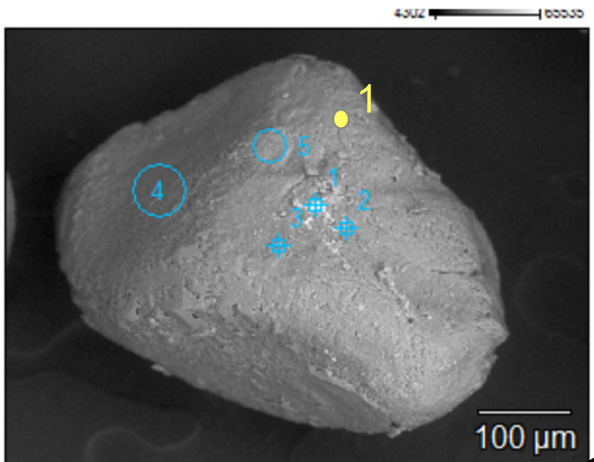


Ulrich, S., Martin Tilton, J., Justicia-Leon, S., Liles, D., Prigge, R., Carter, E., Divine, C., Taggart, D., & Clark, K. (2021). ***Laboratory and initial field testing of the Min-Trap™ for tracking reactive iron sulfide mineral formation during in situ remediation. Remediation. 1–14***. https://doi.org/10.1002/rem.21681

EVONIK
Leading Beyond Chemistry

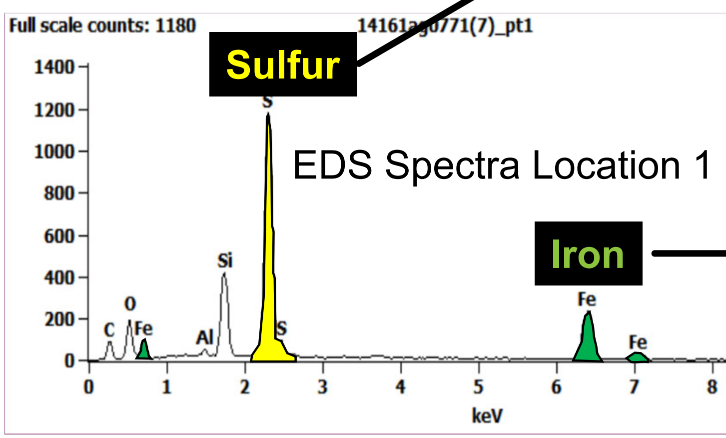
SEM-EDS Results
Following GeoForm™ ER Application

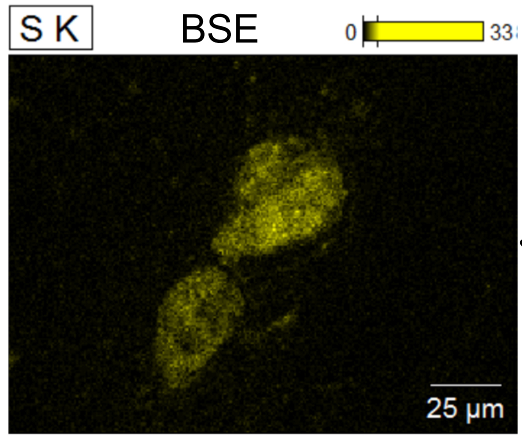
Scanning Electron Microscopy (SEM)-Energy Dispersive Spectroscopy (EDS)



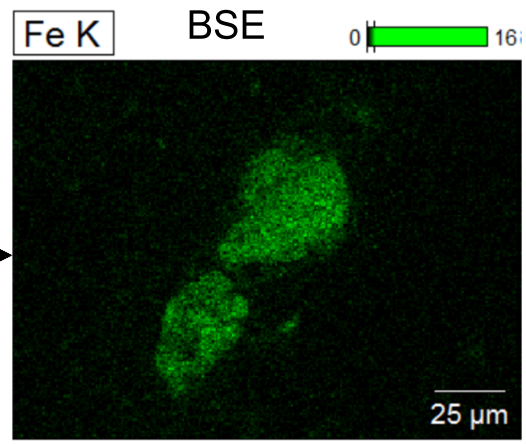
SE EDS Location map

(SE – Secondary Electrons – Show Morphology)

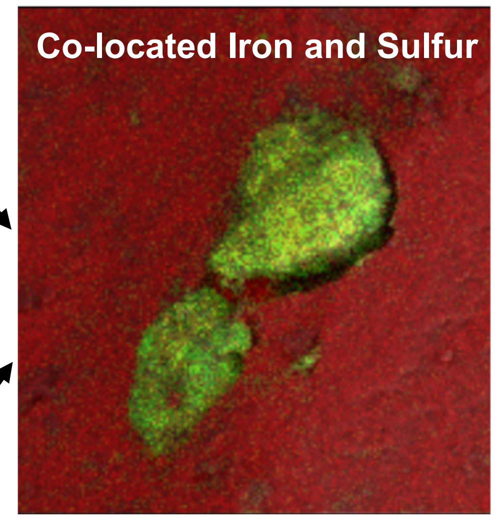




(BSE – Backscatter Electrons)
(Identifies Elements on Surface)



AMIBA Results	
AVS (FeS)	CrES (FeS_2)
51%	49%



X-ray overlay map
red = Si
green = Fe
yellow = S

Treatment Mechanisms for Dissolved Metals and Metalloids

Metal	Adsorption On & Co-precipitation with Iron Corrosion Products	Precipitation as Metal Sulfides/Iron Metal Sulfides	Precipitation as Metal Hydroxides or Iron Metal Oxyhydroxides	Adsorption of organometallic species on activated carbon	Precipitation as Metal Carbonates and Phosphates
As (III, V)	●	●	-	●	-
Cr(VI)	●	-	●	-	-
Pb, Cd, Ni	●	●	●	●	●
Cu, Zn	●	●	●	-	-
Se	●	●	●	-	-
Hg	●	●	-	●	-

EVONIK Leading Beyond Chemistry

MetaFix® and GeoForm® Reagents

MetaFix® Reagents

- Custom blends of ZVI with reactive minerals, carbonates, and adsorbents.
- Track record in treating arsenic, chromium, divalent metals, and mercury.
- Effective under a broad range of pH and Eh conditions.
- Performance not inhibited by high salinity or high acute toxicity.

MetaFix Reagents

GeoForm® Reagents

- Biogeochemical reagents formulated with ZVI, a blend of rapidly and slowly metabolized organic carbon, soluble iron compounds, soluble sulfate, and important nutrients.
- Ensure rapid creation of sulfate reducing conditions.
- Provide long-lasting source of reducing equivalents, ferrous iron, and free sulfide.

GeoForm-ER Reagent

- *Both reagents promote in-situ sulfidation of ZVI which increases the reactivity and longevity of ZVI to treat CVOCs*

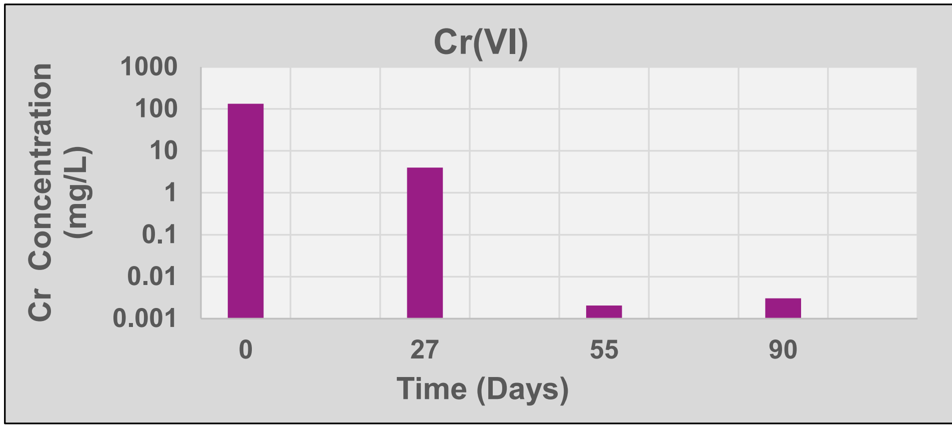
Representative Performance

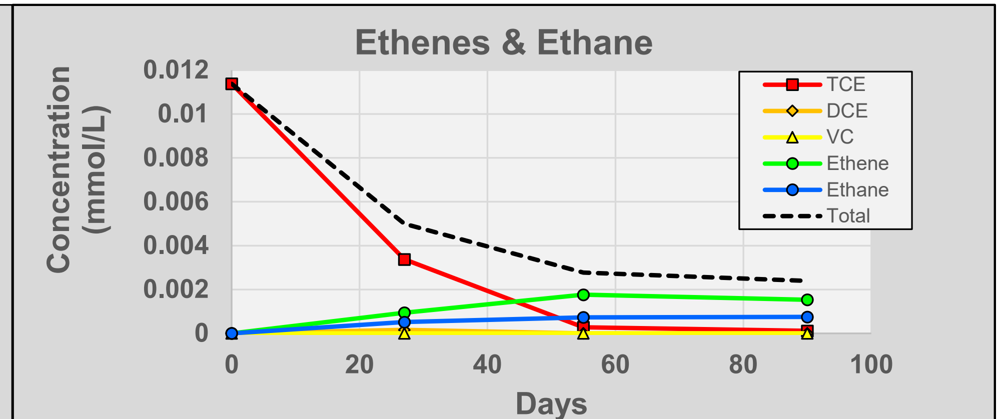
Bench-scale Treatability Results

Field-scale Project Snapshots

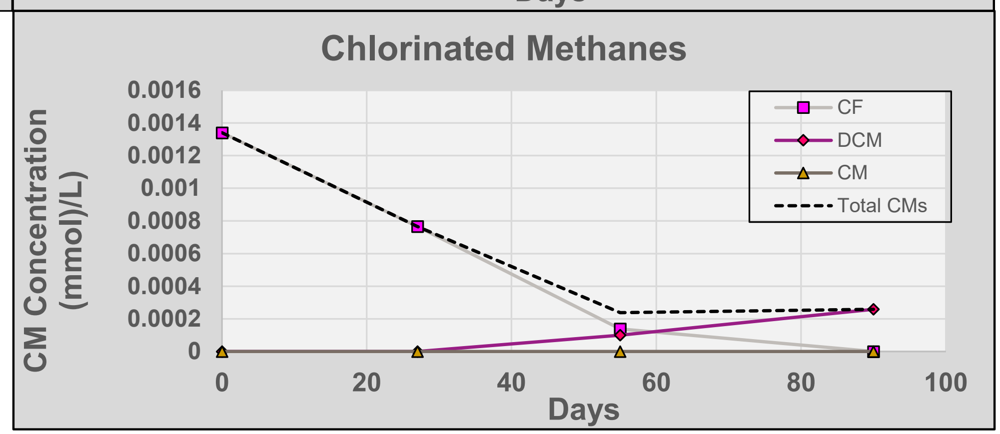
Independent Bench-scale Testing

Treatment of Chlorinated VOCs and Cr(VI)





- MetaFix® reagent used to simultaneously treat both metals and cVOCs
- Cr(VI) reduced from 132 mg/L to 0.003 mg/L
- TCE (1,576 ug/L) and CF (167 ug/L) removed with very little accumulation of typical partial dechlorination products
- Note production of ethene and ethane



Source: Geosyntec, Guelph ON.

EVONIK Leading Beyond Chemistry

Treatability Results - Madison Heights Chromium Site

Glass reaction vessels, 28-day reaction period

Analyte	EP-RW-01-012120	Test 1 Control	Test 2 I-3+EHC Plus (2 wt.%)	Test 3 I-3+EHC Plus (5 wt.%)	Remediation Goal
pH (SU)	6.83	8.36	7.01	6.98	---
ORP (mV)	130	110	100	51	
Chromium, Hexavalent (µg/L)	**302,000**	**268,000**	**91,000**	<10	11
Mercury (µg/L)	**1.2**	<0.084	<0.084	<0.084	0.20
Arsenic (µg/L)	**<167**	**96.1 (J)**	1.8 (J)	1.7 (J)	10
Selenium (µg/L)	**<122**	**124 (J)**	**6.8**	<0.79	5
Cyanide, Free (µg/L)	3.9	**29.6**	1.9 (J)	1.4 (J)	5.2
Trichloroethene (µg/L)	**368**	**221**	1.9	0.37 (J)	200
cis-1,2-Dichloroethene (µg/L)	43.2	46.7	1.4	0.36 (J)	620
trans-1,2-Dichloroethene (µg/L)	<10.9	3.2 (J)	<1.1	<1.1	1,500
Chloroethene (µg/L)	**14.1**	**13.8**	3.3	0.90 (J)	13
Perfluorooctanoic acid (PFOA) (µg/L)	0.0905	0.0827 (J)	0.0218 (J) / 0.0200 (J)	0.0218 (J)	12
Perfluorooctane sulfonate (PFOS) (µg/L)	**20.2 (J)**	**3.47 (J)**	**0.617 (J) / 0.558 (J)**	**0.467 (J)**	0.012

Objectives & Results

- Determine if removal of dissolved Cr(VI) could be achieved at such high initial concentrations.
- Clear dosage response
- Complete removal at 5% w/w
- TCE removal without accumulation of DCE or VC

EVONIK Leading Beyond Chemistry

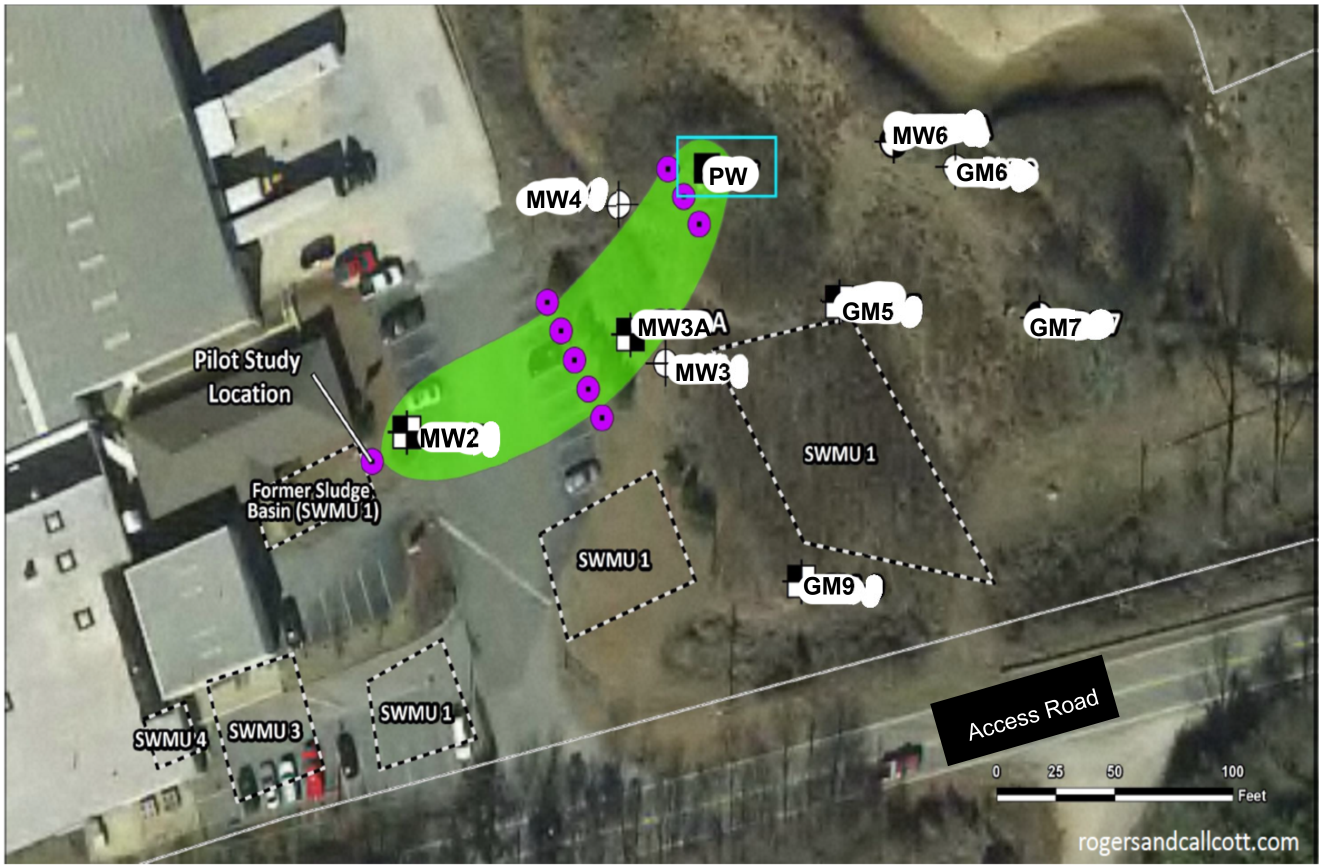
Representative Performance MetaFix® I-7A with GeoForm® ER

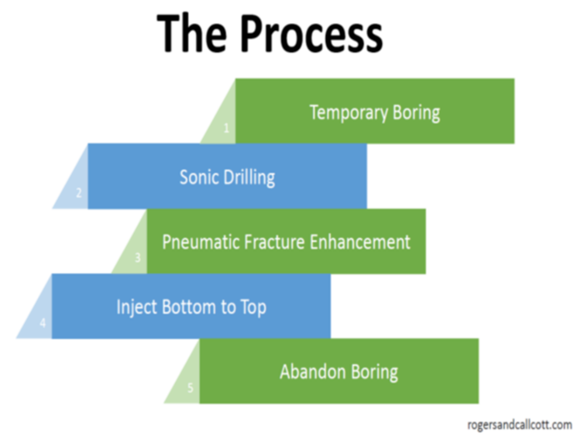
Simultaneous Removal of Dissolved Metals (Cd, Ni, Zn) & cVOCs
Industrial Metal Plating Facility
Southeastern USA

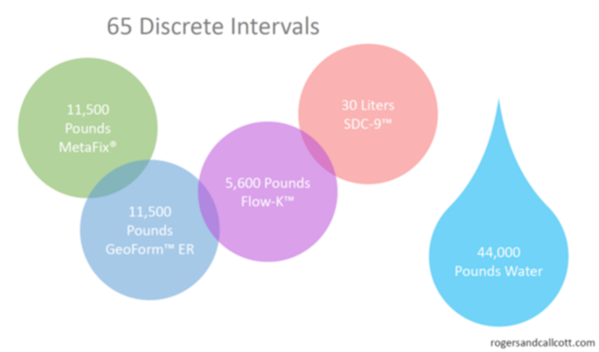
EVONIK
Leading Beyond Chemistry

MetaFix® I-7A + GeoForm® Performance

Full-scale Treatment of Metals and cVOCs



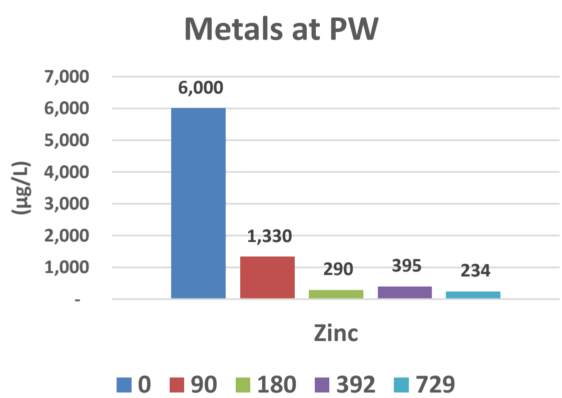


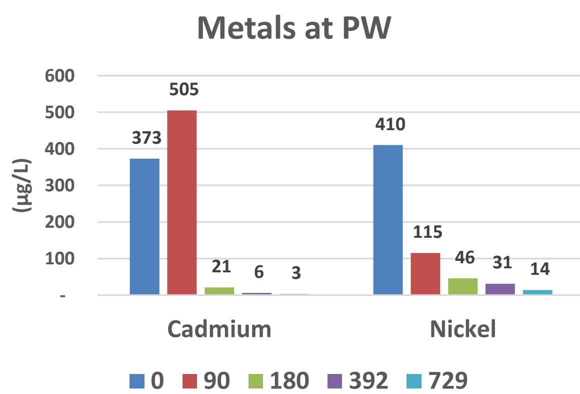


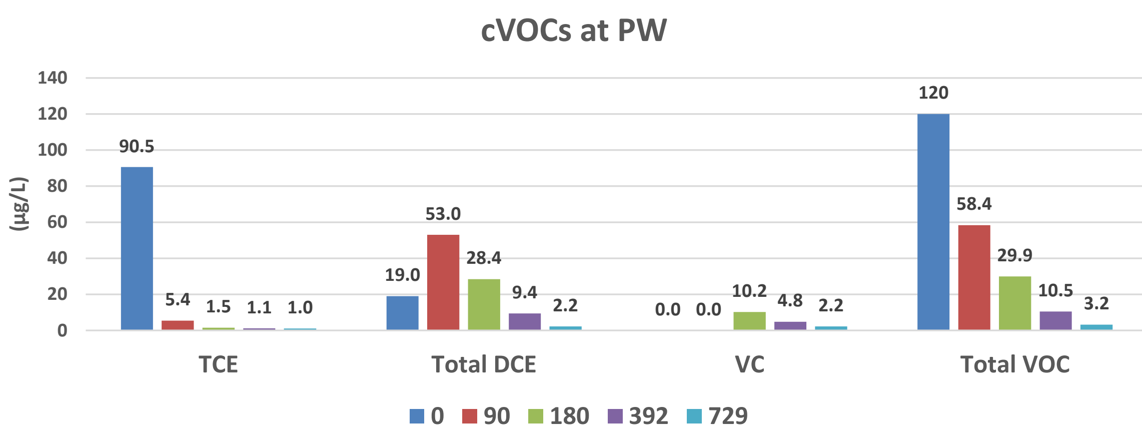
EVONIK Leading Beyond Chemistry

MetaFix® I-7A with GeoForm® ER Project Snapshot

Full-scale Treatment of Metals and cVOCs







Project Summary

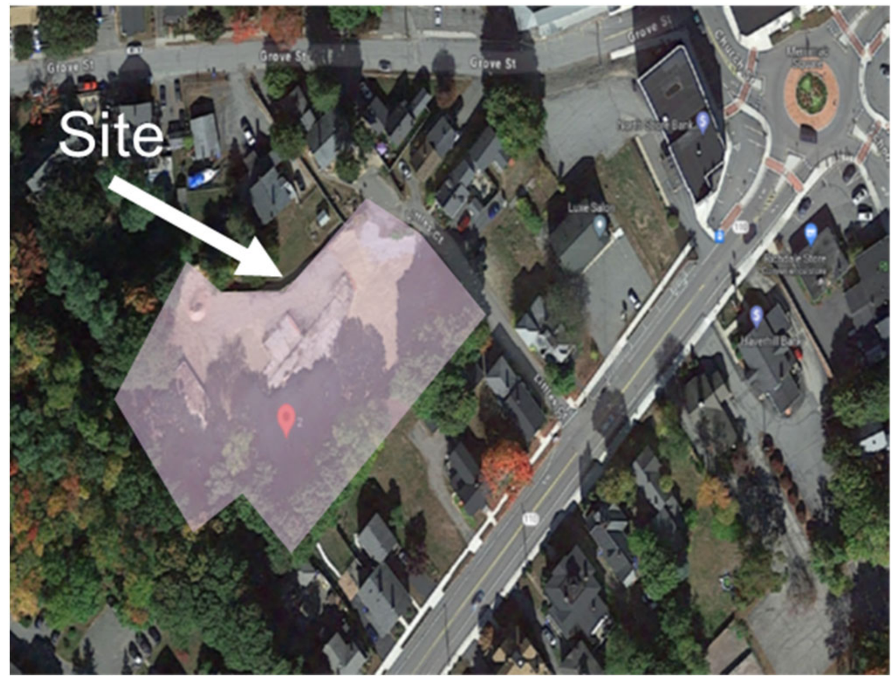
- Low-cost bench-scale treatability testing conducted to ensure effective removal of both metals and cVOCs.
- Pilot-scale demonstration conducted to evaluate injection method and confirm field-scale treatment.
- Full-scale application after evaluation of pilot-scale results.
- Note excellent removal of cadmium, nickel, and zinc.
- Initial increase in cadmium attributed to physical mobilization by high pressure injection.
- Excellent removal of TCE and metabolites.
- Proven ability of our MetaFix® + GeoForm® treatment provides us an important competitive advantage!

EVONIK Leading Beyond Chemistry

Brownfields Redevelopment Site, Merrimac, MA

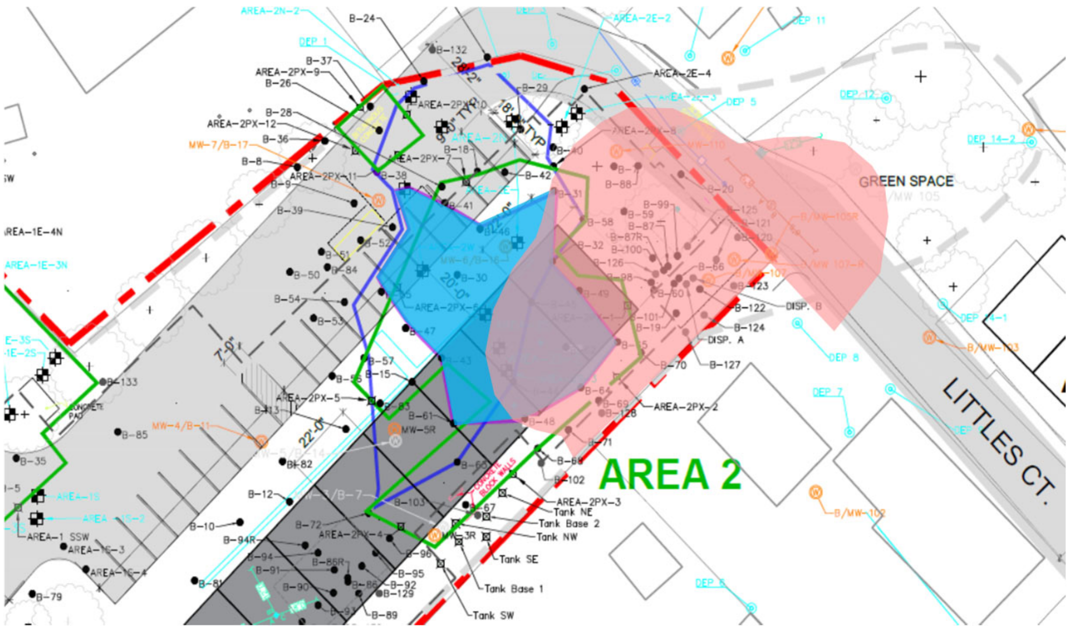
- Coastal Metals Finishing, Inc. operated a plating business in the Town of Merrimac, MA, between 1970 and 2002.
- The town took over the property with the goal of cleaning up and redeveloping it for affordable housing.
- The town was awarded EPA Brownfields Clean Up Grants to remediate chlorinated solvents and heavy metals impacts at the site, and to prevent off-site contaminant migration.

Site Map



- Approximately 1.38-acres
- Surrounded by residential properties

Extents of Leachable Cadmium in Soil and TCE in Groundwater



Groundwater Elevation and Flow Direction

Seepage velocity of 70 ft/yr

Extents of Leachable Cadmium in Soil > 70 mg/kg

Extents of TCE 50 to 1,000 ug/L in GW

Extents of soil excavation

EVONIK Leading Beyond Chemistry

Remediation Plan

Legend

- EHC-M
- GeoForm-S
- GeoForm-ER

Reagents Selected and Application – Oct/Nov 2021

Hot Spot – Central Area	Plume Transects #1-5	Transect #6- Property Boundary
EHC- Metals: slow-release organic carbon, micro-scale zero-valent iron and sulfate.	GeoForm Soluble: Emulsified Lecithin Substrate (ELS™) and a mixture of ferrous iron, sulfate and buffers.	GeoForm ER™ : ZVI, fermentable fibrous organic carbon and sulfate and ferrous iron.
▪ 7,550 lbs of EHC-Metals ▪ 6 L of DHC ▪ 15 injection points ▪ 12-ft spacing	▪ 20,580 lbs of ELS ▪ 3,550 lbs of GeoForm Dry Mix ▪ 43 liters of DHC ▪ 54 injection points ▪ 12-ft spacing	▪ 3,750 lbs of GeoForm ER ▪ 4 L of DHC ▪ 9 injection points ▪ 8-ft spacing

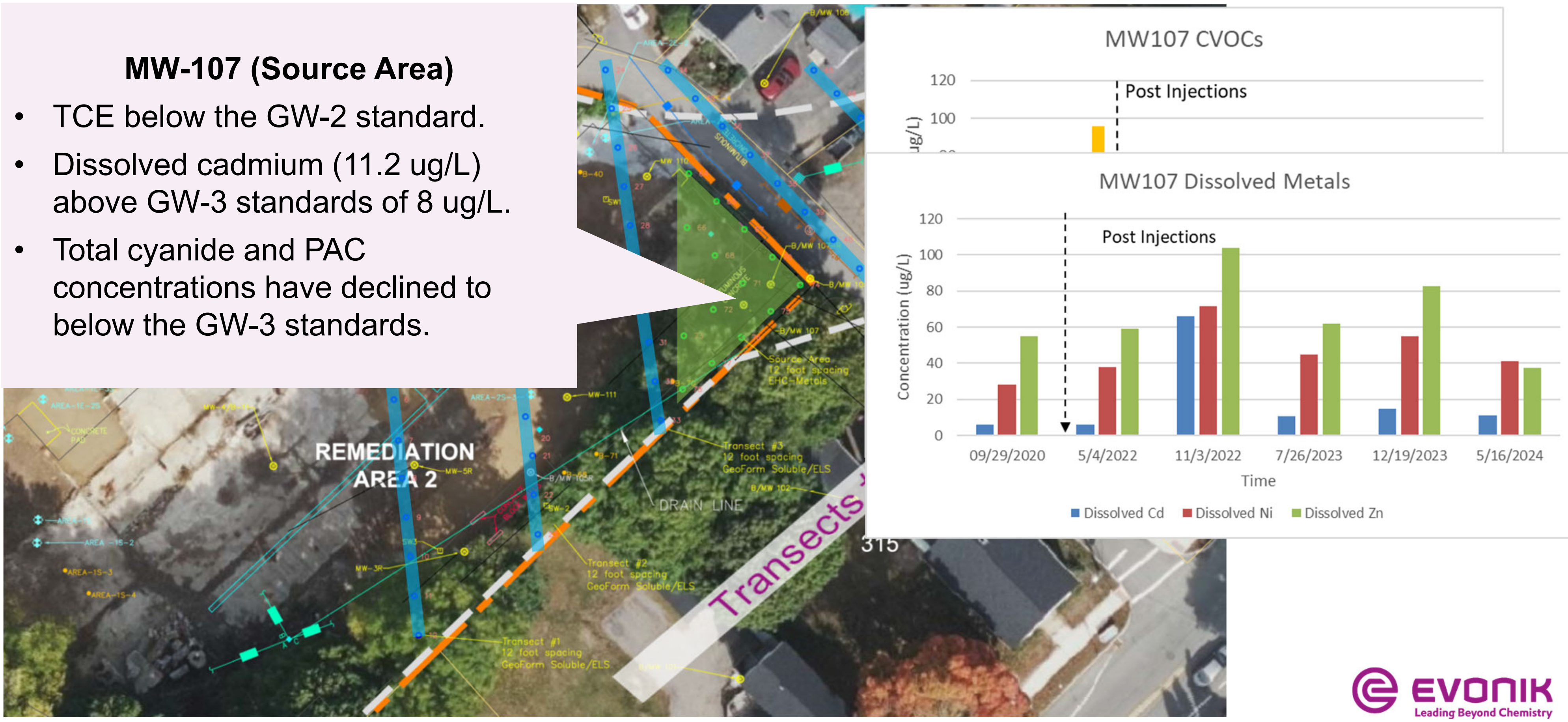
Vertical injection interval was from approx. 3 to 12 ft bgs.

EVONIK Leading Beyond Chemistry

Results as of May 2024

MW-107 (Source Area)

- TCE below the GW-2 standard.
- Dissolved cadmium (11.2 ug/L) above GW-3 standards of 8 ug/L.
- Total cyanide and PAC concentrations have declined to below the GW-3 standards.

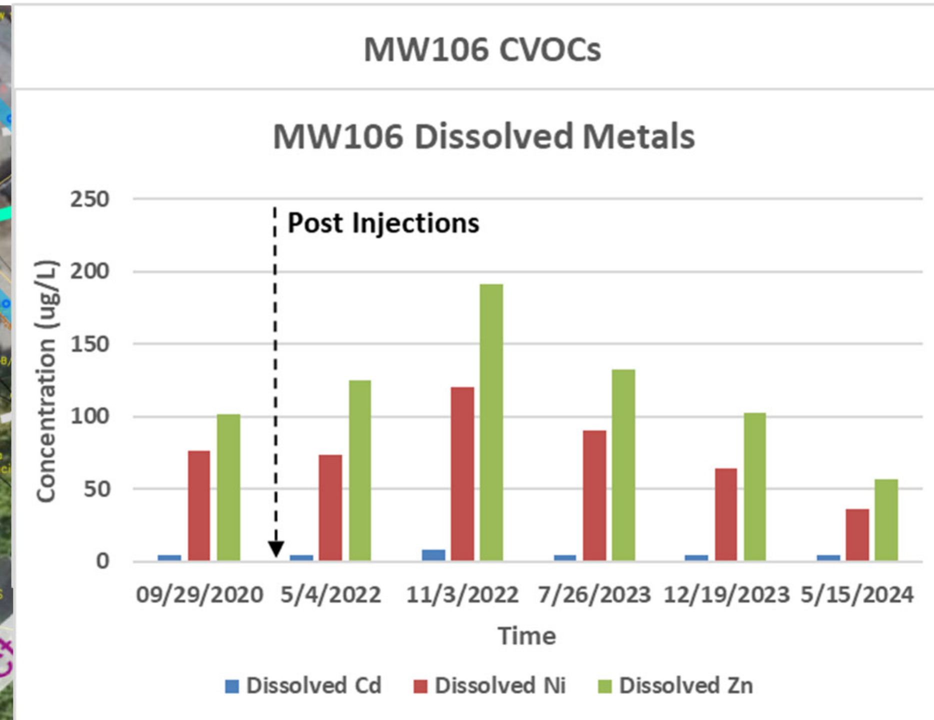


EVONIK
Leading Beyond Chemistry

Results as of May 2024

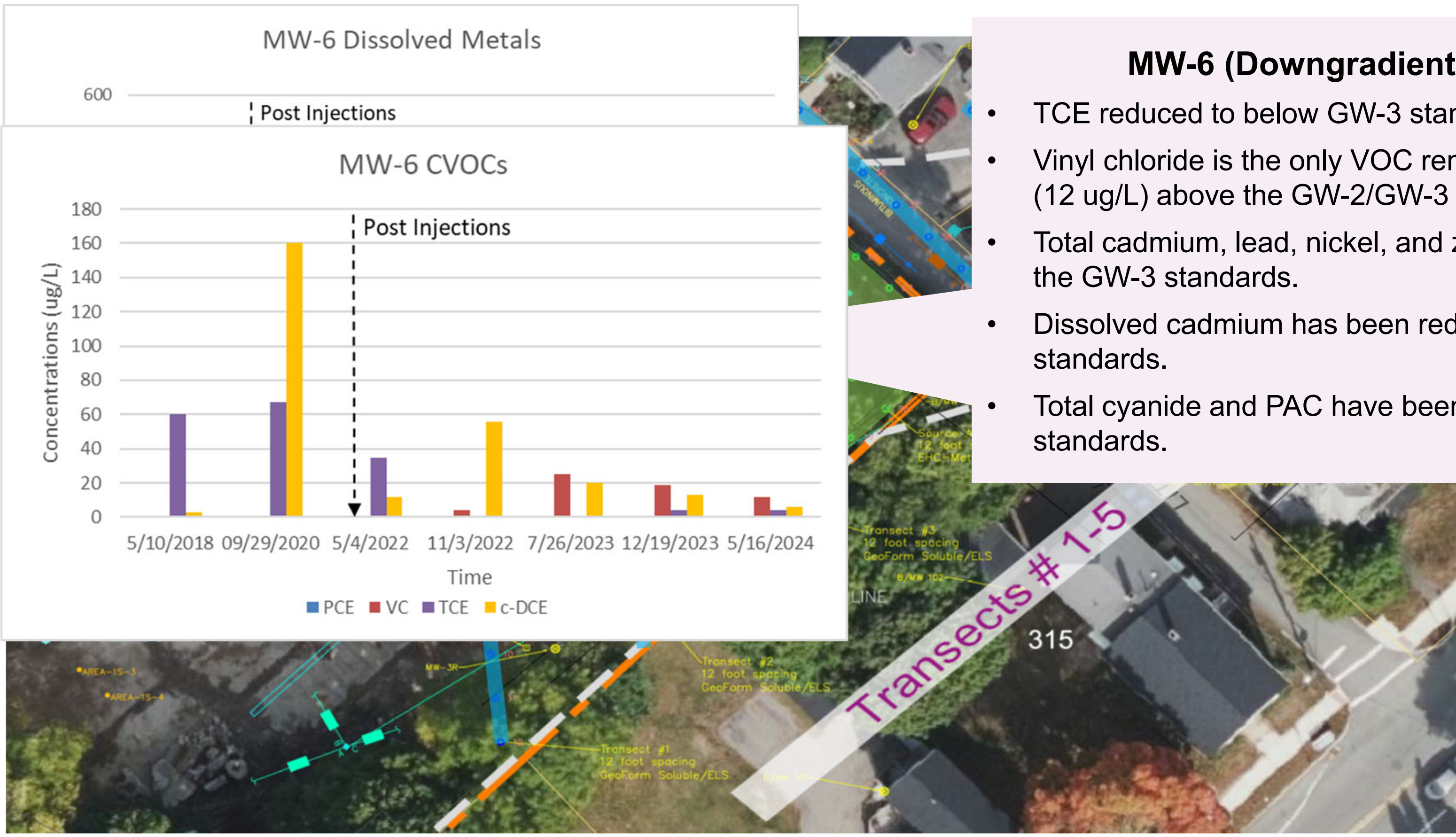
MW-106 (Downgradient of Transect#4)

- TCE reduced to below the GW-3 standards.
- cis-DCE has declined but remains at 25 ug/L, slightly above the GW-3 standard of 20 ug/L.
- Total cadmium, lead, nickel and dissolved cadmium have declined below GW-3 standards.
- Cyanide is below the GW-3 standard.



EVONIK
Leading Beyond Chemistry

Results as of May 2024

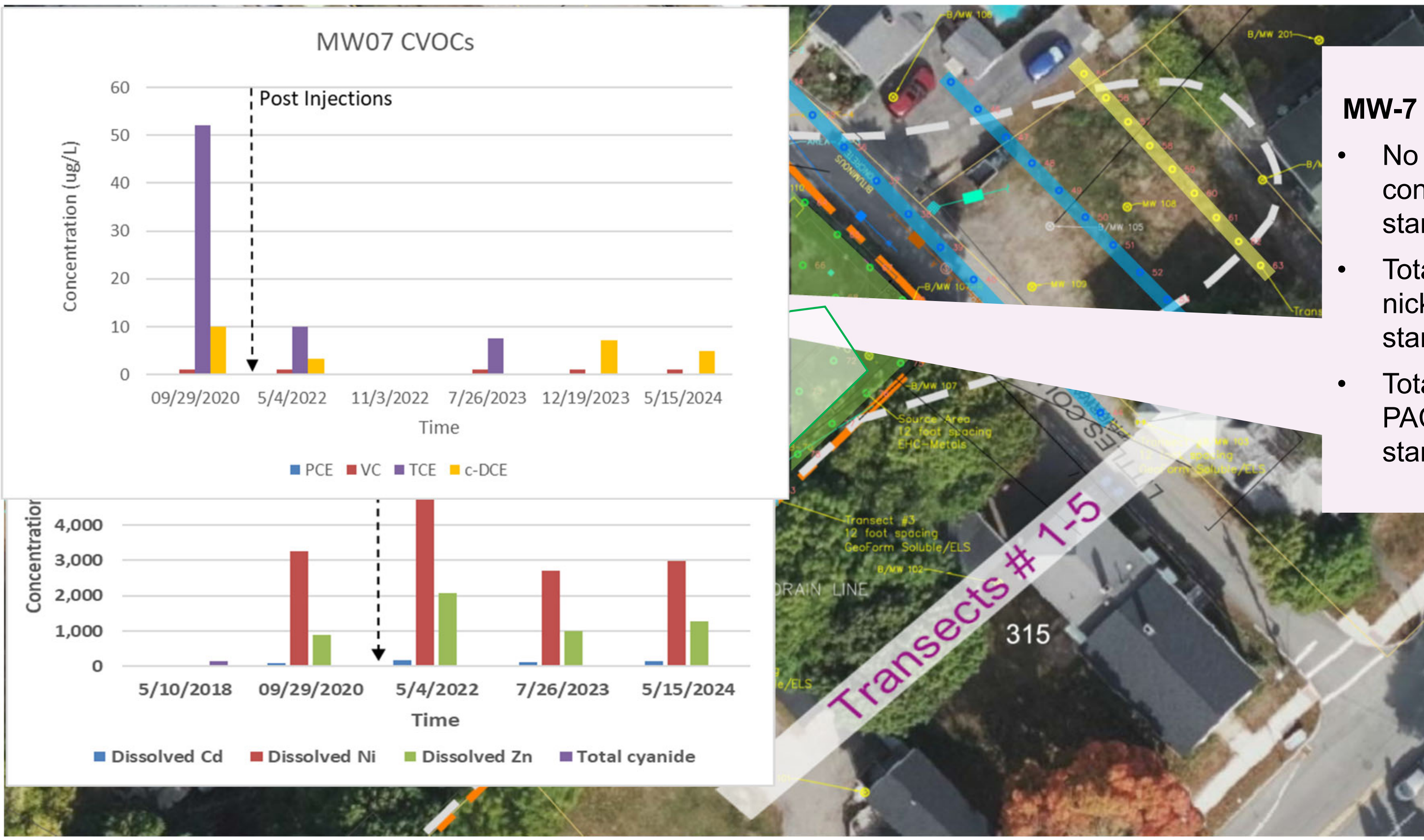


MW-6 (Downgradient from Transect #2)

- TCE reduced to below GW-3 standards.
- Vinyl chloride is the only VOC remaining at a concentration (12 ug/L) above the GW-2/GW-3 standards.
- Total cadmium, lead, nickel, and zinc have been reduced below the GW-3 standards.
- Dissolved cadmium has been reduced to below the GW-3 standards.
- Total cyanide and PAC have been reduced to below the GW-3 standards.

EVONIK Leading Beyond Chemistry

Results as of May 2024



MW-7 (Downgradient of Transect #1)

- No VOCs detected at concentrations above GW-2/GW-3 standards in May 2024.
- Total and dissolved cadmium, nickel, and zinc remain above GW-3 standards.
- Total, dissolved cyanide, and total PAC are below the GW-3 standards.

EVONIK
Leading Beyond Chemistry

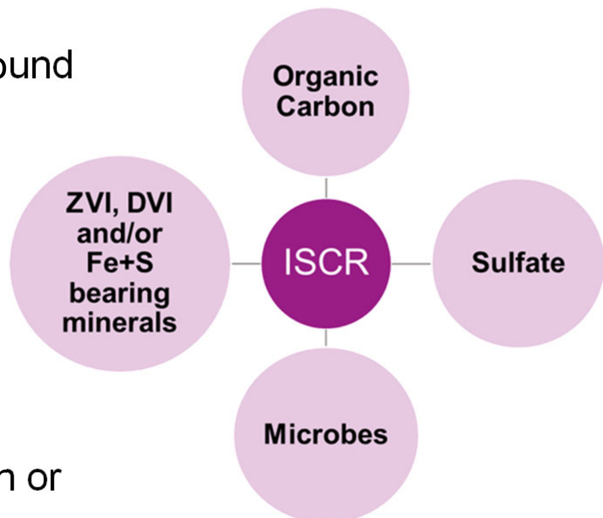
Summary

1. Reagents and processes that promote a combination of adsorption /precipitation/co-precipitation reactions with reductive biogeochemical treatment can enable simultaneous removal of dissolved metals and degradation of CVOCs.

2. Treatment chemistry employed should be carefully considered because rebound may be observed if the treatment chemistry converts dissolved metals into simple precipitates subject to reversal.

3. Susceptibility to this type of rebound can be minimized through use of treatments that generate strong, long-lasting reducing conditions (Redox Capacity).

4. Presence of continuous precipitation and co-precipitation reactions result in occlusion of the metals and thereby shield them from dissolution by oxidation or changes in pH conditions.



EVONIK Leading Beyond Chemistry

Questions

Fayaz Lakhwala, Ph.D.
Evonik Corporation
Soil & Groundwater Remediation
2 Turner Place
Piscataway, NJ 08854

E. Fayaz.Lakhwalal@evonik.com
T. +1 908-613-12443
remediation@evonik.com
www.evonik.com/remediation

Oxidative Destruction

Chemical
- Klozur® Persulfate Portfolio
  - Klozur® SP
  - Klozur® KP
  - Klozur® One
  - Klozur® CR
- Hydrogen Peroxide

Biological:
- Terramend® Reagent
- PermeOx® Ultra
- PermeOx® Ultra Granular

Reductive Destruction

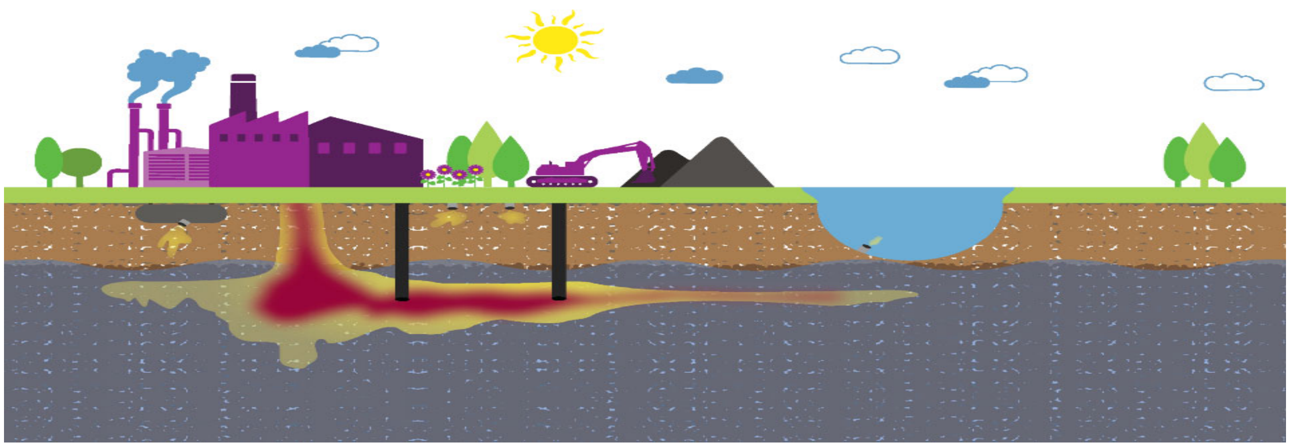
Biological
- ELS® Microemulsion
- ELS® Liquid Concentrate

Biological and Chemical
- EHC ISCR Portfolio
  - EHC® Liquid
  - EHC® Reagent
  - EHC ® Plus
- Daramend® Reagent

Biogeochemical
- GeoForm® Reagents

Physical Stabilization

- MetaFix® Reagents
- ISGS Reagent



EVONIK Leading Beyond Chemistry

Adsorption of Metals on Iron Oxide

- The extent of sorption of several metal cations and anions onto iron oxide is shown as a function of pH for a particular background electrolyte composition.
- It may be seen there that lead sorbs extensively at much lower pH values than zinc or cadmium (Kinniburgh et al., 1976).

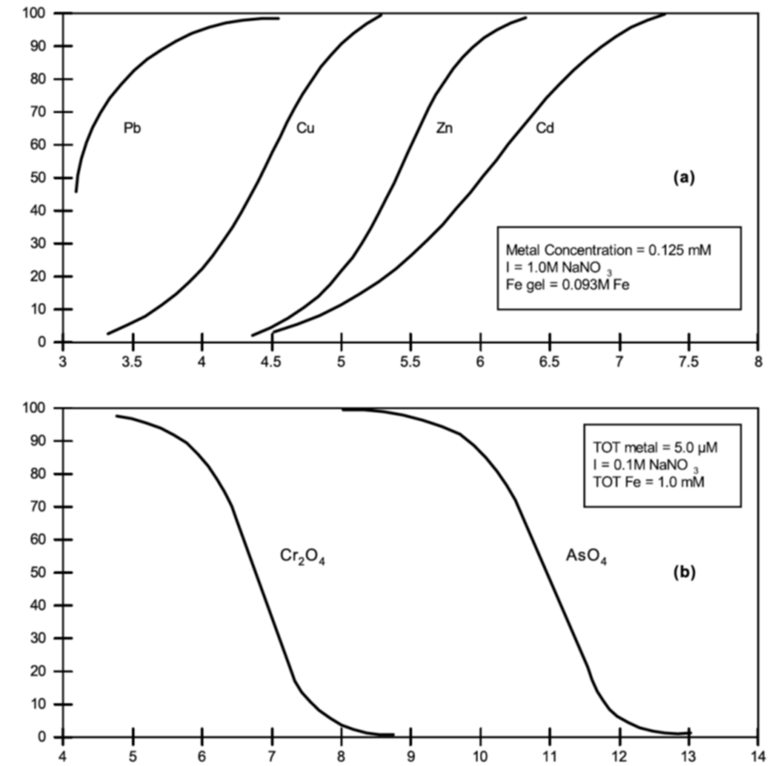
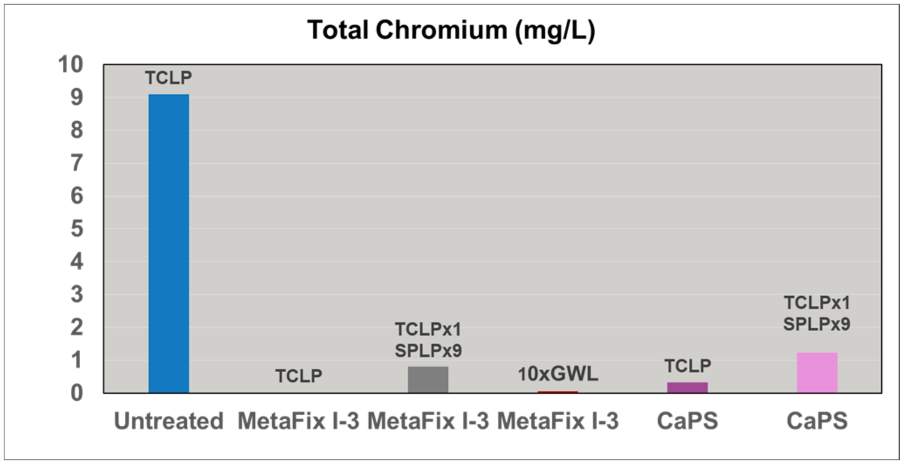


Figure 2. Metal Adsorption to Hydrous Iron Oxide Gels (*a*) Metal Cations (adapted from Kinniburgh et al., 1976) and (*b*) Metal Anions (adapted from Leckie et al., 1980; Honeyman et al., 1984)

Reducing Susceptibility to Metals Rebound

The Importance of Redox Capacity

- Both redox strength and longevity contribute to "Redox Capacity".
- Extremely reducing and long-lasting reagents promote near complete removal of all the oxidized compounds and electron acceptors.
- A reservoir of redox buffers is created which prevents the treated metals to reverse back to an oxidized state.
- As layers of these redox-buffering materials are laid down on the aquifer solids they protect heavy metal precipitates from exposure to oxidizing conditions – process of occlusion.
- Reagents that promote multiple removal mechanisms (physical adsorption, reductive precipitation, enzymatic reduction) can add another degree of resistance to re-solubilization/rebound.



Values (mg/L) are 9.02, 0.02, 0.80, 0.06, 0.33, and 1.24

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

EVONIK Leading Beyond Chemistry

Remediation Goals and Standards

Remediation Goals

- No Significant Risk from CVOCs, cyanide, and metals (cadmium, chromium, lead, nickel, and zinc) in groundwater.
- Reduce the concentrations of dissolved metals and CVOCs in the source area to an extent where their exposure to off-site receptors was mitigated.

MCP GW-2

- Potential for VOCs to migrate into indoor air.

COC	PCE (µg/L)	TCE (µg/L)	c-DCE (µg/L)	VC (µg/L)
GW-2	20	5	20	2

MCP GW-3

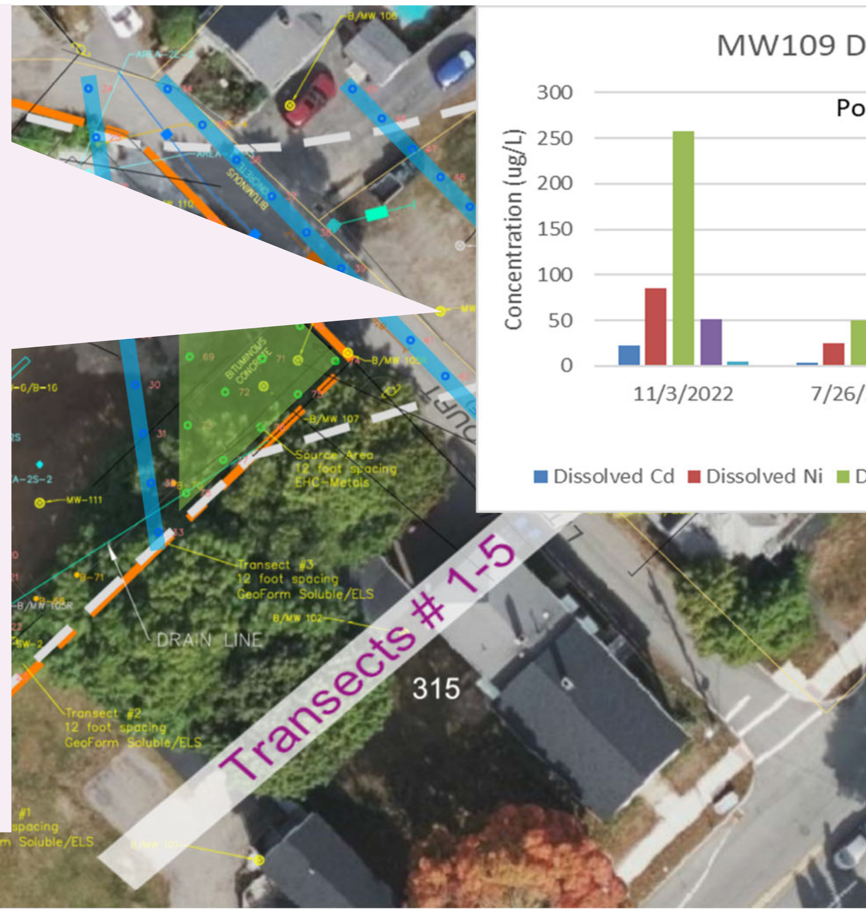
- Potential for contaminated groundwater to discharge to surface water bodies.

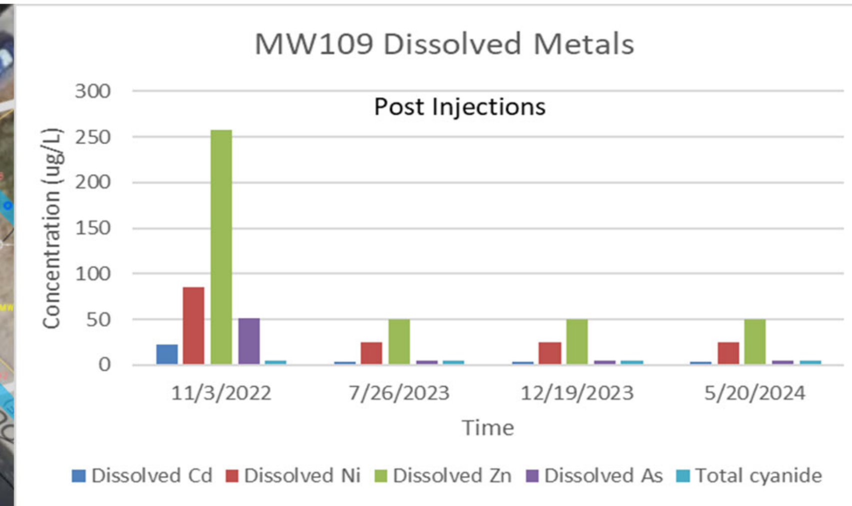
COC	Ni (µg/L)	Zn (µg/L)	Cd (µg/L)	CN (µg/L)
GW-3	200	900	8	30

Results as of May 2024

MW-109 (Downgradient of Transect #4)

- This well was installed at the start of the injection program in 2021.
- No CVOCs were detected above the GW-3 standards.
- All metals were detected below the standards.
- No exceedances of total cyanide and PAC.





EVONIK
Leading Beyond Chemistry