# ISCO / ISCR – Advances and Selection Criteria for 2018?

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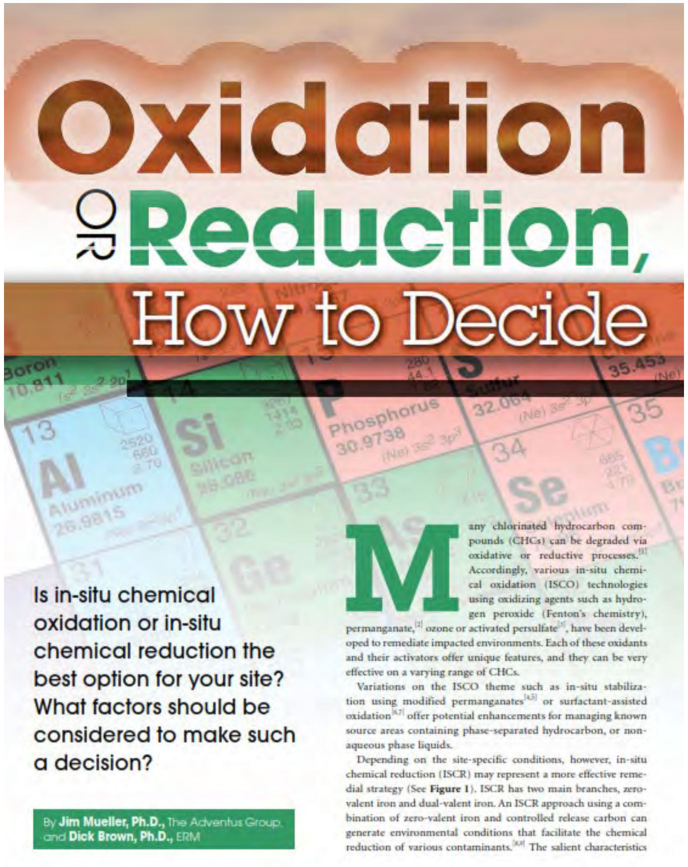
Focused Remediation Seminars
2018

# 10 year Update – References Cited

- Presentation is an update of past publications
- Not a complete analysis: a summary of factors that have been observed to affect technology selection, design and field performance



## Oxidation OR Reduction, How to Decide

Is in-situ chemical oxidation or in-situ chemical reduction the best option for your site? What factors should be considered to make such a decision?

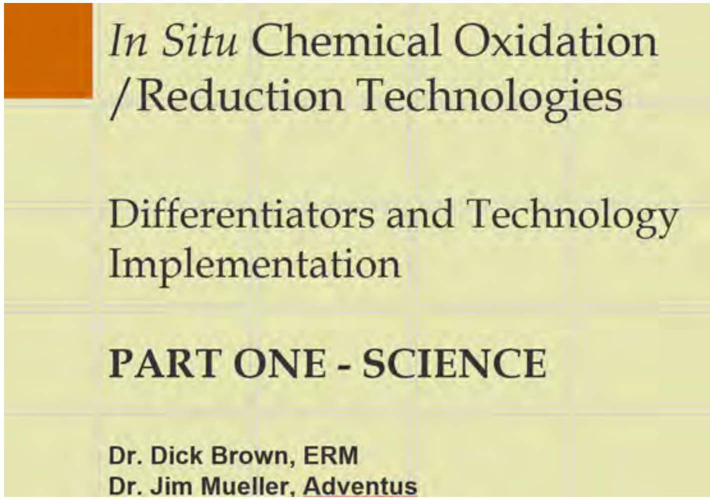
By **Jim Mueller, Ph.D.**, The Adventus Group, and **Dick Brown, Ph.D.**, ERM

Many chlorinated hydrocarbon compounds (CHCs) can be degraded via oxidative or reductive processes.[1] Accordingly, various in-situ chemical oxidation (ISCO) technologies using oxidizing agents such as hydrogen peroxide (Fenton's chemistry), permanganate,[2] ozone or activated persulfate[3], have been developed to remediate impacted environments. Each of these oxidants and their activators offer unique features, and they can be very effective on a varying range of CHCs.

Variations on the ISCO theme such as in-situ stabilization using modified permanganates[4,5] or surfactant-assisted oxidation[6,7] offer potential enhancements for managing known source areas containing phase-separated hydrocarbon, or non-aqueous phase liquids.

Depending on the site-specific conditions, however, in-situ chemical reduction (ISCR) may represent a more effective remedial strategy (See **Figure 1**). ISCR has two main branches, zero-valent iron and dual-valent iron. An ISCR approach using a combination of zero-valent iron and controlled release carbon can generate environmental conditions that facilitate the chemical reduction of various contaminants.[8,9] The salient characteristics

Mueller, J. and R. Brown. 2008. Oxidation or Reduction – How to Decide? Pollution Engineering News, April 2008, pages 51-54



*In Situ* Chemical Oxidation /Reduction Technologies

Differentiators and Technology Implementation

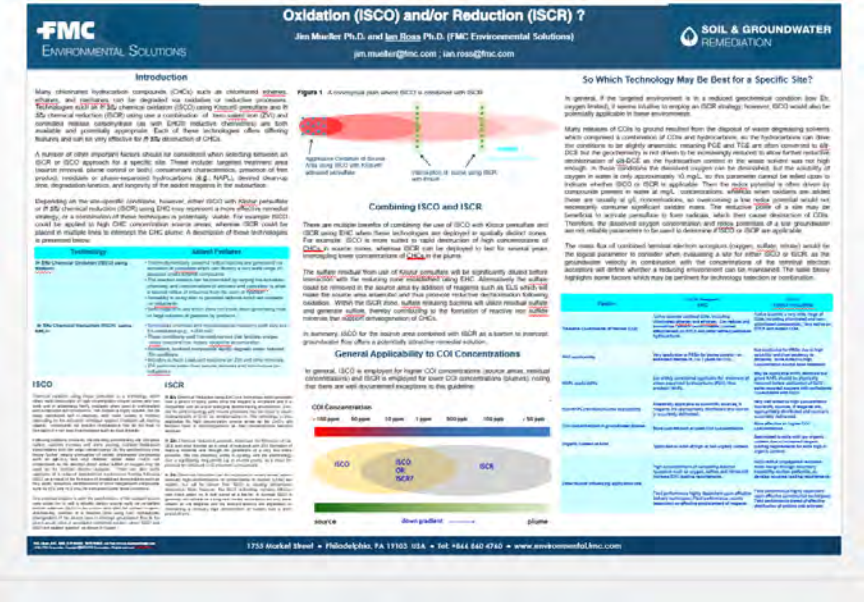
**PART ONE - SCIENCE**

**Dr. Dick Brown, ERM**
**Dr. Jim Mueller, Adventus**

Brown, R and J. Mueller. 2011. Oxidation or Reduction Technologies. to Decide? *Battelle Symposium on Bioremediation and Sustainable Environmental Technologies,* Reno, Nevada; June 27-30, 2011

**All Public Documents and hereby fully credited and referenced**

# 10 year Update – References Cited



## Oxidation (ISCO) and/or Reduction (ISCR) ?

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FMC Environmental Solutions

Soil & Groundwater Remediation

### Introduction

### So Which Technology May Be Best for a Specific Site?

### Combining ISCO and ISCR

### General Applicability to COI Concentrations

Mueller, J. and I. Ross. 2013. ISCO or ISCR: Battelle's Second International Symposium on Bioremediation and Sustainable Technologies, June 10-13, 2013 Jacksonville, Florida.

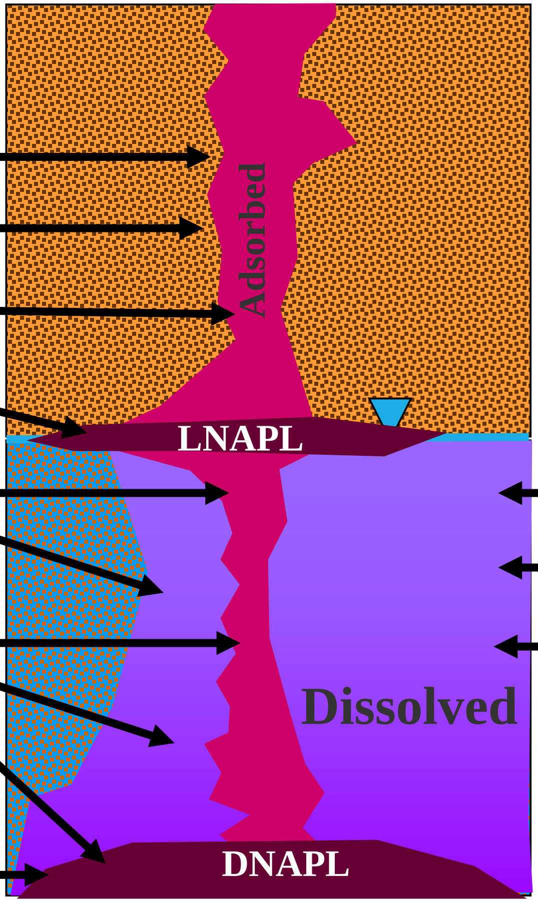
Bryant, D., Moody, W., Turkot, S., Maalouf, G., Sanderson, P., Slack, B., and Knight, D. 2013. Oxidants and reductants join for in-situ remediation. *Pollution Engineering*, May 2013, volume 45(5), pages 20-28.

**All Public Documents and hereby fully credited and referenced**

# Presentation Outline

- Problem Statement
  - We Need ISCO & ISCR Technologies
- What is ISCO?
  - Mode of Action
  - Technologies Available
  - Recognized Limitations (partial oxidation, rebound, longevity, metals)
- What is ERD/ISCR?
  - Mode of Action
  - Technologies Available
  - Recognized Limitations (excessive CH4, heavy metals, ketones)
- Design and Selection Criteria – Lessons Learned
- Summary and Conclusions

# Conventional Remediation Technologies



Excavation
SVE
Aerobic Bio
LNAPL Rec

Air Sparge
PAC/GAC

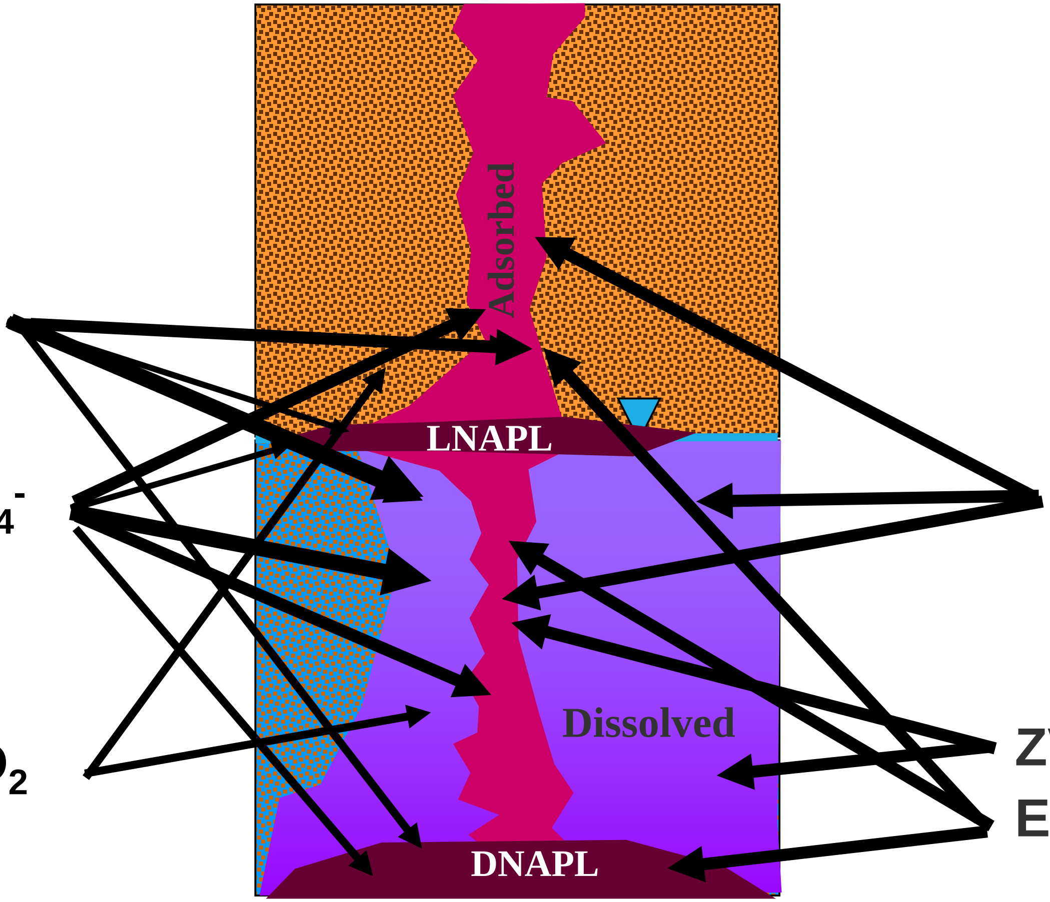
Dual Phase

DNAPL Recovery

Thermal

Pump & Treat
MNA
Anaerobic Bio

# Applicability of ISCO/ISCR Technologies



$S_2O_8^{=}$

$MnO_4^-$

$O_3$

$H_2O_2$

**ISCR**

**ERD**

**ZVI**

**EZVI**

Fast, Effective (terminal destruction),

Cost Efficient and *In Situ*

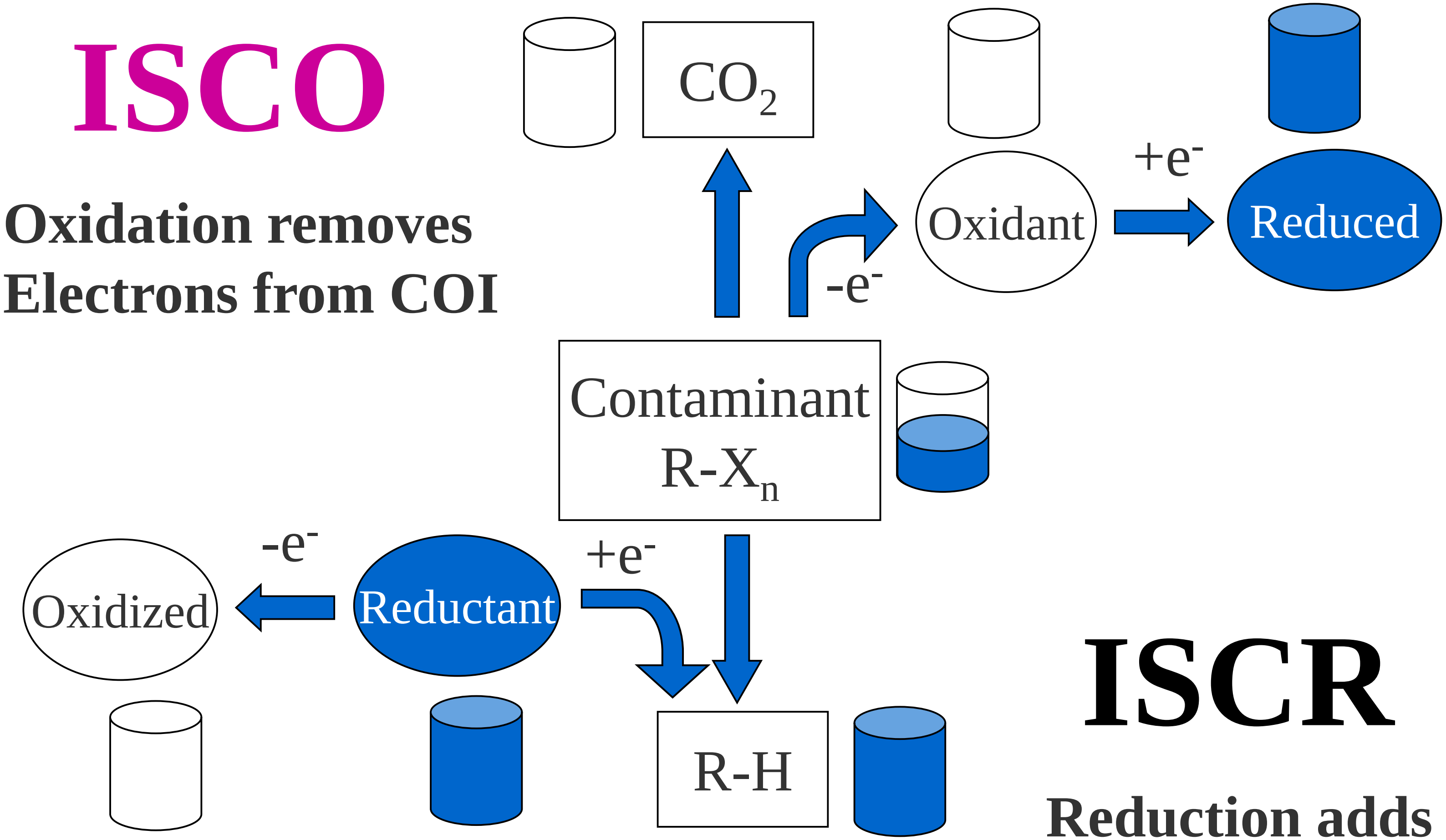
# Why Do We Need ISCO/ISCR?

- Speed
  - Many conventional technologies can take years to complete
  - Long term O&M
- Efficacy
  - Many cannot reach RAO / MCLs
  - Many require treatment / disposal of impacted media
  - Most are ineffective with DNAPLs
  - Ultimately, complete destruction of COI not always achieved
- Cost
  - Many have high O&M
  - Sustainability can be questionable

# Understanding ISCO/ISCR Reactions

## ISCO

**Oxidation removes Electrons from COI**



$CO_2$

Oxidant

$+e^-$

Reduced

$-e^-$

Contaminant

$R\text{-}X_n$

$-e^-$

$+e^-$

Oxidized

Reductant

R-H

## ISCR

**Reduction adds Electrons to COI**

# ISCO = Breaking Chemical Bonds

- Oxidant must be able to accept electrons
  - Capacity = Equivalent weight (MW / No. electrons)
- Ultimate end point is mineralization
  - Partial oxidation is common

| **Bond Type** | **Volts (eV)** |
|---|---|
| Carbon-Carbon (single)<br>Long chain hydrocarbons PAHs, DRO, GRO | 2.5 |
| Carbon-Carbon (one and a half)<br>Aromatic Type - BTEX and PCP | 2.0 |
| Carbon-Carbon (double)<br>HVOCs, PCE, TCE, DCE, VC | 1.5 |
| Carbon-Hydrogen (Alkanes) | 1.0 |

# Oxidation Potentials of Common ISCO

stronger oxidizer

| Oxidation Potentials | Volts |
|---|---|
| Fluorine ($F_2$) | 2.87 |
| Hydroxyl radical (OH●) | 2.80 |
| Persulfate radical ($SO_4$●) | 2.60 |
| Ferrate ($Fe^{+6}$) | 2.20 |
| Ozone ($O_3$) | 2.08 |
| Persulfate ($S_2O_8^{-2}$) | 2.01 |
| Hydrogen peroxide ($H_2O_2$) | 1.78 |
| Permanganate ($MnO_4^-$) | 1.68 |
| Chlorine ($Cl_2$) | 1.49 |
| https://sites.google.com/site/ecpreparation/ferrate-vi | |

**Fenton's**
- **Treats wide range of contaminants**
- **Short subsurface lifetime**
- **Difficult to apply in reactive soils**

**Persulfate**
- **Treats wide range of contaminants**
- **Sulfate radical forms slower than the hydroxyl radical, allowing a larger radius of influence**

**Provect-OX**
- **Generates Ferrate (Fe IV, V, VI possible)**
- **Treats wide range of contaminants**
- **Extended *in situ* lifetime w/ continual production**
- **Avoids Rebound**

**Ozone**
- **Treats wide range of contaminants**
- **Short subsurface lifetime**
- **Limited use in saturated zone**

**Permanganate –**
- **Treats limited range of contaminants**
- **Partial oxidation of TPHs, etc**
- **Long subsurface lifetime**
- **Potential effects on hydrogeology**

Higher oxidation potential = stronger the oxidizer

# Reactivity of Various ISCO Reagents

| Oxidant | Amenable VOC's | Reluctant VOCs | Recalcitrant VOCs | Limitations |
|---|---|---|---|---|
| Peroxide, Old Fenton's | PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA | DCA, $CH_2Cl_2$ | TCA, CT, $CHCl_3$ | Stability (25-95% decomp/hr), low pH |
| Peroxide, New Fenton's | PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA | DCA, $CH_2Cl_2$,TCA, CT, CHCl3 | | Stability (10-50% decomp/hr) |
| Potassium Permanganate | PCE, TCE, DCE, VC, TEX, PAH | MTBE, TBA | TCA, CT, B, $CHCl_3$, DCA, CB, $CH_2Cl_2$ | Soil oxidant demand |
| Sodium Permanganate | PCE, TCE, DCE, VC, TEX, PAH | MTBE, TBA | TCA, CT, B, $CHCl_3$, DCA, CB, $CH_2Cl_2$ | Soil oxidant demand |
| Sodium Persulfate, Fe | PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA | DCA, $CH_2Cl_2$, $CHCl_3$ | TCA, CT | Stability (10-25% decomp/wk), low pH |
| Sodium Persulfate, Base | All VOCs | | | Stability (10-25% decomp/wk), NaOH costs |
| Sodium Persulfate, Heat | All VOCs | | | Stability (10-50% decomp/day), low pH, heating costs |
| Ozone | PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA | | DCA, $CH_2Cl_2$, $CHCl_3$, TCA, CT | Mass Delivery, Volatilization |

# ISCO Issue 1: Non-Beneficial Consumption

$[\text{Oxidant}]_{\text{Required}} =$

$[\text{Stoichiometric Demand}]_{\text{Contaminant}} +$

*[Soil Matrix Demand] +*

*$[\text{Metals}]_{\text{Reduced}}$*

*$[\text{Organic Carbon}]_{\text{Oxidizable}}$*

*$[\text{Decomposition}]_{\text{Oxidant}}$*

Non-Beneficial Consumption

| | Peroxide | Persulfate | Permanganate | Ozone |
|---|---|---|---|---|
| Decomposition | XXXXX | XX | -- | XX |
| SOD - Metals | XXXX | XXXX | XXXX | XX |
| SOD - Organics | --- | ✚ ---- | XXXXX | --- |
| Advection | X | X | X | XX |

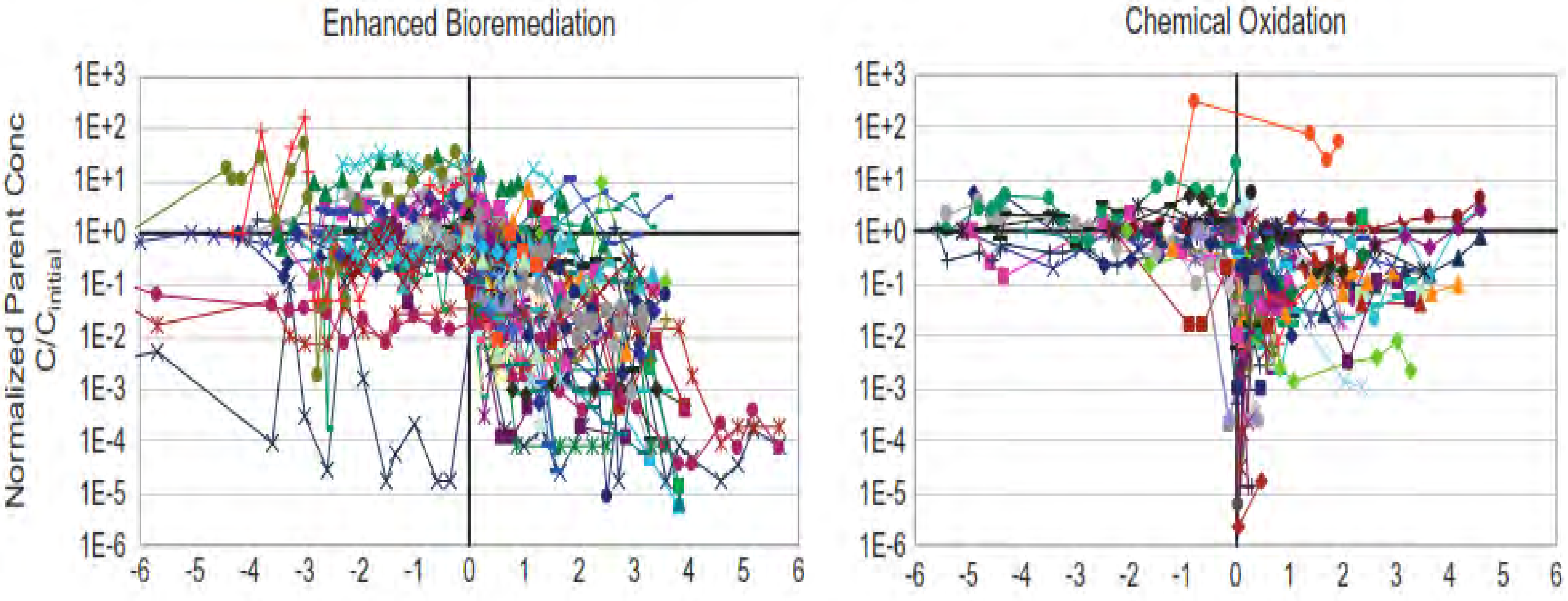
pSOD from non-impacted aquifer = less than accurate

✚ = slow to react

# ISCO Issue 2: Contaminant Rebound

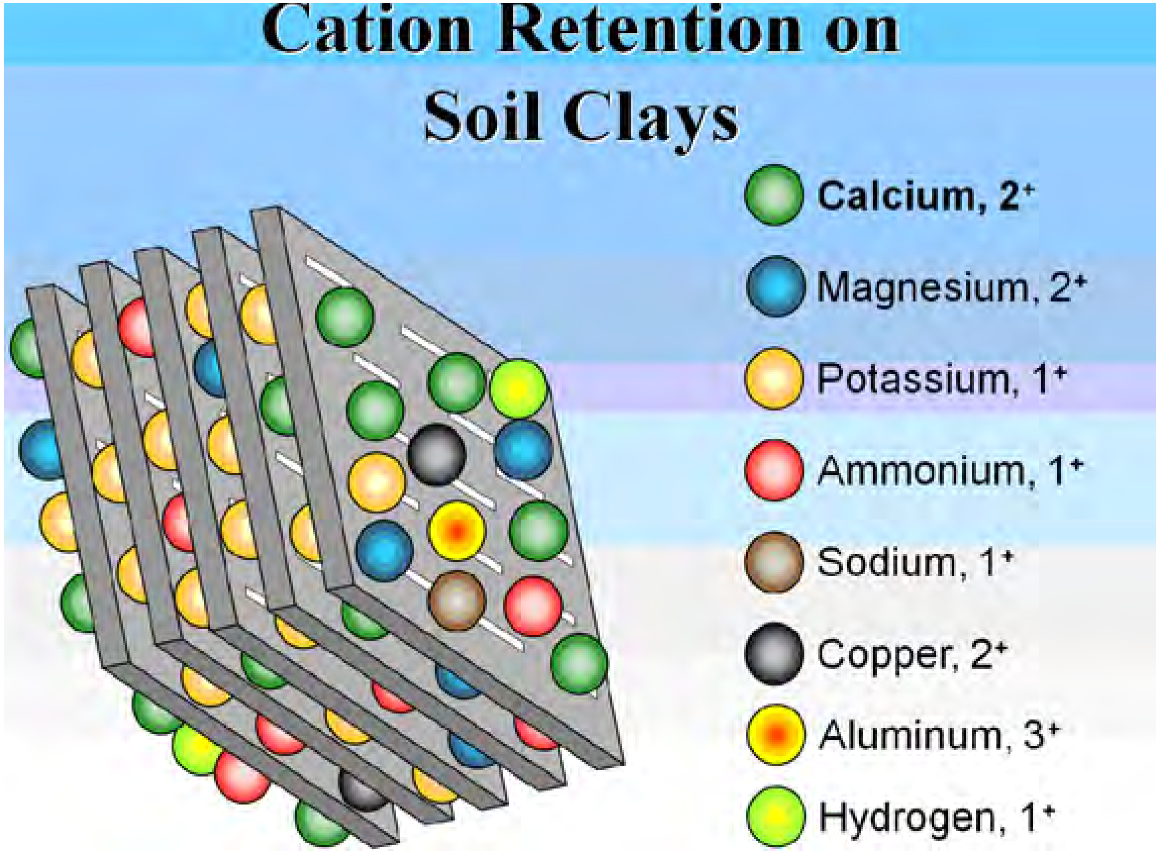
**Figure 1.** Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.

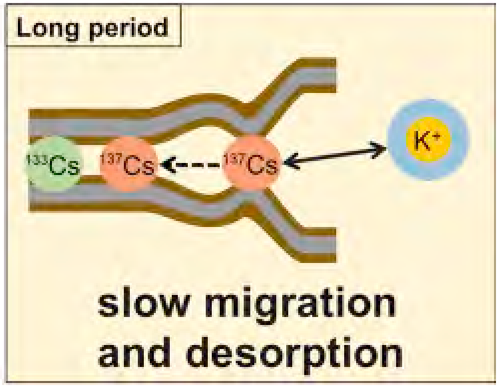
*T.M. McGuire et al.*/ Ground Water Monitoring & Remediation 26, no. 1: 73–84 77

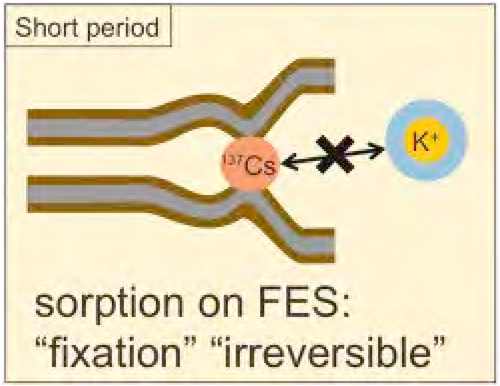


**X-axis showing sampling time (years) relative to initial treatment (Time 0)**

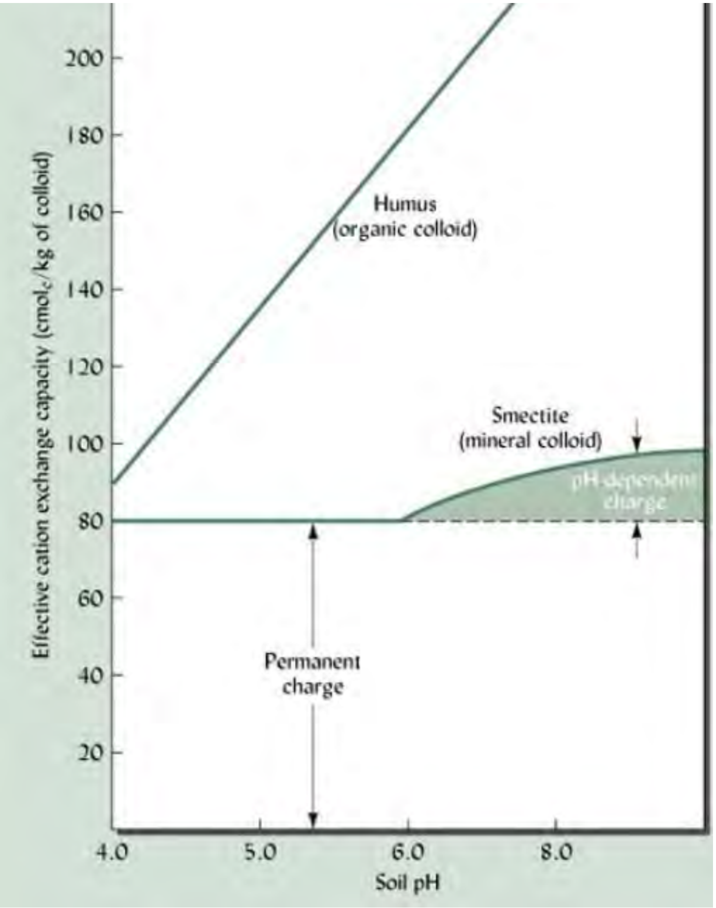
# Rebound from Desorption



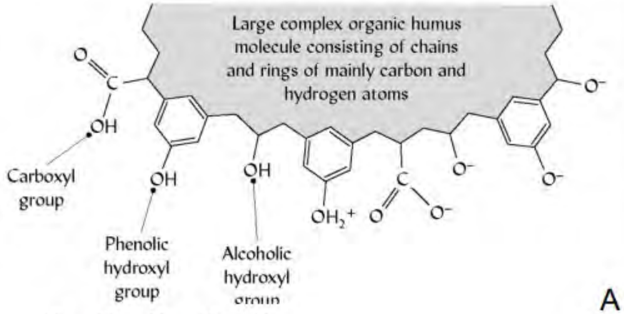


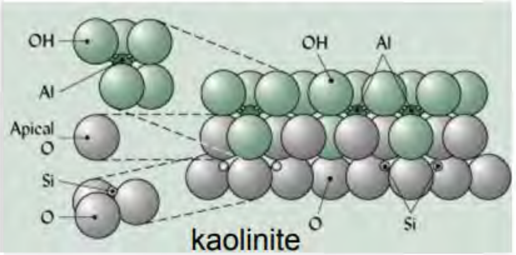


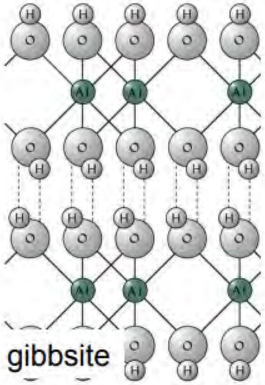
# pH Dependent Rebound



via protonation / deprotonation of hydroxyl groups







A negative charge comes with increasing pH

$$\rangle Al-OH + OH^- \rightleftharpoons \rangle Al-O^- + H_2O$$

$$-C-OH + OH^- \rightleftharpoons -C-O^- + H_2O$$

No charge (soil solids) | (soil solution) | Negative charge (soil solids) | (soil solution)

Negative charge on a compound can increase at higher pH (more protons) due to ionization of hydroxyl and carboxyl groups (not alcohols >18).

# Base-Activated Persulfate and Rebound

Peroxygen Talk

March 2010 - The Use of Lime to Activate Klozur Persulfate and Its Impact on Contaminant Soil Concentrations

Hydrated lime, $Ca(OH)_2$, and in some instances quicklime, CaO, have been used successfully as an activator for Klozur® Persulfate for the treatment of petroleum and chlorinated solvent contaminated soils. Due to its relatively low solubility, the most common method of use with Klozur persulfate is soil blending, either *in situ* or *ex situ*. Lime provides several benefits as an activator, including:

- Relative low cost

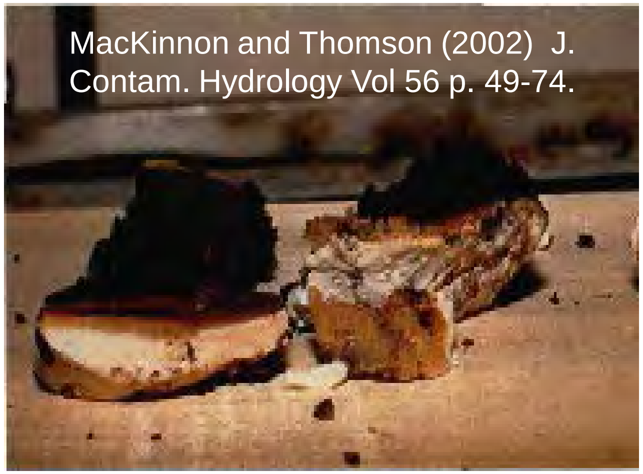
*Philip Block, Ph.D.*

“In conclusion, it is evident that the standard EPA test method 3545 does not adequately account for reversible, lime encapsulation due to a lack of pH adjustment prior to extraction. This may lead to erroneous conclusions that lime application is adequate in remediating contaminated soils, and that it provides equivalent benefit to lime activated persulfate treatment. Adjusting the pH to circum-neutral levels prior to extraction will provide a more accurate estimation of the contaminant destruction that is capable with lime and lime activated persulfate”. FMC (now PeroxyChem) March, 2010.

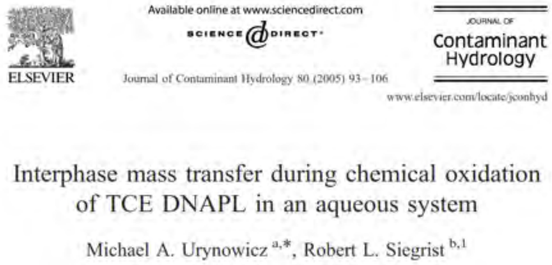
# MnO$_2$ Potential Rebound

**In the presence of an organic compound (R), MnO4 reactions yield an oxidized intermediate (Rox) or CO$_2$ ,… plus MnO$_2$**

$$R + MnO_4^- \rightarrow MnO_2 + CO_2 \text{ or Rox}$$



MacKinnon and Thomson (2002) J. Contam. Hydrology Vol 56 p. 49-74.



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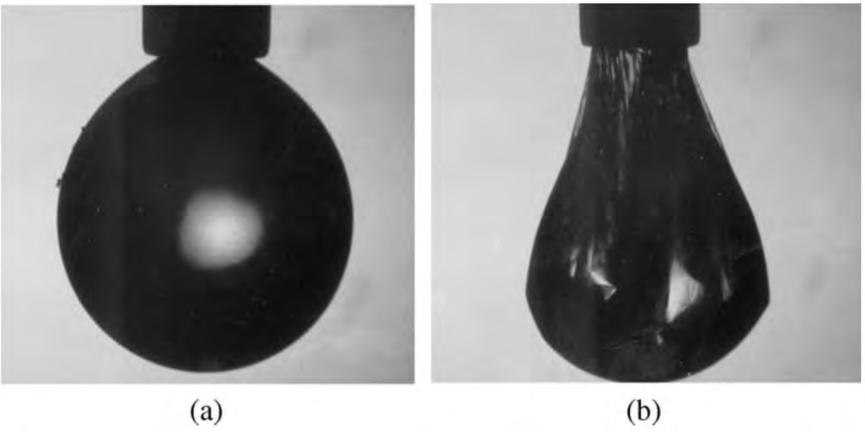
Journal of Contaminant Hydrology 80 (2005) 93–106

JOURNAL OF Contaminant Hydrology

www.elsevier.com/locate/jconhyd

Interphase mass transfer during chemical oxidation of TCE DNAPL in an aqueous system

Michael A. Urynowicz [a,*], Robert L. Siegrist [b,1]

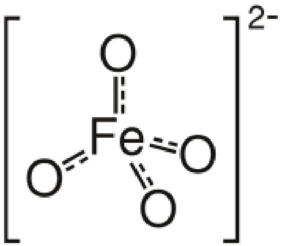


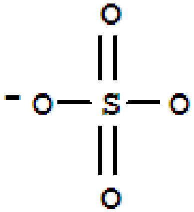
(a) (b)

Fig. 7. (a) Photograph of a TCE droplet suspended in phosphate buffered de-ionized water from the tip of a syringe needle prior to chemical oxidation with $MnO_4^-$. (b) Photograph of a TCE droplet following chemical oxidation with $MnO_4^-$. Needle diameter=0.8 mm.

# What is Provect-OX®?

- **Sodium Persulfate + Ferric Oxide ISCO Reagent**
  - **Chemical Oxidation via Sulfate (SO4•) Radical**
  - **Chemical Oxidation via Ferrate (Fe6+•) Radical**
- **Enhances Biological Attenuation via Sulfate and Iron Reduction Processes**
- **Terminating Reaction Results in Pyrite: An Abiotic Reactive Particle with similar Kinetics to ZVI (BiRD / Pseudo-ISCR)**
- **Easily Transitions from Oxidation to Biological Attenuation to Abiotic Mineralization**
- **Safely Handled Catalyzed Process without the Hazards of Extreme Activators Caustics**





# Provect-OX Oxidation Potentials

Ferrate salts can be prepared from iron salts, hypochlorite and a base:

$$2\ Fe^{+3} + 3\ OCl^{-} + 4\ OH^{-} \rightarrow 2\ \mathbf{FeO_4^{-2}} + 3\ Cl^{-} + 2\ H_2O$$

$$S_2O_8^{-2} + \text{ACTIVATOR}\ [Fe^{+3}] \rightarrow SO_4\bullet^{-} + e^{-} \rightarrow SO_4\bullet^{-2}$$

| Oxidation Potentials | Volts |
|---|---|
| Fluorine ($F_2$) | 2.87 |
| Hydroxyl radical (OH●) | 2.80 |
| Persulfate radical ($SO_4\bullet$) | 2.60 |
| Ferrate ($Fe^{+6}$) | 2.20 |
| Ozone ($O_3$) | 2.08 |
| Persulfate ($S_2O_8^{-2}$) | 2.01 |
| Hydrogen peroxide ($H_2O_2$) | 1.78 |
| Permanganate ($MnO_4^{-}$) | 1.68 |
| Chlorine ($Cl_2$) | 1.49 |

**https://sites.google.com/site/ecpreparation/ferrate-vi**

# Ferrate Chemistry is Complex…

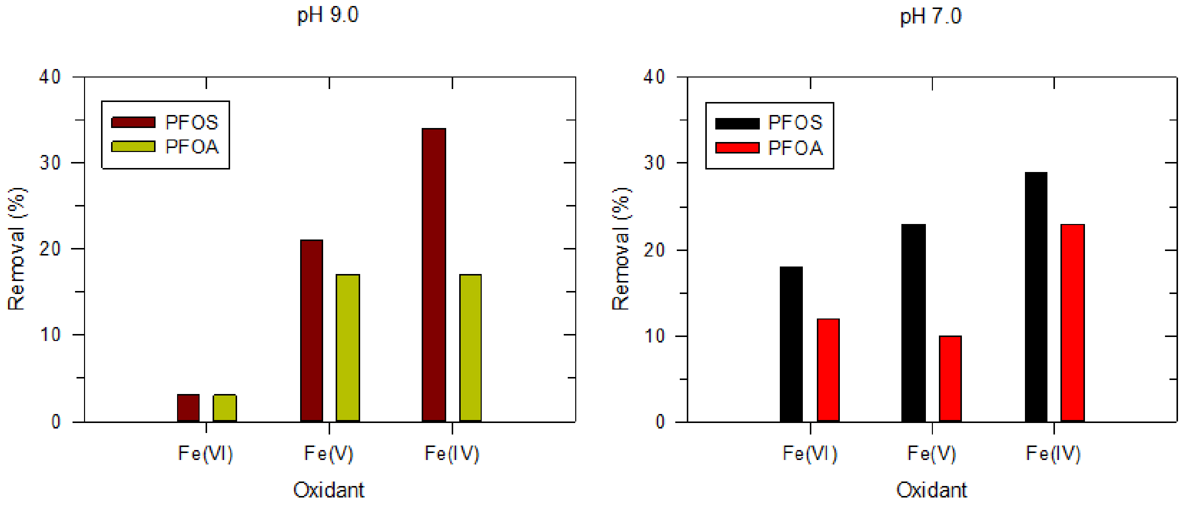
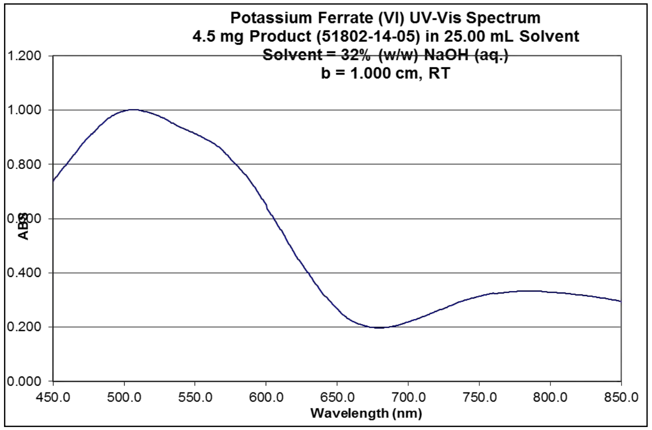


Figure 3. Oxidation of perfluorooctylsulfonate and perfluorooctanoic acid by one application of ferrates at pH 9.0 and 7.0 after five days.



# Provect-OX Reactions

- Sodium Persulfate + Ferric Oxide ISCO Reagent:
  - $S_2O_8^{-2}$ + $Fe^{+3}$ ---------> $Fe^{(+4\ to+6)}$ + $SO_4^{2-}$ + $SO_4^{2-\bullet}$
- Sulfate Reduction of Benzene
  - $C_6H_6$ + 3.75 $SO_4^{2-}$ + 3 $H_2O$ --> 0.37 $H^+$ + 6 $HCO_3^-$ + 1.87 $HS^-$ + 1.88 $H_2S^-$
- Iron Reduction of Benzene
  - $C_6H_6$ + 18 $H_2O$ + 30 $Fe^{3+}$ -------> 6 $HCO_3^-$ + 30 $Fe^{2+}$ + 36 $H^+$
- Terminating Reaction Results in Pyrite:
  - $Fe^{2+}$ + $2S^{2-}$ -------> $FeS_2$ + 2e
- Unique Transition from Oxidation to Biological Attenuation & Abiotic Mineralization

# Provect-OX® Coupled Oxidation w/ Sustained Bioremediation

- List \$1.95 to \$2.05 / lb includes activator
- US Patent 9,126,245

- >\$1.35 / lb persulfate only

- Safely Handled
- All in one bag
- Uses $Fe^{+3}$ as activator
- Conserves Oxidant
- Formation of Reactive Ferrate Species
- Enhances Bioattenuation Fe + $SO_4$
- Encourages the Formation of Pyrite
- Prevents $H_2S$ Formation
- Minimizes Heavy metal mobilization
- No Heat generated = safer

- When Chelated $Fe^{+2}$ used as activator EDTA Consumes the Oxidant
- When Caustic is used as activator
  - Short Lived Reaction
  - $H_2S$ Formed
  - Secondary plumes / metals (Cr)
  - Can generate extreme heat
  - Handling and Safety issues

**pH 10+ Does Not Promote Bio**

**Does Not Manage Rebound**

# Case Study – TPH in Groundwater

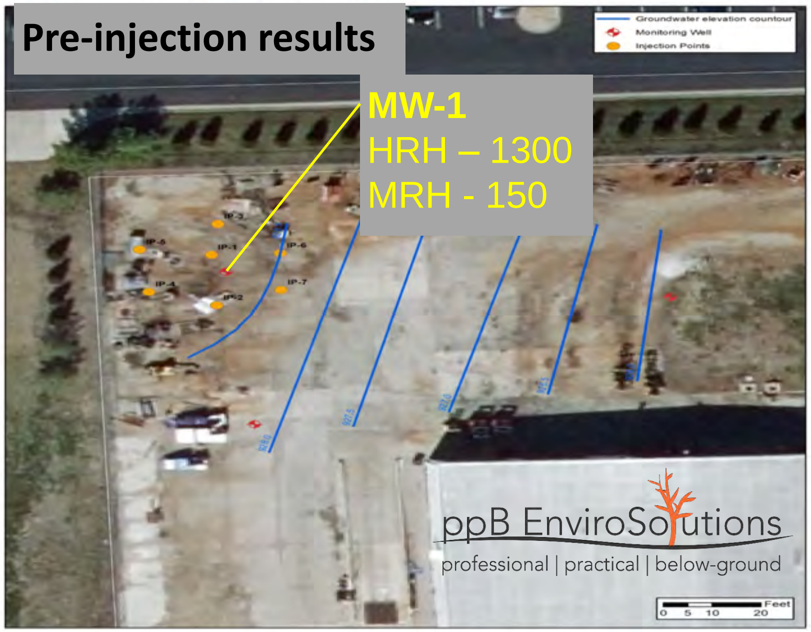
- Relatively low concentration/low risk TPH site (>C9, mid-range and high-range)
- Groundwater testing showed isolated impacts in shallow perched water-bearing zone (DTW 15 to 20 ft bgs)
- Soil sampling did not identify a significant residual source
- Client requested a remediation strategy that would facilitate regulatory site closure quickly due to a pending property transaction (one time injection event)
- Cleanup had to achieve Kansas residential cleanup standards for groundwater

ppB EnviroSolutions

professional | practical | below-ground

# Case Study – TPH in Groundwater

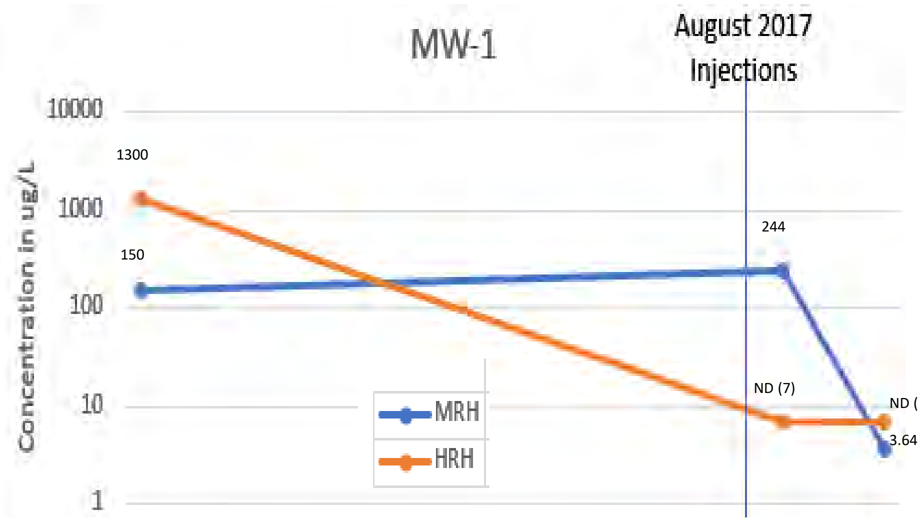
- 2,400 lbs Provect-OX injected
- Approx. 500 ft$^2$ impacted area
- 7 injection points on 12 foot centers
- 2 day injection event
- ROI > 6-ft in clay soils, <50 psi (KHDE)
- RAO <Residential Groundwater Standards
  - TPH-MRH <150 ppb
  - TPH-HRH <1,000 ppb



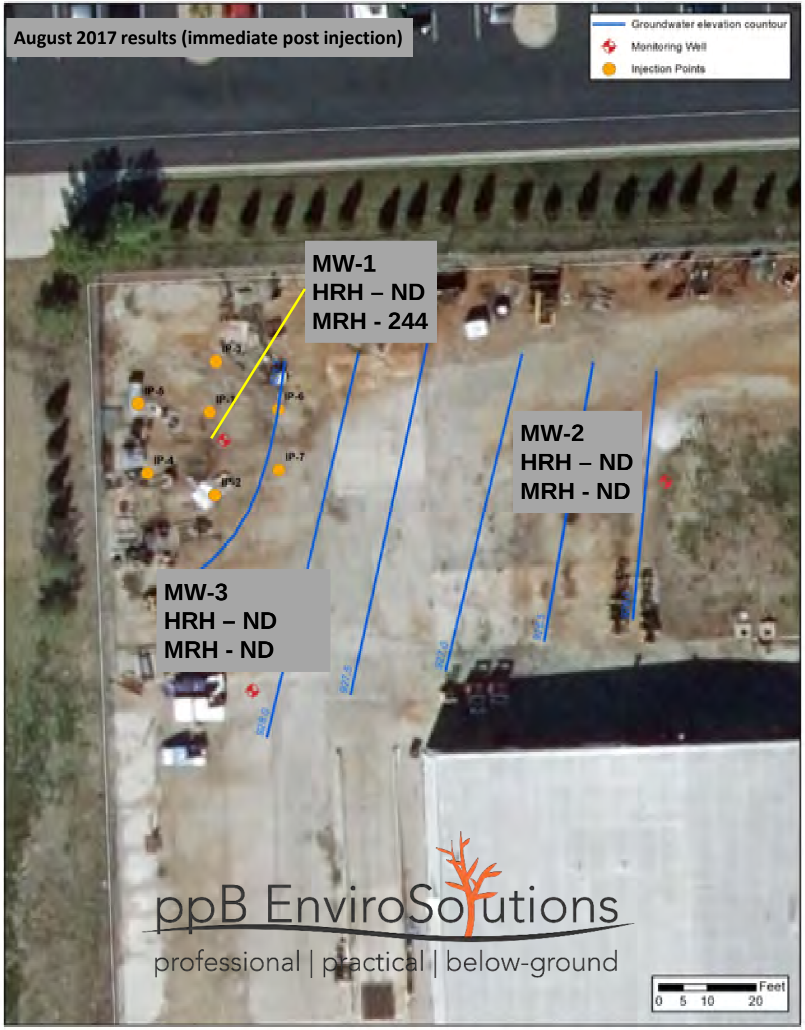
Pre-injection results

**MW-1**
HRH – 1300
MRH - 150

# Results – KS Site TPH



- HRH not detected 1 week after injection event (1,300 to < 7 ppb)
- >97% reduction in MRH 3 months after one injection event (155 to < 4 ppb)
- All groundwater cleanup goals achieved 3 months after injection event
- Total project cost < $50k to date
- Anticipated regulatory closure in 2018



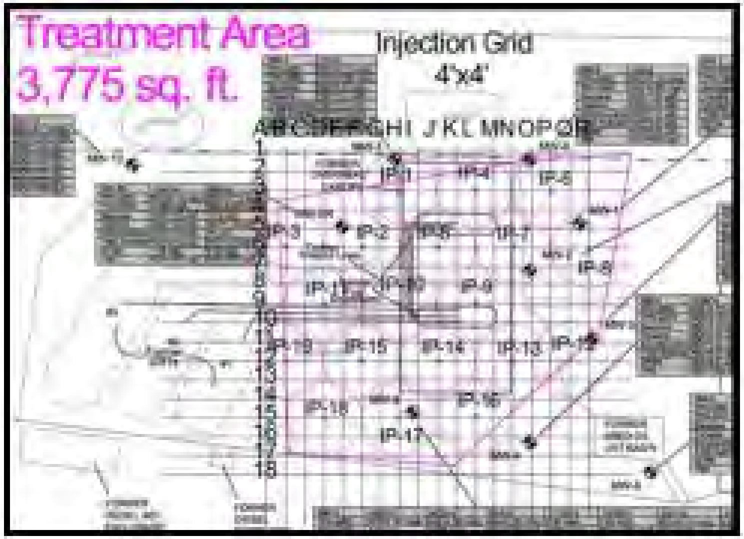
# Provect-OX Site Summaries

- Mendota Site
  - Active facility with desire for one-time application
  - 500 tons of contaminated, vadose zone soil
  - PCE >35,000 mg/kg and Toluene >4,000 mg/kg
  - Goal was to reduce below site-specific soil saturation limits
  - PCE goal ca. 2,000 mg/kg and Toluene goal ca.1,000 mg/kg
- 12,100 lbs Provect-OX
- 15 g / kg soil
- 5 day application period
- Goals reached
  - PCE 38,000 mg/kg to 900 mg/kg
  - Toluene 4,000 to <100 mg/kg

**Courtesy Fehr-Graham, Inc.**

# Provect-OX Site Summaries

- St. Albans, WV Site
    - Former Gas Station
    - Approx. 3,800 sq ft area impacted with BTEX, MTBE, TBA
    - Primarily clay with depth to water ca. 5 ft bgs
    - Treatment interval from 6 to 12 ft bgs
    - Two monitoring wells impacted
    - Goal was significant reductions
- MW-9 Highest Concs. – 1 Year
    - Benzene 77 ug/L to ND
    - Ethylbenzene 66 ug/L to ND
    - MTBE 72 ug/L to ND
    - TBA 1,480 ug/L to ND



**Courtesy Innovative Environmental Technologies, Inc.**

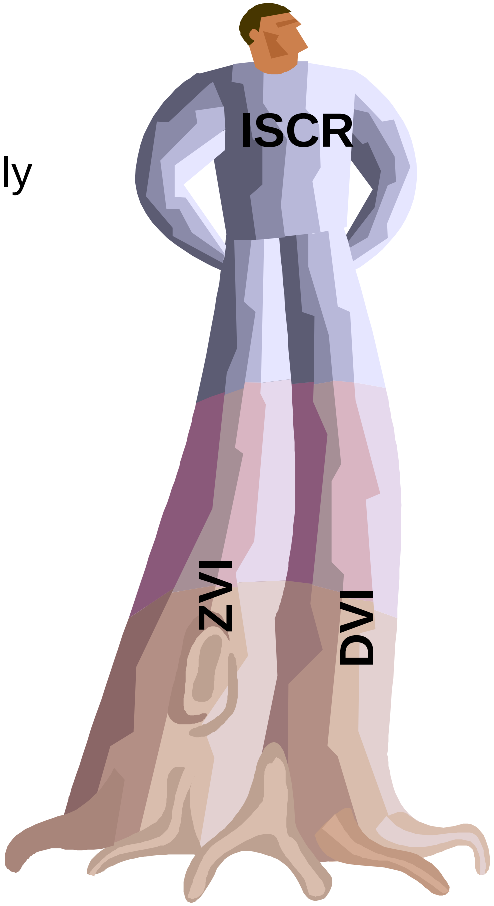
# What is *In Situ* Chemical Reduction?

- In 2004, ISCR was defined as "a synergistic process that combines biotic + abiotic reactions and creates highly reducing, electron-rich conditions" (Mueller and Brown, 2004)
  - ISCR is **not** enhanced anaerobic bioremediation/ERD
  - ISCR is **not** ZVI only or BiRD or *et cetera*

| Process | Amendments |
|---|---|
| **Enhanced Anaerobic Degradation / ERD** | **Molasses, (emulsified) vegetable oils / lecithins, sodium lactate, polylactic acid, whey, simple H release compounds** |
| ***In Situ* Chemical Reduction / ISCR** | **Provect-IR™, ABC®+, EHC®, DARAMEND®** |
| **Antimethanogenic ISCR Reagents** | **Provect-IR®, Provect-IRM®, Aquablok®-CH4, and to some degree ABC-CH4™** |

# ISCR Builds on Decades of Knowledge

1. Biotic processes biodegrade COIs
2. Abiotic processes are based on reduced metals
3. Abiotic process are surface catalyzed
4. Abiotic pathways are different than biological pathways
5. Abiotic processes can be enhanced chemically or biologically



Makinawite FeS,
Pyrite $FeS_2$
Green Rust $[Fe^{2+}{}_6Fe^{3+}{}_2(OH)_{18}\cdot 4(H_2O)]$
Magnetite $Fe^{3+}{}_2Fe^{2+}O_4$
Glauconite $K_{0.6}Na_{0.05}Fe^{3+}{}_{1.3}Mg_{0.4}Fe^{2+}{}_{0.2}Al_{0.3}Si_{3.8}O_{10}(OH)_2$
Biotite $KMg_{2.5}Fe^{2+}{}_{0.5}AlSi_3O_{10}(OH)_{1.75}F_{0.25}$
Siderite $FeCO_3$
Artificially Created
- Steel Slag amended with $Fe^{+2}$
- Cement amended with $Fe^{+2}$
- Minerals treated with $Fe^{+2}{}_{(aq)}$
- Minerals treated with reductants

# Why Add Carbon/ZVI to Reduce ORP?

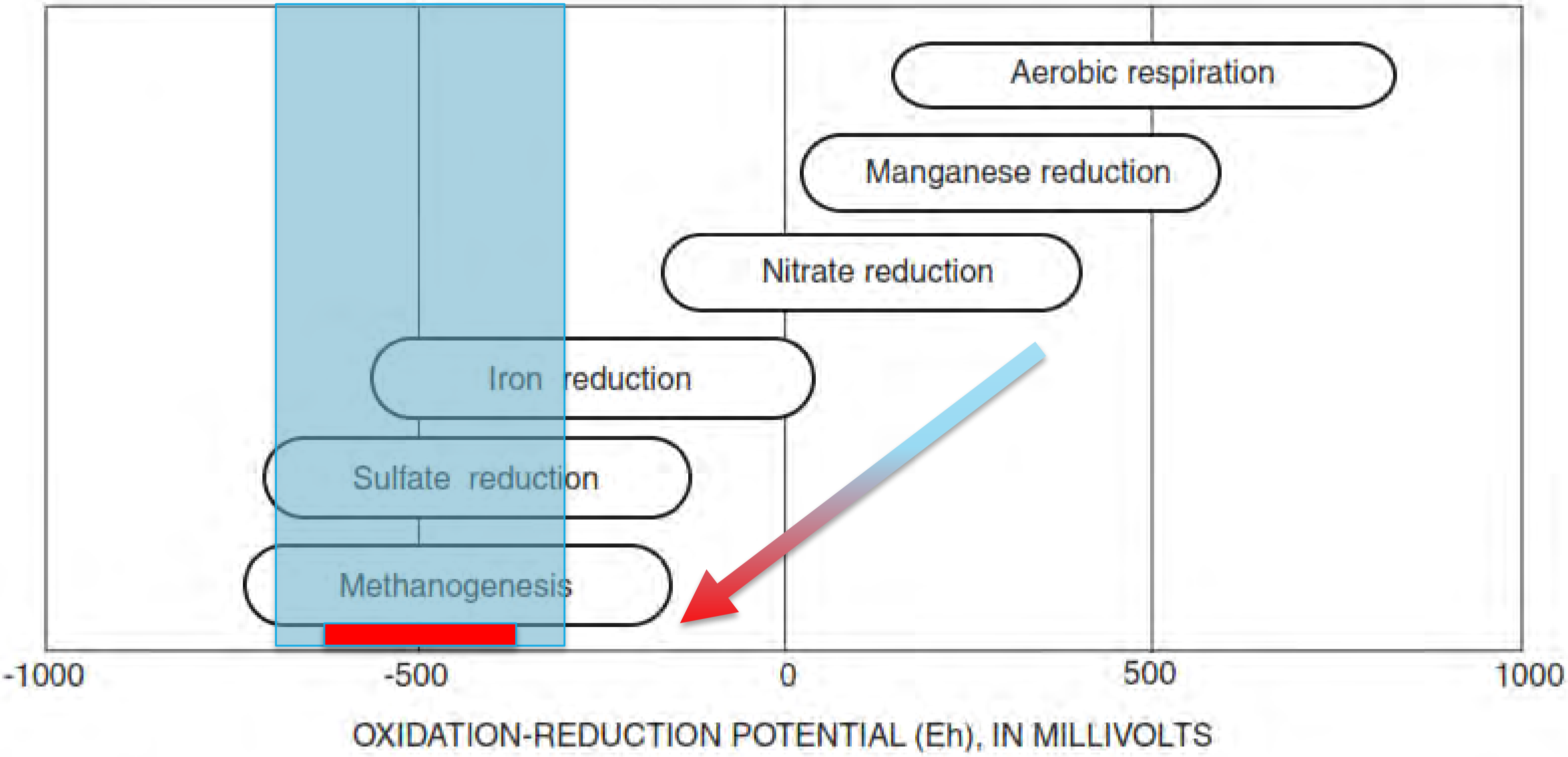
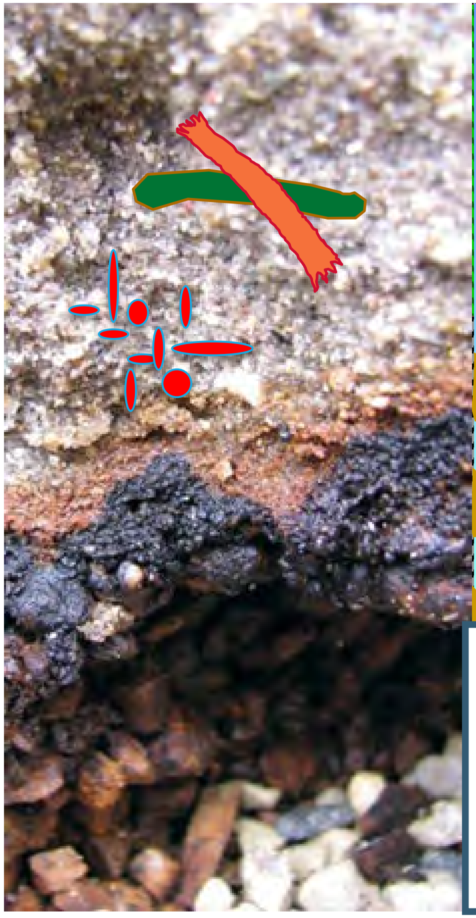
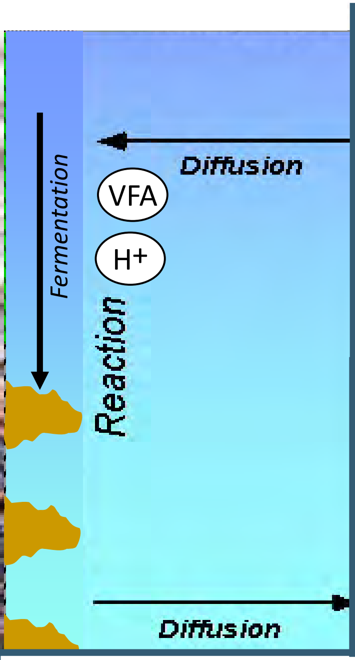


**Figure 2**. Oxidation-reduction potentials for selected microbial processes. (Modified from Stumm and Morgan, 1981.)

# Carbon Fermentation + ZVI Corrosion = ISCR Multiple Reaction Mechanisms





**Production of organic acids (VFAs):** electron donors for reduction of COIs, $O_2$, $NO_3$, $SO_4$

- By preventing basification, reduces precipitate formation on ZVI surfaces to increase rate of iron corrosion /$H_2$ generation / reactivity

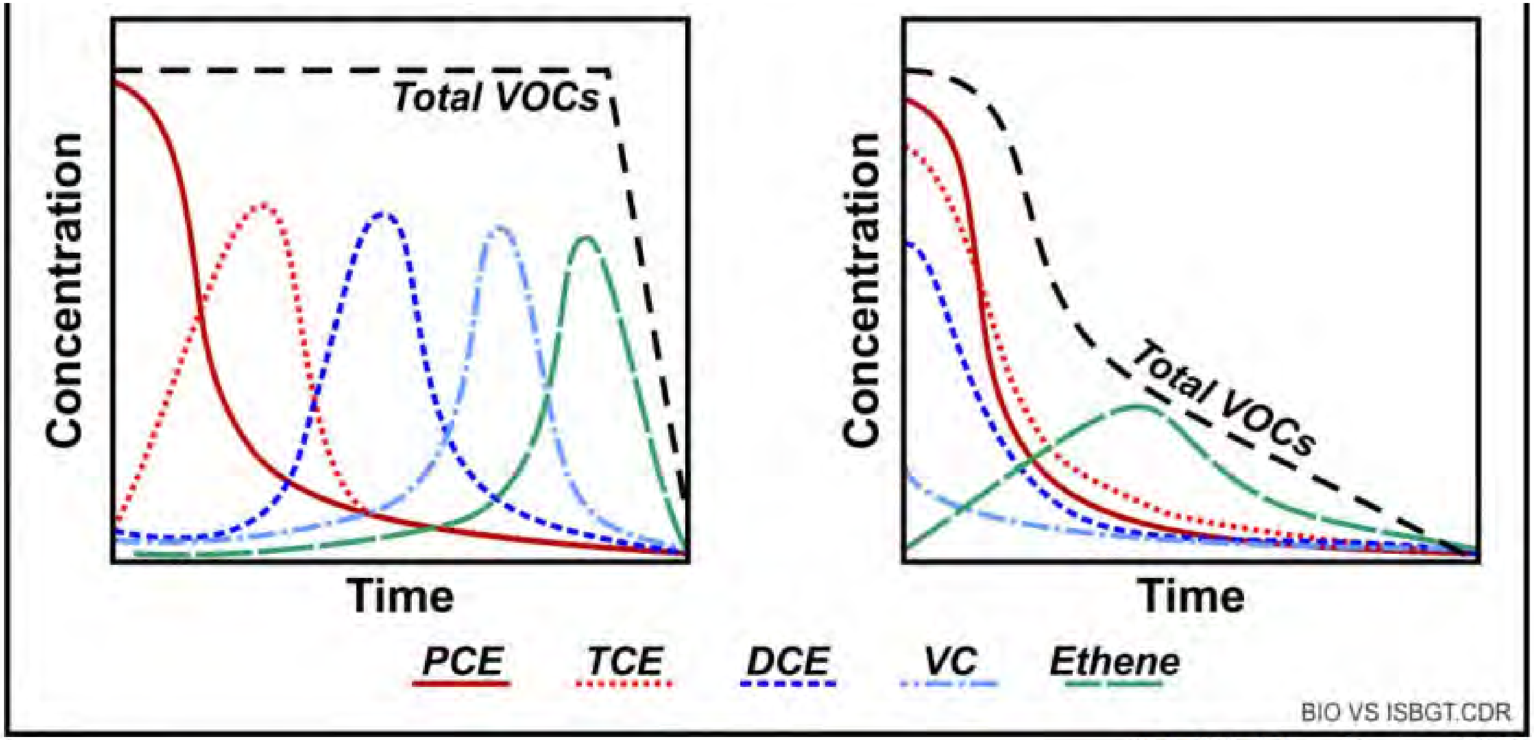
**ZVI Reactions:** $H_2$ and $Fe^{+2}$ and generation

$$Fe^0 \rightarrow Fe^{2+} + 2e^-$$
$$2H_2O \rightarrow 2H^+ + 2OH^-$$
$$2H^+ + 2e^- \rightarrow H_{2(gas)}$$
$$R\text{-}Cl + H^+ + 2e^- \rightarrow R\text{-}H + Cl^-$$

**ISCR = thermodynamic conditions for dechlorination:**

- Combined oxygen consumption from carbon fermentation and iron oxidation → Strongly reduced environment (-250 to -500 mV)
- High electron/$H^+$ pressure

# ERD v. ISCR



(Modified from Brown, 2009)

Figure 2. Abiotic versus Biological Degradation Pattern for Chlorinated Solvents

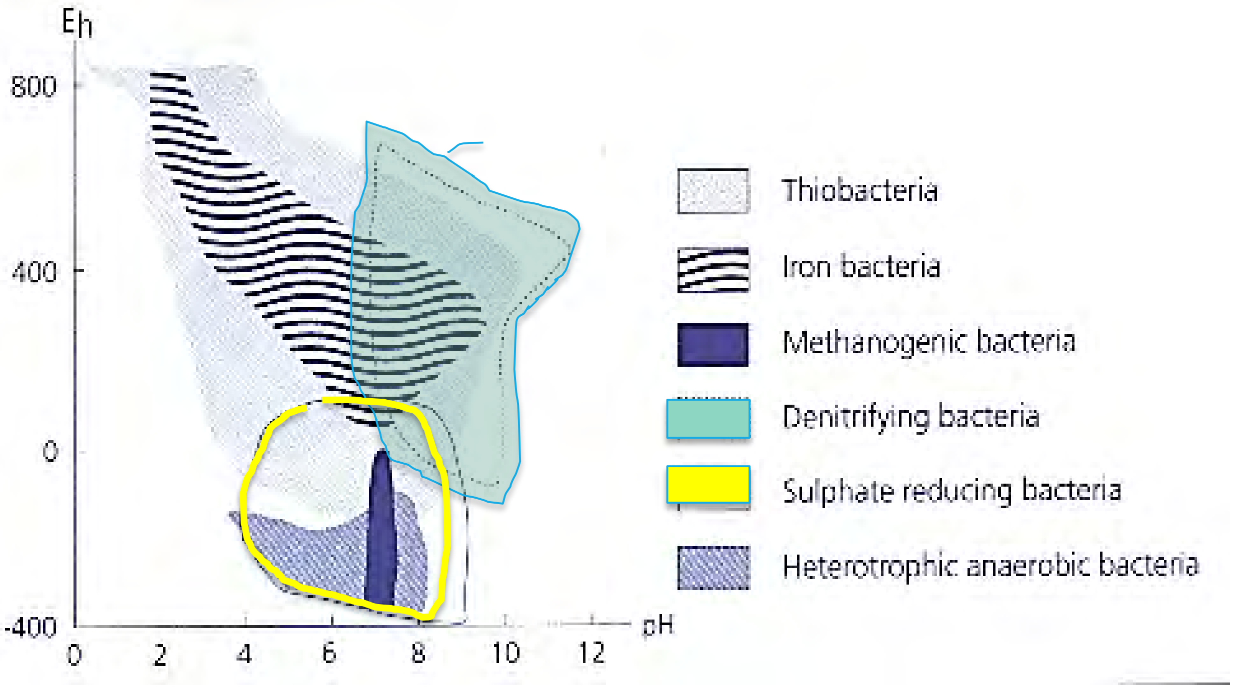
NAVFAC
Naval Facilities Engineering Command
ENGINEERING AND EXPEDITIONARY WARFARE CENTER

TECHNICAL REPORT
TR-NAVFAC EXWC-EV-1601

BIOGEOCHEMICAL TRANSFORMATION HANDBOOK

# Idealized Eh pH Ranges for Microbial Growth

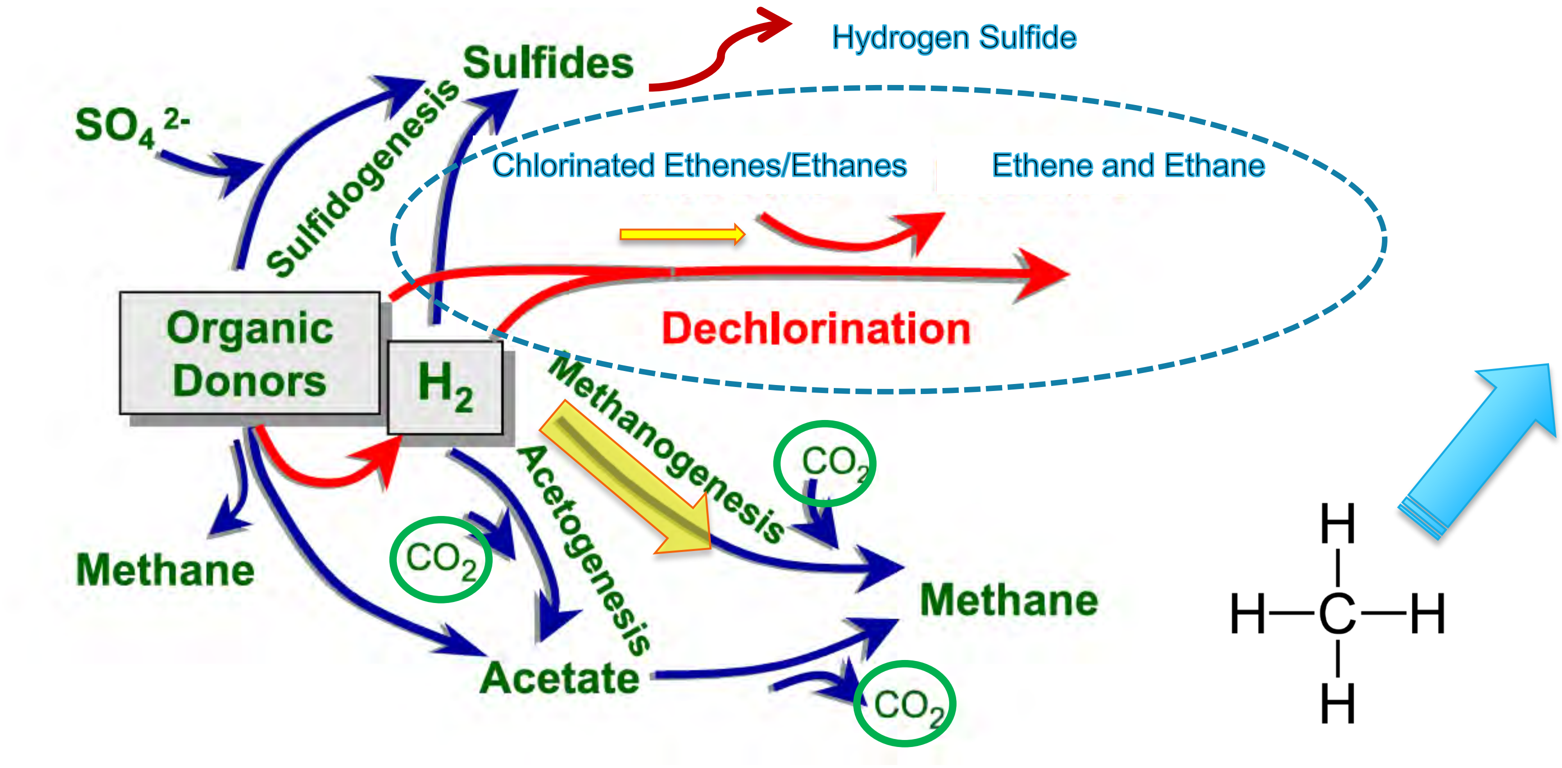
| Microbe | Doubling Times |
|---|---|
| Dehalococcoides spp. | 24 to 48 hours |
| Methanogens with cytochromes | 10 hours |
| Methanogens without cytochromes | 1 hour |



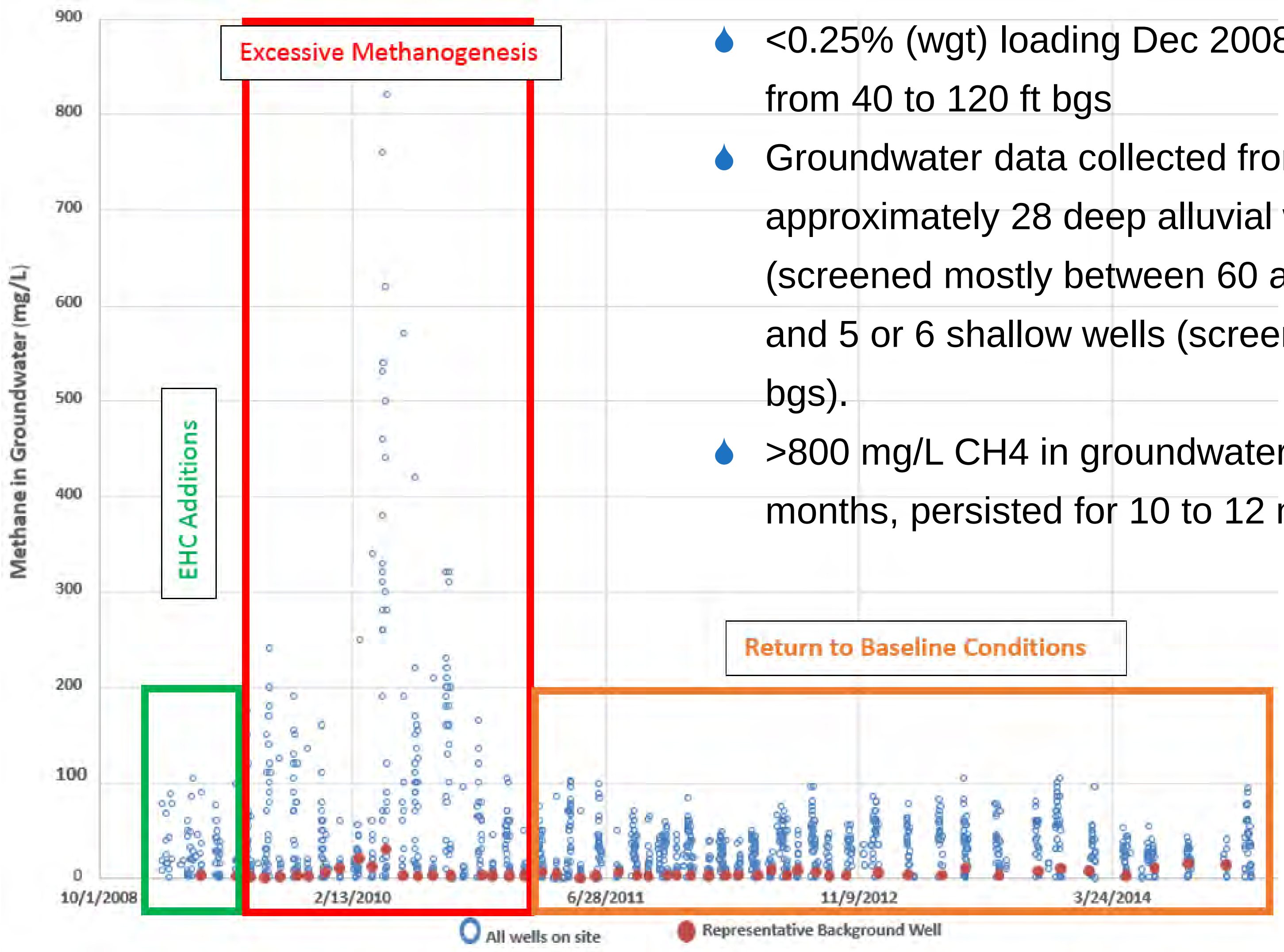
Zajic, 1969. Sigma Aldrich

# Hydrogen is the Currency

- **Where Does it Go? = Cost and Efficiency Issues**: Methanogens dominate anaerobic ecosystems and they can hinder dechlorination by competing for $H_2$ with dechlorinating bacteria (Yang and McCarty, 1998; yellow arrows modified by Provectus).



# Excessive Methane Production

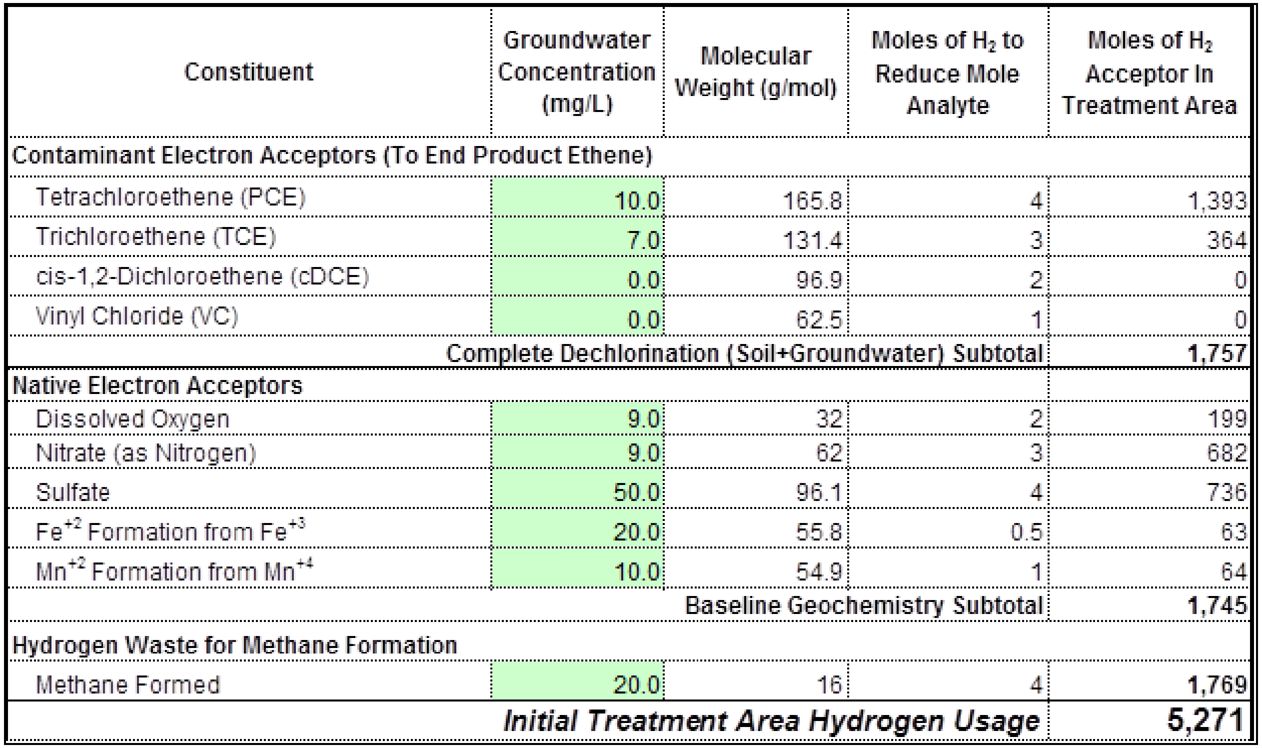


- <0.25% (wgt) loading Dec 2008-May, 2009 from 40 to 120 ft bgs
- Groundwater data collected from approximately 28 deep alluvial wells (screened mostly between 60 and 160 ft bgs) and 5 or 6 shallow wells (screened 25-35 ft bgs).
- >800 mg/L $CH_4$ in groundwater after 6 months, persisted for 10 to 12 months

# Excessive CH4 16 months post EVO

# Issue 1: Cost and Efficiency

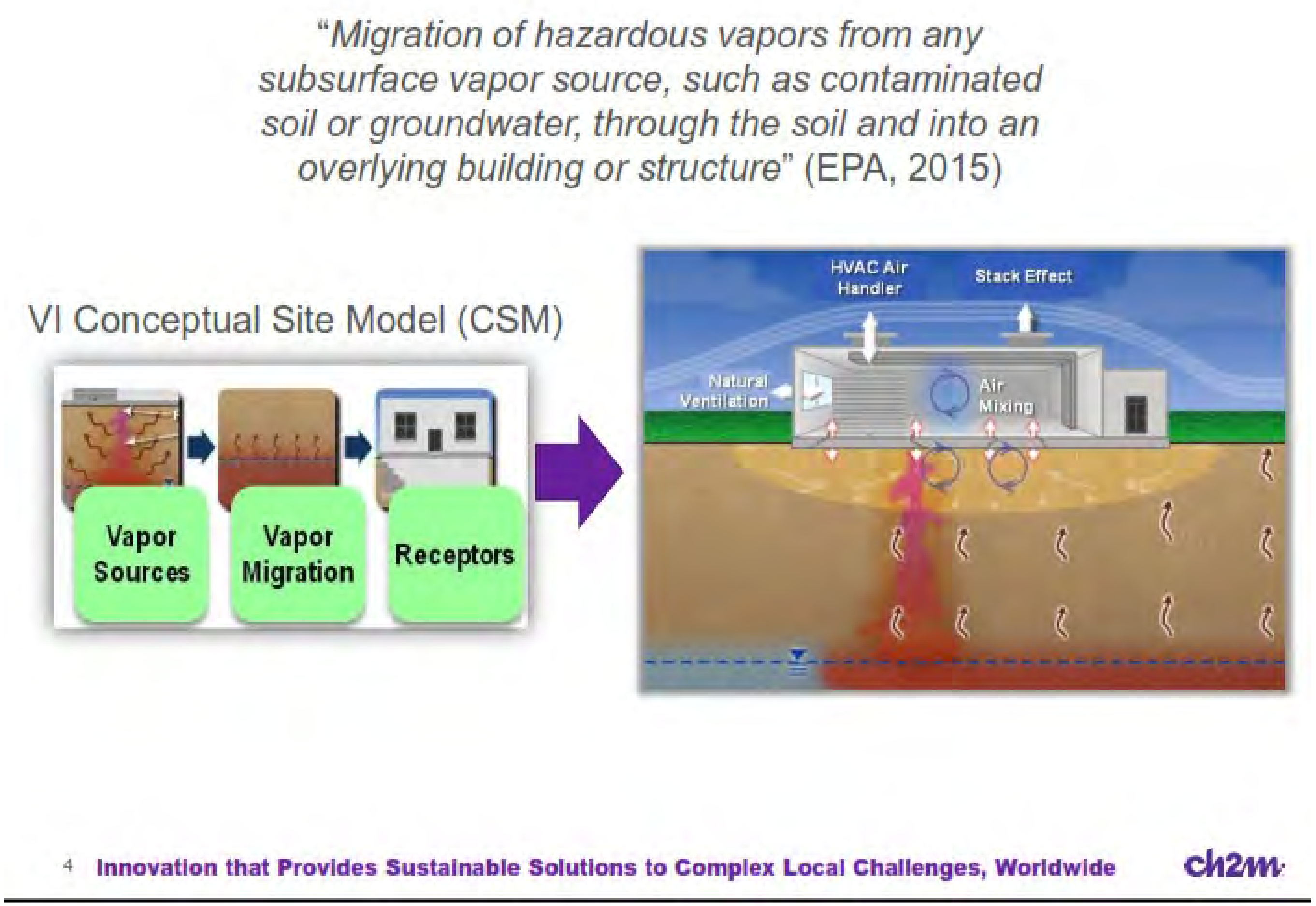
- Production of methane is a direct indication that hydrogen generated from the electron donor amendments was used by methanogens instead of the target microbes (*e.g., Dehalococcoides spp*.), substantially reducing application efficiency.



| Constituent | Groundwater Concentration (mg/L) | Molecular Weight (g/mol) | Moles of $H_2$ to Reduce Mole Analyte | Moles of $H_2$ Acceptor In Treatment Area |
|---|---|---|---|---|
| Contaminant Electron Acceptors (To End Product Ethene) | | | | |
| Tetrachloroethene (PCE) | 10.0 | 165.8 | 4 | 1,393 |
| Trichloroethene (TCE) | 7.0 | 131.4 | 3 | 364 |
| cis-1,2-Dichloroethene (cDCE) | 0.0 | 96.9 | 2 | 0 |
| Vinyl Chloride (VC) | 0.0 | 62.5 | 1 | 0 |
| Complete Dechlorination (Soil+Groundwater) Subtotal | | | | **1,757** |
| Native Electron Acceptors | | | | |
| Dissolved Oxygen | 9.0 | 32 | 2 | 199 |
| Nitrate (as Nitrogen) | 9.0 | 62 | 3 | 682 |
| Sulfate | 50.0 | 96.1 | 4 | 736 |
| $Fe^{+2}$ Formation from $Fe^{+3}$ | 20.0 | 55.8 | 0.5 | 63 |
| $Mn^{+2}$ Formation from $Mn^{+4}$ | 10.0 | 54.9 | 1 | 64 |
| Baseline Geochemistry Subtotal | | | | **1,745** |
| Hydrogen Waste for Methane Formation | | | | |
| Methane Formed | 20.0 | 16 | 4 | **1,769** |
| ***Initial Treatment Area Hydrogen Usage*** | | | | **5,271** |

Even in a highly oxidized setting with relatively high total concentrations of PCE and TCE, generating just 20 mg/L of methane constitutes **greater than 33%** of the total amendment consumption based on moles of $H_2$.

# Issue 2: Vapor Intrusion



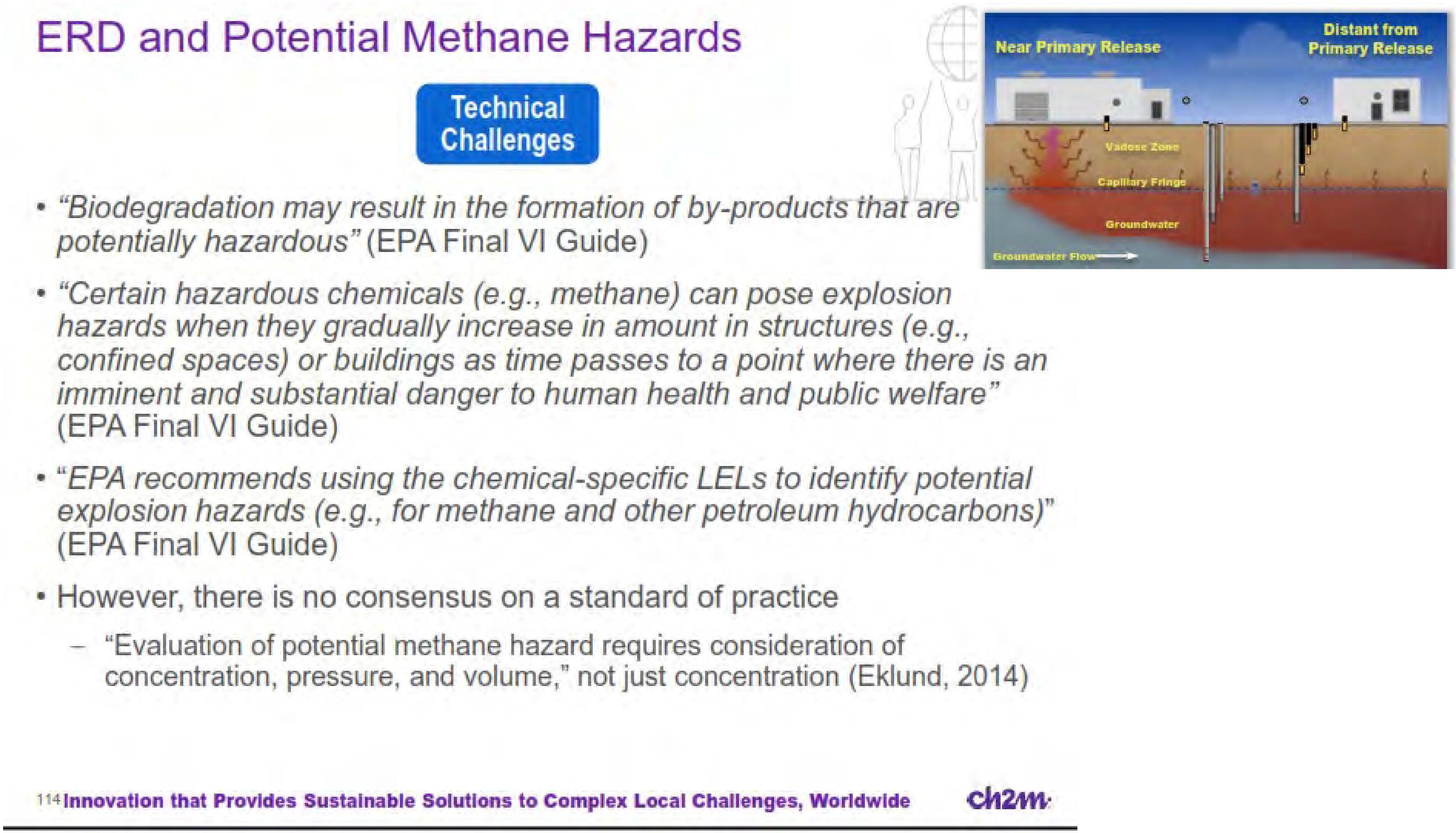
*"Migration of hazardous vapors from any subsurface vapor source, such as contaminated soil or groundwater, through the soil and into an overlying building or structure"* (EPA, 2015)

VI Conceptual Site Model (CSM)

4 **Innovation that Provides Sustainable Solutions to Complex Local Challenges, Worldwide**

ch2m

# Methane Impacts Vapor Intrusion

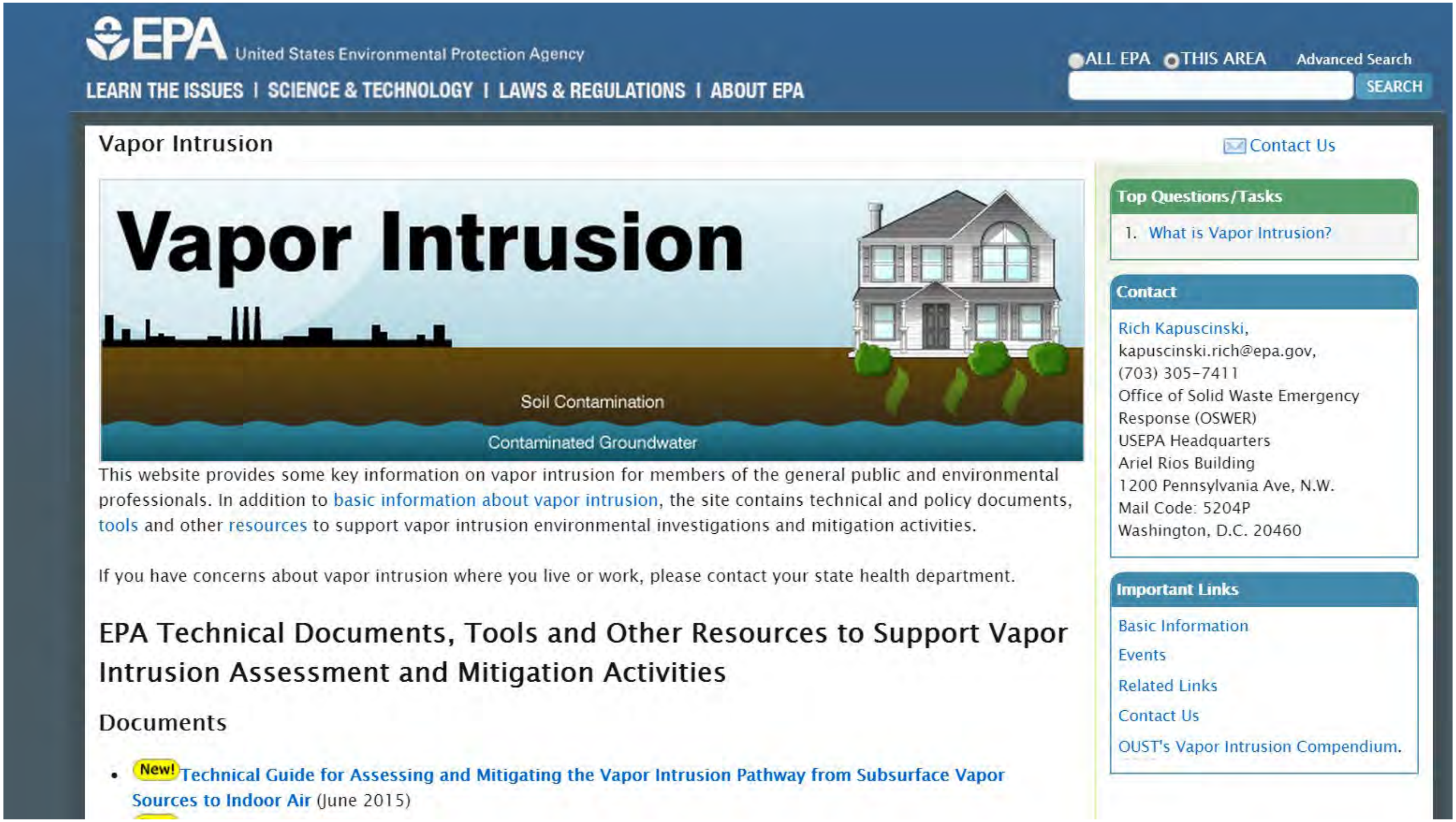


## ERD and Potential Methane Hazards

**Technical Challenges**

- *"Biodegradation may result in the formation of by-products that are potentially hazardous"* (EPA Final VI Guide)
- *"Certain hazardous chemicals (e.g., methane) can pose explosion hazards when they gradually increase in amount in structures (e.g., confined spaces) or buildings as time passes to a point where there is an imminent and substantial danger to human health and public welfare"* (EPA Final VI Guide)
- "*EPA recommends using the chemical-specific LELs to identify potential explosion hazards (e.g., for methane and other petroleum hydrocarbons)*" (EPA Final VI Guide)
- However, there is no consensus on a standard of practice
  - "Evaluation of potential methane hazard requires consideration of concentration, pressure, and volume," not just concentration (Eklund, 2014)

# What Does the US EPA Say?



Vapor Intrusion

This website provides some key information on vapor intrusion for members of the general public and environmental professionals. In addition to basic information about vapor intrusion, the site contains technical and policy documents, tools and other resources to support vapor intrusion environmental investigations and mitigation activities.

If you have concerns about vapor intrusion where you live or work, please contact your state health department.

## EPA Technical Documents, Tools and Other Resources to Support Vapor Intrusion Assessment and Mitigation Activities

### Documents

- New! Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air (June 2015)

**Top Questions/Tasks**

1. What is Vapor Intrusion?

**Contact**

Rich Kapuscinski,
kapuscinski.rich@epa.gov,
(703) 305-7411
Office of Solid Waste Emergency Response (OSWER)
USEPA Headquarters
Ariel Rios Building
1200 Pennsylvania Ave, N.W.
Mail Code: 5204P
Washington, D.C. 20460

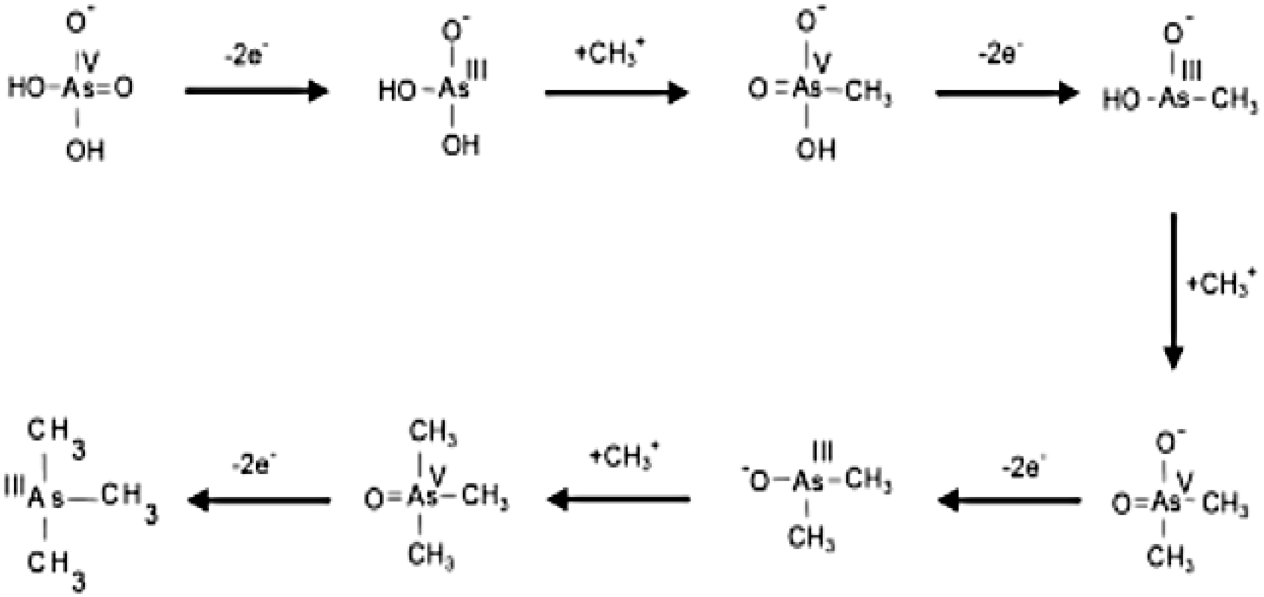
**Important Links**

- Basic Information
- Events
- Related Links
- Contact Us
- OUST's Vapor Intrusion Compendium.

- http://www.epa.gov/oswer/vaporintrusion/

# ISCR Issue 3: Arsenic Mobilization

- Methanogens (and other organisms) methylate metals and they are not able to participate in precipitation reactions.
- Moreover, the overall toxicity of the site is not increased via the generation of methylmetal(loids) as a consequence of the treatment process (example – biomethylation of arsenate).

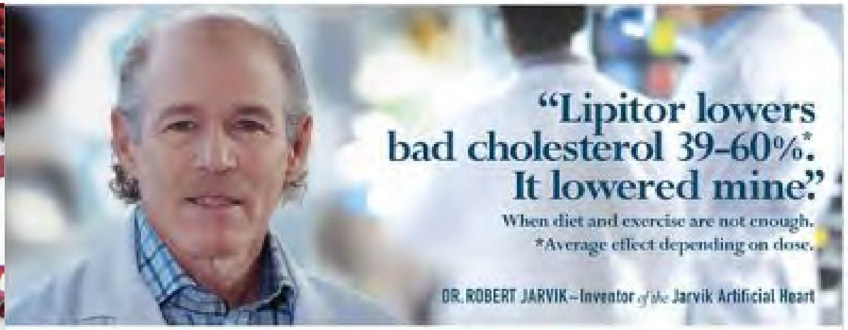


**Challenger mechanisms for biosynthesis or Arsenate (Challenger, 1945)**

# What is Red Yeast Rice (RYR) Extract?

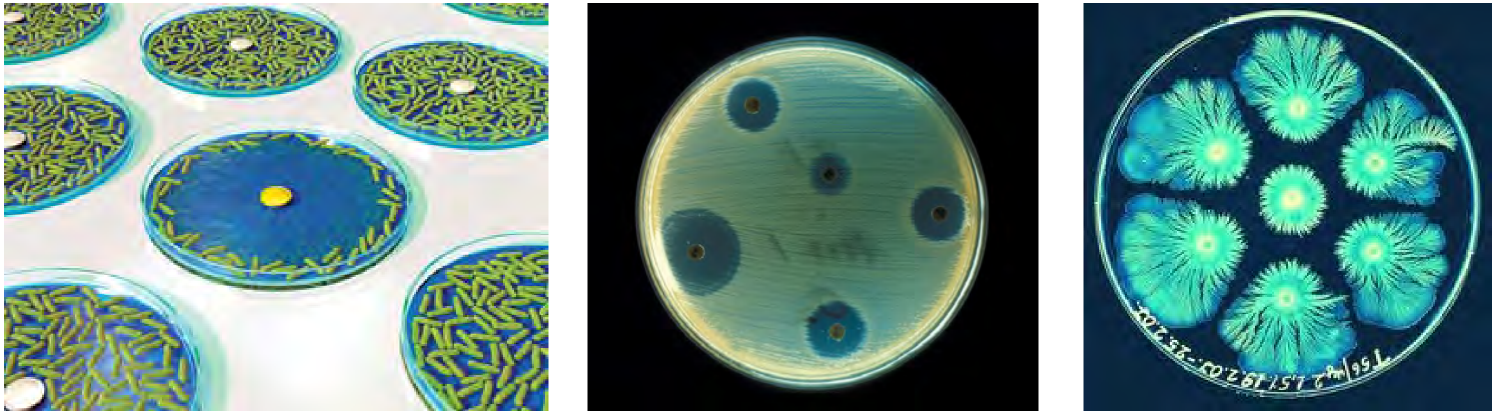
- RYR extract is a substance extracted from rice that has been fermented with a yeast called *Monascus purpureus*.
- RYR extract contains a number of natural statins - most importantly, Monacolin K - otherwise known as Lovastatin® / Lipitor® /etc.
- In addition to Monacolin K, RYR also contains 9 other statins, mono-unsaturated fatty acids, vitamins and other nutrients that will effectively stimulate anaerobic bacteria.
- RYR is used as a food coloring, food additive and preservative, and is widely consumed directly by humans.

[redacted]



Lovastatin is a registered trademark of Merck; Lipitor is a registered trademark of Pfizer

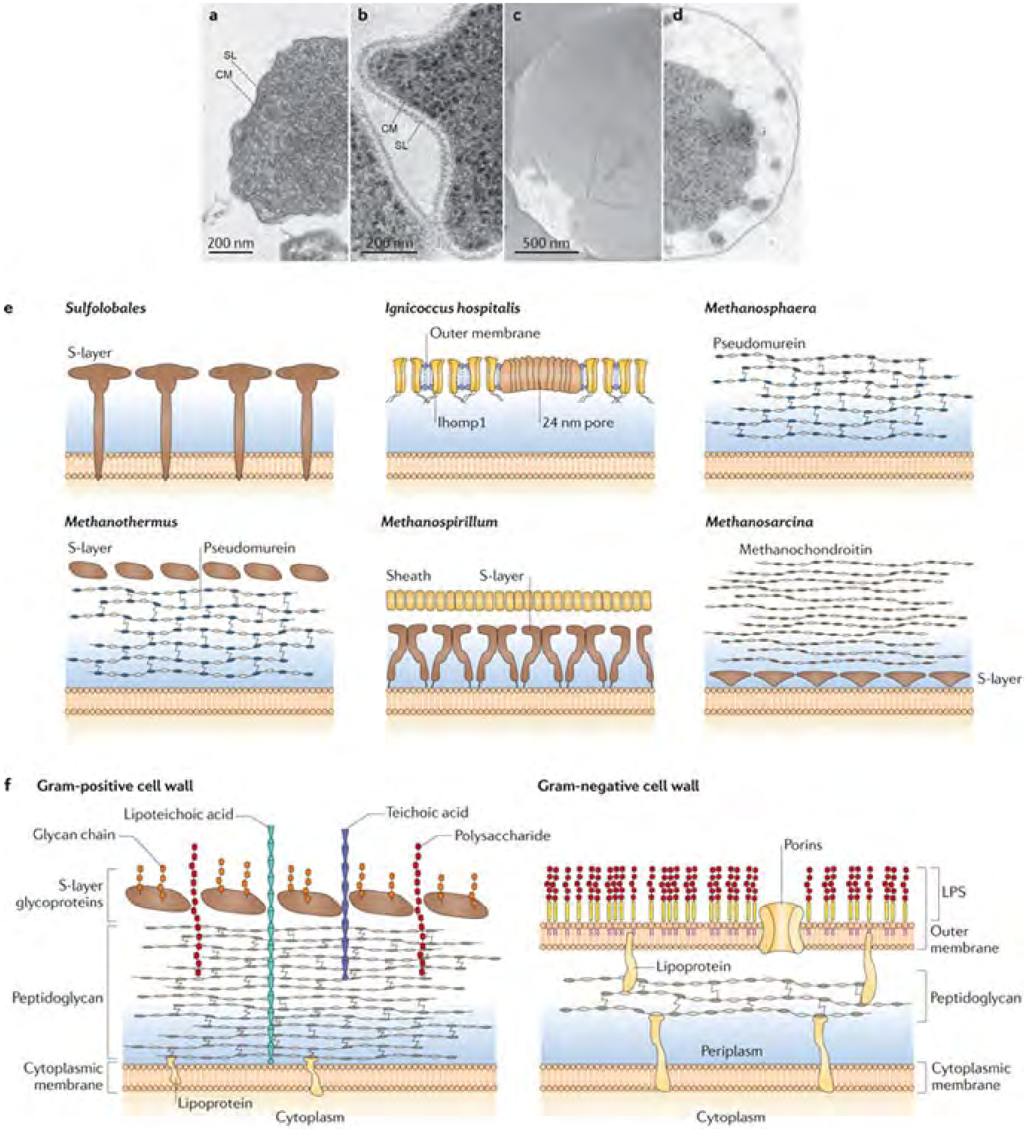
# Why Does RYR Produce Statins?



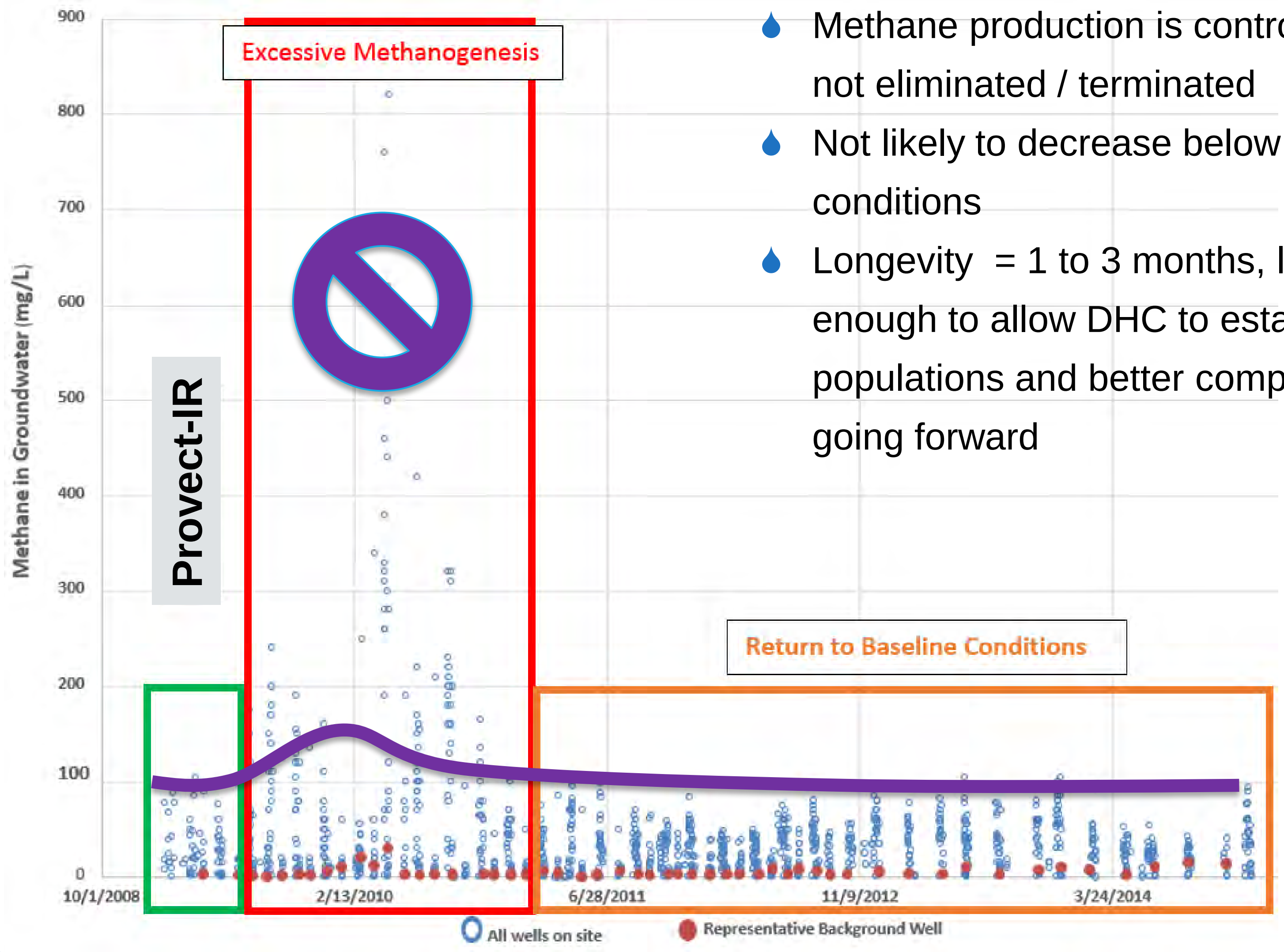
- Many microorganisms produce bioactive compounds that inhibit / regulate the growth and development of other organisms
- Example, antibiotics such as penicillin which is produced by mold of *Penicillium* genus

# How Does RYR Control Methanogens?

- Bacteria cell walls contain peptidoglycan (murein).
- Methanogens cell walls contain pseudomurein.
- Pseudomuerin is biosynthesized via activity similar to that of 3-hydroxyl-3-methylglutaryl-coenzyme A (HMG-CoA) reductase, which is a key enzyme in the cholesterol biosynthesis pathway in humans (Alberts *et al.*, 1980).



# Controlled Methanogenesis



- Methane production is controlled, not eliminated / terminated
- Not likely to decrease below current conditions
- Longevity = 1 to 3 months, long enough to allow DHC to establish populations and better compete going forward

# Provect-ERD CH4 Ole® Ego

2016.08.29 11:11

## Liquid, Antimethanogenic ERD reagent

**Photograph 1**. Provect-ERD CH4™ 15:1 Water:Oil (Left), 85% Carbon + 4% AMR Self-Emulsifiable Oil Concentrate (Middle), and 85% Carbon Self-Emulsifiable Oil Concentrate, no AMR (Right).

### Product Data

The materials are all combined at our own manufacturing facilities in the USA (and Europe) at proportions and formulations optimized for a given site. ERD-CH4$^{TM}$ is manufactured using 100% food grade ingredients that provide fast- and slow-release characteristics. Provect-CH4$^{®}$ antimethanogenic reagent (AMR) is typically added at three to five weight percent of the mass of the fermentable carbon. The common dosage of ERD-CH4 provides groundwater concentrations of 1,000 to 3,000 ppm TOC plus a minimum 150 ppm of AMR within the targeted treatment area.

| | |
|---|---|
| Color | Translucent Yellow |
| Density (lbs. / gal) | 7.75 to 8.46 (varies based on AMR) |
| Physical State | Liquid |
| Odor | Earthy |
| Viscosity (Brookfield, 30 rpm @25°C) | 50-100 cps |
| pH – 1% w/v in water | 7.3 |

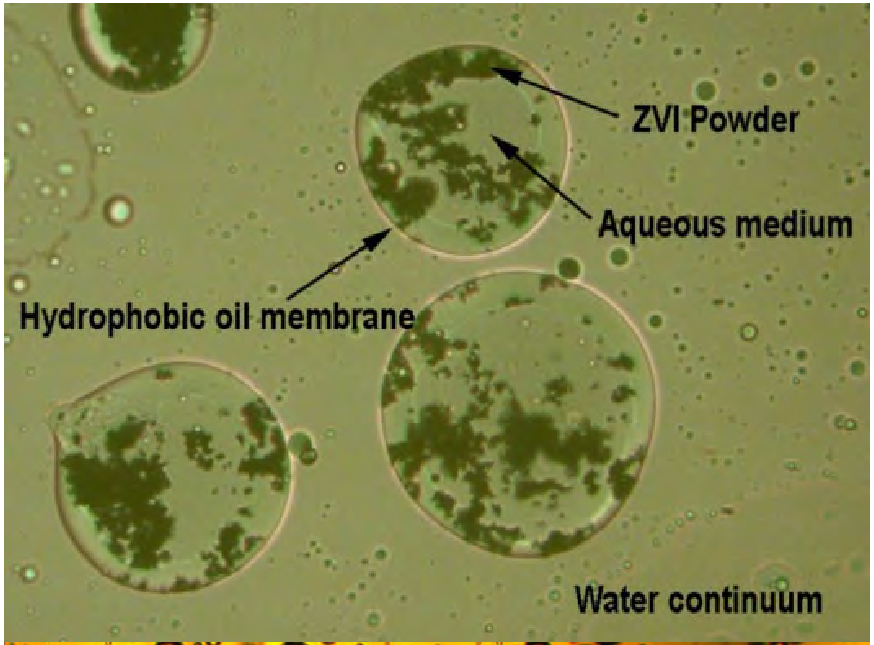
| **Oil Sample** | **Al** | **P** | **S** | **Zn** | **Fe** | **Mg** | **Ca** | **Na** | **K** |
|---|---|---|---|---|---|---|---|---|---|
| Self-Emulsifiable Vegetable Oil | 1.2 to 1.3 | 1,265 to 1,751 | 17.2 to 28.2 | 19.6 to 39.7 | 1,4 to 2.3 | 138 to 143 | 135 to 187 | 15.4 to 15.9 | 507 to 954 |

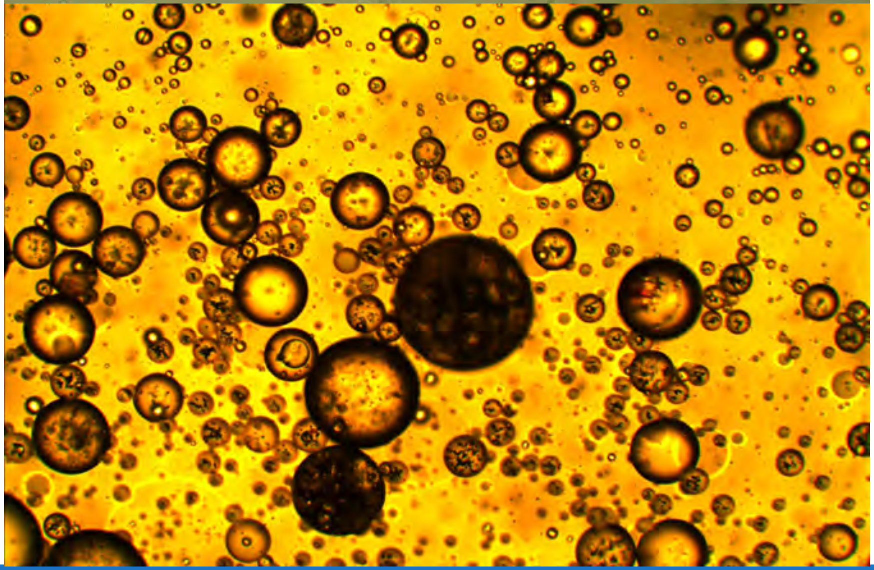
- **All units mg/kg oil**

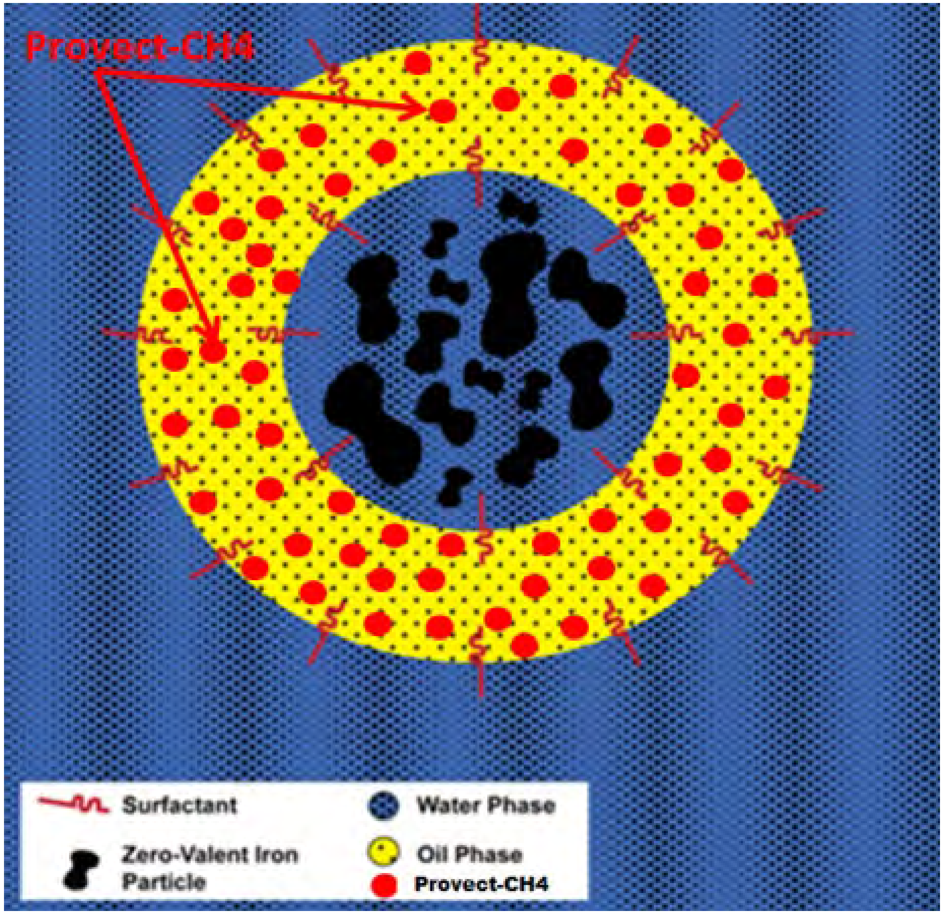
# Provect-IR® Solid, Antimethanogenic ISCR Reagent

- Provect-CH4 AMR Technology
- Multiple, Complex, Hydrophilic, Timed-Release organic carbon source (plant materials, Kelp, Ca Propionate) @ 390 g H donor / lb product
- 15% (wgt) Small (ave. 25 µm) ZVI particles ca. 25 ft surface area / lb
- Integrated Vitamins, minerals and nutrients (yeast extract) specially selected for anaerobes
- Chemical oxygen scavenger to maintain ZVI
- Package in 50 lb <u>safety</u> bags or 2,000 lb supersacs.

# EZVI-CH4™ AMR DNAPL Technology

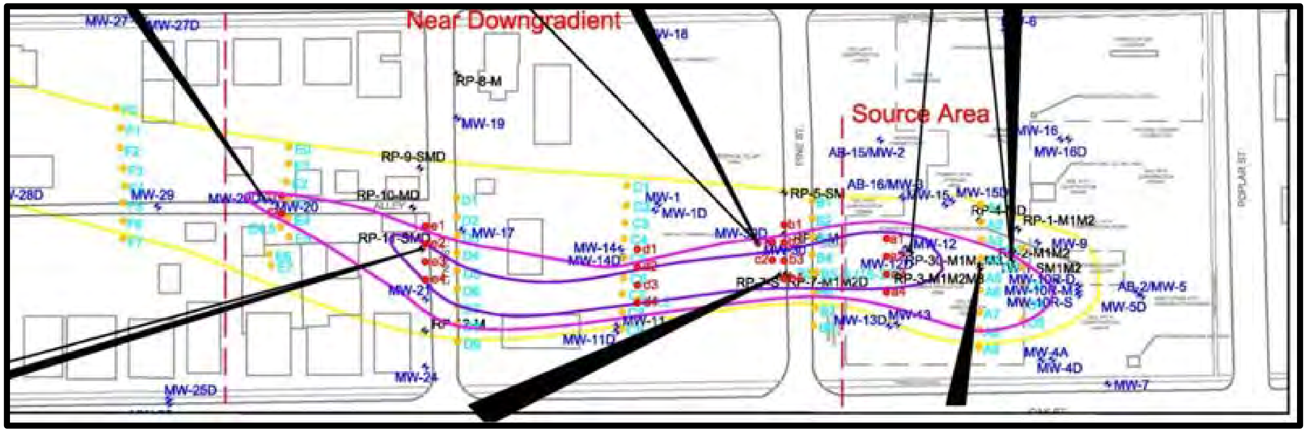






# Provect-CH4 Site Summary

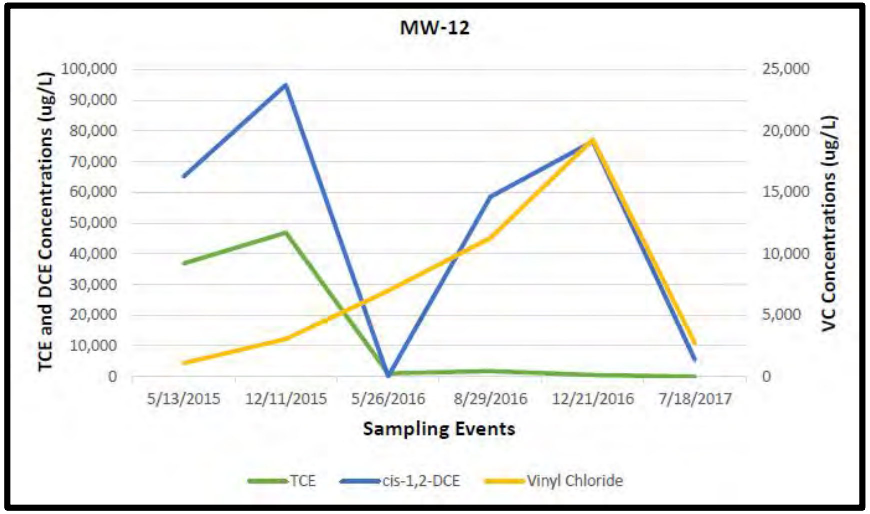
- Seymour Former Manufacturing Facility
  - Maximum cVOCs of 60,000 ug/L
  - Impacts extend to residential area
  - Primarily sand with clay and silt lenses
  - Excavation, thermal, and original ISCR technologies
  - Continued destruction of plume with methane control
- Emulsified vegetable oil (2 injections) with Provect-CH4
- 85% reductions with 1.9 ppm of methane produced

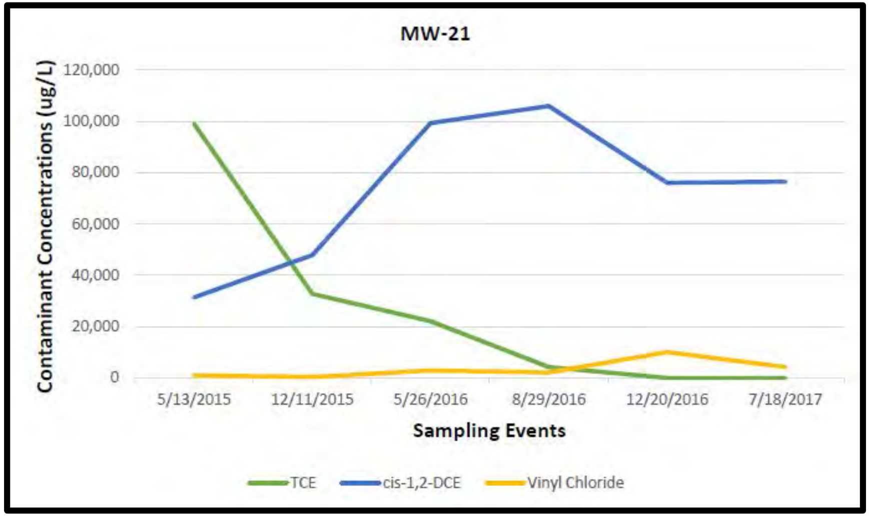


Courtesy Mundell & Associates

# Provect-IR / EZVI Site Summary

- East Orange, NJ Site
  - Former Manufacturing Facility
  - TCE concentrations greater than 99,000 ug/L – IR, EZVI and ZVI
  - Red-brown clayey silts with fine sand layers
  - Depth to groundwater ca. 20 ft bgs
  - Goal was to limit downgradient plume migration
  - 600 days of cVOC and geochemical monitoring; full case study



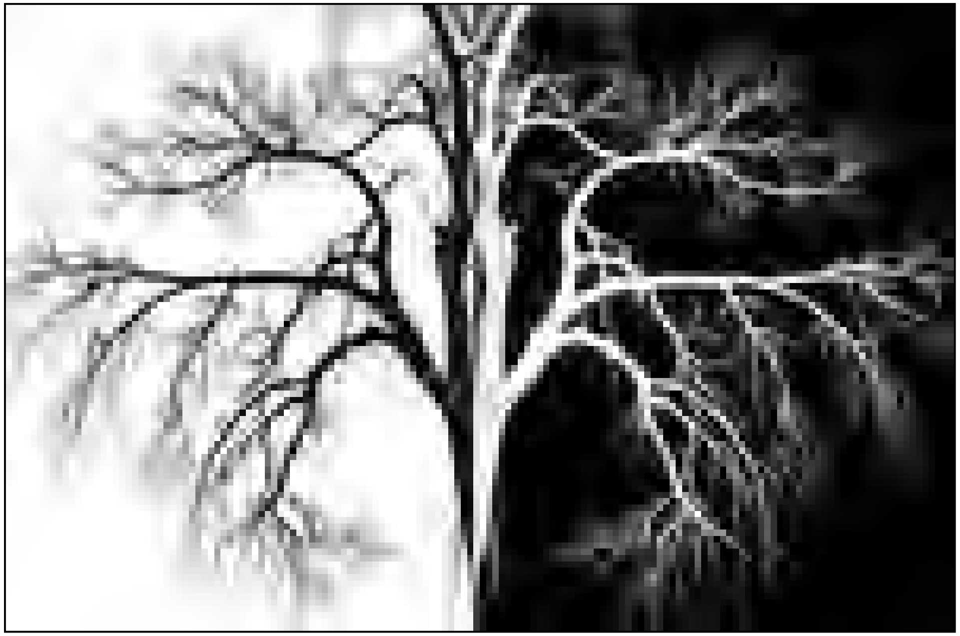


**Courtesy Innovative Environmental Technologies, Inc.**

# ISCO / ISCR – How to Decide in 2017?

ISCO and ISCR are electron transfer reactions. They are mirrors of each other. They can both be used for treating a number of contaminants, especially chlorinated solvents. However, for a given site, they may not be equally effective. Neither technology is universally applicable.

So - How does one determine which technology to apply?



# ISCO or ISCR – Five Selection Criteria

**Dosage Loading**

**Reagent Choice**

**Strategy and Distribution**

**Success is *enough reagent in contact* with the contaminant for a *long enough period of time* to *react effectively***

**Persistence**

**Contaminant Destruction**

# Reagent Selection and Dosage

- Contaminant Type and Concentration
- Contaminant Distribution
- Aquifer Lithology / Hydrogeology / Biogeochemistry
  - DO/ORP
  - pH
  - TOC / SOD / COD
  - Nitrate / Sulfate
  - Reduced metals
- Performance Criteria
- Site Logistics
  - Health & Safety requirements
  - Constructability

# Contaminant Concentration

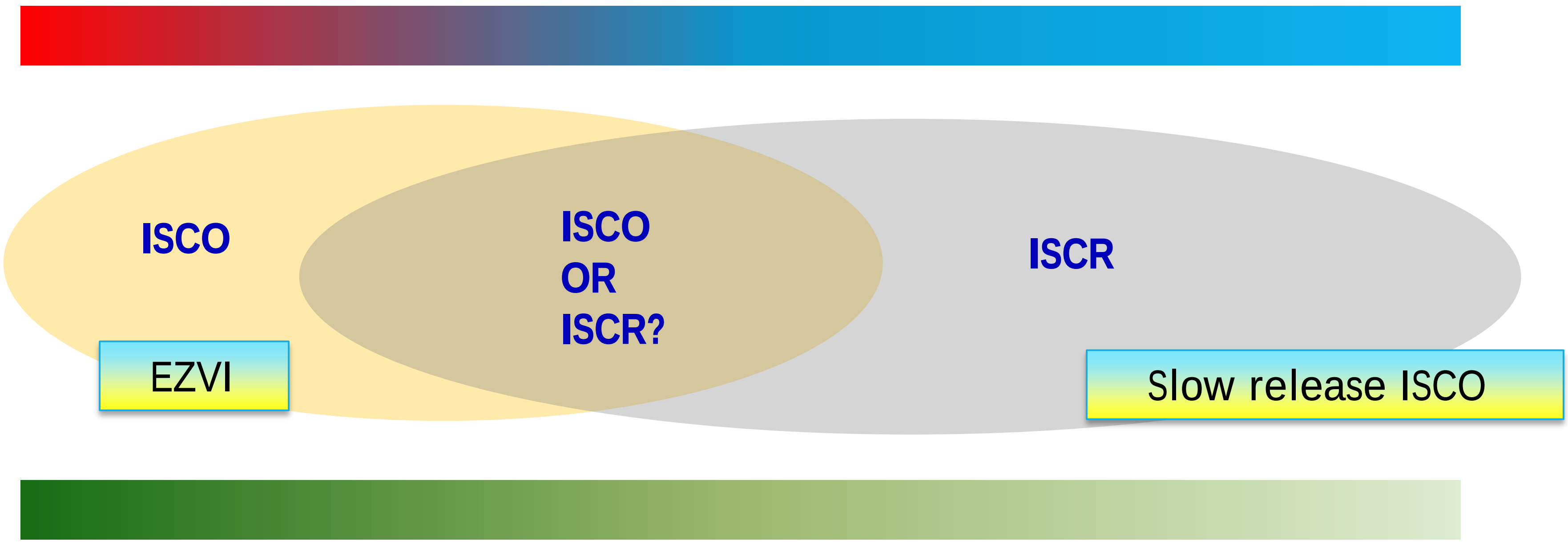
| Media | COI Concentrations | ISCO | ISCR |
|---|---|---|---|
| **Soil** | Low Level Impacts<br>Up to 10 mg/kg | Yes | Yes |
| | Mid Level Impacts<br>> 10 mg/kg | Yes | **Yes** |
| | High Level Impacts<br>NAPL | Yes | **EZVI** |
| **Groundwater** | Low Level Impact<br><1 ppm | No | Yes |
| | Mid Level Impacts<br>1 ppm to 100 ppm | Yes | Yes |
| | High Level Impacts<br>>100 ppm | Yes | **EZVI** |

Changes from 2008

# Contaminant Distribution

**Contaminant Concentration**

**> 100 ppm** **50 ppm** **10 ppm** **1 ppm** **500 ppb** **100 ppb** **< 50 ppb**



**ISCO**

**ISCO**
**OR**
**ISCR?**

**ISCR**

EZVI

Slow release ISCO

**source** **down gradient** → **plume**

**Contaminant Source**

Changes from 2008

Mueller *et al*., 2009, 2010, 2011, 2012

# Contaminant Distribution

| | ISCR | ZVI | ISCO |
|---|---|---|---|
| **PRB Applicability** | Yes<br>(3 to >5 yrs) | Yes<br>(>12 yrs) | Typically not applicable (short longevity) |
| **Widespread Plume Treatment** | More cost efficient at lower COI concentrations | Multiple PRBs possible | May not be cost effective at low concentrations |
| **Hot Spot Treatment** | Can apply to hot-spots | EZVI applicable to NAPL | Yes |
| **Source with NAPL** | | Iron or iron/ clay can be mixed into NAPL zones | Typically not applicable due to cost |

Changes from 2008

# Aquifer Biogeochemistry

- Geochemistry
  - **high organic carbon favors ISCR**

- Soil oxidant demand (SOD)
  - **>10 mg/kg favors ISCR**

- Competing electron acceptors (CEAs)
  - **$O_2 >$ Mn(IV) $> NO_3^- >$ Fe(III) $> SO_4^{2-} > CO_2$**
  - **Sulfate > 100 mg/L favors ISCO**

- Is there a concern from secondary plumes
  - **sodium, sulfate, iron, purple color etc.**

- Toxic intermediates and daughter products
  - **Less likely with ISCO; more likely with ISCR**

- Methane VI and other issues
  - **Less likely with ISCO;**
  **more likely with Conventional ISCR**

Factors that can be managed, but will increase cost

Regulatory Drivers

# Summary

## ISCO

Multiple Oxidants Available

- ✓ Different reaction pathways
  - Non-Contaminant Specific
  - Oxidant Specific
  - Geochemical effects
- ✓ None naturally occurring

Limited Reagent Lifetime

- Non-Beneficial Consumption
- Rebound issue improved
- Slow release reagents

Non-selective reactions

- Partial oxidation
- End products are $CO_2$, Water +
- Sulfuric acid possible

## ISCR

ZVI DVI (added, created or natural)

- ✓ Reaction pathways
  - β elimination primary reaction
  - Combination of electron reactions

Longer Reagent Lifetime

- Minimal Non-Beneficial Consumption
- DO and Nitrate

More selective reactions

- Known catabolites
- End products are dechlorinated organics +
- CO, CO2, CH4

# Conclusions

## Weight of Evidence Approach

- Selecting ISCO or ISCR requires site-specific evaluation
- Best choice usually has the fewest undesirable factors that can be overcome or managed most easily /cost effectively

## 2018 updates

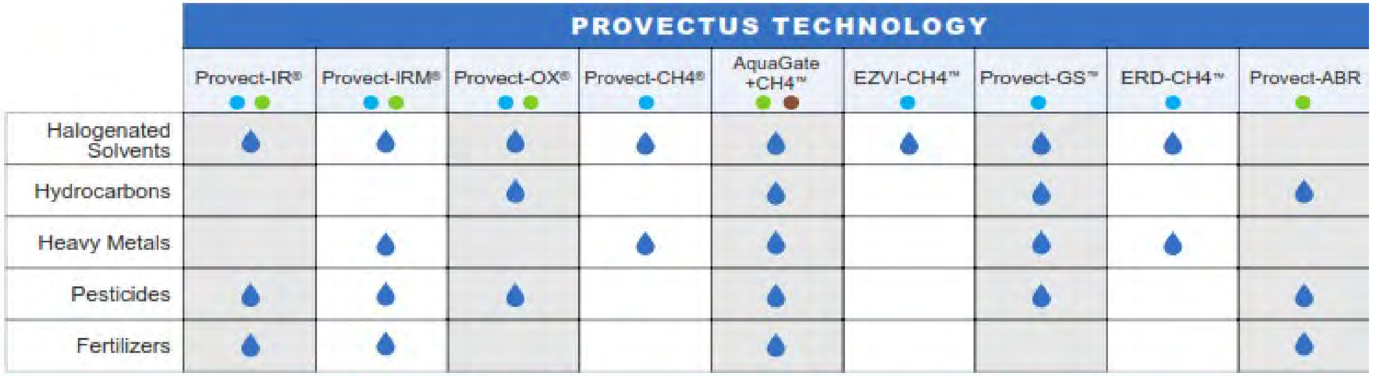
- ISCO integrated with multiple biological processes = rebound
- Slow release ISCO reagents = longevity / kinetics challenge
- Antimethanogenic ERD ISCR technologies
- Sequestration technologies

## Reminder:

– Presentation is an update of multiple past reports/publications

– Not a complete analysis, but a summary of factors that have been observed to affect technology selection, design and field performance

# Provectus Environmental Products, Inc



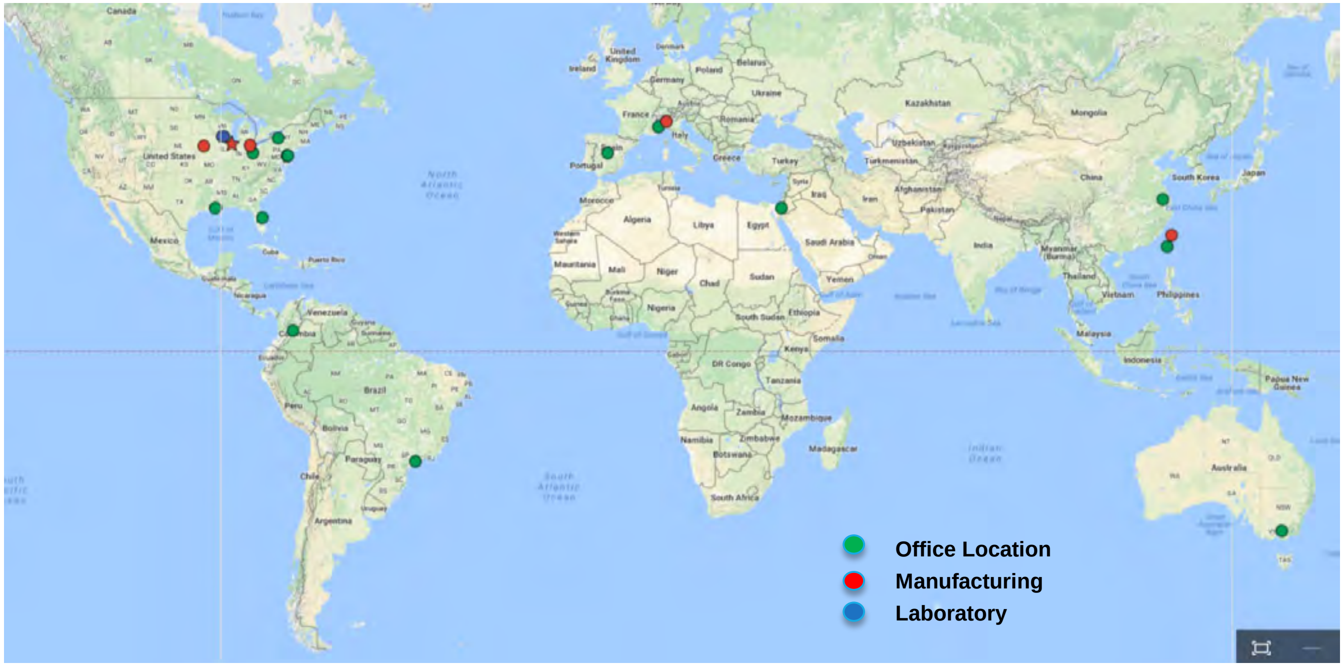
| | PROVECTUS TECHNOLOGY | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Provect-IR® 🔵 🟢 | Provect-IRM® 🔵 🟢 | Provect-OX® 🔵 🟢 | Provect-CH4® 🔵 | AquaGate +CH4™ 🟢 🟤 | EZVI-CH4™ 🔵 | Provect-GS™ 🔵 | ERD-CH4™ 🔵 | Provect-ABR 🟢 |
| Halogenated Solvents | 💧 | 💧 | 💧 | 💧 | 💧 | 💧 | 💧 | 💧 | |
| Hydrocarbons | | | 💧 | | 💧 | | 💧 | | 💧 |
| Heavy Metals | | 💧 | | 💧 | 💧 | | 💧 | 💧 | |
| Pesticides | 💧 | 💧 | 💧 | | 💧 | | 💧 | | 💧 |
| Fertilizers | 💧 | 💧 | | | 💧 | | | | 💧 |

🔵 Groundwater Applications 🟢 Surface Soil Applications 🟤 Sediment Applications

**We Now Sell ZVI**

# Provectus Environmental Products

- **Complimentary Site Evaluation**
- **Complimentary review of quarterly field performance data with every project**
- **Laboratory Treatability Studies**
- **Turn-Key, Pay-for-Performance Contracting Options**
- **Project Specific Guarantees and Warranties**



- **USA (Illinois, New Jersey, Ohio, Pennsylvania, Louisiana)**
- **Australia, Brazil, China, Colombia, Israel, Italy, Spain and Taiwan**

# Overview of Provectus' Patent Estate (IET)

| Application / Patent Number | Title | Filing Date | Issue Date |
|---|---|---|---|
| 7,129,388 and 7,531,709 and 9,427,786 | Method for Accelerated Dechlorination of Matter; Parts 1 and 2. | | 10/31/2006 and 5/12/2009 and 8/30/2016 |
| 7,828,974 | Method for the Treatment of Ground Water and Soils Using Dried Algae and Other Dried Mixtures | | 11/9/2010 |
| 8,147,694 | Method for the Treatment of Ground Water and Soils Using Mixtures of Seaweed and Kelp | | 4/3/2012 |
| 8,766,030 | Utilization of Ferric Ammonium Citrate for In Situ Remediation of chlorinated Solvents | | 7/1/2014 |
| 9,221,699 | Method for Inhibition of Methane Production During Anaerobic Reductive Dechlorination | | 12/29/2015 |
| 9,126,244 | Use of Encapsulated Substrates to Control the Release Rates of Organic Hydrogen Donors | | 9/8/2015 |
| 9,126,245 B2 | Chemical Oxidation and Biological Attenuation Process for the Treatment of Contaminated Media | | 9/8/2015 |
| 7,044,152 | Apparatus for In Situ Remediation Using a Closed Delivery System | | 5/11/16 |
| 62/024,640<br>15/325,864 | Method and Composition for Inhibiting Methanogenesis During In Situ Sediment Treatment | 06/15/2015 | |
| 9,637,731 | Method and Composition for Inhibiting Heavy Metal Methylation During In Situ Remedial Actions | | 5/2/2017 |
| 15/269,903 | Inhibition of Methanogenesis to Control Wood-Boring Insects and Pestilence | 9/19/2016 | |
| 15/408,145 | Inhibition of Methanogenesis During Environmental Applications | 1/17/2017 | |

8 issued patents; 5 Pending Patents (as of January, 2016)

# My Background (Mueller)

- B.S., M.S.  SIU Carbondale – 1983/1985
- Ph.D. Clemson University -1988
- Post Doctoral Studies US EPA GBERL (1988 – 1991)
- SBP Technologies, Inc.→ RF Weston (1991 to 1997)
- Dames & Moore → URS (1997 to 2002)
- Malcolm Pirnie, Inc. (2002 to 2003)
- WR Grace → Adventus Americas, Inc. → FMC Corporation → Peroxychem/JPM  (2003 to April, 2014)
- Provectus Environmental Products – May, 2014 (acquired patents on CH4 inhibitors, ISCR  and ISCO)

# ISCO Issue 3: Longevity of Reagents

Chemosphere

Volume 150, May 2016, Pages 239–247

## A five-year performance review of field-scale, slow-release permanganate candles with recommendations for second-generation improvements

Mark Christenson[a, b], Ann Kambhu[c], James Reece[b], Steve Comfort[b], Laurie Brunner[d]

[a] AirLift Environmental, LLC, 5900 N. 58th, Suite 5, Lincoln, NE 68507, USA

[b] School of Natural Resources, University of Nebraska, Lincoln, NE 68583-0915, USA

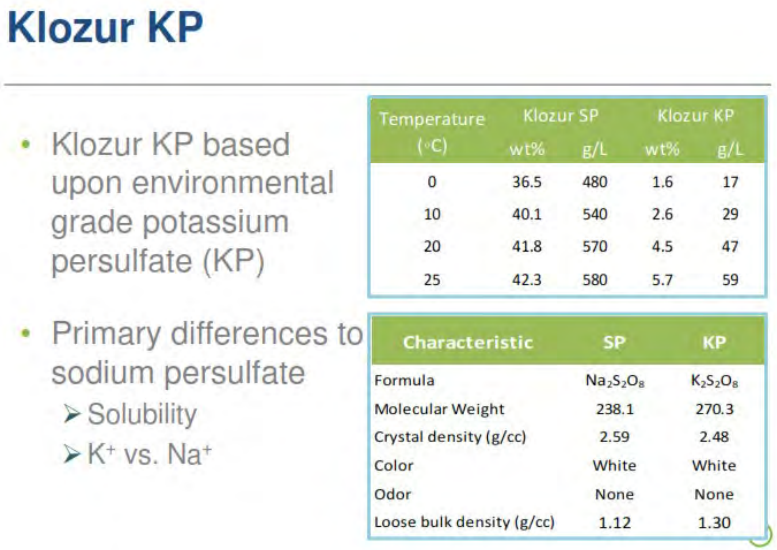
[c] Department of Civil Engineering, University of Nebraska, Lincoln, NE 68583-0531, USA

[d] Nebraska Department of Environmental Quality, Waste Management Division, Lincoln, NE 68509-8922, USA

Received 14 December 2015, Revised 26 January 2016, Accepted 31 January 2016, Available online 21 February 2016

**Figure 2.** **(A)** Field plot of the permeable reactive barrier of SRPCs and monitoring wells; each SRPC location received five candles stack on top of each other; and **(B)** photograph of permanganate candles.

# Longevity of ISCO Reagents – KP?

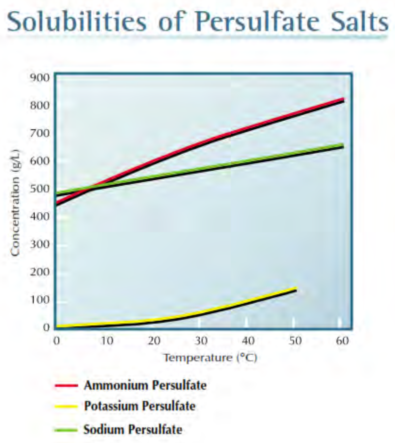


## Klozur KP

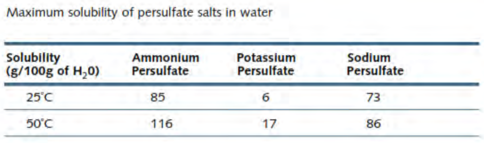
- Klozur KP based upon environmental grade potassium persulfate (KP)
- Primary differences to sodium persulfate
  - ➢ Solubility
  - ➢ K⁺ vs. Na⁺

| Temperature (°C) | Klozur SP wt% | Klozur SP g/L | Klozur KP wt% | Klozur KP g/L |
|---|---|---|---|---|
| 0 | 36.5 | 480 | 1.6 | 17 |
| 10 | 40.1 | 540 | 2.6 | 29 |
| 20 | 41.8 | 570 | 4.5 | 47 |
| 25 | 42.3 | 580 | 5.7 | 59 |

| Characteristic | SP | KP |
|---|---|---|
| Formula | $Na_2S_2O_8$ | $K_2S_2O_8$ |
| Molecular Weight | 238.1 | 270.3 |
| Crystal density (g/cc) | 2.59 | 2.48 |
| Color | White | White |
| Odor | None | None |
| Loose bulk density (g/cc) | 1.12 | 1.30 |

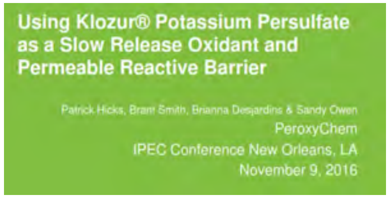


Solubilities of Persulfate Salts



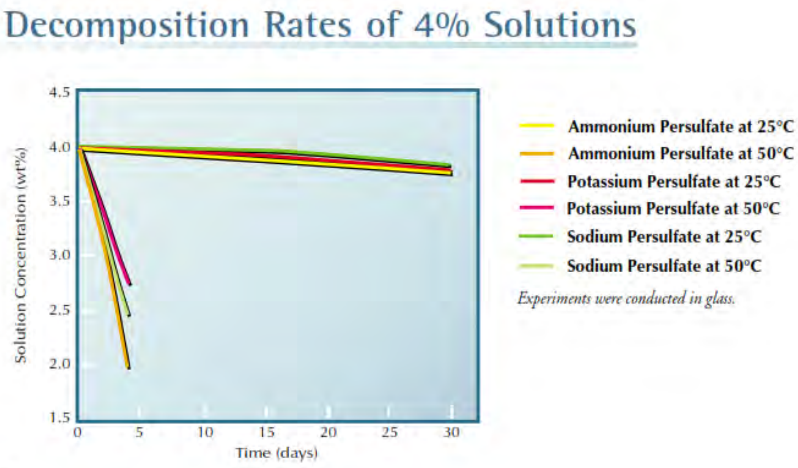
Maximum solubility of persulfate salts in water

| Solubility (g/100g of $H_2O$) | Ammonium Persulfate | Potassium Persulfate | Sodium Persulfate |
|---|---|---|---|
| 25°C | 85 | 6 | 73 |
| 50°C | 116 | 17 | 86 |



**Using Klozur® Potassium Persulfate as a Slow Release Oxidant and Permeable Reactive Barrier**

Patrick Hicks, Bram Smith, Brianna Desjardins & Sandy Owen
PeroxyChem
IPEC Conference New Orleans, LA
November 9, 2016



Decomposition Rates of 4% Solutions

*Experiments were conducted in glass.*

- Potassium persulfate (Hoag, 1998) espoused for slow release ISCO
  - – Solubility < 30,000 mg/L at average GW temp 11 C
  - – Kinetics historically questioned

# Kinetics of KP…

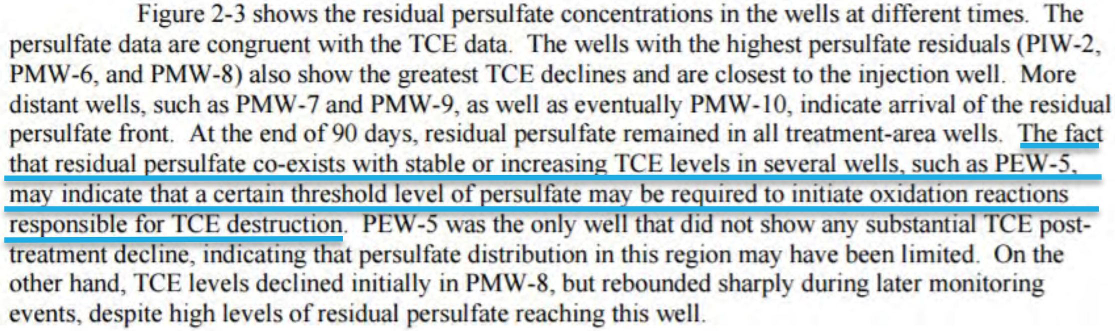
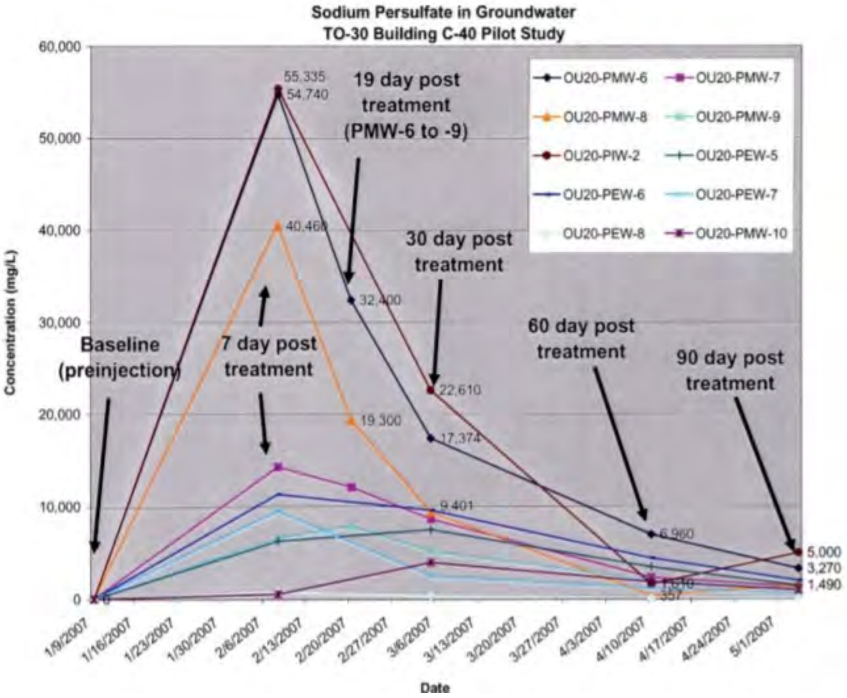
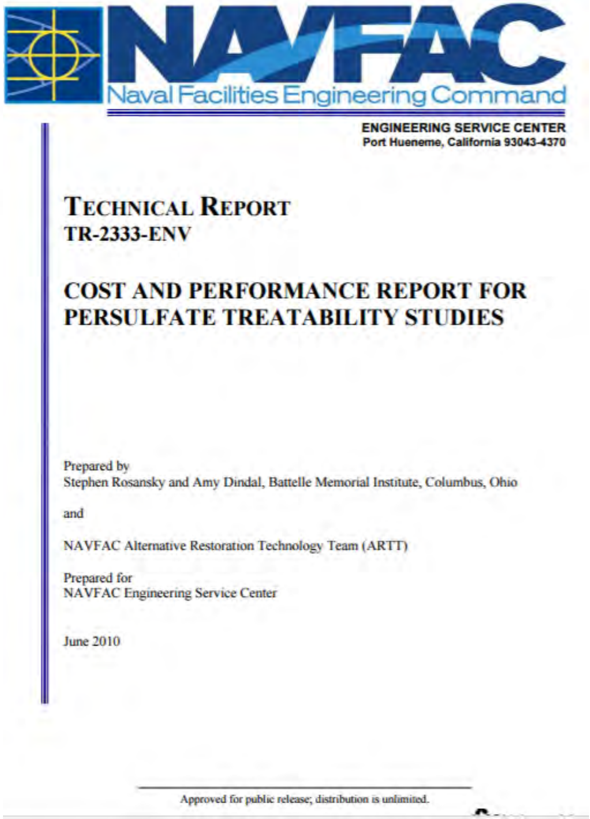


Figure 2-3 shows the residual persulfate concentrations in the wells at different times. The persulfate data are congruent with the TCE data. The wells with the highest persulfate residuals (PIW-2, PMW-6, and PMW-8) also show the greatest TCE declines and are closest to the injection well. More distant wells, such as PMW-7 and PMW-9, as well as eventually PMW-10, indicate arrival of the residual persulfate front. At the end of 90 days, residual persulfate remained in all treatment-area wells. The fact that residual persulfate co-exists with stable or increasing TCE levels in several wells, such as PEW-5, may indicate that a certain threshold level of persulfate may be required to initiate oxidation reactions responsible for TCE destruction. PEW-5 was the only well that did not show any substantial TCE post-treatment decline, indicating that persulfate distribution in this region may have been limited. On the other hand, TCE levels declined initially in PMW-8, but rebounded sharply during later monitoring events, despite high levels of residual persulfate reaching this well.





NAVFAC
Naval Facilities Engineering Command

ENGINEERING SERVICE CENTER
Port Hueneme, California 93043-4370

TECHNICAL REPORT
TR-2333-ENV

COST AND PERFORMANCE REPORT FOR
PERSULFATE TREATABILITY STUDIES

Prepared by
Stephen Rosansky and Amy Dindal, Battelle Memorial Institute, Columbus, Ohio

and

NAVFAC Alternative Restoration Technology Team (ARTT)

Prepared for
NAVFAC Engineering Service Center

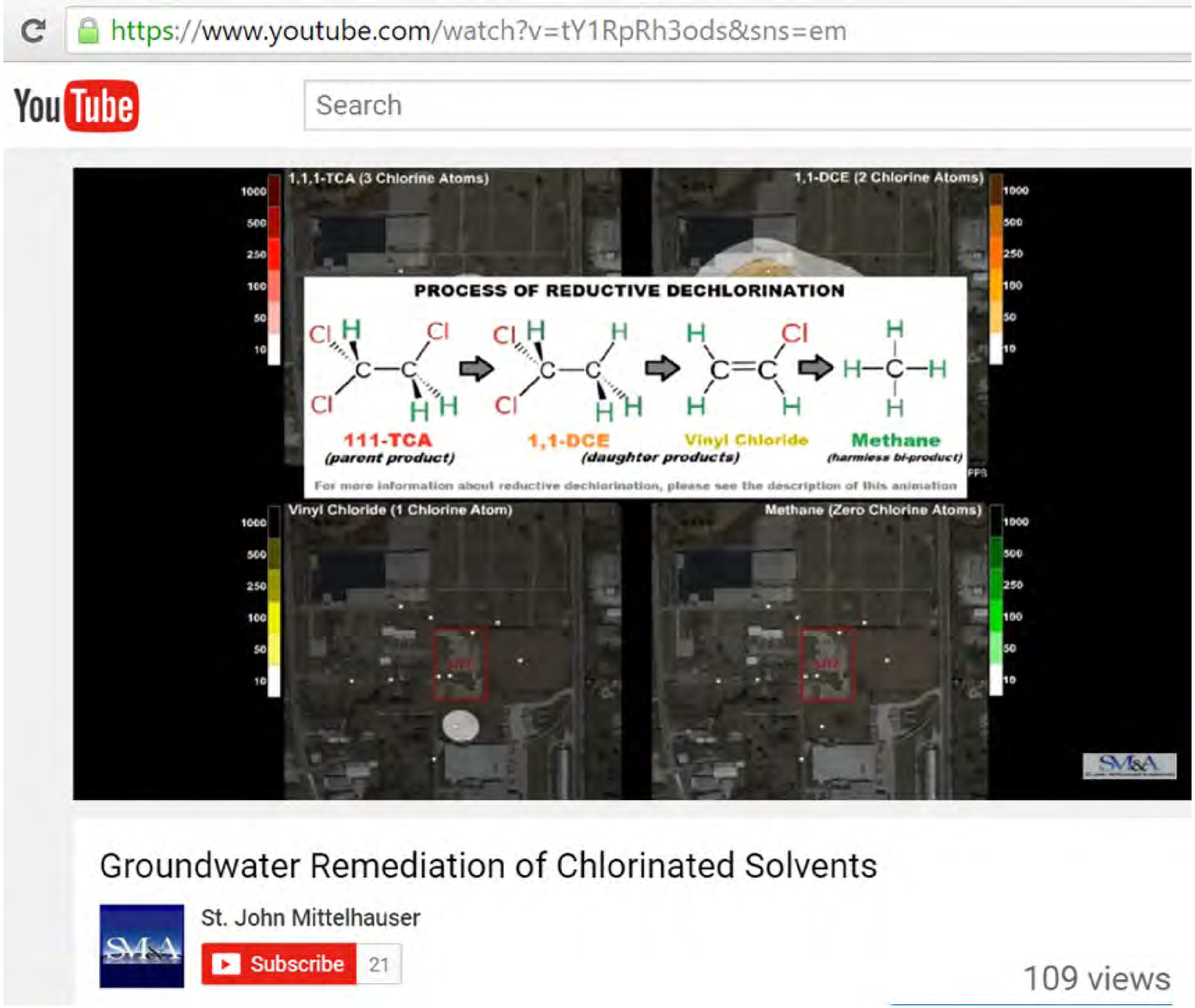
June 2010

Approved for public release; distribution is unlimited.

Page 8 – North Island, CA

Ion Chromatography may be more accurate than the field test kits used

# Vapor Intrusion / H&S



https://www.youtube.com/watch?v=tY1RpRh3ods&sns=em

Groundwater Remediation of Chlorinated Solvents

St. John Mittelhauser

109 views

# EVO Case Study

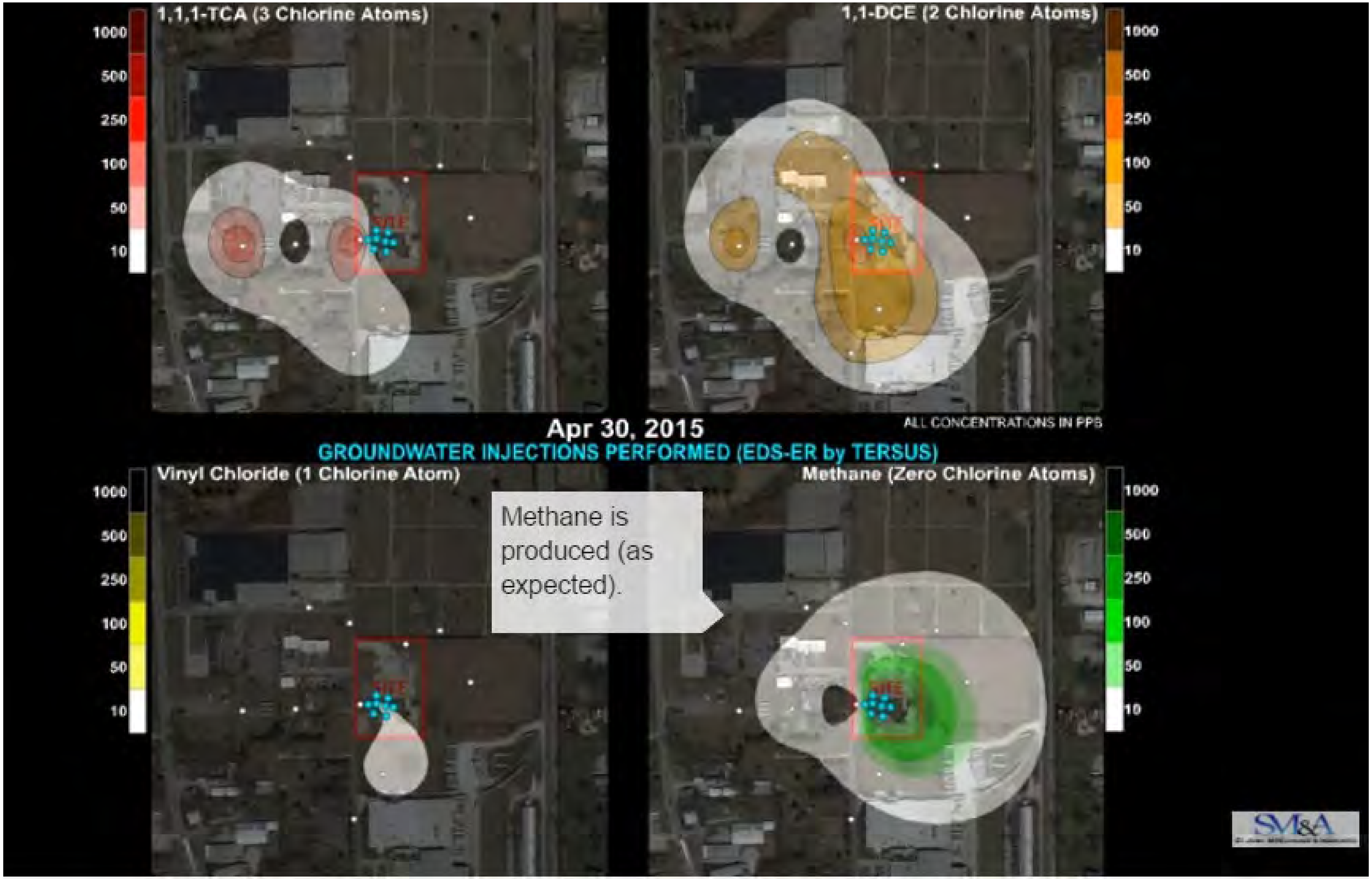
Groundwater injections were performed at 8 well locations on Aug. 13, 2014.

Aug 13, 2014

GROUNDWATER INJECTIONS PERFORMED (EDS-ER by TERSUS)

ALL CONCENTRATIONS IN PPB

# EVO Case Study - 8 months



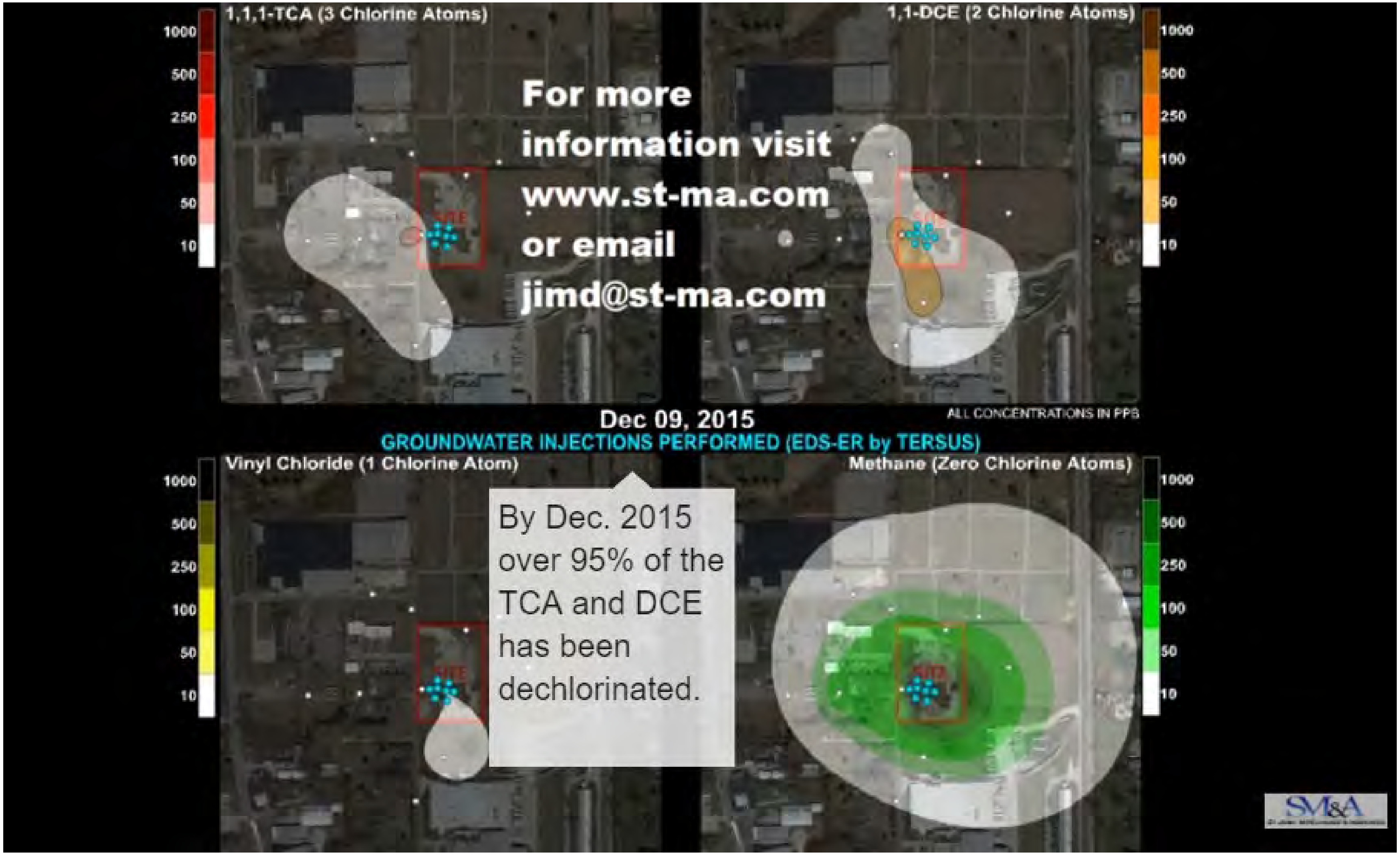
Apr 30, 2015

GROUNDWATER INJECTIONS PERFORMED (EDS-ER by TERSUS)

ALL CONCENTRATIONS IN PPB

Methane is produced (as expected).

# EVO Case Study - 16 months



For more information visit www.st-ma.com or email jimd@st-ma.com

By Dec. 2015 over 95% of the TCA and DCE has been dechlorinated.