provectus
ENVIRONMENTAL PRODUCTS™

Integrating More Efficient *In Situ* Technologies to Best Meet RAOs

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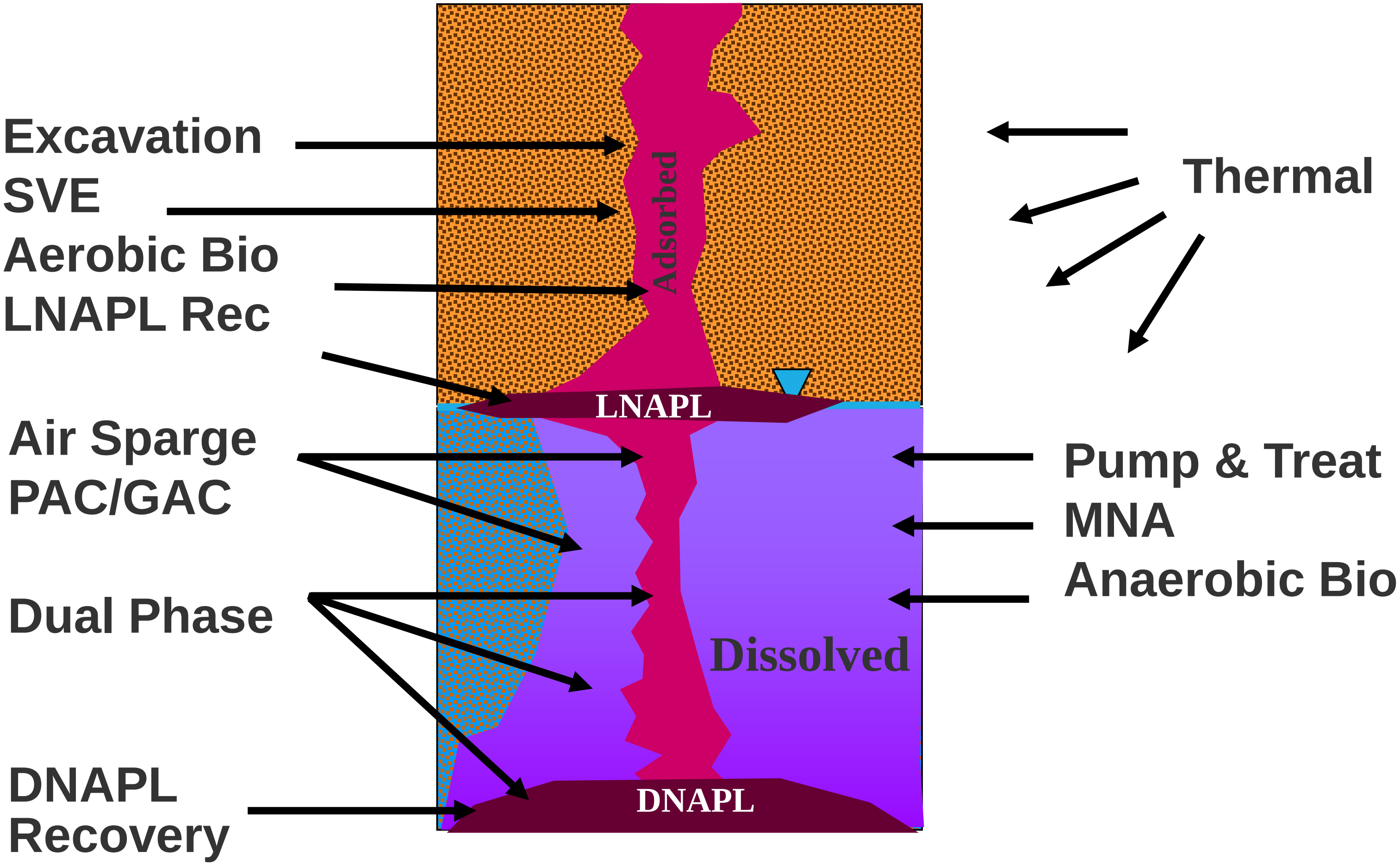
focusedremediationseminars

Focused Remediation Seminars
2019

Presentation Outline

- Problem Statement
  - We Need ISCO & ISCR Technologies
  - We Can Improve our ISCO & ISCR Technologies
- What is ISCO?
  - Mode of Action
  - Recognized Limitations (partial oxidation, rebound, longevity, metals)
  - Case Studies using Improved Technologies
- What is ERD/ISCR?
  - Mode of Action
  - Recognized Limitations (excessive CH4, heavy metals, ketones)
  - Case Studies using Improved Technologies
- Summary and Conclusions

Conventional Remediation Technologies



Excavation
SVE
Aerobic Bio
LNAPL Rec

Air Sparge
PAC/GAC

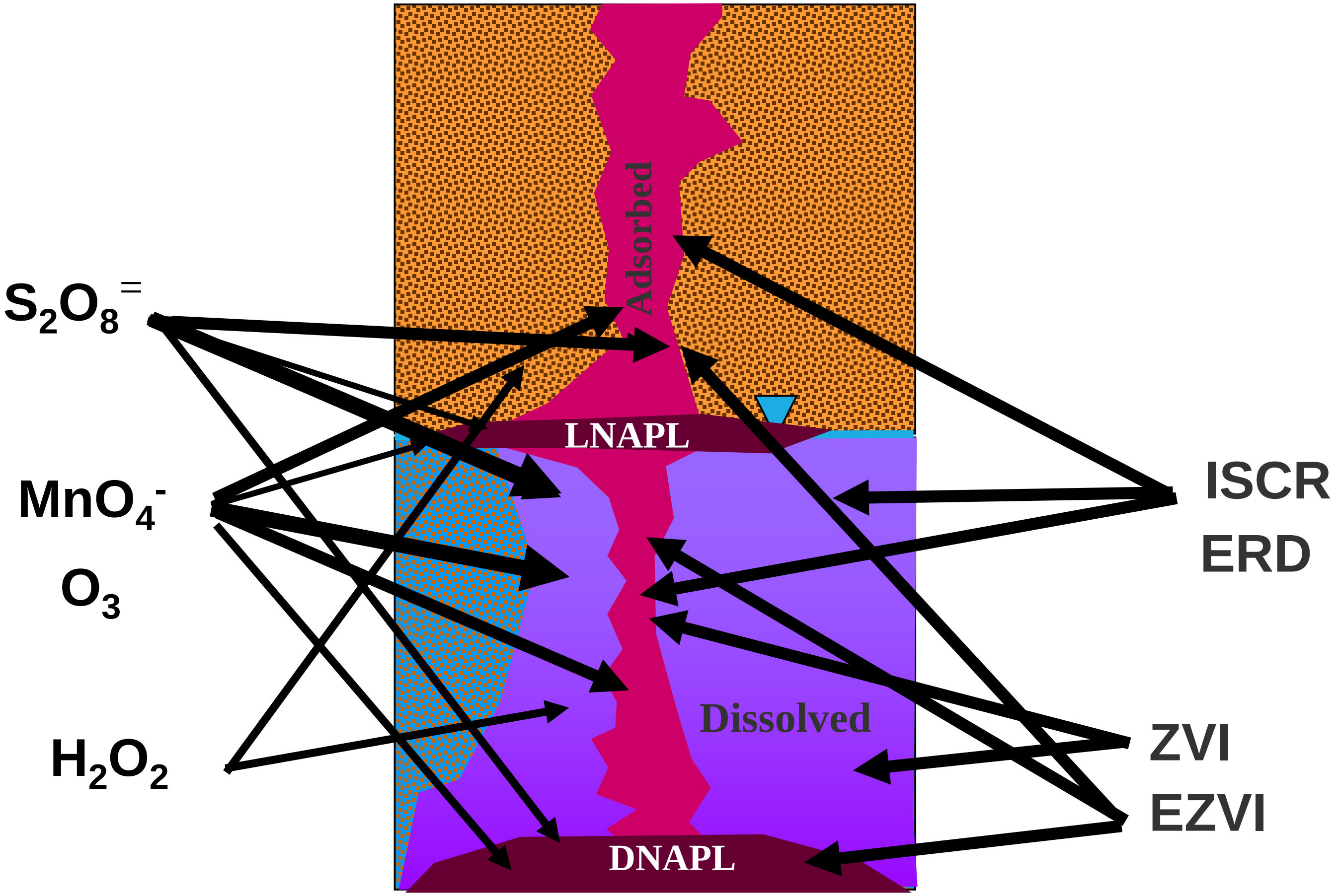
Dual Phase

DNAPL
Recovery

Thermal

Pump & Treat
MNA
Anaerobic Bio

Applicability of ISCO/ISCR Technologies



Fast, Effective (terminal destruction),

Cost Efficient and *In Situ*

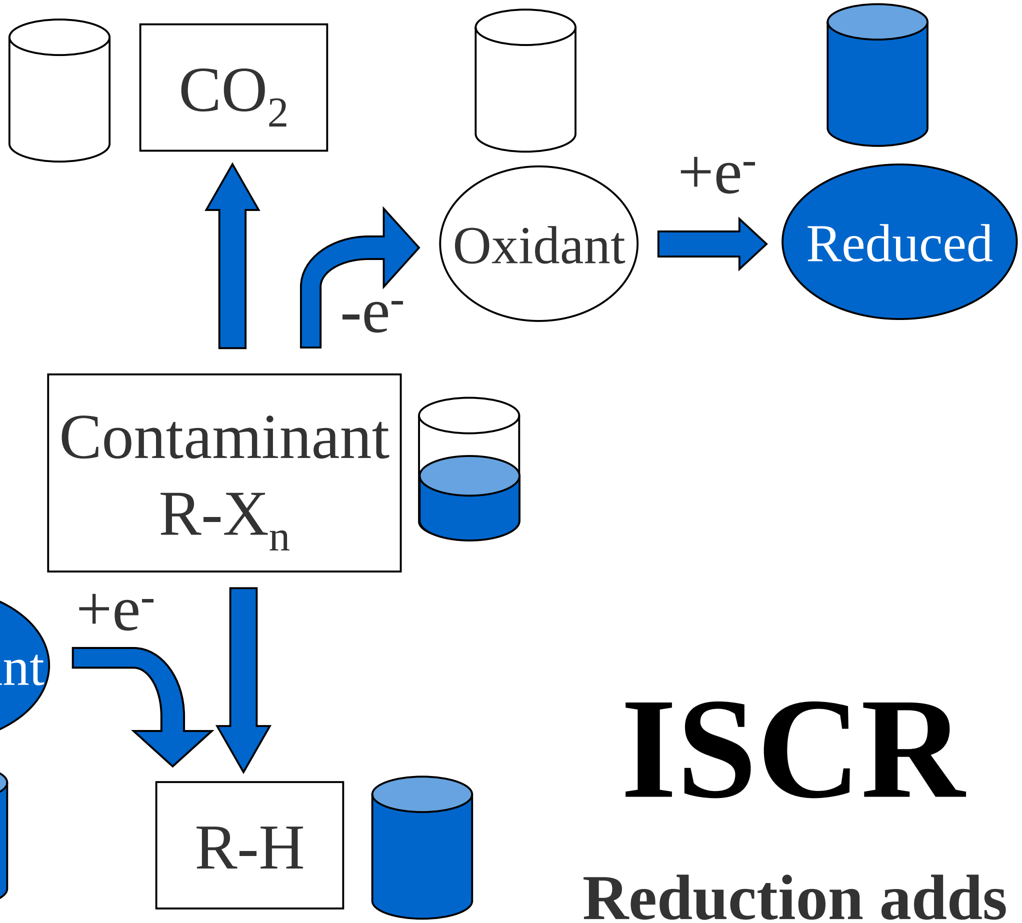
Why Do We Need ISCO/ISCR?

- 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

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) Long chain hydrocarbons PAHs, DRO, GRO	2.5
Carbon-Carbon (one and a half) Aromatic Type - BTEX and PCP	2.0
Carbon-Carbon (double) 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

Limitations with Conventional ISCO

- Non-Beneficial Consumption of Oxidant
  - Oxidants can be self-consuming
  - Soil Oxidant Demands can be very high and very significant
- Use of Extreme Activation Chemistries
  - pH extremes are simply not conducive to biological activity
  - pH extremes can mobile heavy metals creating secondary plumes
  - Many COI not always achieved
- Lack of Longevity
  - Oxidants last days to weeks (months for permanganate)
  - Persulfate activators also do not persist
- These lead to… Contaminant Rebound
  - Observed at most every ISCO site that uses conventional reagents
  - Ineffectiveness and inefficiency represents angst, time and money

Why Do Contaminants Rebound?

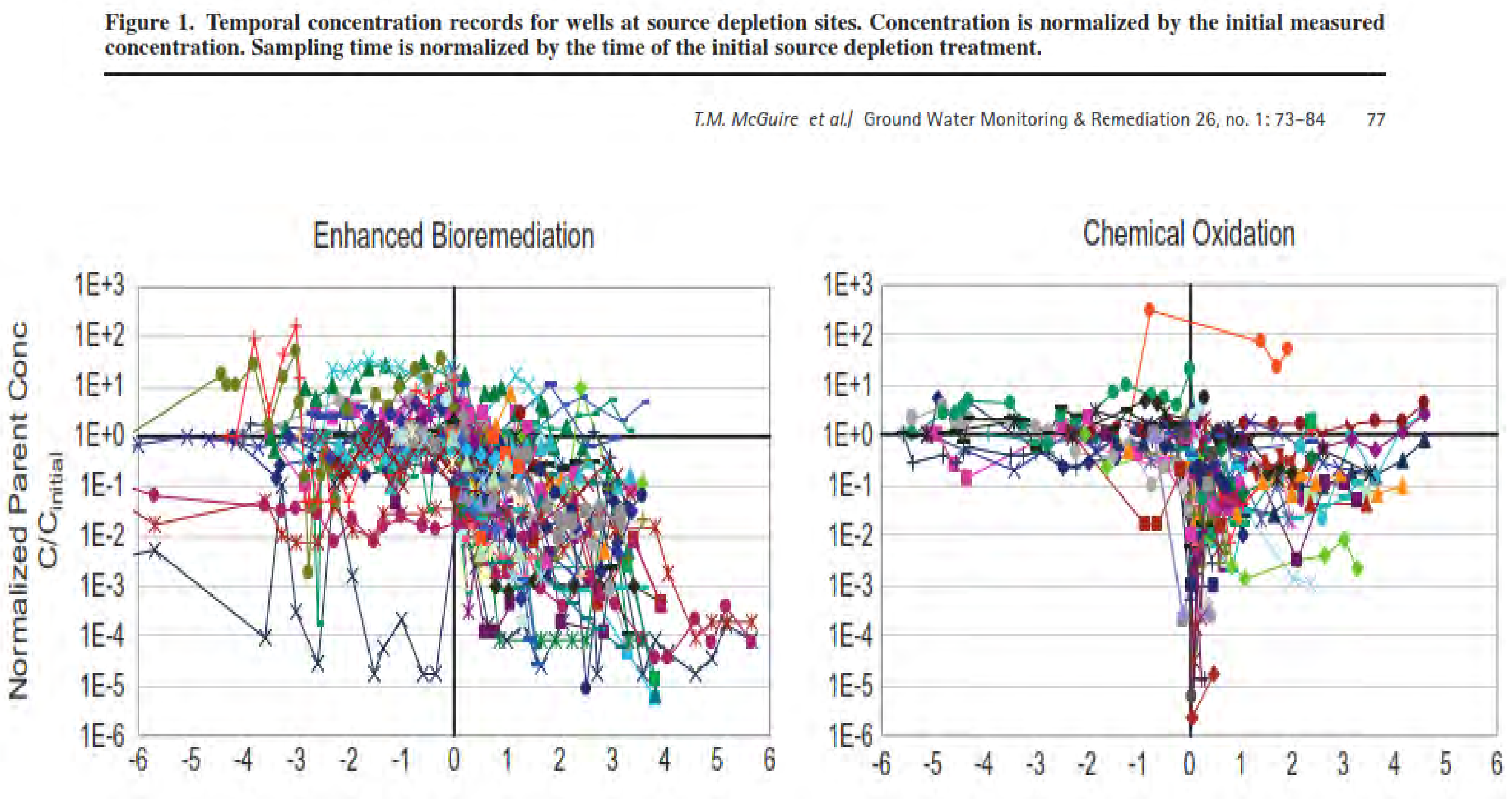
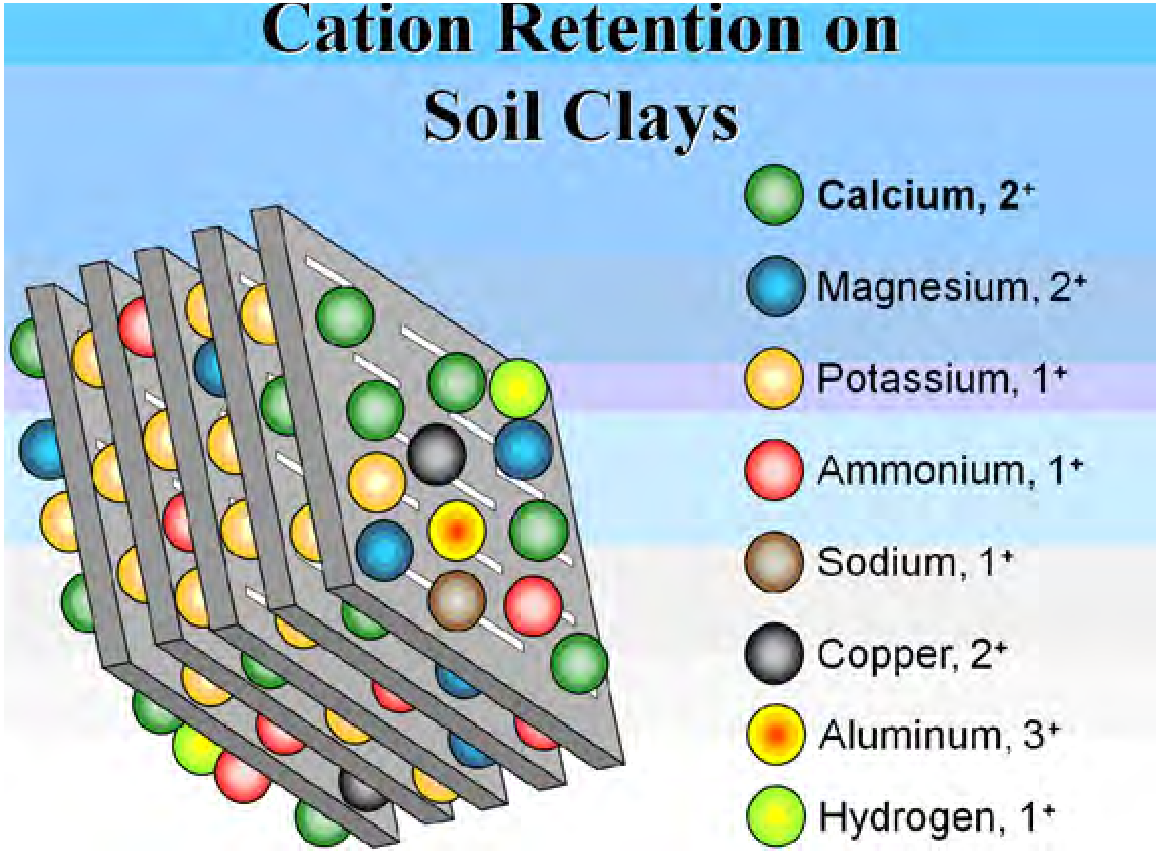


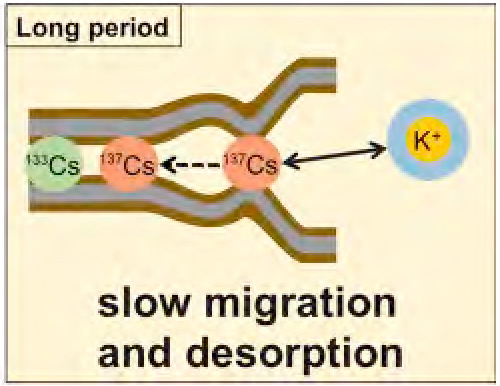
Figure 1. Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.

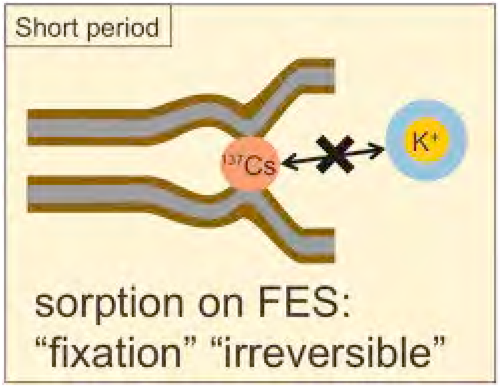
T.M. McGuire et al./ Ground Water Monitoring & Remediation 26, no. 1: 73–84 77

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

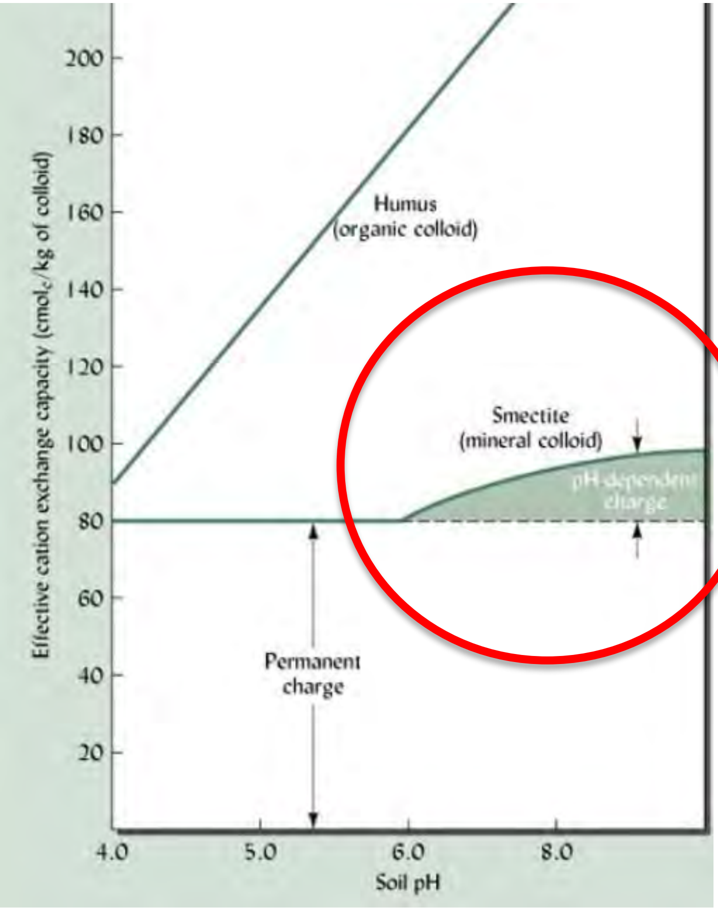
Rebound from Desorption



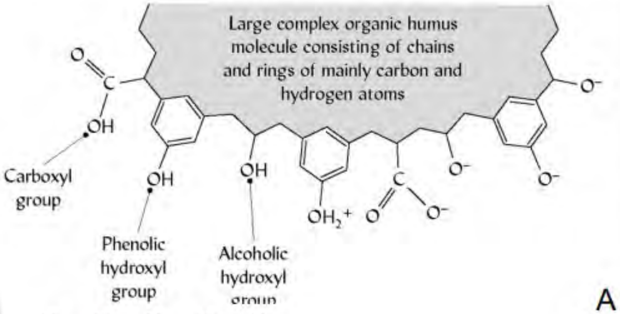


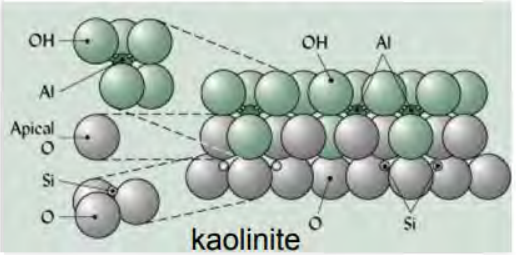


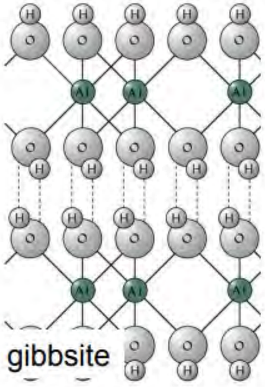
pH Dependent Rebound



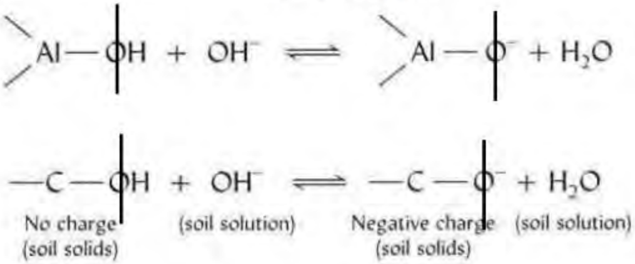
via protonation / deprotonation of hydroxyl groups







A negative charge comes with increasing pH



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

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

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

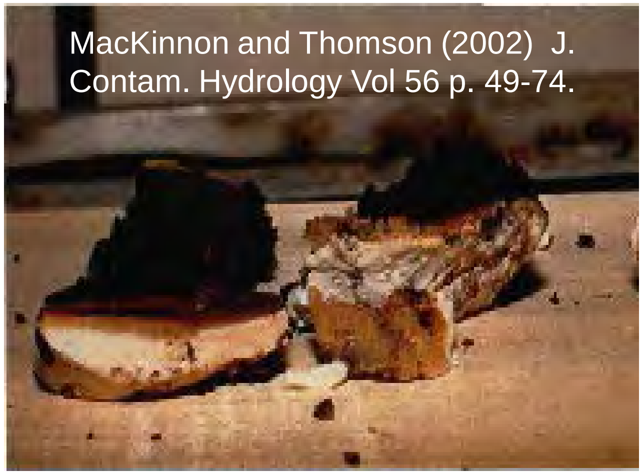
Philip Block, Ph.D.

"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.

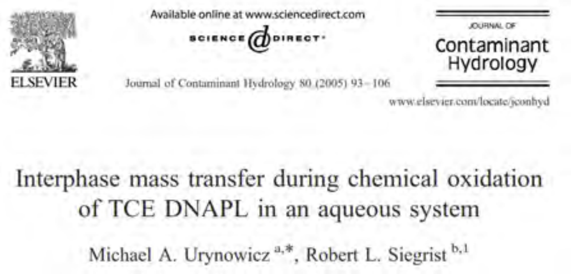
MnO_2 Potential Rebound

In the presence of an organic compound (R), MnO4 reactions yield an oxidized intermediate (Rox) or CO_2 ,… plus MnO_2

$R + MnO_4$- $\rightarrow$ $MnO_2 + CO_2$ 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

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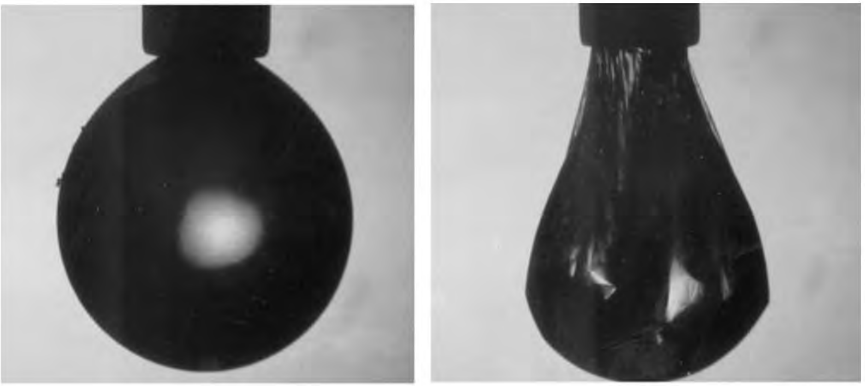
Interphase mass transfer during chemical oxidation of TCE DNAPL in an aqueous system

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

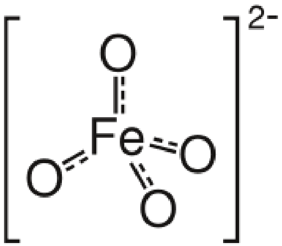


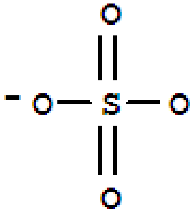
(a) (b)

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●)	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…

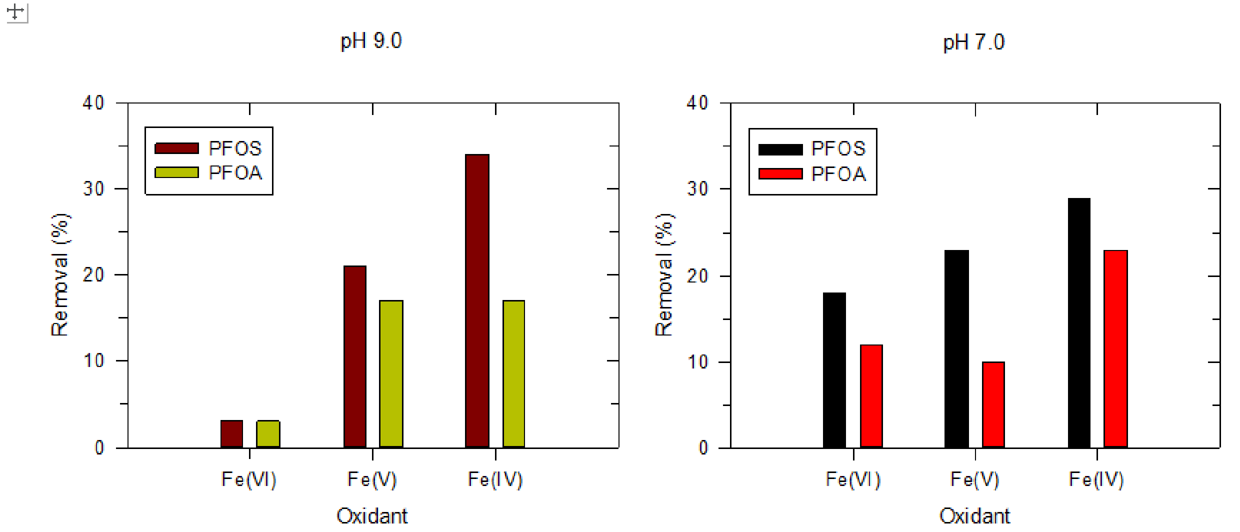
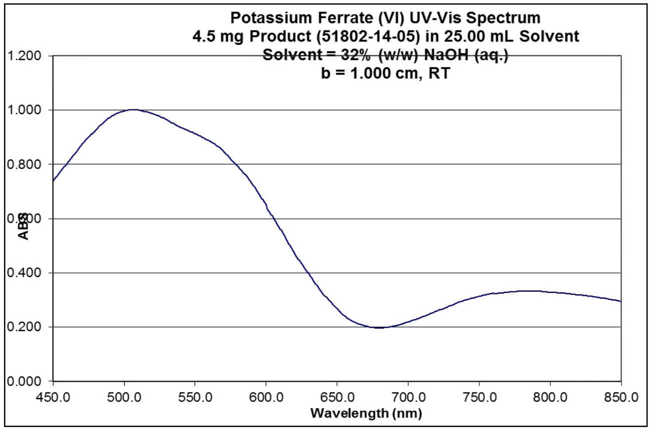


Figure 3. Oxidation of perfluorooctylsulfonate and perfluorooctanoic acid by one application of ferrates at pH 9.0 and 7.0 after five days.



Provect-OX Integrated Reactions

Sodium Persulfate + Ferric Oxide ISCO Reagent:

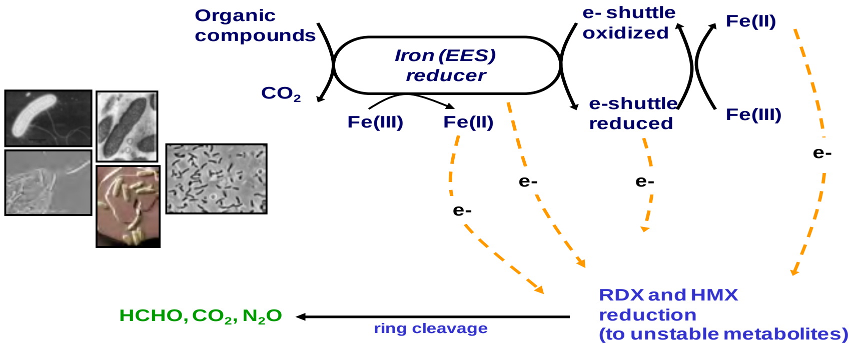
- $S_2O_8^{-2} + Fe^{+3} \text{---------}> Fe^{(+4\ to +6)} + SO_4^{2-} + SO_4^{2-\bullet}$

Sulfate Reduction of Benzene

- $C_6H_6 + 3.75\ SO_4^{2-} + 3\ H_2O \text{-->} 0.37\ H^+ + 6\ HCO_3^- + 1.87\ HS^- + 1.88\ H_2S^-$

Iron Reduction of Benzene

- $C_6H_6 + 18\ H_2O + 30\ Fe^{3+} \text{-------}> 6\ HCO_3^- + 30\ Fe^{2+} + 36\ H^+$



Adapted from Kwon and Finneran , Biodegradation, 2008 , V19(5), Page 705

Generates Reaction Minerals *In Situ* (e.g., Mackinawite)

- $Fe^{2+} + 2S^{2-} \text{-------}> FeS_2 + 2e$

Longevity of ISCO Reagents – POX2

- Na persulfate solubility = 55.6 g/100 mL at 20C
- K persulfate has solubility of 5 g/100 mL at 20C
- K persulfate can provide an extended release of oxidant for many months versus weeks

provect-OX® 2

Extended Release, Self-Activating ISCO / Enhanced Bioremediation Reagent

- Buffered, self-activating ISCO + sustained bioremediation technology
- Allows permeable reactive barrier (PRB) approaches
- Introduction to excavations that include access limitations (e.g., buildings, roads, etc.)

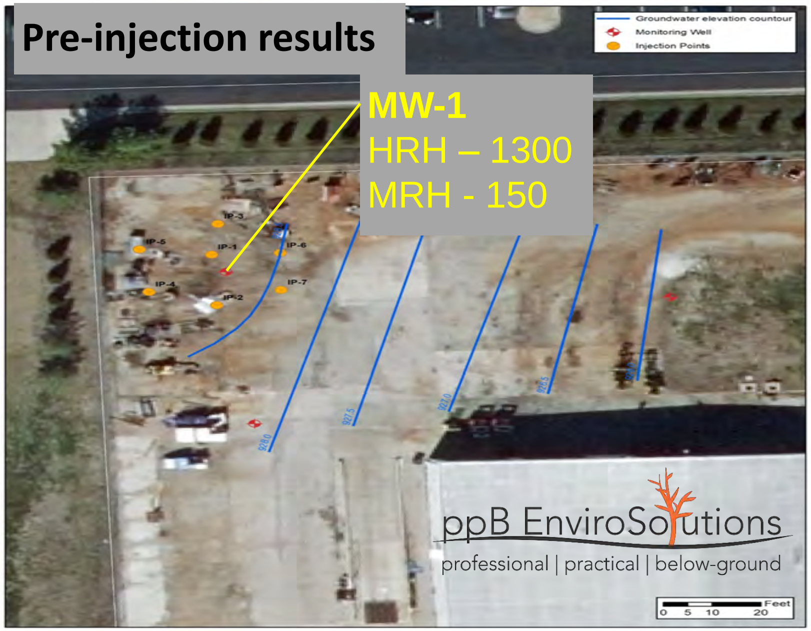
Provect-OX Case Study 1
TPH in Groundwater, Kansas

- 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 1 – Remedial Design

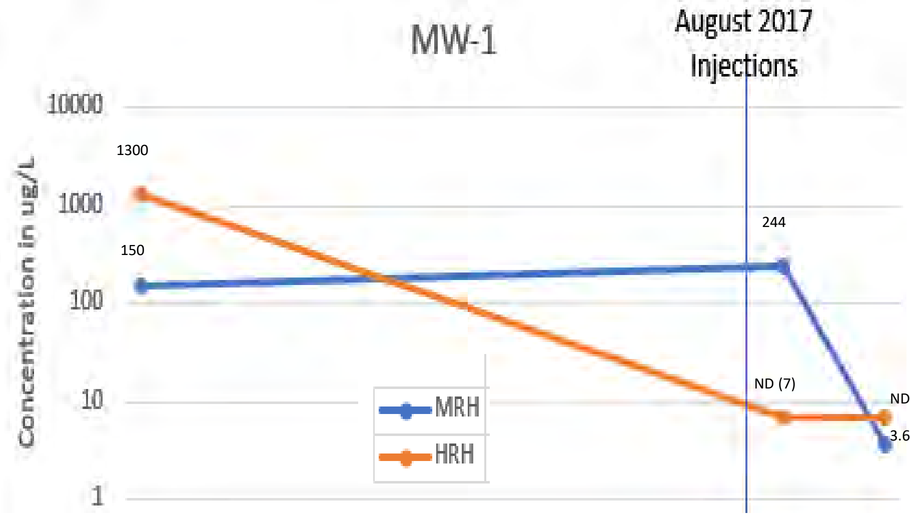
- 2,400 lbs Provect-OX injected
- Approx. 500 ft^2 impacted area
- 7 injection points on 12 foot centers
- 2 day injection event
- ROI > 6-ft in clay soils, <50 psi (KHDE)
- RAO <Residential Groundwater Standards
  - TPH-MRH <150 ppb
  - TPH-HRH <1,000 ppb



Pre-injection results

MW-1
HRH – 1300
MRH - 150

Case Study 1 - Results




August 2017 results (immediate post injection)

MW-1
HRH – ND
MRH - 244

MW-2
HRH – ND
MRH - ND

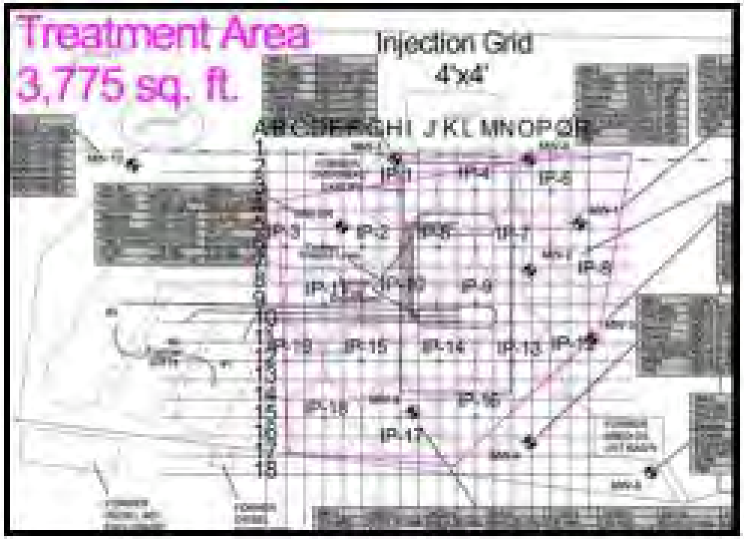
MW-3
HRH – ND
MRH - ND

- 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
- Received regulatory closure < 1 year

ppB EnviroSolutions
professional | practical | below-ground

Provect-OX Case Study 2
Former Gas Station, West VA

- 3,775 ft^2 area impacted by BTEX (max 77 ppb), MTBE (max 72 ppb), TBA (max 1,480 ppb)
- Primarily clay with water at 5 ft bgs
- Treatment interval from 6 to 12 ft bgs
- RAO = significant reductions
- 7,300 lbs of Provect-OX
- Applied via 19 direct push points
- Two monitoring wells targeted

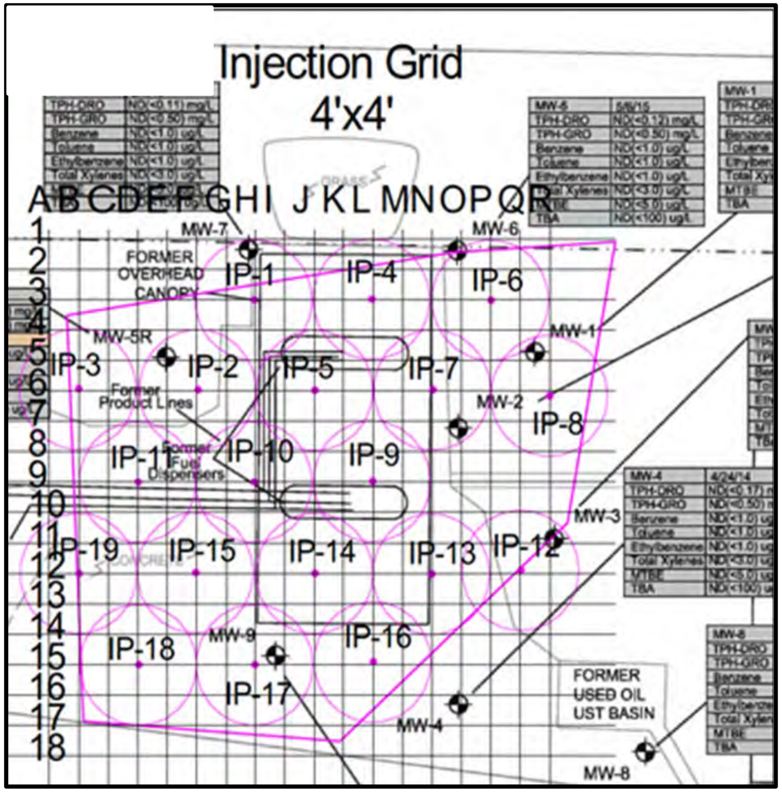


Courtesy Innovative Environmental Technologies, Inc.
Design and Implementation

Case Study 2 – Results

- MW-9 (Highest Conc) – 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

- MW-5R – 2 Year
  - Benzene 12.2 ug/L to 2.01
  - Ethylbenzene 36 ug/L to ND
  - Sulfate 1,350 mg/L
  - Iron 38.1 mg/L



Provect-OX Case Study 3
Soil Mixing CHC/TPH Impacts

- 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
- 5 day application period
- Goals reached
- <$25K; <30 days
  - PCE 38,000 mg/kg to 900 mg/kg
  - Toluene 4,000 to <100 mg/kg

Courtesy Fehr-Graham, Inc.

Provect-OX Case Study 4
F-7 Listed Waste, Closed Landfill

- 25,000 USG Liquid Waste (leachate) Annually
  - Benzene, MEK and *para* 1,4-DCB main COIs (>500 ppb)
  - MCB, TCE and 1,2-DCA also present (<500 ppb)

- Historically, waste drummed and shipped off site
- Changes in Regulatory Policy increased disposal cost 10x
- Landfill owner/operator wanted on-site treatment options

Example Landfill from www.hdrinc.com

Provect-OX Case Study 4 - Results

- Batch reactor treatment
  - 45 USG (375 lbs) F-7 in HDPE drum
  - 22.5 lbs Provect-OX (6% wgt basis)
  - Intermittent mixing for 8 days
- >87% removal all COIs 5 to 8 days
- Cost $0.85/USG or $500/week

Analyte* (Method)	Sampling Time	Unit Values = mg/L		
	0 (untreated)	Day 2	Day 5	Day 8
Metals ICP/TCLP EPA 6010 (preparation 3010 / leachate 1311)				
Arsenic	4.4	5.9	7.6	6.6
Chromium	<0.10	0.12	0.13	<0.10
Selenium	<0.50	0.53	0.80	<0.50
Volatile Organics EPA 8260				
Benzene	0.62	<0.05	<0.05	<0.05
Chlorobenzene	0.25	<0.05	<0.05	<0.05
Lab 1,2-Dichlorobenzene	1.11	0.75	0.25	<0.05
MEK	170	83	22	2
1,2-Dichloroethane	0.43	<0.05	<0.05	<0.05

Provect-OX Coupled Oxidation w/ Sustained Bioremediation

- Sulfate radical and ferrate (site-specific)
- Safely handled; all in one bag or supersack
- Uses Fe^{+3} as activator
  - No heat generated = safer
  - Conserves oxidant
  - Enhances bioattenuation Fe + SO_4
  - Encourages the formation of pyrite
  - Minimizes heavy metal mobilization
- Terr-OR buffer / reactive ferrate stabilizer

provect-OX®

>1

Self-Activating ISCO / Enhanced Bioremediation Reagent

- When Chelated Fe^{+2} used as activator EDTA Consumes the Oxidant
- When Caustic is used as activator
  - Short lived reaction
  - Secondary plumes / metals (Cr)
  - Can generate heat
  - Handling and safety issues (50% sodium hydroxide)
- pH 10+ Does Not Support Biological reactions
- Does Not Manage Rebound

provect-OX®

2

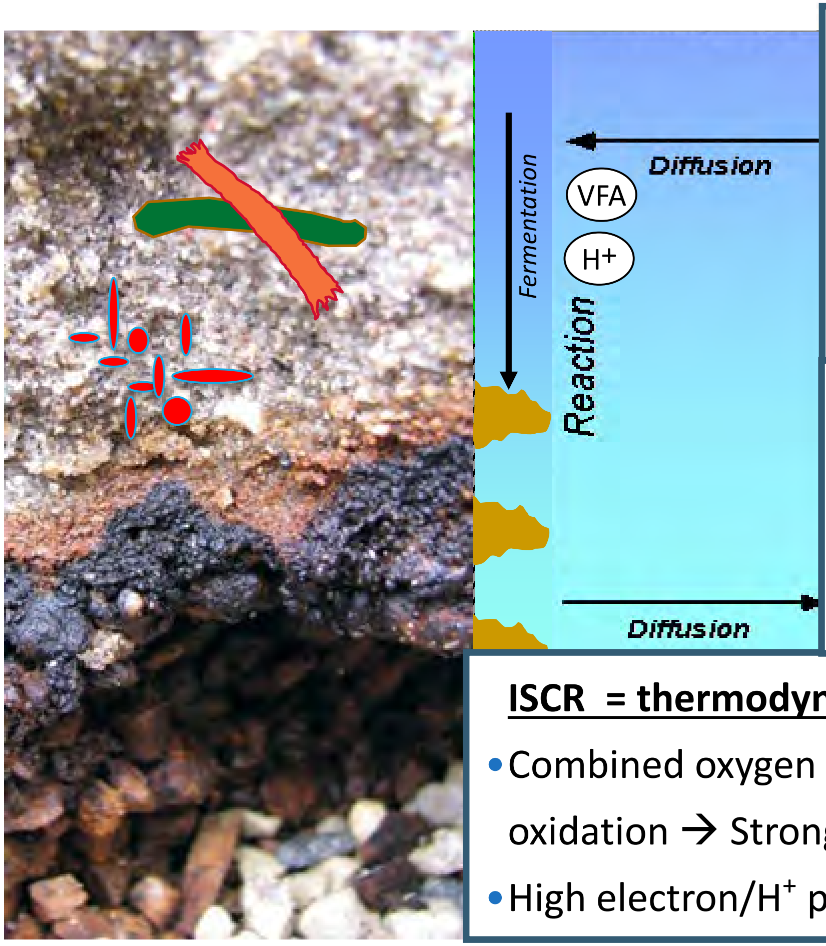
Extended Release, Self-Activating ISCO / Enhanced Bioremediation Reagent

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™**

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

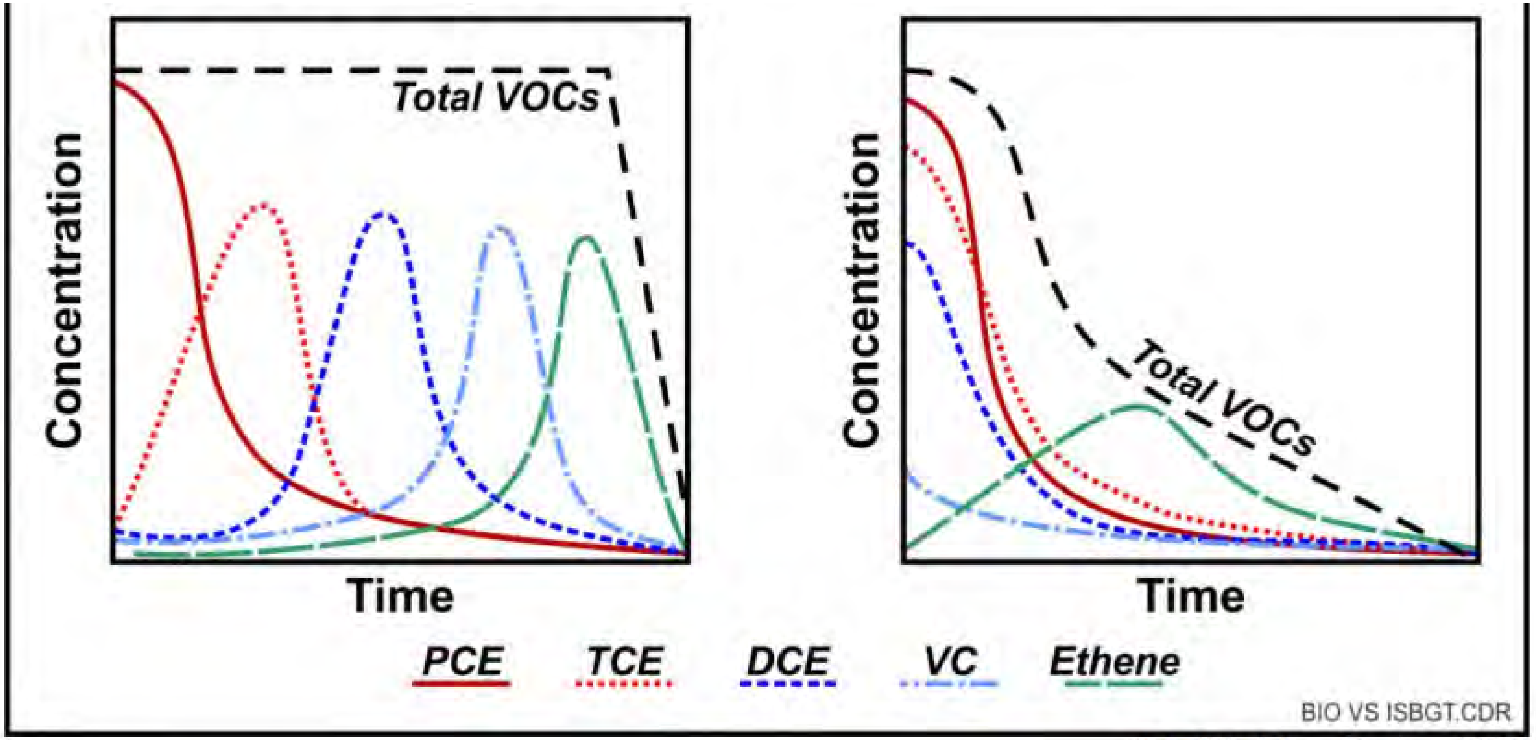
ZVI Reactions: H_2 and Fe^{+2} and generation

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

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

Why Add Carbon/ZVI to Reduce ORP?

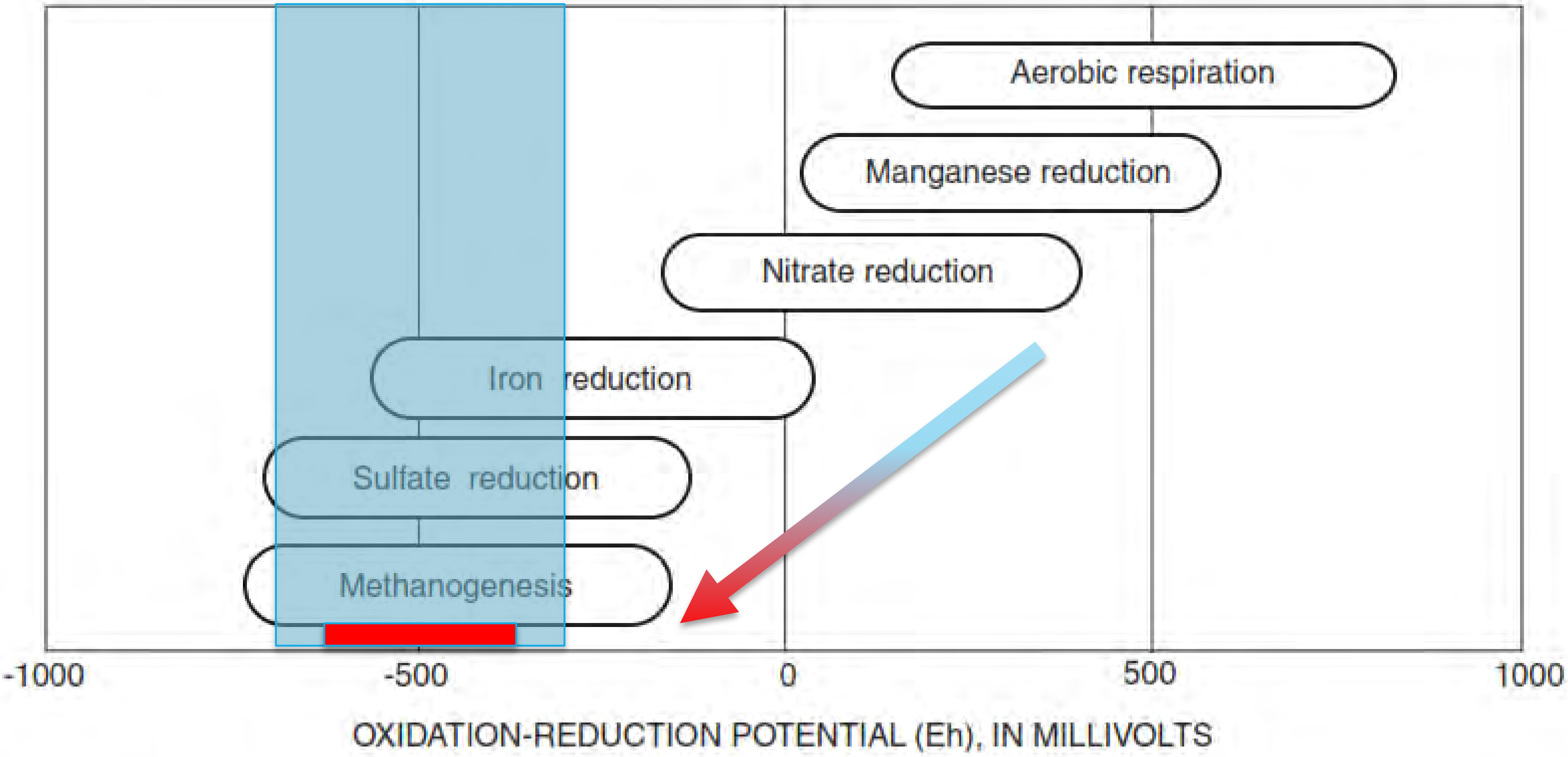
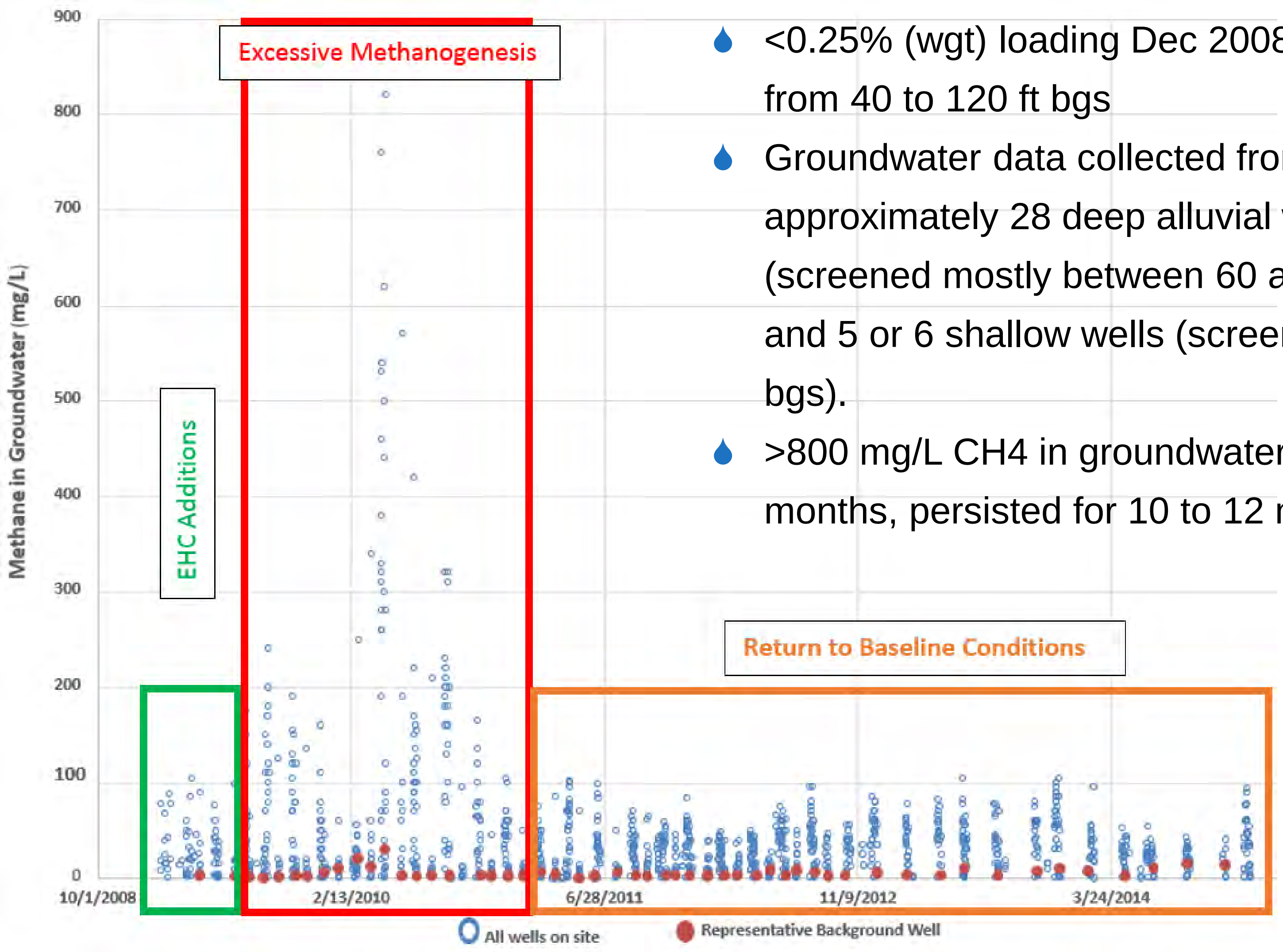


Figure 2. Oxidation-reduction potentials for selected microbial processes. (Modified from Stumm and Morgan, 1981.)

Excessive Methane Production

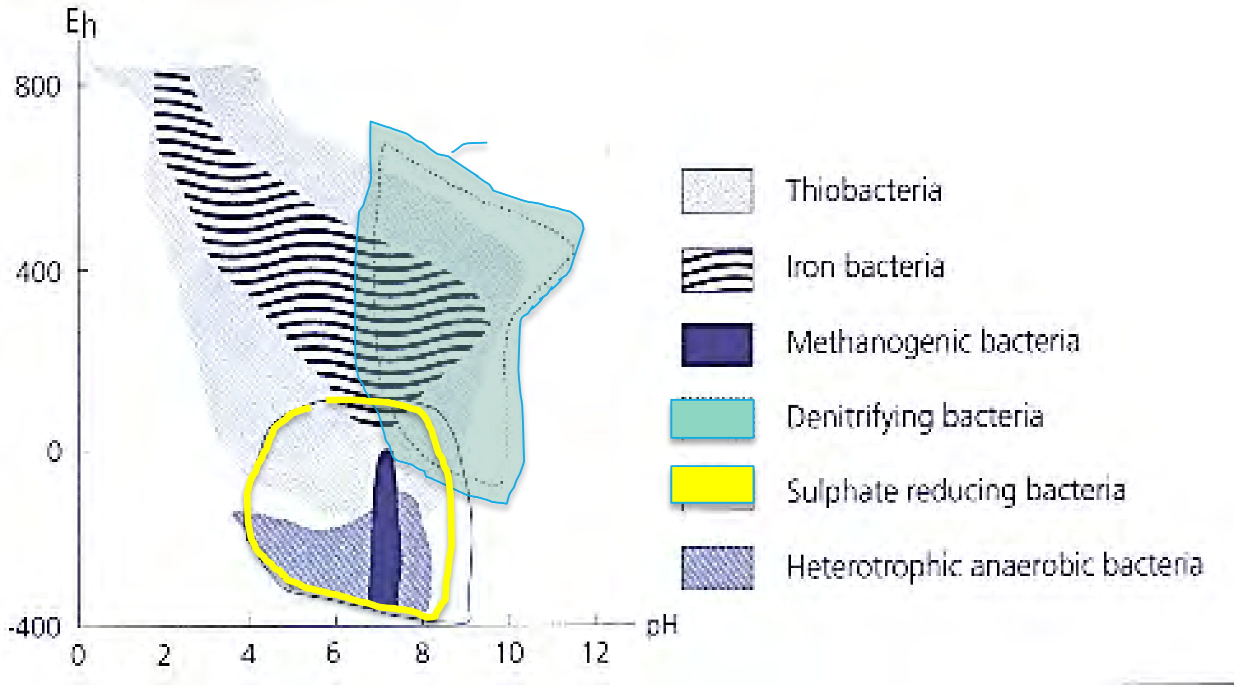


- <0.25% (wgt) loading Dec 2008-May, 2009 from 40 to 120 ft bgs
- Groundwater data collected from approximately 28 deep alluvial wells (screened mostly between 60 and 160 ft bgs) and 5 or 6 shallow wells (screened 25-35 ft bgs).
- >800 mg/L CH4 in groundwater after 6 months, persisted for 10 to 12 months

Excessive CH4 16 months post EVO

Idealized Eh pH Ranges for Microbial Growth

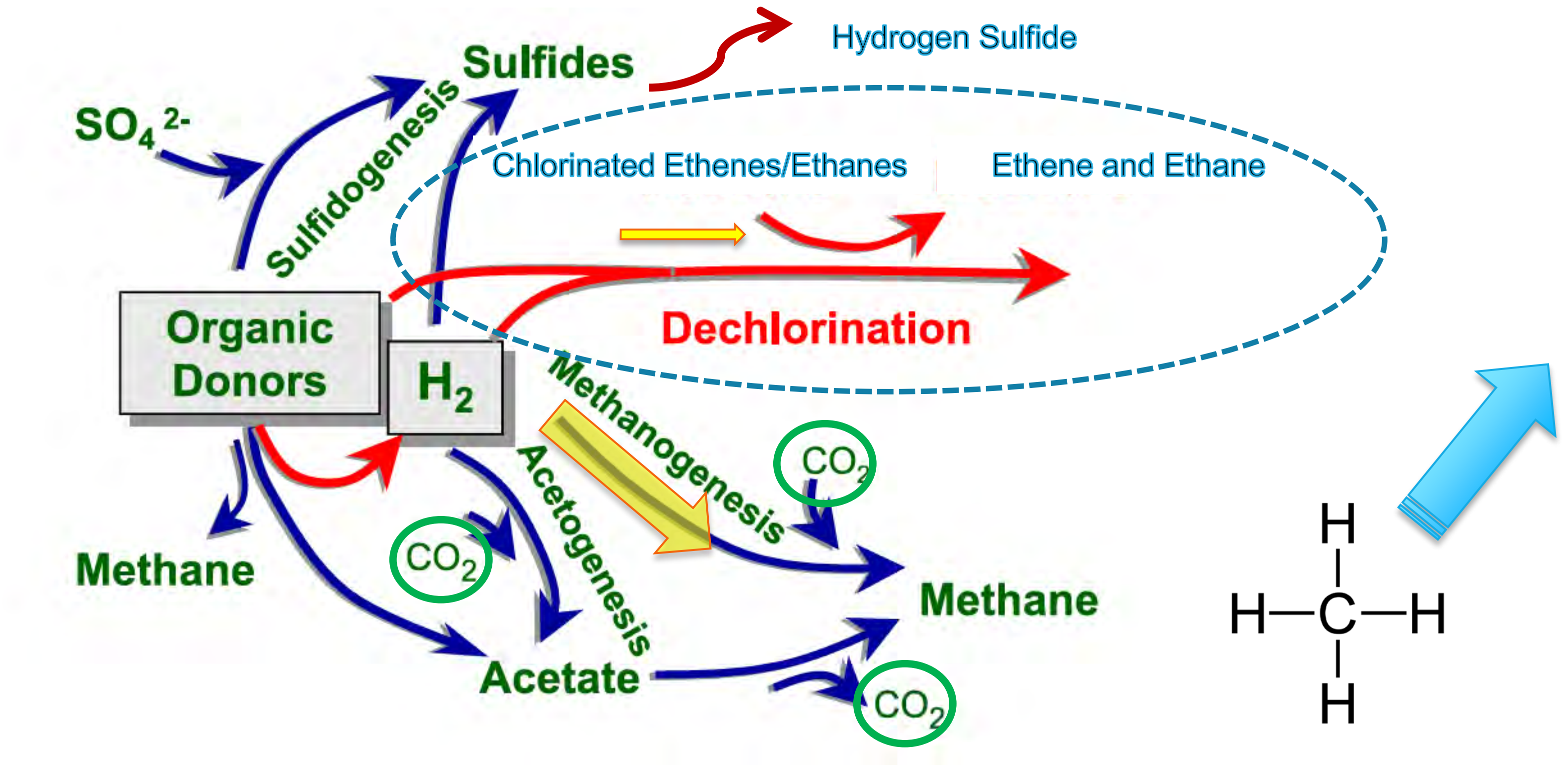
Microbe	Doubling Times
Dehalococcoides spp.	24 to 48 hours
Methanogens with cytochromes	10 hours
Methanogens without cytochromes	1 hour



Zajic, 1969. Sigma Aldrich

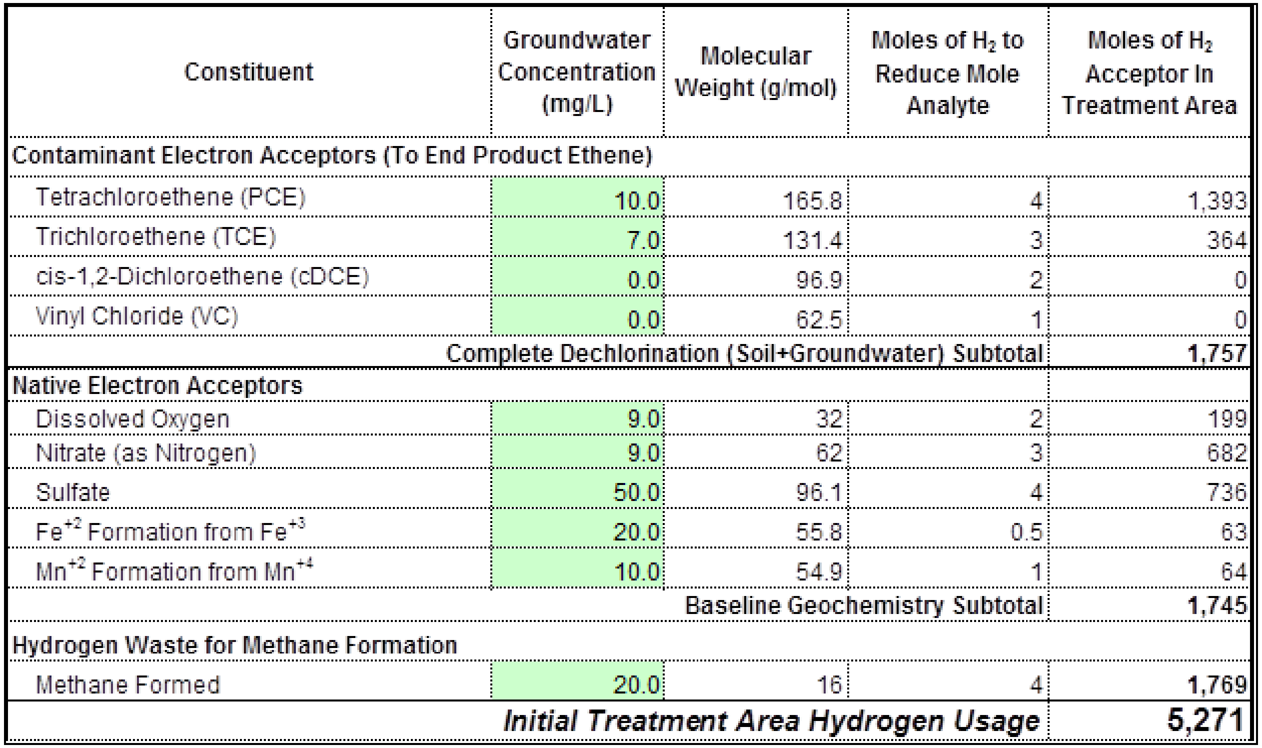
Hydrogen is the Currency

- **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).



Issue 1: Cost and Efficiency

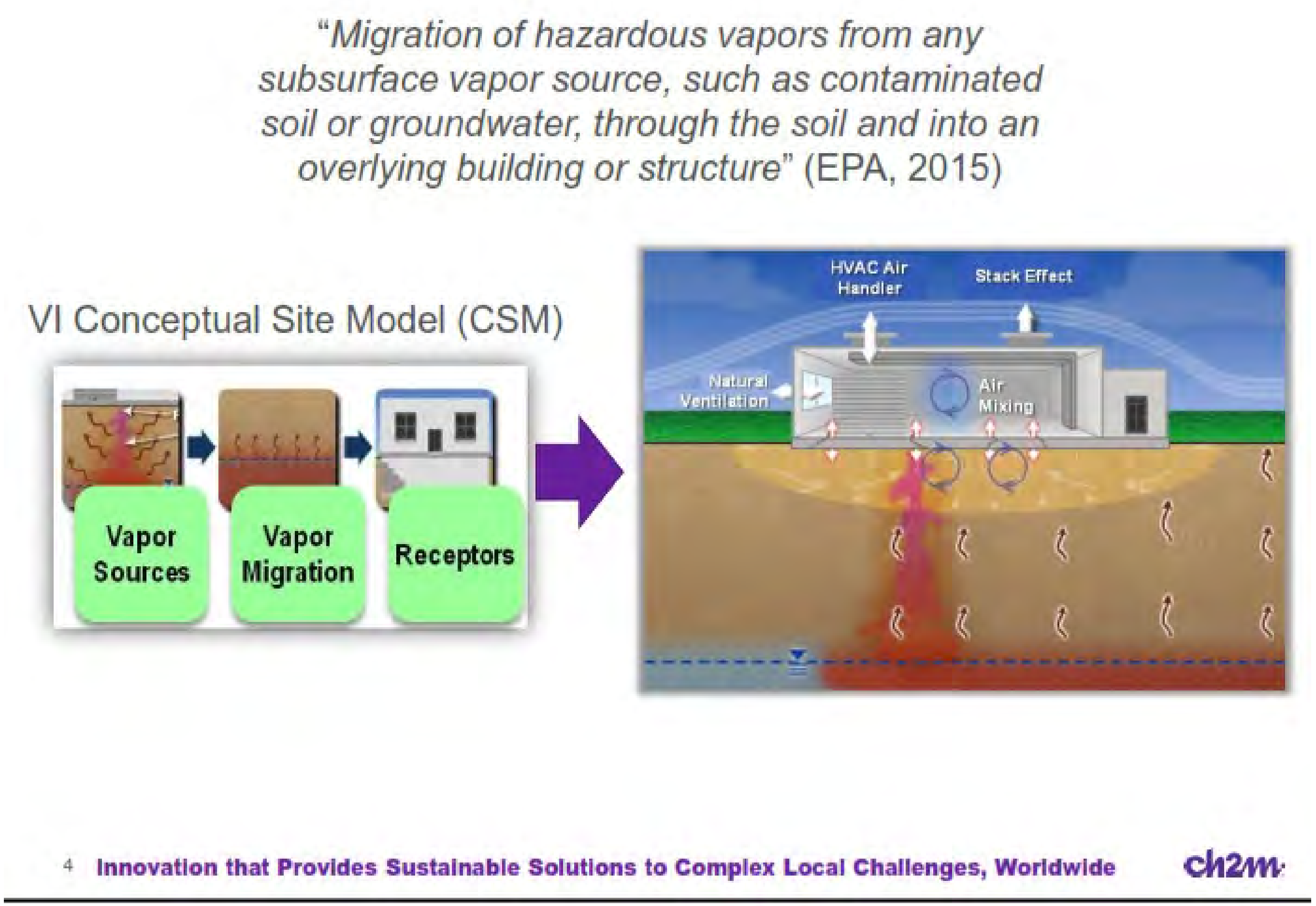
- Production of methane is a direct indication that hydrogen generated from the electron donor amendments was used by methanogens instead of the target microbes (*e.g., Dehalococcoides spp*.), substantially reducing application efficiency.



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

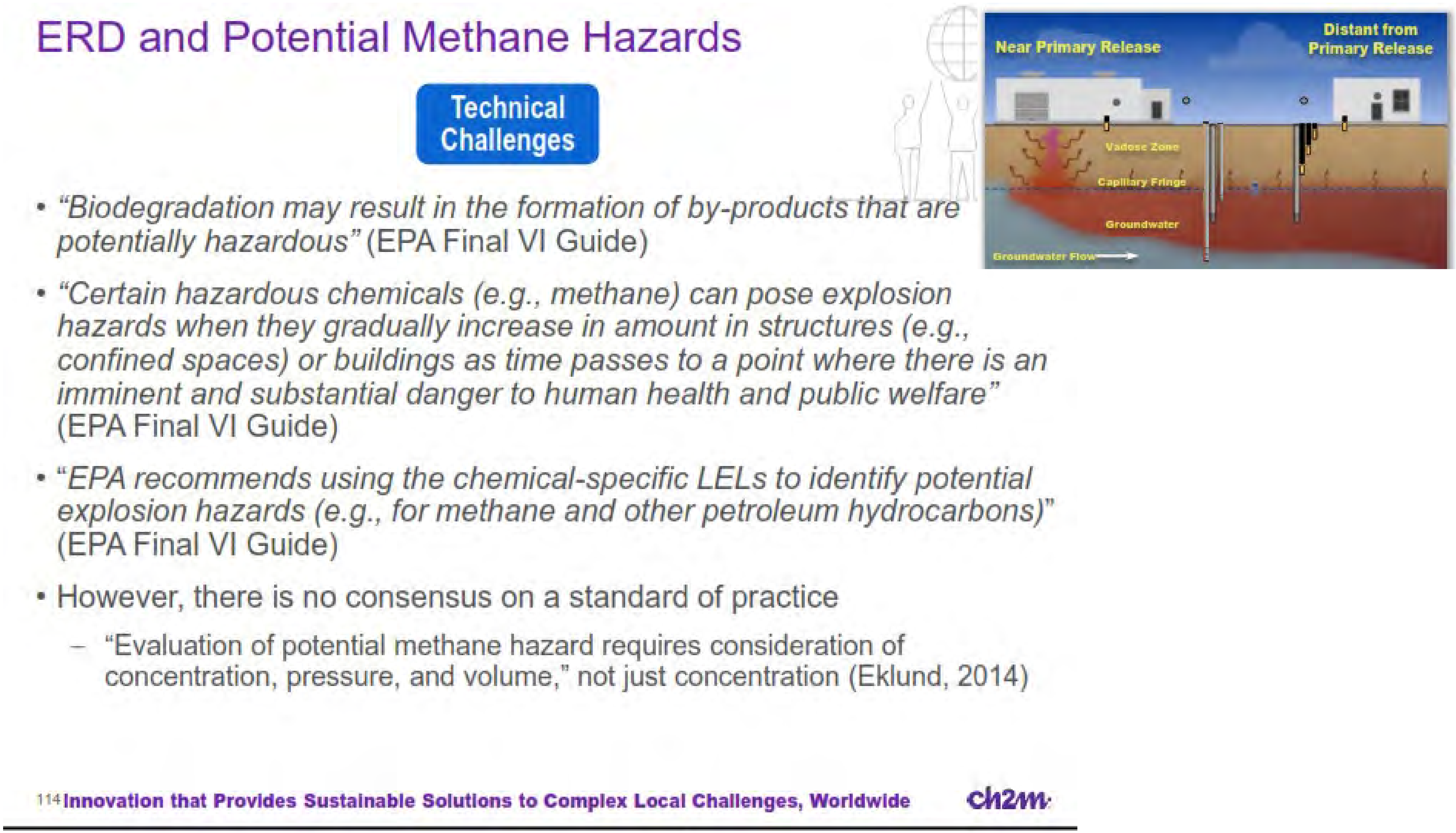


"Migration of hazardous vapors from any subsurface vapor source, such as contaminated soil or groundwater, through the soil and into an overlying building or structure" (EPA, 2015)

VI Conceptual Site Model (CSM)

4 **Innovation that Provides Sustainable Solutions to Complex Local Challenges, Worldwide** ch2m

Methane Impacts Vapor Intrusion

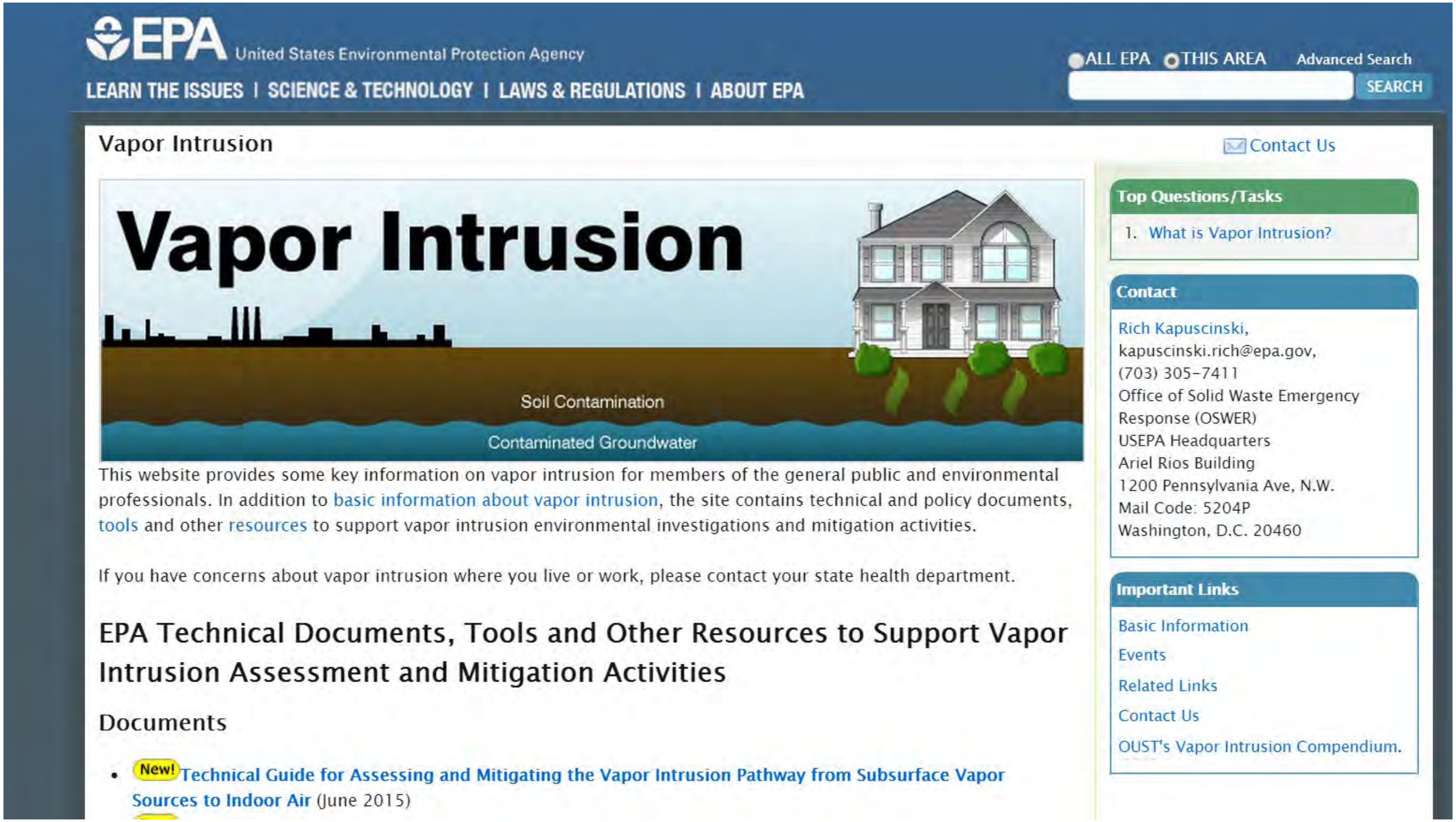


ERD and Potential Methane Hazards

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

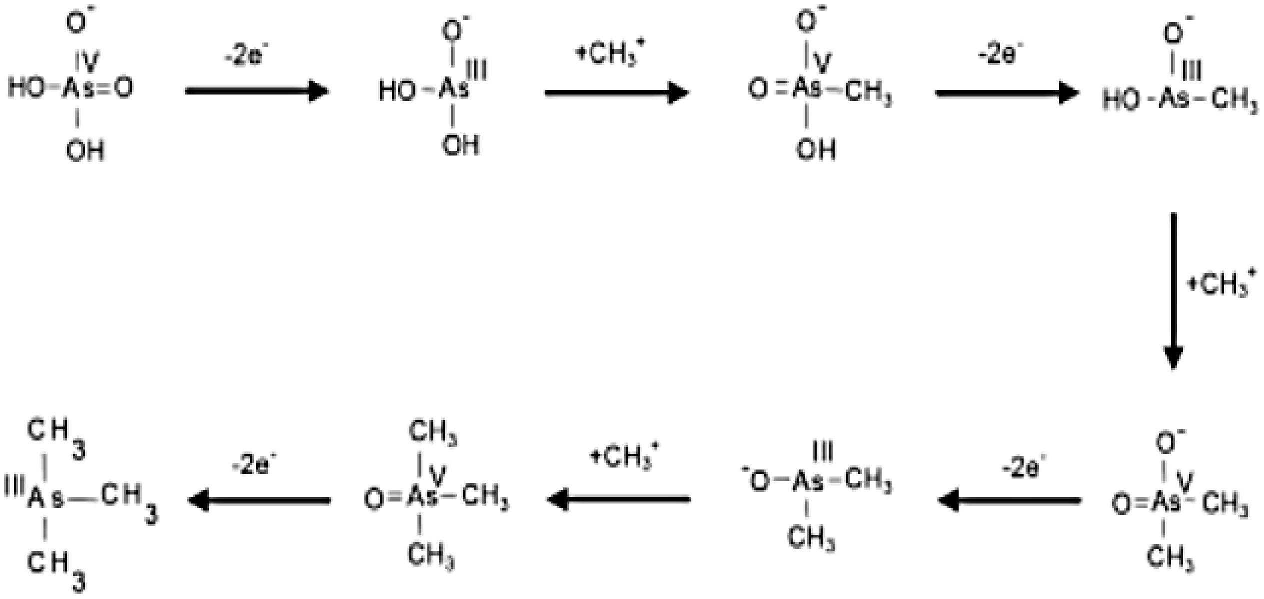
Important Links

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

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

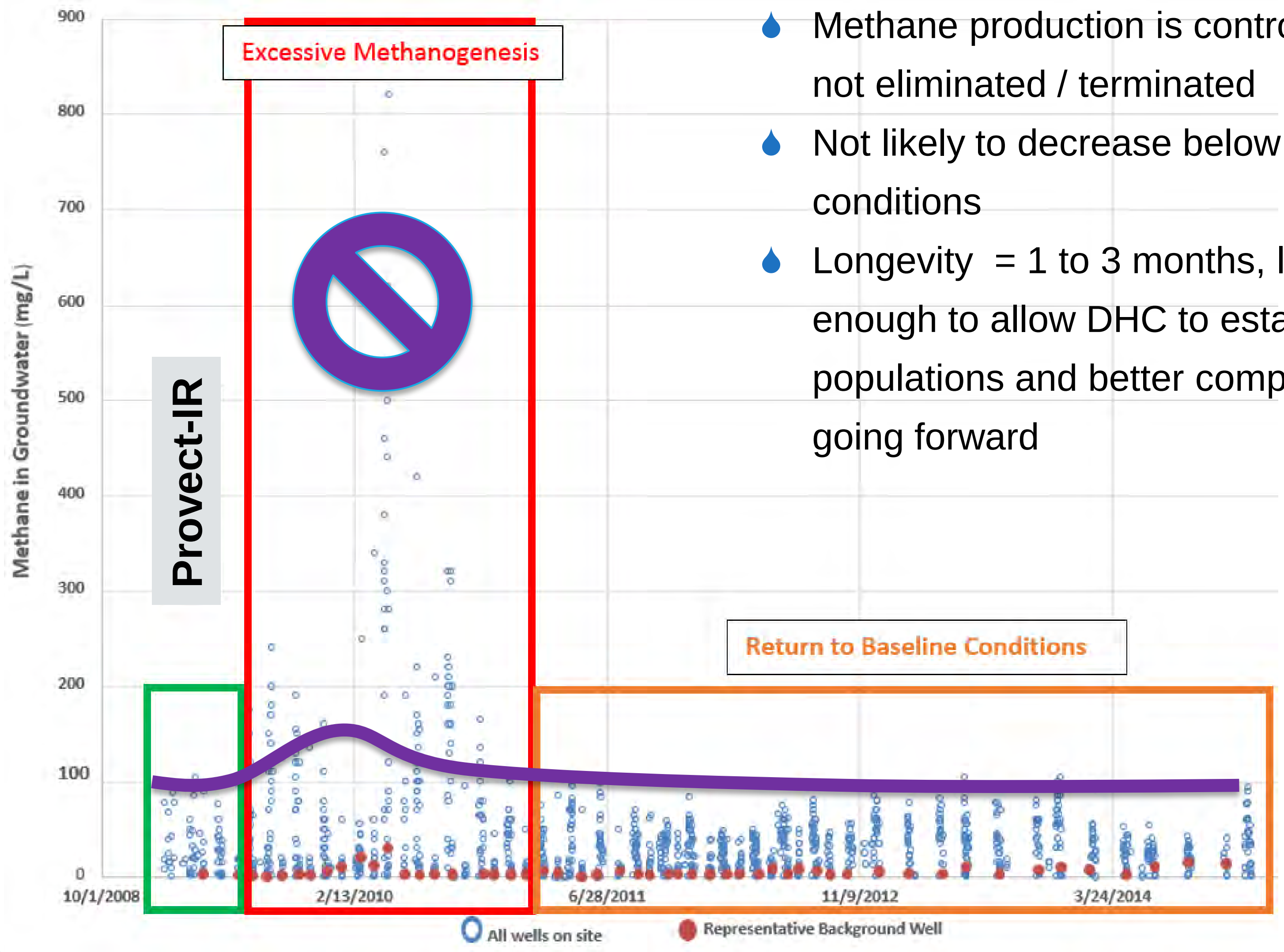
ISCR Issue 3: Arsenic Mobilization

- 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)

Controlled Methanogenesis

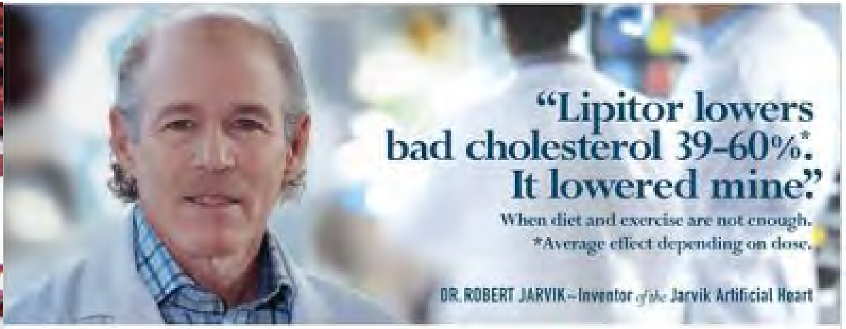


- Methane production is controlled, not eliminated / terminated
- Not likely to decrease below current conditions
- Longevity = 1 to 3 months, long enough to allow DHC to establish populations and better compete going forward

What is Red Yeast Rice (RYR) Extract?

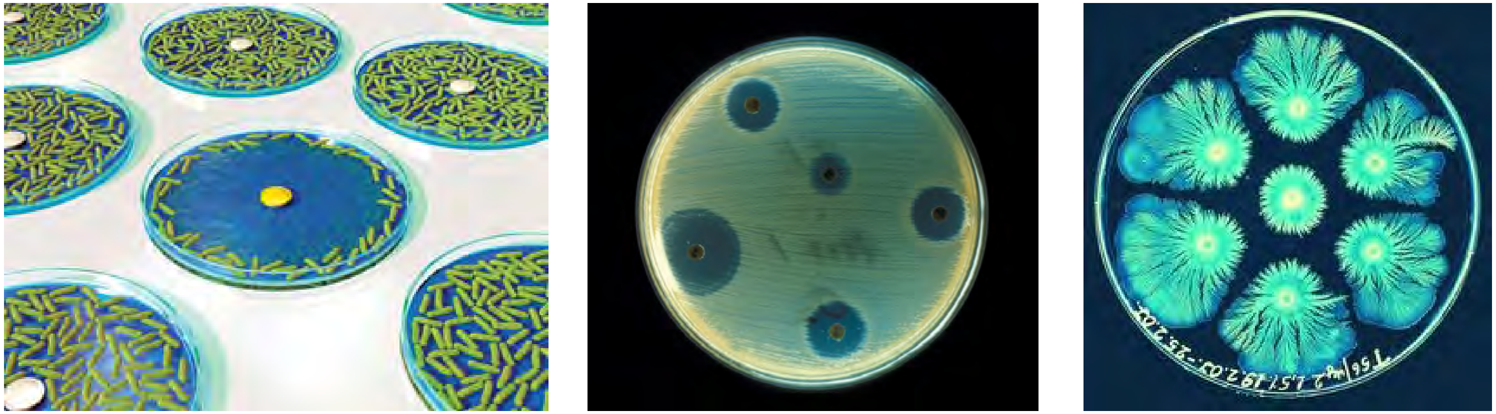
- RYR extract is a substance extracted from rice that has been fermented with a yeast called *Monascus purpureus*.
- RYR extract contains a number of natural statins - most importantly, Monacolin K - otherwise known as Lovastatin® / Lipitor® /etc.
- In addition to Monacolin K, RYR also contains 9 other 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

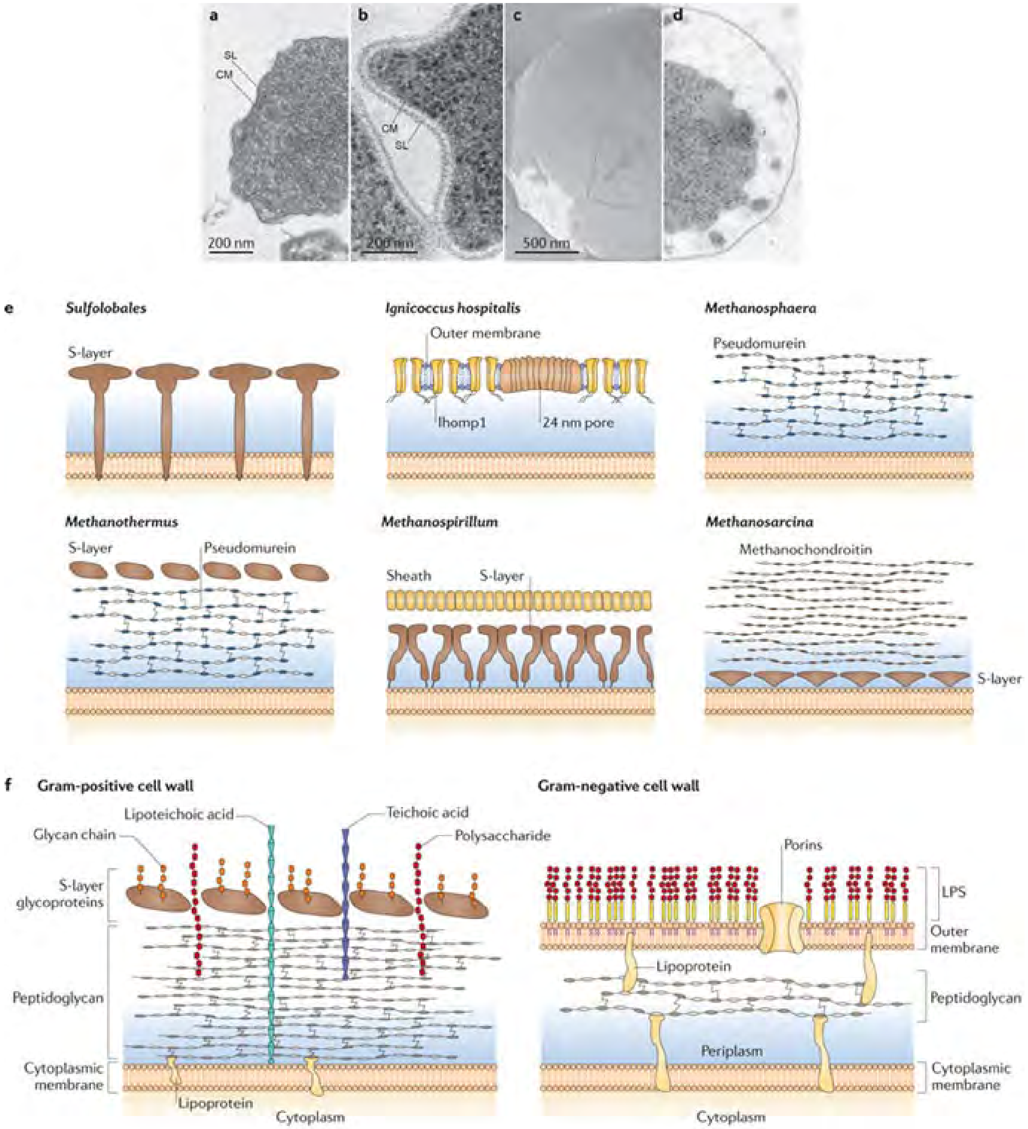
Why Does RYR Produce Statins?



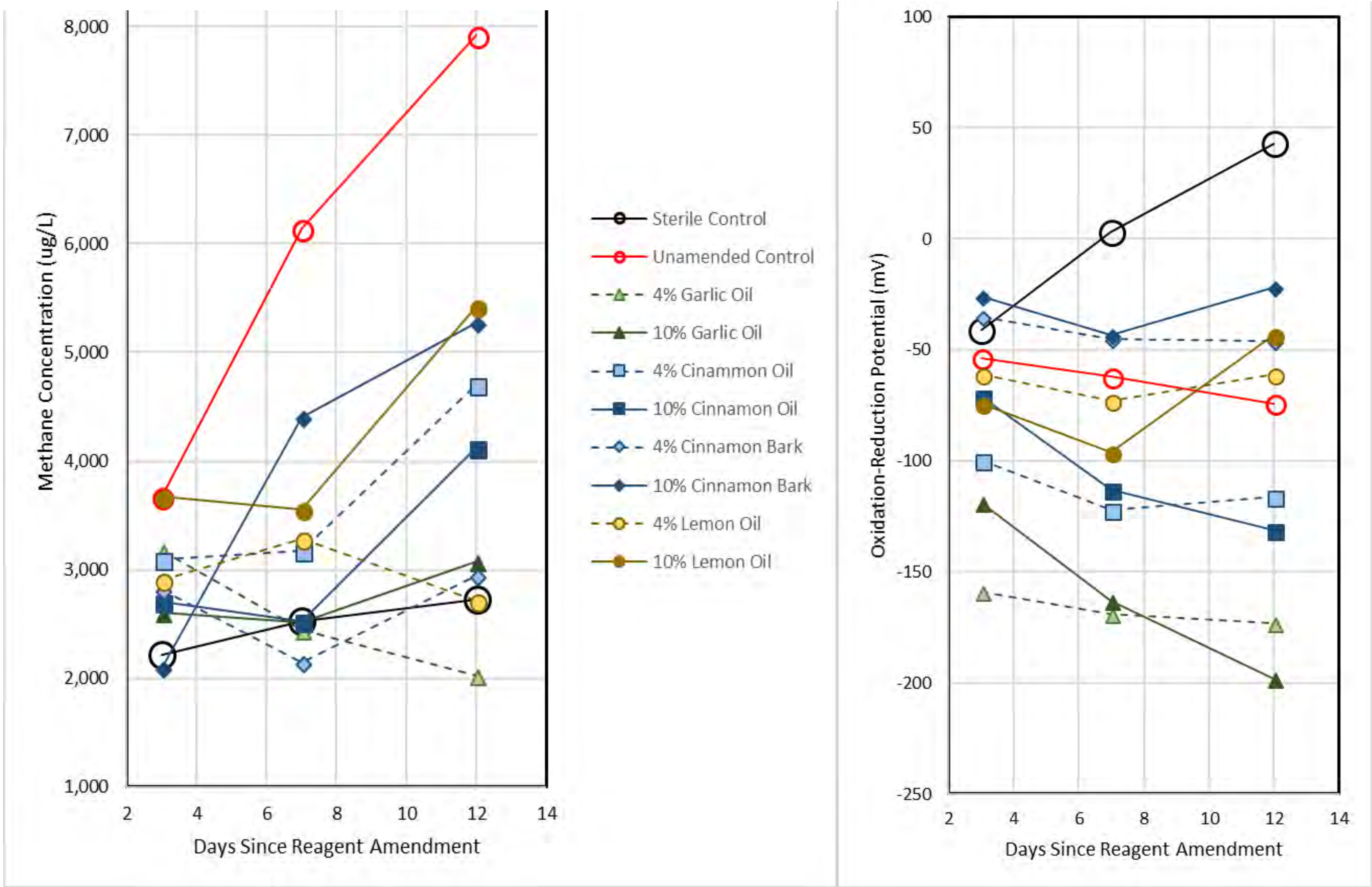
- Many microorganisms produce bioactive compounds that inhibit / regulate the growth and development of other organisms
- Example, antibiotics such as penicillin which is produced by mold of *Penicillium* genus

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).

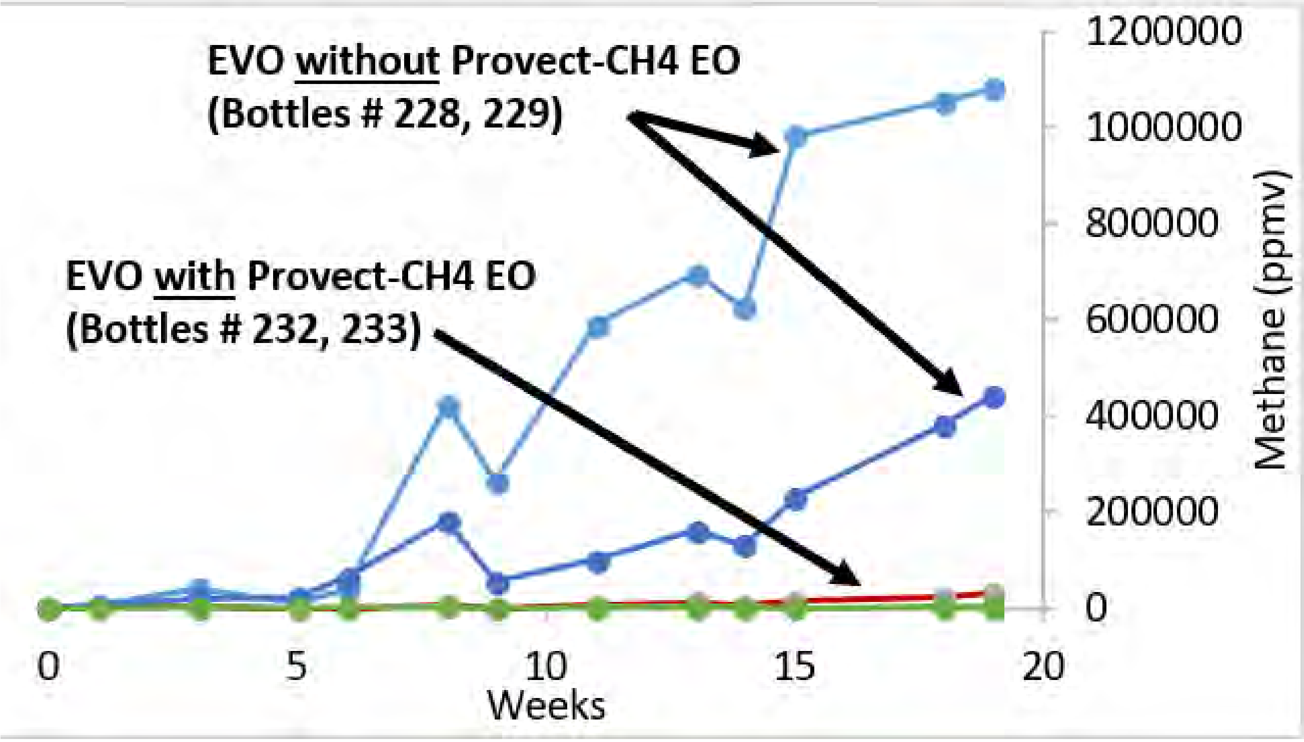


Oil-Based AMRs: Initial Studies



AMR Studies - Clemson Univ.

- 50 g aquifer solids
- 30 ml groundwater
- 40 mM EVO
- +/- 250 ppm AMR
- 10 µmol TCE
- DHC added


EVO without Provect-CH4 EO (Bottles # 228, 229)

EVO with Provect-CH4 EO (Bottles # 232, 233)

19 weeks incubation cumulative methane production

- **No AMR** CH4 >100,000 ppmV closed headspace; > 900 µmol (> 480 ppm) in water
- **+ AMR** CH4 <10,000 ppmV closed headspace; < 10 µmol (< 5 ppm) in water
- **90 to >99% reduction in methane production with Provect-CH4 Ego**

AMR Studies - DVGW Germany

CH4	EVO	PV
mg/L	2.75	0.09
umol	145	15
ppmv	1,450	150
Day 142		

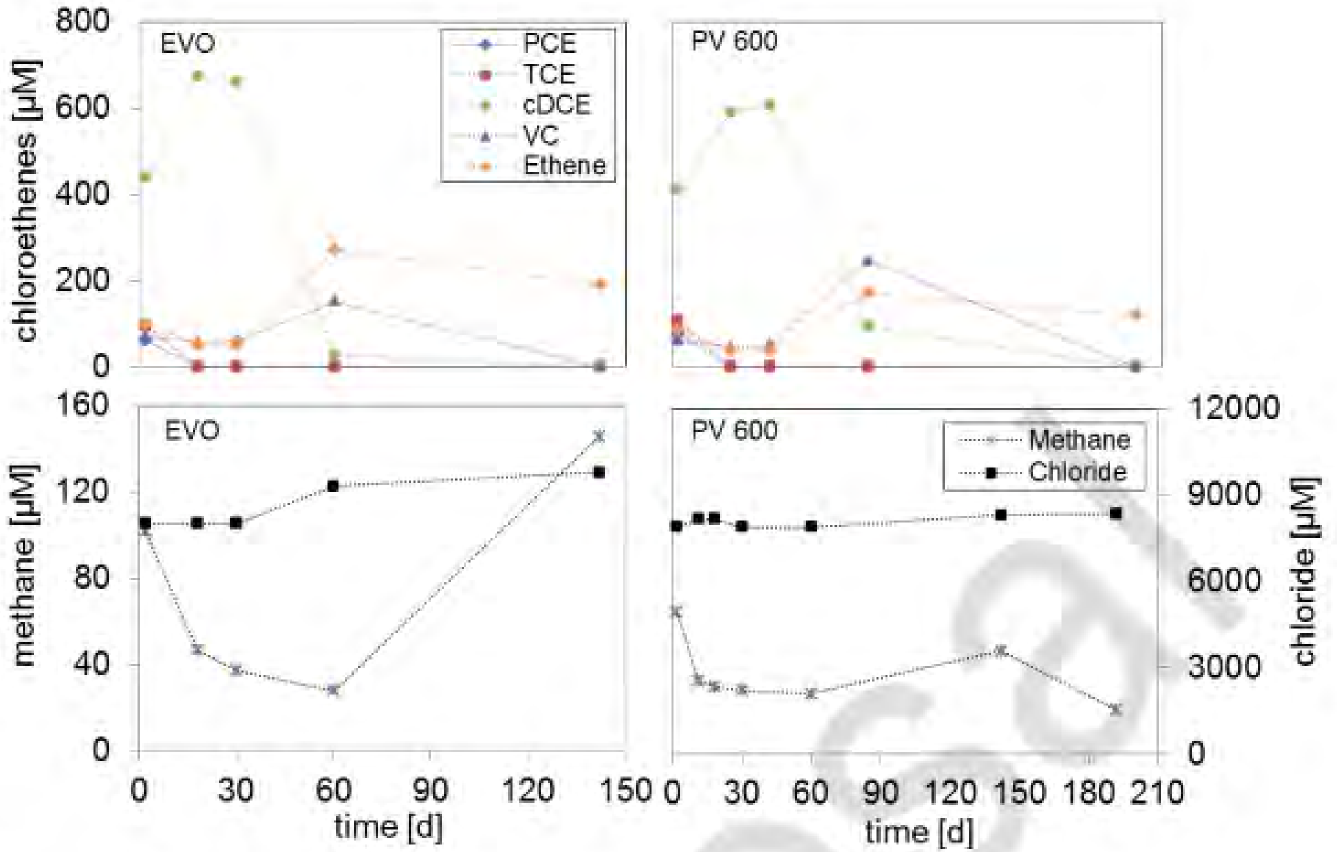


Figure 5-8: **Chloroethene, methane and chloride concentrations in the microcosms with EVO and with Provect-CH4™**

AMR Studies - DVGW Germany

CH4	EVO	PV
mg/L	2.75	0.09
umol	145	15
ppmv	1,450	150
mcrA	**2E6**	**1E2**
DHC dco	**5E6**	**3E6**
DHB deha	**1E3**	**6E3**
Day 142		

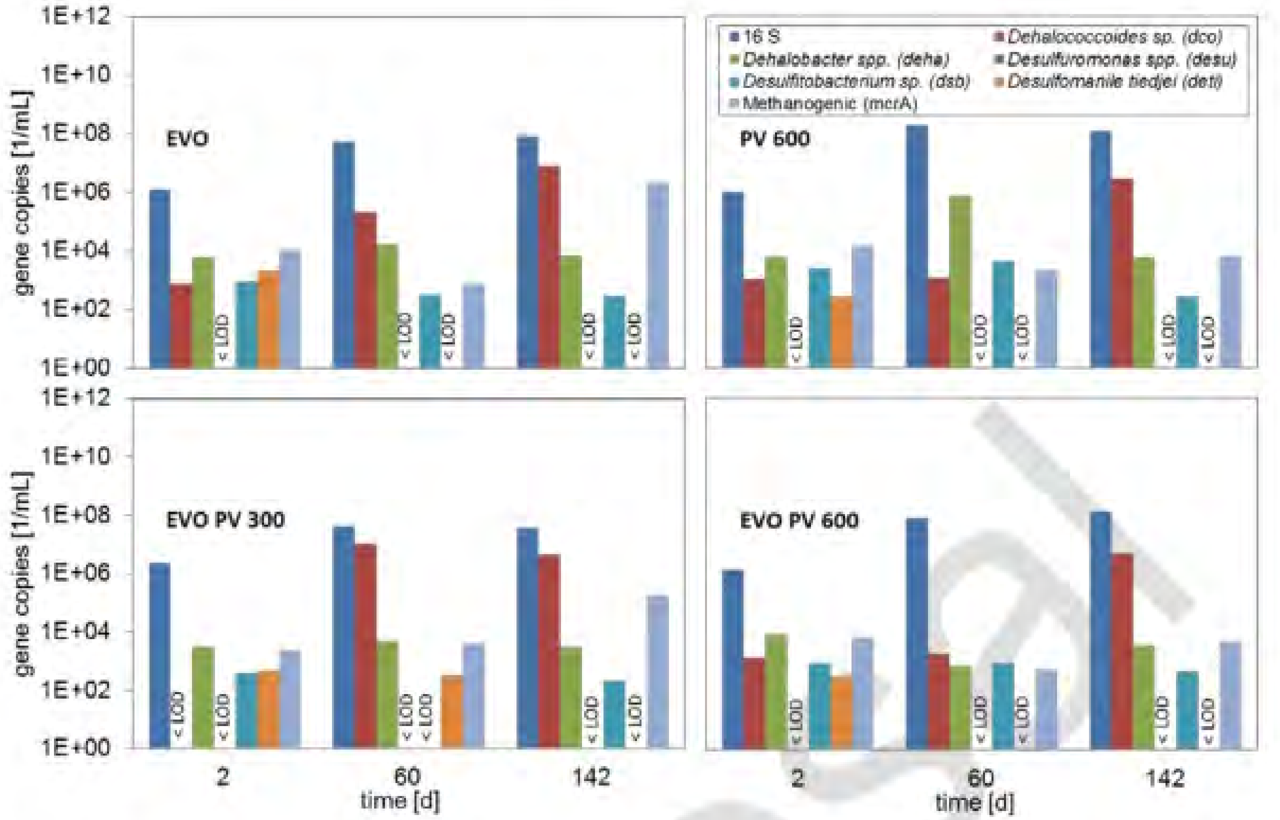


Figure 5-7: qPCR results for the microcosms EVO with and without Provect-CH4™ (limit of detection (LOD) = 10 copies/mL)

Provect-ERD CH4 Ole® Ego

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™ 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

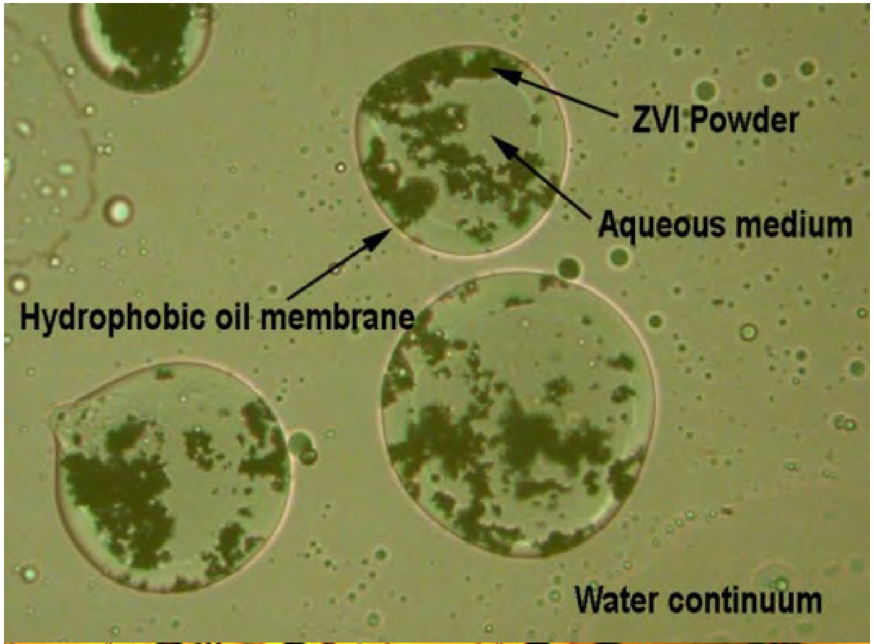
Oil Sample	**Al**	**P**	**S**	**Zn**	**Fe**	**Mg**	**Ca**	**Na**	**K**
Self-Emulsifiable Vegetable Oil	1.2 to 1.3	1,265 to 1,751	17.2 to 28.2	19.6 to 39.7	1,4 to 2.3	138 to 143	135 to 187	15.4 to 15.9	507 to 954

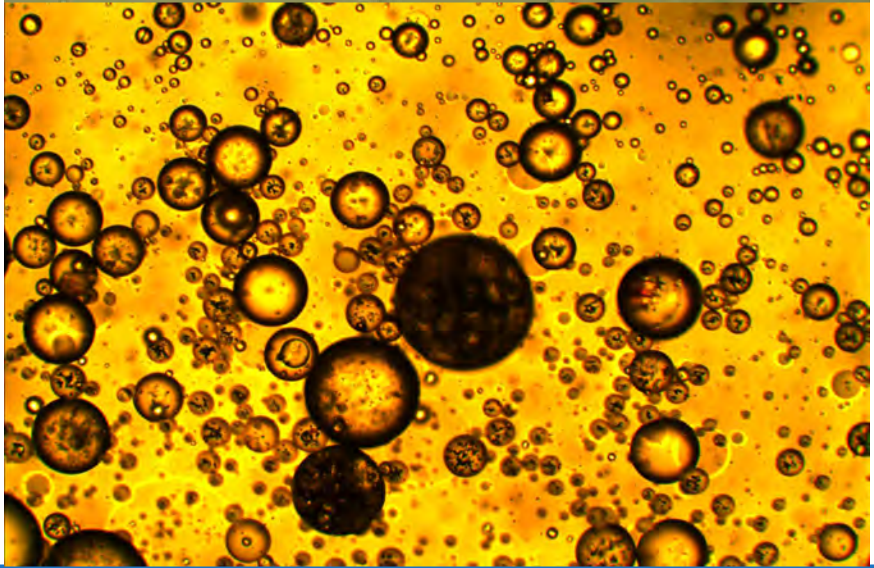
- **All units mg/kg oil**

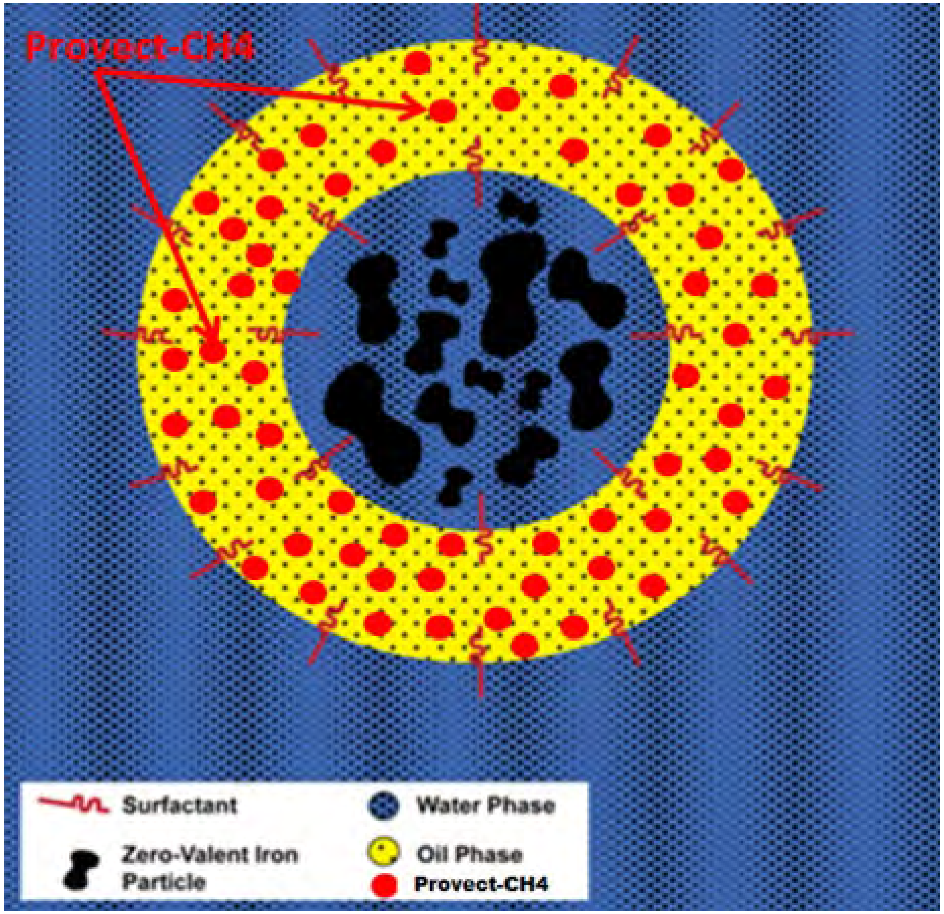
Provect-IR® Solid, Antimethanogenic ISCR Reagent

- 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

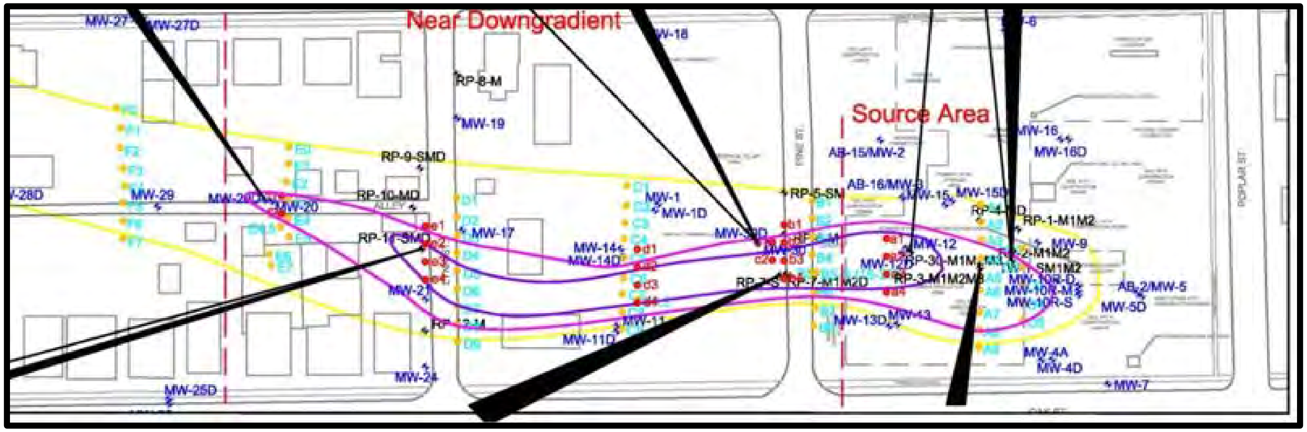






Provect-CH4 Case Study
Industrial Site, Indiana

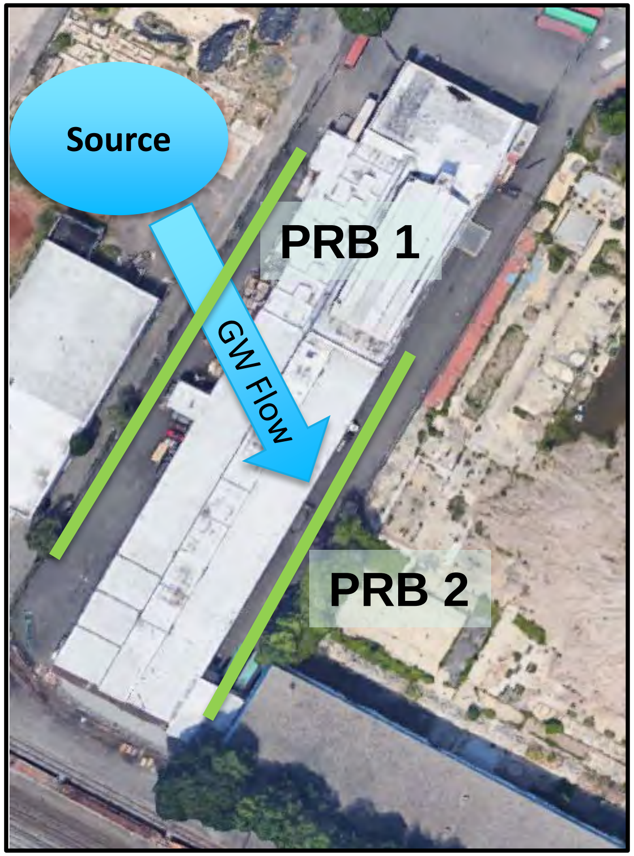
- Seymour Former Manufacturing Facility
  - Maximum cVOCs of 60,000 ug/L
  - Impacts extend to residential area
  - Primarily sand with clay and silt lenses
  - Excavation, thermal, and original ISCR technologies
  - Continued destruction of plume with methane control
- Emulsified vegetable oil (2 injections)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



Courtesy Mundell & Associates

Antimethanogenic ISCR Case Study Northern NJ

- Site Conditions and Scope
  - Target downgradient property
  - TCE, DCE and VC impacts
  - Fine sands, silt and clay underlain by bedrock
  - Treatment interval 15 to 60 ft bgs
  - Significant mass reduction, limiting further off-site migration
  - AMRs included
  - Freezing conditions with snowfall



Case Study – Northern NJ

Final Scope of Work

- 58 direct push points
- Ca. 140,000 lbs of IR
- Two Provect-IR Barriers
- Two mobilizations
- Sea containers to store IR
- Facility open during injection

Reactive Barrier 1

Daily Truck Deliveries

Reactive Barrier 2

Case Study – Northern NJ

Groundwater Results

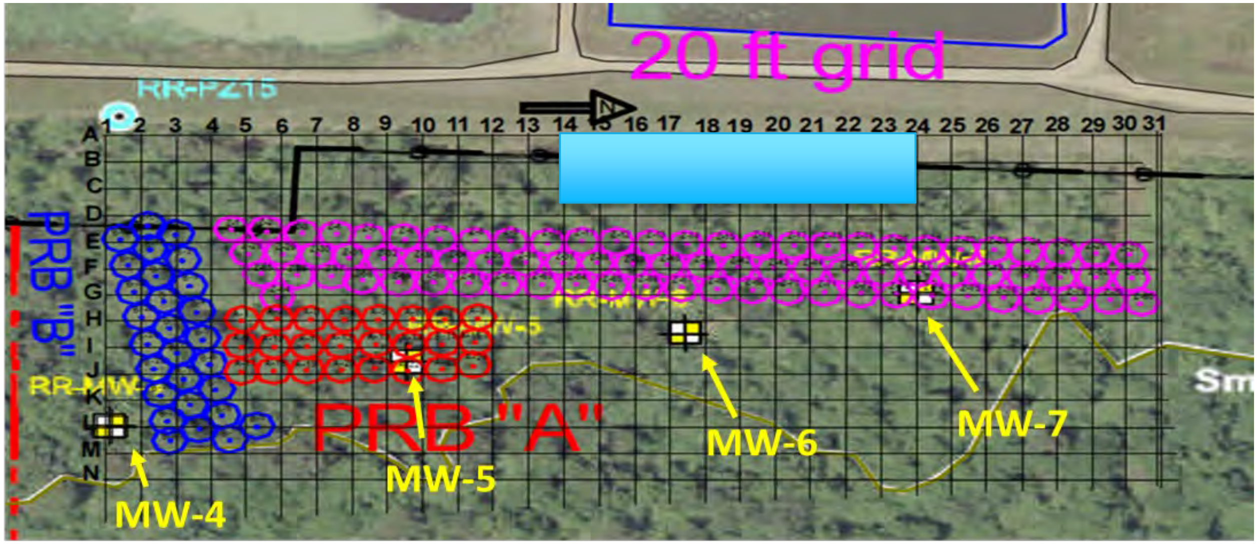
- 1 Year of Monitoring
- TCE Reduced >99%
- Reductions in DCE and VC
- Provect-IR lifespan >10 years
- CH4 ca. 0.50 to < 5 ppm

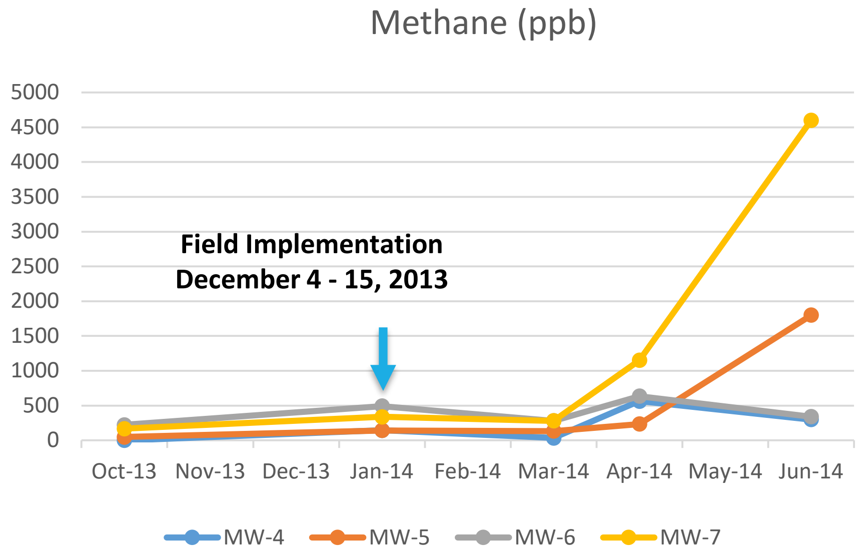
	MW-33D		
	7/12/17	9/18/18	
VOC (µg/l)			% Reductions
Trichloroethene	184,000	17.9	99.99%
cis-1,2-Dichloroethene	66,000	2,530	96.17%
Vinyl chloride	1,360	925	31.99%

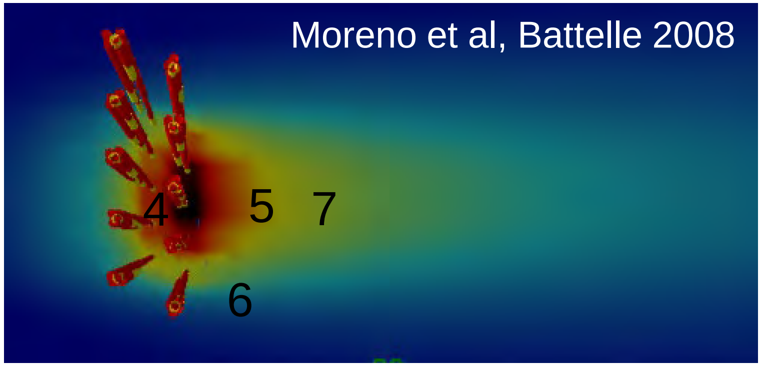
	MW-29D		
	7/13/18	9/17/18	
VOC (µg/l)			% Reductions
Trichloroethene	18,800	4.5	99.98%
cis-1,2-Dichloroethene	10,200	168	98.35%
Vinyl chloride	156	52.8	66.15%

	MW-34D		
	7/12/18	9/17/18	
VOC (µg/l)			% Reductions
Trichloroethene	3,600	1	99.98%
cis-1,2-Dichloroethene	620	6.5	98.95%
Vinyl chloride	24.5	1.8	92.65%

Interpreting Field Data






Moreno et al, Battelle 2008

- 🟦 Biotic: Biostimulation
- 🟨 Abiotic: Indirect iron effects
- 🟥 ISCR = Greatly reduced redox
- ⬛ Abiotic: Direct ZVI effects

Case Study: Provect-IR®

- Active Dry Cleaning Facility, southern Michigan
- Shallow groundwater 5 ft bgs confined by a clay layer at 12 ft bgs.
- PCE (max. 35 ppm) and TCE (max. 14 ppm) along with an accumulation of anaerobic catabolites *cis* 1,2-DCE (max. 25 ppm) and some VC (max. 4 ppm).
- Source area up to 70 ppm total CVOCs
- Groundwater migrates through a sandy aquifer into a damaged storm sewer.
- A sanitary sewer feeder from the active dry cleaner exacerbating the PCE migration problem by allowing warm water with potential contaminants and surfactants to enter the groundwater.
- Consultant and Agency selected Provect-IR over conventional ERD and ISCR reagents known to induce methane production.

Provect-IR Field Pilot: Focused on CH4

Table 1. Summary of Provect-IR Applications for Field-Scale Pilot Test

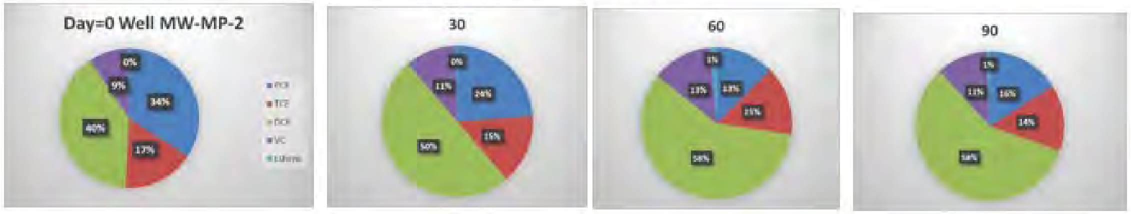
Depth Interval (ft bgs)	Amount of Provect-IR Injected (lb)			
	Point 1	Point 2	Point 3	Point 4
11 to 12	75	100	100	150
9 to 10	75	100	100	100
7 to 8	50	50	50	50
TOTAL	200	250	250	300

Figure 1. Pilot Test Area

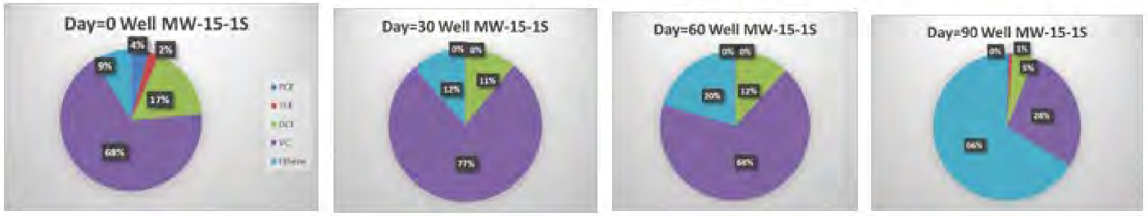
Active Dry Cleaner – 90 Days

- Total CVOCs reduced by 62 to >99%
- No accumulation of DCE or VC as dead-end catabolites
- No groundwater methane accumulation during any sampling event (ranged from 1.7 mg/L @ Time=0 to a high of 2.2 mg/L @ 60 days after Provect-IR additions.
- Soil gas methane baseline <20 ppmv to a high of 94 ppmv 30 days after the injection event (Day 60 and Day 90 <20 ppm)

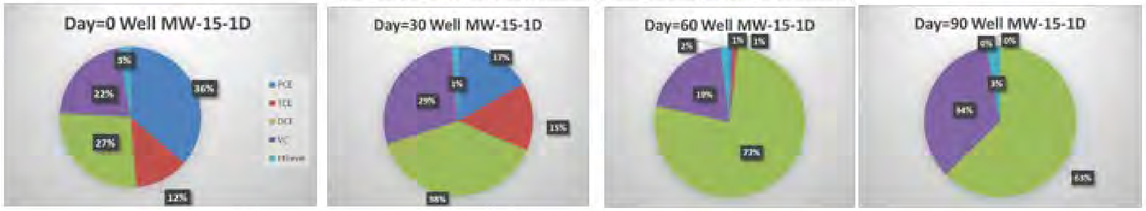
Well MW-MP-2 Source Area



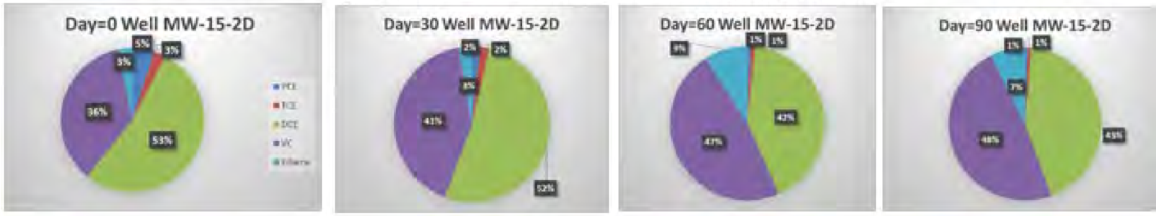
Well MW-15-1S (shallow, 5 feet downgradient)



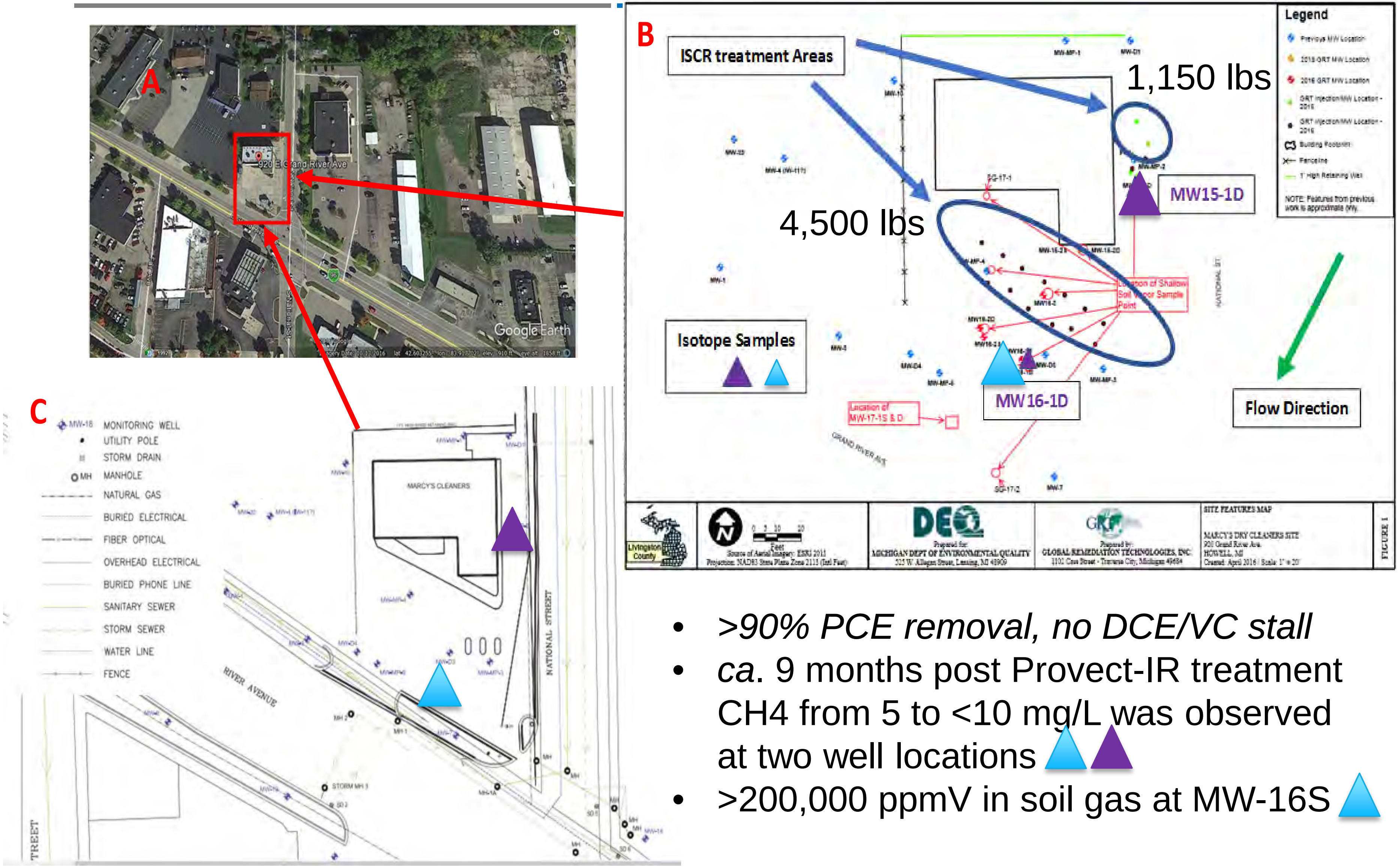
Well MW-15-1D (deep, 5 feet downgradient)



Well MW-15-2D (deep, 20 feet downgradient)



Phase II Implementation (March 2016)

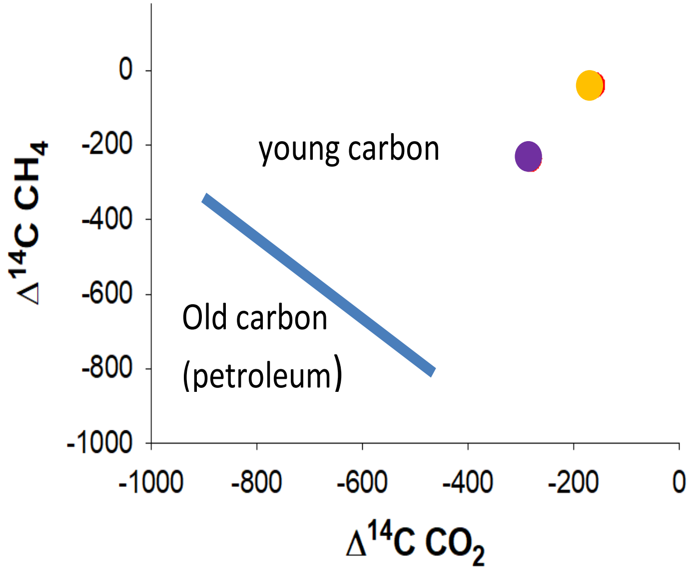


- *>90% PCE removal, no DCE/VC stall*
- *ca*. 9 months post Provect-IR treatment CH4 from 5 to <10 mg/L was observed at two well locations ▲▲
- >200,000 ppmV in soil gas at MW-16S ▲

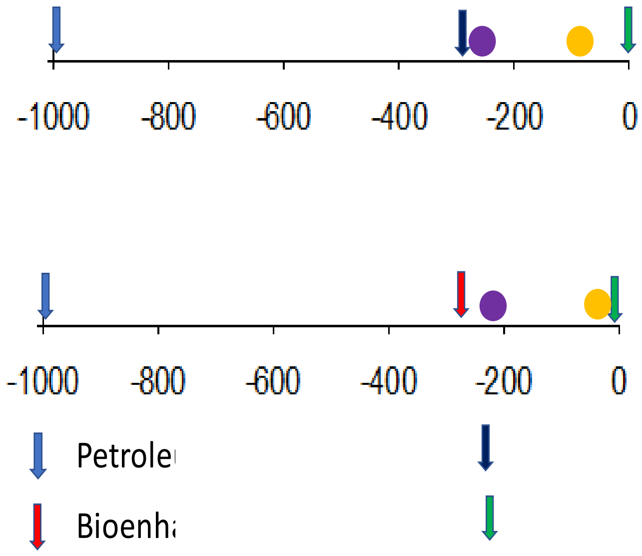
Origin of CH4 After 9 Months

$\Delta^{14}C$ and $\delta^{13}C$ Data Review

Sample Identification	Type	F Modern	Fm Err	Age (years)	Age Err	$\delta^{13}C$	$\Delta^{14}C$
MW-16-1D-CO2, groundwater	CO2	0.8469	0.0020	1,340	20	-71.48	-159.96
MW-15-1D-CO2, groundwater	CO2	0.7261	0.0024	2,570	25	-16.65	-279.81
MW-16-1D-CH4, groundwater	CH4	0.9669	0.0019	270	15	-57.96	-40.95
MW-15-1D-CH4, groundwater	CH4	0.7677	0.0016	2,120	15	-60.61	-238.54

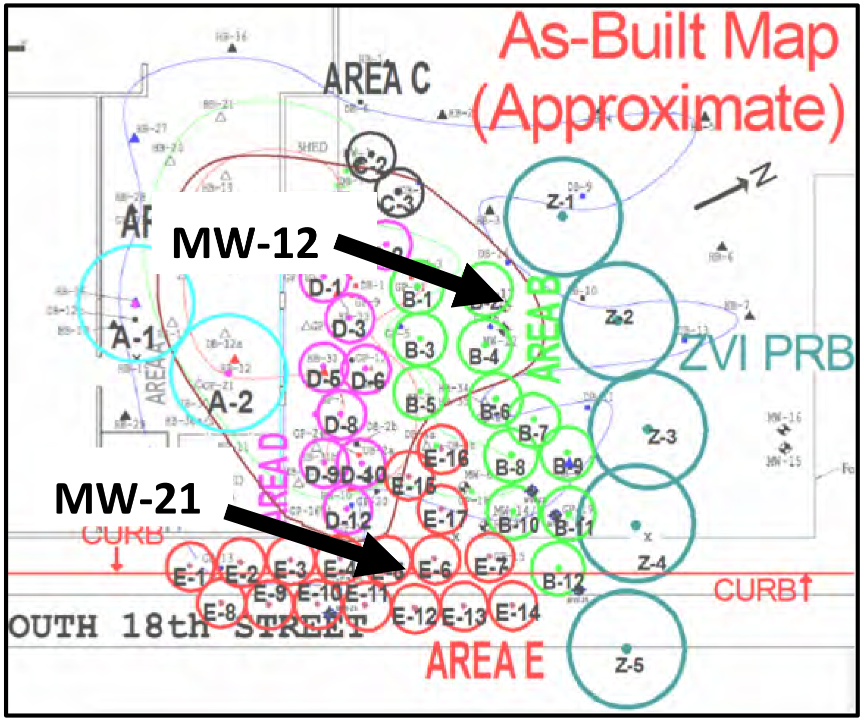


Potential CO$_2$ and CH$_4$ $\Delta^{14}C$ Source Values



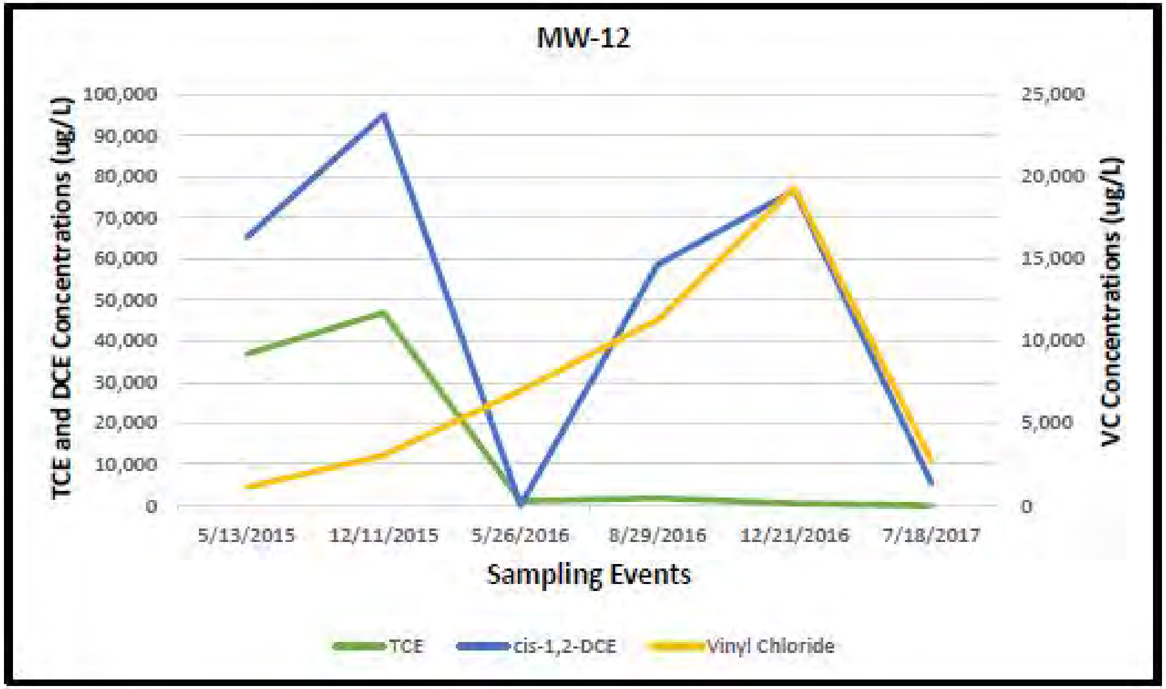
Combined Provect-IR / EZVI Case Study
East Orange, New Jersey

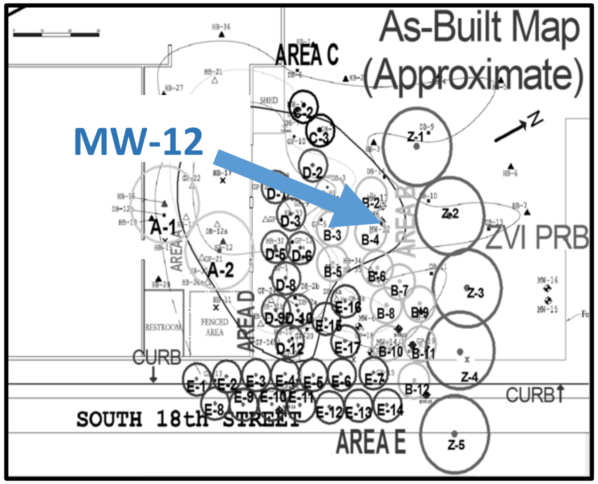
- Former Manufacturing Facility
- Historical use & release TCE
- Primarily clay, silts, fine sands
- Treatment interval 17 to 27 ft bgs
- Source Area: EZVI applied
- Plume Area: “Provect-IR”
- MW-12 and MW-21 TCE Source
- Goal was limit plume migration

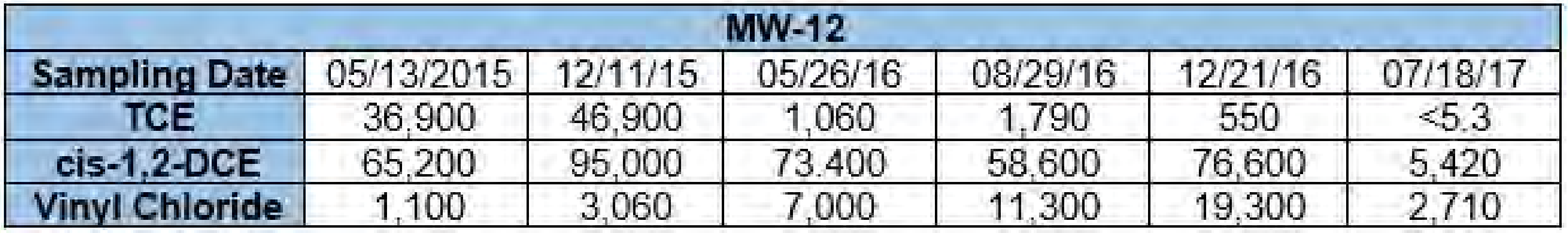


Courtesy Innovative Environmental Technologies, Inc.

Results MW-12 (treated area)

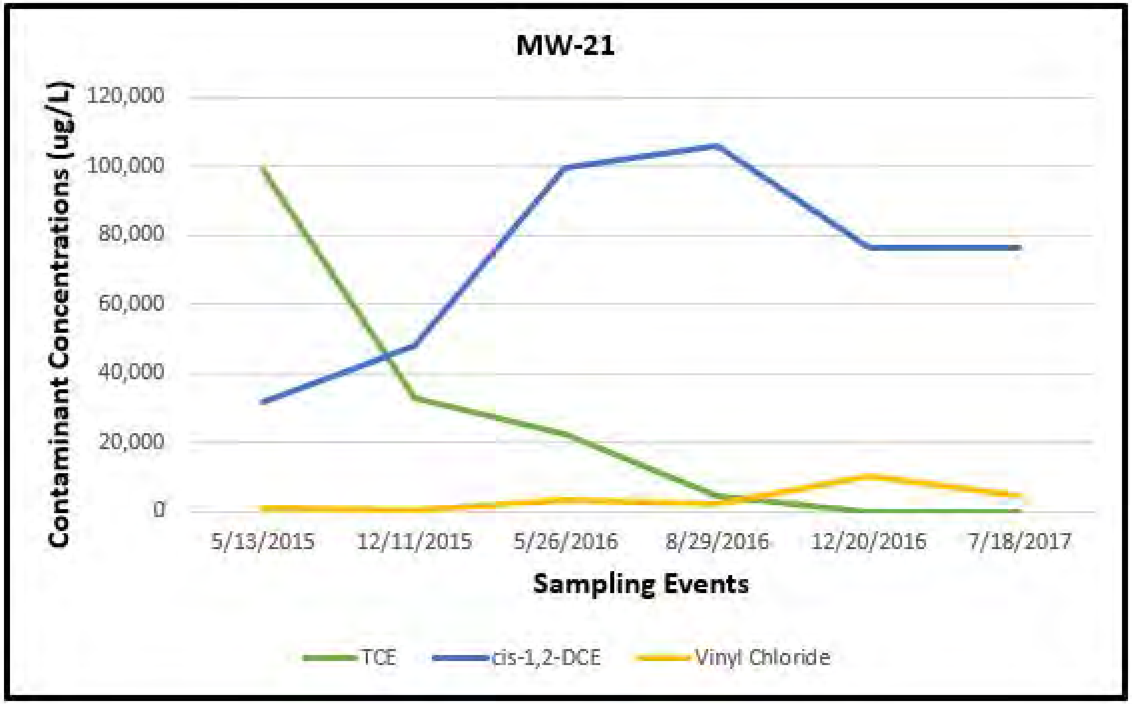


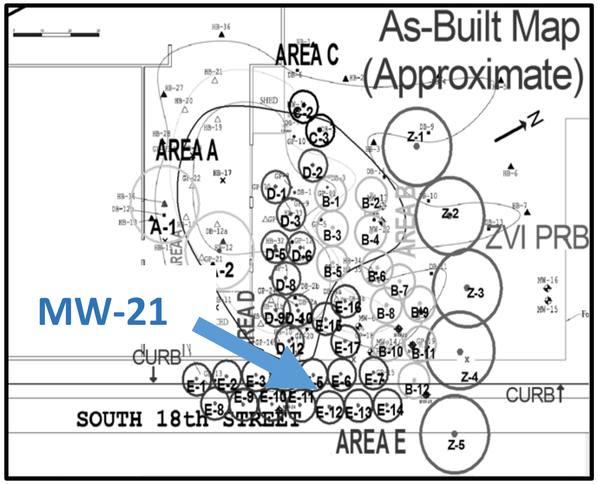


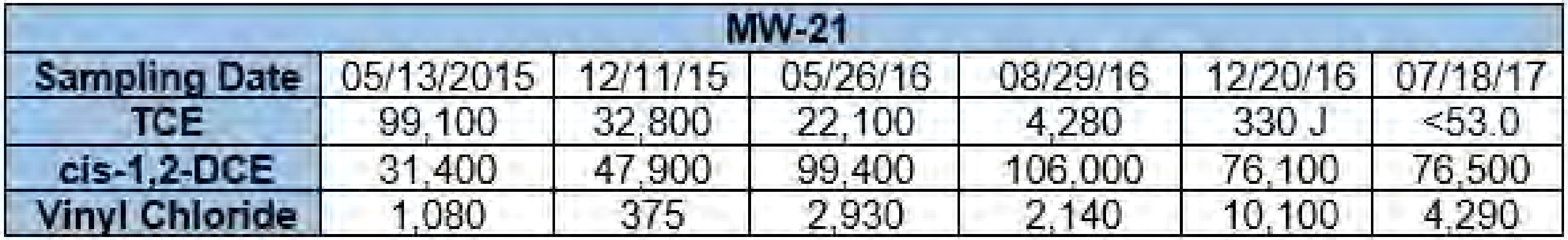


MW-12						
Sampling Date	05/13/2015	12/11/15	05/26/16	08/29/16	12/21/16	07/18/17
TCE	36,900	46,900	1,060	1,790	550	<5.3
cis-1,2-DCE	65,200	95,000	73,400	58,600	76,600	5,420
Vinyl Chloride	1,100	3,060	7,000	11,300	19,300	2,710

Results MW-21 (side gradient)





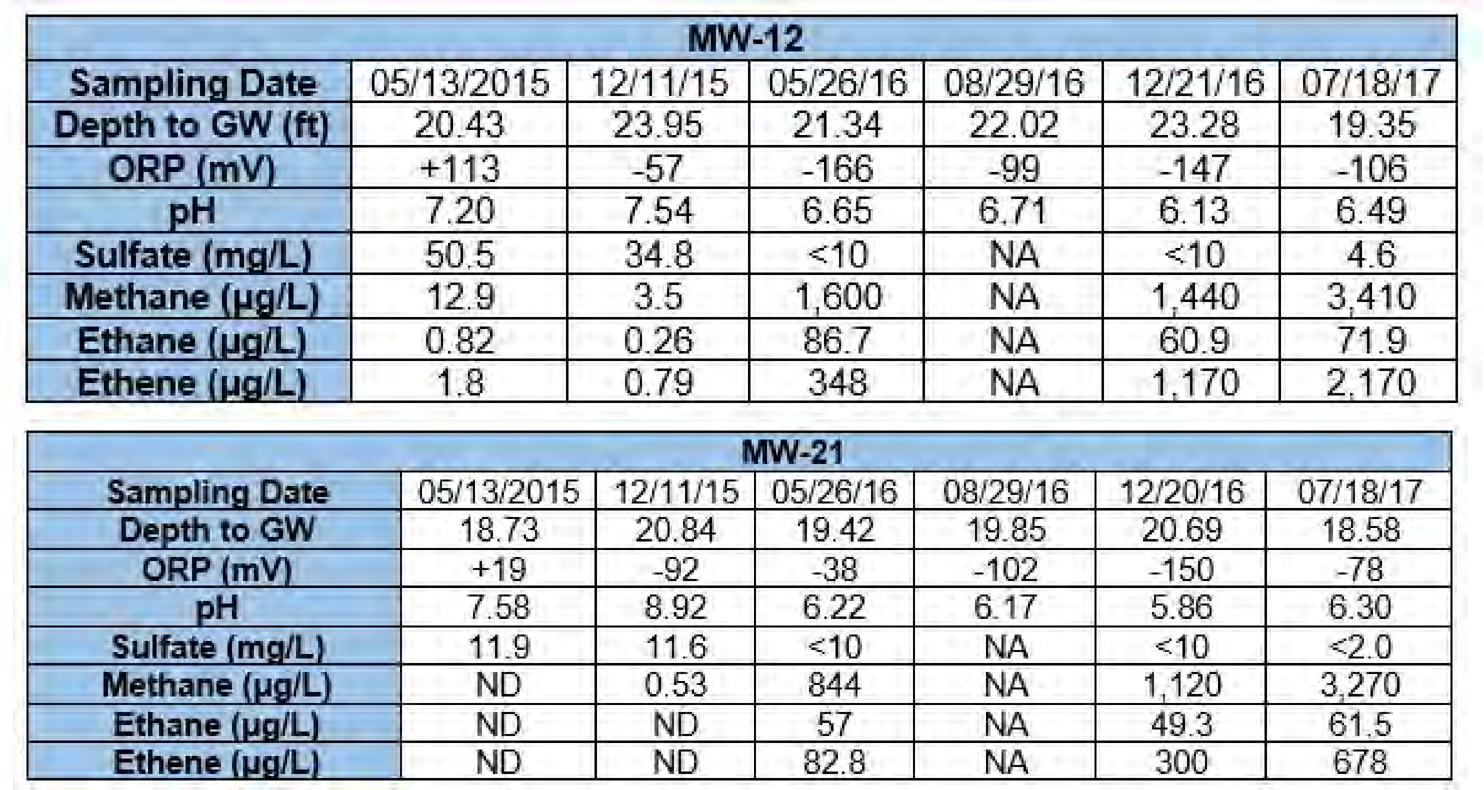


MW-21						
Sampling Date	05/13/2015	12/11/15	05/26/16	08/29/16	12/20/16	07/18/17
TCE	99,100	32,800	22,100	4,280	330 J	<53.0
cis-1,2-DCE	31,400	47,900	99,400	106,000	76,100	76,500
Vinyl Chloride	1,080	375	2,930	2,140	10,100	4,290

Case Study – East Orange, NJ

Field Parameters and Geochemical Data

- ORP still reducing 2 years after injection
- Dissolved gasses continue to increase
- Methanogenesis controlled (ca. < 10 ppm) for > 2 years



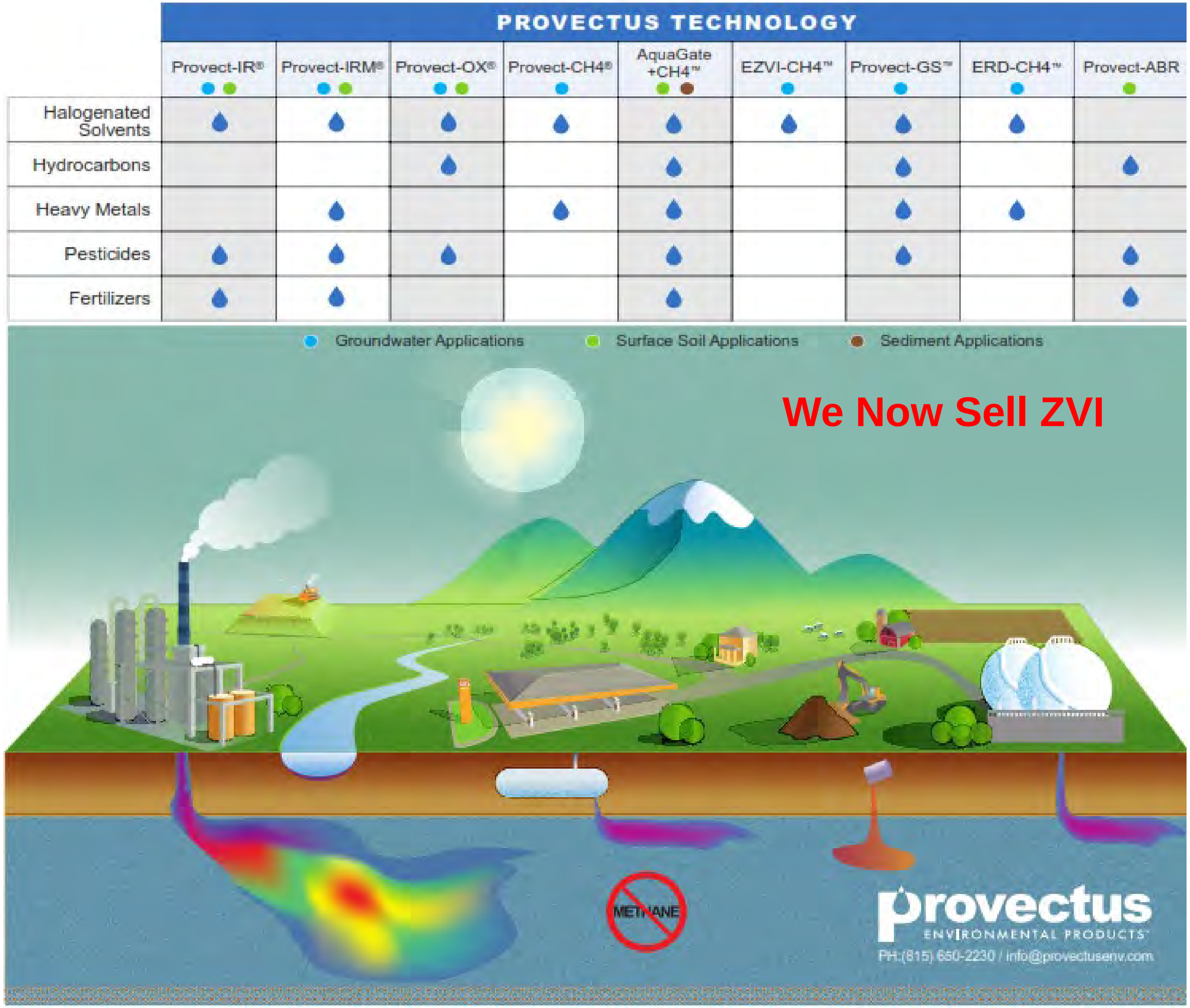
MW-12						
Sampling Date	05/13/2015	12/11/15	05/26/16	08/29/16	12/21/16	07/18/17
Depth to GW (ft)	20.43	23.95	21.34	22.02	23.28	19.35
ORP (mV)	+113	-57	-166	-99	-147	-106
pH	7.20	7.54	6.65	6.71	6.13	6.49
Sulfate (mg/L)	50.5	34.8	<10	NA	<10	4.6
Methane (µg/L)	12.9	3.5	1,600	NA	1,440	3,410
Ethane (µg/L)	0.82	0.26	86.7	NA	60.9	71.9
Ethene (µg/L)	1.8	0.79	348	NA	1,170	2,170

MW-21						
Sampling Date	05/13/2015	12/11/15	05/26/16	08/29/16	12/20/16	07/18/17
Depth to GW	18.73	20.84	19.42	19.85	20.69	18.58
ORP (mV)	+19	-92	-38	-102	-150	-78
pH	7.58	8.92	6.22	6.17	5.86	6.30
Sulfate (mg/L)	11.9	11.6	<10	NA	<10	<2.0
Methane (µg/L)	ND	0.53	844	NA	1,120	3,270
Ethane (µg/L)	ND	ND	57	NA	49.3	61.5
Ethene (µg/L)	ND	ND	82.8	NA	300	678

Summary

- Natural statins in RYR, essential plant oils and other materials can be used to effectively and specifically control methanogenic activity
- The methane control technology has been integrated into various products designed for the environmental remediation industry
  - **Provect-CH4®** ERD Supplement / Methane Inhibitor
  - **ERD-CH4® Ole Ego™** Liquid, Antimethanogenic ERD Reagent
  - **Provect-IR®** Solid, Antimethanogenic ISCR Reagent
  - **Provect-IRM®** Antimethanogenic ISCR Reagent for Metals
  - **AquaGate®-CH4™** Antimethanogenic *In Situ* Sediment Capping Technology
  - **EZVI-CH4™** Antimethanogenic Source Area / DNAPL Treatment
- The main benefit is improved performance = “better gas mileage”
- Other potential benefits relate to safety, regulatory compliance, and sustainability

Provectus Environmental Products, Inc



PROVECTUS TECHNOLOGY

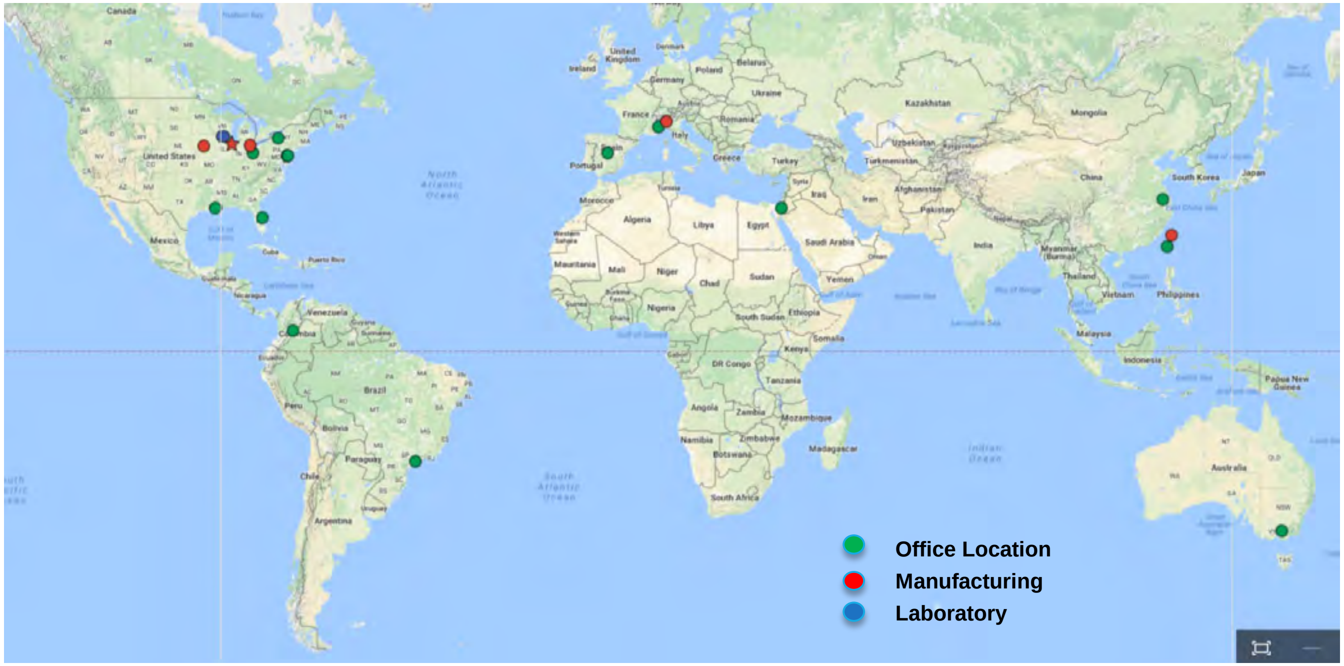
	Provect-IR® 🔵 🟢	Provect-IRM® 🔵 🟢	Provect-OX® 🔵 🟢	Provect-CH4® 🔵	AquaGate +CH4™ 🟢 🟤	EZVI-CH4™ 🔵	Provect-GS™ 🔵	ERD-CH4™ 🔵	Provect-ABR 🟢
Halogenated Solvents	💧	💧	💧	💧	💧	💧	💧	💧	
Hydrocarbons			💧		💧		💧		💧
Heavy Metals		💧		💧	💧		💧	💧	
Pesticides	💧	💧	💧		💧		💧		💧
Fertilizers	💧	💧			💧				💧

🔵 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)**
- **Australia, Brazil, China, Colombia, Israel, Italy, Spain and Taiwan**