



# Remediation of Chlorinated Hydrocarbons in an Urban Setting: Managing Methane Production during an ISCR Remedial Approach

**Ohio Brownfield Conference**

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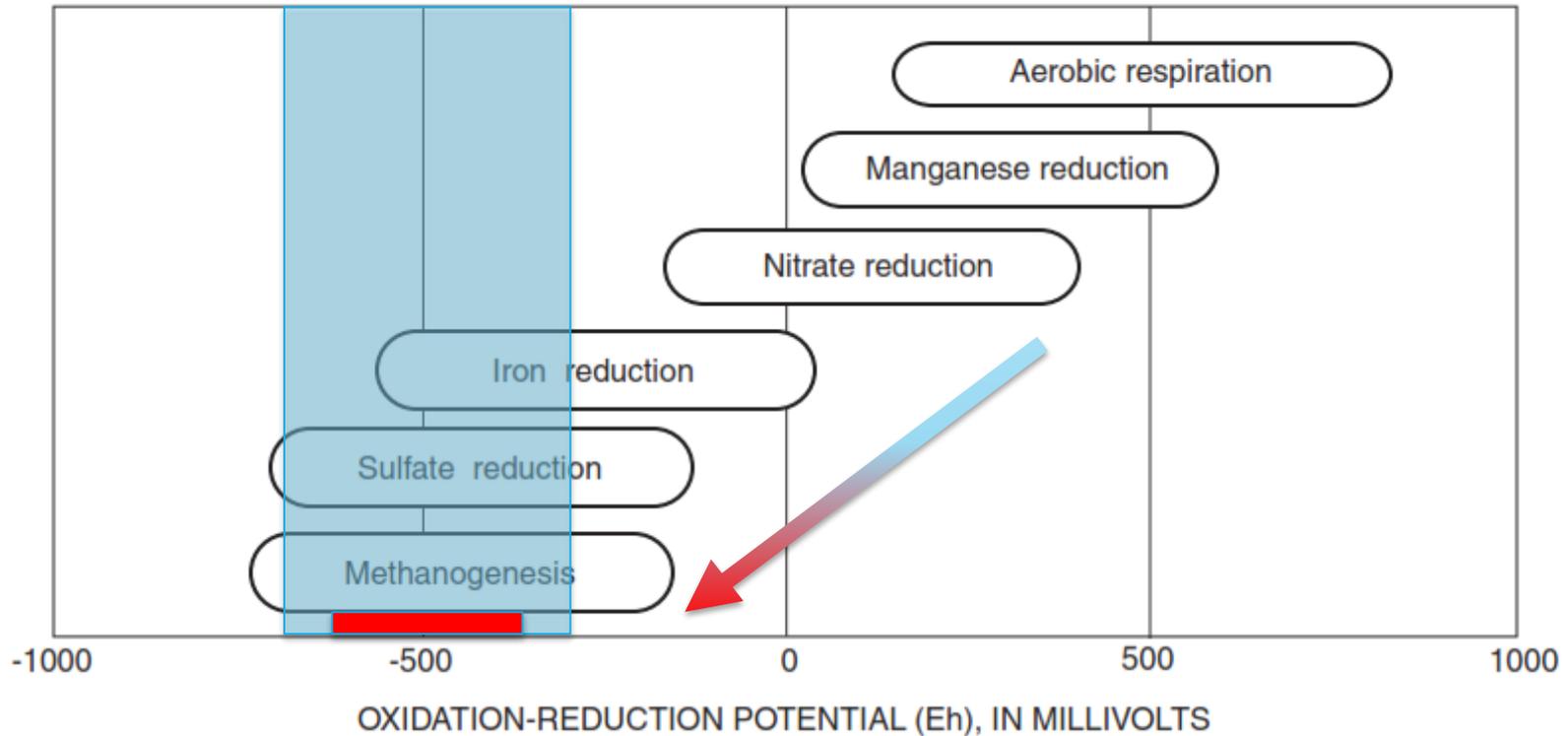
# Presentation Outline

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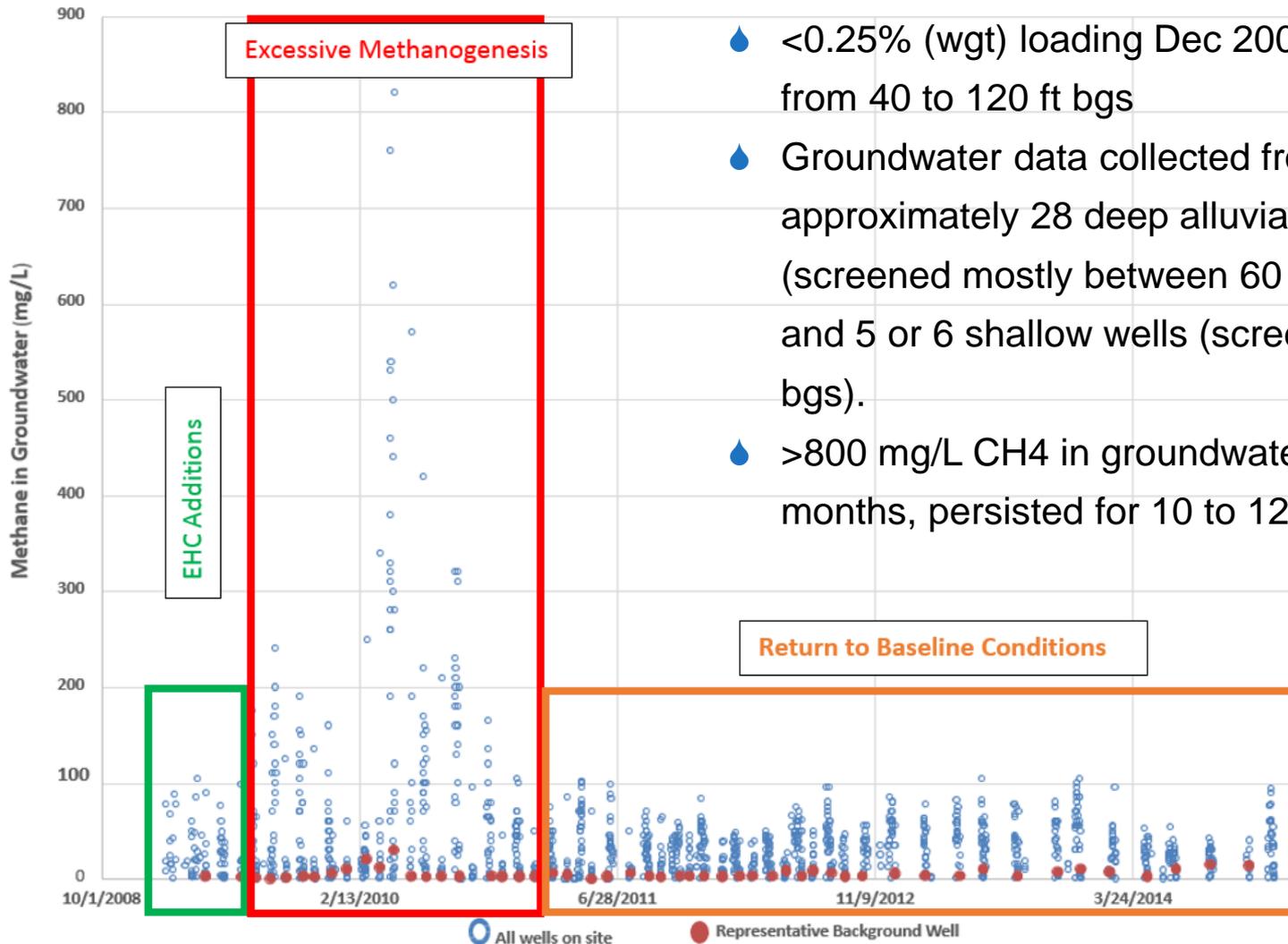
- 💧 Introduction – what is the problem with methane?
- 💧 How can we actively control methanogens?
  - **Provect-CH4<sup>®</sup>** Methane Inhibitor
  - **Provect-IR<sup>®</sup>** Solid, Antimethanogenic ISCR Reagent
  - **Provect-IRM<sup>®</sup>** Antimethanogenic ISCR/Heavy Metal Immobilization Reagent
  - **EZVI-CH4<sup>™</sup>** Antimethanogenic Reagent for CHC DNAPL
  - **AquaBlok-CH4<sup>®</sup>** Antimethanogenic
- 💧 **Case Studies - dry cleaning sites in urban settings**
  - **Former site – Georgia**
  - **Active site – Michigan**
  - Recently active site – Wisconsin / New Mexico
- 💧 **Summary and Conclusions**

# Why Reduce ORP?



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

# Example of Excessive Methane



- <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<sub>4</sub> in groundwater after 6 months, persisted for 10 to 12 months

# What is a Methanogen?

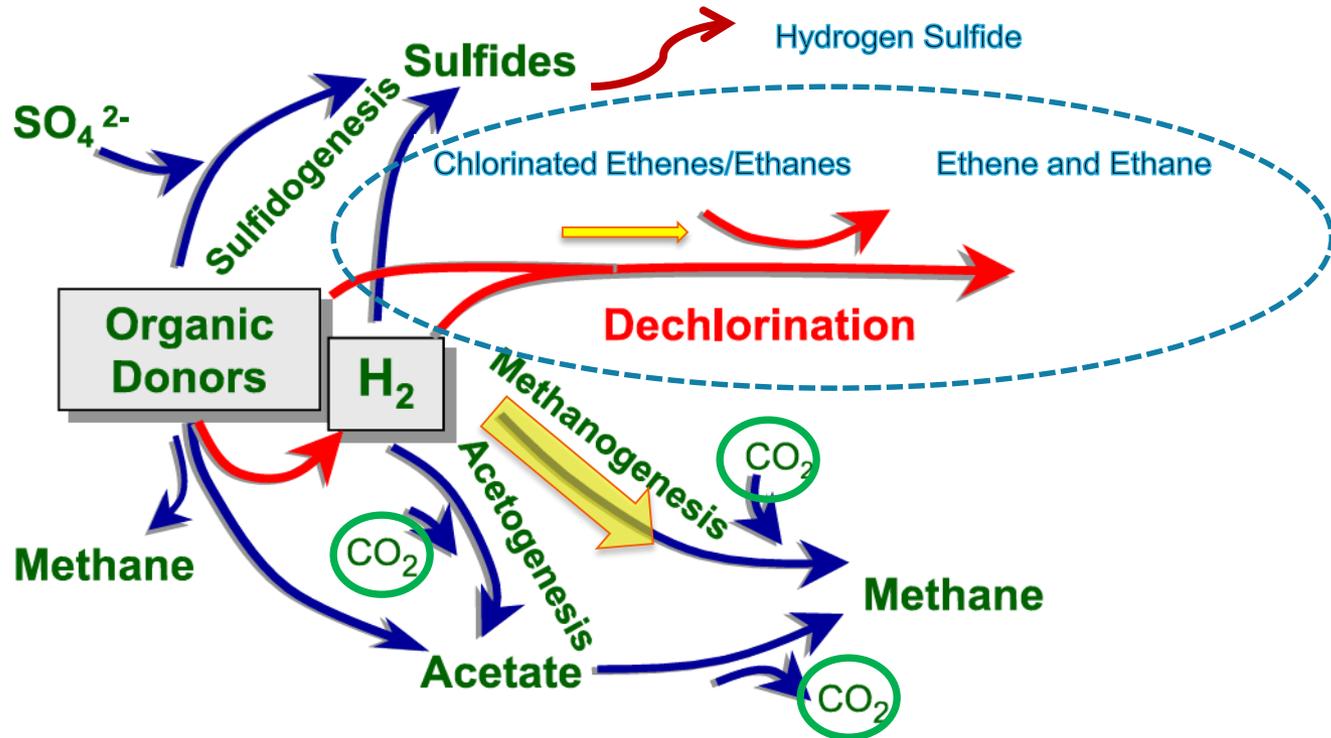
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- Methanogens are microorganisms that produce methane
- Methanogens are Archaea (Woese and Fox, 1977) and hence, from a genetic perspective, *Dehalococcoides ethenogenes* are as different from methanogens as you are.
- Methanogens are often dominant as compared to DHC spp. and acetogens: averaging 2% to 15% of all soil microbes (Bates, *et. al.*, 2011)
  - Even at biostimulated populations of DHC rising to  $>10^8$  cells/L Archaea populations can be orders of magnitude greater in number
- Methanogens are important members of synergistic, fickle anaerobic communities = we need some

# What is The Problem With Methanogens?

- 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).





# What is The Problem With Methanogens?

- ◆ **Cost and Efficiency Issues:** 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 <sub>2</sub> to Reduce Mole Analyte	Moles of H <sub>2</sub> Acceptor In Treatment Area
<b>Contaminant Electron Acceptors (To End Product Ethene)</b>				
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
<b>Complete Dechlorination (Soil+Groundwater) Subtotal</b>				<b>1,757</b>
<b>Native Electron Acceptors</b>				
Dissolved Oxygen	9.0	32	2	199
Nitrate (as Nitrogen)	9.0	62	3	682
Sulfate	50.0	96.1	4	736
Fe <sup>+2</sup> Formation from Fe <sup>+3</sup>	20.0	55.8	0.5	63
Mn <sup>+2</sup> Formation from Mn <sup>+4</sup>	10.0	54.9	1	64
<b>Baseline Geochemistry Subtotal</b>				<b>1,745</b>
<b>Hydrogen Waste for Methane Formation</b>				
Methane Formed	20.0	16	4	1,769
<b>Initial Treatment Area Hydrogen Usage</b>				<b>5,271</b>

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<sub>2</sub>.

# What is The Problem With Methane?



- 💧 **Potential Health and Safety Issues (in Some Situations):**
  - ✓ Methane is explosive, with an LEL of 5% and an UEL of 15%.
  - ✓ Induces vapor intrusion – indoor air issues
- 💧 **New and Emerging State and Federal Guidelines and Regulations**

The screenshot shows the EPA website page for Vapor Intrusion. The header includes the EPA logo and navigation links. The main content area features a large title 'Vapor Intrusion' and an illustration of a house with a cross-section showing 'Soil Contamination' and 'Contaminated Groundwater'. Below the illustration is a paragraph of introductory text and a link to contact the state health department. A sidebar on the right contains 'Top Questions/Tasks', 'Contact' information for Rich Kapuscinski, and 'Important Links'.

**EPA** United States Environmental Protection Agency  
LEARN THE ISSUES | SCIENCE & TECHNOLOGY | LAWS & REGULATIONS | ABOUT EPA

Vapor Intrusion [Contact Us](#)

## Vapor Intrusion

Soil Contamination  
Contaminated Groundwater

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**

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**Important Links**

- [Basic Information](#)
- [Events](#)
- [Related Links](#)
- [Contact Us](#)
- [OUST's Vapor Intrusion Compendium.](#)

# Yes – Methane is Important



# Presentation Outline

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💧 Introduction – what is the problem with methane?

💧 **How can we actively control methanogens?**

- **Provect-CH4<sup>®</sup>** Methane Inhibitor
- **Provect-IR<sup>®</sup>** Solid, Antimethanogenic ISCR Reagent
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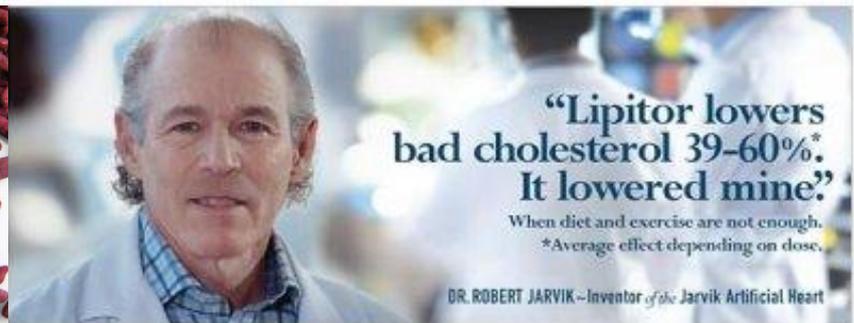
💧 **Case Studies - dry cleaning sites in urban settings**

- Former site – Georgia
- Active site – Michigan
- Recently active site - Wisconsin

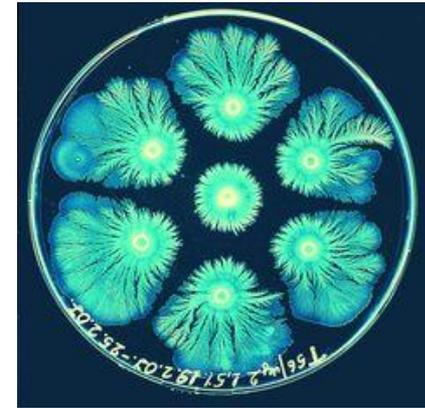
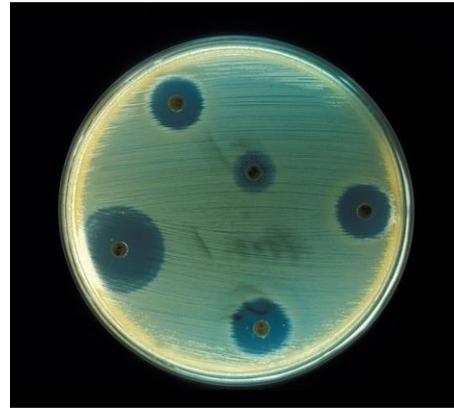
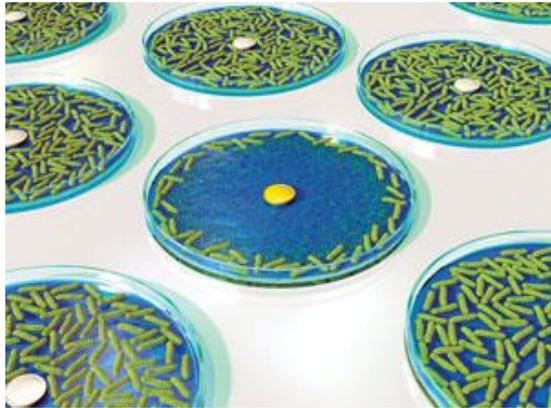
💧 **Summary and Conclusions**

# What is Red Yeast Rice (RYR) Extract?

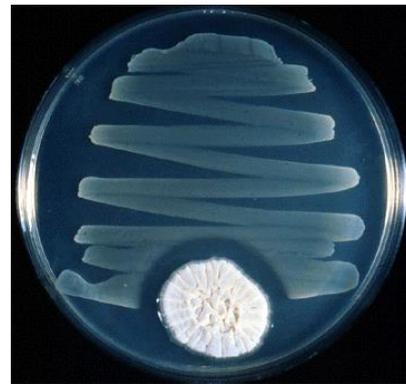
- ◆ RYR extract is a substance extracted from rice that has been fermented with a yeast called *Monascus purpureus*.
- ◆ RYR extract contains a number of natural statins - most importantly, Monacolin K - otherwise known as Lovastatin® / Lipitor® /etc.
- ◆ In addition to Monacolin K, RYR also contains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



# Why Does RYR Produce Statins?

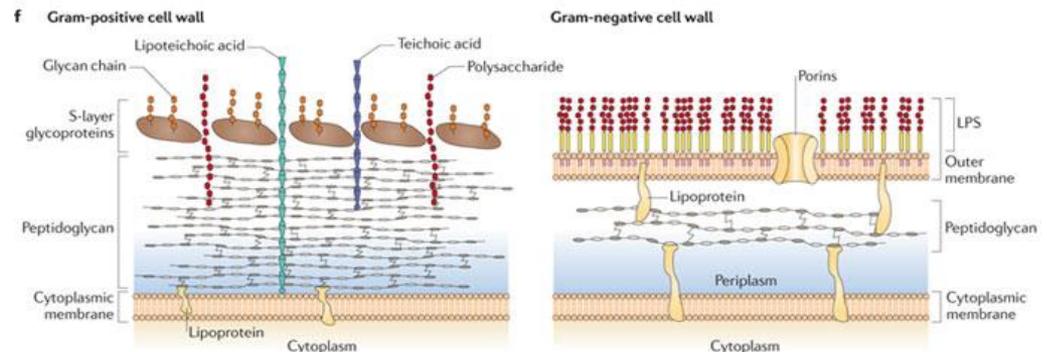
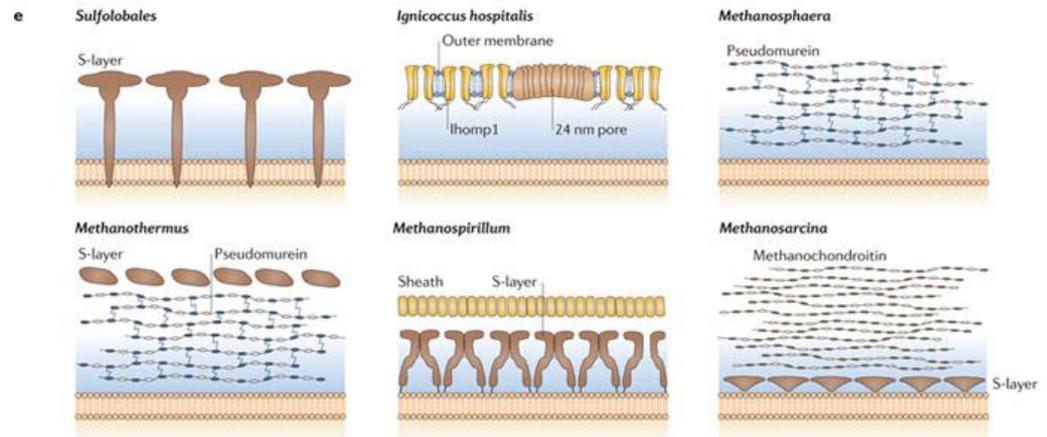
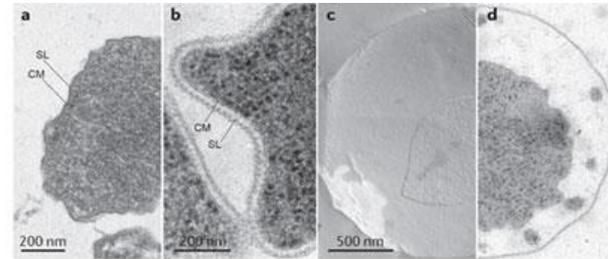


- ◆ Many microorganisms produce bioactive compounds that inhibit / regulate the growth and development of other organisms
- ◆ Example, antibiotics such as penicillin which is produced by mold of *Penicillium* genus



# How Does RYR Control Methanogens?

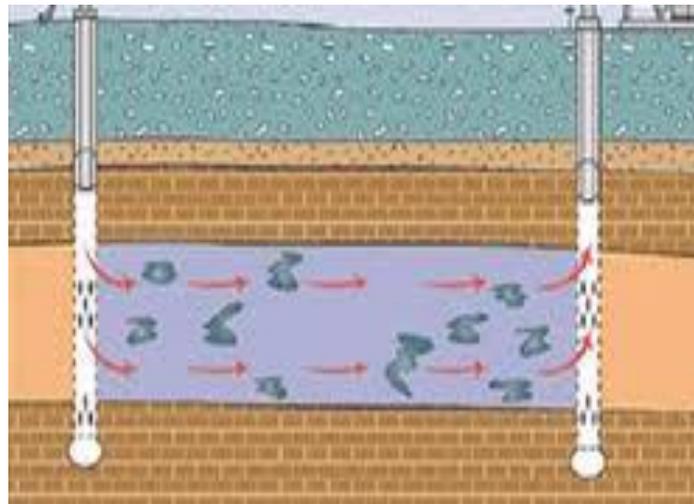
- ◆ Bacteria cell walls contain peptidoglycan (murein).
- ◆ Methanogens cell walls contain pseudomurein.
- ◆ Pseudomurein is biosynthesized via activity similar to that of 3-hydroxy-3-methylglutaryl-coenzyme A (HMG-CoA) reductase, which is a key enzyme in the cholesterol biosynthesis pathway in humans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



# What is Provect-CH4<sup>®</sup> Methane Inhibitor / ERD Supplement?



- ◆ Proprietary combination of Red Yeast Rice (RYR) extract specially selected for the environmental industry
- ◆ Cold water soluble powder that is safe and easy to handle
- ◆ Packaged and sold in 55.1 lb (25 kg) drums
- ◆ Used as an ERD Supplement; component to ABC-CH4<sup>®</sup>, Provect-IR<sup>®</sup> Provect-IRM<sup>®</sup>, EZVI-CH4<sup>™</sup> and AquaGate<sup>®</sup>-CH4<sup>™</sup>
- ◆ Multiple patents issued / pending





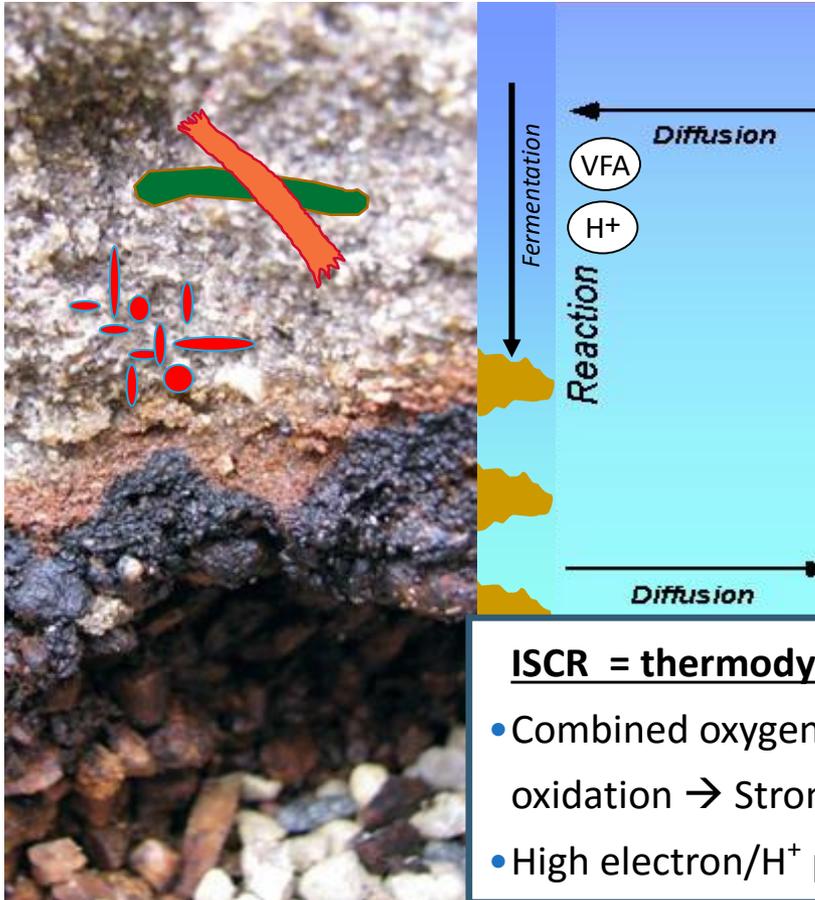
# Provect-IR<sup>®</sup> Solid, Antimethanogenic ISCR Reagent



- ◆ Multiple, Complex, Hydrophilic, Timed-Release organic carbon source (plant materials, Kelp, Ca Propionate) @ 390 g H donor / lb product
- ◆ 10% (wgt) Small (ave.10  $\mu\text{m}$ ) ZVI particles = 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 safety bags or 2,000 lb supersacs.



# Carbon Fermentation + ZVI Corrosion = ISCR Multiple Reaction Mechanisms

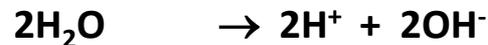
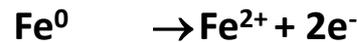


**Production of organic acids (VFAs):** electron donors for

reduction of COIs, O<sub>2</sub>, NO<sub>3</sub>, SO<sub>4</sub>

- By preventing basification, reduces precipitate formation on ZVI surfaces to increase rate of iron corrosion /H<sub>2</sub> generation / reactivity

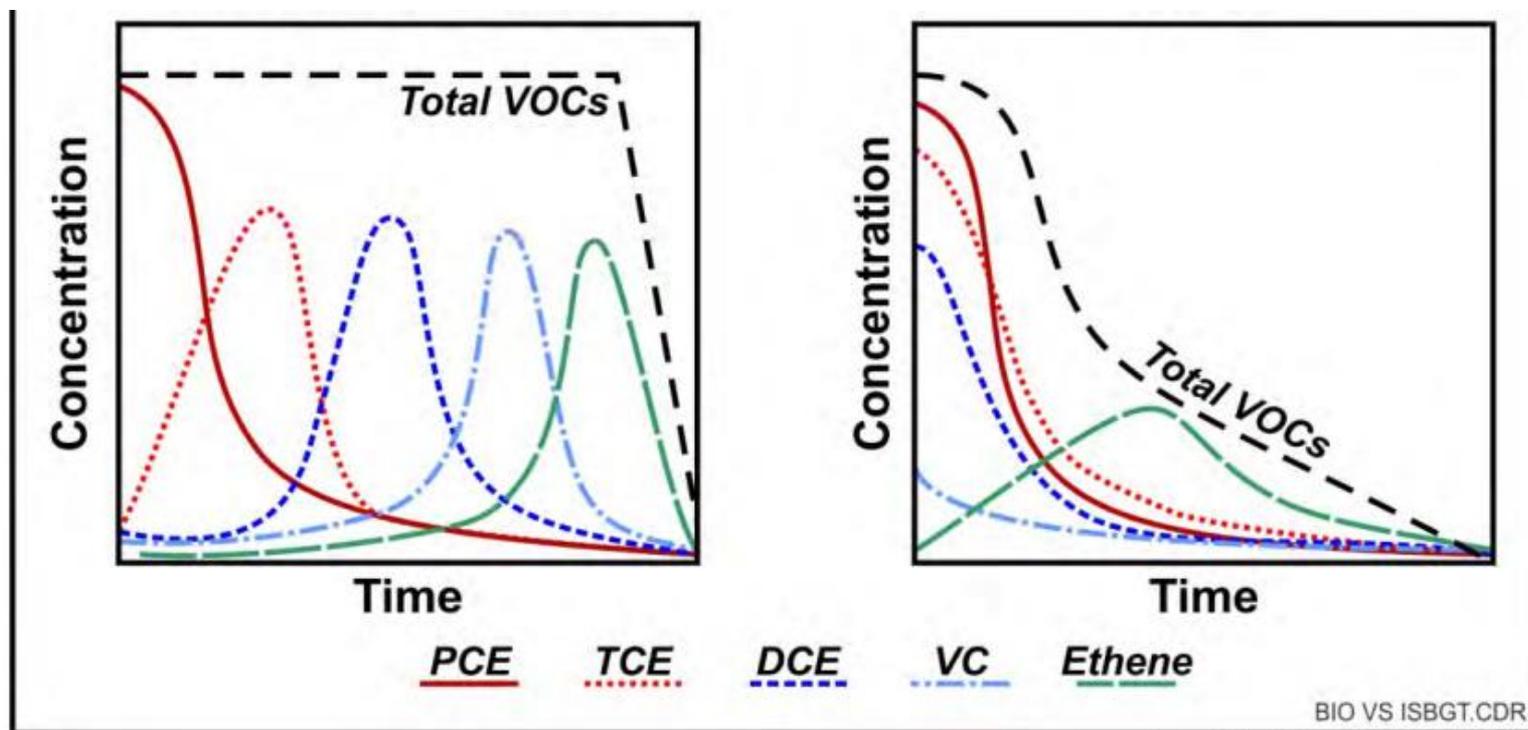
**ZVI Reactions:** H<sub>2</sub> and Fe<sup>2+</sup> and generation



**ISCR = thermodynamic conditions for dechlorination:**

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

# ERD v. ISCR



(Modified from Brown, 2009)

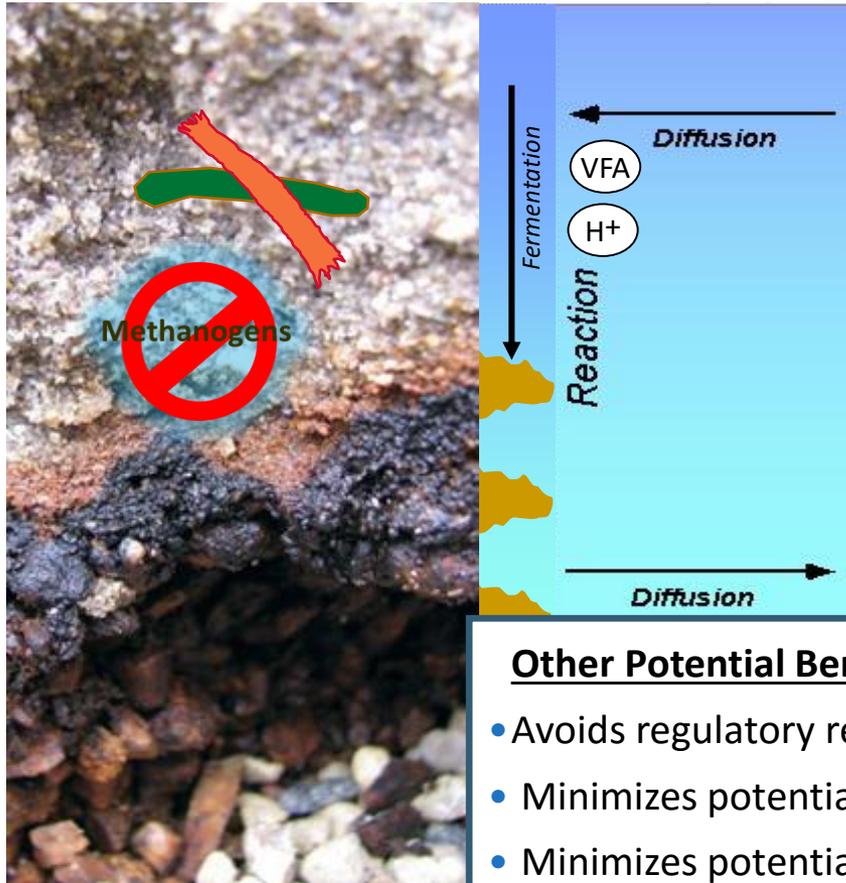
**Figure 2. Abiotic versus Biological Degradation Pattern for Chlorinated Solvents**



TECHNICAL REPORT  
TR-NAVFAC EXWC-EV-1601

BIOGEOCHEMICAL TRANSFORMATION HANDBOOK

# Benefits of Provect-IR Antimethanogenic ISCR



## More Efficient:

- Calculated minimum 30% more efficient use of hydrogen donor (Mueller *et al*, 2014)
- Allows for slower-growing acetogens and DHC-type microbes an opportunity to compete

## Safer Remedial Actions:

- Elevated methane concentrations (>1,000 ppm) can exceed current and pending regulations of < 10 to <28 ppm in groundwater and/or 0.5% v/v methane in soil gas (*e.g.*, 10% of the LEL) and/or indoor air regulations (methane is flammable between 5 and 15% v/v)

## Other Potential Benefits:

- Avoids regulatory reporting (DOI?) and Contingency planning (AS/SVE gas)
- Minimizes potential for methylation of Hg and other heavy metals
- Minimizes potential for secondary COI issues

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# Former Dry Cleaner Site - Georgia



## ◆ Former Dry Cleaner Site near Atlanta, GA

- ◆ Combinations of sodium lactate, ethyl lactate, emulsified oils, and ZVI added in 2004 (3), 2005 (4), 2006 (2) - legal issues and delays - 2013 (1)
- ◆ Residual PCE, TCE and c-DCE concentrations required additional treatment
- ◆ Excessive CH<sub>4</sub> production previously noted

## ◆ Repeat ABC applications in July, 2014

- ◆ 2,500 lbs (250 USG) ABC added via 3 DPT points proximal to MW-4
- ◆ 2,500 lbs ABC (250 USG) + 37 lb Provect-CH<sub>4</sub> added via 3 DPT points proximal to MW-207 (targeted 50 to 75 ppm within the PRB zone)



# Well Head and Dissolved Gas Analysis (6 weeks post treatment)



**Dissolved Gas Analysis (Method RSK 175) = 65% less CH4 at MW-207**

Well Location	Pre-injection (ppm)		6 weeks Post-Injection (ppm)	
	CH4	PCE	CH4	PCE
MW-4	13.7	170	10.2	--
MW-207s	11.8	1,200	4.2	--

- Thermo/Foxboro TVA-1000B PID/FID Analyzer (PID sensitive to 2,000 ppm CH4; FID sensitive to 50,000 ppm CH4)
- LandTec GEM5000 Landfill Gas (LFG) Meter (infrared detector calibrated to 15% methane)



**Well Head Gas Analysis = Provect CH4 = >98% less CH4**

Well Location	CH4 PID (ppm)	CH4 FID (ppm)	CH4 TGA %	CO2 %	O2 %	Balance (N) Est. %
<b>MW-4</b>	<b>ABC Only</b>					
0 min	297	>50,000	34.8	65.2	0.0	0.0
5 min	439	>50,000	35.6	61.0	0.2	3.2
<b>MW-207s</b>	<b>Provect CH4 added</b>					
0 min	82	Out of range	0.5	1.0	12.7	85.8
5 min	41	1,599	0.4	0.7	20.2	78.7

# Active Dry Cleaner Site - Michigan



- ◆ 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



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

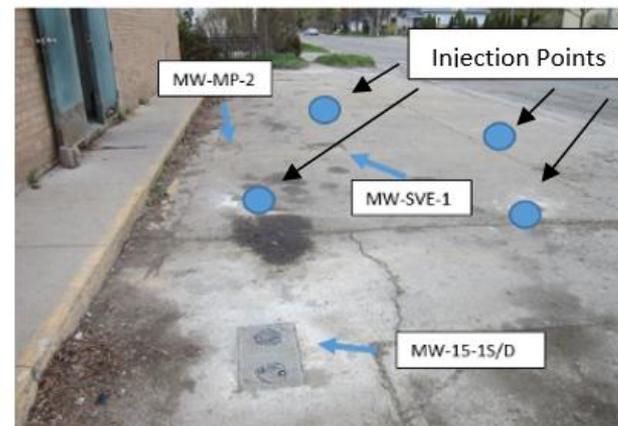


# Provect-IR – Field Study



Groundwater samples were acquired from four well locations MW-MP-2, MW-15-1S, MW-15-1D, and MW-15-2D at Day = 0, immediately after the injection event (Day=1), and 30, 60 and 90 days after injections were completed. Groundwater samples were collected utilizing low-flow sampling techniques and a DEQ-approved groundwater sampling method per RRD Operational Memorandum No. 2. The samples were properly preserved, packed and delivered to the DEQ Environmental Laboratory and analyzed for:

- pH – Excessive fermentation can acidify aquifer and impede microbiological activity
- Turbidity – Excessive turbidity may compromise data and indicate methane bubbles (above the saturation level)
- Water Level – Influence during injection can give estimate of Radius of influence (ROI)
- DO/ORP – Rapid reductions in redox should be observed in treatment zone giving ROI
- Dissolved gasses (CH<sub>4</sub>, CO<sub>2</sub>, ethane and ethene) – Documents effectiveness
- VOCs – Documents effectiveness and ROI along with mass loading
- Total and Dissolved metals to include iron, calcium, magnesium, manganese and Michigan 10 metals
- Anion Scan (chloride, sulfate, nitrate and nitrite)
- Total Organic Carbon – TOC Indicates the presence of ISCR reagents and microbiological activity

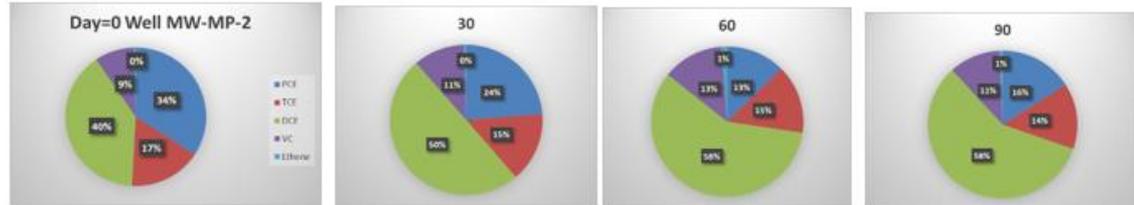


# Active Dry Cleaner – 90 Days

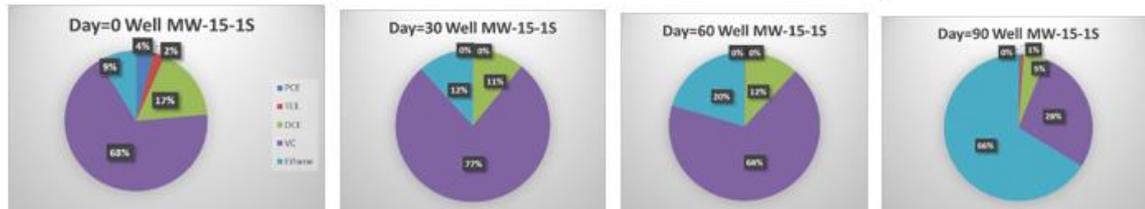


- Total CVOCs reduced by 62%
- No accumulation of DCE or VC as dead-end catabolites
- No groundwater methane during any sampling event (ranged from 1.7 mg/L at Time=0 to a high of 2.2 mg/L 60 days after Provect-IR additions).
- Soil gas methane baseline <20 ppmv to a high of 94 ppmv 30 days after the injection event (Day 60 and Day 90 <20 ppm)
- Full scale implementation April-May 2016

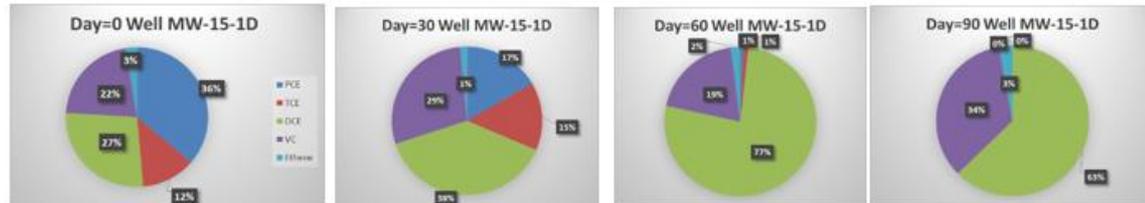
Well MW-MP-2 Source Area



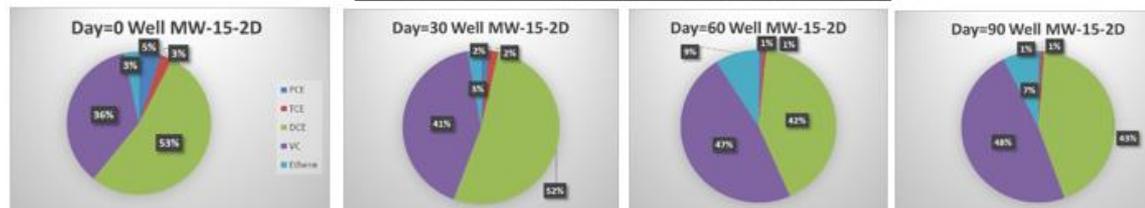
Well MW-15-1S (shallow, 5 feet downgradient)



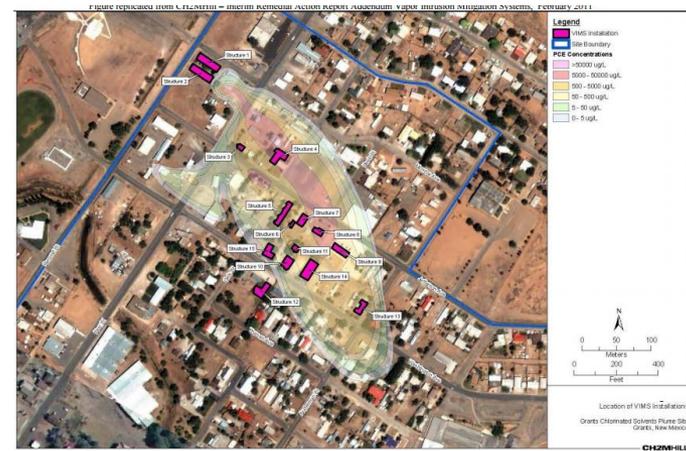
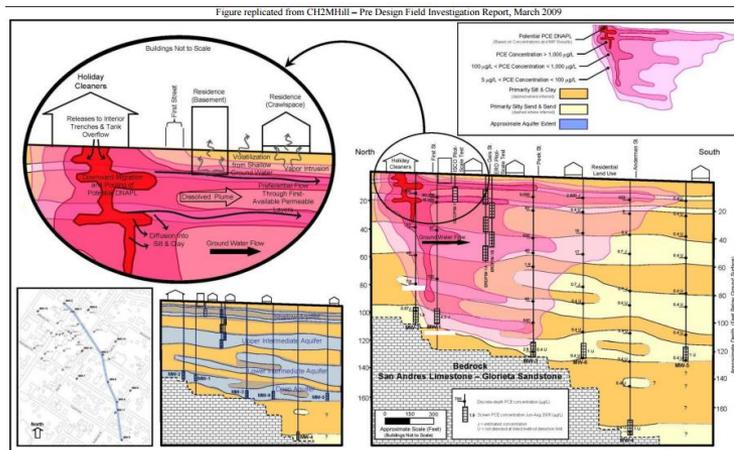
Well MW-15-1D (deep, 5 feet downgradient)



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



# Potential Savings – Large Dry Cleaning Superfund Site, New Mexico



[http://www.epa.gov/region6/6sf/newmexico/grants/nm\\_grants\\_5yr\\_review\\_9-13.pdf](http://www.epa.gov/region6/6sf/newmexico/grants/nm_grants_5yr_review_9-13.pdf),

“Elevated methane levels have been observed around the ERD treatment areas with the potential for buildup beneath impervious surfaces”  
 “secondary arsenic issues need to be addressed”

Item	Current	Potential	Savings (% / est \$)
Injection Wells	550+	550+	0/0
Substrate / event	15,000 USG EVO	11,000 USG EVO	30% / \$60,000
Field Time / event	100%	80%	
	30 days @ 15k/d	24 days @15k/d	\$90,000 per event

SAVINGS PER EVENT = \$150,000 x 3 injection events over time = \$450,000

Estimates in Table were NOT reviewed or approved by design engineers and represent preliminary estimates as of June 4, 2015

# So, is Methanogenesis Important?



## 💧 Some say...

- ✓ We never see problems
- ✓ My site is remote
- ✓ Our amendments don't make methane
- ✓ It's bad to stop methanogens
- ✓ Our clients don't worry about it
- ✓ We will just add more reagent

## 💧 You decide

- ✓ Look at your own data
- ✓ Evaluate your site conditions – VI concerns?
- ✓ Co-metabolism of CHCs is slow, and it mostly stalls at DCE/VC = worse than what you started with
- ✓ Experienced clients understand the value added
- ✓ What do your regulators say ...

## Response

mostly because we never looked  
ignores efficiency issue  
then they are not working well  
it's beneficial to control them  
then YOU better worry about it...  
\$\$ not acceptable to our clients

# Summary

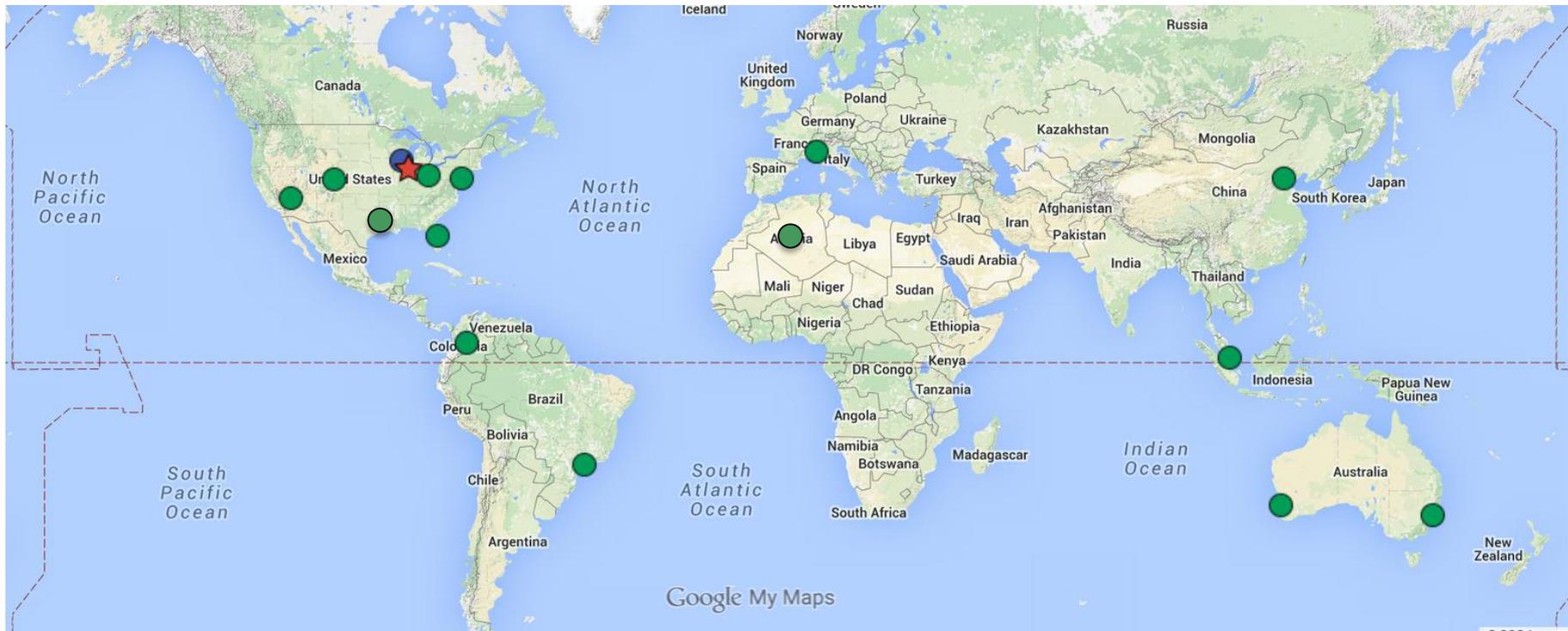
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- **Natural statins in RYR extracts (as prepared) can be used to effectively and specifically control methanogenic activity**
- **The methane control technology has been integrated into various products designed for the environmental remediation industry**
  - **Provect-CH4®** ERD Supplement / Methane Inhibitor
  - **ABC-CH4®** 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 / CHC DNAPL Treatment
- **The main benefit is improved performance = “better gas mileage”**
- **Other potential benefits relate to safety, regulatory compliance, and sustainability**

# Provectus Environmental Products

- ◆ Complimentary Site Evaluation
- ◆ Complimentary review of quarterly field performance data for 1 year with every project
- ◆ Laboratory Treatability Studies
- ◆ Turn-Key, Pay-for-Performance Contracting Options
- ◆ Project Specific Guarantees and Warranties



- ◆ USA (Illinois, Ohio, Pennsylvania, Louisiana)
- ◆ Australia, Brazil, China, Colombia, Italy, Singapore, Spain