Remediation of an active Dry Cleaning Operation in an Urban Setting: Need to Manage Methane Production during Remedial Action

45th Annual Environmental Show of the South
Gatlinburg, TN – Wednesday April 20, 2016
4:00 to 4:20 pm

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Presentation Outline

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

What is a Methanogen?

- 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

Why Reduce ORP?

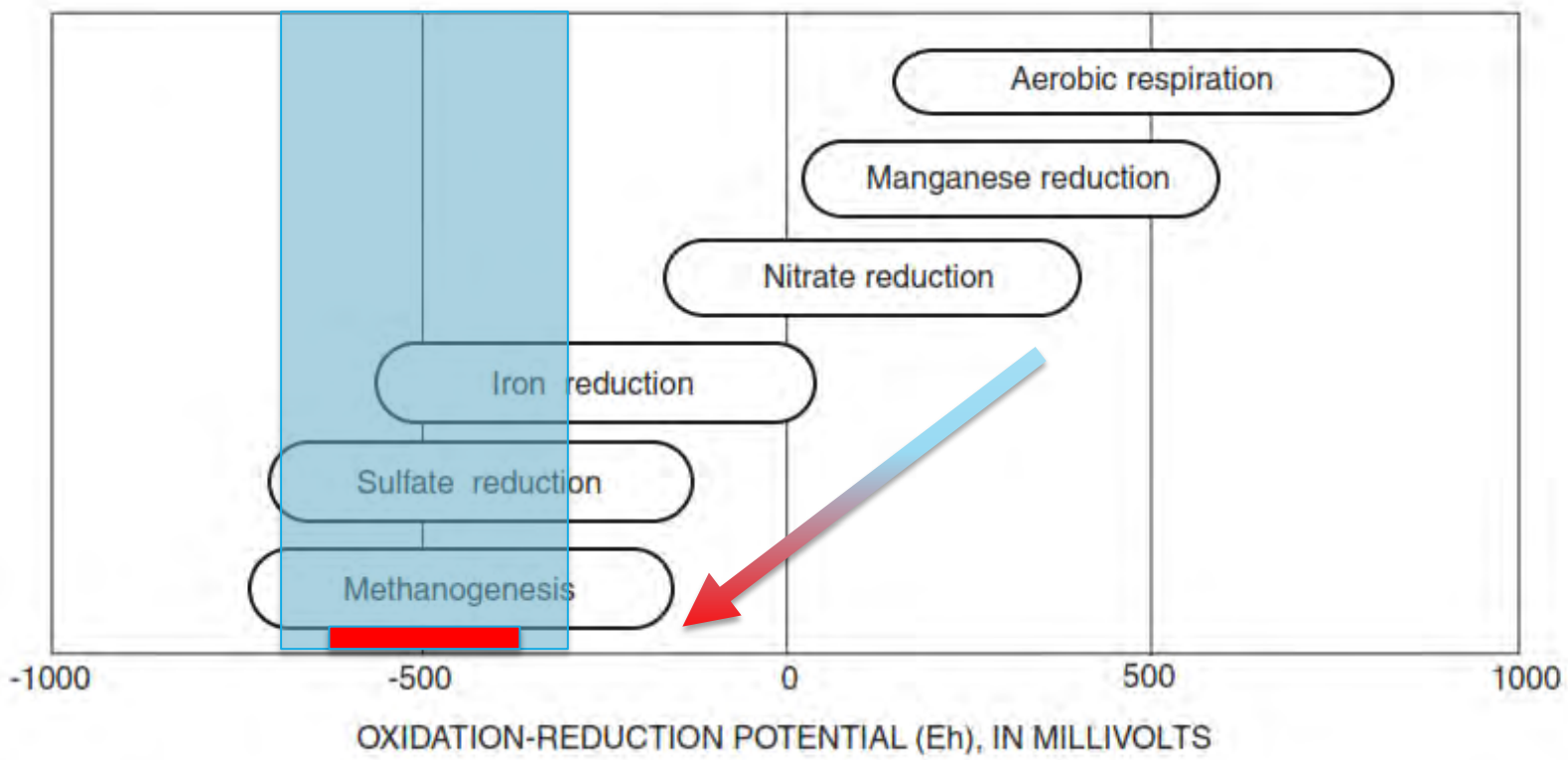
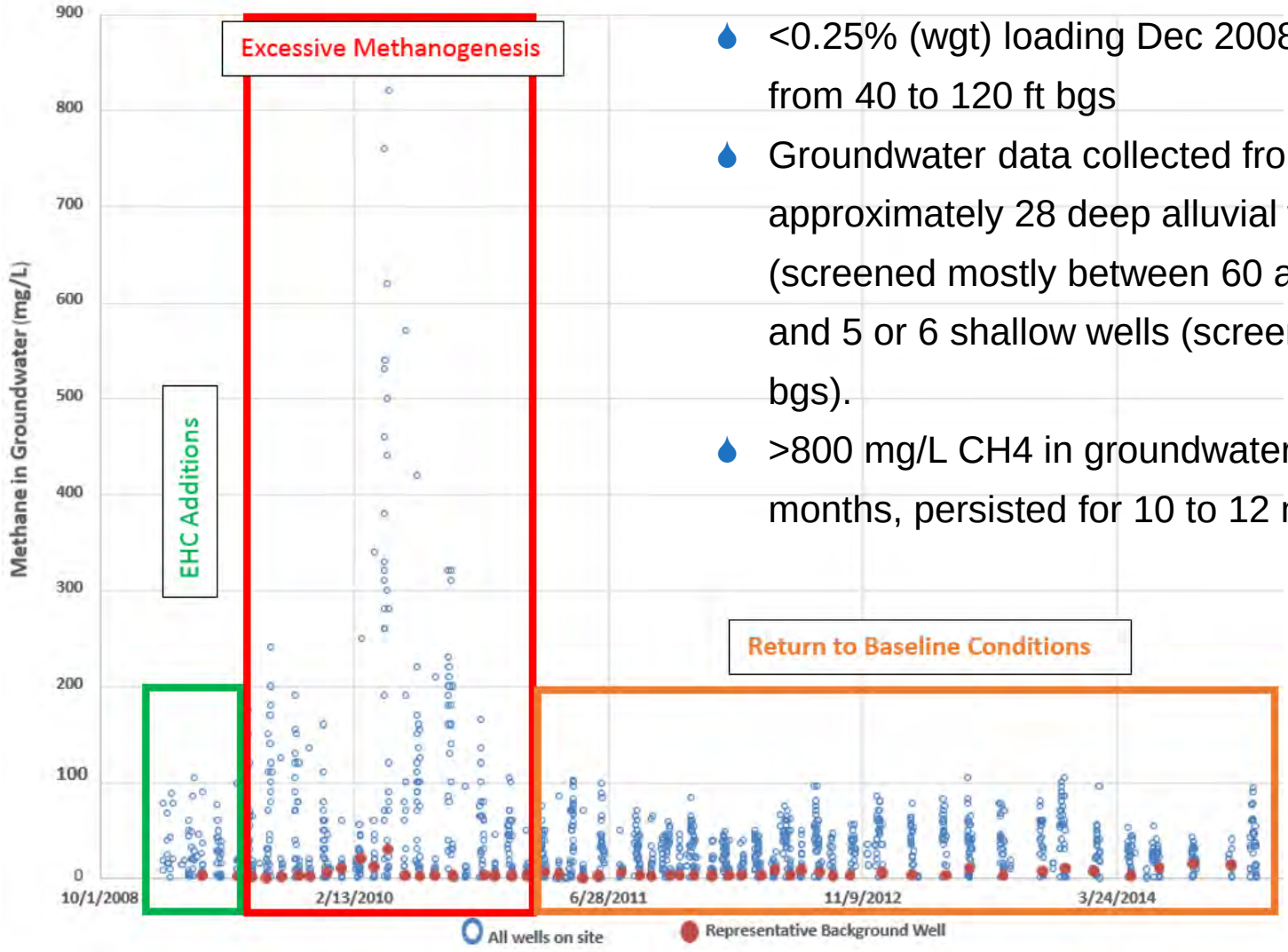


Figure 2. Oxidation-reduction potentials for selected microbial processes. (Modified from Stumm and Morgan, 1981.)

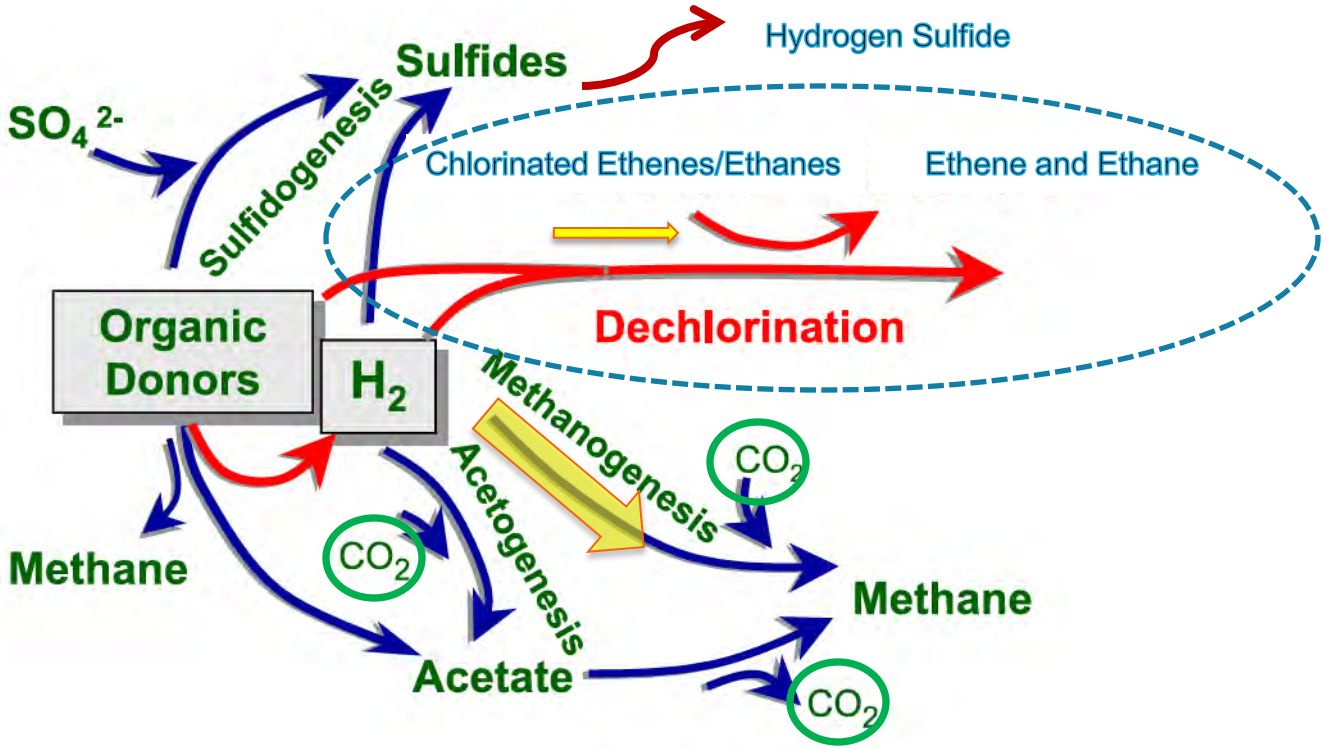
Example of Excessive Methane



- <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 CH4 in groundwater after 6 months, persisted for 10 to 12 months

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_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.

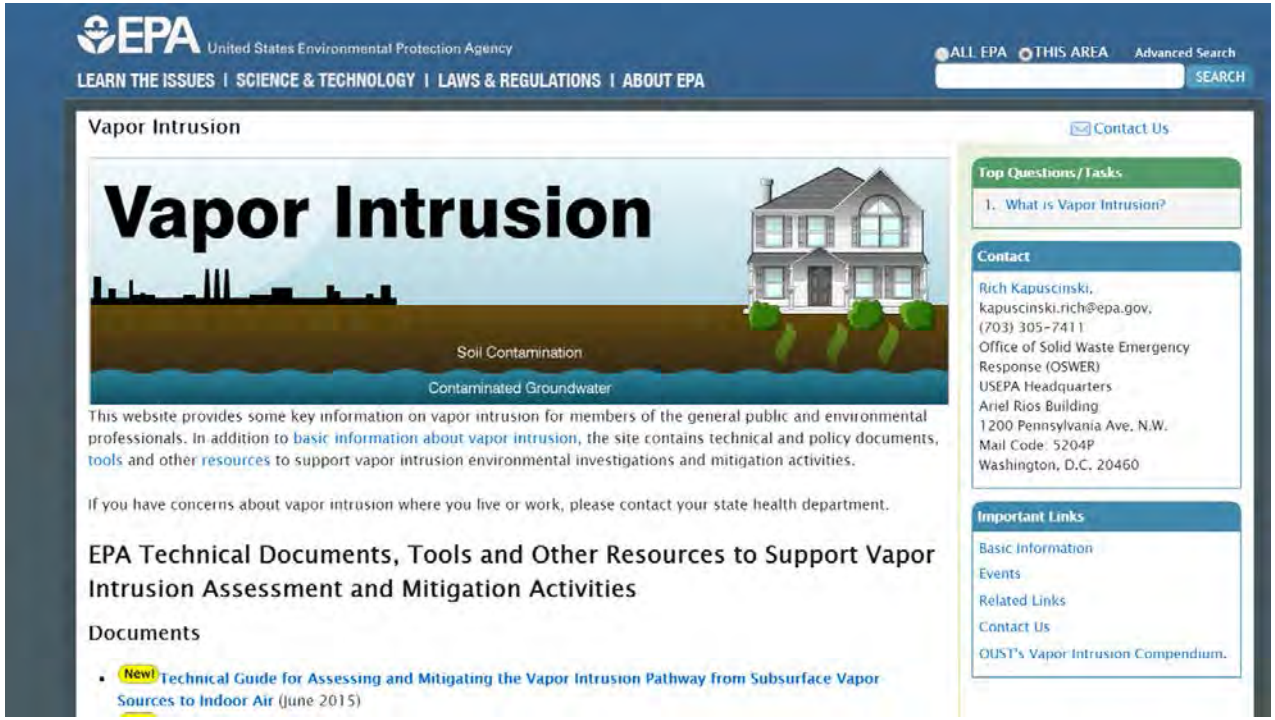
What is The Problem With Methane?

- ***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**



Yes – Methane is Important

especially in urban settings

- **Safety**
- **Performance**
- **cost**

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- How can we actively control methanogens?
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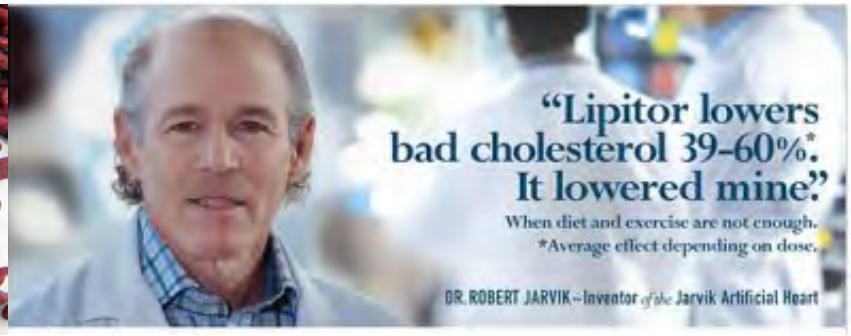
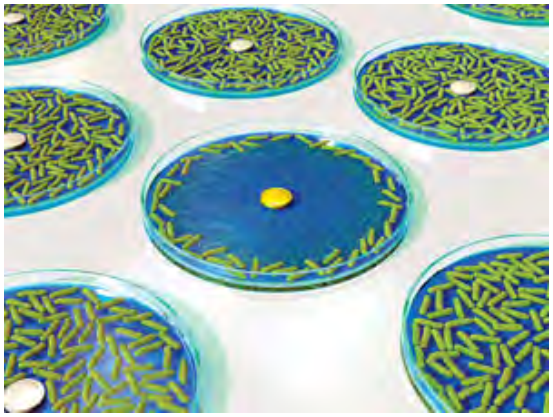
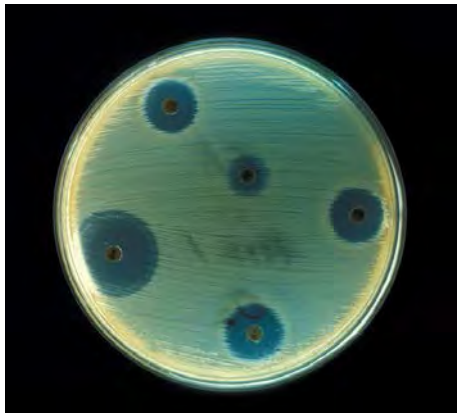
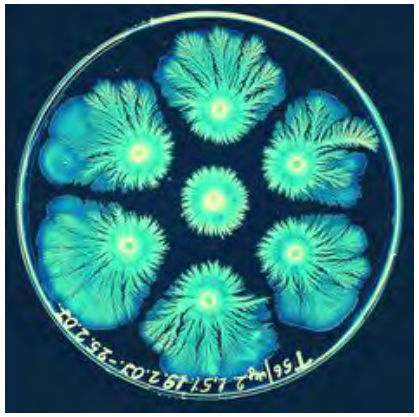
What is Red Yeast Rice (RYR) Extract?

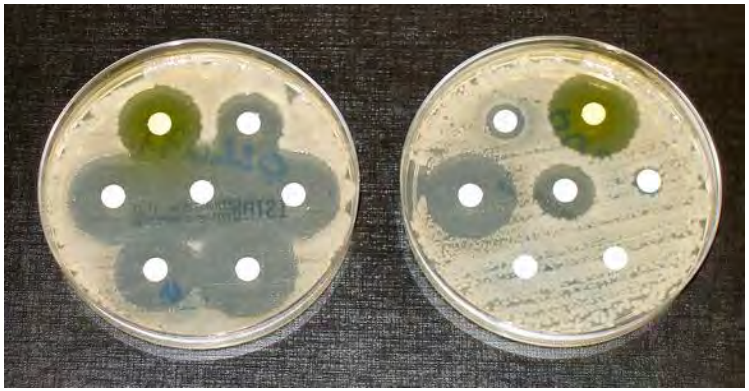
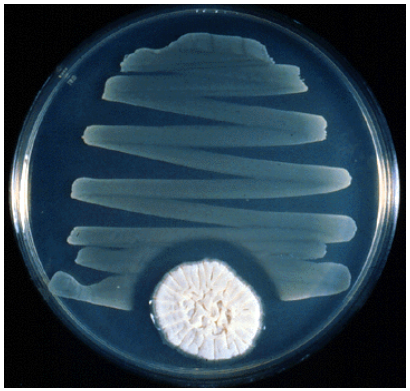
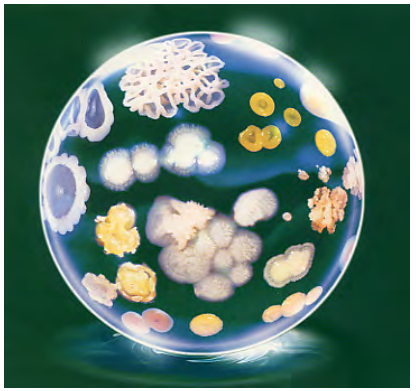
- RYR extract is a substance extracted from rice that has been fermented with a yeast called *Monascus purpureus*.
- RYR extract contains a number of natural statins - most importantly, Monacolin K - otherwise known as Lovastatin® / Lipitor® /etc.
- In addition to Monacolin K, RYR also contains 9 other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

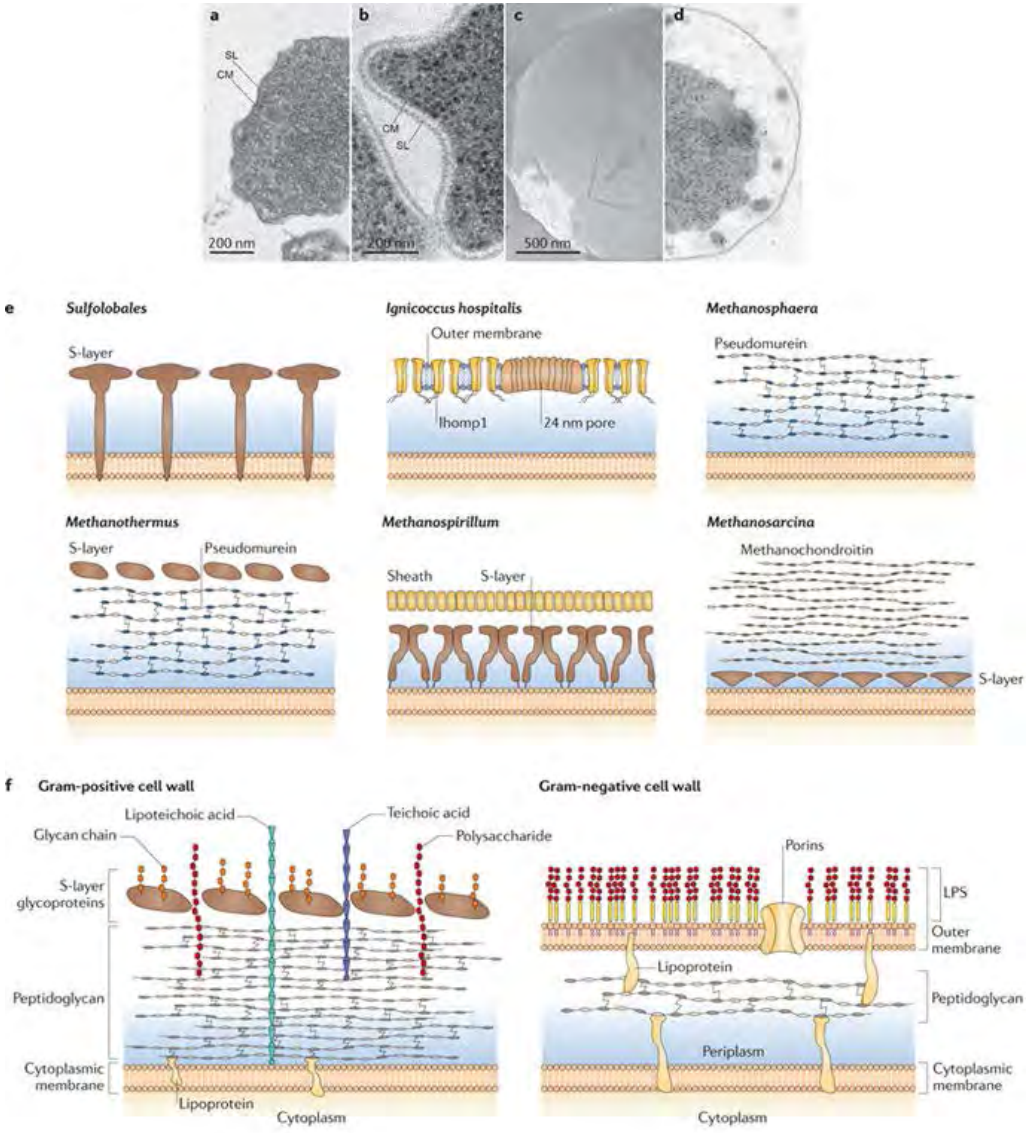




- Many microorganisms produce bioactive compounds that inhibit / regulate the growth and development of other organisms
- Example, antibiotics such as penicillin which is produced by mold of *Penicillium* genus

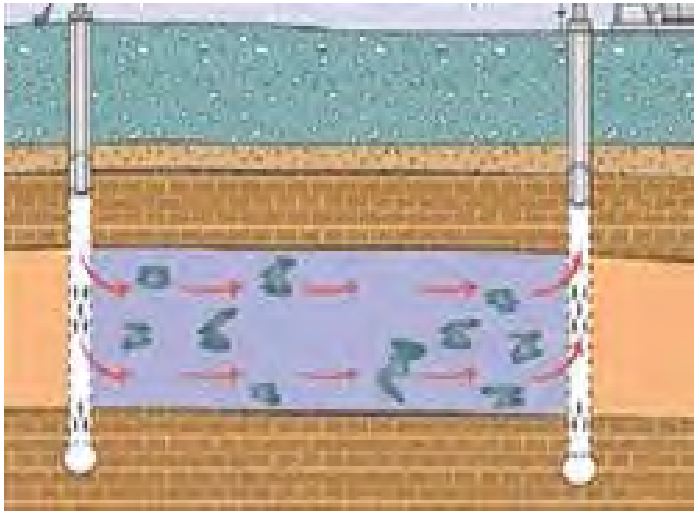
How Does RYR Control Methanogens?

- Bacteria cell walls contain peptidoglycan (murein).
- Methanogens cell walls contain pseudomurein.
- 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).



What is Provect-CH4®
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®, Provect-IR® Provect-IRM®,EZVI-CH4™ and AquaGate®-CH4™
- Multiple patents issued / pending

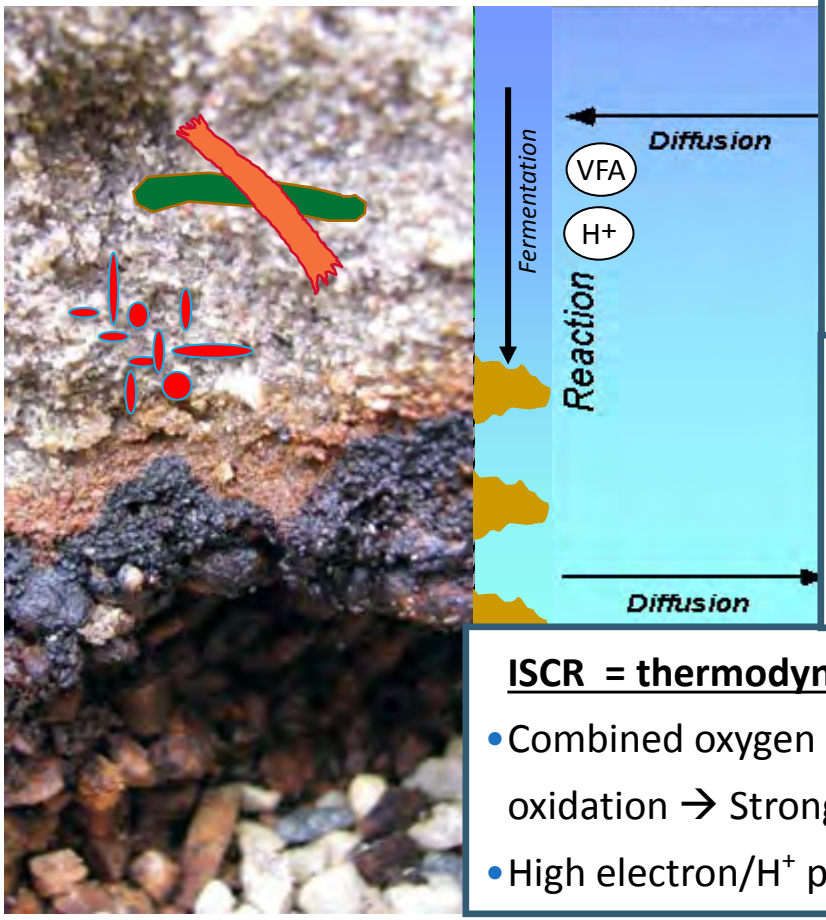



Chris

Provect-IR® 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 µm) 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_2, NO_3, SO_4

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

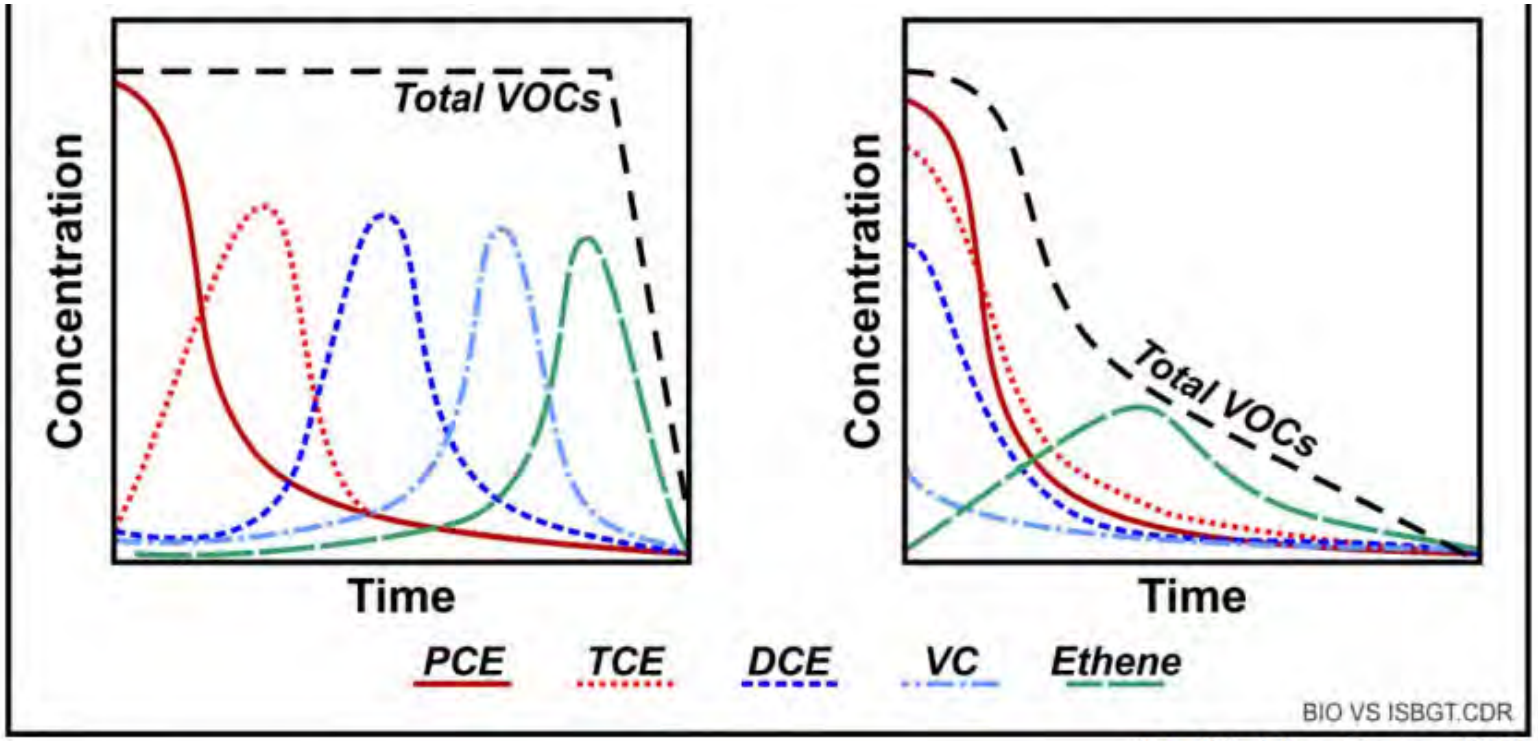
ZVI Reactions: H_2 and Fe^{+2} and generation

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

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)

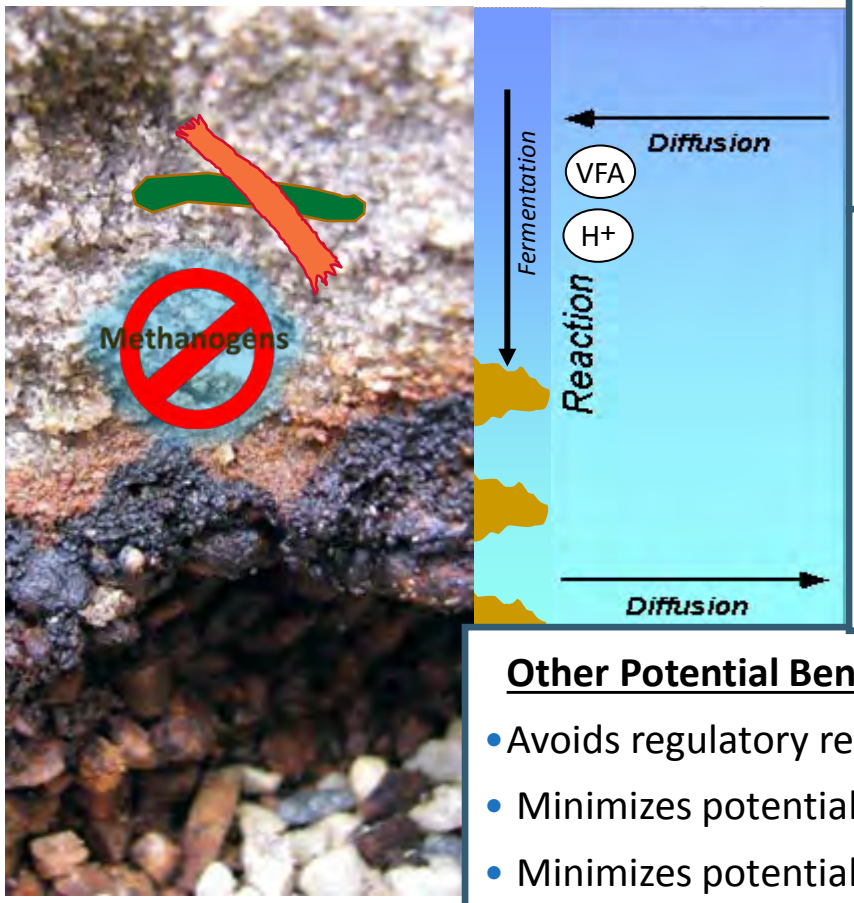
Figure 2. Abiotic versus Biological Degradation Pattern for Chlorinated Solvents

NAVFAC
Naval Facilities Engineering Command
ENGINEERING AND EXPEDITIONARY WARFARE CENTER

TECHNICAL REPORT
TR-NAVFAC EXWC-EV-1601

BIOGEOCHEMICAL TRANSFORMATION HANDBOOK

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 CH4 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-CH4 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) = 35% CH4 compared to MW-4

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. %
MW-4	ABC Only					
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
MW-207s	Provect CH4 added					
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

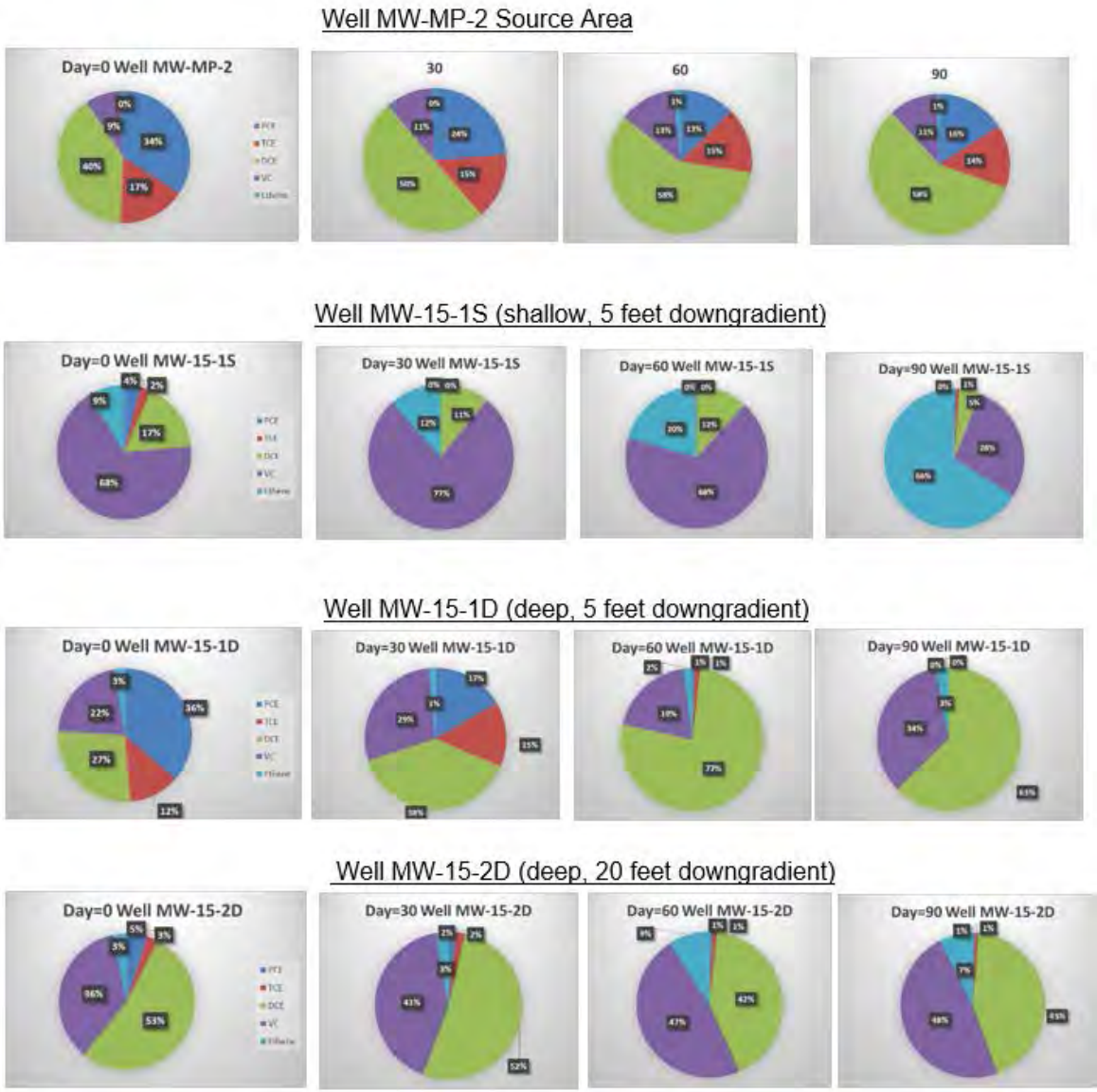
Groundwater samples were acquired from four well locations MW-MP-2, MW-15-1S, MW-15-1D, and MW-15-2D at Day = 0, immediately after the injection event (Day=1), and 30, 60 and 90 days after injections were completed. Groundwater samples were collected utilizing low-flow sampling techniques and a DEQ-approved 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 compromises 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_4, CO_2, 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 March 2016



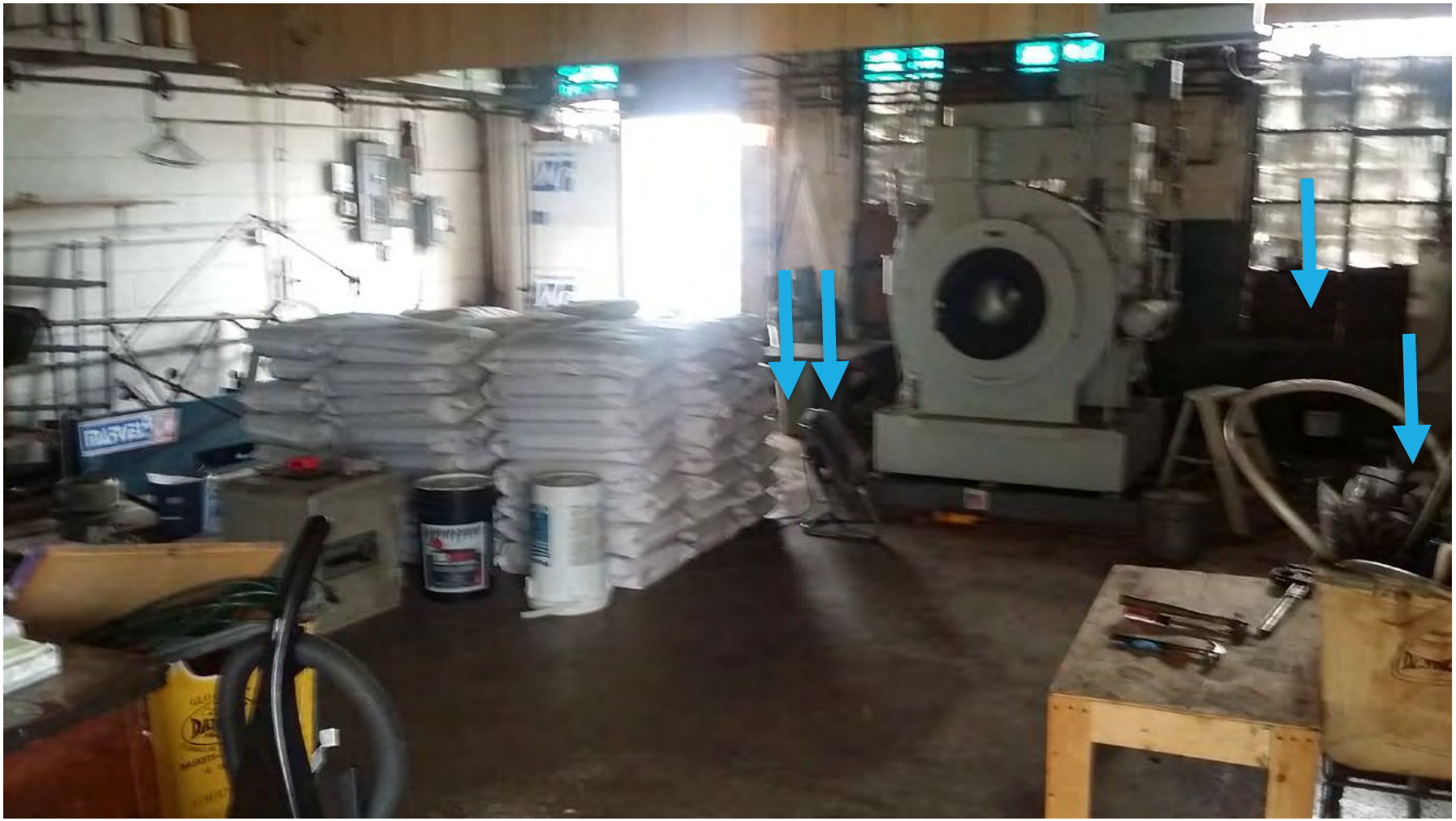
Yes – Methane is Important

especially in urban settings

- **Safety**
- **Performance**
- **cost**

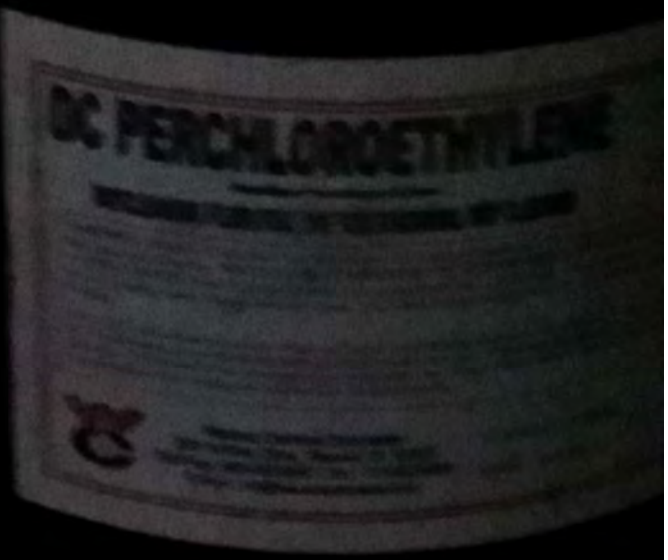
Recently Active Dry Cleaner - WI

Recently Active Dry Cleaner - WI



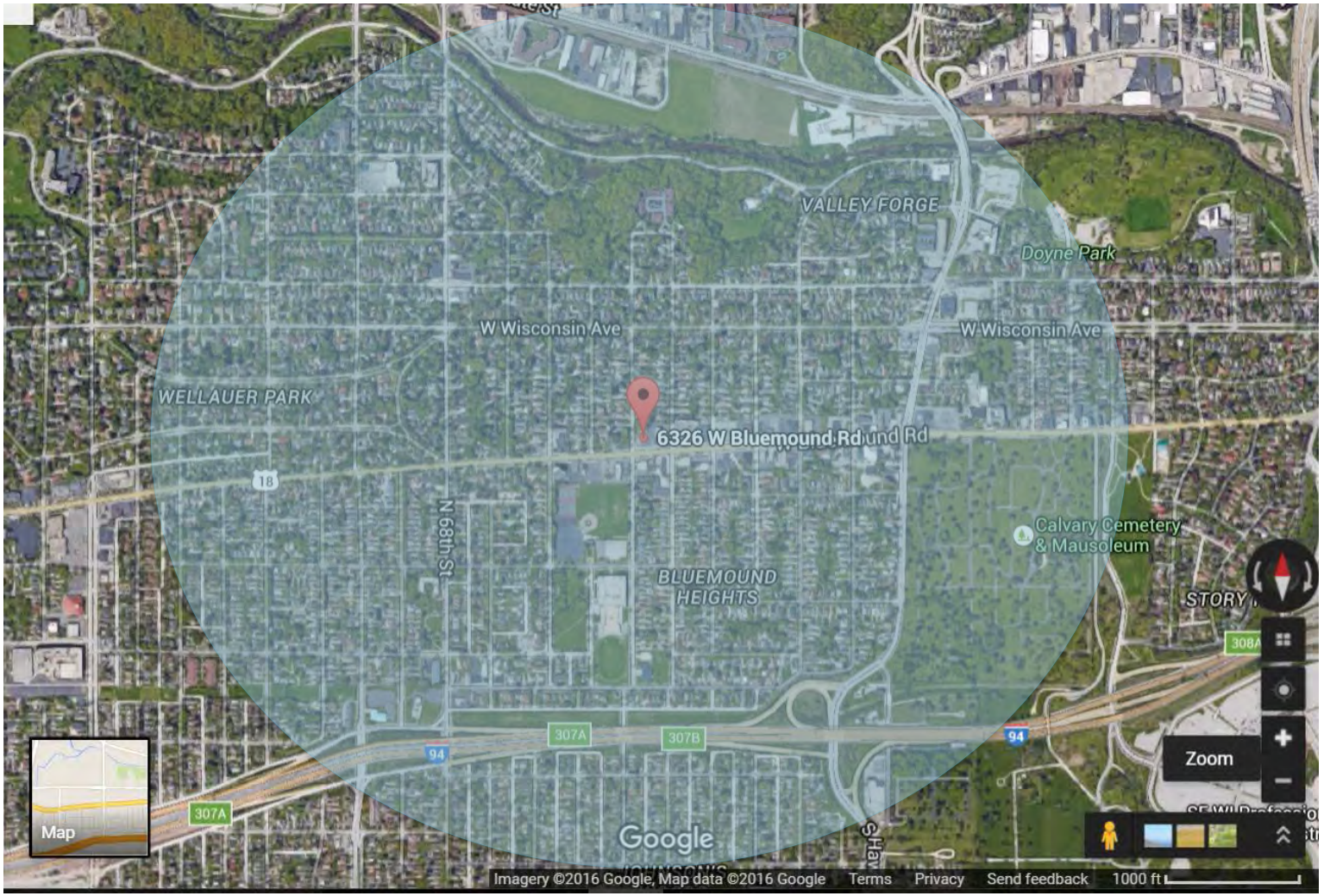
Recently Active Dry Cleaner - WI

100 g PCE will yield a plume
100 m x 100 m x 3m deep
(no partitioning; n=0.2)

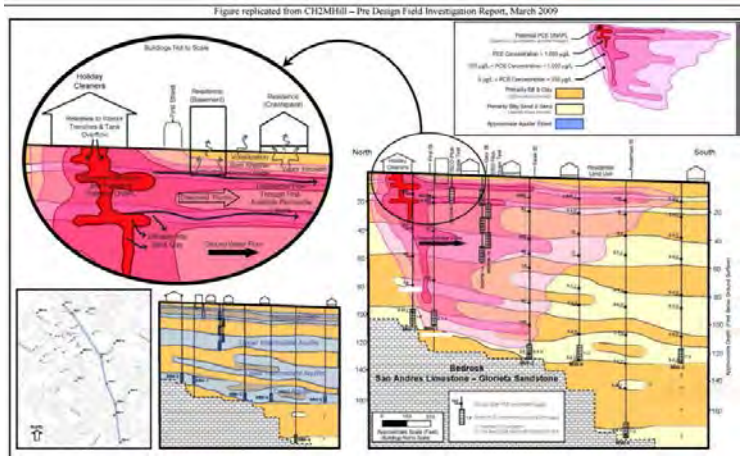


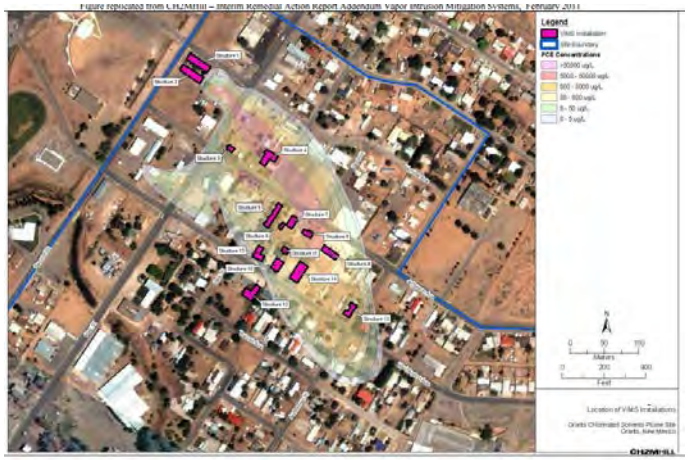
- Sump and drain had >55 USG sludge >2% PCE
- > 7,000 g PCE
- 7,000 m plume potential

Large Plume Potential



Potential Savings – Large Dry Cleaning Superfund Site, New Mexico





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 andrepresent preliminary estimates as of June 4, 2015

So, is Methanogenesis Important?

Some say…	Response
✓ We never see problems	mostly because we never looked
✓ My site is remote	ignores efficiency issue
✓ Our amendments don't make methane	then they are not working well
✓ It's bad to stop methanogens	it's beneficial to control them
✓ Our clients don't worry about it	then YOU better worry about it…
✓ We will just add more reagent	$$ not acceptable to our clients

You decide

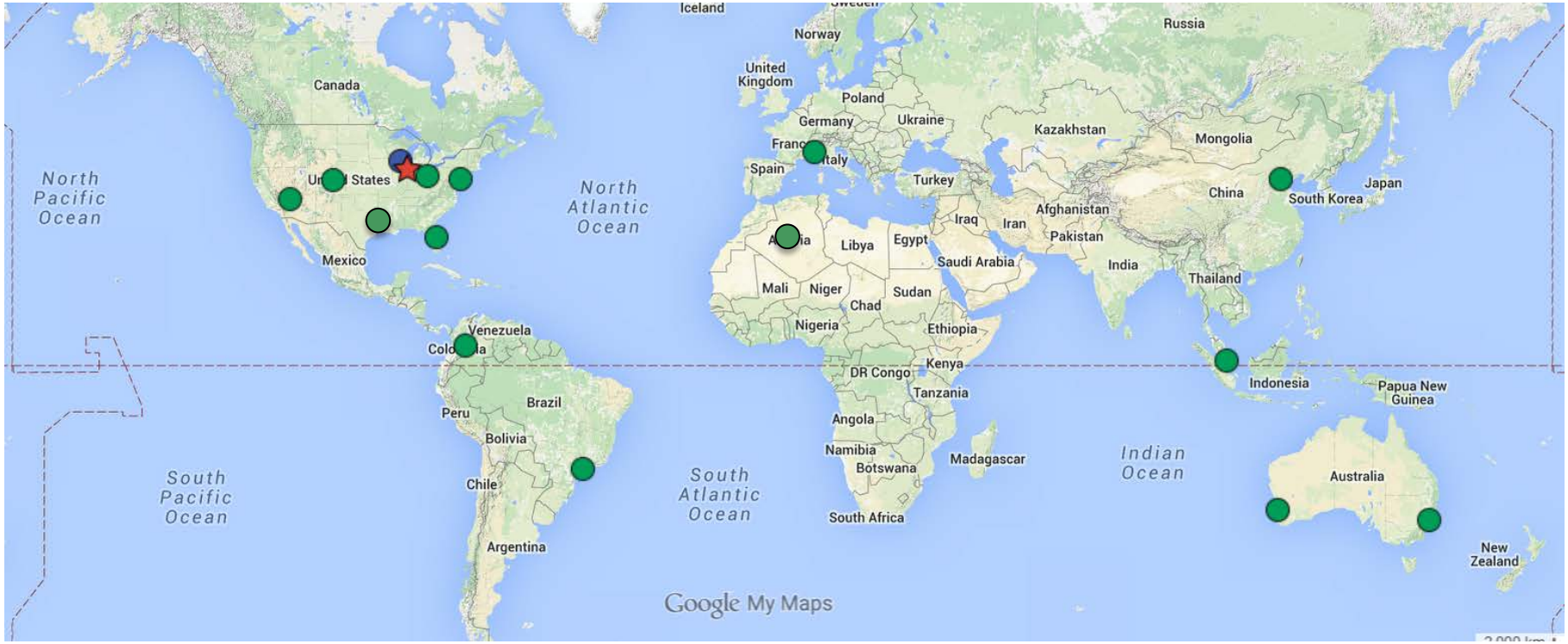
- ✓ Look at your own data
- ✓ Evaluate your site conditions – VI concerns?
- ✓ Co-metabolism of CHCs is slow, and it mostly stalls at DCE/VC = worse than what you started with
- ✓ Experienced clients understand the value added
- ✓ What do your regulators say …

Summary

- **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