

Antimethanogenic Supplements for ERD Amendments

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INTRODUCTION

Enhanced reductive dehalogenation (ERD) has demonstrated success in the *in situ* remediation of numerous sites impacted by various constituents, most commonly chlorinated ethenes. One seemingly universal phenomenon has been the biological production of methane, especially during the early phases of the process. There are recognized benefits to methanogens and of limited methanogenesis; however, excessive methane production represents a costly waste of amendment (generating just 20 mg/L of methane constitutes greater than 33% of the total amendment consumption based on moles of H₂; Mueller *et al.*, 2014). Moreover, excessive and extended production of methane can result in elevated groundwater concentrations (as high as ca. 1,000 ppm have been reported) which can lead to accumulation in soil gas subsequently impacting indoor air, accumulating in basements, under slabs/foundations and/or migrate along utility corridors. Accordingly, State-specific regulations for methane in groundwater have been promulgated, and remedial practitioners proactively design costly contingencies for conventional ERD implementation in the event that methane exceeds a threshold level ranging from 1 to 10 ppm groundwater.

APPROACH

Active measures to control the production of methane can offer multiple advantages in terms of cost, treatment efficiency, treatment time and safety. Such measures have included the use of slowly released carbon sources, excess nitrate/sulfate, ethylsulfonates, ethylformate, low level toxins, *et cetera* but these are not specific to methanogens and the efforts have met with limited success.

Recently, the use of statins as effective inhibitors of protein and enzyme systems specific to Archaea (*i.e.*, methanogens) was described for environmental applications (Scalzi *et al*, 2013, 2014).

Provect-CH₄™ provides a unique source of Monacolin K and other natural statins that interfere with the biosynthesis of psuedomurein (found only in Archaea) which prevents cell wall biosynthesis. Hence, growth and proliferation of methanogens is limited: this inhibitory affect is not observed in other microbes (bacterial cell walls are composed of peptidoglycan, or murein). When added to liquid ERD amendments such as (emulsified) oils, lecithin, sugars, lactates or any other hydrogen donor, the production of methane is thereby minimized. This enhances reductive dechlorination reactions by allowing slower-growing *Dehalococcoides* spp. to better compete. Moreover, minimizing the production of methane improves cost effectiveness, treatment efficiency, treatment time, and overall safety

Primary Benefit = Saves Money

- More efficient = less amendment required (\$) and less field time required (\$)

Other Potential Benefits

- Reduced COI migration
- Reduced heavy metal mobilization
- Improves safety



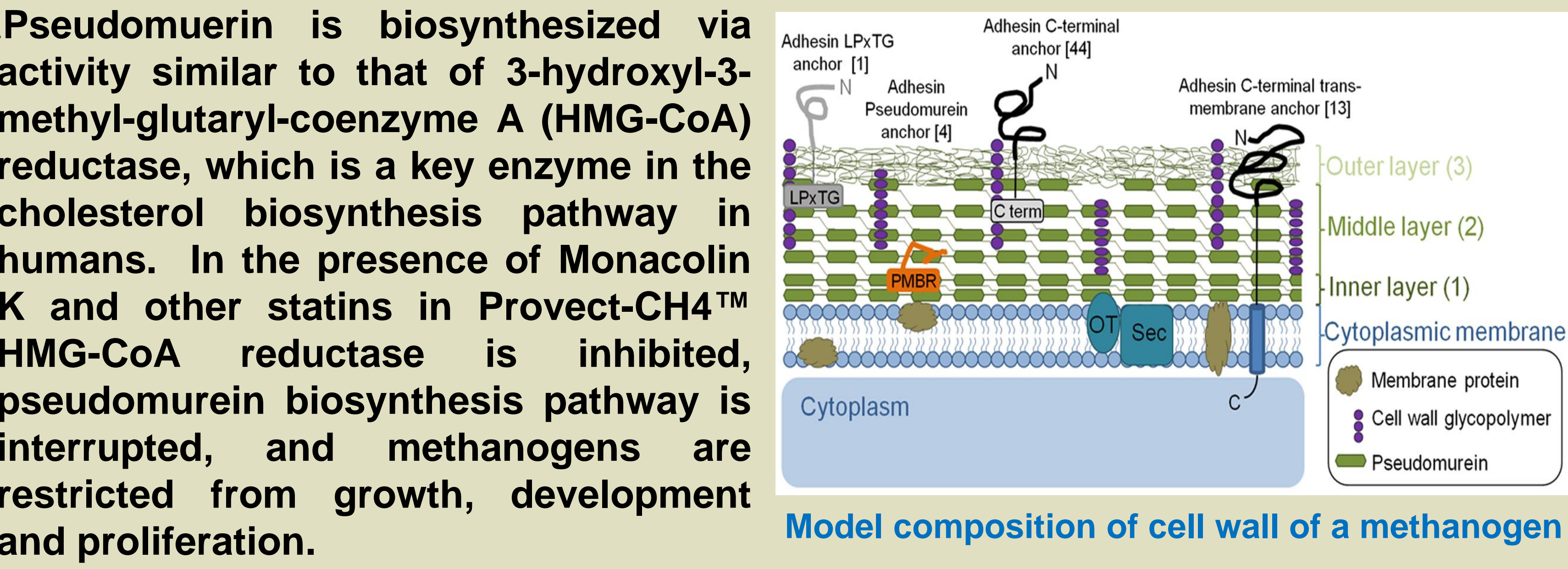
WHAT IS A METHANOGEN?

- Methanogens are microorganisms that produce methane
- They are ubiquitous, and they are often dominant in numbers, averaging 2% to 15% of all soil microbes
- They are important members of synergistic, fickle anaerobic communities
- They are genetically unique and belong to their own domain, Archaea
- They can double cell numbers in one hour and are problematic when overactive

HOW CAN WE CONTROL METHANOGENS?

Provect-CH₄™ is a proprietary amendment for environmental remediation applications that includes Red Yeast Rice (RYR) Extract. RYR extract contains a number of natural statin compounds, including Monacolin K (also known as Lovastatin), that effectively inhibit methanogens while permitting other biodegradation processes to occur.

Mode of Action: Research has demonstrated that these statins specifically inhibit the growth and development of Archaea hence minimizing methanogenic activity. Bacteria cell walls contain peptidoglycan (murein), whereas the cell walls of methanogens cell walls contain pseudomurein.



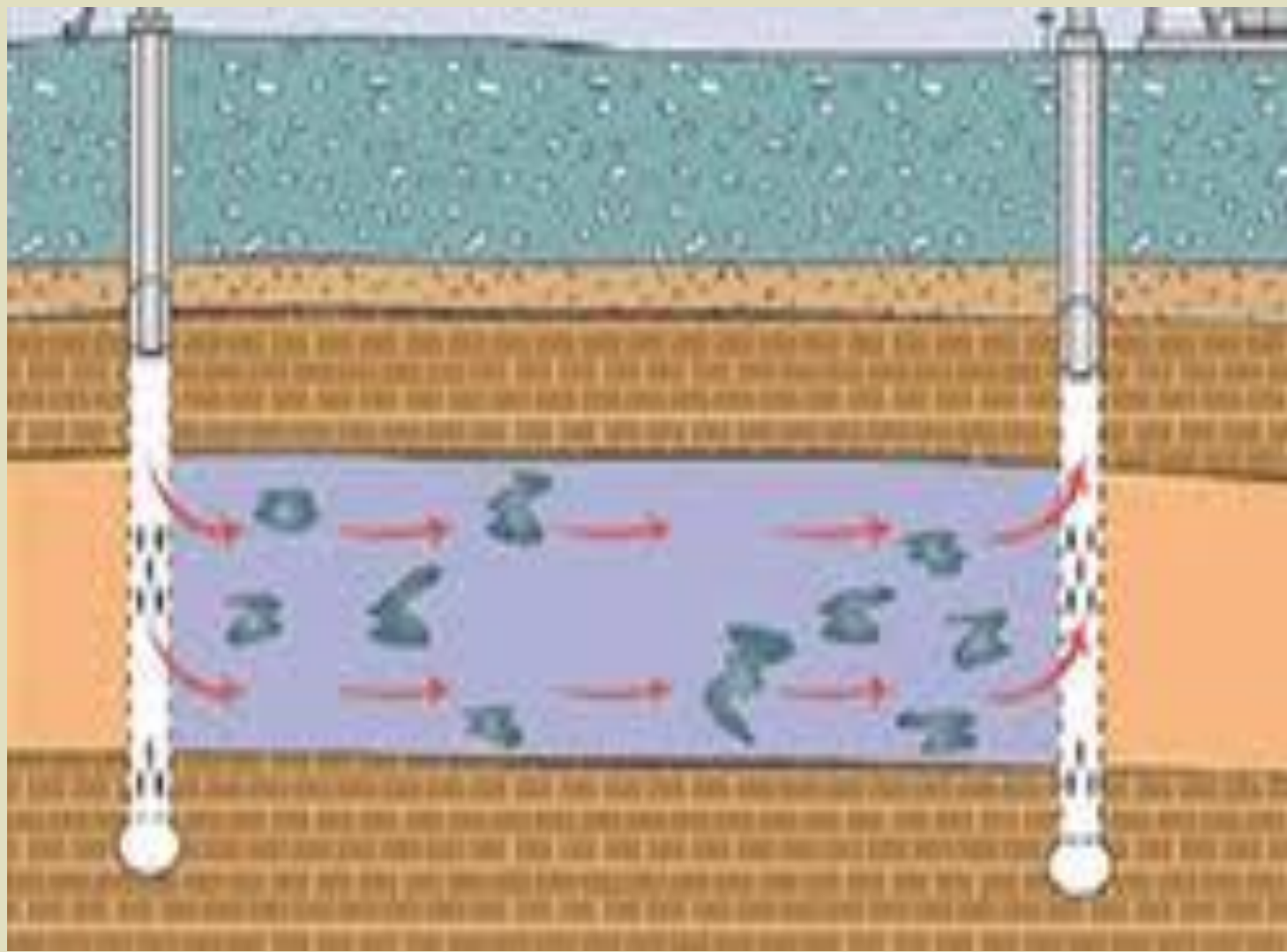
ANTIMETHANOGENIC TECHNOLOGIES

We integrated methane control features into various amendments to create safer, more efficacious remedial technologies (see below).

Technology	Use and Application
ABC-CH ₄ ™	Liquid, antimethanogenic ERD reagent
Provect-IR™	Solid, antimethanogenic ISCR reagent
Provect-IRM™	Solid, antimethanogenic ISCR reagent for simultaneous immobilization of heavy metals
Provect-CH ₄ ™	Methane control technology to supplement conventional ERD and conventional ISCR amendments
AquaGate-CH ₄ ™	Antimethanogenic <i>in situ</i> sediment capping technology
EZVI-CH ₄ ™	Antimethanogenic DNAPL treatment technology

SUPPLEMENTS FOR ERD AMENDMENTS

Provect-CH₄™ is an antimethanogenic reagent that can be added to conventional ERD amendments to: i) **increase efficiency** and ii) **improve overall performance**.



Former Dry Cleaner Site - 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
- Repeated ABC applications in July, 2014 via 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)

Results/ Conclusions

- 65% less CH₄ in groundwater samples
- >90% less CH₄ in well-head space (soil) gas
- >95% removal of COIs after 6 months (data not shown)
- Overall reduction on Material cost approximately 15%

Safer. Less Expensive. Improved Performance.

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)	
	CH ₄	PCE	CH ₄	PCE
MW-4	13.7	170	10.2	--
MW-207s	11.8	1,200	4.2	--

- ThermoFisoxboro TGA-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 10% methane)

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

Well Location	CH ₄ PID (ppm)	CH ₄ FID (ppm)	CH ₄ TGA (%)	CO ₂ (%)	O ₂ (%)	Balance (M 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 CH ₄ 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