# Antimethanogenic, Liquid ERD Amendment for Safer, More Efficient Remedial Actions

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## INTRODUCTION

There are recognized benefits to methanogens and of limited methanogenesis. For example, i) methanogens are known to play important roles in synergistic microbial ecology, ii) their metabolic activity can help maintain anoxic conditions in treatment zones (through seasonal changes), and iii) the activity of methane mono-oxygenases and other enzymes can stimulate co-metabolic activity of chlorinated solvents in redox-recovery zones. Hence, limited production of methane is part of a healthy ERD/ISCR application. 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 in groundwater concentrations (as high as 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. As a result, many 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

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 specifically limited *i.e.,* this inhibitory affect is not observed in other microbes (bacterial cell walls are composed of peptidoglycan, or murein). This enhances reductive dechlorination reactions by allowing slower-growing *Dehalococcoides* spp. to better compete

Provect-CH4 can be added as a supplement to the conventional liquid ERD substrates and/or conventional solid ISCR amendments to control the production of methane:

- Vegetable Oils (VO)
- Lecithin
- Emulsified Vegetable Oils (EVO) / Lecithin
- Sugars (Lactate, Dextrose, Glucose)
- Other “Hydrogen Releasing Compounds”
- Plant- Based Carbon Sources (cellulose, hemicellulose)
- Conventions Carbon + ZVI ISCR amendments

By minimizing the production of methane, this improves cost effectiveness, treatment efficiency, treatment time, and overall safety of these amendments.

- Improved efficiency = Saves $
  less amendment required ($) and less field time required ($)
- Reduced COI Migration potential (methane driving)
- Reduced heavy metal mobilization *(e.g.*, secondary As plumes As)

## WHAT IS ABC-CH4™?

Anaerobic BioChem (ABC®) is a patented (Rice *et al,* 1999) mixture of hydrogen donors, nutrients, and buffer to accelerate the anaerobic biodegradation of halogenated solvents in groundwater. It contains Dipotassium Phosphate for micronutrients and pH buffering + Potash or bicarbonate for pH control + 60% water soluble carbon consisting of:

- Glycerin as fast-release H donors
- Soluble lactic acid as mid-release H donors
- Ethyl lactate as a green solvent and H donor
- Dissolved Fatty acids as long-term release H donors

Since 2003, millions of pounds of ABC® have been used on hundreds of sites throughout the world. Over time the essential ingredients of ABC have been refined, and the materials formulated specifically for the unique geochemistry, biology, and hydrogeology of a given site.

ABC-CH4™ represent a significant technology advancement. It combines the proven chemistry of ABC® with the power of the Provect-CH4™ methanogen inhibitors to yield a truly unique liquid, antimethanogenic ERD reagent. This is the only liquid ERD reagent specifically designed to actively control the production of methane.

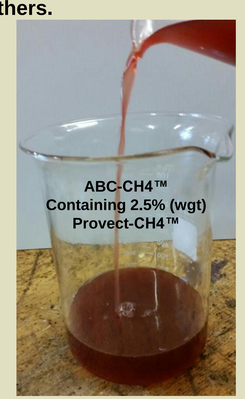
## ABC-CH4 APPLICATION GUIDELINES

Theoretical hydrogen demand of a subsurface system are based on the redox equations specified in Stumm and Morgan (1996) using site-specific data for the parameters that participate in redox reactions: dissolved oxygen, nitrate, sulfate, ferrous hydroxide, manganese dioxide, contaminant species (*e.g.,* PCE, TCE, *et cetera*), as well as pH and redox potential. From our experience, this value is usually a significant underestimate of the amount of hydrogen required for the system,. Other factors that increase the required hydrogen dose over the theoretical dose include compound concentration heterogeneity (both ambient species and contaminant species), relevant bacteria heterogeneity (presence, viability and density), dynamic conditions (groundwater recharge and flow), application limitations (inherently non uniform distribution of hydrogen due to access methods like injection), hydrogen conversion inefficiencies (hydrogen in a molecule of amendment is rarely converted with 100% efficiency), and others.

From our experience at hundreds of sites, typically application dose ranges from approximately 0.05 to 0.15 lbs of amendment per cubic foot of aquifer.

ABC-CH4™ contains 2.5% (wgt basis) Provect-CH4™ to yield a targeted 50 ppm methane inhibitor in groundwater.

Shipped in 5 USG pails, 55SUG drums, or 250/325 USG totes as a pre-mixed liquid that can be easily applied via injection wells or networks




- Viscosity = 10 cP at 20 C
- Specific Gravity = 1.14

## CASE STUDY

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 Data from the MW-4 (water depth 11.9 ft bgs; pressure 0.11 in) treated with an ERD substrate only had over 30% CH4 in the headspace gas as measured by the GEM5000 LFG meter (note – TVA detectors exceeded their level of sensitivity and shut down). By comparison, the well headspace gas in MW-207s (water depth 18 ft bgs; pressure 0.24 in) had only 0.5% CH4 (Table 1a). Dissolved methane concentrations were reduced by about 60% in the presence of the methane inhibitors (Table 1b). After ca. 6 months, both systems effectively removed site COIs without excessive accumulation of Catabolites (some data not shown)

- 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)
- Estimated Cost Savings >15%

Table 1a. Well Head Gas Analysis at a Former Dry Cleaner Site in Georgia (6 weeks post ERD application).

| Well Location | CH4 PID (ppm) | CH4 FID (ppm) | CH4 TGA % | CO2 % | O2 % | Balance (N) % |
|---|---|---|---|---|---|---|
| MW-4 | | | | | | |
| 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 | | | | | | |
| 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 |

Table 1b. Dissolved Gas Analysis at a Former Dry Cleaner Site in Georgia (Method RSK 175).

| Well Location | Pre-Injection (ppm) | | 6-Wks Post-Injection (ppm) | | 6-Months Post-Injection (ppm) | |
|---|---|---|---|---|---|---|
| | CH4 | PCE | CH4 | PCE | CH4 | PCE |
| MW-4 | 13.7 | 170 | 10.2 | Lost | 5.6 | <0.01 |
| MW-207s | 11.8 | 1,200 | 4.2 | Lost | 7.9 | <0.03 |

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