Technology for Inhibiting Methanogenesis during *In Situ* Sediment Treatment

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AquaBlok® Composite Particle System

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Presentation Outline

- How do Methanogens Impact Sediment Capping?
  - Methanogens are ubiquitous and grow rapidly when stimulated
  - Methane induces contaminant migration and can breach caps
  - Methanogens can methylate heavy metals (Hg, As, Sn, etc)
- Integrated Technologies
  - AquaBlok® *In Situ* Sediment Capping Technology
  - Engineering designs to control methane and COI migration
  - Provect-CH4™ Methanogen Inhibitor
  - AquaBlok-CH4™ Antimethanogenic Sediment Cap
- Case Study (Example Field Application)
- Conclusions

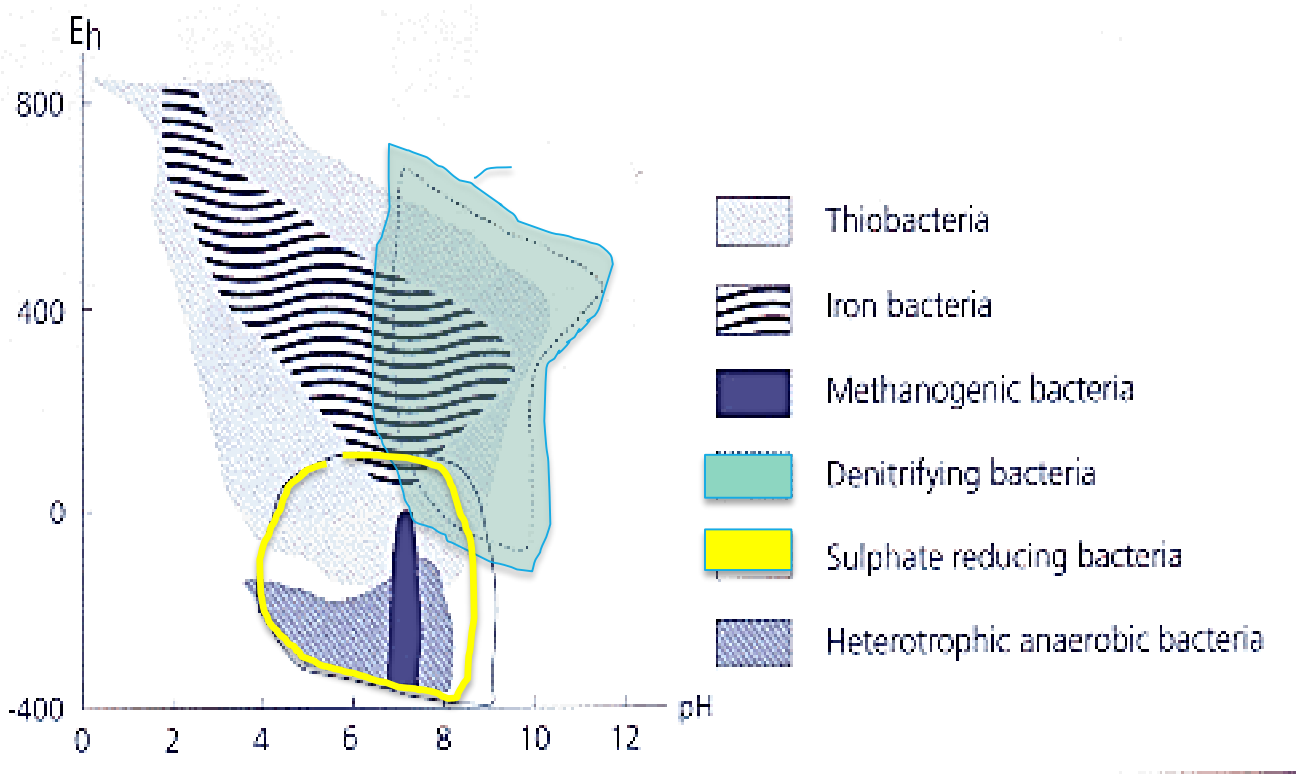
What is a Methanogen?

- 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

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

Issues with Methane Generation

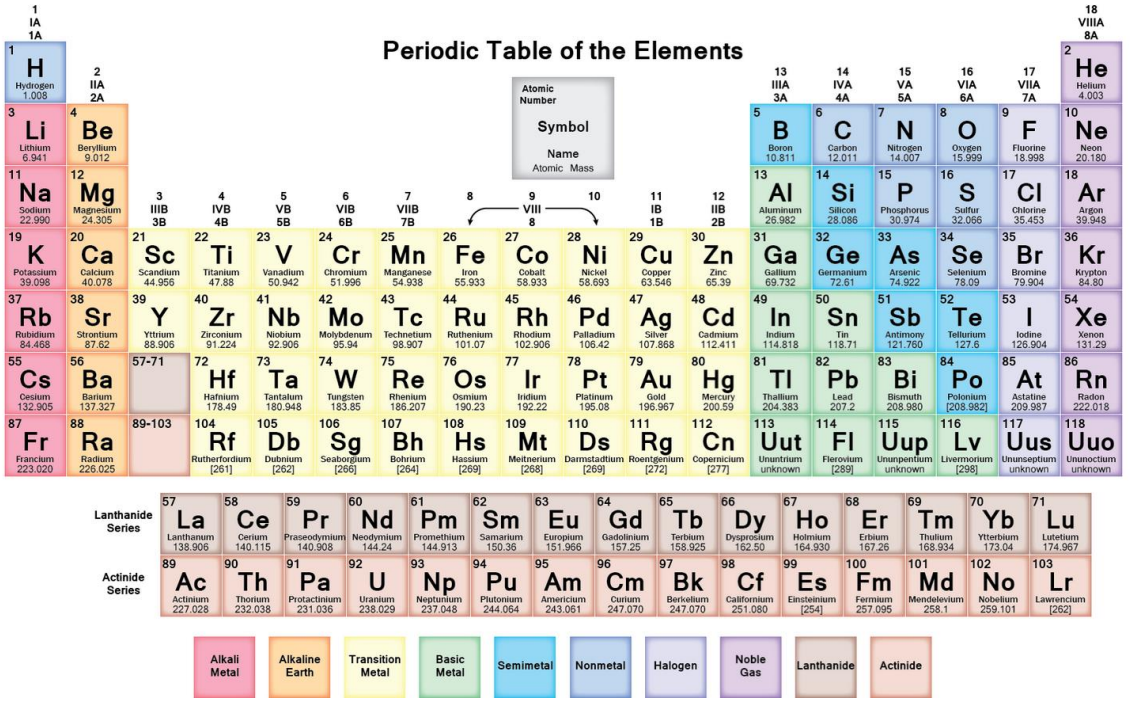
- Typically there is a short term stimulation of methanogenic /microbial activity as a result of disturbing sediments, etc
- Methane gas ebullition causes cap breaching and induced migration = sheen
- Can result in the generation of methylmetal(loids)

Biomethylation of Heavy Metals

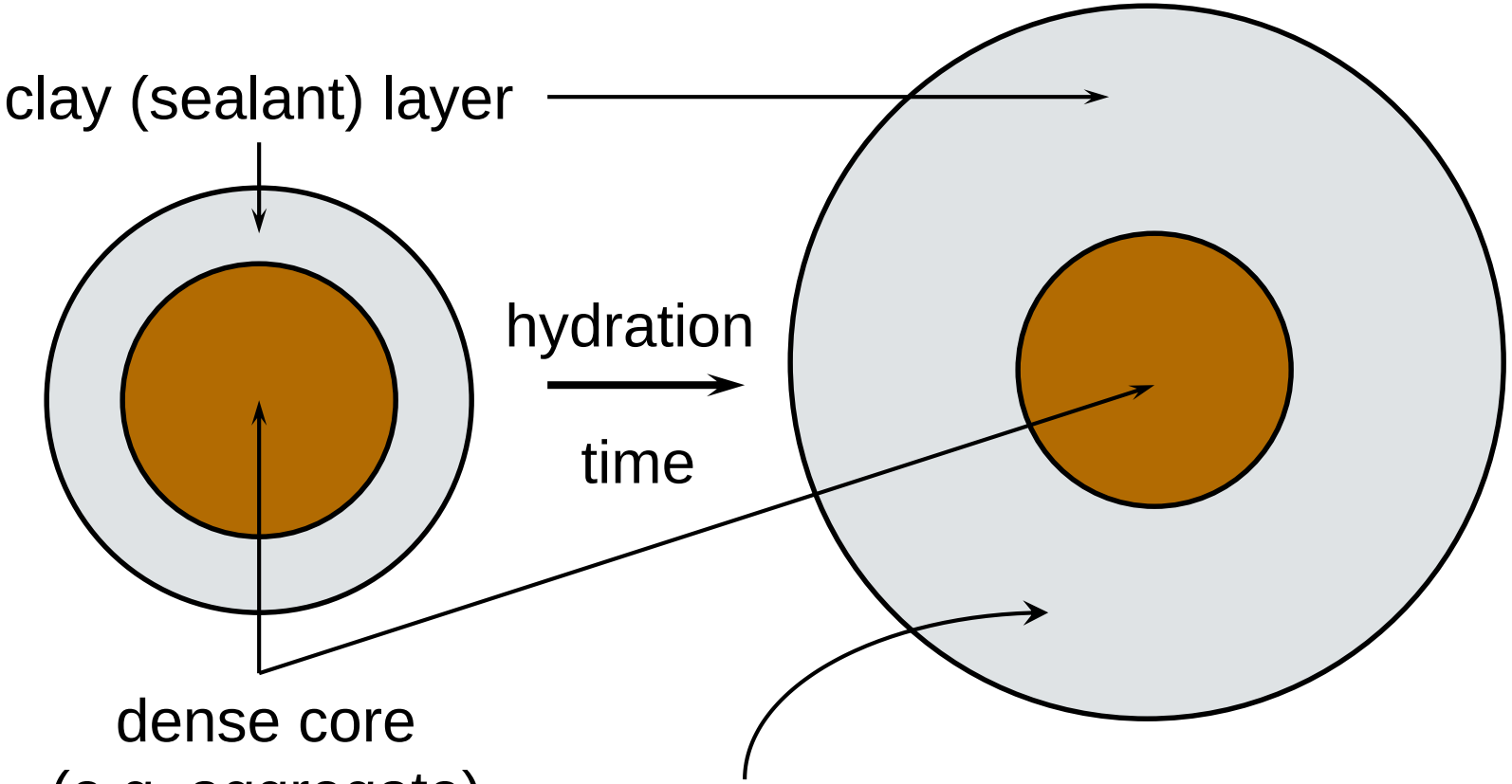
- With the possible exception of Pb almost all Group IV, V and VI elements can be biomethylated (Bentley and Chasteen, 2002).
- Methylmetal(loids) are usually volatile and more toxic than their inorganic counterparts due to increased water solubility and hydrophobicity (*e.g.,* methylmercury).
- Microorganisms are primarily responsible for the biosynthesis of organo-metals (Challenger, 1945), and the activity of methanogens is a main source of their production (Michalke, *et al*., 2006).

Volatile methylmetal(loids) may produced by Growing Cultures of Methanogens (Archaea).

*** As, Hg, Sn and Pb are of particular interest**



AquaBlok® *In Situ* Capping Technology



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AquaBlok Placement Methods

Basic Product Behavior in Water

Recontamination is Not Due to Flux Through the Cap

Split-core from Section A (2.5 yrs after placement)

New sediment Deposits

AquaBlok Clean Cap Layer

Discrete boundary

Contaminated Sediment

AquaBlok® Composite Particle System

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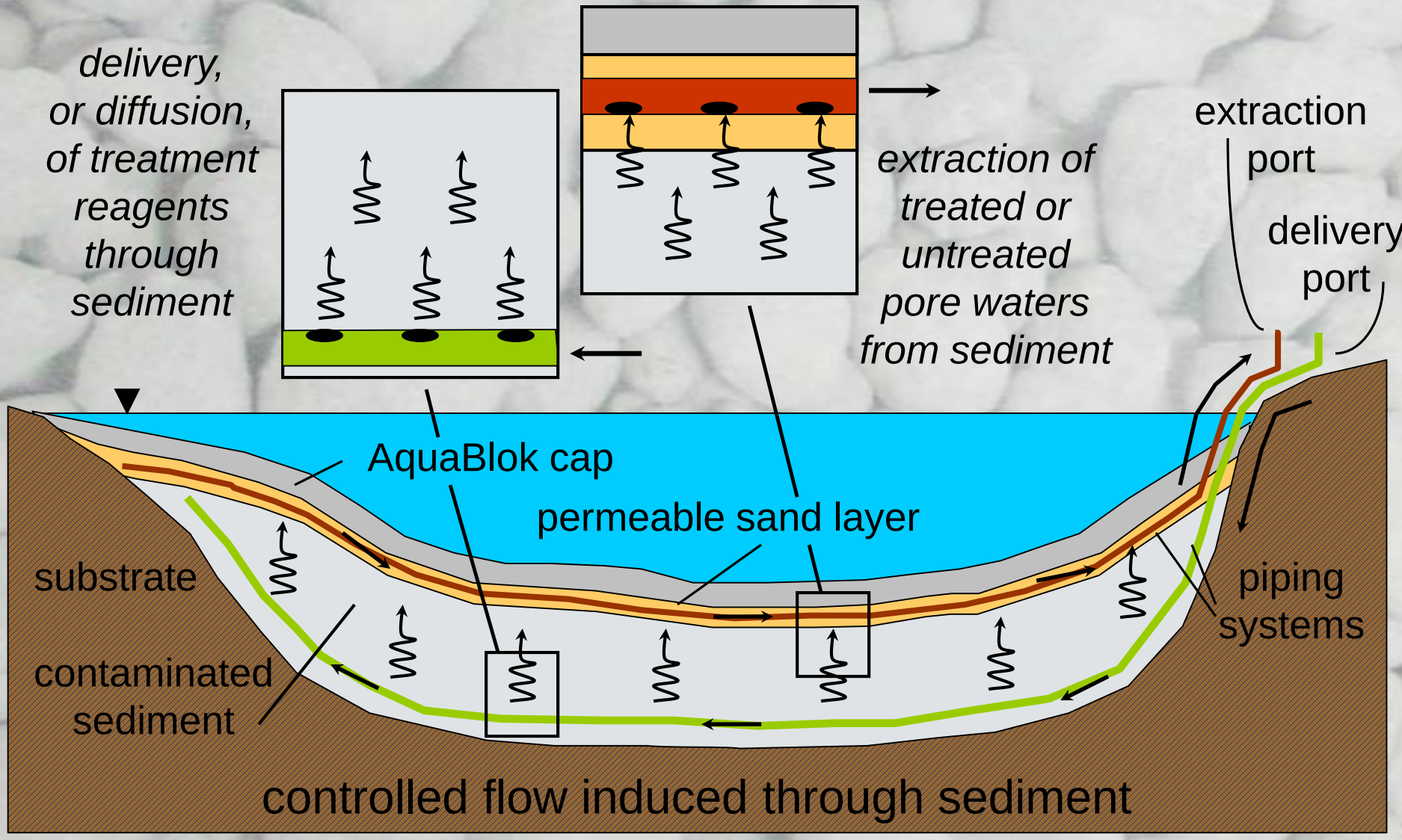
Facilitating *In Situ* Sediment Treatment



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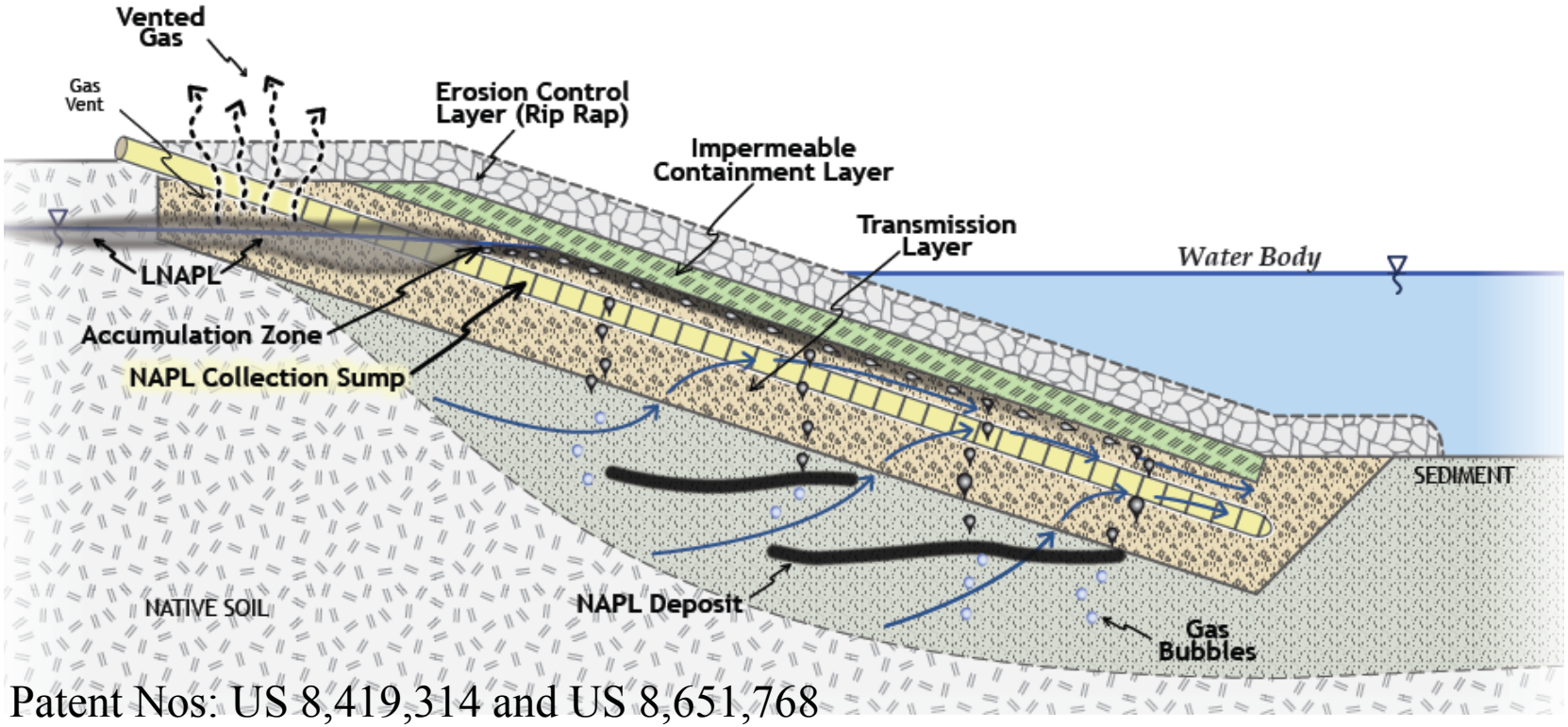
Conceptual Design - NAPL Trapping Cap

A sediment capping system made of geological materials (clay, sand, gravel, boulders) that can be used to capture NAPL permanently and predictably as it migrates from sediments



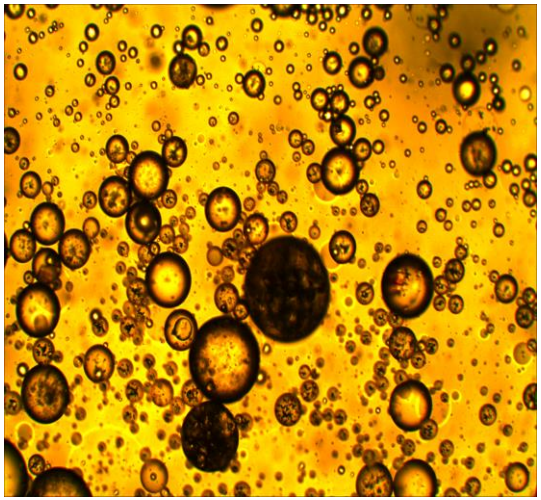
Patent Nos: US 8,419,314 and US 8,651,768

* NAPL Trapping Cap was designed by TRC

AquaBlok®
Composite Particle System

Provect-CH4™ Methane Inhibitor

- Proprietary combination of Red Yeast Rice (RYR) extract specially prepared 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 pending



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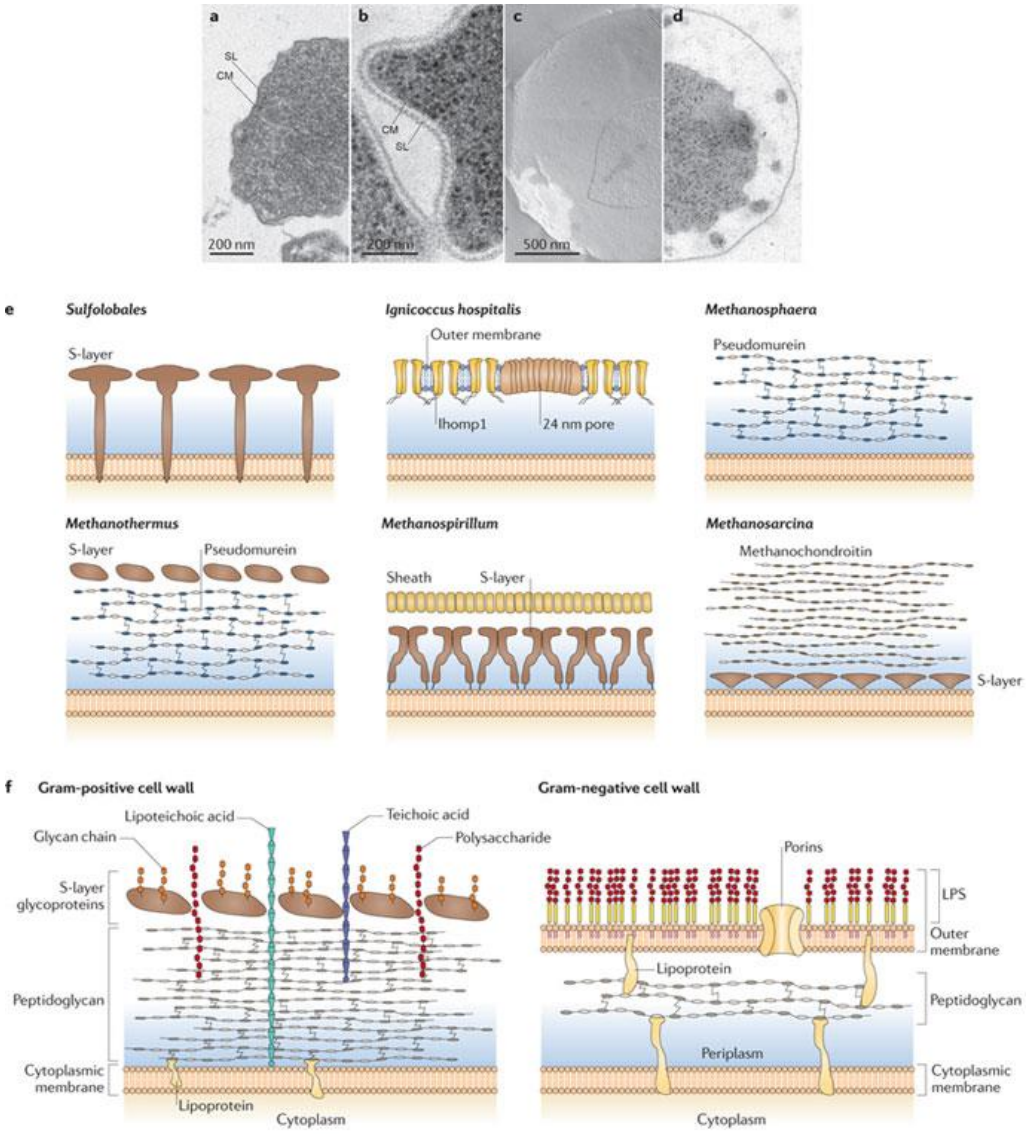
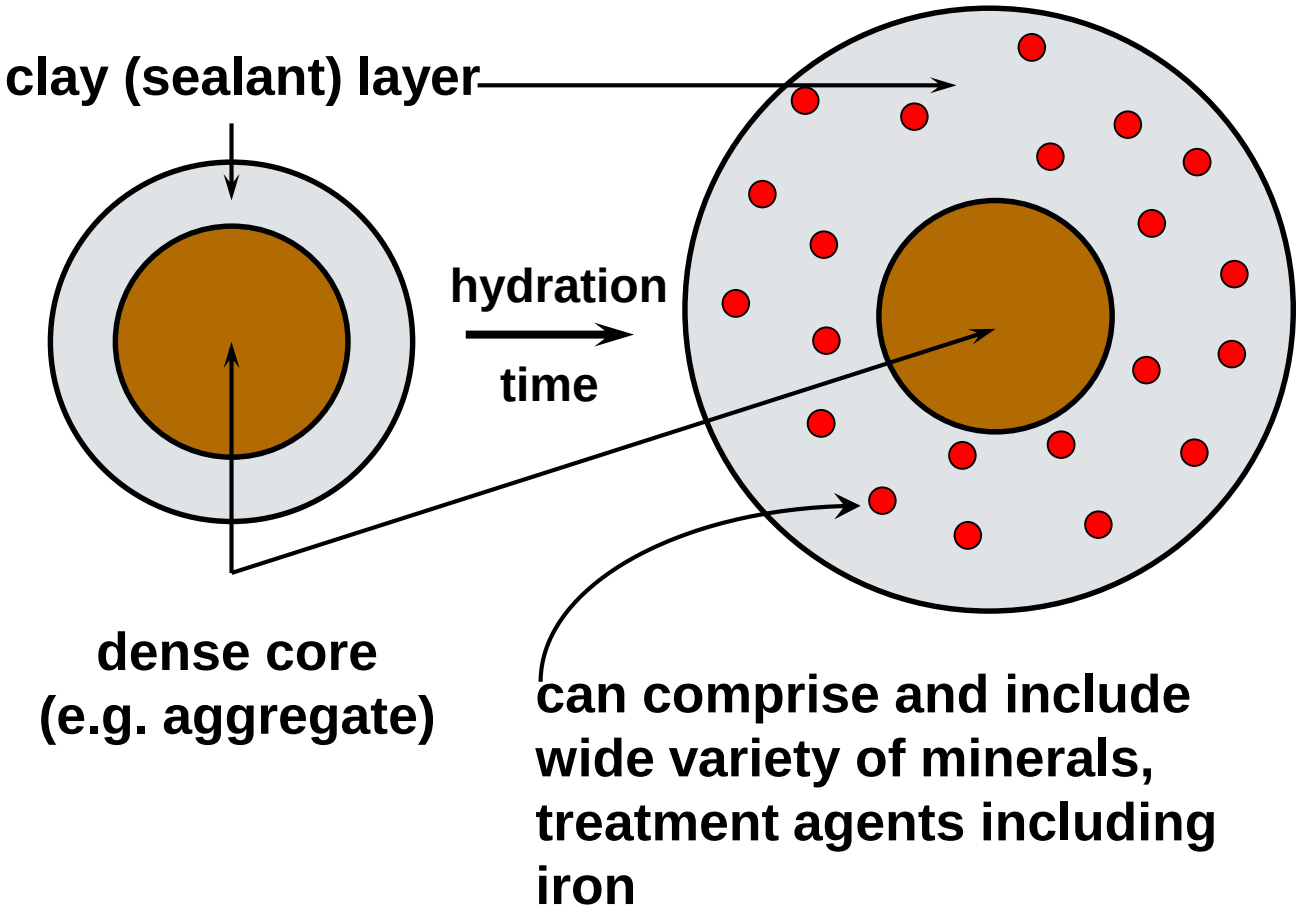
Provect-CH4 will Control Methanogens

- 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).

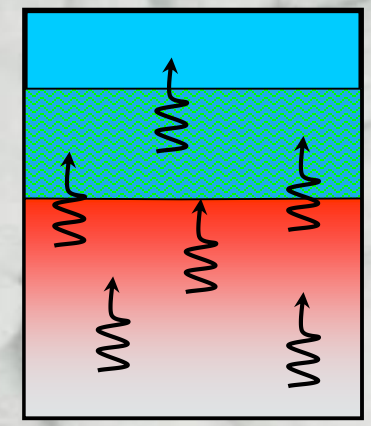


AquaGate-CH4™ Particle



Horizontal Reactive Barrier (hPRB) for *In Situ* Sediment Treatment

Contiguous Reactive Cap or funneling *of contaminant-bearing sediment pore waters beneath low-permeability cap through* ***Reactive Gates***



higher-permeability treatment "**gates**" (includes reactive medium, ZVI, buffering agents, microbes, or other materials)

AquaBlok+ ™ Reactive Cap

Reactive Gates & AquaBlok™ Cap

Impacted Sediment

predominant direction of ground water flow

AquaBlok™ Composite Particle System

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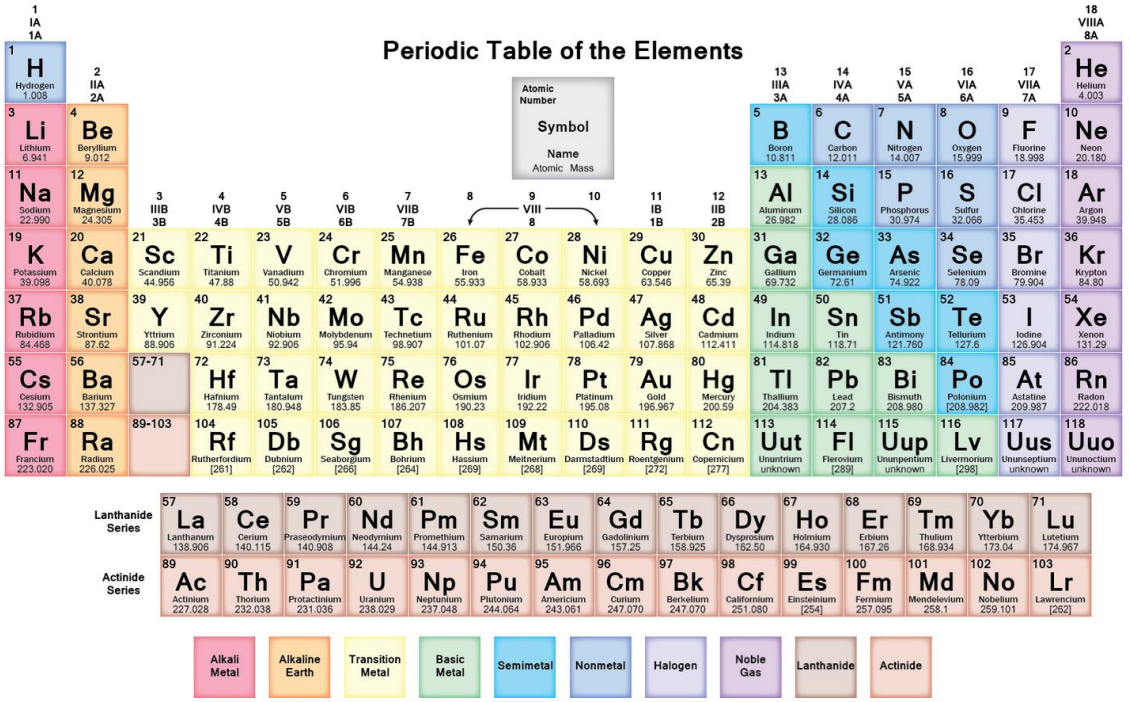

Illegal Gold Mining – Latin America

www.npr.org/sections/goatsandsoda/2015/05/17/398765777/who-did-this-to-perus-jungle

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A massive gold mining zone in eastern Peru has turned thousands of acres of rain forest into wastelands. This strip of mining in La Pampa is 5 miles wide and 40 miles long.

Jason Beaubien/NPR

www.npr.org/sections/goatsandsoda/2015/05/17/398765777/who-did-this-to-perus-jungle

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An aerial photo shows the environmental destruction in the wake of illegal gold mining in the Peruvian Amazon.

Courtesy of Gregory Asner, Carnegie Institution for Science

Mercury Contaminated Sediments

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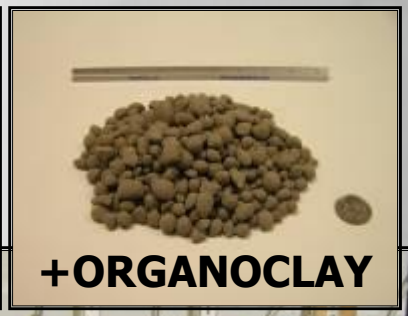
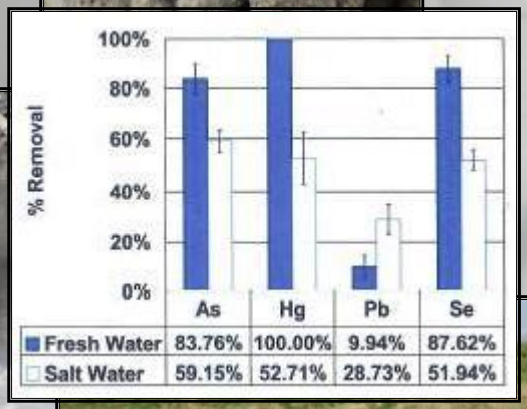
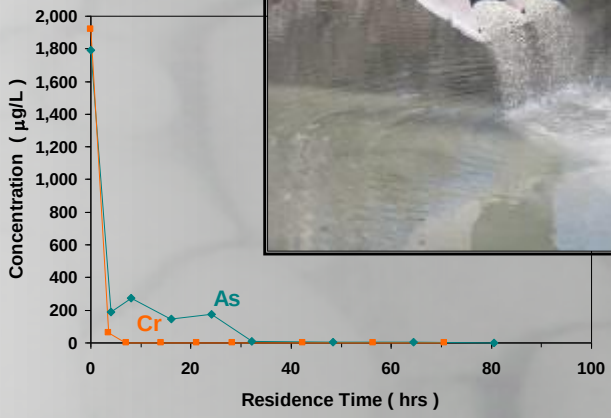
In-Situ Treatment & Biological Applications







Reactive AquaGate Materials

Contaminant	Treatment Materials
PAHs, BTEX, PCBs	Activated Carbon, Oxygen Delivery, Rubber
Gasoline	Oxygen Delivery, Nutrients
CVOCs	ZVI*, Provect-IR*, Bimetallic, A/C
Metals, Ammonia	ZVI*, Provect-IRM*, Organic Carbon, Zeolites, Ferric Sulfides, A/C
Acid Mine Drainage	Provect-IRM*, Organic Carbon
Nitrate	Provect-IR*, Organic Carbon
Methane control – all COIs	Provect-CH4™

* Provectus Environmental Products

Case Study - Funnel & Gate Approach

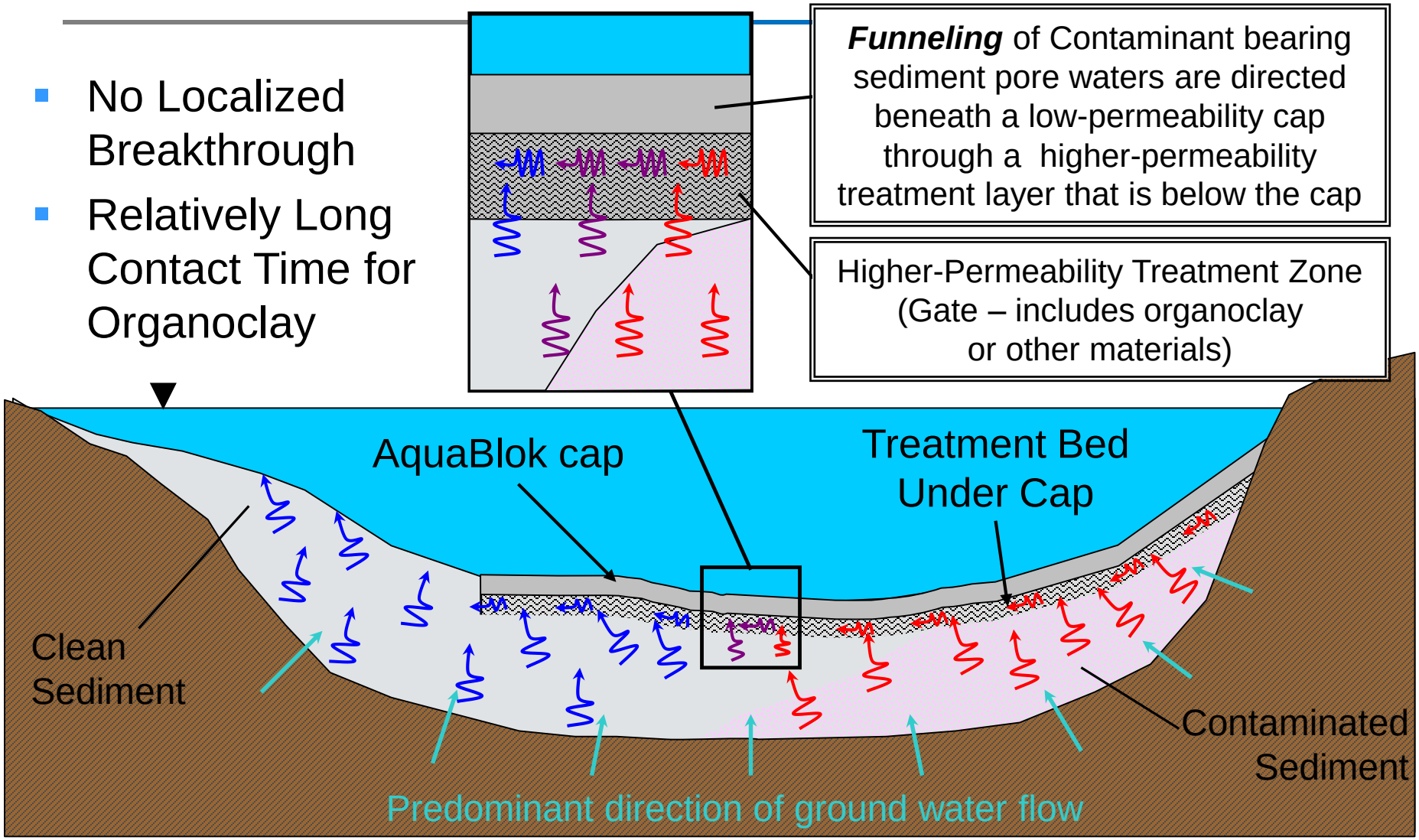
Site Location: *U.S. EPA Region 2*
Confidential Site – New York State

- **Setting/Purpose:** Canal/River (freshwater). MGP Site – PRB and low permeability barrier/cap over contaminated sediments. Site area was approximately 4,000 square feet.
- **Contaminant(s) of Concern:** Coal Tar associated with historic MGP site, including PAH (polynuclear aromatic hydrocarbons) and DNAPL (Dense Non-Aqueous Phase Liquids).
- **AquaBlok Cap Design/Site Area:** Multi-layer design comprised of a one inch basal layer AquaBlok+ORGANOCLAY PRB covered with a hydrated layer (~6 inches in target thickness) of AquaBlok 3070FW. The cap was then armored with a two-inch layer of AASHTO #2 stone.
- **Method of AquaBlok Placement:** Shore-based excavator

Example of Sheen

Key Objectives:

- No Localized Breakthrough
- Relatively Long Contact Time for Organoclay



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Placement of Low-Permeability Cover Layer & Armor Stone

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Completed AquaBlok Cap with Armor Stone

AquaBlok Cap Following Spring

Summary

- A variety of treatment materials are available to effectively reduce bioavailability of contaminants in sediments.

- Funnel and reactive gate technology provides:
  - isolation of contaminated sediment
  - treatment of contaminated sediment pore water
  - better protection of uncontaminated water bodies and aquifers than sediment removal or non-reactive caps

- Technology is applicable to:
  - contaminated sediments
  - contaminated groundwater discharging into water bodies
  - contaminated water bodies recharging groundwater
  - wide range of contaminants

Cost Factors

- **Location**
- **Size of Area**
- **Desired Thickness of (hydrated) Layer**
- **Contaminant Capping/Treatment Strategy**
- **Sediment Layer Thickness / Consolidation**
- **Energy Level of Site**
- **Access to Installation Area**
- **Slopes/Stabilization**

Order of Magnitude Cost:

Std. AquaBlok: $1.50 – 4.50 / SF for Material & Installation
$110 – 250 / US Ton (Based on 85lb/CF Bulk Density)

Positions Available….

- Hydrogeologists
- Geologists
- Engineers
- Microbiologists
- Environmental Scientists
- Business Development
- Sales & Marketing

A Career – not just a job

Microsoft….. Google…… Provectus