RemTech 2019

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Perspectives on Emerging Contaminants: Technology Advances and Field Applications in Remediation of Emerging Contaminants

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Geosyntec Consultants International

Presenting Today

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Assessment / Remediation / Regulatory

Emerging Contaminants Then and Now…

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2003

- MTBE and Oxygenates
- 1,4-Dioxane
- Perchlorate
- NDMA
- Pharmaceuticals
- PFOS
- APEOs
- Emerging Pathogens

Sedlak and Alverez-Cohen, Overview of Emerging Contaminants, Env. Eng. Science, 2003

Almost…2019

- TBA
- 1,4-Dioxane
- Perchlorate
- Pharmaceuticals
- PFAS (PFOS & many others)
- PDBEs
- Energetics
- Selenium
- 1,2,3-Trichloropropane
- Sulfolane
- Microplastics
- Pathogens, new Pesticides…

PFAS

Groundwater Remediation Options

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Ex Situ Options

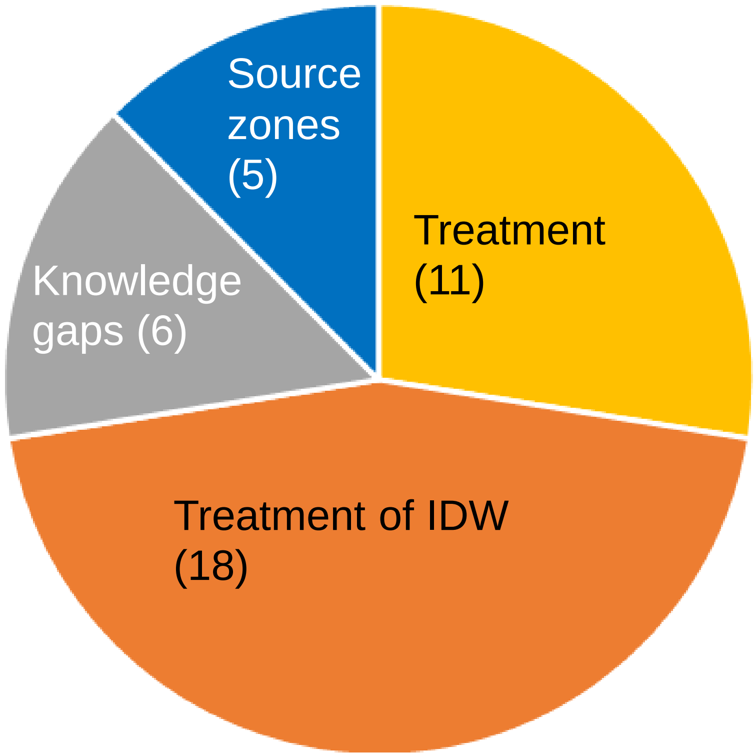
- Established
- GAC/Resins/RO/IX
  - Compound specific
  - Sensitive to water quality
  - Scale-specific
- Under Development
  - STAR-X (for IDW)
  - Physical (ball milling)
  - Chemical Oxidation
  - Chemical Reduction
  - Electrochemical

In Situ Options

- Under Development
- Treatment trains with Oxidation/low pH
- Sorption / Sequestration for PRBs or other configurations
  - GAC/Resins, Polymers
- Many other maybes, but no success stories yet

Remedial Trends

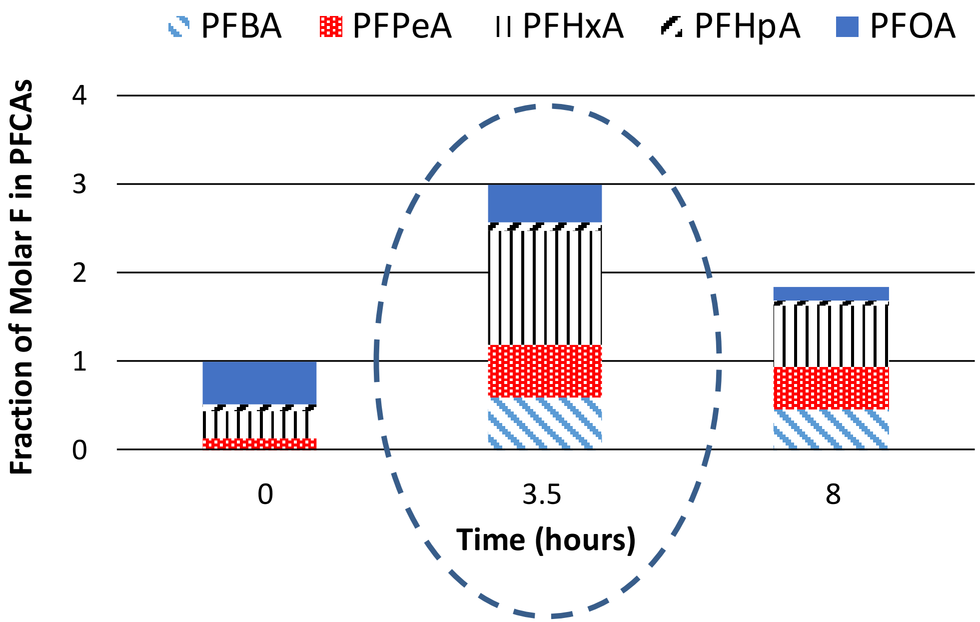
- Ex situ treatment processes most common
  - GAC, IX – site-specific
- Some R&D progress with innovative ex situ and in situ tools
  - US DOD/DOE R&D – treatment growing focus
  - IDW treatment also key focus

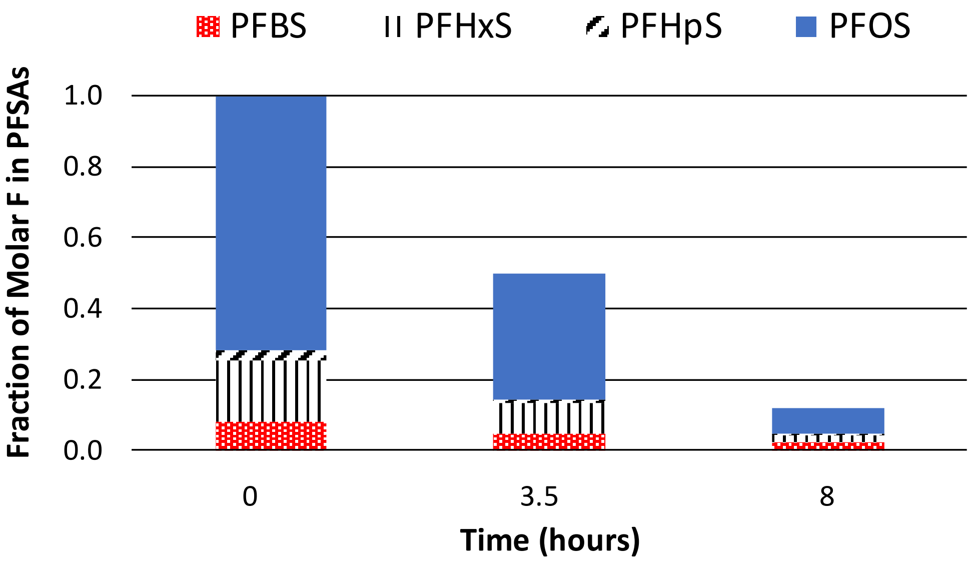


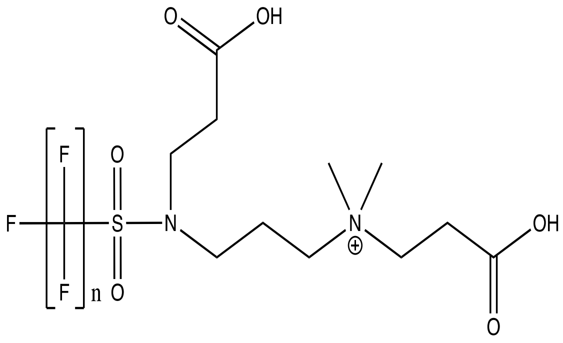
PFAS projects funded by SERDP/ESTCP in FY2018

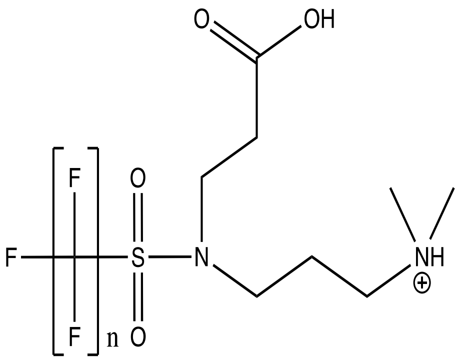
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Contaminated-Groundwater-SONs/In-Situ-and-Ex-Situ-Remediation

Electrochemical Oxidation of AFFF-Impacted Groundwater using Boron-Doped Diamond Anodes









Oxidation of precursor compounds
present in AFFF results in transient formation of perfluorinated carboxylates

Schaefer et al., ES&T (2018)

R&D – In Situ Treatment Train

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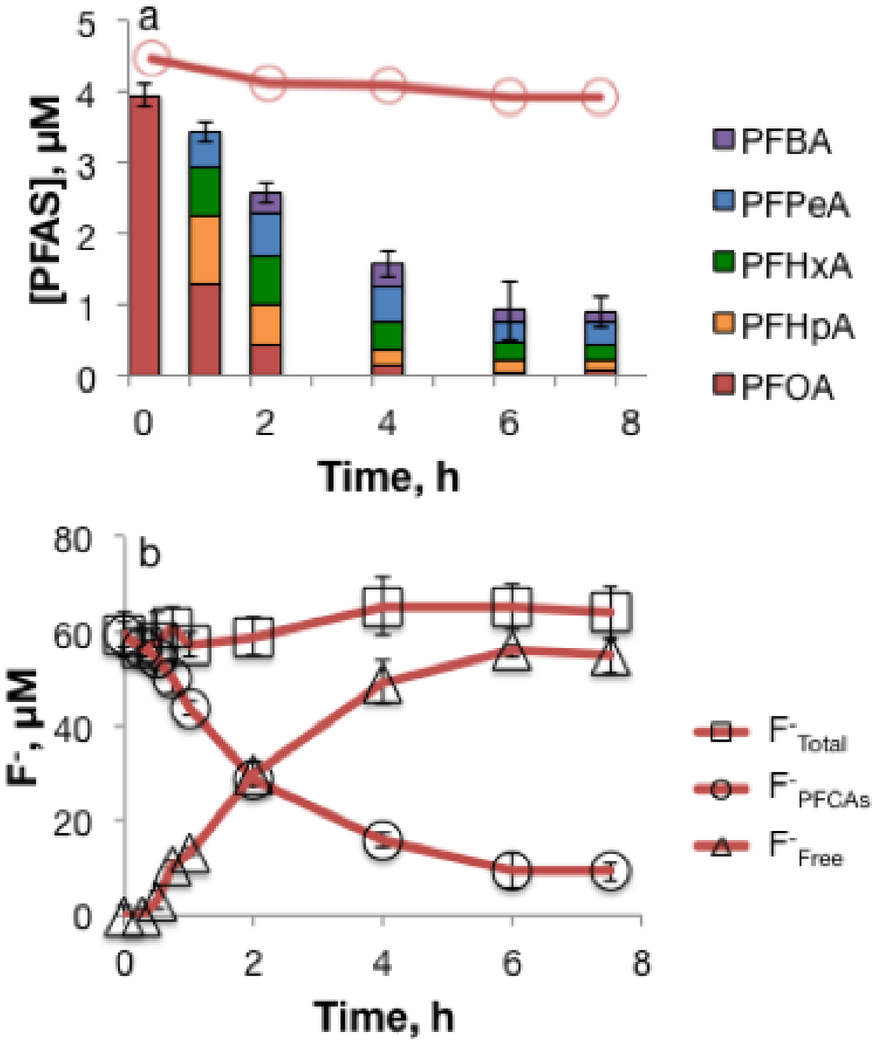
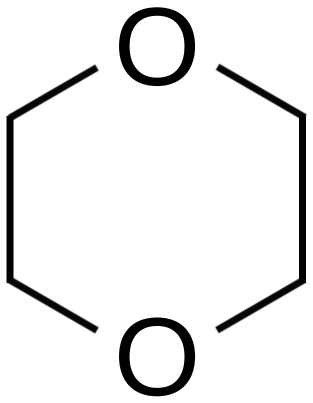
- **Thermally Enhanced Low-pH ISCO / P&T treatment train**
  - Fully degrades PFOA and other PFCAs
  - Fully degrades polyfluorinated precursors
  - Not expected to degrade PFOS and other PFSAs
  - 1 month treatability study removed 90% PFCAs and precursors
- **Field pilot at NAS Jacksonville**
- **ESTCP Funded Project, team includes**
  - Dr. David Sedlak, University of California at Berkeley
  - Dr. John Kornuc, NAVFAC EXWC
  - Dr. Rula A. Deeb, Bruce Marvin, Elisabeth Hawley, Geosyntec Consultants



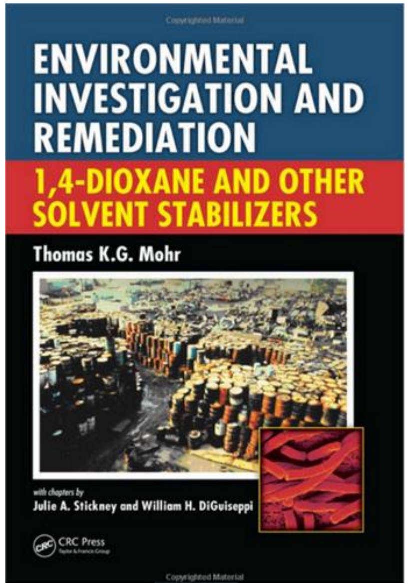
Laboratory results from UC Berkeley

1,4-Dioxane

1,4-Dioxane Background Information



- Emerging contaminant that keeps on emerging (avg. DW detection rate = 13%)
- Animal carcinogen and suspected human carcinogen
- Solvent, wetting agent & stabilizer for chlorinated solvents (1,1,1-TCA)
- High Solubility → Large Plumes
- Poor removal by GAC, air stripping
  - Log K_{OW} = -0.32*
  - Henry's LC = 2.2 x 10^{-5} atm-m^3/mol*
- Proposed Health Canada Guidelines published Sept 2018 with MAC of 50 µg/L, no CCME standard



https://www.canada.ca/en/health-canada/programs/consultation-1-4-dioxane-drinking-water/document.html#a715

Groundwater Remediation Options

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Ex Situ Options

- Bioreactors
  - Effective
  - Applicable to wide range of concentrations
  - Cultures under development
- Advanced Oxidation
  - Effective in laboratory studies
  - Field applications
- Sorbent/Resins
  - Specialized vendor products
  - GAC not effective

In Situ Options

- Bioremediation
  - Cultures under development
- Chemical oxidation (ISCO)
- Phytoremediation
- Thermal
- Electrokinetics
- Large, dilute plumes - unique challenges for remediation

Geosyntec led R&D: Bioreactor Field Application at Landfill Site

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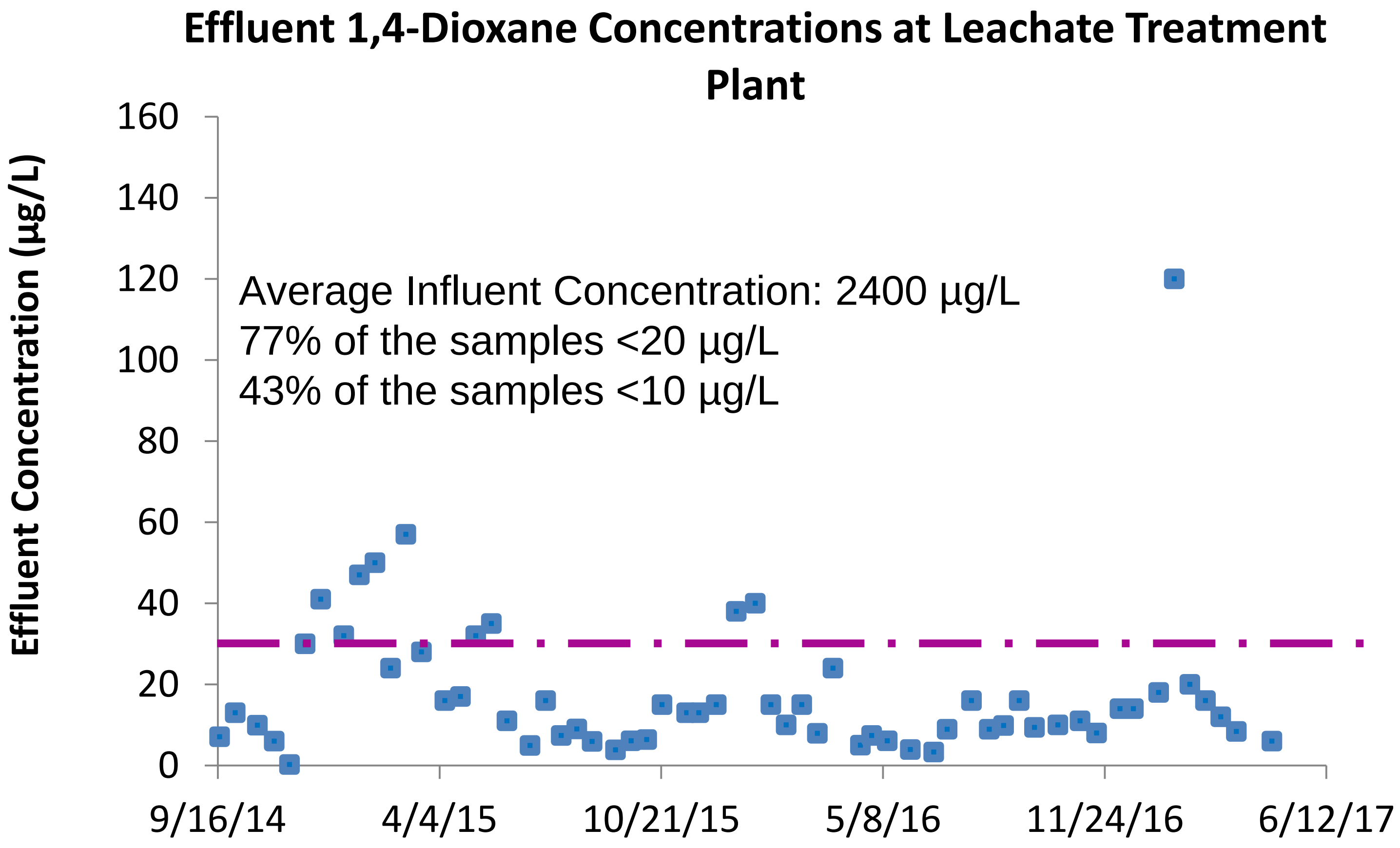
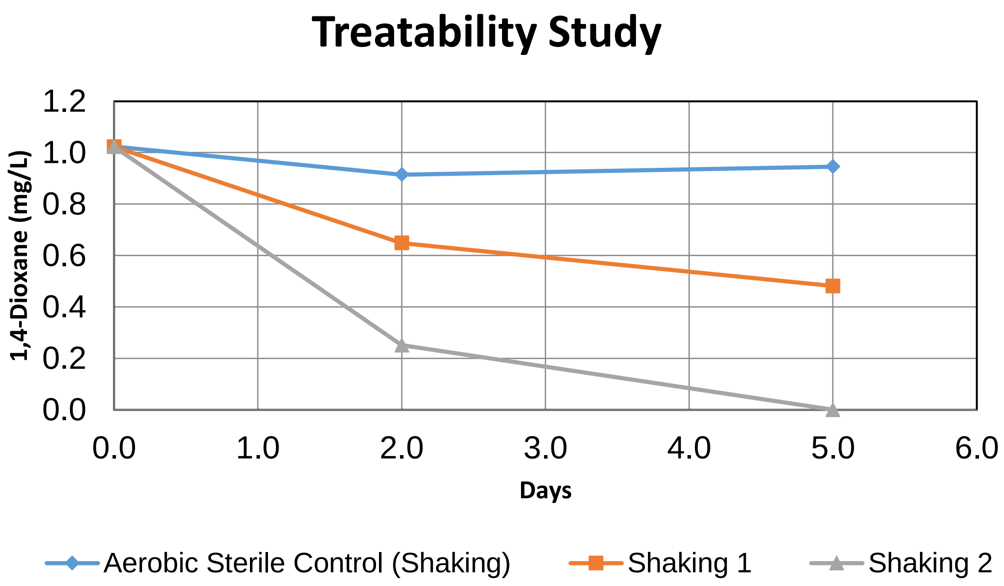


- Bioaugmentation culture for in situ aerobic bioremediation also under development at SiREM

1,4-Dioxane Culture Development

- Mixed culture
- Aerobic degradation
- Degrades up to 1,000 mg/L to <20 ug/L
- Requires DO for effective treatment



Engineered Phytoremediation - *TreeWells*®

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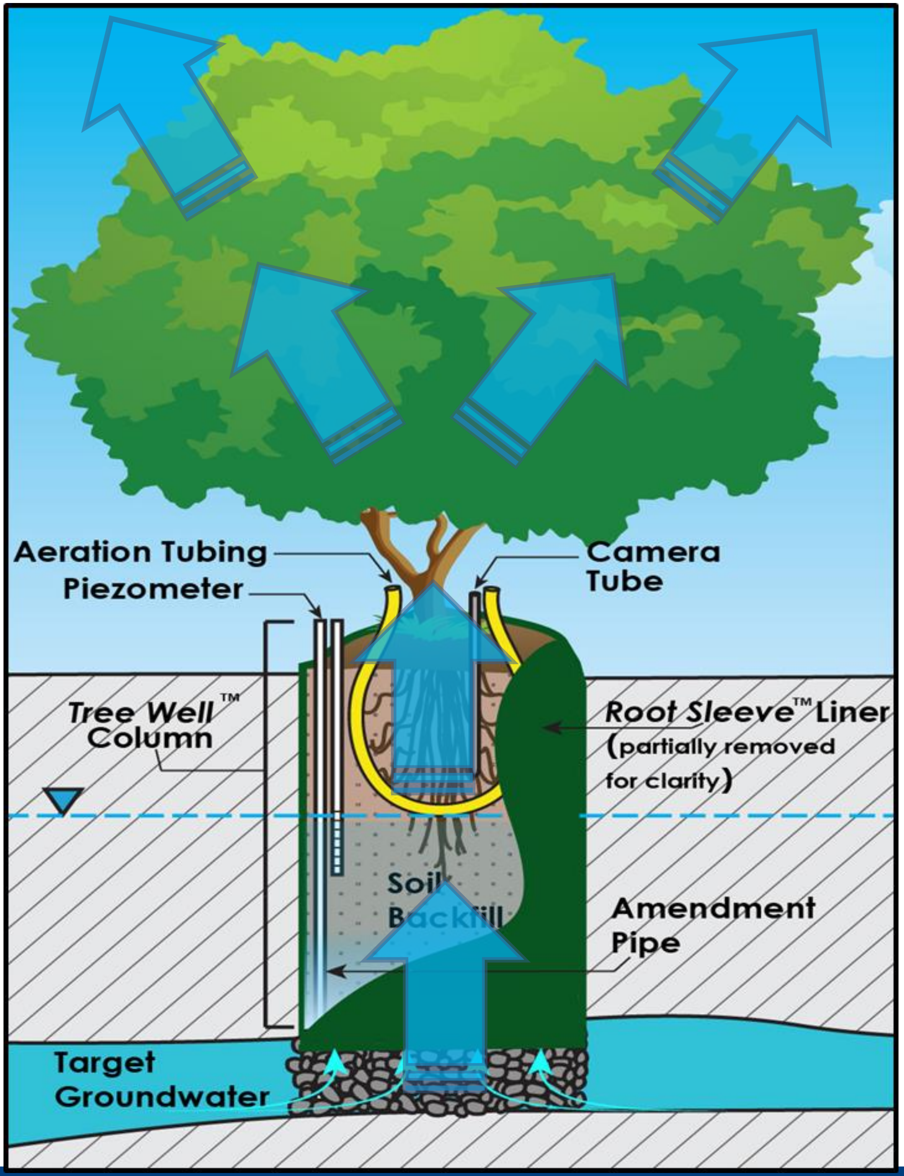

- Developed and patented by Dr. Edward (Edd) Gatliff of Applied Natural Sciences, Inc. (ANS), licenced to Geosyntec
- Targets *specific* groundwater by directing root growth downward
- Effectively treats a wide range of contaminants
- Overcomes challenges to conventional phytoremediation
- Pre-treatment option (reactive treatment media – ZVI, etc.)
- Optimizes growing conditions
- Highly adaptable – can be tailored to specific site conditions
- *Active* treatment – in a *passive* manner

It is a designed, engineered approach to using plants to address contaminant issues. Not just “Plant a tree and hope for the best.”

Case Study – Sarasota, Florida

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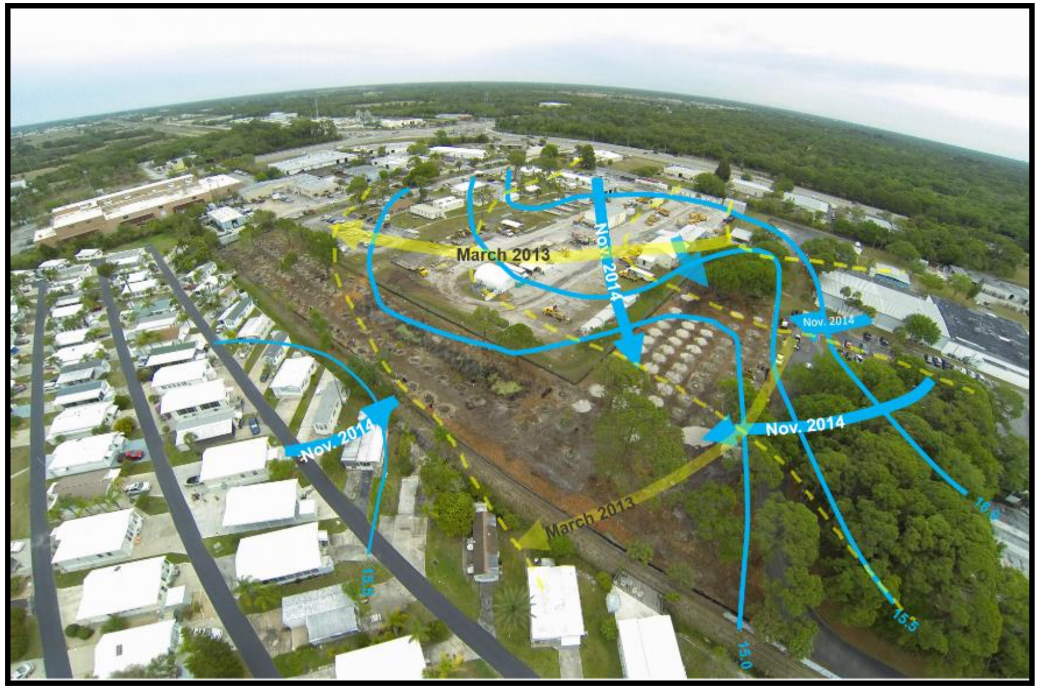
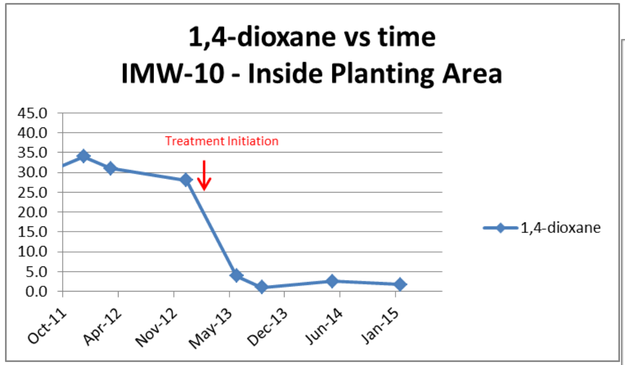
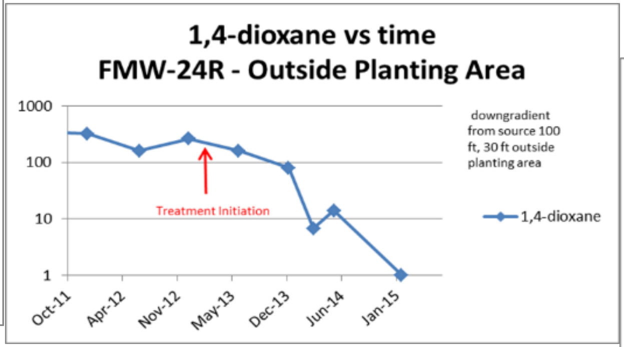
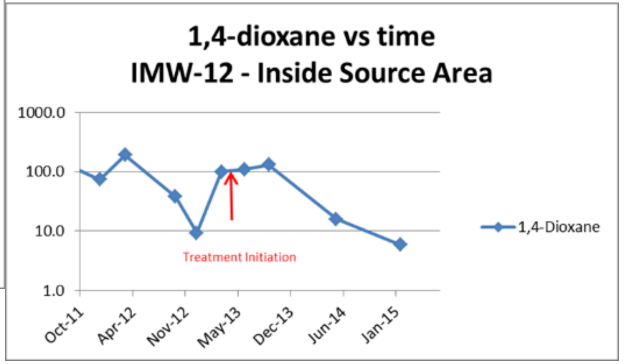


- Comparison of GW flow at time of *TreeWell* system installation (Yellow) vs. 18 months post-installation (Blue)
- Gradient reversal in only two growing seasons
- Experience at Sarasota with predicted groundwater response versus actual has been applied to modeling of other sites with similar success

- Dissolved-phase concentrations have decreased significantly and rapidly since implementation







- 154 *TreeWell* units planted in 2013

All indicated concentrations in µg/L

Perchlorate

Perchlorate Uses

Military and Space Applications (rockets, boosters, flares)

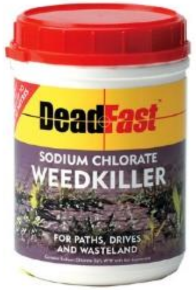
Explosives	Pyrotechnics (fireworks)
Safety (road) flares	Airbag Inflators (igniter)
Matches	Lithium Perchlorate Batteries
Medical Devices	Electropolishing/Metal Etching
Leather Tanning Agent	Mordant for Dyes & Fabrics
Electronic Tubes	Lab Dessicant/Digesting Agent
Photography	

Fertilizers (Chilean Nitrate)

Evaporite Deposits (natural) Lightning (natural)







Common Release Mechanisms

Manufacturing Site Activities

- Production processes – mixing, grinding, building wash-down
- Propellant hogout/bore-out
- Waste handling and disposal (open burn, landfill)

Training Range Activities

- Firing Points
- Impact Areas

Storage & Disposal Areas

Perchlorate Characteristics

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- Highly soluble
- No sorption to soil
- Limited natural degradation
- Disperses in surface drainages
- Infiltrates to groundwater
- Migrates long distances (many kilometers) in groundwater
- Biodegrades with organics present

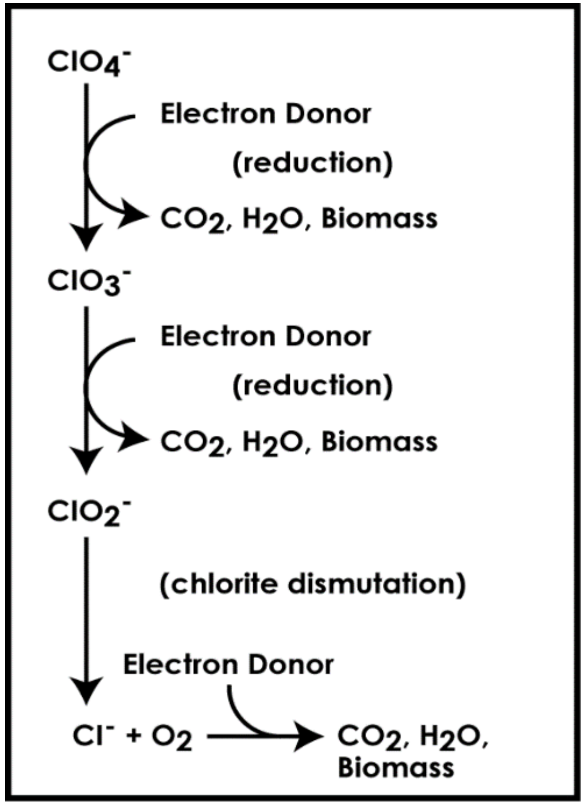
Environmental Microbiology (2004) **6**(5), 517–527 doi:10.1111/j.1462-2920.2004.00598

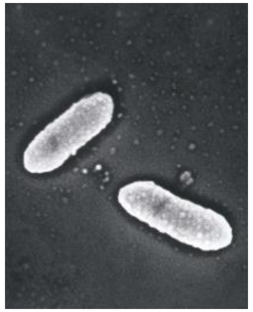
Perchlorate-reducing microorganisms isolated from contaminated sites

Alison S. Waller,[1] Evan E. Cox[2] and Elizabeth A. Edwards[1]*
[1]*Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, M5S 3E5, Canada.*
[2]*GeoSyntec Consultants, Inc., 130 Research Lane, Suite 2, Guelph, Ontario, N1G 5G3, Canada.*

Summary

An extensive microcosm survey of perchlorate-contaminated sites was undertaken to assess the ability of indigenous microorganisms to degrade perchlorate. Samples from 12 contaminated sites and from one pristine location were analysed. Perchlorate was degraded to below detection limit in all electron donor-amended microcosms. Perchlorate-reducing microorganisms (PRMs) were numerous at most of these sites. Sixteen distinct PRMs were isolated that





Groundwater Remediation Options

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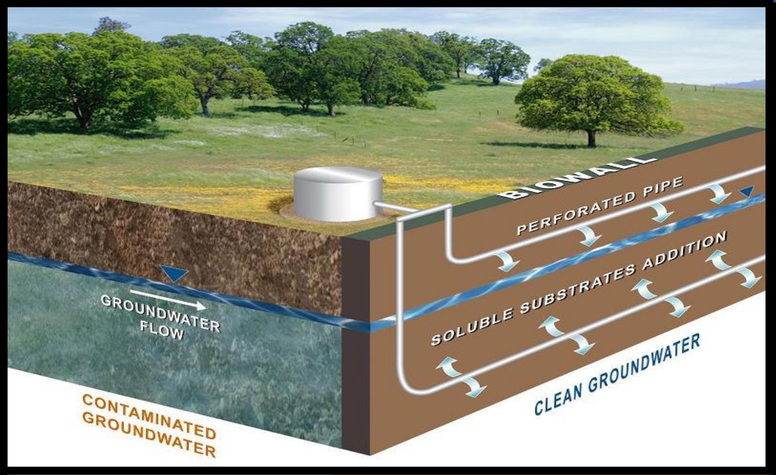

Ex Situ

- **Tailored GAC**
  - <50 μg/L
- **Ion Exchange**
  - <500 μg/L
- **Bioreactors (FBR, FFR)**
  - >500 μg/L <100,000 μg/L
- **Reverse Osmosis/EDR**
  - >100,000 μg/L

In Situ

- **Bioremediation**
  - <1,000 mg/L
- **Phytoremediation**
  - <10 mg/L
- **Electrokinetics**
  - <100 mg/L
  - Coupled with either bioremediation or extraction

Innovative Soil Bioremediation

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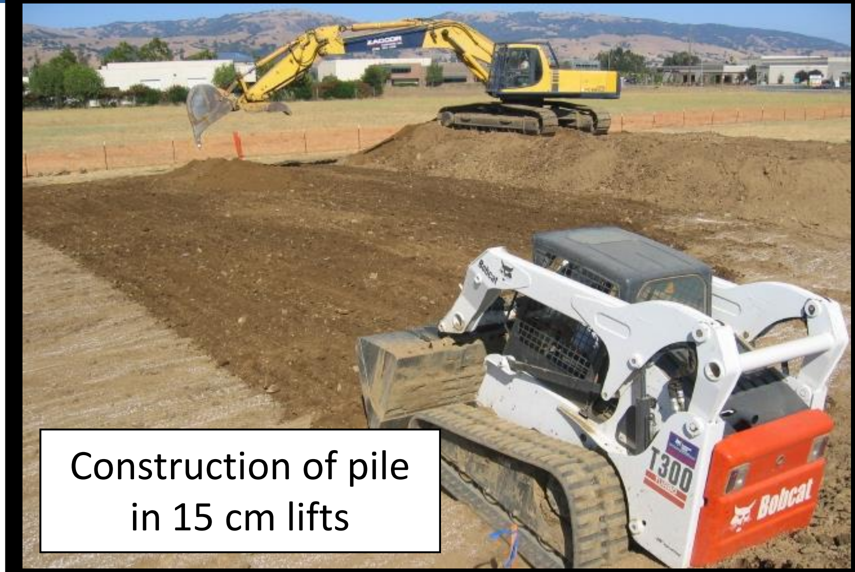
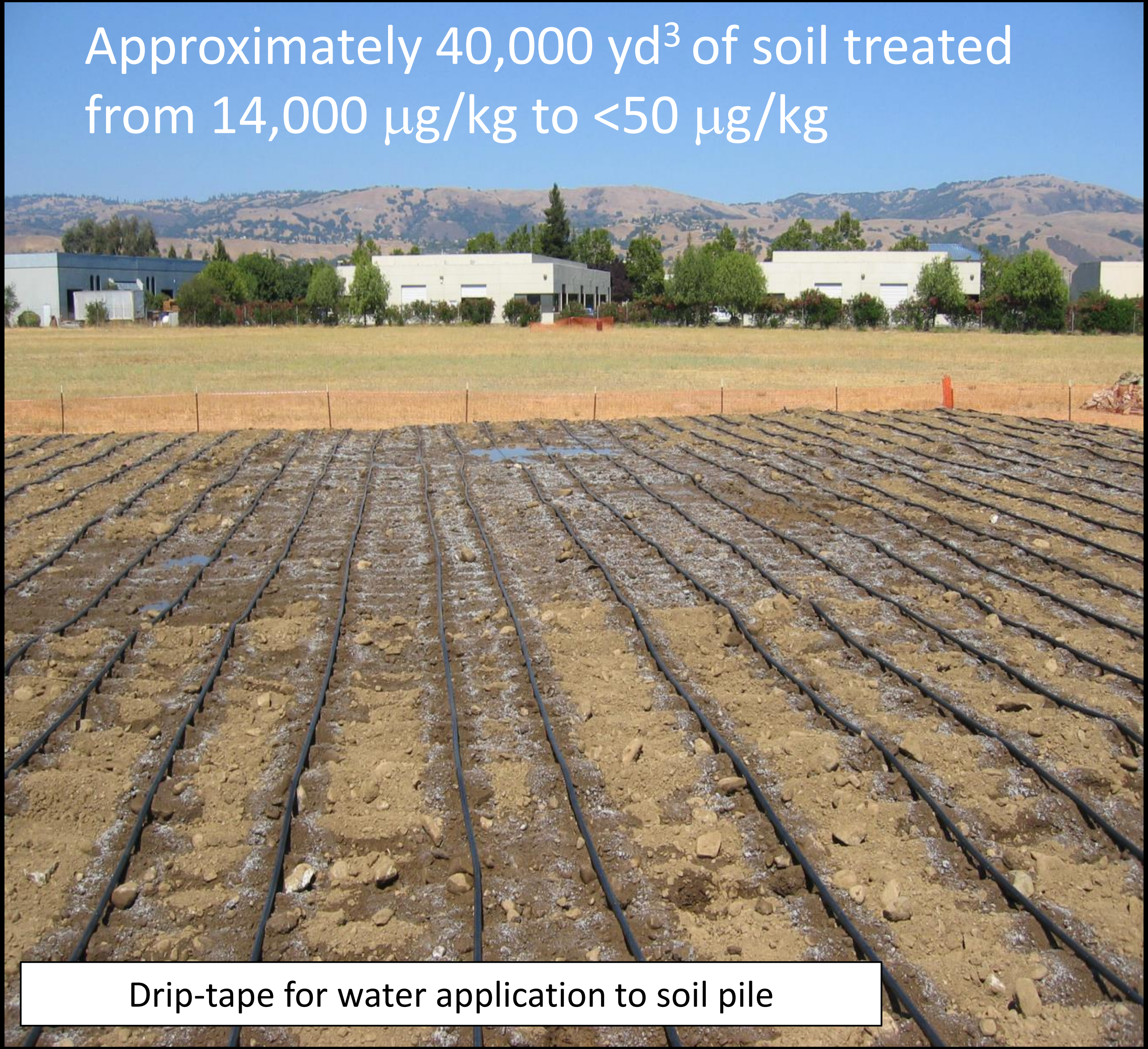


Construction of pile in 15 cm lifts

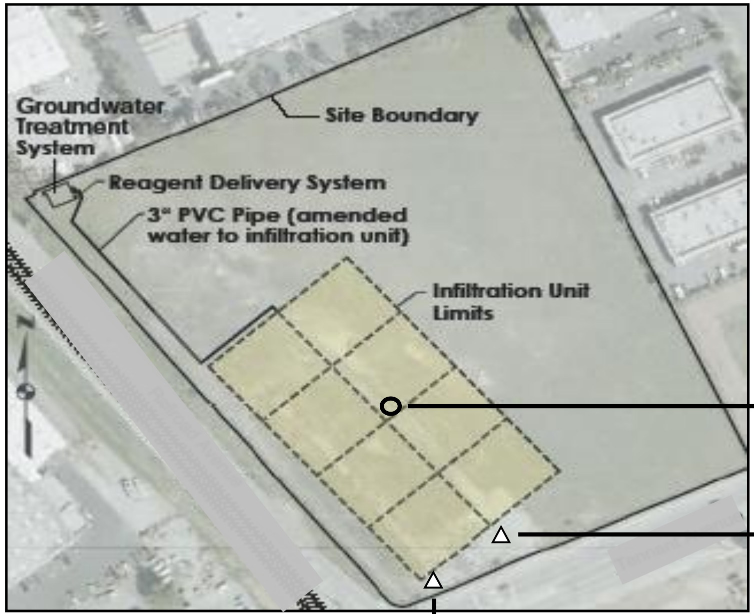
Electron donor being applied to the top of a construction lift

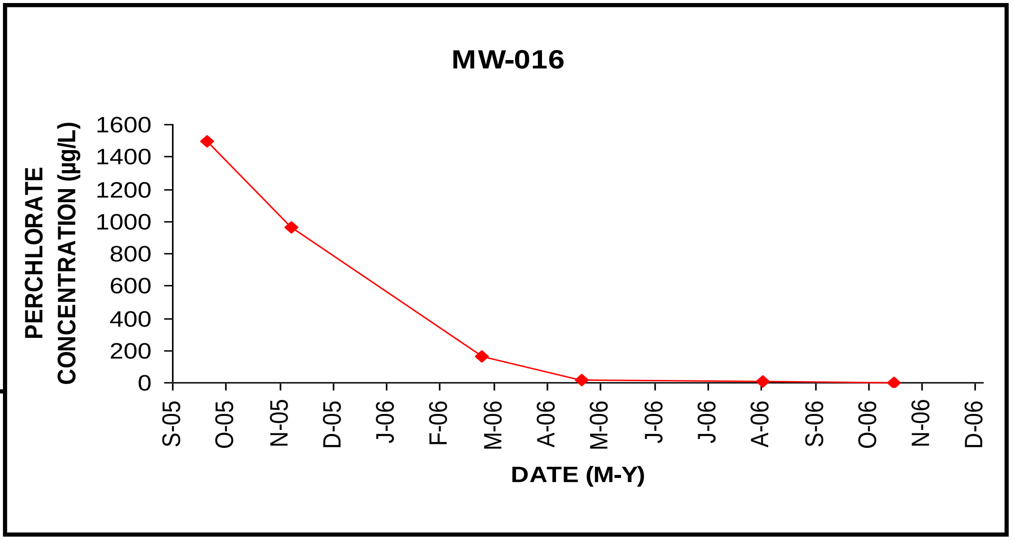
Approximately 40,000 yd^3 of soil treated from 14,000 µg/kg to <50 µg/kg

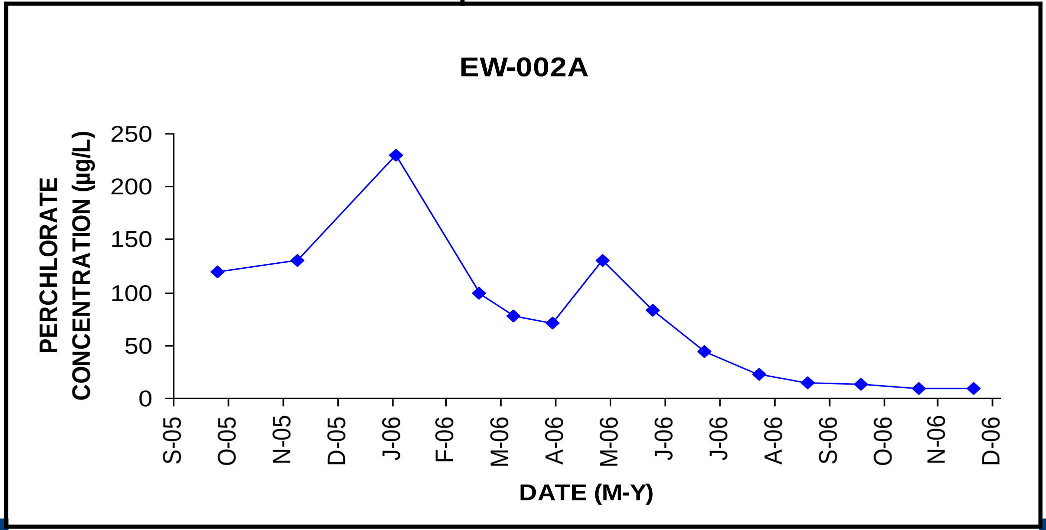


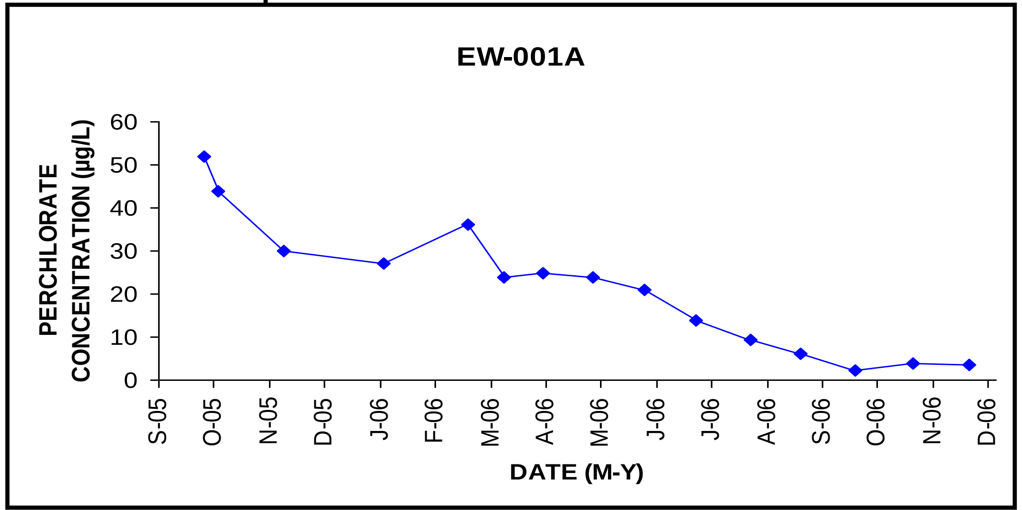
Drip-tape for water application to soil pile

Improvement of Groundwater Quality Following Soil Remediation









Selenium

Selenium Releases to the Environment

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- Naturally occurring non-metal in rock, including organic rich shale and coal areas
- Typically in insoluble reduced form, released when oxidized by exposure to air
- Present in process and surface water runoff from:
  - Coal and other mining sites (phosphate, gold)
  - Power industry - coal combustion flue gas desulfurization (FGD) water
  - Oil refineries
  - Land redevelopment of former wetland/anoxic areas where rock types contain Se
- Ecological toxicity – Se can cause embryo mortality in birds and larval deformities in fish

Selenium Characteristics/Behaviour

- Typically released as soluble selenate or selenite
- Elemental selenium is less soluble and can be precipitated under reducing redox conditions
- Biological reduction is an effective removal mechanism

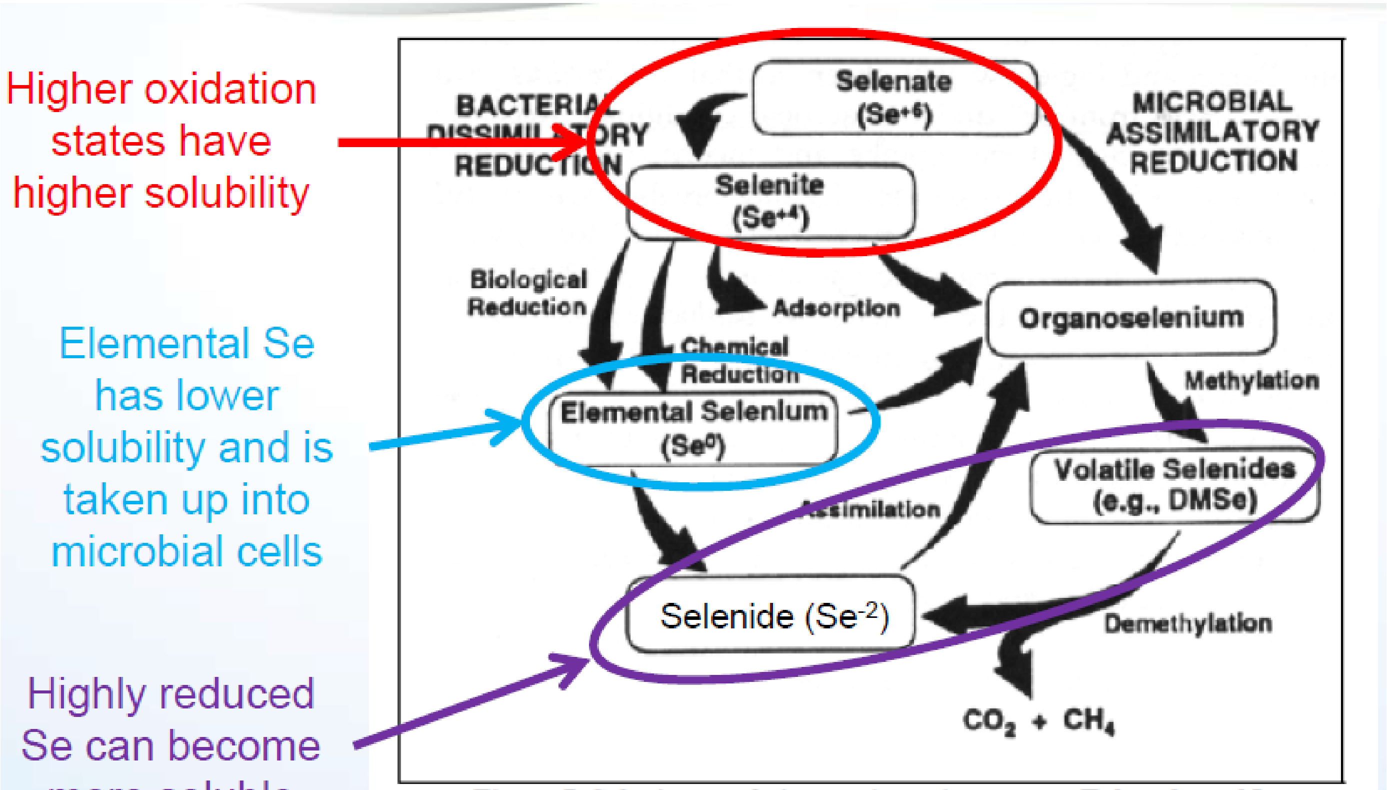

Figure 7. Selenium cycle in anoxic environments. Taken from 35.

SeO_4^{2-}	→	SeO_3^{2-}	→	Se
Se(VI)		Se(IV)		Se(0)

Groundwater Remediation Options

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Ex Situ

- **ZVI Canister**
  - <50 µg/L, low flow
- **Ion Exchange**
  - <100 µg/L, low flow
- **Bioreactors (FBR, FFR)**
  - <500 µg/L

In Situ

- **ZVI PRB**
  - <100 µg/L, low flow
- **Engineered Wetland**
  - <500 µg/L, low flow
- **Bioremediation**
  - <1,000 µg/L (high flow)
- **TreeWells?**
  - Possibly coupled with either bioremediation or ZVI (low flow)

Technology Innovation – Gravel Bed Bioreactors

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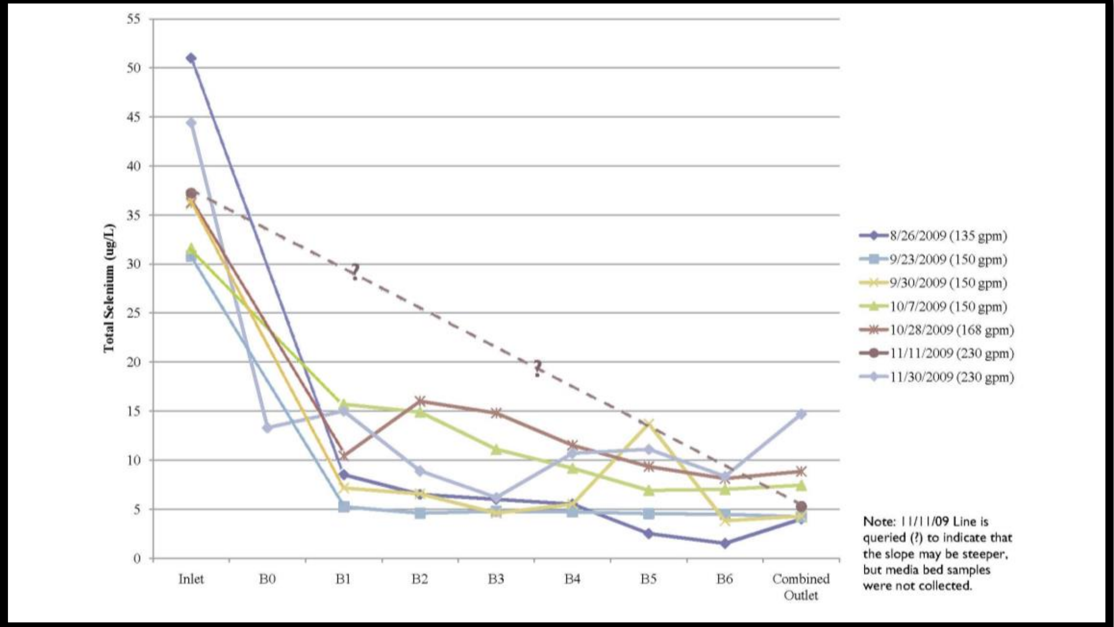
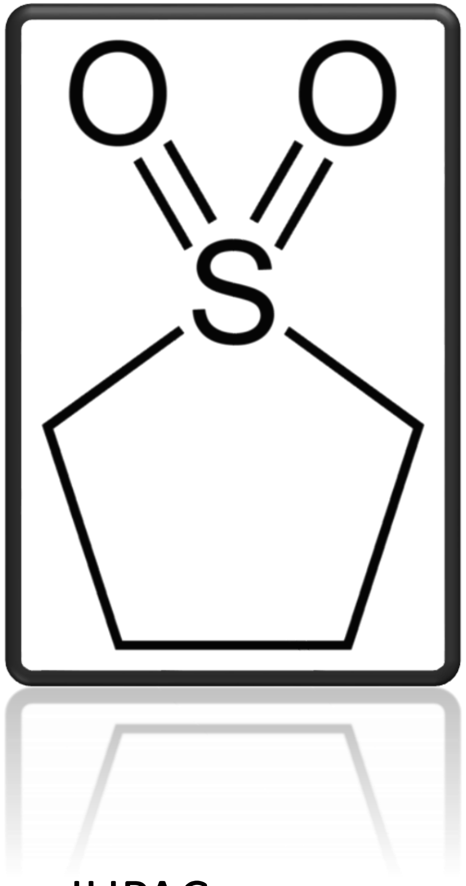
Photo 1 | Construction procedure of the biofilter cell: geomembrane liner installation for the bottom of the cell (inset photo). Startup placement of geogrids and matrix tank modules (above).



Sulfolane

Sulfolane Uses & Characteristics

- **Uses**
  - Initial use: Purifying butadiene
  - Sweetening of “acidic” or “sour” natural gas (Shell Sulfinol® Process) – Removes CO_2, H_2S, mercaptans
  - Extraction of aromatics (BTEX) from refinery stream
  - Production of insecticides, herbicides, fungicides
  - Process solvent in pharmaceutical manufacturing
- **Interesting Characteristics**
  - Density driven properties, can act as a DNAPL
  - Fairly soluble, limited sorption
  - Can migrate long distances (many kilometers) in groundwater



IUPAC name:
Thiolane, 1,1-dioxane

Soil/Groundwater Treatment Options

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Thermal Remediation/ Air Sparge/SVE
- Thermally stable solvent (287.3°C)
- Low Henry's low coefficient/low vapor pressure = low volatility
- Not proven, nor cost-effective for large scale remediation systems

Anaerobic Bioremediation
- Microbial anaerobic ring cleaving not energetically efficient for sulfolane
- Not cost-effective for large scale remediation systems

Chemical Oxidation
- Susceptible to destruction by chemical oxidation induced by free-radicals. More effective with oxidant (H_2O_2) + UV
- Not proven in large scale treatment systems

Adsorption
- Low K_{oc} value (0.07); high carbon usage at high concentrations/flow rates
- Outcompeted by other more sorptive organics
- Used in smaller point-of-use systems at low concentrations

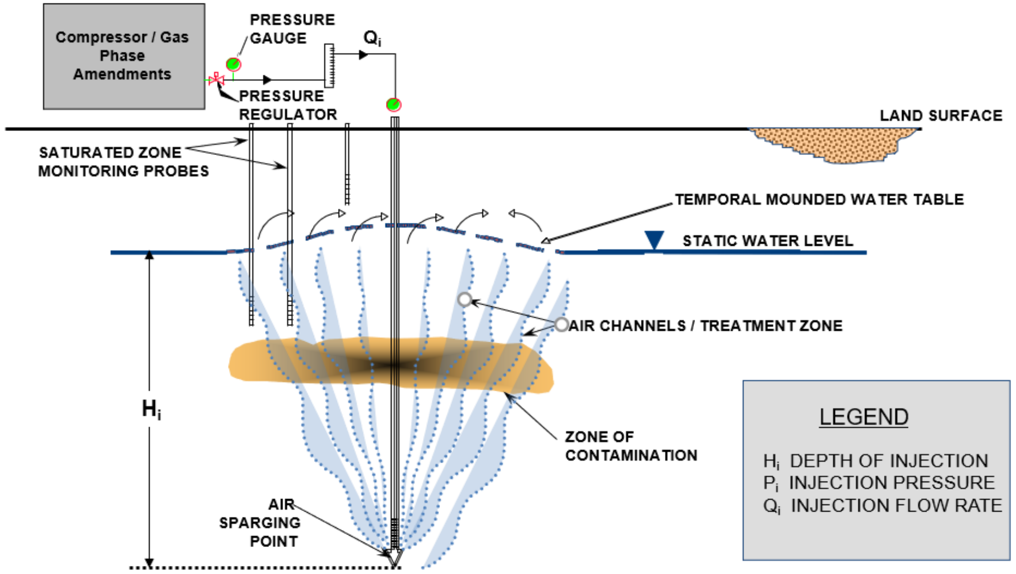
Aerobic Bioremediation/Bio - Sparge
- Microbial aerobic ring cleaving energetically efficient therefore readily degradable
- Applied at large scale groundwater treatment systems

Aerobic Bioremediation Options

- **Bioreactors**
  - Microbial film on either fixed or fluidized media
  - Generally used for < 10 mg/L sulfolane
  - Footprints vary, capital cost can be high
  - O&M costs tend to be high

- **Aerated Lagoons**
  - Microbial culture established in water/floc
  - Treats >>> mg/L sulfolane
  - Very large footprint

- **In Situ Biosparging**
  - Sparge air or oxygen into subsurface to promote oxidation
  - Typically <10 mg/L sulfolane



*Graphic courtesy: Princeton Groundwater Remediation Course

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Thank you for listening!

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