Environmental Solutions

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In Situ and Ex Situ Treatment Technologies for 1,4-Dioxane

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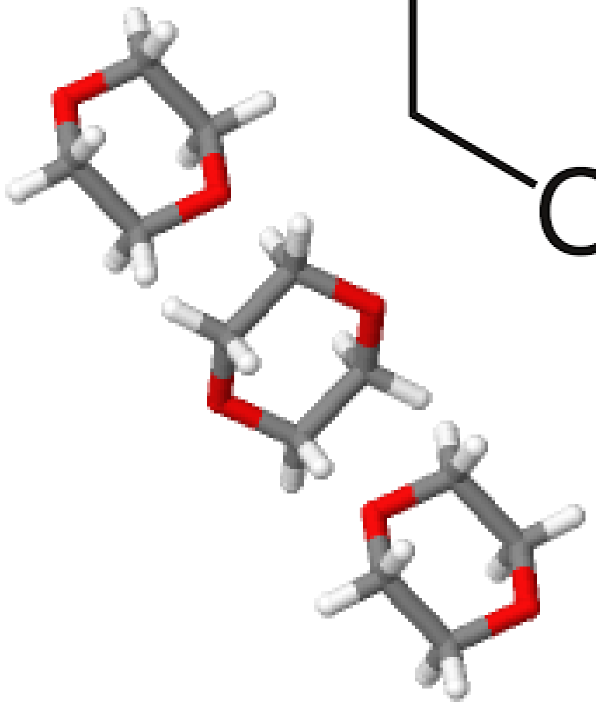
Overview

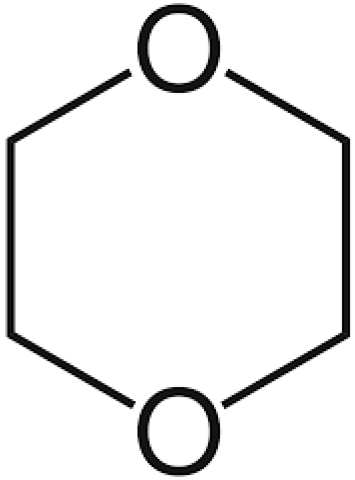
- 1,4-Dioxane is not PFAS or GenX
  - Conventional destructive treatment options
  - Sorptive treatment options
  - Emerging treatment options

- 1,4-Dioxane
  - Present in many waste streams including wastewater
  - This presentation will tend to focus on treatment at environmental sites

Why is 1,4-Dioxane Special?

- 1,4-Dioxane REALLY likes water
  - Miscible in water
  - Polar compound
  - Once in water, it wants to stay there (partitioning coefficients):
    - Negative Log K_{ow} (-0.27)
    - Low Henry's Coef (4.8 x 10^{-6} atm m^3/mole)
- 1,4-Dioxane is often co-mingled with other contaminants that have very different characteristics
  - Trichloroethene (TCE)
  - 1,1,1-Trichloroethane (1,1,1-TCA)





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Soil-Groundwater Partitioning

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- While primarily associated with groundwater, 1,4-dioxane has a low affinity for organic carbon

- Assuming F_{oc} of 0.005 (5,000 mg/Kg)
  - 1,4-Dioxane is primarily in the aqueous phase
  - Other contaminants are primarily sorbed to soil

$$K_d = K_{oc} * F_{oc}$$

Contaminant	Contaminant Distribution (%)	
	GW	Soil
1,4-Dioxane	70%	30%
PCE	21%	79%
TCE	19%	81%
DCE	51%	49%
1,1,1-TCA	27%	73%
1,1-DCA	43%	57%
1,2-DCA	51%	49%
Carbon Tetrachloride	19%	81%
1,2-Dichlorobenzene	6%	94%
Benzene	40%	60%
Toluene	18%	82%

Treatment Technologies

Remedial technologies typically exploit some aspect of the contaminant:

- Partitioning Coefficients:
  - Vapor pressure:
    - Air Sparging/Soil Vapor Extraction (AS-SVE)
    - Thermally enhanced SVE
  - Organic Partitioning Coefficients
    - Activated Carbon
    - Etc
  - Henry's Law
    - Air stripping
    - SVE
- Chemical transformations
  - Bioremediation
  - Chemical oxidation
  - Chemical reduction
  - Chemical precipitation/Metals stabilization

A good engineer/scientist can get most technologies to "work." Questions are how well, how efficient and at what cost?

Partitioning Coefficients

Characteristics	Ratio/Comparison	Units	1,4-Dioxane	1,1,1-TCA
Vapor Pressure	Gas - Pure Phase	mm Hg @ 20 °C	29	96
Henry's Law	Gas/Water	atm-m3/mole	4.8×10^{-6}	1.8×10^{-2}
K_{ow}	Octanol/water	dimensionless	0.54	302
K_{oc}	Organic Carbon/Water	dimensionless	17	110

EPA Technical Fact Sheet: 1,4-Dioxane, Nov 2017

Watts “Hazardous Wastes: Sources, Pathways, Receptors,” Wiley, 1998

Air Stripping

Contaminant	Henry's Law Constant (atm-m3/mole @ 25 °C)
1,4-Dioxane	4.8×10^{-6}
TCE	9.1×10^{-3}
1,1,1-TCA	1.8×10^{-2}
1,1-DCE	2.1×10^{-2}
1,2-DCA	9.1×10^{-4}

- 1,4-Dioxane favors the aqueous phase
- Treatment would require large systems
- NOT FAVORABLE

Vapor Extraction

- Pure phase vapor extraction
  - 1,4-dioxane has lower vapor pressure than many other contaminants
  - Less efficient treatment possible

Contaminant	Vapor Pressure (mm Hg @ 20°C)
1,4-Dioxane	29
TCE	58
1,1,1-TCA	96
1,1-DCE	495
1,2-DCA	64

- Soil Vapor Extraction (SVE)
  - 1,4-Dioxane also partitions into moisture in soil
  - Effectively air stripping
    - NOT FAVORABLE
- Extreme SVE
  - Increase temperature
    - Beneficial non-linear response
  - Increase PVs flushed
- Not expected to be common remedy but a level of treatment likely

Sorption Technologies

- 100% of “typical” carbon requirement
  - 99% 1,4-dioxane on carbon at equilibrium

- Carbons are expected to act differently
  - Need to consider sorption capacity
  - 1,4-dioxane capacity low compared to most other contaminants
  - Low efficiency treatment possible

- Specific sorbents
  - DOW Ambersorb563™
  - >99% removal observed
  - Higher capacity

Bioremediation

- Aerobic co-metabolic treatment
  - i.e-Propane, ethane, isobutane, etc
- Aerobic-direct treatment
  - Bench scale evidence
  - Specific microbes
- Anaerobic
  - Still needs to be proven
- Kinetics:
  - Aggressive biosystem
    - Half life: “days”
  - Less aggressive system
    - Half life: “months”
- Common co-contaminants found to inhibit:
  - 1,1-DCE>TCE>TCA
- Common co-contaminants may not be treated
- Has promise as a remedy, but likely very complex, potential inhibition

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Chemical Oxidation

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- Activated Persulfate
  - Excellent
- Hydrogen peroxide
  - Excellent
- Ozone
  - Excellent
- Permanganate
  - Limited kinetics (half life of ~1 month at ~10 g/L)

Radical	Reaction Rate
Hydroxyl Radical	3.1×10^9
	2.5×10^9
Sulfate Radical	7.2×10^7
	1.6×10^7

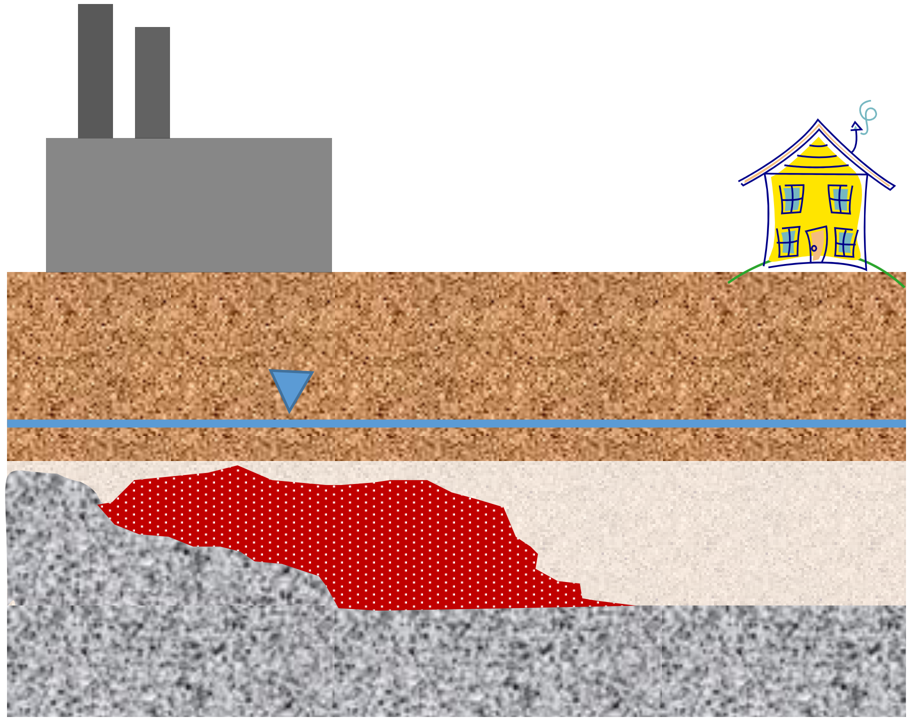
Certain activation methods for persulfate and hydrogen peroxide are known to also treat 1,1,1-TCA, DCA(s), TCE and DCE

Treating 1,4-Dioxane

Design Fundamentals

- Sufficient reagents

- Establish contact



Chemical oxidation, reduction, and bioremediation work by establishing contact between a sufficient mass of reagents with the contaminant mass in the subsurface

Sufficient Mass

- All transformative technologies (ISCO, ISCR, Bioremediation, etc) work by:
  - Adding a sufficient mass of reagents for the mass of contamination
  - Establishing contact of that mass with the contaminant

- Transformative technologies will react with:
  - Target demand
  - Non-target demand

- No system is completely efficient = Safety Factors
  - Remediation has inherent uncertainties (contaminant mass, contaminant distribution, reagent distribution, etc)
  - Application of reagents

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Establishing Contact

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- Contact is critical for chemical reaction to occur.
- Number of contaminant molecules and oxidant radicals influence potential contact in the aquifer.
- Contaminant partitioning between soil and groundwater largely dependent upon fraction of organic carbon on soil (F_{oc}).
- 1,4-Dioxane tends to be in aqueous phase more than other contaminants.

Establishing Contact

- Reagents and contaminants must contact each other
  - Contamination on soils
    - Injection or soil mixing of reagents
  - Contamination in groundwater
    - Permeable reactive barriers (PRBs)
      - Transects or source areas
      - Injected or trenched
    - Recirculation
    - Pull-push
    - Injection (can work, but may displace some GW)

Establishing Contact

KLOZUR® SP

Aqueous Reagents

"Solid" Contaminants

Injection Strategy

Aqueous Contaminants

"Solid" Reagents

KLOZUR® KP

PRB Strategy

Aqueous and Solid Reagents

Aqueous and "Solid" Contaminants

Soil Mixing

Case Study

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Former Industrial Facility in the Northeast

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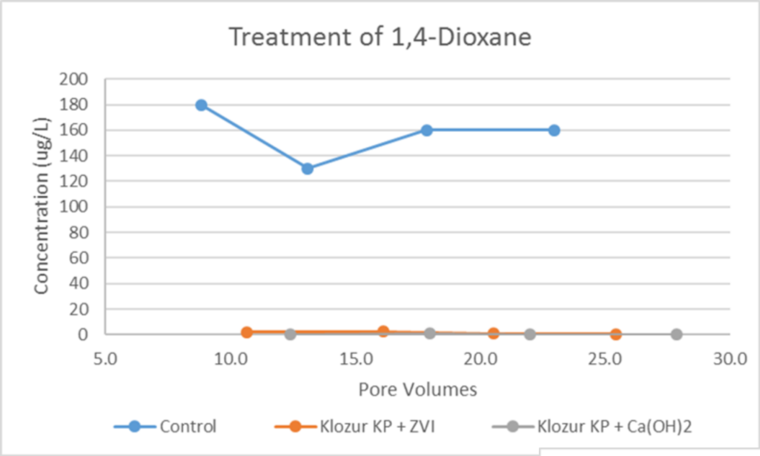
- Consultant: AECOM
- Residual 1,4-dioxane, TCA , and TCA daughter products
  - 1,1,1-Trichloroethane and 1,1,2-Trichloroethane (TCAs)
  - 1,1-DCA and 1,2-DCA
  - 1,1-DCE
- Silty soils with sand lenses
- Klozur KP PRB selected to establish contact with aqueous phase reagents

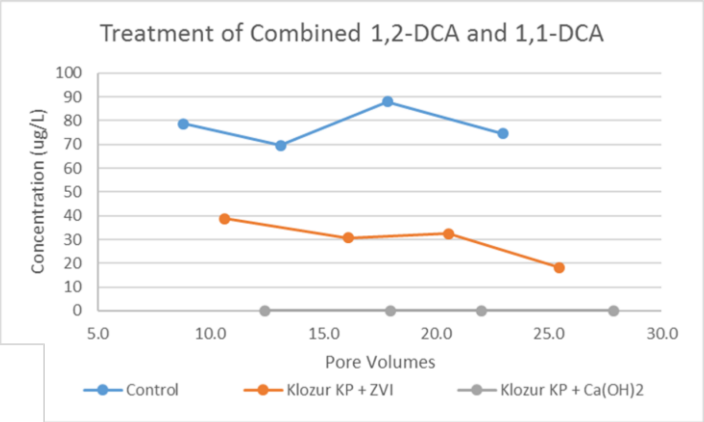
Klozur KP: Column Bench Test

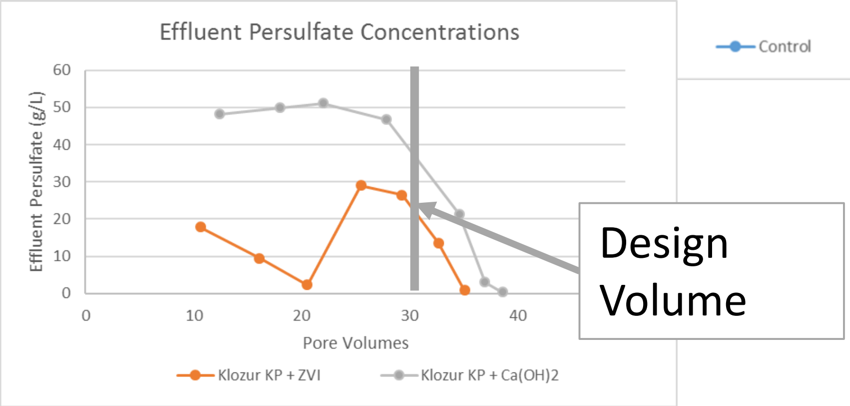
1) Oxidative pathway
   - 1,4-Dioxane

2) Reductive Pathway
   - DCA(s)

3) KP persisted intended 30 PVs





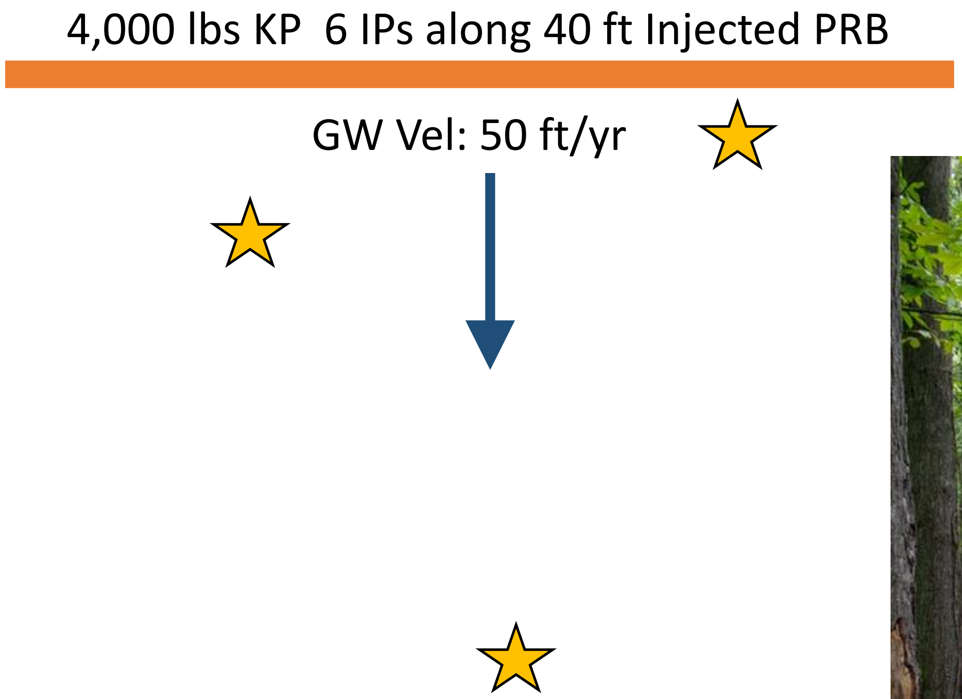


Pilot Study

- Pilot Conducted Early December 2017

- Injected PRB (40 ft)
  - Solid slurry
  - 6 DPT points
  - 20 to 30 ft bgs
  - Designed for 6 month persistence

- Reagents:
  - Klozur KP
  - Klozur SP
  - Hydrated Lime
  - 25% NaOH



Persistence and Distribution

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4,000 lbs Klozur KP 6 IPs along 40 ft Injected PRB

GW Vel: 50 ft/yr

- Monitoring wells downgradient in targeted vertical interval:
  - Location 1 (~3 ft)
  - Location 2 (~10 ft)
  - Location 3 (~25 ft)

Event	Location 2	
	Persulfate (g/L)	pH
Baseline	NA	7.2
3 month	3	6
8 month	2.5	6.8

Event	Location 1	
	Persulfate (g/L)	pH
Baseline	NA	6.9
3 month	7.2	12
8 month	14.2	12

Event	Location 3	
	Persulfate (g/L)	pH
Baseline	NA	7.2
3 month	NA	NA
8 month	8	6.5

Treatment

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4,000 lbs Klozur KP 6 IPs along 40 ft Injected PRB

GW Vel: 50 ft/yr

Event	Location 1: Contaminant Concentrations (µg/L)				
	DCA	DCE	1,4-Dioxane	VOCs*	Reduction VOCs (%)
Baseline	21	40	30	115	0%
3 month	0.2	nd	nd	0.2	99.8%
6 month	0.2	nd	nd	0.2	99.8%

* Detected VOCs not including acetone

Event	Location 2: Contaminant Concentrations (µg/L)				
	DCA	DCE	1,4-Dioxane	VOCs*	Reduction VOCs (%)
Baseline	44	72	55	184	0%
3 month	10	11	nd	26	86%
6 month	16	nd	16	34	82%

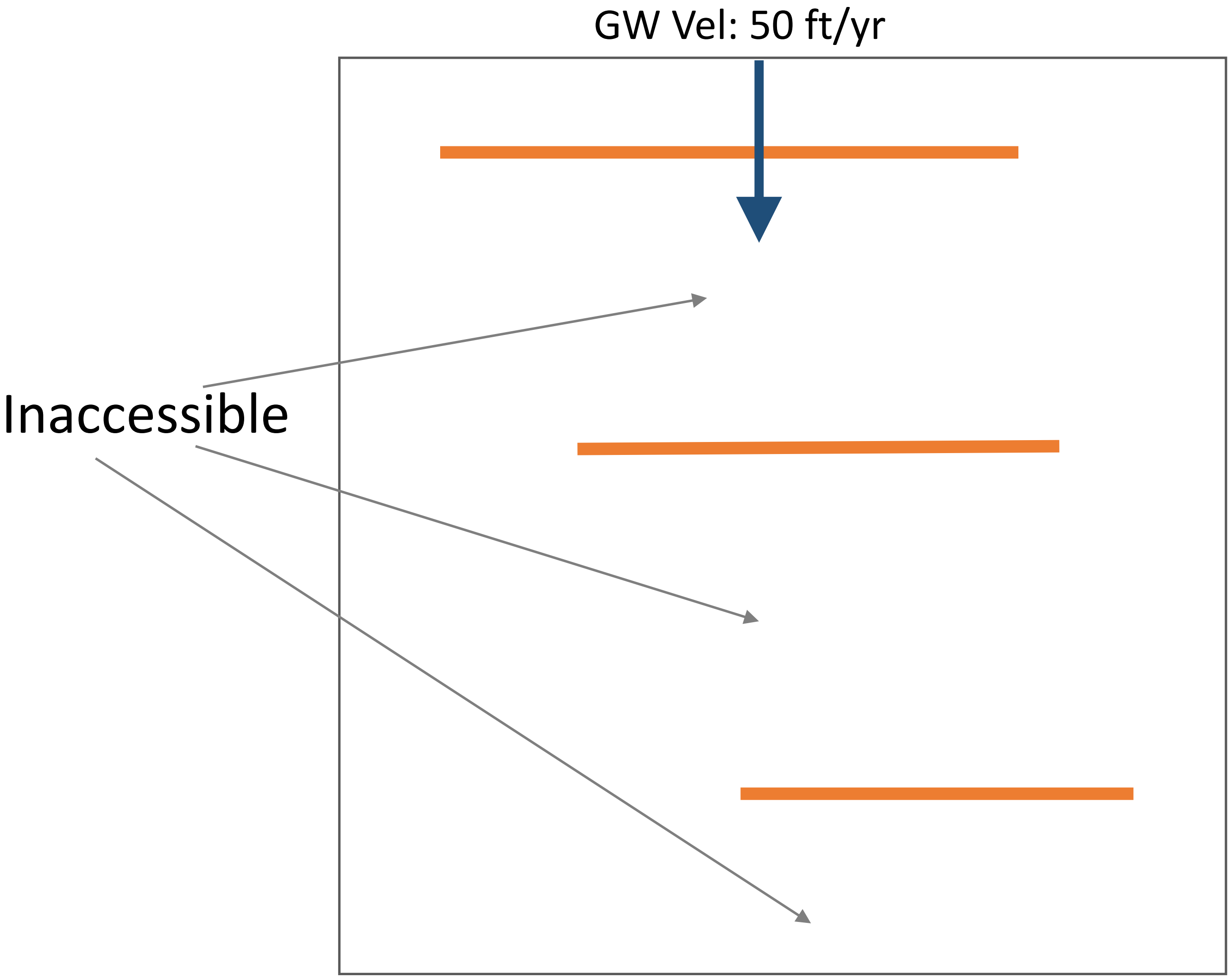
* Detected VOCs not including acetone

Event	Location 3: Contaminant Concentrations (µg/L)				
	DCA	DCE	1,4-Dioxane	VOCs*	Reduction VOCs (%)
Baseline	89	270	200	610	0%
3 month	46	82	69	216	65%
6 month	63	30	110	230	62%

* Detected VOCs not including acetone

Full Scale

- Implemented August 2018
- Three transects/PRBs
- Largely targeting 1,4-Dioxane
- Cut off source long enough and clean inaccessible zones



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Summary

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- Current technologies for 1,4-Dioxane
  - Primary
    - Sorption-resins
    - Chemical oxidant
  - Developing
    - Bioremediation
  - Have been tested:
    - Extreme SVE
- 1,4-Dioxane is different from most contaminants
  - Affinity for water
  - Typically co-mingled
- Treatment is more than technologies
  - Establish contact
  - Sufficient reagents at all times
- Treatment of 1,4-Dioxane and co-mingled contaminants is ongoing

Questions

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