Keys to Successful Treatment of 1,4-Dioxane with Klozur® Persulfate

Brant Smith, Technical Applications Manager: ISCO
PeroxyChem
PeroxyChem is a company of Evonik Industries AG

April/May 2020

Field-Proven Portfolio of Remediation Technologies

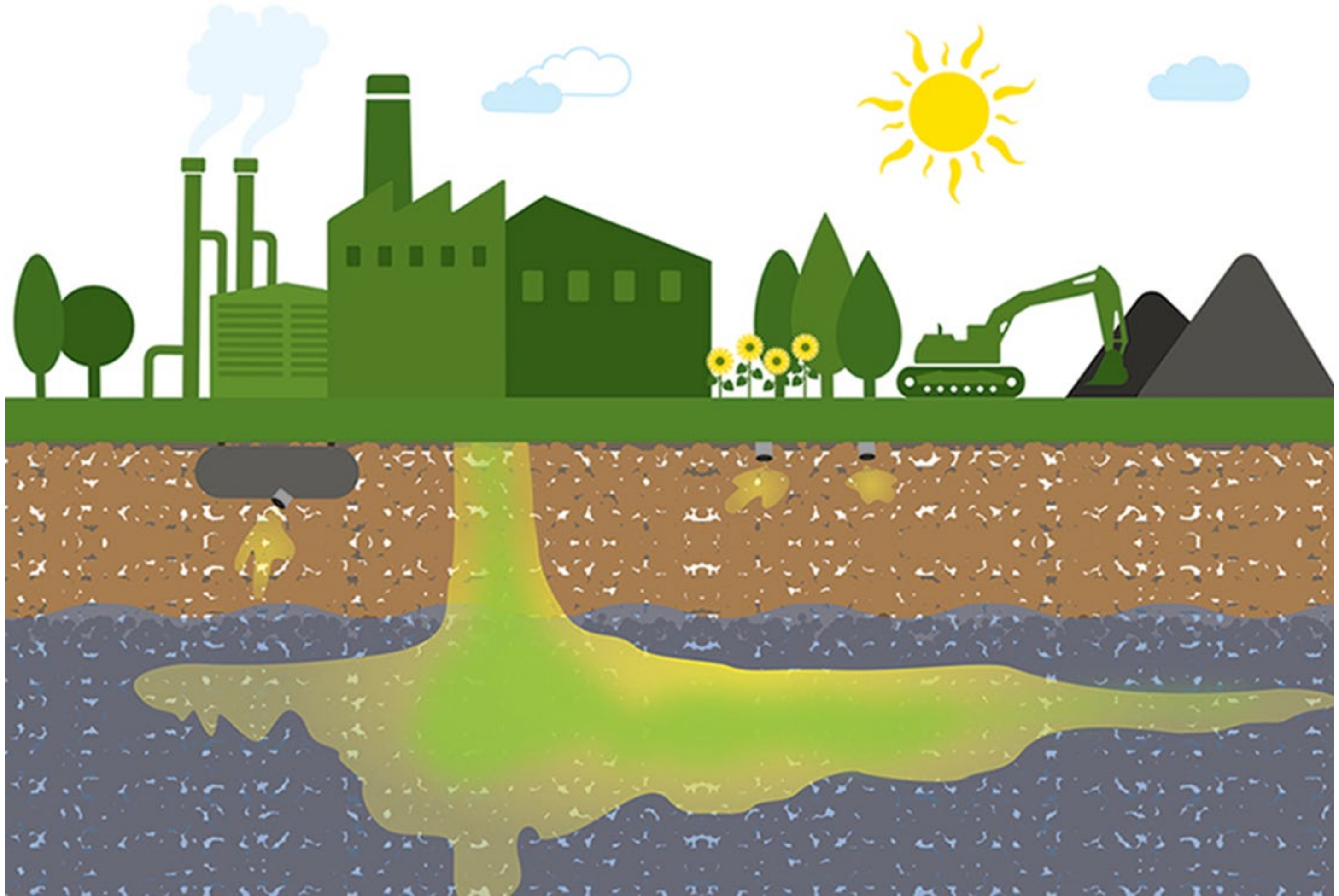
Chemical Oxidation
- Klozur® Persulfate Portfolio
- Hydrogen Peroxide

Chemical Reduction
- EHC® Reagent
- EHC® Liquid
- Daramend® Reagent
- Zero Valent Iron
- GeoForm™ Reagents

Aerobic Bioremediation
- Terramend® Reagent
- PermeOx® Ultra

Enhanced Reductive Dechlorination
- ELS® Microemulsion
- ELS® Concentrate

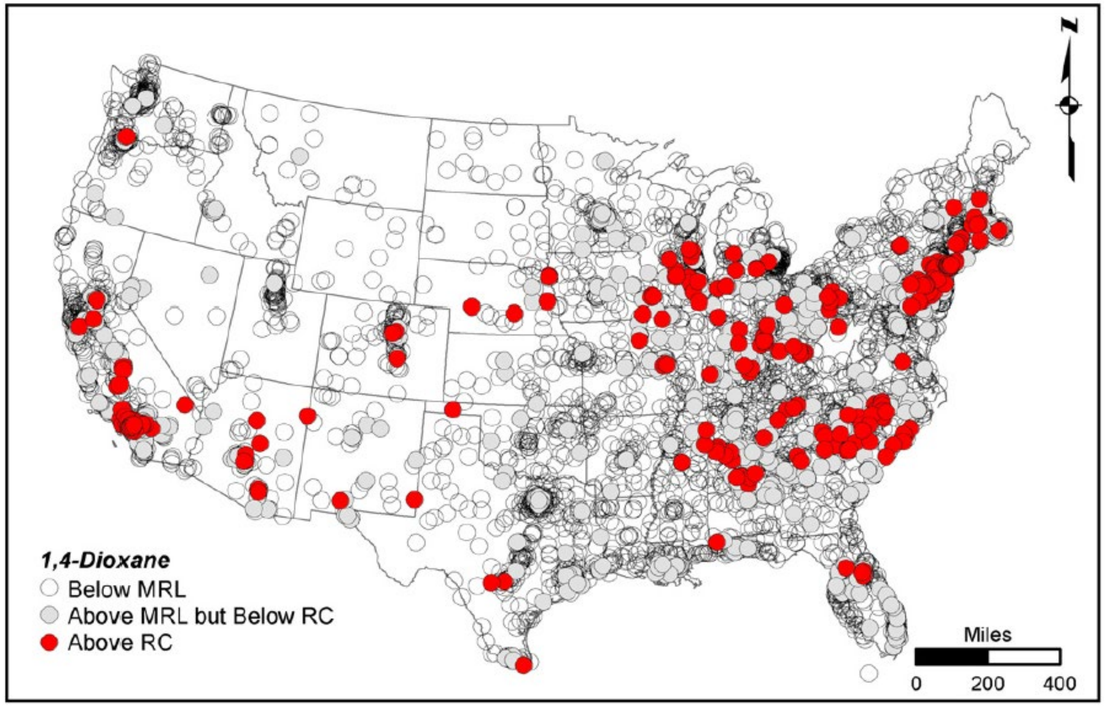
Metals Remediation
- MetaFix® Reagents



Outline

- 1,4-Dioxane overview
- Treatment with Klozur® persulfate
- Why is 1,4-Dioxane different?
  - Key characteristics
  - How to establish contact
- Case Study
- Summary

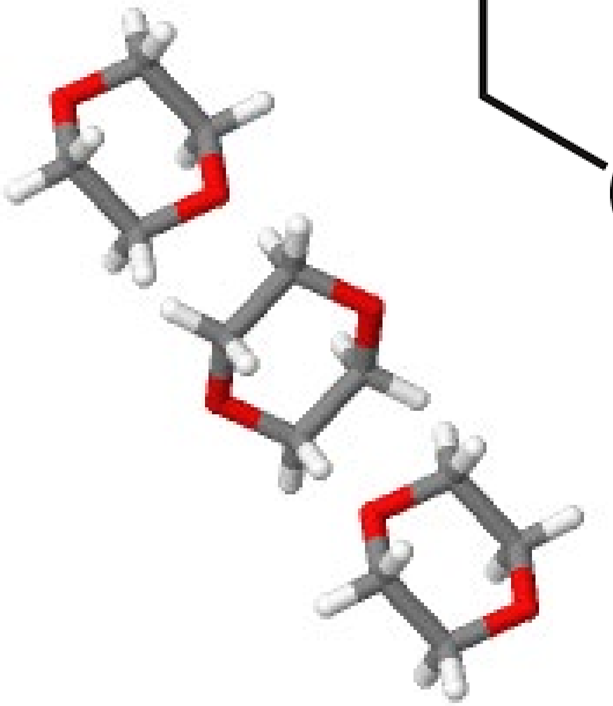
Drinking Water Occurrence of 1,4-dioxane based on EPA UCMR3

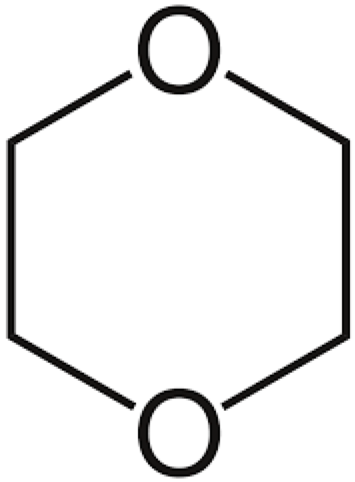


Adamson et al (2017)

1,4-Dioxane

- Industrial chemical
- Heterocyclic ether
- Has been identified as an “Emerging Contaminant”





Common Uses for 1,4-Dioxane

PeroxyChem

- Solvent
  - Inks and adhesives
  - Specialized analytics
  - Cellulose acetate membrane production
- Chlorinated solvent stabilizer
- Also found in:
  - Gluten-free bread (ethyl hydroxyethyl cellulose)
  - Ice cream (polysorbate 60)
  - Paints, detergents, coolants, de-icers, etc
  - Detergents
  - Personal Care Products

1,4-Dioxane still in use today

2015 US EPA Toxic Release Inventory listed 25 manufacturers and 4-5M lbs of waste

Environmental Releases

PeroxyChem

- Stabilizer for chlorinated solvents
  - 1,1,1-Trichloroethane (TCA)
    - % level concentrations of 1,4-dioxane
  - Trichloroethene (TCE) debated

- 1,4-Dioxane found at 193 sites of 589 (Adamson, 2016)
  - Co-occurring contaminants
  - At sites where 1,4-Dioxane was included in analytical program, it was detected at:
    - 52 percent of TCE sites
    - 70 percent of TCA sites

Health Risks and Standards

PeroxyChem

- Short-term exposure: nausea, drowsiness, headache, and irritation of the eyes
- Chronic exposure: dermatitis, eczema, drying and cracking of skin, liver and kidney damage
- *Likely human carcinogen*

State	Guideline (µg/L)	Source
Alaska	77	AL DEC 2016
California	1.0	Cal/EPA 2011
Colorado	0.35	CDPHE 2017
Connecticut	3.0	CTDPH 2013
Delaware	6.0	DE DNR 1999
Florida	3.2	FDEP 2005
Indiana	7.8	IDEM 2015
Maine	4.0	MEDEP 2016
Massachusetts	0.3	MADEP 2004
Mississippi	6.09	MS DEQ 2002
New Hampshire	0.25	NH DES 2011
New Jersey	0.4	NJDEP 2015
North Carolina	3.0	NCDENR 2015
Pennsylvania	6.4	PADEP 2011
Texas	9.1	TCEQ 2016
Vermont	3.0	VTDEP 2016
Washington	0.438	WA ECY 2015
West Virginia	6.1	WV DEP 2009

US EPA, 2017

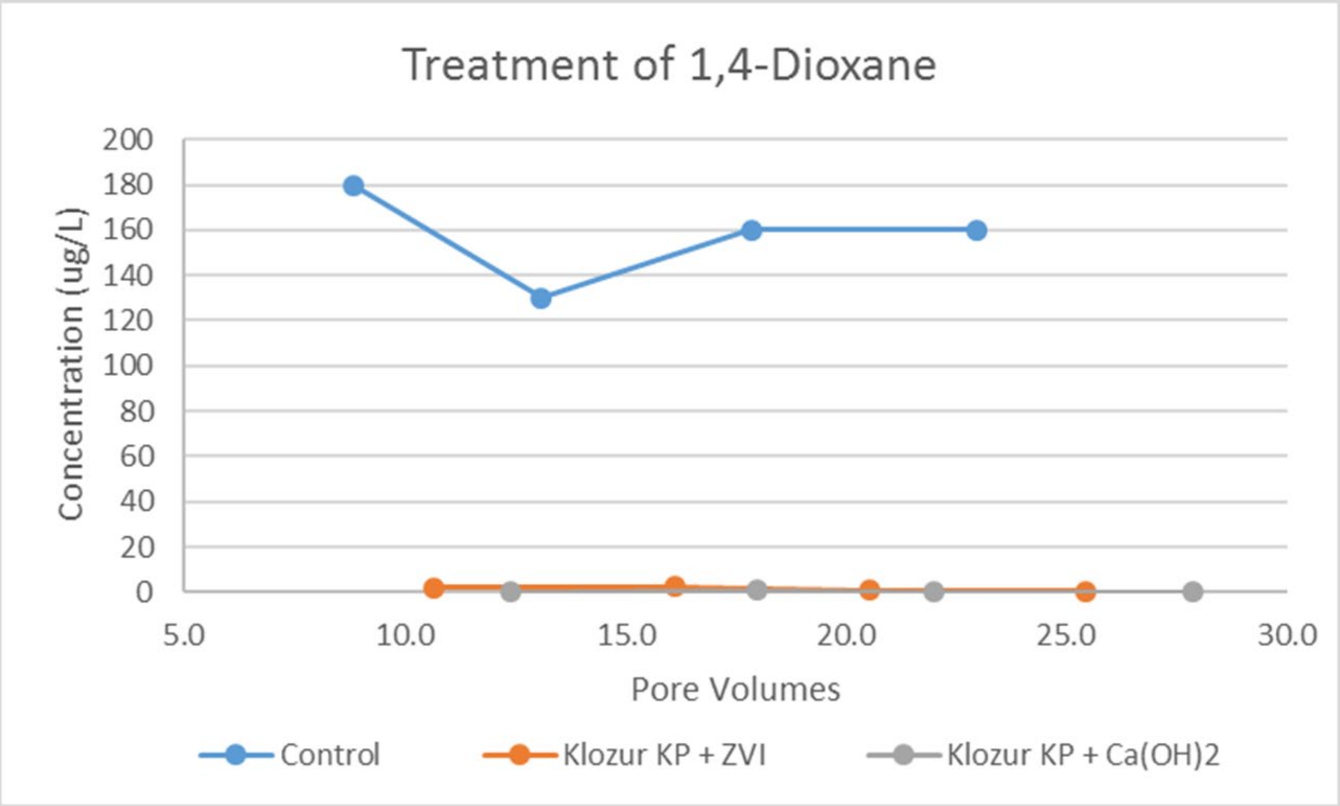
Is it Treatable?

- Several references regarding how difficult it is to treat 1,4-dioxane
  - Air stripping/SVE are not favorable
    - Low Henry's Coefficient (4.8 x 10^{-6} atm m^3/mole)
  - Bioremediation
    - Cometabolic treatment of 1,4-dioxane
    - 1,4-Dioxane treatment can be inhibited by comingled contaminants (Zhang et al (2016))
    - Sequential treatment technologies for 1,4-dioxane and chlorinated compounds
  - Non-radical based ISCO can be have slow kinetics

- Numerous studies confirm rapid successful treatment with activated persulfate (Zhong et al (2015); Felix-Navarro et al (2013); Zhao et al (2014); Kambhu et al (2017); Smith et al, (2018); Cashman et al, (2019); etc)
  - Rapid treatment with sulfate and hydroxyl radicals

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

Continuous Treatment of 1,4-Dioxane in Flow Through System



- Consultant: Weston Solutions
- Former chemical waste storage and bulking facility
- Residual 1,4-dioxane and 1,1,1-Trichloroethane (1,1,1-TCA) daughter products
  - 1,1-Dichloroethane (1,1-DCA)
  - 1,2-Dichloroethane (1,2-DCA)
  - 1,1-Dichloroethene (1,1-DCE)
- Soil matrix of clayey till was bench tested. Site includes sand lenses.

Smith et al. (2018)

What Makes 1,4-Dioxane Different?

PeroxyChem

1. 1,4-Dioxane REALLY likes water
   - Miscible in water
   - K_{oc} and K_{ow}

2. Diffusion of high aqueous concentrations
   - Creation of secondary sources

3. Often comingled with TCA, DCA(s), TCE and DCE
   - Oxidative vs reductive treatment technologies

1. 1,4-Dioxane Really Likes Water

PeroxyChem

Once in water, it wants to stay there

- K_{oc} = Partitioning Coefficient with Organic Carbon and Water
- K_{ow} = Partitioning Coefficient with Octanol and Water

Compound	Solubility (mg/L)	Log K_{ow}	Log K_{oc}	K_{oc}
1,4-Dioxane	Miscible	-0.27	1.23	17
1,1,1-TCA	657	2.48	2.04	110
TCE	1,312	2.71	2.22	166
1,1-DCE	3,920	2.07	1.58	38
1,1-DCA	5,060	1.79	1.73	53

EPA (2017); EPA Partitioning Doc
Watts (1998)

1. Partitioning Applied

- K_d = Soil/GW Distribution Coefficient

$$K_d = Ko_c * foc = \frac{Soil\ (\frac{g}{Kg})}{GW\ (\frac{g}{L})}$$

- Retardation Factor
  - Times faster GW is compared to contaminant transport

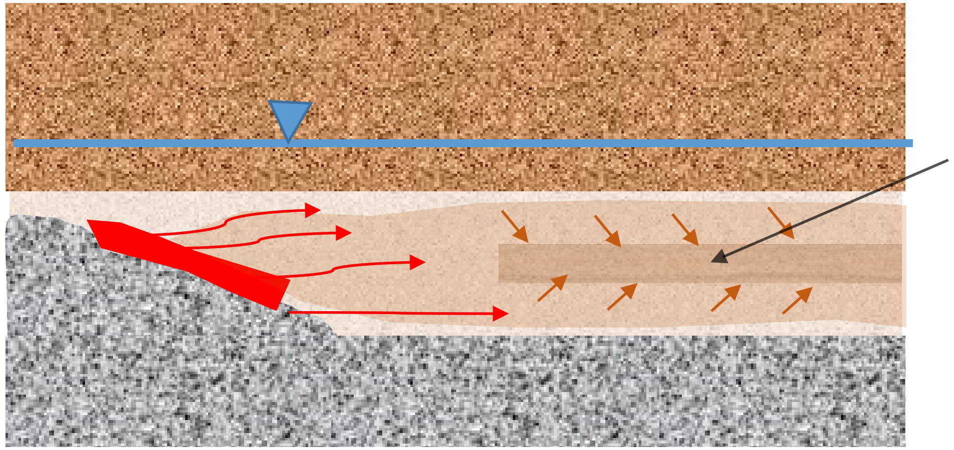
$$R = 1 + \frac{\rho B}{n} * Kd$$

Contaminant	EPA K_{oc}	F_{oc}	Contaminant Distribution (%) GW	Contaminant Distribution (%) Soil	R[1]
1,4-Dioxane	17	0.005	70%	30%	1.8
1,1,1-TCA	110	0.005	27%	73%	6.5
DCE	38	0.005	51%	49%	2.9
TCE	166	0.005	19%	81%	9.3
1,1-DCA	53	0.005	43%	57%	3.7
Note:	1. Assuming 1.5 g/cm^3 soil bulk density and effective pore volume of 0.15				

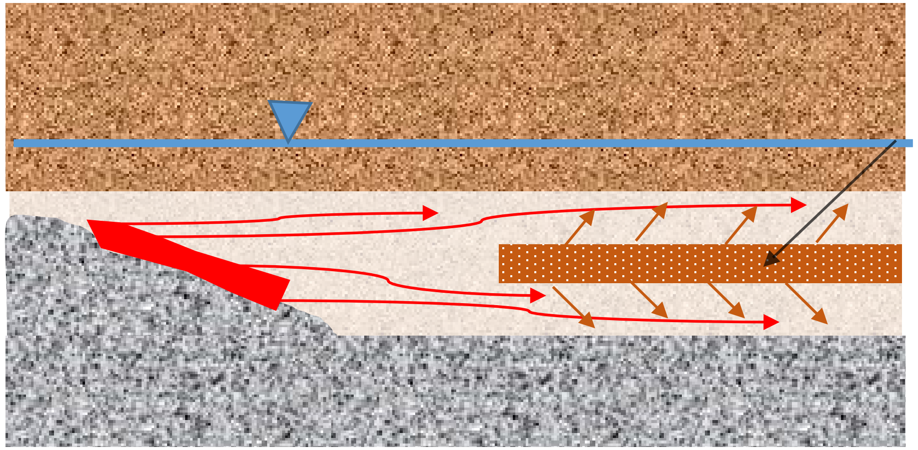
Foc = Fraction of organic carbon on soils
pB = Bulk density of soil
n = Effective porosity

2. Diffusion into Less Permeable Soils

PeroxyChem



Early release



Older Plume

Potential TCA DNAPL source area evolution

1. Negative K_{ow}/Miscible solubility limit, high concentrations of 1,4-Dioxane flood into aqueous phase
2. High concentrations of aqueous phase 1,4-dioxane diffuse into lower permeable units
3. 1,4-Dioxane back diffuses from lower permeable units once concentration gradient reverses

Adamson (2017)

3. Comingled Contaminants

PeroxyChem

- Common contaminants comingled with 1,4-Dioxane:
  - 1,1-Trichloroethane (TCA)
    - 1,1-Dichloroethene (1,1-DCE)
    - 1,1-Dichloroethane and 1,2-dichloroethane (1,1-DCA & 1,2-DCA)
  - Trichloroethene (TCE)

- TCA and DCA(s) are best treated via a reductive pathway

- 1,4-Dioxane is typically treated by oxidative pathway
  - Hydroxyl and sulfate radicals

Degradation Pathways

PeroxyChem

Oxidative (radicals)	Either	Reductive
Petroleum Hydrocarbons	PCE, TCE, DCE and VC	Carbon Tetrachloride
MGP Residuals	Chlorobenzenes	1,1,1-Trichloroethane
BTEX	Phenols	Dichloroethanes
PAHs	Select Pesticides	Select Pesticides
Oxygenates	Select Fluorinated Compounds	Select Energetics
1,4-Dioxane	PCBs	
	Select Energetics	

Activation Methods: Alkaline, Hydrogen Peroxide, and Heat

Activation Method: Iron Chelate

Key Characteristic Summary

PeroxyChem

- 1,4-Dioxane has different characteristics compared to many common contaminants
  - Impacts fate, transport and even conceptual models

- Comparitively 1,4-Dioxane
  - Is in Groundwater
    - But, soil can not be ignored (K_{oc} = 17)

  - At some sites you will need primary focus in on soils
    - High organic content
    - Source zones with low perm soils where TCA DNAPL had been present

- 1,4-Dioxane is usually comingled with other contaminants
  - Activated persulfate can treat common comingled contaminants and 1,4-dioxane

Treatment with Klozur® Persulfate

Treatment with Klozur® Persulfate

PeroxyChem

- Properly activated persulfate can treat 1,4-dioxane and common comingled contaminants

- Primary questions are:
  - Which Klozur persulfate technology?
  - How to establish contact?

ISCO works by establishing contact between a sufficient mass of activated oxidant with the contaminant mass in the subsurface

Klozur® Persulfates

PeroxyChem

KLOZUR® SP

- Environmental grade sodium persulfate

KLOZUR® KP

- Environmental grade potassium persulfate

Key Differences:

- Solubility
- Na^+ vs K^+ residual

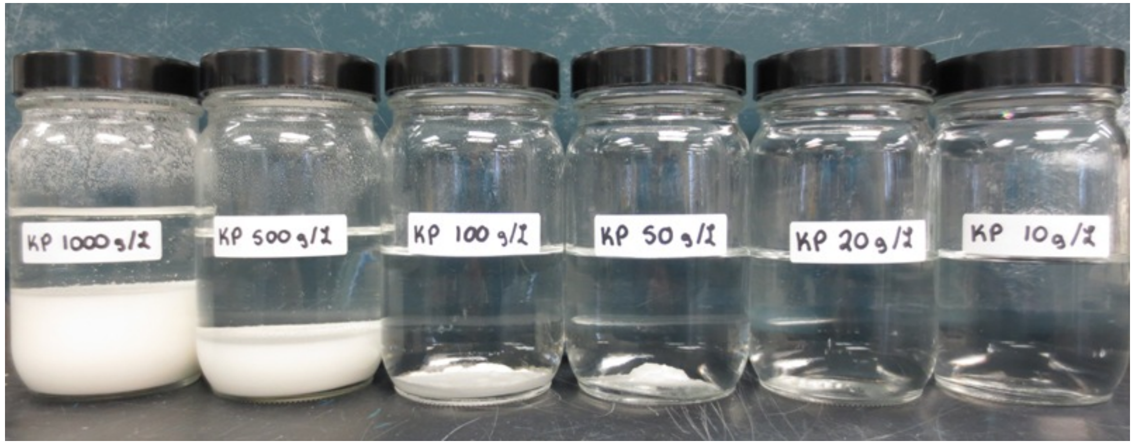
Temperature (◦C)	Klozur SP		Klozur KP	
	wt%	g/L	wt%	g/L
0	36.5	480	1.6	17
10	40.1	540	2.6	29
20	41.8	570	4.5	47
25	42.3	580	5.7	59

Characteristic	SP	KP
Formula	$Na_2S_2O_8$	$K_2S_2O_8$
Molecular Weight	238.1	270.3
Crystal density (g/cc)	2.59	2.48
Color	White	White
Odor	None	None
Loose bulk density (g/cc)	1.12	1.30

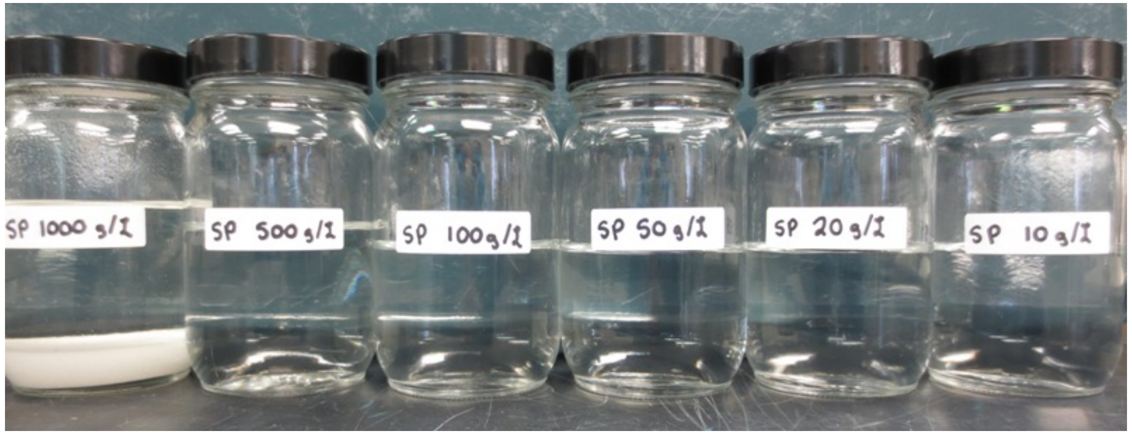
Solubility Limited Release Static System

Reactors at ~20◦C

Klozur KP Solubility = 47 g/L

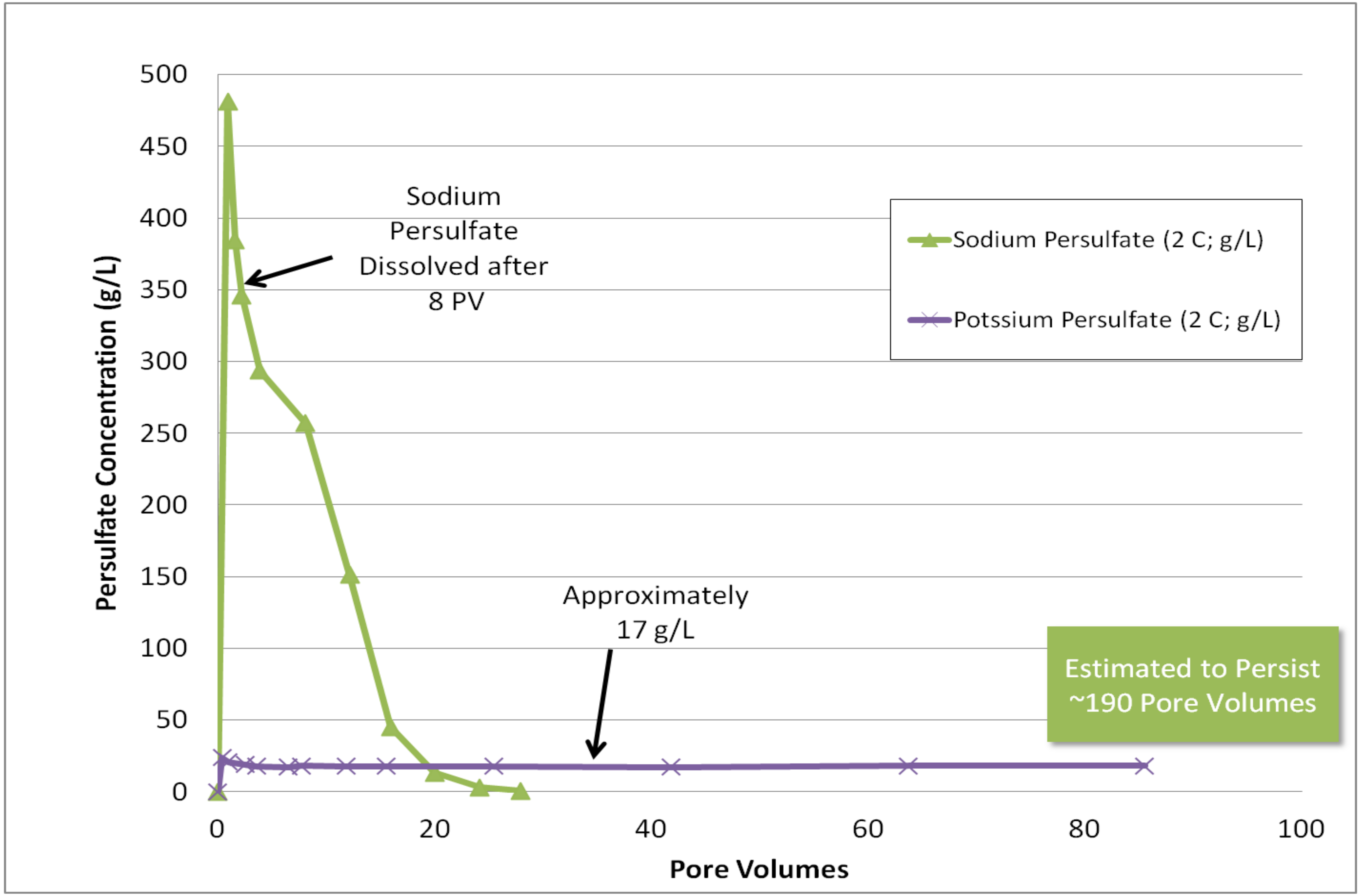


Klozur SP Solubility = 570 g/L



Column Study (2◦C) Effluent Persulfate Conc.

- Dissolution of Persulfate
  - 2 ◦C
- Klozur SP
  - Peak at theoretical maximum
- Klozur KP
  - Sustained at theoretical maximum



PeroxyChem

Common Activators

KLOZUR® SP

Alkaline activators

- Injection: 25% NaOH
- Soil mixing: 25% NaOH, $Ca(OH)_2$ or Portland cement

KLOZUR® KP

Alkaline activators

- Slurry injection: $Ca(OH)_2$
- Soil mixing: 25% NaOH, $Ca(OH)_2$ or Portland cement

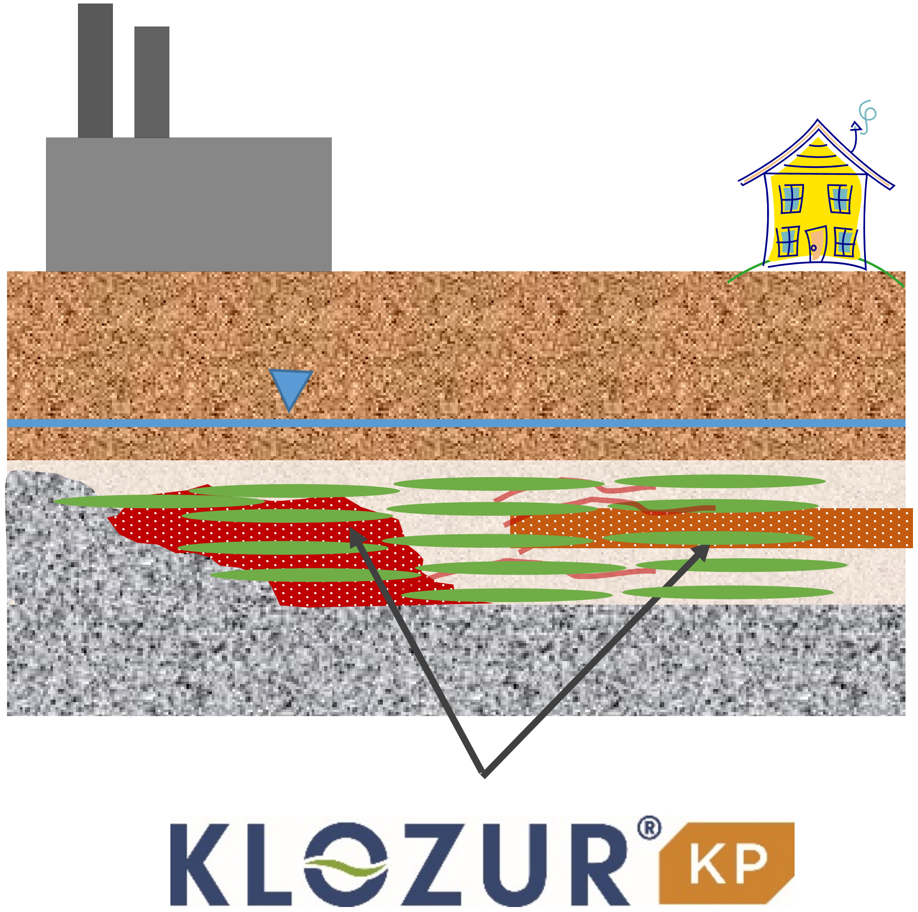
Alkaline activation is known to generate oxidative radicals needed to treat 1,4-dioxane and reductive radicals to treat other common co-contaminants

Common Methods of Establishing Contact

TCA and 1,4-Dioxane Source Zone

- Fracture in Klozur KP
  - Low levels of Klozur SP, as needed
  - Activators: Hydrated Lime, etc

Courtesy of FRx



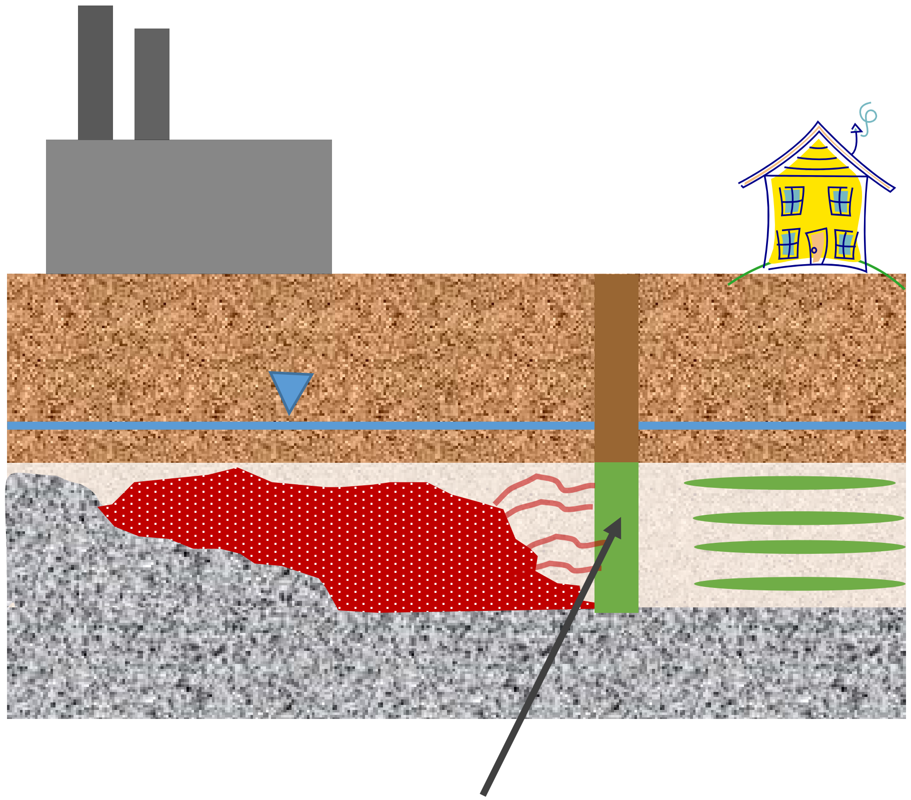
Hydrated lime activator (typical)

- Soil mix in Klozur SP/KP
  - Activators: Hydrated Lime, 25% NaOH, etc.

PeroxyChem

1,4-Dioxane Low GW Flux Plume

- Klozur KP Permeable Reactive Barrier (PRB)
- Fracture in Klozur KP/SP blend
  (illustration on previous slide)
  - Permeable reactive barrier (PRB)
  - Source zone treatment with offset grid to address mass on soils in addition to mass in GW

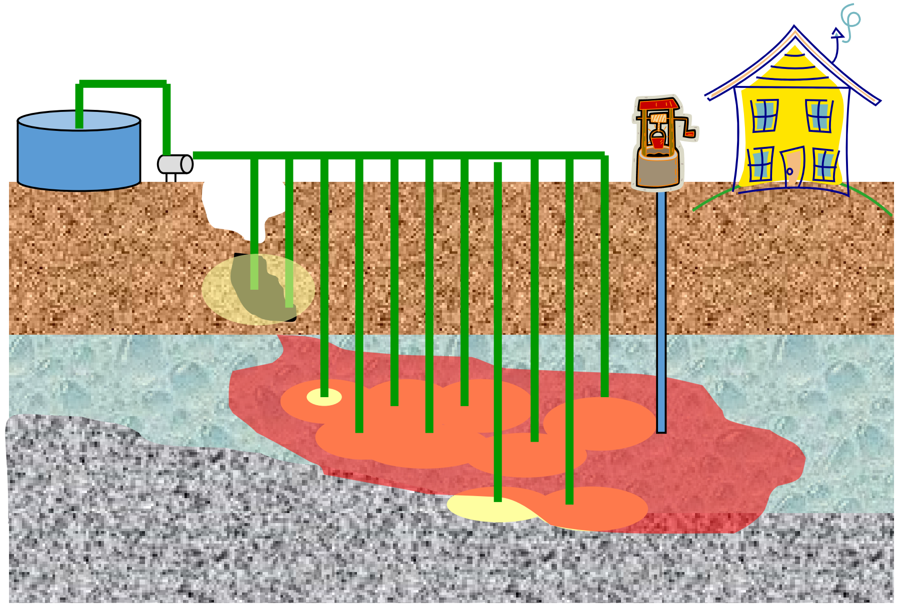


KLOZUR® KP

Hydrated lime activator (typical)

High GW Flux Plume/On Soils

- Klozur SP with injection strategy aimed at establishing contact with particular geologic formation
  - Concern regarding displacement of aqueous phase contamination
  - High f_{oc}, etc
  - Why is 1,4-Dioxane still in a high GW flux plume?
    - Look for sources such as NAPL or back diffusion from low permeable soils



- Potential strategies to treat GW
  - Outside/in strategy
  - Recirculation
  - "Chaotic" mixing
  - Subsurface mixing (certain soils)

Soil Mixing Benefits

- Establishes contact
  - Typically more rapid treatment
- Low permeable material
- Minimizes impact of site heterogeneity
- Homogenizes soil and contaminant
- Can be combined with ISS

Courtesy of Bill Lang

1,4-Dioxane Case Study

Former Industrial Facility in the Northeast

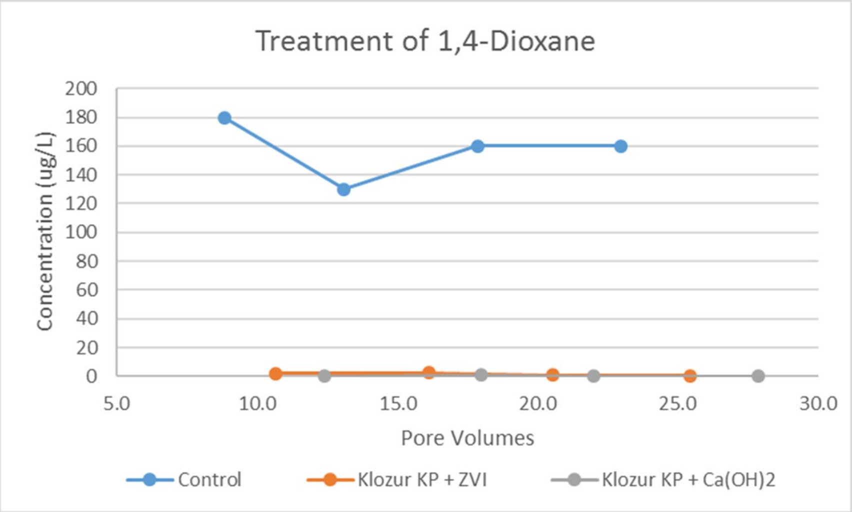
- Consultant: AECOM
- Residual 1,4-dioxane, TCA , and TCA daughter products
  - 1,1,1-Trichloroethane and 1,1,2-Trichloroethane (TCAs)
  - 1,1-DCA and 1,2-DCA
  - 1,1-DCE
- Silty soils with sand lenses
- Klozur KP PRB selected to establish contact with aqueous phase reagents

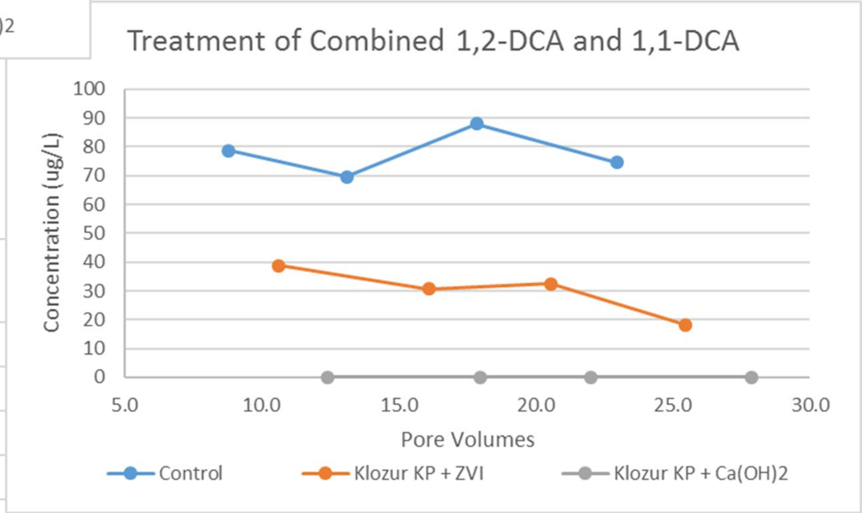
Klozur KP: Column Bench Test

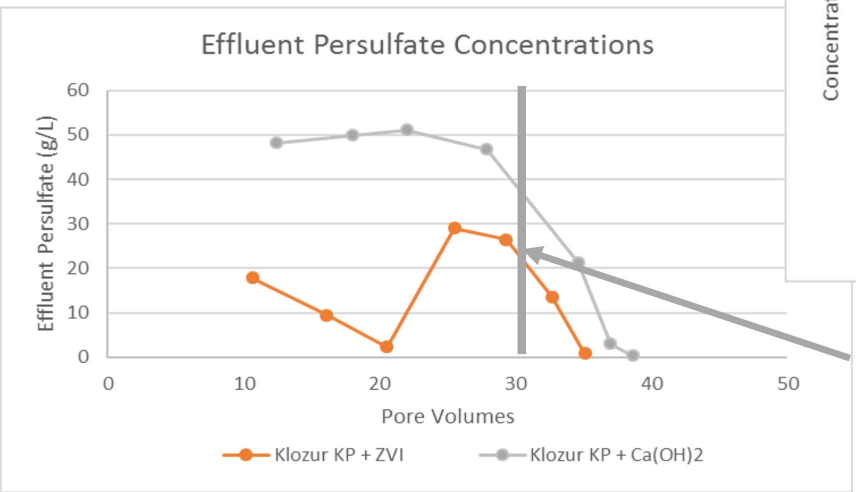
1) Oxidative pathway
   - 1,4-Dioxane

2) Reductive Pathway
   - DCA(s)

3) KP persisted intended 30 PVs



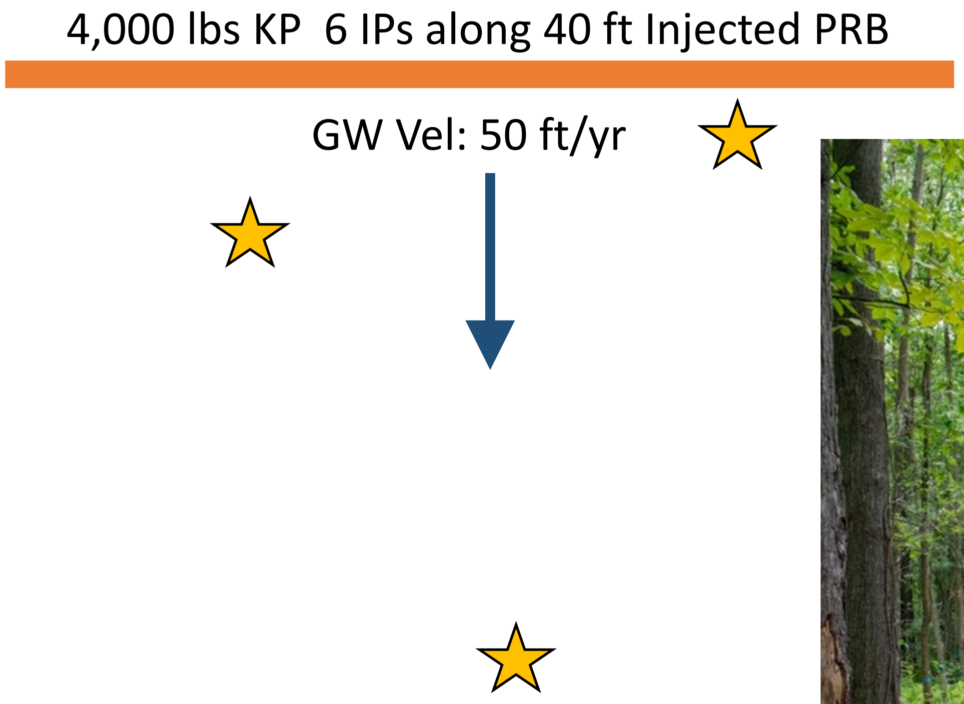




Design Volume

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

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

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

GW Vel: 50 ft/yr

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

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

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

Treatment

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%

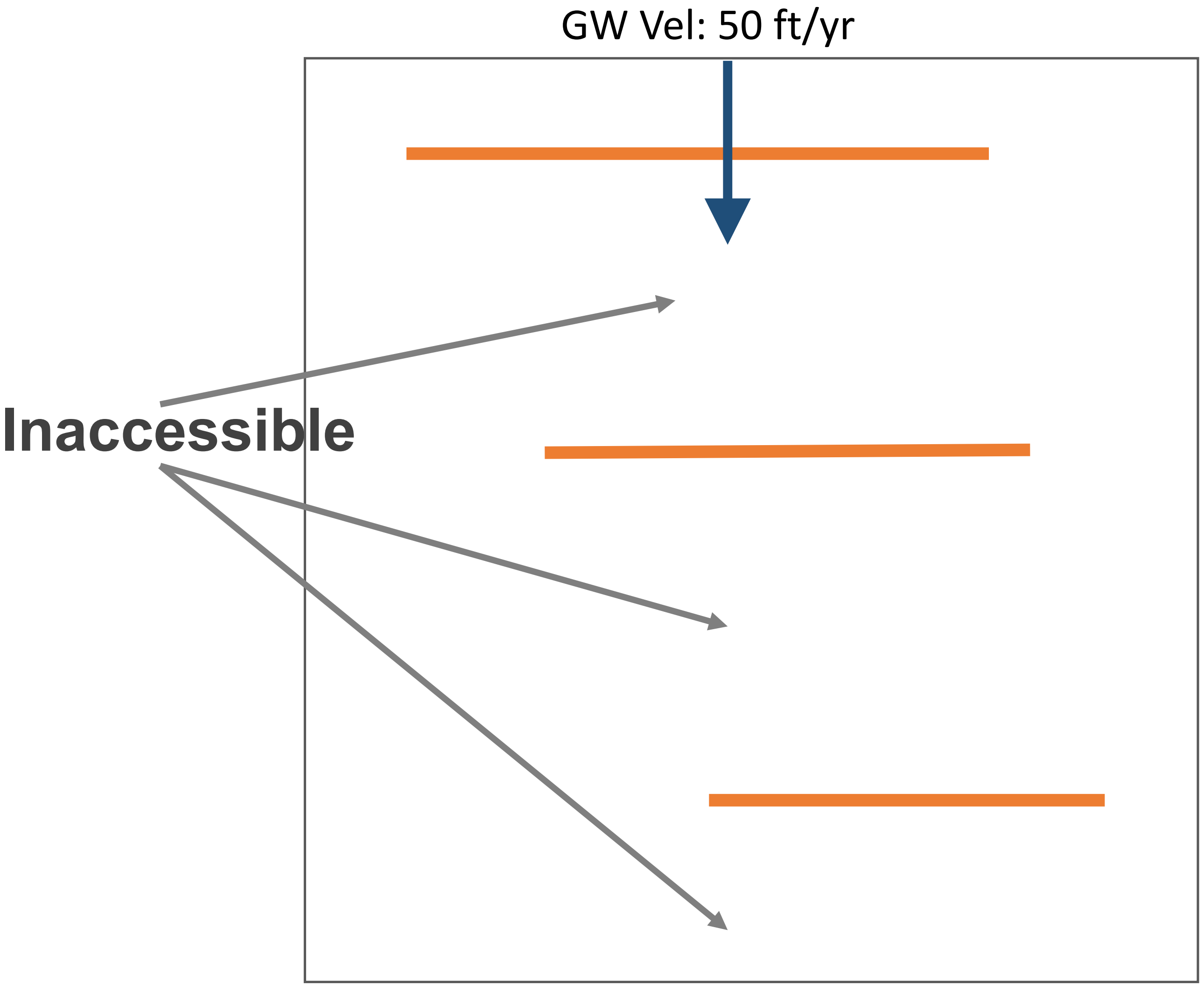
* Detected VOCs not including acetone

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

- Ongoing
- Three transects/PRBs
- Largely targeting 1,4-dioxane
- Cut off source long enough and clean inaccessible zones



Summary

PeroxyChem

- 1,4-Dioxane and common comingled contaminants have been successfully treated by alkaline activated persulfate
- 1,4-Dioxane prefers aqueous phase compared to most common contaminants
  - Keys to establishing contact
- Klozur KP can be used as solid state oxidant to treat aqueous phase contaminants
- Klozur SP can still be used if contact can be established

Bibliography

PeroxyChem

- Adamson, D., Newell, C., Mahedra, S., Bryant, D., and Wong, M. (2017) “In Situ Treatment and Management Strategies for 1,4-Dioxane Contaminated Groundwater,” SERDP Project ER-2307
- Adamson, D.T., Pina, E.A., Cartwright, A.E., Rauch, S.R., Anderson, R.H., Mohr, T., and Connor, J.A. (2017) “1,4-Dioxane drinking water occurrence data from the third unregulated contaminant monitoring rule,” Sci. of the Total Environ., 596-597, 236-245
- Adamson, D. (2016) “Fact Sheet” New Developments in 1,4-Dioxane Site Management,” SERDP Project ER-2307
- Cashman, M.A., Kirschenbaum, L., Holowachuck, J., and Boving, T.B. (2019) “Identification of hydroxyl and sulfate free radicals involved in the reaction of 1,4-dioxane with peroxone activated persulfate oxidant,” J. of Haz. Mater., 380, 120875
- Kambhu, A., Gren, M., Tang, W., Comfort, S., and Harris, C (2017) “Remediating 1,4-dioxane-contaminanted water with slow-release persulfate and zerovalent iron,” Chemosphere, 175, 170-177
- Mohr, T.K.G., DiGuiseppi, W.H., Anderson, J.K., and Hatton, J.W., (2020) “Environmental Investigation and Remediation: 1,4-Dioxane and Other Solvent Stabilizers,” 2nd Edition, CRC Press, New York
- Smith, B.A., Kammer, L., Soukup, J., Letts, C., Sadeghi, V., Lyon, P., and Pac, T. (2018) “Evaluation of Potassium Persulfate as a Permeable Reactive Barrier at Three Different Sites,” Eleventh International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, Palm Springs, CA
- US EPA (2017) “Technical Fact Sheet-1,4-Dioxane” EPA 505-F-17-011, November 2017
- Watts, R.J. (1998) “Hazardous Wastes: Sources, Pathways, and Receptors,” John Wiley & Sons, New York
- Zhang, S., Gedalanga, P.B., and Mahedra, S. (2016) “Biodegradation Kinetics of 1,4-Dioxane in Chlorinated Solvent Mixtures,” Environ. Sci. & Tech., 50, 9599-9607
- Zhao, L., Hou, H., Fugii, A., Hosomi, M., and Li, F., (2014) “Degradation of 1,4-dioxane in water with heat- and Fe2+ activated persulfate oxidation,” Environ. Sci. Pollut Res, 21, 7457-7465
- Zhong, H., Brusseau, M.L., Wang, Y., Yan, N., Quig, L., and Johnson, G.R. (2015) “In-situ activation of persulfate by iron filings an degradation of 1,4-dioxane,” Water Research, 83, 104-111