



Remediation of 1, 4-Dioxane



Presented by
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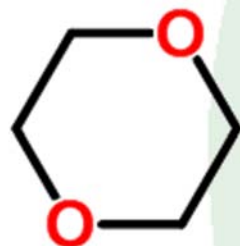
Agenda

- Basic properties of 1,4-dioxane with respect to remediation
- A discussion of applicable reliable remedial technologies with case studies
 - Ex situ
 - Advanced oxidation
 - Sorption
 - In situ
 - In situ chemical oxidation
- Promising remedial technologies
 - Phytoremediation
 - Thermally enhanced soil vapor extraction
 - Bioremediation



Molecular Structure of 1,4-Dioxane

Molecular Formula: $C_4H_8O_2$



1,4-dioxane is a synthetic, volatile, colorless liquid that is miscible with water, most organic solvents, aromatic hydrocarbons and oils. It is used primarily as a stabilizer in chlorinated solvents. 1,4-dioxane is also used as a solvent for numerous commercial products and as a wetting/dispersing agent in textile processing. [Recent article on a large plume in MI where 1,4-dioxane was used in processes for the manufacture of medical filters.](#)



Basic Properties of 1,4-Dioxane in the Environment

Compound	Solubility (mg/L)	Koc (cm ³ /g)	Henry's Law Const. (unitless)	Vapor Pressure (mmHg)	Water Quality Criteria ug/L
MtBE	51,000	7.26	0.025	245	13
PCE	200	155	0.753	24	5
Benzene	179	59	0.227	76	5
1,4-Dioxane	miscible	17	0.0002	37	3*

* = Levels may be lowered e.g. NJDEP Interim Ground Water Quality Criteria is now **0.4 ug/L**

- What do these properties mean?
 - Volatile as a residual product
 - Very soluble in groundwater
 - When dissolved, not easily adsorbed, therefore is not readily retarded in soils
 - When dissolved, prefers to be in aqueous vs. vapor phase i.e. not easily stripped out of groundwater
 - TYPICALLY MEASURED ON LEADING EDGE OF PLUME



Ex Situ Technologies

- Advanced oxidation
 - key is formation of radical chemistry
- Sorption
 - key is synthetic materials



Advanced Oxidation Case Study

New Jersey

- Landfill leachate and groundwater extraction system (50-100 gpm)
- 1,4-dioxane up to 322 ug/L (has attenuated over time)
- Water is currently treated using powdered activated carbon/sand filtration (ZIMPRO Process)
- Advanced Oxidation Process (AOP) being added to address 1,4-dioxane that is not treated by ZIMPRO
- Bromide up to 1,300 ug/L



AOP Process

- Reaction between H_2O_2 and O_3 produces hydroxyl free radical ($\bullet\text{OH}$) – proven effective on 1, 4-dioxane
- Bromate (BrO_3^-) is a common disinfection by-product
 - Formed during common water treatment process (e.g., chlorination, direct ozonation, AOP, etc.)
 - Naturally occurring bromide ions (Br^-) in the raw ground water/surface water source is the pre-cursor to bromate formation.
 - MCL for bromate is 10 ug/L in drinking water
- There is no GWQC for bromate in the New Jersey Administrative Code (NJAC 7:9C) Ground Water Quality Standard (GWQS)



Oxidant Dosing and Impact on Bromate Control / Balancing Act

- The molar ratio of hydrogen peroxide to ozone ($\text{H}_2\text{O}_2:\text{O}_3$) can be adjusted to minimize the formation of bromate. Typically, by increasing the amount of hydrogen peroxide relative to a fixed dose of ozone (i.e., increasing molar ratio of $\text{H}_2\text{O}_2:\text{O}_3$), the ozone will be more completely reacted with the hydrogen peroxide, and bromate formation will be reduced
- However, the trade-off is that the excess hydrogen peroxide can now react with the hydroxyl radicals (i.e., termed hydroxyl radical “scavenging”), which reduces the treatment efficiency of 1,4-dioxane
- Could use UV instead of ozone to avoid bromate but that has its own issues



1,4-Dioxane Destruction Results

Test Scenario	Impact on 1,4-Dioxane			Impact on Bromate		
High Spike, 240 ug/L 1,4-dioxane O₃ Dose = 5, 10, 13, 20mg/L H₂O₂:O₃ Ratio = 1.0 (all scenarios) 7 injection nozzles except the 20 mg/L ozone dose which used 9 nozzles.	O ₃ (mg/L)	H ₂ O ₂ (mg/L)	Final 1,4-dioxane (ug/L)	O ₃ (mg/L)	H ₂ O ₂ (mg/L)	Final Bromate (ug/L)
	5	3.6	48	5	3.6	64
	10	7.1	6.6	10	7.1	190
	13	9.2	1	13	9.2	290
	20	14.2	1	20	14.2	430
	<u>Result:</u> 1,4-dioxane destruction is more effective as ozone dose is increased.			<u>Result:</u> Bromate conc. <u>increased</u> significantly as ozone dose increased.		
<u>Conclusions:</u> Hydrogen peroxide/ozone molar ratio requires optimization to reduce bromate formation. Also, likely to require more nozzle injection points to reduce bromate while achieving desired 1,4-dioxane destruction (7 to 9 nozzles used in Round 1, increased to 20 and 30 in Round 2).						



Bromate Formation Control Results

Test Scenario	Impact on 1,4-Dioxane			Impact on Bromate		
High Spike, 240 ug/L 1,4-dioxane O ₃ Dose = 10.7 mg/L H ₂ O ₂ Dose = 19.0 and 30.4 mg/L H ₂ O ₂ :O ₃ Ratio = 2.5 and 4.0 20/30 injection nozzles	Molar Ratio	2.5	4.0	Molar Ratio	2.5	4.0
	No. Inj. Noz.	Final 1,4-dioxane (ug/L)		No. Inj. Noz.	Final Bromate (ug/L)	
	20	3.4	10.0	20	12	3
	30	7.2	21.0	30	4.9	2.2
	Result: 1,4-dioxane destruction is <u>less</u> effective as MR increases and as no. of injection nozzles increase.			Result: Bromate concentration <u>decreases</u> as MR increases and as no. of injection nozzles increase.		

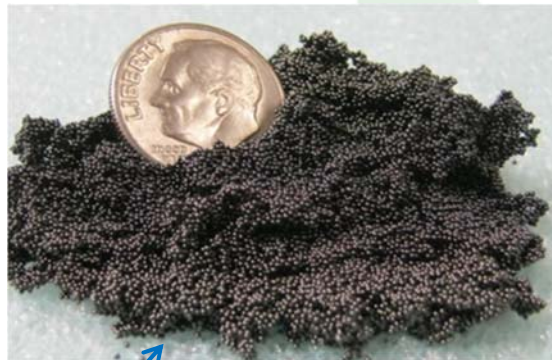
Conclusions: Increasing the molar ratio of hydrogen peroxide to ozone reduces the bromate formation and bromate was reduced to below 10 ug/L in some scenarios. However, 1,4-dioxane destruction becomes less efficient. In addition, increasing the number of injection nozzles also reduces bromate, but reduces the 1,4-dioxane destruction.



Sorption



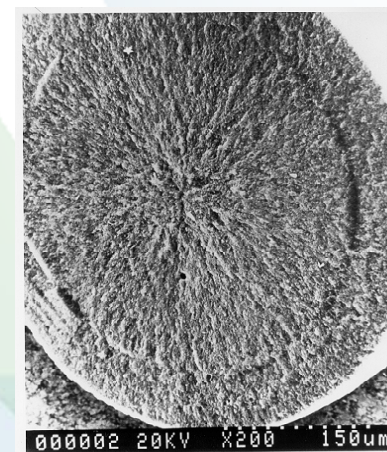
- GAC limited effectiveness on 1,4-dioxane – cost effective?
- Synthetic Media can be used to collect various contaminants from liquids, vapor or atmospheric streams and be reused indefinitely



AMBERSORB™ 560

Properties of Dow's AMBERSORB™ 560

- Hydrophobic
- Unique pore size distribution
- High affinity for organic compounds: (**simple** adsorption mechanism)
- Can achieve non-detect effluent concentration at substantial loading rates
- Can typically reuse (thermally regenerate in-place) indefinitely
- Durable structure

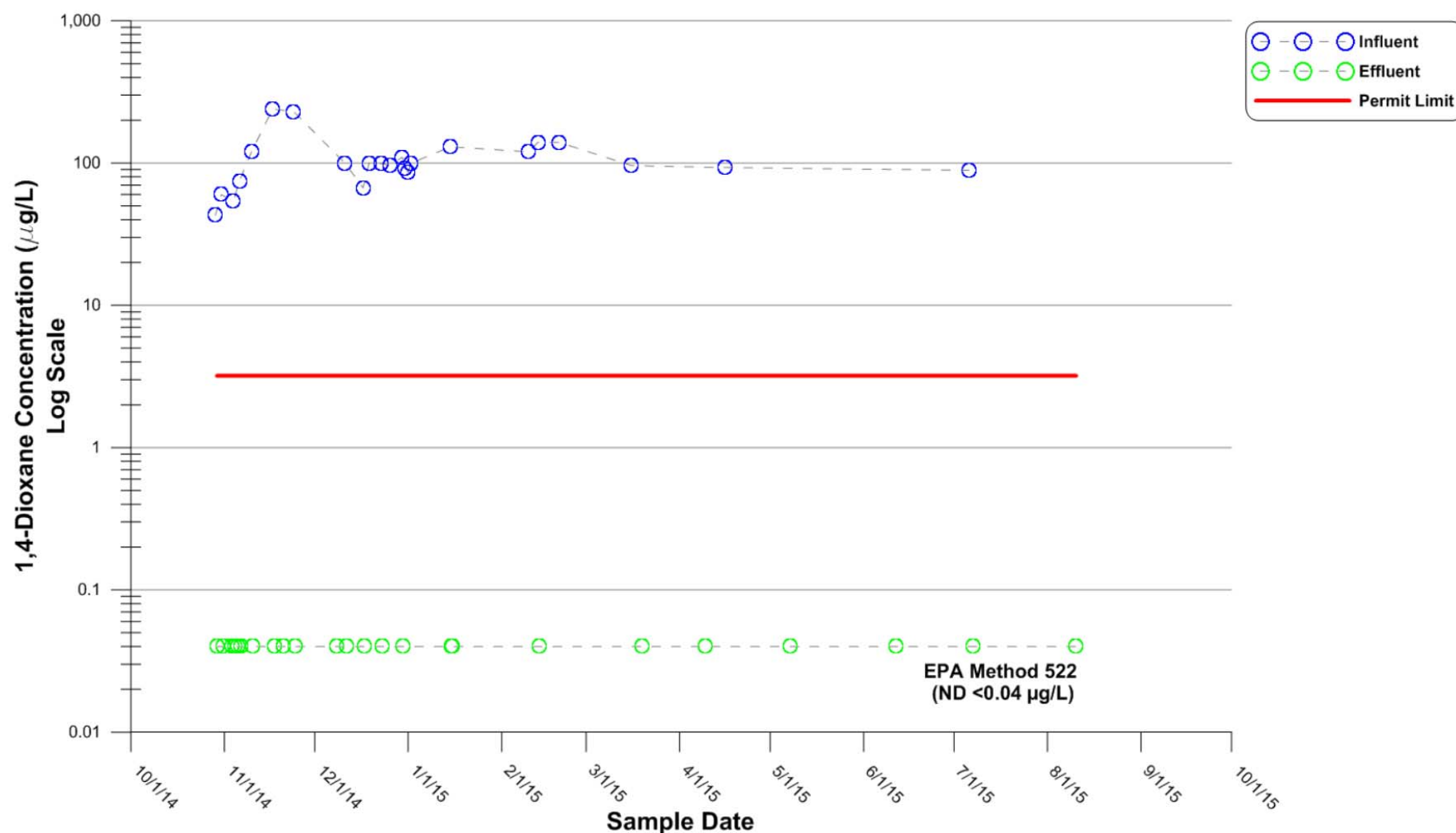


St. Petersburg, FL 140-gpm System

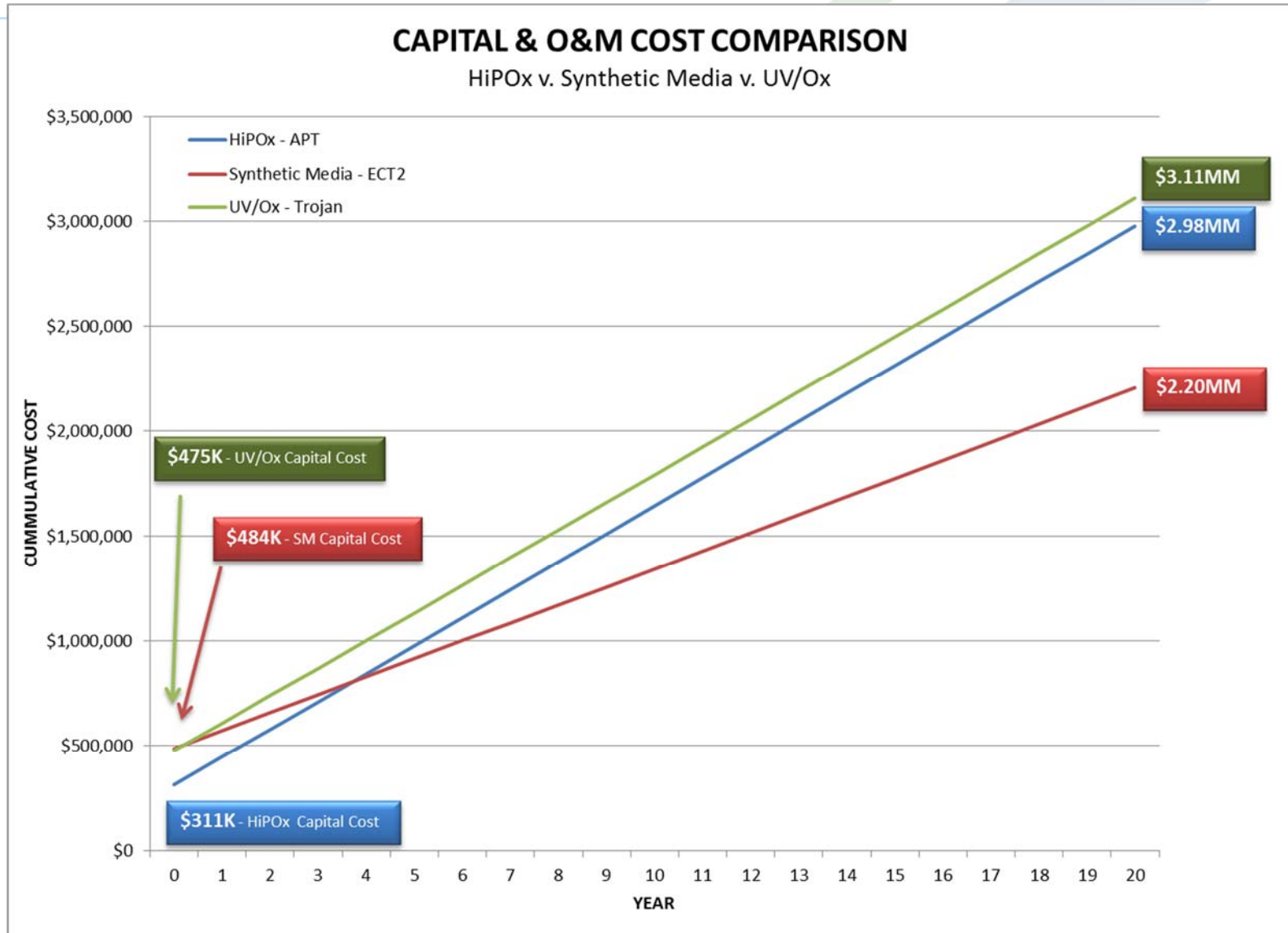
- Design Basis:
 - Flow = **100-175 gpm**
 - 1,4-dioxane = **2,535 ug/L MAX more typically 100's ug/L**
 - Total Organics = **17,450 ug/L**
 - Iron = **6-30 mg/l**



Influent and Effluent 1,4-Dioxane



Cost Comparison 20 gpm System, CA



In Situ Technologies

- In situ chemical oxidation
 - Generally, key again is radical chemistry



XDD CASE STUDY

The Problem: Solvent Contamination

- Source Area:

- 30 x 60 feet area
- 15 feet thick
- Silty sands – dual level system

<u>Compound</u>	<u>Historical Max. Conc.</u> <u>(ug/L)</u>
1,1,1-TCA	101,000
PCE	20,000
1,4-Dioxane	3,000

- Located beneath active manufacturing plant

- Treatment Goal:

- Reduce groundwater to below 1 mg/L in source
- Goal based on protection of downgradient receptor



The Solution: ISCO Treatment

- Selected Alkaline Activated Persulfate (AAP) for safety reasons
 - Greater in-situ stability
 - Reduced potential for gas evolution
- Evaluated AAP on bench scale
 - Soil buffering capacity
 - 2 to 4 g NaOH/Kg Soil
- Two injection events

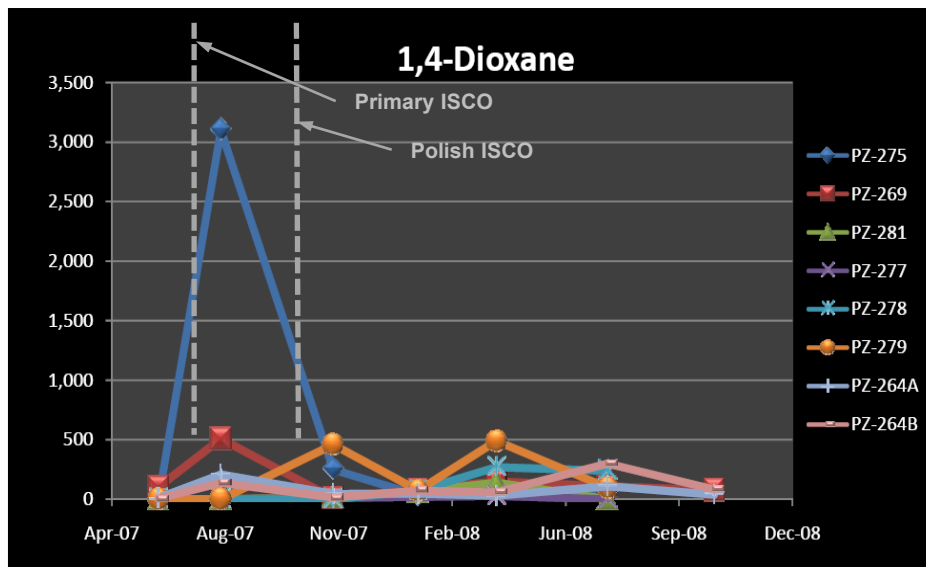
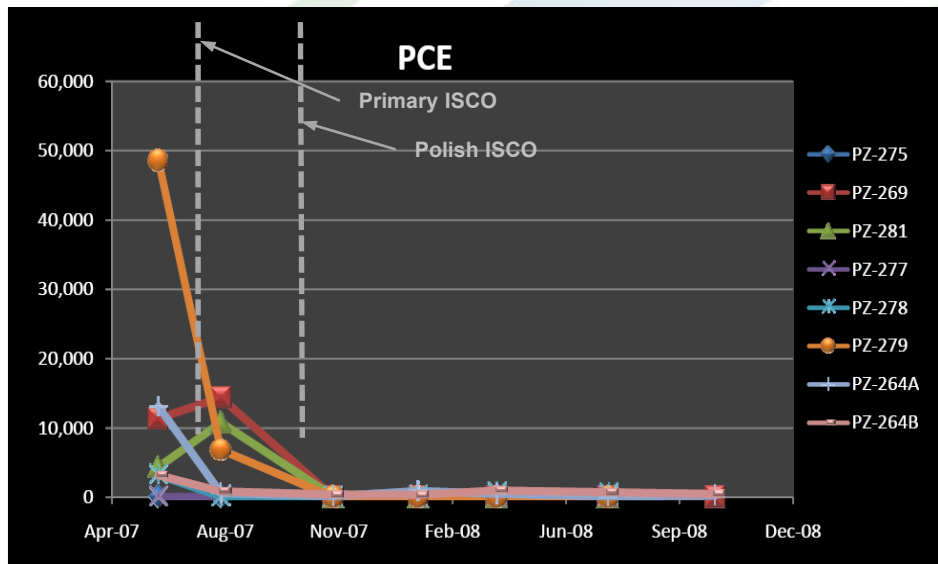
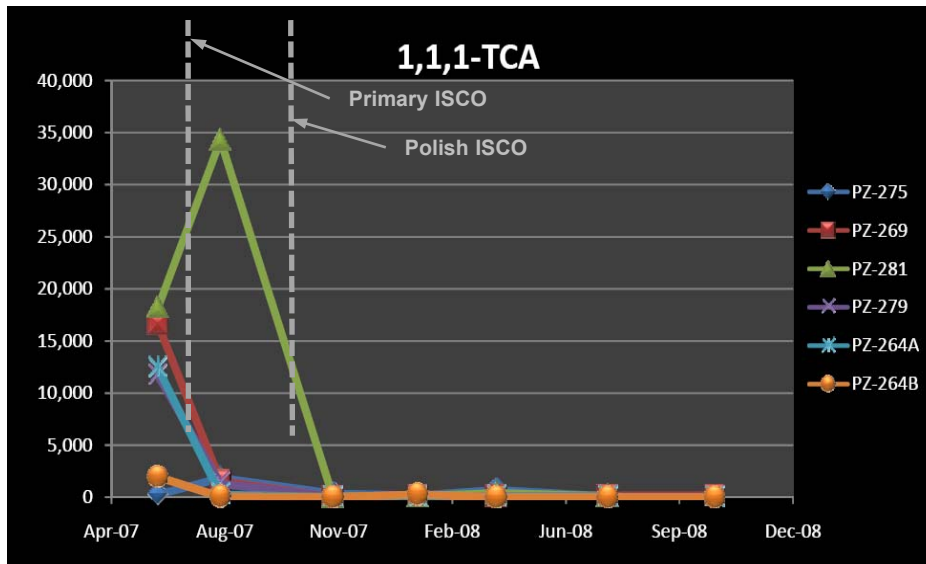
❖ **NaOH Mass < Soil Buffering Capacity + acid generated by persulfate reaction**

❖ **31,000 Kg Klozur
(sodium persulfate)**

❖ **15,300 Kg Sodium
Hydroxide (NaOH)**



Long Term Monitoring Results-VOCs



- 2-3 Orders Magnitude Reduction from baseline
- Target compounds remain below 1 mg/L objective
- Target compounds dropped to low ug/L level and remained over number years post treatment



In Situ Chemical Oxidation

Other:

- Persulfate / Permanganate Slow Release Cylinders
 - SERDP funded Laboratory Study
- Other hydroxyl radical chemistry
 - Peroxide / ozone systems
 - Other catalyzed peroxide / Fenton's type systems



Promising Remedial Technologies

- Phytoremediation
 - primarily removal by transpiration
- Thermally enhanced SVE
 - remove water and 1,4-dioxane from vadose zone – ESTCP study
- **Bioremediation - both ex- and in situ**



1,4-Dioxane Bioremediation

- Bioremediation

- Aerobic

- Few organisms use 1,4 dioxane as an energy source
 - THF/Propane/others as energy: co-metabolic processes
 - Activity common with monooxygenase enzymes

- Anaerobic (Nitrate, Iron, Sulfate, and Methanogenic)

- SERDP Study in 2007 results: no degradation?



1,4-Dioxane Bioremediation

- MNA Evaluation CA GeoTracker + Air Force Sites / Wells (ES&T, 2015, 49, 6510–6518)
 - Only 30% of 193 CA sites had a statistically significant source decay term
 - About 23% of CA sites had order of magnitude reduction in max. vs. recent 1,4 dioxane levels, very few with higher than 2 or 3 order reduction
 - 30% of 441 AF wells with decreasing trends, 70% with stable, no trend or increasing trend (increasing was 9%)
 - AF wells : attenuation correlated positively with dissolved oxygen, and negatively for CVOCs and metals
 - Median half-Life 20-48 months for statistically significant attenuating sites / wells



[illegible]

-  : @XDD_LL
-  : XDD Environmental