Ferrous Sulfide - A New Activation Chemistry for Persulfate

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Technical Presentation Outline

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- Persulfate Activation Methods
- Combined Remedies: Chemical Oxidation & Bioremediation
- Treatability Studies & Field Experience
- Conclusions

1. Selection and Loading

2. Delivery and Distribution

Performance is:
applying *enough oxidant* *in contact* with the contaminant for a *long enough period of time* to *react effectively*

3. Contact and Persistence

4. Reaction and Contaminant Destruction

Available Oxidants

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Oxidant	Advantages	Drawbacks
Permanganate (MnO_4^-) 1.7 mV	Stable solid or liquid Flexible (0 – 40%)	Purple color Limited reactivity
Persulfate (unactivated) (SO_4^{-2}) 2.1 mv **Persulfate (activated)** + ($SO_4^{-\cdot}$) 2.6 mV	Stable solid Flexible (0 – > 56%) Increased reactivity	Limited reactivity Limited transport
Ozone (O_3) 2.1 mV	Gaseous	Limited transport Specialized equipment
Hydrogen Peroxide *(unactivated)* (H_2O_2) 1.8 mv ***(activated – Modified Fenton's)*** + ($OH_{\cdot}$) 2.8 mv	Stable liquid Cost Clear solution Increased reactivity	Low concentration Rapid decomposition Limited transport Gas pressure release Heat

Reactivity (i.e., "strength")

Oxidant Misconceptions

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- In porous media, the application of oxidants **will not "clog"** the formation (< 10% void infilling at high loading). Due to small pore throats and limited connectivity, this is not necessarily true in low permeability materials or fractured media
- Oxidation **does not sterilize** formation, biota recovers quickly and fully
- Effective and appropriate **delivery is critical** to ISCO success
- Oxidant can **persist** in presence of contaminant
- Excess oxidizer lead to **false negative** confirmatory samples (also may damage to lab equipment)
- Treatment trains - biological methods (ERD using QRS™ or SRS®) provide **follow-up** to ISCO

ISCO with Sodium Persulfate

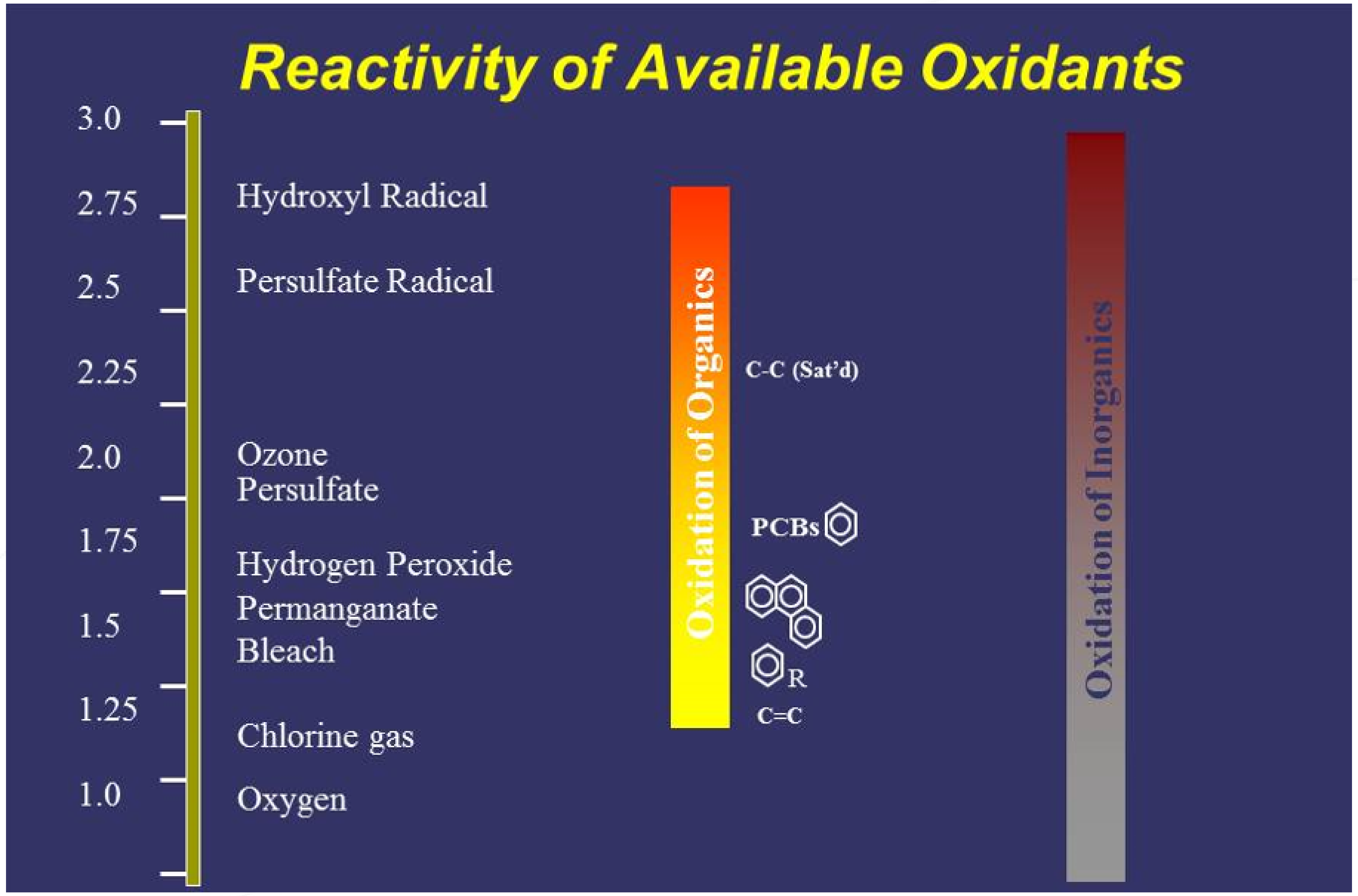
- Two Reaction Pathways

activated (radical) - $S_2O_8^{-2}$ + TSI-FSA™ → $S_2O_8^{-}$, SO_4^{-}•, OH•, O_2^{-}

- Why Activation?

unactivated (oxidation) – $S_2O_8^{-2} + 2H^{+} + 2e^{-} \rightarrow 2H_2SO_4^{-}$

1. combined oxidative and reductive pathways
2. stronger, kinetically fast, localized
3. degrade recalcitrant compounds (Cl-ethanes, CT, pesticides, etc.)



Commonly Used Persulfate Activation Methods

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Method	Drawbacks	Patent Holder
Sodium Hydroxide	Hazardous (pH, worker safety)	Evonik (Block et al.)
Fe-EDTA	Requires 160 to 600 mg/L Iron	Evonik (Block et al.)
Hydrogen Peroxide	Rapid decomposition of persulfate and peroxide	Evonik (Sethi et al.)
Stabilized Hydrogen Peroxide	Precise monitoring and control of pressure and temperature	Cronk (JAG)
Carbohydrate	Licensed technology	ISOTEC (Watts et al.,)
Ferrous Sulfide TSI-FSA™	Limited field experience	**None**

Comparative Activator Costs

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Activation Method Mass Required	Cost (USD)	
Sodium Hydroxide (29,000 # @ 50%)	$26,240	+ 8X
Fe-EDTA (630 #)	$360	- 1X
Hydrogen Peroxide (83,000 # @ 50%)	$55,500	+ 25X
Stabilized Hydrogen Peroxide	$26,700	+12X
Carbohydrate	$3,500	+0.5 X
Ferrous Sulfide TSI-FSA™ (1,300 #)	**$2,145**	**-**

- Application of 8 pallets (17,600 pounds sodium persulfate) at 15% injection concentration
- Does not include taxes, shipping or application costs

Combined Remedies:
Chemical Oxidation & Bioremediation

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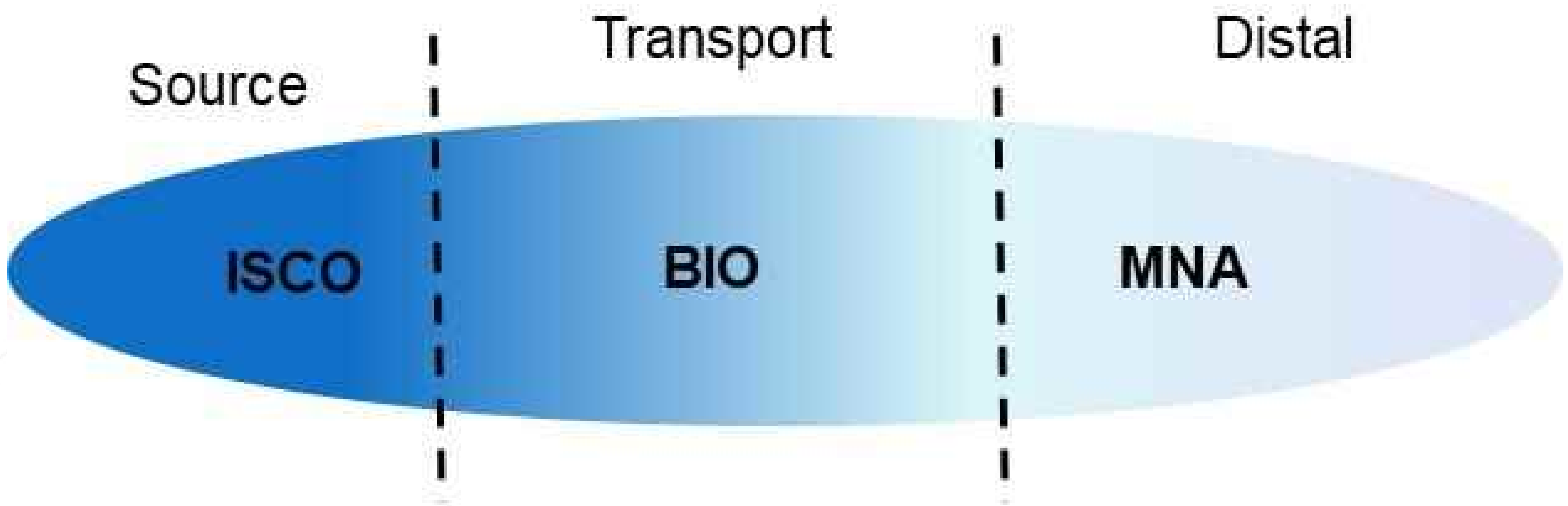
- Two Reaction Pathways Technology Coupling – "Best of Both Worlds"
  - maximize effectiveness while minimizing cost
  - spatially – sequentially over distance
  - temporally – sequentially over time
  - better respond to changes in conditions
  - mutually supportive
- Remedial Life Cycle Approach



Treatability Studies

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1. Aqueous treatment of spiked 1,4-dioxane, benzene, naphthalene, and tetrachloroethene (PCE)

2. Batch Study for Gasoline

3. Batch Study for PAHs

4. Treatability Results for Chlorinated

1. Spiked Aqueous Only Treatability Study

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Treatment Study Design	Persulfate Consumption	1,1,1-TCA	1,4-Dioxane	Benzene	CCl_4	NAP	PCE
Spiked Concentration *(ug/L)*		**2,900**	**4,600**	**3,400**	**2,500**	**4,300**	**2,100**
Control		13.8%	-30.4%	11.8%	20.0%	16.3%	14.3%
50 g/L persulfate 2.1 g/L TSI-FSA™	11.9%	**99.7%**	**>95.9%**	**>99.9%**	90.8%	**>99.9%**	**>99.9%**
50 g/L persulfate 0.64 g/L NaOH	9.5%	58.6%	**>95.0%**	**>99.9%**	**99.8%**	**>99.9%**	**>99.9%**

28-day treatability study (percent reduction vs. T_0 concentration)

- ~90% persulfate persisted for both activations
- Both activations removed all 1,4-dioxane, benzene, naphthalene (NAP), and tetrachloroethene (PCE)
- TSI-FSA™ gave better treatment of 1,1,1-TCA. NaOH better for carbon tetrachloride (CCl4)

2. Batch Study Persulfate Activation for Gasoline

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Treatment Study Design	Persulfate Consumption	Benzene	NAP	C_6-C_{10} TPH GRO	Total VOCs
Control		39.3%	16.8%	1.1%	24.7%
LOW 0.5 g/L TSI-FSA™	78.1%	80.5%	19.1%	36.4%	57.7%
MODERATE 2.1 g/L TSI-FSA™	78.6%	71.9%	1.0%	36.4%	43.6%
HIGH 3.7 g/L TSI-FSA™	82.6%	**91.9%**	**24.8%**	**57.5%**	**79.5%**
VERY HIGH 10.5 g/L TSI-FSA™	85.0%	79.1%	-7.2%	19.5%	53.0%
12.6 g/L NaOH	100.0%	18.9%	17.7%	-4.9%	13.6%

Day 35 – Mass balance compared to control (soil & groundwater)

- 50 g/L persulfate consumed completely with NaOH
- Persulfate losses with TSI-FSA™ ranged from 78.1 to 85%
- Better removal of benzene, GRO, and total VOCS with TSI-FSA™ than NaOH
- Very high TSI-FSA™ loading reduced treatment efficiency

3. Batch Studies for PAHs

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Treatment Study Design	Persulfate Removal (%)	Sum PAHS *(mG/KG)*	Removal vs. Control (%)
Starting Concentration		**413,777**	
Control		258,033	37.6%
Sodium persulfate 6 g/L NaOH	56.2%	**28,069**	**93.2%**
Sodium persulfate **LOW** 0.5 g/L TSI-FSA™	53.2%	**40,673**	**90.2%**
Sodium persulfate **MODERATE** 2.5 g/L TSI-FSA™	54.2%	103,887	74.9%
Sodium persulfate **HIGH** 4.0 g/L TSI-FSA™	54.2%	86,393	79.1%
Control		170,399	58.8%
Sodium persulfate unactivated	52.2%	159,826	61.4%
Potassium persulfate unactivated	42.9%	165,453	60.0%
Potassium persulfate **LOW@** 0.5 g/L TSI-FSA™	47.6%	67,106	83.8%

21-day treatability study (50 g/L sodium and potassium persulfate KPS with various activations)

- Best treatment of PAHs with sodium persulfate activated by NaOH (93.2%), followed by LOW TSI-FSA™ (90.2%)
- Moderate persulfate consumption
- TSI-FSA™ can activate potassium persulfate

4. Treatability Results for Chlorinated Ethenes

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Soil and groundwater contaminated with TCE, cis-1,2-DCE, and VC)

- Two 14-day Studies completed using various doses of
  - Sodium persulfate with TSI-FSA™ activation
  - Sodium persulfate using Calcium hydroxide ($Ca(OH)_2$) activation

Treatment Study Design	Cis-DCE (ug/L)	TCE (ug/L)	VC (ug/L)	NPS (g/L)
Treatment Study 1	171	8.06	8,910	
Control	44.9%	52.2%	81.6%	
25 g/L sodium persulfate 1.0 g/L TSI-FSA™	**>98.8%**	>97.5%	**>99.9%**	5.7%
50 g/L sodium persulfate 1.0 g/L TSI-FSA™	**>98.8%**	>97.5%	**>99.9%**	41.8%
50 g/L sodium persulfate 2.0 g/L TSI-FSA™	**>98.8%**	**>97.6%**	**>99.9%**	44.3%
Treatment Study 2	3,050	3	12,700	
Control 2.5 g/L $Ca(OH)_2$	73.0%	-238.3%	80.6%	
10 g/L sodium persulfate 5.3 g/L $Ca(OH)_2$	93.9%	-73.6%	**98.8%**	67.7%
25 g/L sodium persulfate 6.5 g/L $Ca(OH)_2$	96.0%	-32.6%	**99.8%**	47.3%
50 g/L sodium persulfate 8.7 g/L $Ca(OH)_2$	**98.0%**	**-9.5%**	**99.9%**	55.6%

Treatability Study Conclusions

- TSI-FSA^{TM} activation shown to be effective for –
  - chlorinated ethanes (1,1,1-TCA, DCA)
  - chlorinated ethenes (PCE, TCE, DCE isomers and vinyl chloride)
  - chlorinated methanes (chloroform and methylene chloride)
  - 1,4-dioxane
  - carbon tetrachloride
  - GRO/DRO – BTEX, MTBE, NAP (DRO confirmation treatabilty in process (June 2024))
  - pesticides
- May provided better treatment and less activator vs. other activation chemistries at reduced cost
- Optimal loadings of TSI-FSA^{TM} appear to be between 2 and 8% of the persulfate

Active Manufacturing Yard
Southern New Jersey

- Site Description:
  - Residual BTEX contamination from historical UST
  - Pre-treatment (2021) concentrations
    - Benzene: 1,200 ug/L
    - Ethylbenzene: 1,400 ug/L
    - Toluene: 9,300 ug/L
    - Xylene: 15,000 ug/L
    - TICs: 13,700 ug/L
- Permanent Re-injectable Points (RIPs) installed in targeted areas (collaboration with client based on historical delineation)

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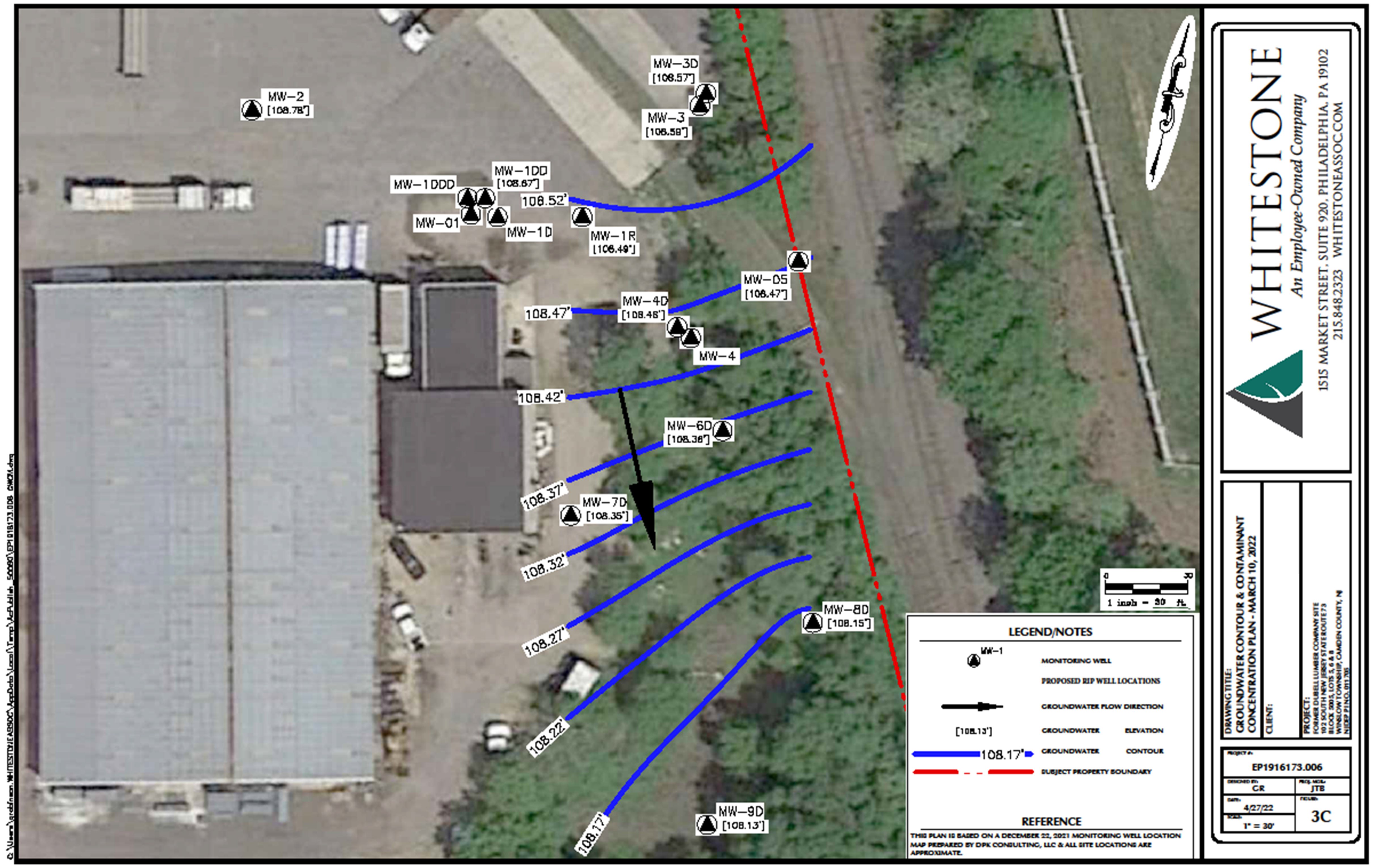
- Site lithology:
  - Overburden medium to coarse sands,
  - **Medium to find sands to ~ 30 ft bgs**
  - Tighter fine sands and intermittent clay at 40 ft bgs
- Two source area wells - MW-1 & MW-4
- Treatment Interval: 10 - 30 ft bgs
- Treatment area: 75' x 125'
- Two injection events
  - December 2021
  - August 2022



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- **December 2021** Event:10,140 lbs. TSI-SPS, 10,970 gallons of injectate (11%)
  - Injection into 10 RIPs and 20 temporary injection points (TIPs)
  - Injection Duration: 9 Days
- **August 2022** Event: 12,620 lbs. TSI-SPS, 13,710 gallons of injectate (11%)
  - Injection into 15 RIPs targeting and 20 TIPs (DPT)
  - Treatment Interval: 10- 30 ft bgs
  - Injection Duration: 5 Days
- **Challenges**:
  - Surfacing from shallow injection intervals
  - Logistics with Site operations
  - Tighter/deeper pressures, water source 350 ft away

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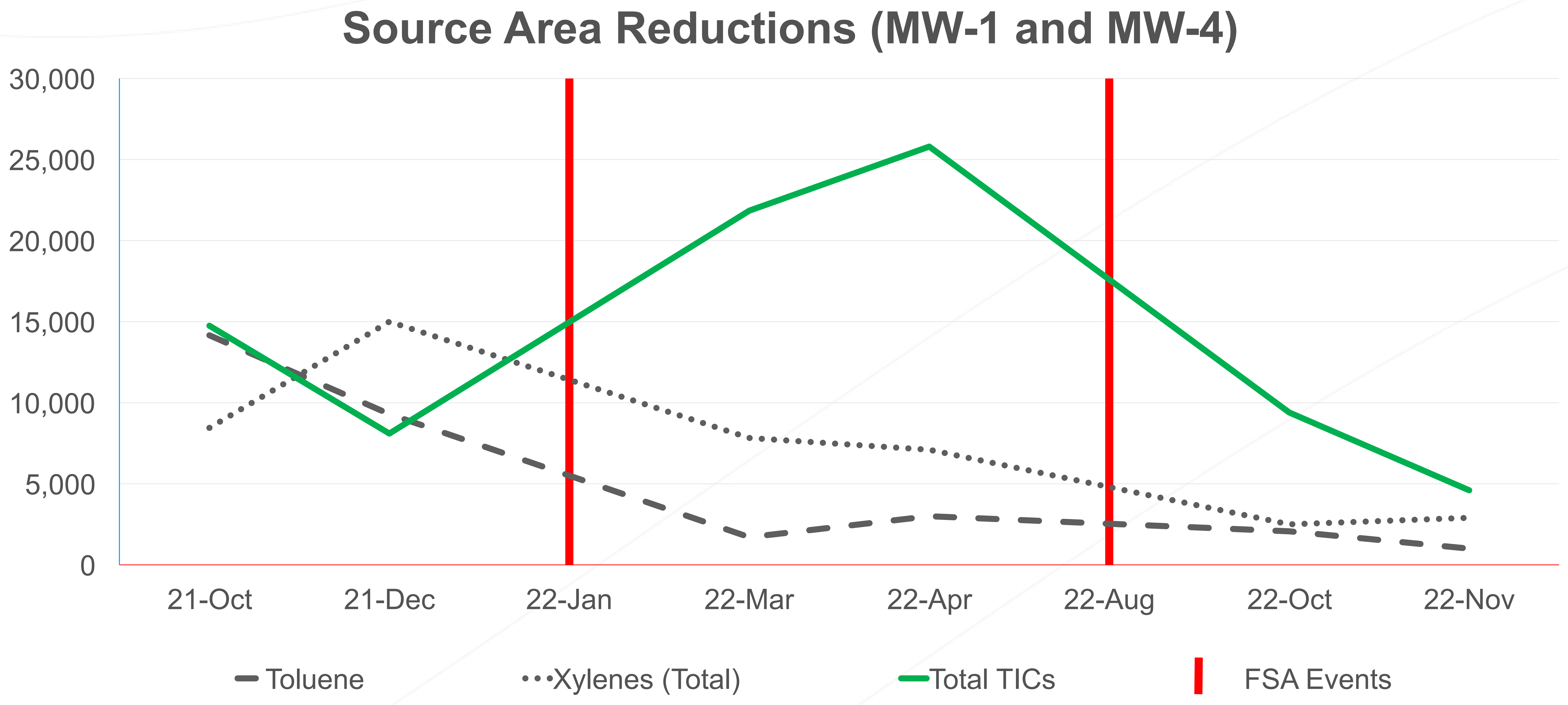

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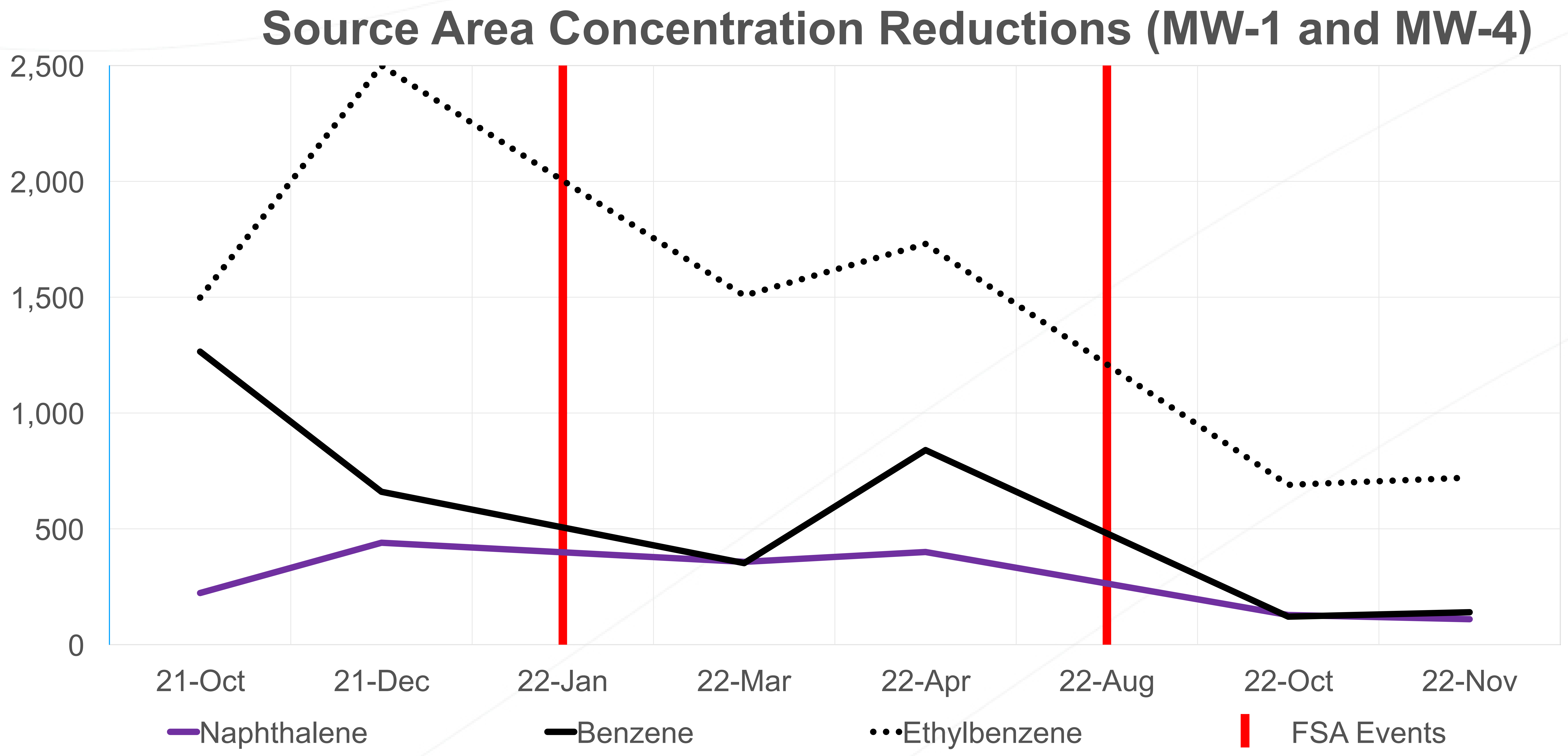

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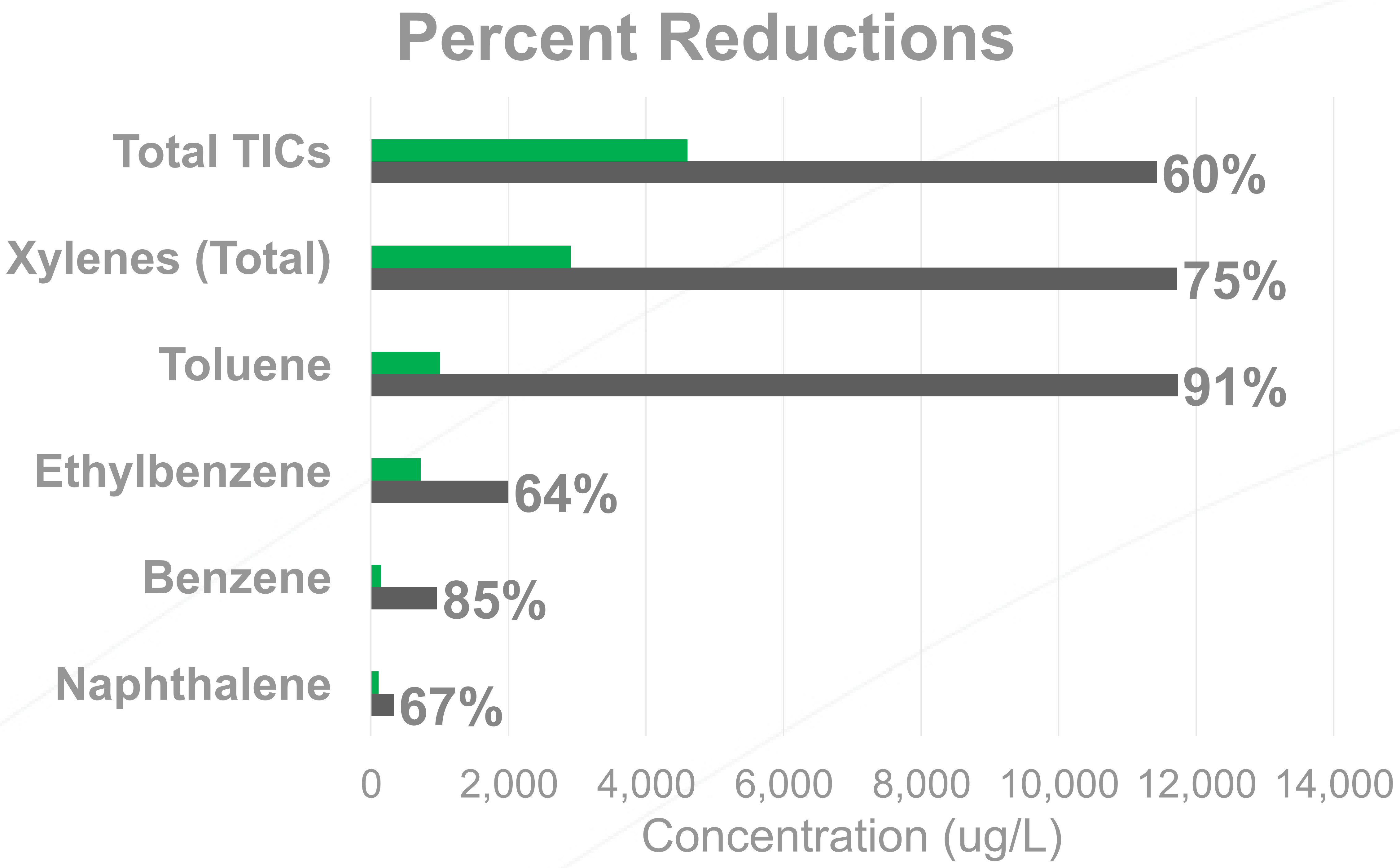
- Results:
  - 85% reduction of Benzene
  - 91% reduction in Toluene
  - 64% reduction in Ethylbenzene
  - 75% reduction in Xylene.
- Naphthalene increased following first injection event, reduced 67% overall
- TICs increased following first injection event, reduced by 60% overall



Based on post injection data, source area injections have been halted and residual downgradient plume injection events have occurred utilizing colloidal carbon

Ferrous Sulfide Activated (FSA) Persulfates

- Ideal for the remediation of higher concentration media - source areas and hot spots
- Lower pH injections - greater safety for the injection crew
- Provides extended activation of the persulfates in groundwater
- Simpler to store and inject
- Less activator required at reduced cost
- Less wear and tear on injection equipment
- Ease of transition to/from bioremediation

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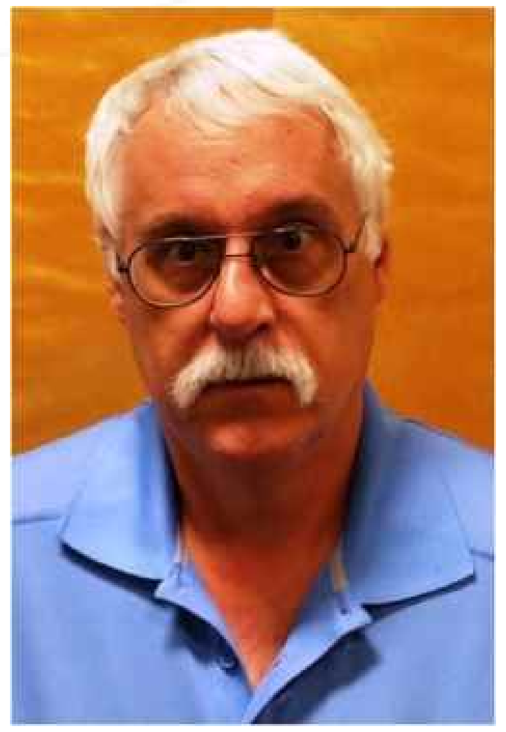
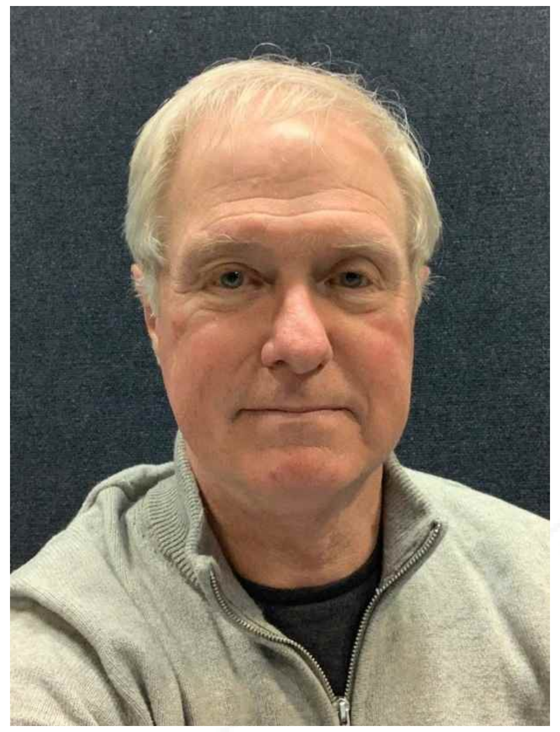
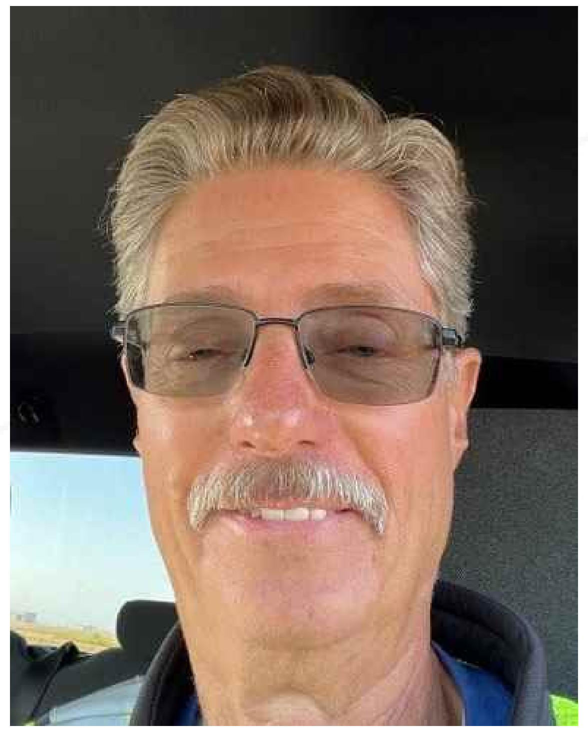
Questions?







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