

# **Confirmation of MTBE Destruction (not Volatilization) When Sparging with Ozone**

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# ABSTRACT

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Laboratory testing demonstrated that ozone ( $O_3$ ) can destroy MTBE and TBA in groundwater. MTBE was completely removed from water sparged with  $O_3$  or  $N_2$ , but acetone—a by-product of MTBE oxidation—was formed only in the ozone tests. The mass of acetone in the spiked DI test indicated stoichiometric conversion of MTBE to acetone. In tests using groundwater, acetone increased, then decreased, indicating production then destruction of acetone. TBA was completely removed from ozone tests using groundwater, but only 42-75% removed from  $N_2$  tests, implying that at least some TBA was destroyed by  $O_3$ .

# INTRODUCTION

# Site Background

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- **Petroleum distribution facility in California**
- **Groundwater contains up to**
  - **5,000  $\mu\text{g/L}$  methyl t-butyl ether (MTBE)**
  - **2,000  $\mu\text{g/L}$  t-butyl alcohol (TBA), and**
  - **20,000  $\mu\text{g/L}$  gasoline range petroleum hydrocarbons (TPH-g)**

# Ozone Basics--I

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- **Oxidizing gas that reacts with a wide range of organic compounds**
- **Iron and other metals may enhance effectiveness by generating hydroxyl radicals**
- **May be applied in situ to treat GW or vadose zone contaminants**
- **Gaseous nature of ozone raises concerns about mechanism of contaminant removal (destruction versus volatilization)**

## Ozone Basics--II

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- Complete mineralization possible:



- Dose requirements are: 8.2 g O<sub>3</sub> / g MTBE and 8.5 g O<sub>3</sub> / g TBA

# Factors to Consider When Evaluating Ozone

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- Contaminants can be **destroyed**
- Ozone is a gas—volatilization may occur
- Ozone reactions are rapid (seconds to minutes)
- Ozone is **non-selective**
- Ozone will oxidize dissolved metals
  - Iron will form solid hydroxides
  - Mn may oxidize to permanganate

# Study Objectives

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- **Determine whether  $O_3$  can remove contaminants from GW**
- **Determine whether removal is due to destruction or volatilization**
- **Assess whether metals present in soil and GW can enhance effectiveness of ozone**

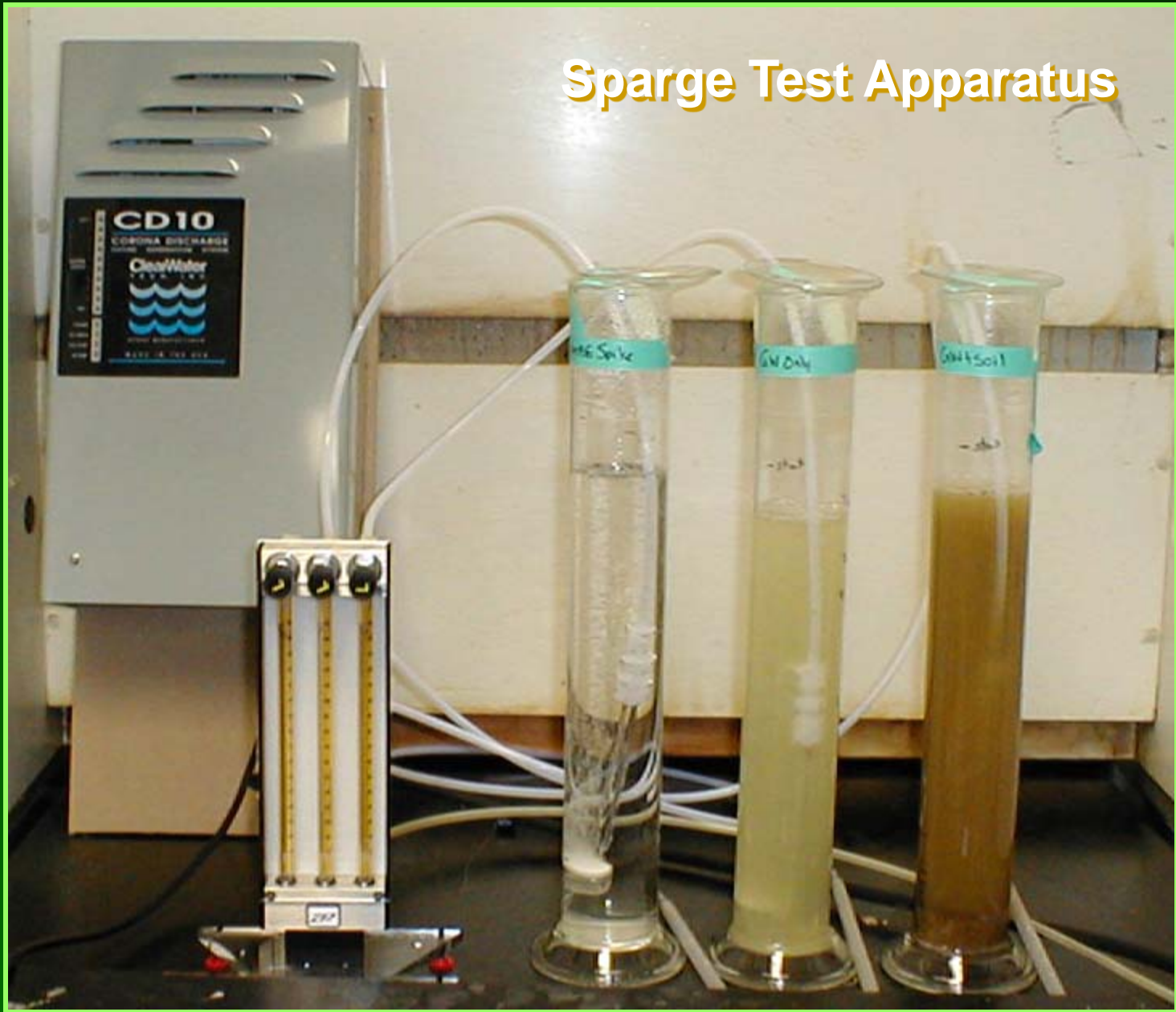


# **EXPERIMENTAL PROCEDURES**

## Sparge Tests

- **GW, GW+Soil, and Deionized (DI) water spiked with MTBE were sparged with O<sub>3</sub> or with nitrogen (N<sub>2</sub>) (*Table 1*)**
  - Approximately 0.76% Ozone
  - 800 mL/min flow to each reactor
- **Aqueous samples collected periodically and analyzed for TPH-g, MTBE, TBA, and acetone**

# Sparge Test Apparatus



# Table 1. Description of Sparge Tests

Test	Water Type	Soil	Sparge Gas
1A 1B (Control)	Spiked DI	None	O <sub>3</sub> N <sub>2</sub>
2A 2B	Site GW	None	O <sub>3</sub> N <sub>2</sub>
3A 3B	Site GW	Site Soil	O <sub>3</sub> N <sub>2</sub>

# RESULTS AND DISCUSSION

## Table 2. COC Concentrations ( $\mu\text{g/L}$ ). Test 1 (Spiked DI Water)

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Time	MTBE		TBA		Acetone	
	O <sub>3</sub>	N <sub>2</sub>	O <sub>3</sub>	N <sub>2</sub>	O <sub>3</sub>	N <sub>2</sub>
0	9,600	14,000	< 200	840	< 400	< 400
3	170	3,100	53	<2,000	890	110,000*
6	< 5	330	< 100	< 2000	5,000	91,000*
24	< 5	< 5	< 100	< 2000	6,700	59,000*

\* High acetone concentrations due to contamination

# Table 3. COC Concentrations ( $\mu\text{g/L}$ ). Test 2 (GW only)

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Time	MTBE		TBA		Acetone	
Hrs	O <sub>3</sub>	N <sub>2</sub>	O <sub>3</sub>	N <sub>2</sub>	O <sub>3</sub>	N <sub>2</sub>
0	4,300	4,100	1,700	1,600	< 200	< 200
3	< 1	< 100	110	<2,000	1,100	130,000*
6	< 0.5	< 50	< 10	< 1,000	810	90,000*
24	< 0.55	< 10	< 5	400	160	7,600*

\* High acetone concentrations due to contamination

**Table 4. COC Concentrations ( $\mu\text{g/L}$ ).  
Test 3 (GW+Soil)**

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<b>Time</b>	<b>MTBE</b>		<b>TBA</b>		<b>Acetone</b>	
<b>Hrs</b>	<b>O<sub>3</sub></b>	<b>N<sub>2</sub></b>	<b>O<sub>3</sub></b>	<b>N<sub>2</sub></b>	<b>O<sub>3</sub></b>	<b>N<sub>2</sub></b>
<b>0</b>	<b>3,900</b>	<b>3,600</b>	<b>1,600</b>	<b>1,600</b>	<b>&lt; 400</b>	<b>&lt; 200</b>
<b>3</b>	<b>1.3</b>	<b>16</b>	<b>140</b>	<b>1,100</b>	<b>1,500</b>	<b>&lt; 20</b>
<b>6</b>	<b>&lt; 1</b>	<b>&lt; 0.5</b>	<b>26</b>	<b>1,100</b>	<b>1,200</b>	<b>&lt; 20</b>
<b>24</b>	<b>&lt; 0.5</b>	<b>&lt; 0.5</b>	<b>&lt; 5</b>	<b>700</b>	<b>310</b>	<b>&lt; 20</b>



**TABLE 1. DCE, TCE in Groundwater Treated with  $\text{KMnO}_4$**

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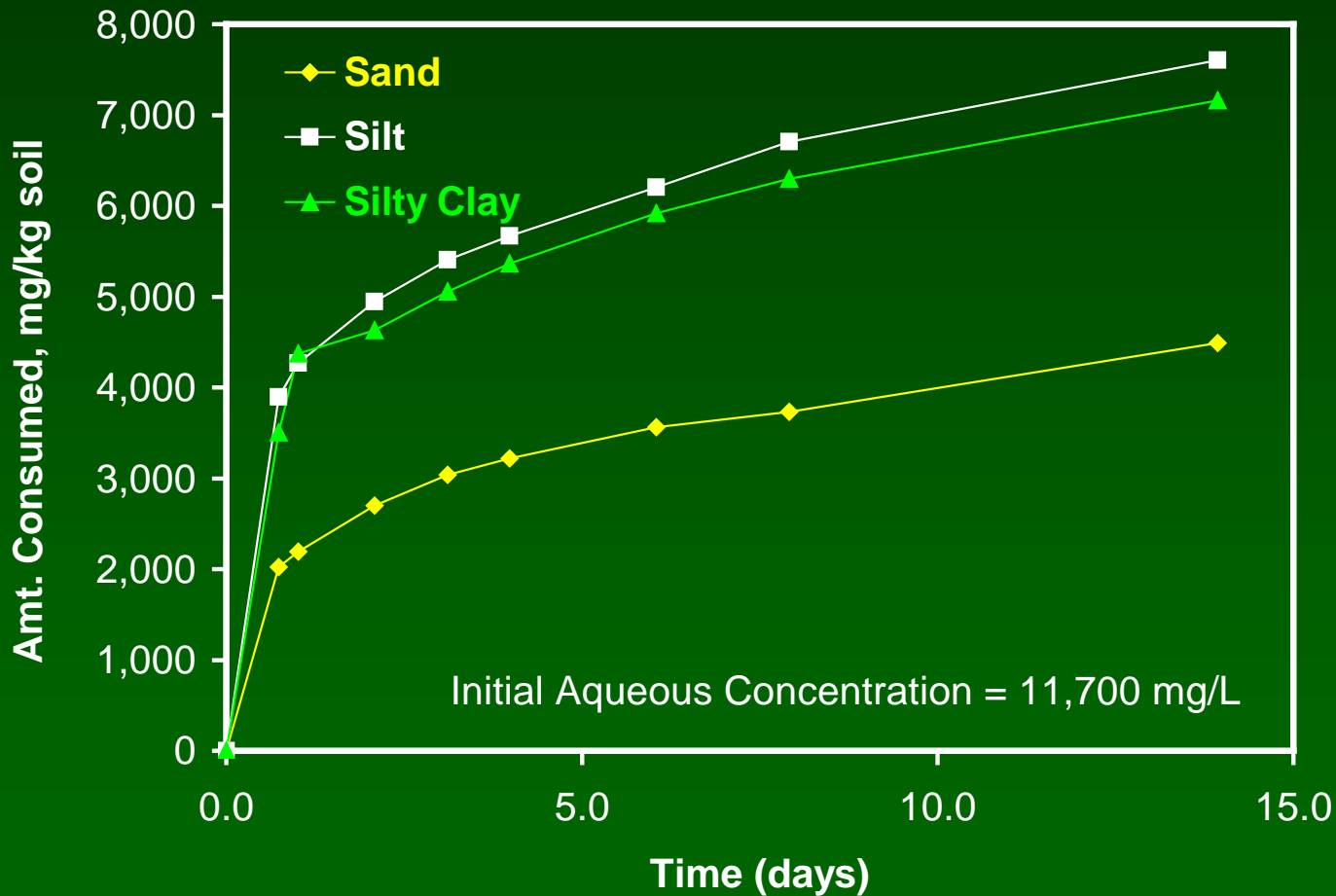
<b>Test</b>	<b>DCE, mg/L</b>	<b>TCE, mg/L</b>
<b>0X-Stoichiometric Dose (0mg/L <math>\text{KMnO}_4</math>)</b>	<b>1.9</b>	<b>0.18</b>
<b>2X-Stoichiometric Dose (16.1mg/L <math>\text{KMnO}_4</math>)</b>	<b>0.026</b>	<b>0.013</b>
<b>5X-Stoichiometric Dose (40.3mg/L <math>\text{KMnO}_4</math>)</b>	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>

## **KMnO<sub>4</sub> Dose Requirements--Soil**

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**As shown in Figure 1 and Table 2, site soils consumed a significant amount of KMnO<sub>4</sub>. The rate of consumption was initially fast, presumably due to rapid reaction of easily oxidizable species such as natural organic matter. This is consistent with the faster rate seen in the silt and clay, which had a higher organic carbon content than the sand (Table 3).**

# FIGURE 1. Consumption of $\text{KMnO}_4$ by Soil



# TABLE 2. Rate of $\text{KMnO}_4$ Consumption

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Soil	Initial Rate (0-1 days), mg/kg/day	Later Rate (1-14 days), mg/kg/day
Sand	2288 ( $r^2 = 0.962$ )	162 ( $r^2 = 0.924$ )
Silt	4447 ( $r^2 = 0.966$ )	244 ( $r^2 = 0.932$ )
Clay	4419 ( $r^2 = 0.994$ )	218 ( $r^2 = 0.956$ )

# TABLE 3. Selected Parameters of Site Soils

Material	TOC, mg/kg*	Cr(VI) Reducing Capacity, mg/kg	Total Cr, mg/kg
Sand	239	1,380	93
Silt	690	3,450	92
Clay	587	3,380	86
KMnO <sub>4</sub> **	n/a	n/a	63

\* TOC=Total Organic Carbon; \*\* EM Science, Guaranteed Reagent

## Formation of Cr(VI)

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As shown in Table 4, Cr(VI) was formed in batch tests in which site soils were exposed to  $\text{KMnO}_4$ . The amount of Cr(VI) measured was greater than the amount present in the  $\text{KMnO}_4$ , implying that some soil chromium was oxidized.

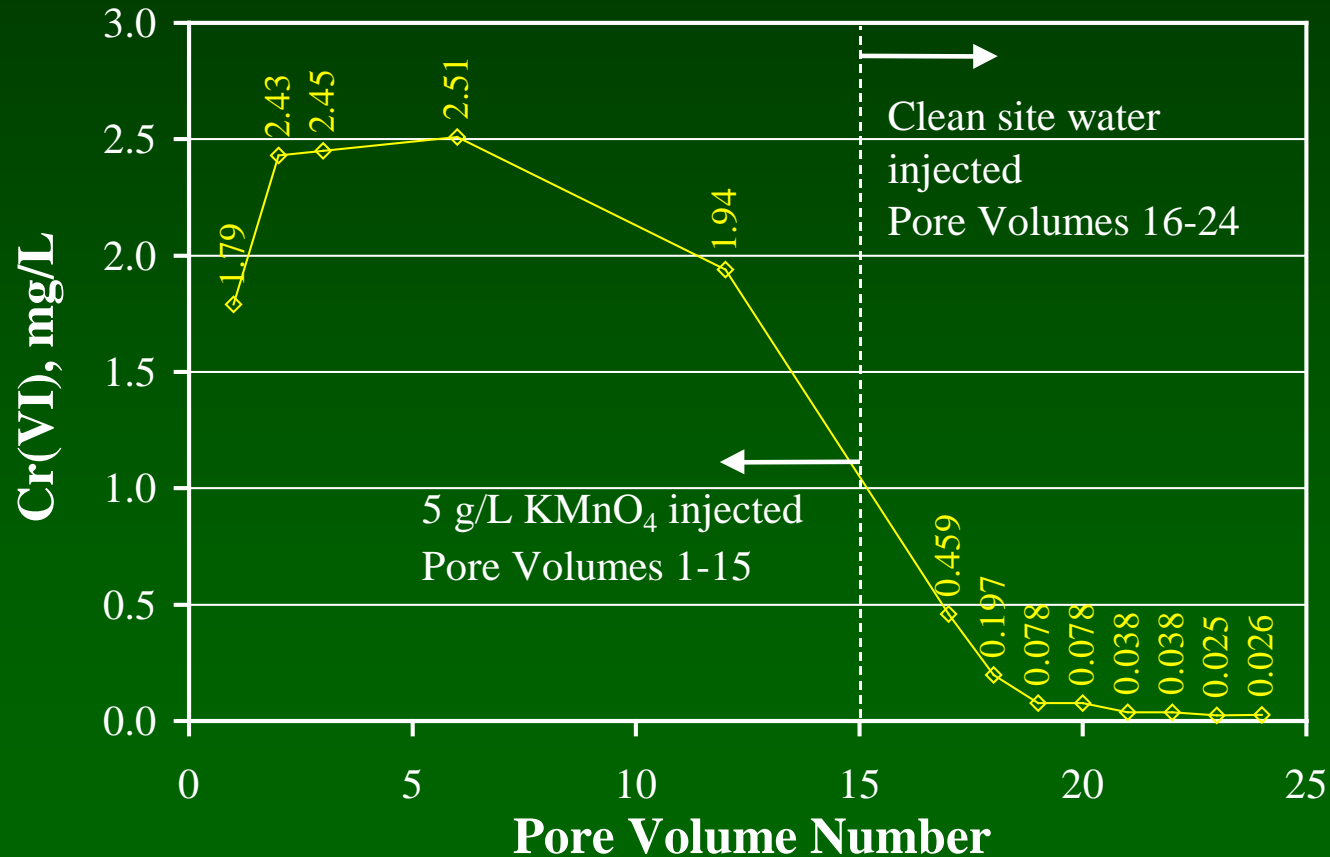
Figure 2 confirms the results of the batch test. Note that Cr(VI) concentration decreased sharply once  $\text{KMnO}_4$  application ceased.

# TABLE 4. Aqueous Cr(VI) in Batch Tests with Soil Exposed to $\text{KMnO}_4$ .

Soil (g/L $\text{KMnO}_4$ added)	Cr(VI), mg/L (colorimetric)	Cr(VI), mg/L (ion chromatography)
Sand (0.5)	0.81	0.69
Silt (0)	< 0.05	n.a.
Silt (1)	0.84	n.a.
Clay (0)	< 0.05	n.a.
Clay (1)	0.81	n.a.

n.a. = not analyzed

# FIGURE 2. Cr(VI) in Column Effluent





# **Fate of Cr(VI)--Addition of Reducing Agents**

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**In a batch test designed to simulate injection of  $\text{KMnO}_4$  into the subsurface followed by injection of a reducing agent,  $\text{KMnO}_4$ -treated soil was washed with a reducing agent, then clean site water. Soil treated with  $\text{FeSO}_4$  or ascorbic acid had less Cr(VI) in the aqueous phase than soil treated with clean site water or molasses (Table 6). This indicates that application of a reducing agent after treatment with  $\text{KMnO}_4$  can hasten the removal of Cr(VI).**

# TABLE 5. Effect of Reducing Agents on [Cr(VI)]

Cummulative Time (days)	3	4	5	12	13	20
Replicate	Cr(VI), $\mu\text{g/L}$					
	After KMnO <sub>4</sub>	After Reductant	After Clean Water			
1-Fe(II)	234	< 10	< 10	< 10	n.a.**	< 10
2-Ascorbic Acid	225	28	< 10	< 10	n.a.	< 10
3-Molasses	242	40	12	< 10	n.a.	< 10
4-Clean Site Water	221	42	13	20	n.a.	< 10
5-None*	240	230	214	81	n.a.	< 10
6-None*	248	n.a.	n.a.	n.a.	155	< 10
7-None*	237	n.a.	n.a.	n.a.	153	< 10
8-None*	240	n.a.	n.a.	n.a.	163	13

\* KMnO<sub>4</sub> solution not added

\*\* n.a. = not analyzed

# **Fate of Cr(VI)--Natural Attenuation**

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**In the batch test to assess the effect of reducing agents, some replicates were exposed to  $\text{KMnO}_4$ , but were otherwise untreated. After 13 days, the aqueous Cr(VI) had decreased, suggesting natural attenuation was occurring (Table 5, “None”).**

**To confirm this, soil was saturated with site water was spiked with Cr(VI). After 7 days, Cr(VI) in the porewater was measured. As shown in Table 6, the concentration decreased by 43%.**

## TABLE 6. Natural Attenuation

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	Cr(VI) in pore water, mg/L
<b>Initial* (Day 0)</b>	<b>1.2</b>
<b>Final (Day 7)</b>	<b>0.68</b>
<b><i>% Removed</i></b>	<b><i>43%</i></b>

\*Clean site water spiked with Cr(VI); used to saturate soil.

# CONCLUSIONS

- **KMnO<sub>4</sub> effectively removed contaminants from site groundwater**
- **KMnO<sub>4</sub> dose is controlled by soil KMnO<sub>4</sub> demand**
- **Soil chromium was oxidized to Cr(VI) upon exposure to KMnO<sub>4</sub>**
- **Cr(VI) naturally attenuated in laboratory tests**
- **Formation and attenuation of Cr(VI) must be considered when evaluating KMnO<sub>4</sub> injection**