Laboratory Investigations of Mechanisms for 1,4-Dioxane Destruction by Ozone in Water

Ann Louise Sumner (Battelle, Columbus, Ohio, USA) Michelle Simon (U.S. EPA, Cincinnati, Ohio, USA)

Chlorinated and Recalcitrant Compound Conference Monterey, California

May 25, 2010

## **Outline of Presentation**

- Introduction of oxidation for 1,4-Dioxane
- Cooper Drum Field Project and Results
- Laboratory studies to investigate results
- Experimental Methods
- Summary and Conclusion

## **Previous Presentations 2006 Battelle Monterey Conference**

- Sadeghi VM, Gruber DJ, Yunker E, Simon M, Gustafson D. 2006a. In Situ Oxidation of 1,4-Dioxane with Ozone and Hydrogen Peroxide. Proceedings, Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, USA, May 22-25, Paper D-31.
- Schreier CG, Sadeghi VM, Gruber DJ, Brackin J, Simon M, Yunker E. 2006b. In-Situ Oxidation of 1,4-Dioxane. Proceedings, Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, USA, May 22-25, Paper D-21.

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## Site Background

- Cooper Drum Company Superfund Site
- Located in South Gate, Los Angeles County
- Chlorinated ethenes (TCE; PCE; 1,2-DCE; 1,1-DCE; VC)
- Chlorinated ethanes (1,1-DCA; 1,2-DCA)
- Benzene
- 1,4-dioxane (more recent discovery: April 2004)

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## 1,4-Dioxane

*Stable Chemical Structure* 



### Air Stripping?



Low volatility

#### Separation/Adsorption?



High solubility in water

From Sadeghi et al. 2006

#### **Bioremediation?**

Not easily biodegradable

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## **Oxidant Strengths**

Oxidant	Oxidation Potential (Volts)	
Hydroxyl radical (OH°)	2.8	
Sulfate radical $(SO_4^{-\circ})$	2.5	
Ozone	2.1	
Sodium persulfate	2.0	
Hydrogen peroxide	1.8	
Permanganate	1.7	
Chlorine	1.4	
Oxygen	1.2	

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#### **Mechanisms for Oxidation With Ozone**

Direct Ozone Reaction with Alkenes and Formation of an Ozonide

 $O_3 + RC=CR \rightarrow RCOCR + O_2$ 

Ozone Reaction with Hydroxide Ion can form the Hydroxyl Radical

 $O_3 + OH^- \rightarrow O_2 + 2OH^\circ$ Radical formation may occur in presence of organic soil compounds (soil humics, carboxylic acids, alcohols, etc.)

Ozone Reaction with Hydrogen Peroxide can form the Hydroxyl Radical

 $2 O_3 + H_2O_2 \rightarrow 2OH^{\circ} + 3O_2$ 

From Sadeghi et al. 2006

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## O<sub>3</sub> versus \*OH

- Literature implies that ozone is too slow to be effective in 1,4D destruction on its own
- AOP use hydrogen peroxide to increase concentration of hydroxyl radical
- But it is hard to get H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> to mix in porous media and then degrade COC

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#### Hard to measure \*OH directly

- Short half life
- Analytical limitations
- Use chemical probe
  - any compound that reacts readily with \*OH
    - at a known rate
    - easily measured
    - salicylic acid (SA) was selected as the chemical probe. Salicylic acid (SA) reacts readily with \*OH radicals to produce the stable products 2,3-dihydroxybenzoic acid (DHBA), 2,5-DHBA, and catechol.

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# **TABLE 1.** Expected reactions, reported rates, and relativedecay rates

Reaction Number	Reaction	Rate Constant, k (M <sup>-1</sup> s <sup>-1</sup> )	Relative Decay Rates (k <sub>SA</sub> /k <sub>1,4D</sub> )	Reference
1	°OH + SA	5 x 10 <sup>9</sup>	2.1 - 4.5	Karnik et al., 2007
2	°OH + 1,4D	1.1 x 10 <sup>9</sup> 2.4 x 10 <sup>9</sup>		Anbar et al.,1996 Thomas, 1966
3	O <sub>3</sub> + SA	3.1 x 10 <sup>3</sup>	9.4 x 10 <sup>3</sup>	Hoigne and Bader, 1983 (II)
4	O <sub>3</sub> + 1,4D	0.32 (at pH 2)		Hoigne and Bader, 1983 (I)

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## Laboratory Apparatus



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- \*OH chemistry plays a significant role in the destruction of 1,4-dioxane by treatment with O3,
  - even in deionized water
  - in the absence of potential catalysts
- Future Work
  - Perform in porous media

## Acknowledgements & Disclaimer

- Funding for this study was provided by the U.S. EPA National Risk Management Research Laboratory under Contract # EPC05057, Task Order 32, Work Assignment 2. The authors acknowledge the expertise of Raj Mangaraj and A.J. Savage who performed the HPLC/MS/MS analyses.
- The extended abstract summarizes recent research and does not present U.S. EPA policy.

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## THANK YOU! QUESTIONS?



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