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

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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.

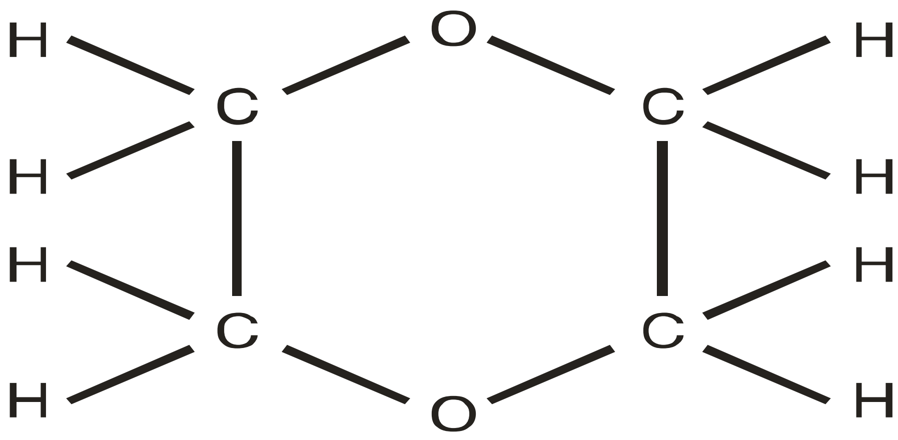
- Schreier CG, Sadeghi VM, Gruber DJ, Brackin J, Simon M, Yunker E. 2006b. In-Situ Oxidation of 1,4-Dioxane. Proceedings, Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, USA, May 22-25, Paper D-21.

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)

1,4-Dioxane

Stable Chemical Structure



Air Stripping?

Low volatility

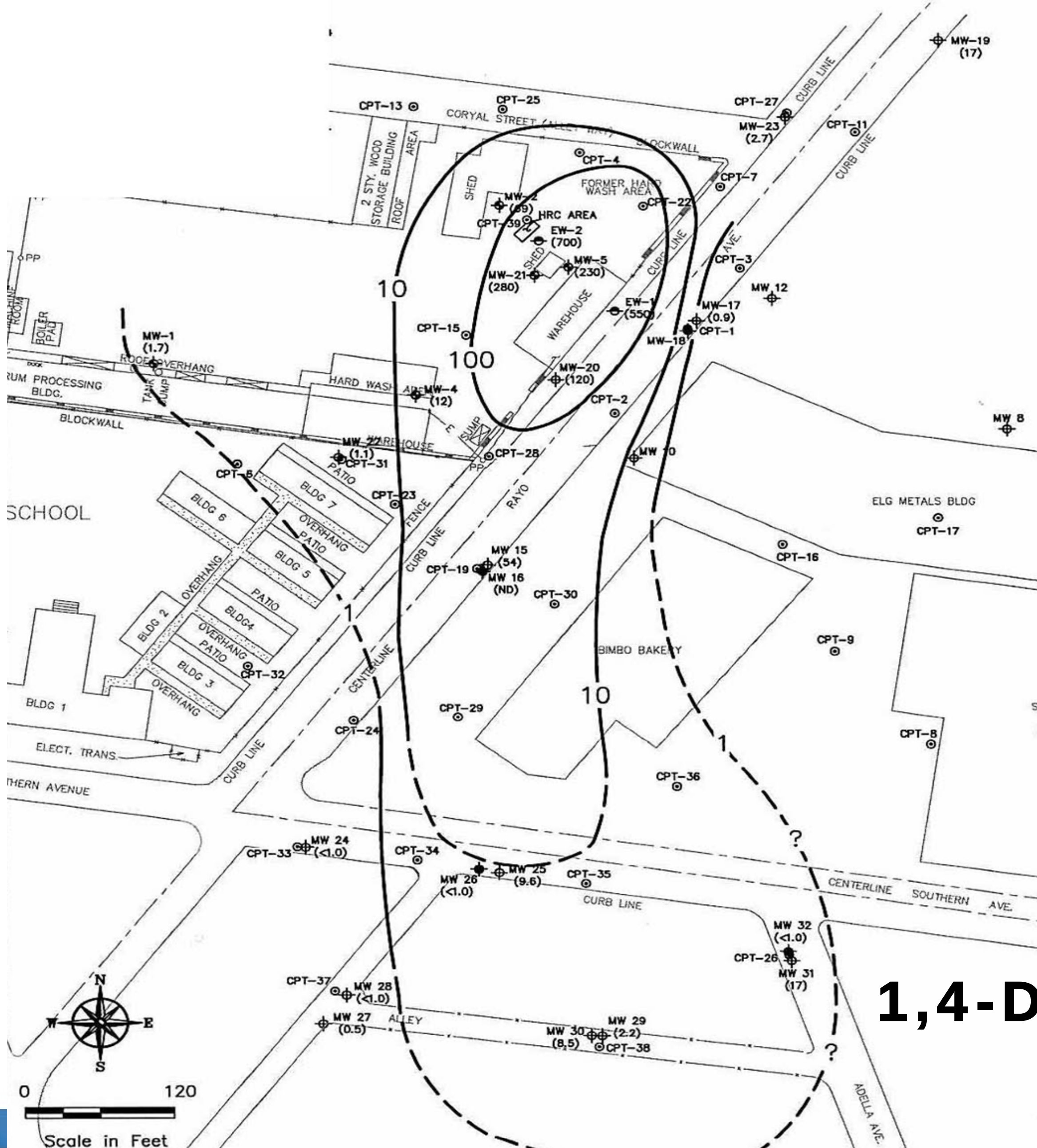
Separation / Adsorption?

High solubility in water

From Sadeghi et al. 2006

Bioremediation?

Not easily biodegradable


MW-19 (17)
CPT-13
CPT-25
CORYAL STREET
CPT-27
MW-23 (2.7)
CURB LINE
CPT-11
2 STY. WOOD STORAGE BUILDING
ROOF AREA
SHED
CPT-4
FORMER HAND WASH AREA
CPT-7
MW-2 (69)
HRC AREA
CPT-22
CPT-39
EW-2 (700)
MW-5 (230)
MW-21 (280)
CPT-3
MW 12
WAREHOUSE
EW-1 (550)
MW-17 (0.9)
CPT-1
MW-18
10
100
CPT-15
MW-1 (1.7)
ROOF OVERHANG
BOILER PAD
DRUM PROCESSING BLDG.
HARD WASH AREA
MW-4 (12)
MW-20 (120)
CPT-2
BLOCKWALL
MW 8
MW 22 (1.1)
CPT-31
WAREHOUSE
CPT-28
MW 10
CPT-6
BLDG 7
BLDG 6
RAYO
SCHOOL
PATIO
CPT-23
FENCE
OVERHANG
ELG METALS BLDG
CPT-17
CPT-16
BLDG 5
CURB LINE
MW 15 (54)
CPT-19
MW 16 (ND)
CPT-30
BLDG 2
BLDG4
BLDG 3
CPT-32
1
CENTERLINE
BIMBO BAKERY
CPT-9
10
BLDG 1
CPT-29
CPT-24
CPT-8
ELECT. TRANS.
CPT-36
SOUTHERN AVENUE
MW 24 (<1.0)
CPT-33
CPT-34
MW 25 (9.6)
MW 26 (<1.0)
CPT-35
CURB LINE
CENTERLINE SOUTHERN AVE.
?
MW 32 (<1.0)
CPT-26
MW 31 (17)
CPT-37
MW 28 (<1.0)
MW 27 (0.5)
ALLEY
MW 30 (8.5)
MW 29 (2.2)
CPT-38
N
W
E
S
0
120
Scale in Feet
ADELLA AVE.

1,4-Dioxane

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

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

O_3 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_2O_2 and O_3 to mix in porous media and then degrade COC**

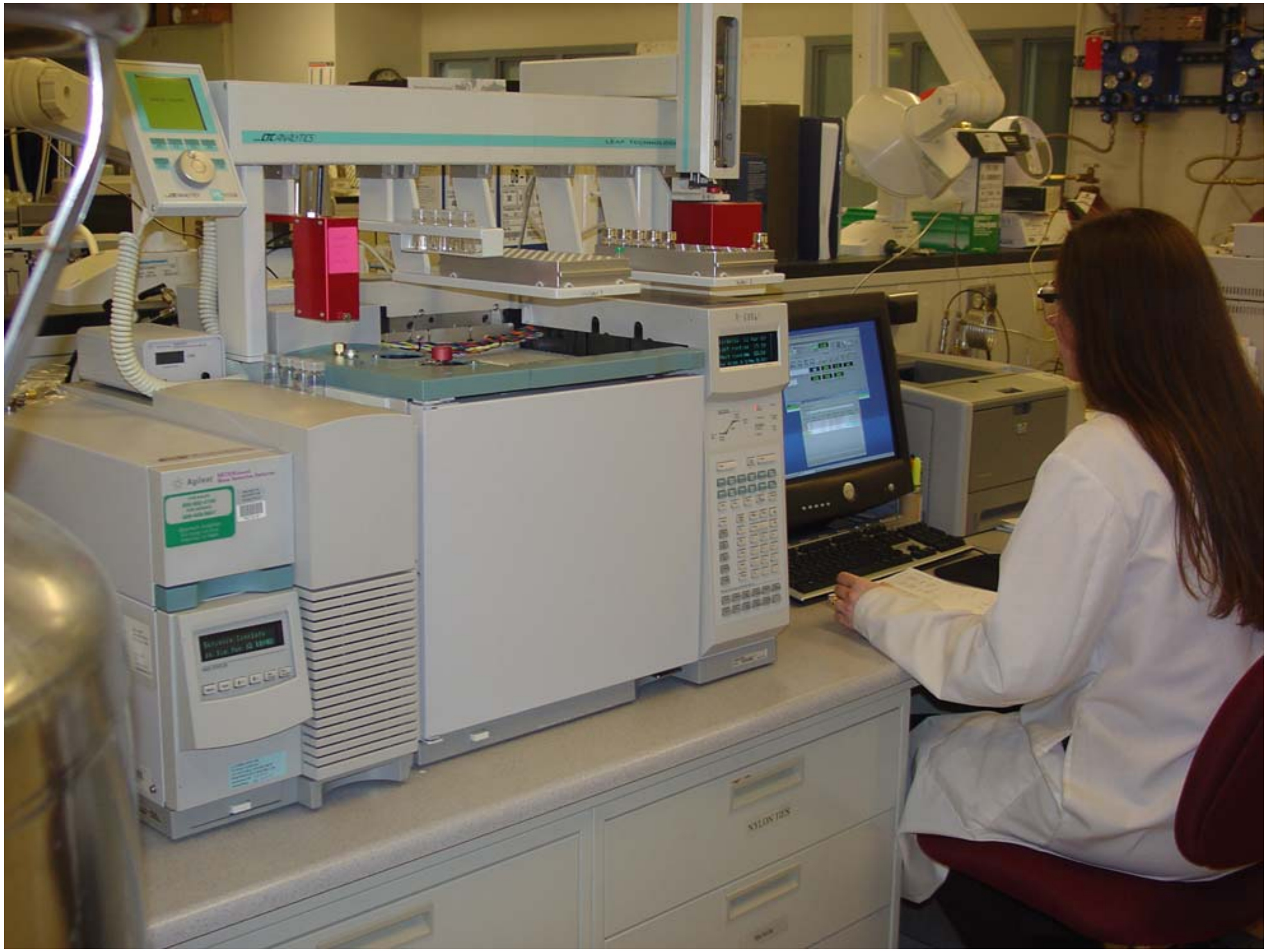
- Hard to measure *OH directly
  - Short half life
  - Analytical limitations
- Use chemical probe
  - any compound that reacts readily with *OH
    - at a known rate
    - easily measured
    - salicylic acid (SA) was selected as the chemical probe. Salicylic acid (SA) reacts readily with *OH radicals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

TABLE 1. Expected reactions, reported rates, and relative decay rates

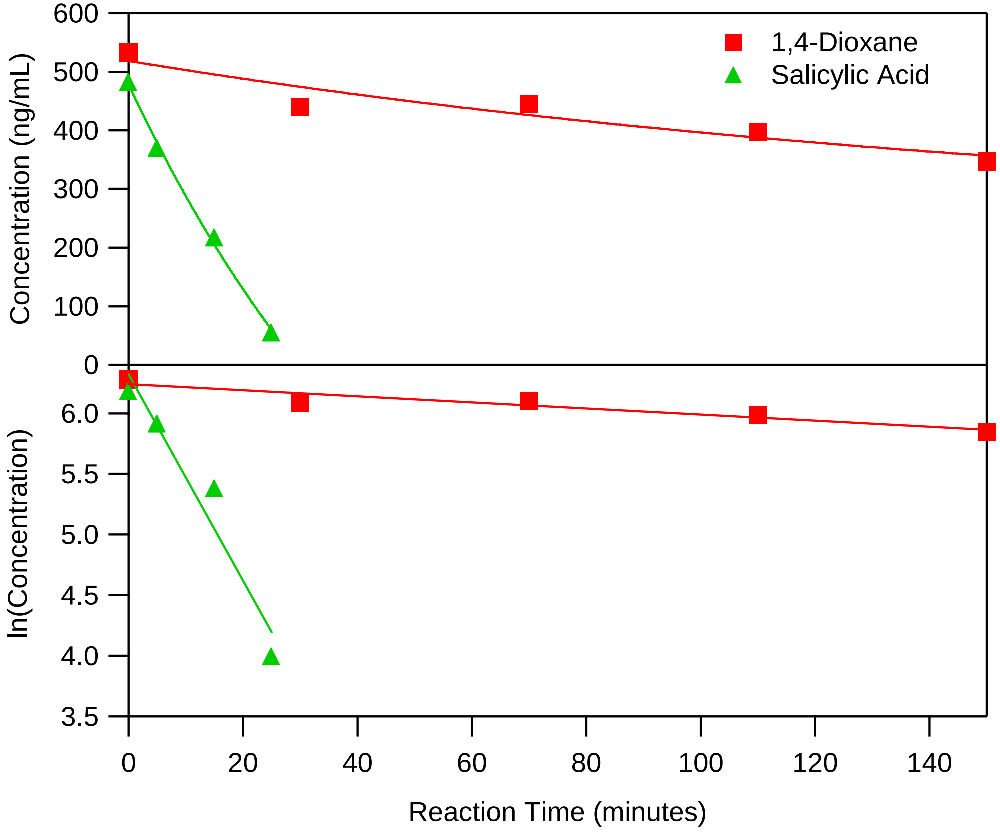
Reaction Number	Reaction	Rate Constant, k ($M^{-1}s^{-1}$)	Relative Decay Rates ($k_{SA}/k_{1,4D}$)	Reference
1	ºOH + SA	5×10^9	2.1 - 4.5	Karnik et al., 2007
2	ºOH + 1,4D	1.1×10^9 2.4×10^9		Anbar et al.,1996 Thomas, 1966
3	O_3 + SA	3.1×10^3	9.4×10^3	Hoigne and Bader, 1983 (II)
4	O_3 + 1,4D	0.32 (at pH 2)		Hoigne and Bader, 1983 (I)

Laboratory Apparatus

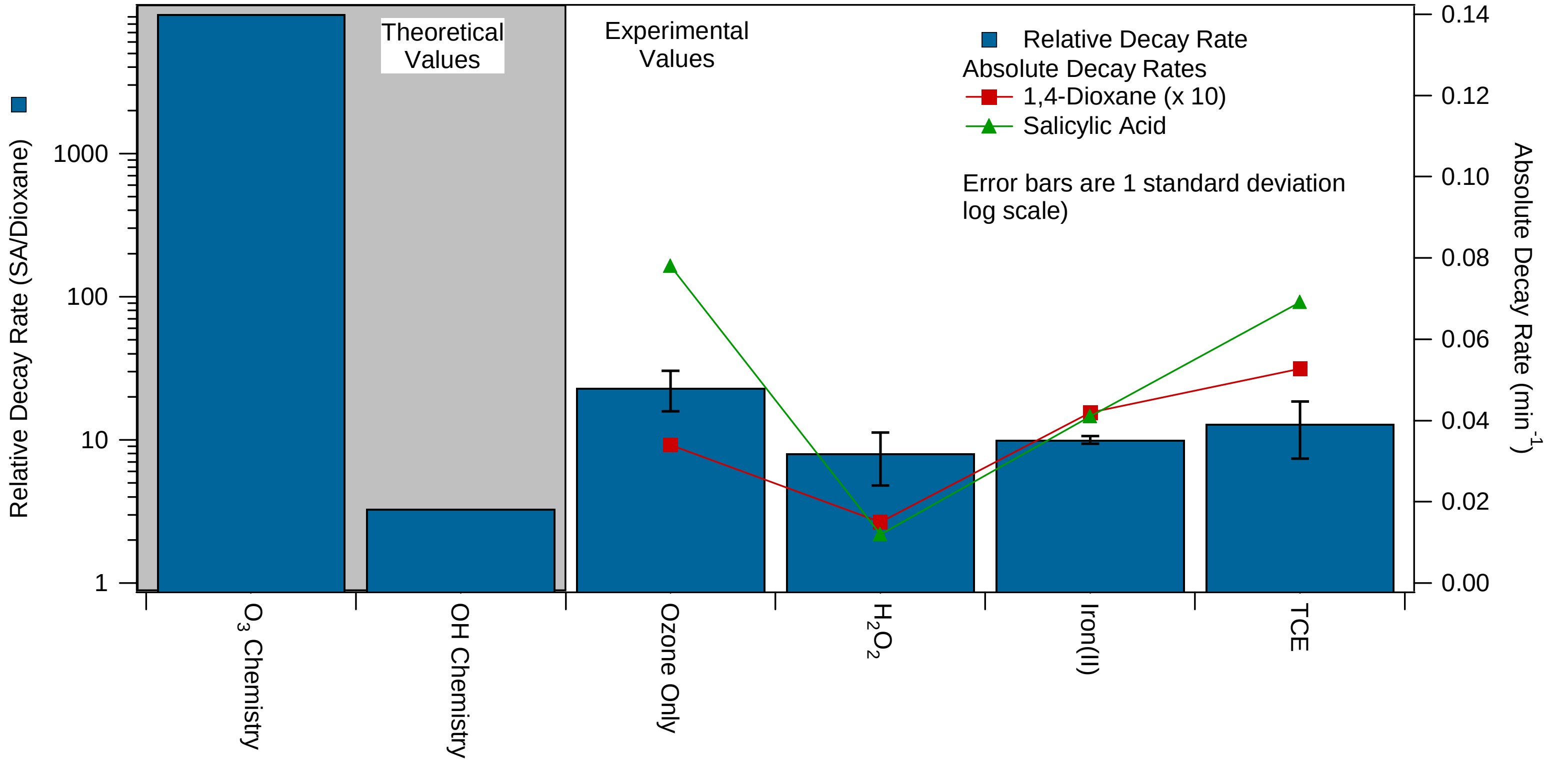
SPME GC/MS



HPLC MS/MS


1,4-Dioxane
Salicylic Acid
Concentration (ng/mL)
600
500
400
300
200
100
0
ln(Concentration)
6.0
5.5
5.0
4.5
4.0
3.5
0
20
40
60
80
100
120
140
Reaction Time (minutes)

Results



Relative Decay Rate (SA/Dioxane)
1000
100
10
1
Theoretical Values
Experimental Values
Relative Decay Rate
Absolute Decay Rates
1,4-Dioxane (x 10)
Salicylic Acid
Error bars are 1 standard deviation
log scale)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Absolute Decay Rate (min-1)
O3 Chemistry
OH Chemistry
Ozone Only
H2O2
Iron(II)
TCE

Conclusions

- *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

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- The extended abstract summarizes recent research and does not present U.S. EPA policy.

THANK YOU!
QUESTIONS?