

In Situ Oxidation of 1,4-Dioxane (Laboratory Results)



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ABSTRACT

Laboratory testing demonstrated that ozone (O₃) alone was as effective as a mixture of O₃ and hydrogen peroxide (H₂O₂) at destroying 1,4-dioxane in site groundwater. Application of 940 mg O₃ reduced the concentration of 1,4-dioxane from 680 micrograms per liter (µg/L) to < 3 µg/L. The same results were achieved by treating with 940 mg O₃ and 0.07-0.35% H₂O₂. Ozonation of deionized water spiked with 1,4-dioxane resulted in destruction of 75% of 1,4-dioxane, while ozonation (under the same conditions) of mixtures of deionized water, 1,4-dioxane, and one additive produced complete destruction. The additives tested were constituents of site groundwater: ferrous iron (2 mg/L), chelated iron (2 mg/L iron), and alkalinity (1000 mg/L as CaCO₃). These results imply that although ozone can partially destroy 1,4-dioxane, compounds naturally present in this site's groundwater can enhance the effectiveness of ozone in the same manner as H₂O₂. The effect of O₃ and O₃+H₂O₂ on secondary water quality was similar for most parameters evaluated. The exception was bromate, a higher concentration of which was produced by O₃ alone.

BACKGROUND

The Site: Cooper Drum Superfund site in South Gate, Los Angeles County, California.

The Chemicals of Concern: 1,4-dioxane (~ 400 µg/L), a stabilizer for chlorinated solvents. Trichloroethene (TCE) and other chlorinated volatile organic compounds (VOCs).

Proposed Treatment: *In situ* chemical oxidation using ozone (O₃) plus hydrogen peroxide (H₂O₂)

- Reaction between O₃ and H₂O₂ generates the hydroxyl radical (OH[•])
- Destroys a wide range of organic compounds, including chlorinated solvents and 1,4-dioxane
- Generally more effective toward 1,4-dioxane than ozone alone
- Less likely than ozone alone to have secondary effects such as formation of bromate (from bromide) or formation of hexavalent chromium (from soil chromium)

STUDY OBJECTIVES

- Compare removal of chemicals of concern (COCs) by O₃ alone and by O₃+H₂O₂
- Determine whether removal is due to volatilization or destruction
- Measure effect of O₃+H₂O₂ on bromate, Cr(VI), and dissolved metals
- Evaluate the ability of naturally occurring compounds (rather than H₂O₂) to enhance effectiveness of O₃

METHODS

O₃ Generation: 26-31 mg O₃/L air (1.2-1.4 % v/v) was generated using a corona discharge ozone generator with extra dry air as the feed gas.

COC Removal Tests (assess COC removal, mechanism of removal, secondary effects)

- Batch tests were performed using the conditions in Table 1.
- Two sets of tests: Set B tests to confirm Set A results and evaluate 1,4-dioxane loss via sparging
- Analyses
 - Set A Tests: VOCs, 1,4-dioxane, bromate, bromide, hexavalent chromium [Cr(VI)] and metals in water; VOCs in off-gas
 - Set B Tests: 1,4-dioxane in soil and water



TABLE 1. Conditions for COC Removal Tests^a.

Test	Initial H ₂ O ₂ , %	Sparge Gas ^b	O ₃ Dose ^c , mg
Set A Tests			
Control-A	0	None	0
Ozone-A	0	Ozone	940
O3+H2O2-Low	0.07	Ozone	940
O3+H2O2-High	0.35	Ozone	940
Set B Tests			
Control-B	0	None	0
Nitrogen	0	Nitrogen	0
Ozone-B	0	Ozone	1,100

^aAll tests used 100 g site soil and 1,000 mL site groundwater. ^bAll tests sparged at a flowrate of 200 mL/minute for 180 minutes. ^cO₃ concentration was 26 mg O₃/L air for Set A tests and 31 mg O₃/L air for Set B tests

Potential "O₃ Enhancer" Tests

- Batch tests were performed using the conditions in Table 2.
- Potential "enhancers" are compounds that are present at site (chelated iron may be present due to previous remediation activities)
- Analyses: 1,4-dioxane in water and soil, if applicable

TABLE 2. Conditions for Potential "O₃ Enhancer" Tests^a.

Test	Soil, g	Water, mL	Enhancer
Control-C	None	1,000 mL spiked DI ^b	None
Ferrous Iron	None	1,000 mL spiked DI	2 mg/L iron ^c
Chelated Iron	None	1,000 mL spiked DI	2 mg/L iron ^d
Bicarbonate	none	1,000 mL spiked DI	1,000 mg/L as CaCO ₃
Olefins (TCE)	None	1,000 mL spiked DI	500 µg/L TCE ^e
Groundwater Only	None	1,000 mL site groundwater ^f	None
Soil	100g site soil	1,000 mL spiked DI	None

^aO₃ dose per test was 1,100 mg; all tests sparged with 25 mg/L O₃ in air at 250 mL/minute for 180 minutes. ^bDI water spiked with approximately 400 µg/L 1,4-dioxane. ^cAdded as ferrous sulfate heptahydrate; ^dAdded as Grow-More™ agricultural iron (iron EDTA), which is 13% iron by weight; ^eDI water also spiked with about 100 µg/L trichloroethene (TCE), an olefin present at the site; ^fSite groundwater less settleable solids

Analytical Procedures

The analytical methods used are shown in Table 3.

TABLE 3. Analytical Procedures.

Analyte	Method
VOCs	USEPA 8260B
1,4-dioxane	USEPA8260 with direct injection
Bromide and bromate	USEPA 300
Cr(VI)	colorimetric
Metals	USEPA 6020

RESULTS AND DISCUSSION

COC Removal/Mechanism of Removal: Aqueous VOC and 1,4-dioxane concentrations are shown in Table 4. No VOCs were seen in the off-gases above the detection limit of 0.4 µg/L. Set B test results are shown in Table 5. In short

- complete removal of VOCs and 1,4-dioxane was seen in all Set A and Set B tests employing O₃ or O₃+H₂O₂.
- 1,4-dioxane not removed by nitrogen (N₂) in Set B tests
- no VOC seen in off-gases of Set A tests
- no VOCs seen in O₃-treated soil in Set B tests.

The results imply that

- O₃ and O₃+H₂O₂ appear equally effective at removing 1,4-dioxane from site materials. Possibly, iron naturally present in groundwater enhanced the effectiveness of O₃—Bowers and Miller (2002) demonstrated that O₃ can react with iron and manganese to generate hydroxyl radicals.
- 1,4-dioxane removal from site materials by O₃ alone is reproducible, since similar results were obtained in the Set A and Set B tests
- VOC and 1,4-dioxane removal was due to destruction, not volatilization, since no VOCs were seen in off-gases and 1,4-dioxane was removed by O₃, but not by N₂, an inert gas.

TABLE 4. COC Removal. Set A Tests.

Analyte	Aqueous Concentration, µg/L			
	Control-A	Ozone-A	O ₃ +H ₂ O ₂ -Low	O ₃ +H ₂ O ₂ -High
1,4-dioxane	680	< 3	< 3	< 3
1,1-DCE	23	< 1	< 1	< 1
trans-1,2-DCE	6	< 1	< 1	< 1
1,1-DCA	39	< 1	< 1	< 1
cis-DCE	160	< 1	< 1	< 1
1,2-DCA	< 5	< 1	< 1	< 1
TCE	420	< 1	< 1	< 1
bromoform	< 5	1.4	< 1	< 1

TABLE 5. COC Removal. Set B Tests.

Test	1,4-Dioxane Concentration, ppb*	
	Soil	Water
Untreated material	< 50	690
Control-B	110	600
Nitrogen-B	110	600
Ozone-B	< 50	< 3

* "ppb" = parts per billion = "µg/kg" for soil and "µg/L" for water

Evaluation of Ozone Enhancers: Results are shown in Table 6 In short

- partial (75%) removal of 1,4-dioxane was seen in the control, which contained no enhancer
- complete (> 99%) removal of 1,4-dioxane was seen for all potential enhancers except olefins (TCE) in all Set A and Set B tests employing O₃ or O₃+H₂O₂
- complete removal was seen with site groundwater only and with site soil only.

The results imply that

- the better-than-expected results for O₃ only in the Set A and Set B tests (COC Removal) are not due to application of excess O₃ because a similar O₃ dose applied to DI water spiked with 1,4-dioxane (Control C test) resulted only in 75% removal of the 1,4-dioxane.
- several compounds naturally present in soil and groundwater can enhance the effectiveness of O₃ toward 1,4-dioxane destruction in the same way that H₂O₂ enhances O₃.
- the enhancers are present in both soil and groundwater since 1,4-dioxane reacted more quickly in groundwater than in DI water and because addition of site soil to 1,4-dioxane-spiked DI water enhanced the removal of 1,4-dioxane
- TCE (an olefin) did not affect 1,4-dioxane removal by O₃ as much as the other enhancers, possibly due to competition for the O₃

TABLE 6. Potential O₃ Enhancers.

Test	1,4-Dioxane Concentration, ppb*	
	Soil	Water
Untreated spiked DI	not applicable	400
Control-C (no enhancer)	not applicable	98
Ferrous Iron	not applicable	< 3
Chelated Iron	not applicable	< 3
Bicarbonate	not applicable	< 3
Olefins (TCE)*	not applicable	69
Groundwater Only	not applicable	< 3
Soil	< 50	< 3

* "ppb" = parts per billion = "µg/kg" for soil and "µg/L" for water

Secondary Effects: Results of water quality parameters analyses taken of the Set A tests are shown in Table 7. In short

- Bromate was generated in both the O₃ and the O₃+H₂O₂ tests, but the amount formed was greater in the O₃ only test. Other parameters affected by both treatments were copper, chromium, manganese, iron, nickel, barium and tungsten
- vanadium increased only in the O₃+H₂O₂ tests
- selenium increased only in the O₃ test.

The results imply that

- Adverse effects on water quality that may be associated with O₃ may be eliminated or lessened by using O₃+H₂O₂
- O₃+H₂O₂ may adversely affect some water quality parameters that are not usually affected by O₃.

TABLE 7. Secondary Effects.

Analyte	Units	Control-A	O ₃ -A	O ₃ +H ₂ O ₂ -Low	O ₃ +H ₂ O ₂ -High
Bromate	µg/L	< 25	232	46	78
Bromide	µg/L	2,310	1,910	2,260	4,170
Cr(VI)	µg/L	< 1.00	9.98	< 10*	< 10*
H ₂ O ₂ , residual	mg/L	0	< 1	~ 400	~ 2,000
Metals					
vanadium	µg/L	27	30	130	160
chromium (total)	µg/L	< 5	12	< 5	6.6
manganese	µg/L	2,400	< 10	180	190
iron	µg/L	2,400	1,900	1,200	1,200
cobalt	µg/L	< 5	< 5	< 5	5.5
nickel	µg/L	66	29	18	26
copper	µg/L	30	40	26	79
arsenic	µg/L	25	29	25	26
selenium	µg/L	7.0	18	7.4	9.6
molybdenum	µg/L	150	160	150	140
barium	µg/L	31	19	18	16
tungsten	µg/L	10	< 5	< 5	< 5
pH	--	7.37	8.15	8.16	8.20

Be, Al, Zn, Ag, Cd, Sb, Hg, Ti, Pb were not detected in any test.

CONCLUSIONS

- O₃ was as effective as O₃+H₂O₂ at removing 1,4-dioxane from site soil and groundwater
- Iron, bicarbonate and possibly other compounds present in soil and groundwater can enhance the effectiveness of O₃
- Removal of VOCs and 1,4-dioxane was due to destruction, not volatilization
- O₃+H₂O₂ may prevent or minimize some of the adverse effects associated with O₃ only, but may also have adverse effects of its own

REFERENCE

Bower, K. C. and C. M. Miller. 2002. "Filter Sand-Phosphate Buffer Effect on 2,4-Dinitrotoluene Ozonation," *J. Environ. Eng.* February: 131-136.