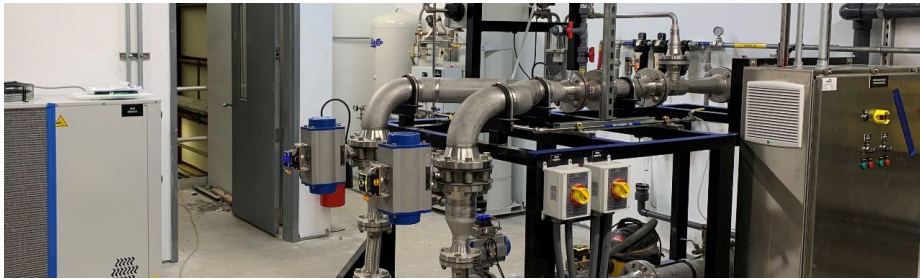


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# Winning the Battle Against 1,4-Dioxane with Ozone Advanced Oxidation



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# Agenda

1. What is 1,4-Dioxane?
2. Project Background
3. Treatability Studies
4. Cost Comparison of Treatment Options
5. Full Scale Results
6. UVT for Process Control
7. Conclusions

# 1,4-Dioxane is a clear, synthetic organic chemical found in many consumer products and historically used in chlorinated solvents



## The Dirty Dozen

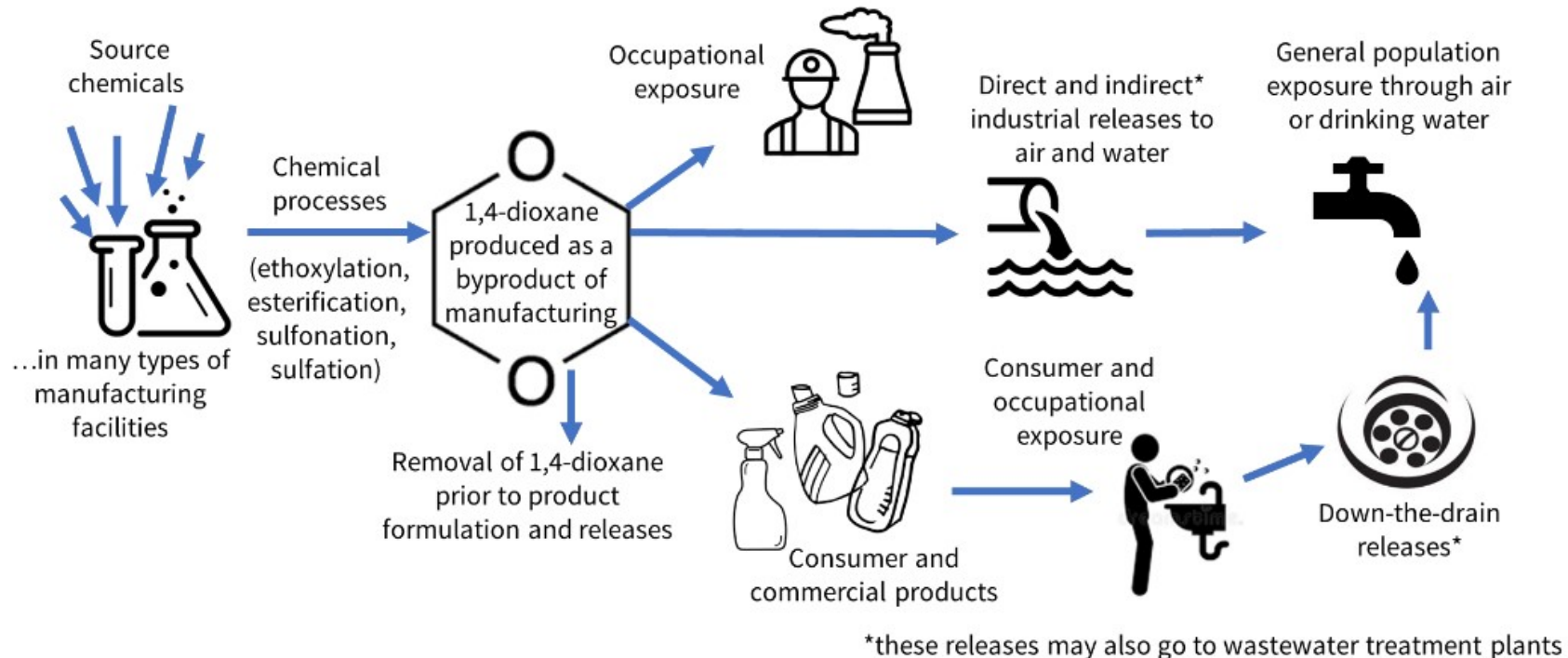
Products with the Highest Levels of Probable Carcinogen 1,4-Dioxane

1	Victoria's Secret Bombshell Body Wash	2	Victoria's Secret Love Body Wash	3	Tide Original Detergent	4	Ivory Snow 2X Ultra Detergent	5	Dreft Stage 1/ Newborn Detergent	6	Gain Original Detergent
											
17,000 ppb		16,000 ppb		14,000 ppb		11,000 ppb		10,000 ppb		10,000 ppb	
7	Tide Simply + Oxi Detergent	8	The Home Store Lemon Scented Dish Soap	9	Baby Magic Hair and Body Wash	10	Up&Up (Target) Free + Clear Dish Soap	11	Persil Original Detergent	12	Pantene Pro-V Nature Fusion Shampoo
											
8,300 ppb		7,700 ppb		7,600 ppb		6,400 ppb		6,100 ppb		5,500 ppb	

Reference: <https://www.citizenscampaign.org/14dioxane>

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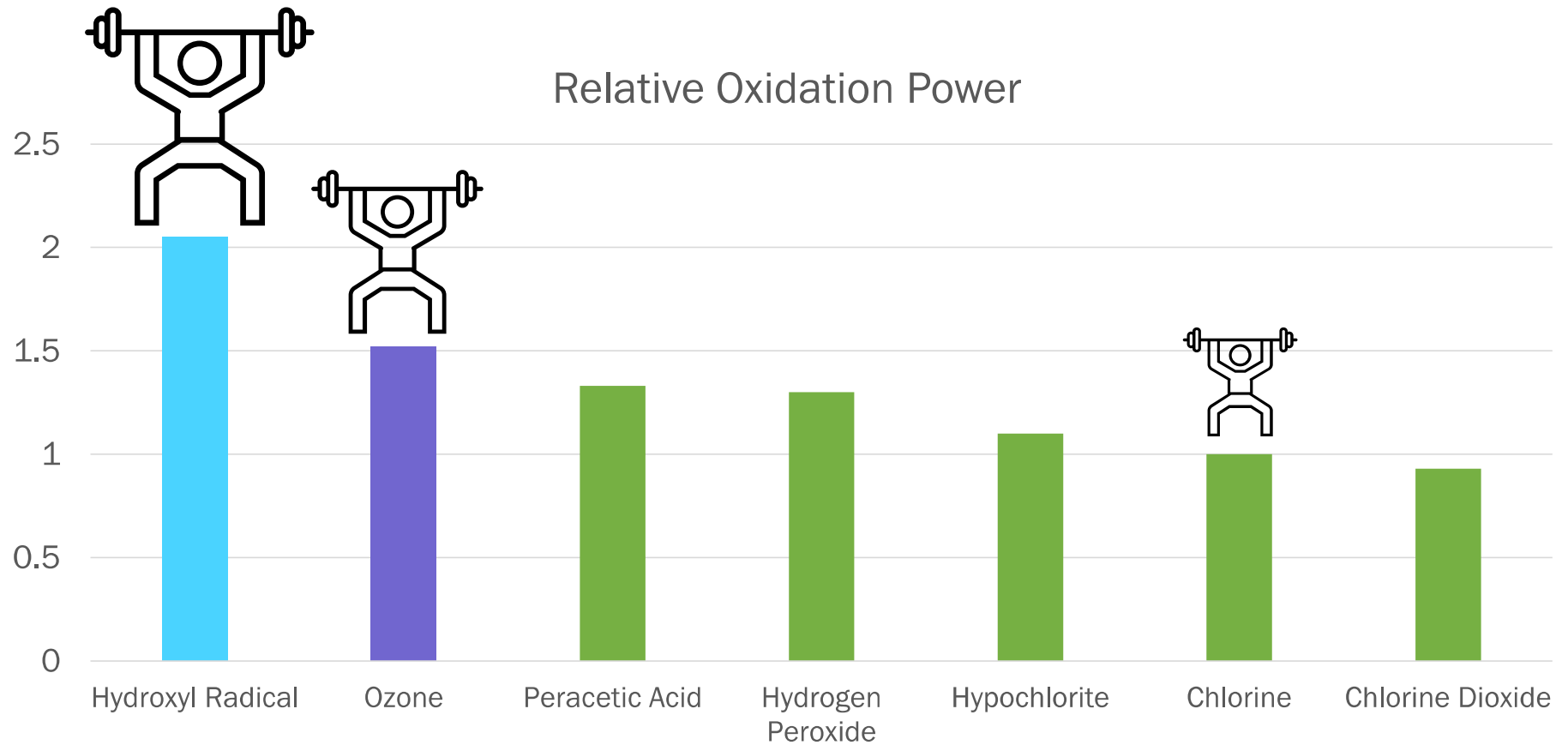
# 1,4-dioxane gets into the water cycle through multiple and related pathways



**Figure 1-2. Production of 1,4-Dioxane as a Byproduct and Potential Exposure Pathways**

Reference: EPA Draft Supplement to the Risk Evaluation for 1,4-Dioxane, July 2023

# Hydroxyl radicals have more oxidation power than other common chemicals used in water treatment.



**This project began with a process evaluation to determine best replacement option for an aging UV-AOP system.**



# Advanced Oxidation Process Treatment Objectives

- Organics removal
- 1,4-dioxane is 'controlling compound'
- Also removes: SVOCs, PCB congeners
- Design feed water 1,4-dioxane concentration      285 µg/L
- Design treated water 1,4-dioxane concentration      <0.63 µg/L

# General water quality includes low bulk organics, but high 1,4-D and poor UV Transmittance.

Parameter	Units	UV-H <sub>2</sub> O <sub>2</sub> Test	O <sub>3</sub> -H <sub>2</sub> O <sub>2</sub> Batch Test <sup>1</sup>	O <sub>3</sub> -H <sub>2</sub> O <sub>2</sub> Semi-batch Test
1,4-Dioxane	µg/L	166	108	185-218
pH	SU	7.91	7.61	7.83
UV Transmittance (UVT)	%	74	81	73
Total Organic Carbon (TOC)	mg/L	2.9	3.2	2.5
Chemical Oxygen Demand (COD)	mg/L	16	12	12
Alkalinity	mg/L as CaCO <sub>3</sub>	210	209	193
Dissolved Iron	mg/L	0.055	NA	0.040

<sup>1</sup>Values from diluted sample prior to ozone stock solution addition



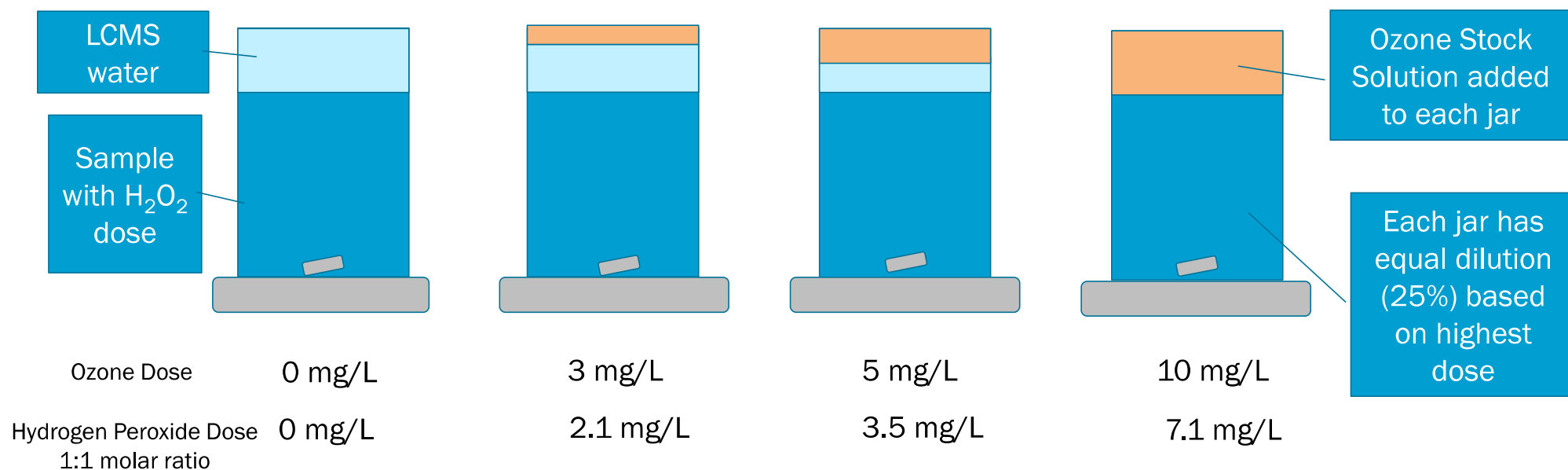
# UV-Peroxide Bench Scale Tests

## UV Batch Reactor

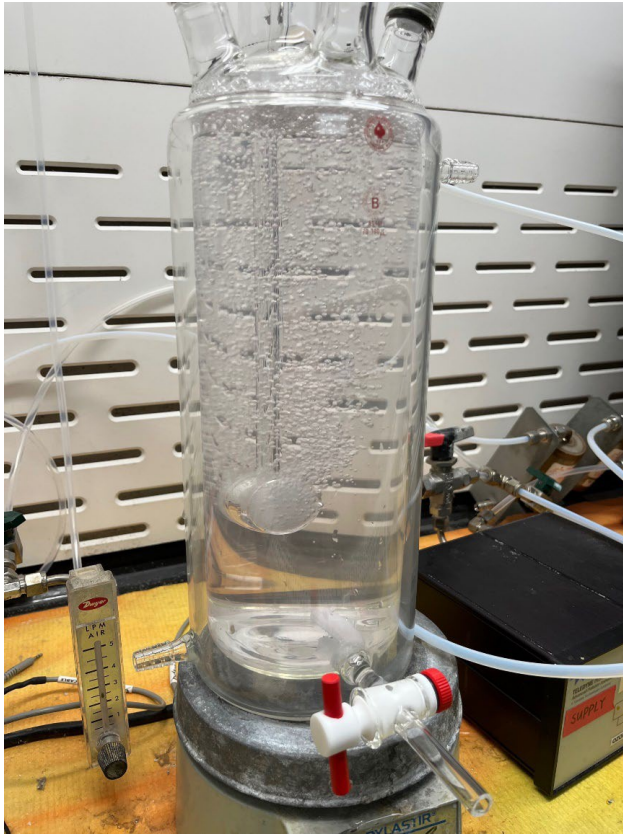
- 40 W low-pressure lamp
- Three UV doses (500, 2000, and 3500 mJ/cm<sup>2</sup>)
- Three hydrogen peroxide doses (25, 35, and 50 mg/L)



# Ozone-Peroxide Bench Scale Tests – Batch method should consider dilution of the sample with the stock solution



# Ozone-Peroxide Bench Scale Tests – Semi-Batch Method relies on multiple instruments for calculating transferred ozone dose



## Semi-Batch Method

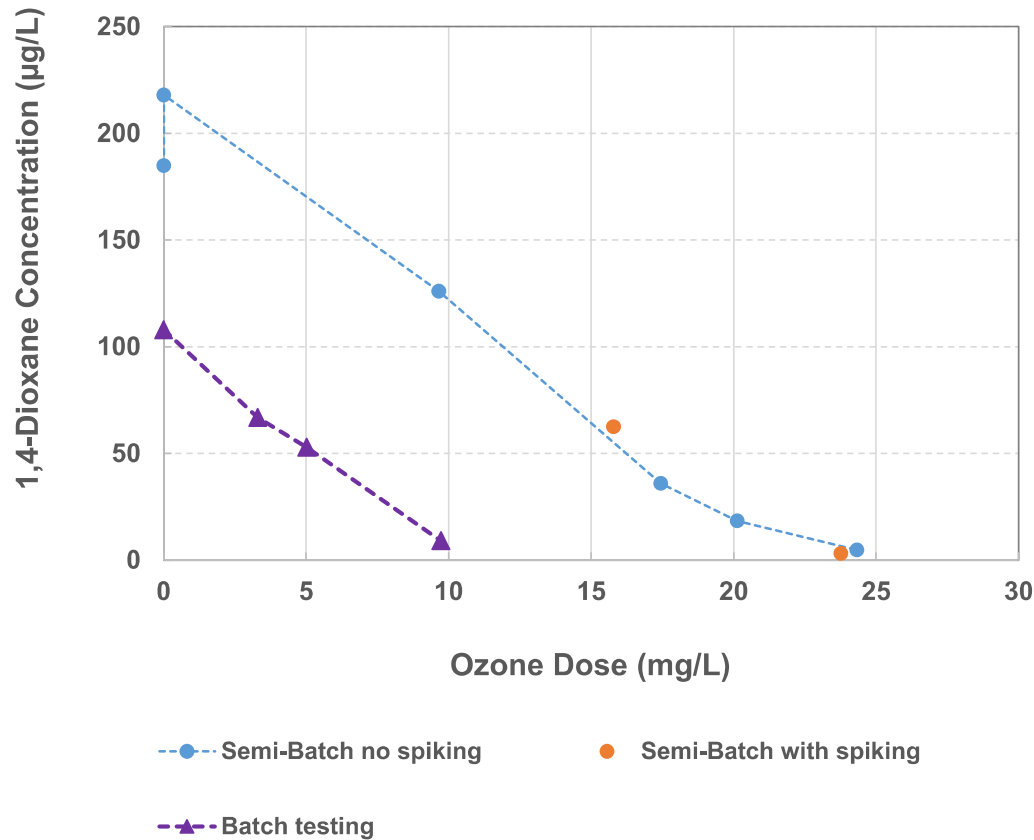
- Directly ozonate sample (10 mg/L to 25 mg/L, no dilution)
- Pre-dosed with hydrogen peroxide at 1:1 molar ratio
- Continuous measurement of gas flow and ozone concentration into and out of reactor
- Sum each time step to calculate ozone transferred to sample

# Ozone-Peroxide Bench Scale Tests – Challenge Testing

- Spiked samples with compounds sometimes found in this water matrix
  - 100  $\mu\text{g}/\text{L}$  of 2-chloroaniline
  - 100  $\mu\text{g}/\text{L}$  of azobenzene
  - 25 of  $\mu\text{g}/\text{L}$  bis(2-ethylhexyl)phthalate (DEHP)
- Spiked chemicals removed and no impact on 1,4-Dioxane removal efficacy



# Bench test results showed that increasing ozone and peroxide dose decreases 1,4-Dioxane concentration



## Notes

1. Batch and semi-batch tests conducted on two different water samples from full scale facility
2. Batch test 1,4-Dioxane  
Initial 144 µg/L  
Diluted 108 µg/L
3. Semi-batch test 1,4-Dioxane  
Initial 202 µg/L

# UV-AOP predicted to cost twice as much as Ozone-AOP

UV-Peroxide		
Criteria	Unit	Value
Flowrate	gpm	60 – 120
Design UV Dose	mJ/cm <sup>2</sup>	2000
Design Peroxide Dose	mg/L	35
Budget Capital Cost	US \$	\$1.3M
Annual Costs	US \$/yr	\$86 – 104k
Present Value 20 yr Life Cycle Cost	US \$	\$2.5 – 2.8M

Ozone-Peroxide		
Criteria	Unit	Value
Flowrate	gpm	60 – 120
Design O <sub>3</sub> Dose	mg/L	15
Design Peroxide Dose	mg/L	15
Budget Capital Cost	US \$	\$0.42M
Annual Costs	US \$/yr	\$25 – 31k
Present Value 20 yr Life Cycle Cost	US \$	\$0.8 – 0.9M

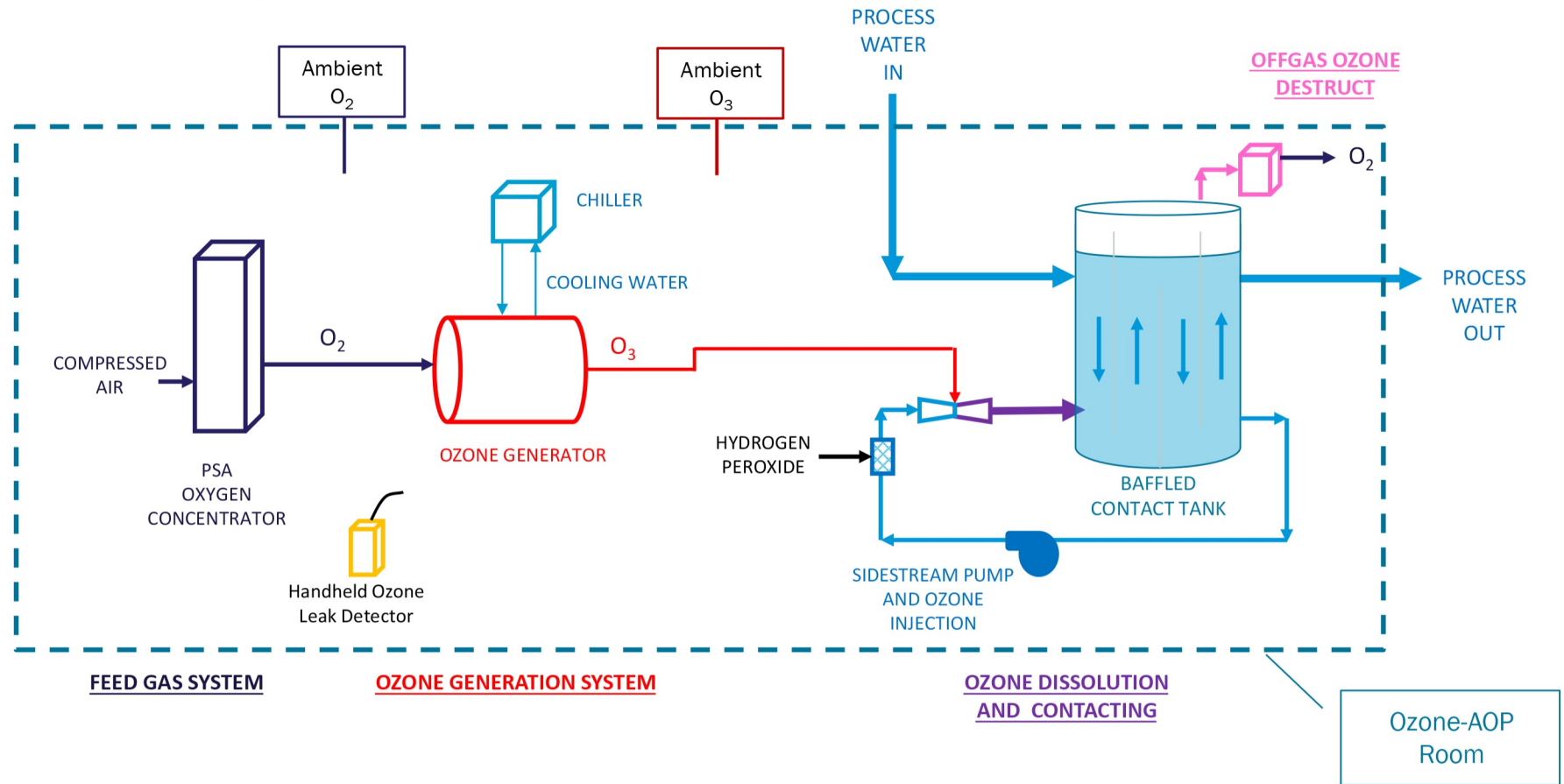
Budget cost estimates from April 2020

UV - major annual costs include power, lamp and ballast replacement

# Ozone-AOP System Design Criteria

- Process Flow Range 50 – 90 gpm (189 – 341 lpm)
- Hydrogen Peroxide Dose 7.1 – 21.3 mg/L
- Transferred Ozone Dose 10.0 – 30.0 mg/L
- Ozone Generator Production 7 – 38 pounds per day (132 – 718 g/hr)
- Ozone-in-oxygen Gas Concentration 8 to 12 percent by weight
- Ozone Dissolution Method Sidestream Injection
- Ozone Mass Transfer Efficiency Greater than or equal to 90 percent

# Ozone-AOP Systems involve multiple components





# Full scale installation provides functionality in a small space

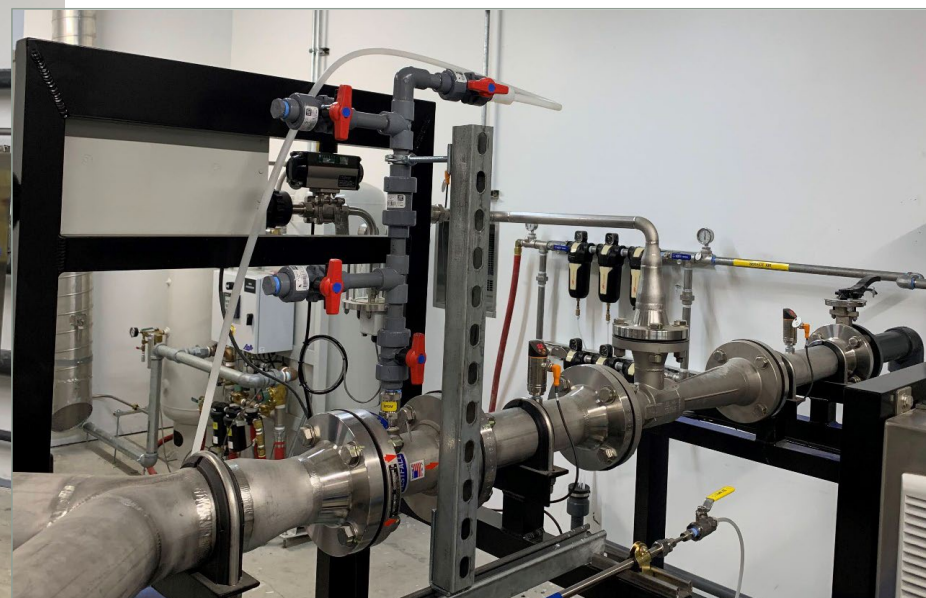


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# Injection skid provides streamlined design for ozone and peroxide dosing



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# Contactor and Destruct Unit

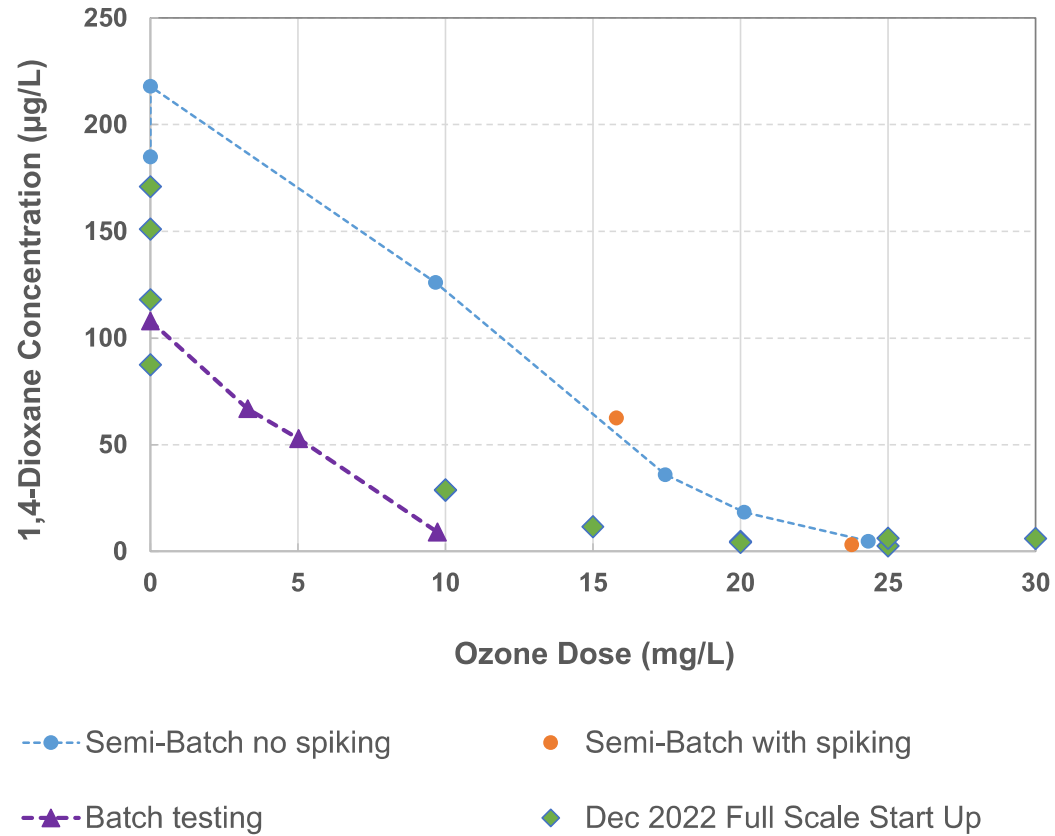


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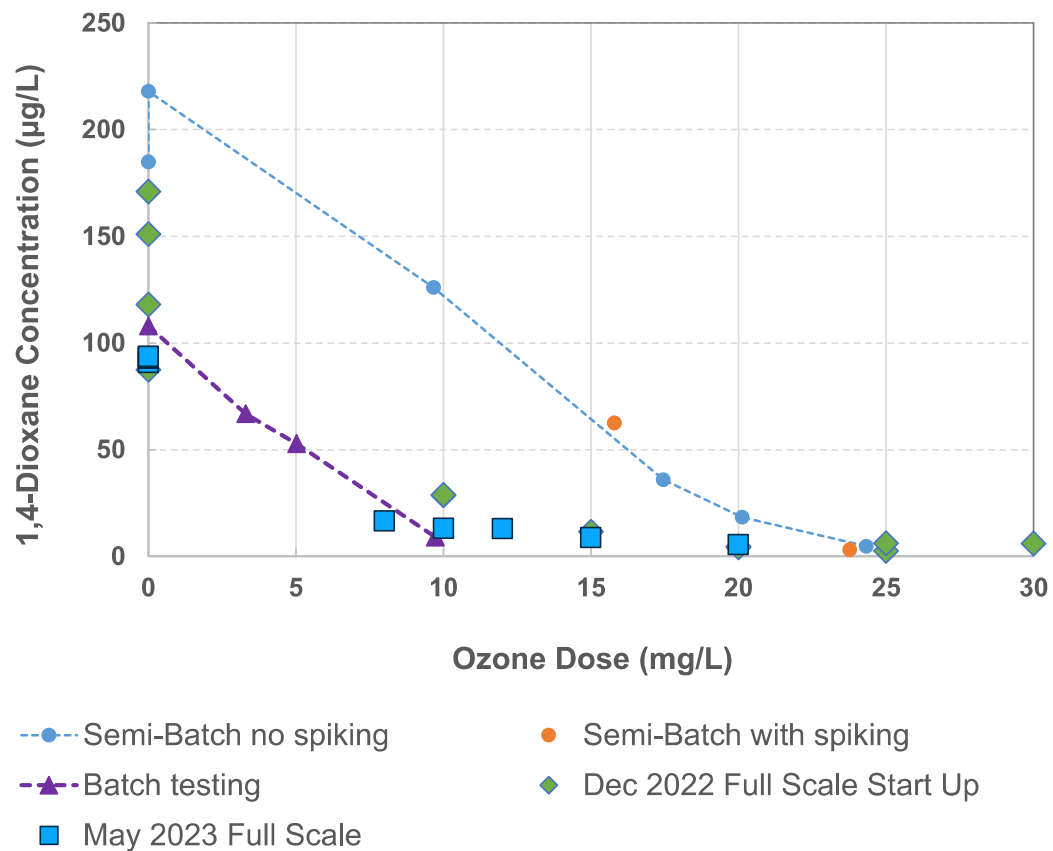


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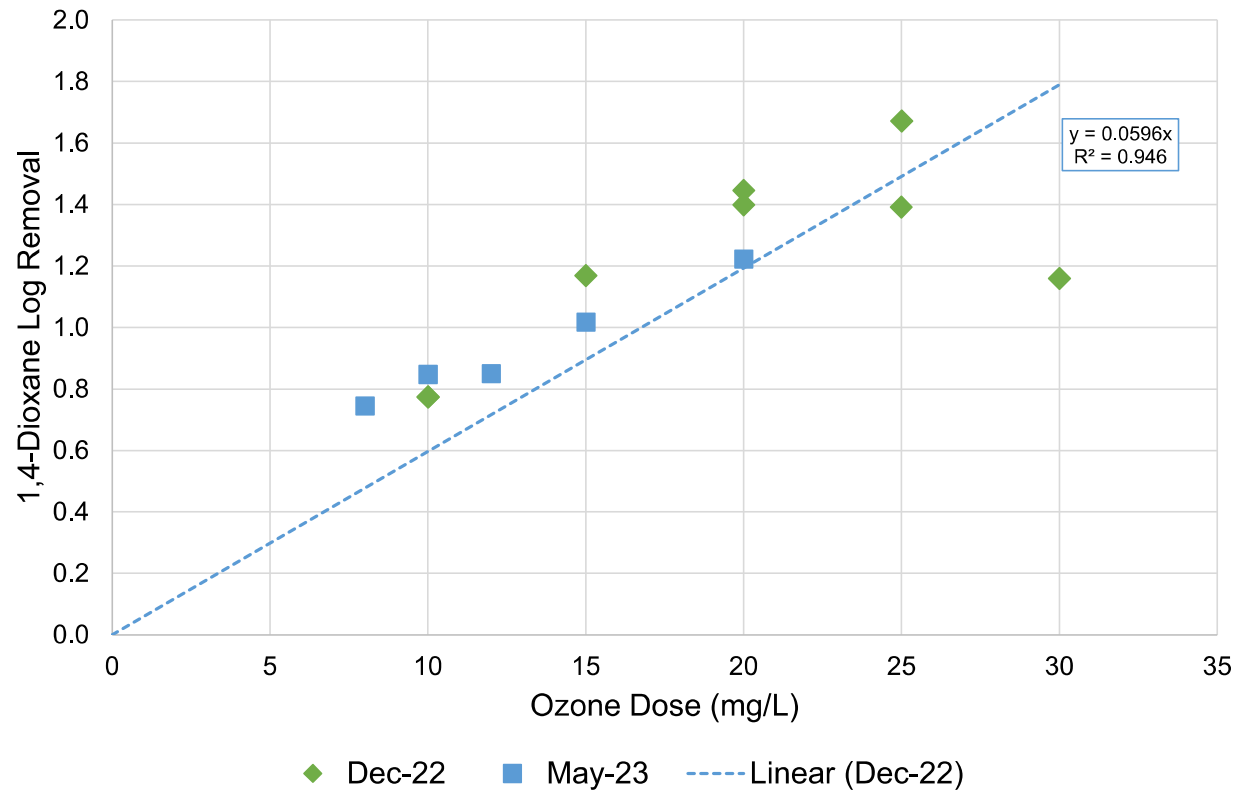
# Full scale results show better performance than semi-batch predictions



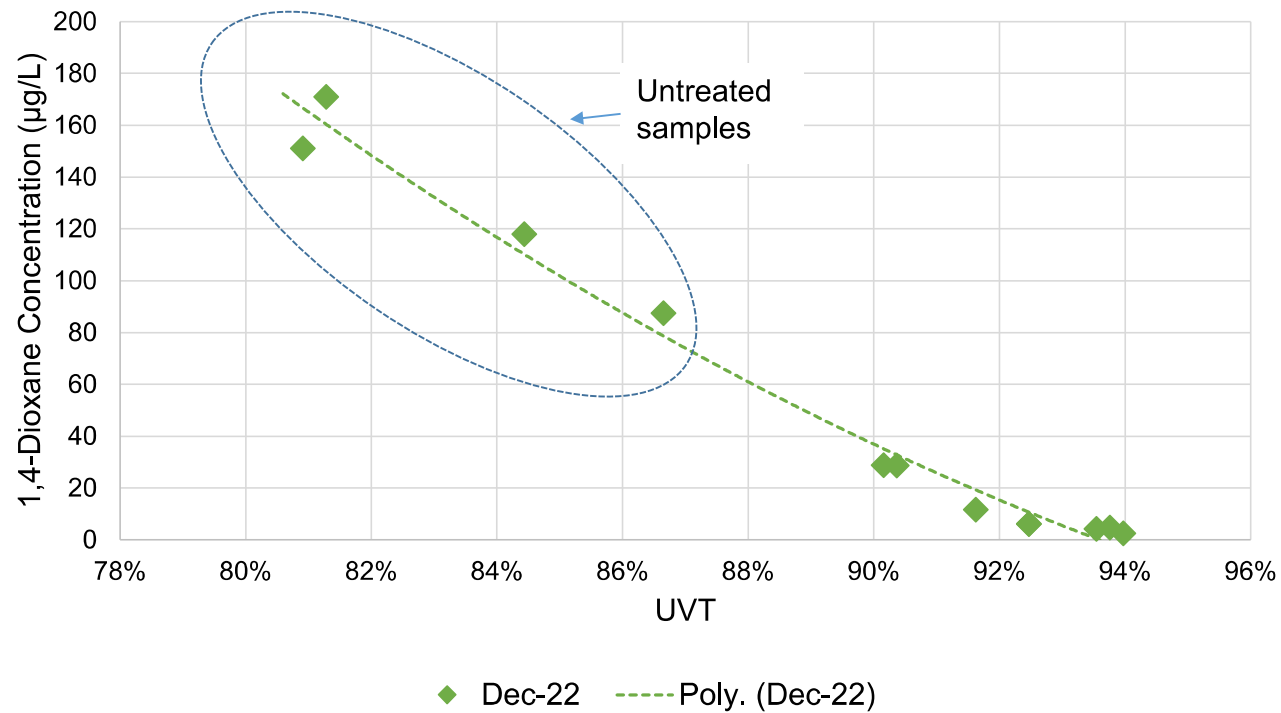
# Repeat testing after six months closely match start up tests and batch results



# Log removal is linear with ozone dose until reaching diminishing return at 25 mg/L

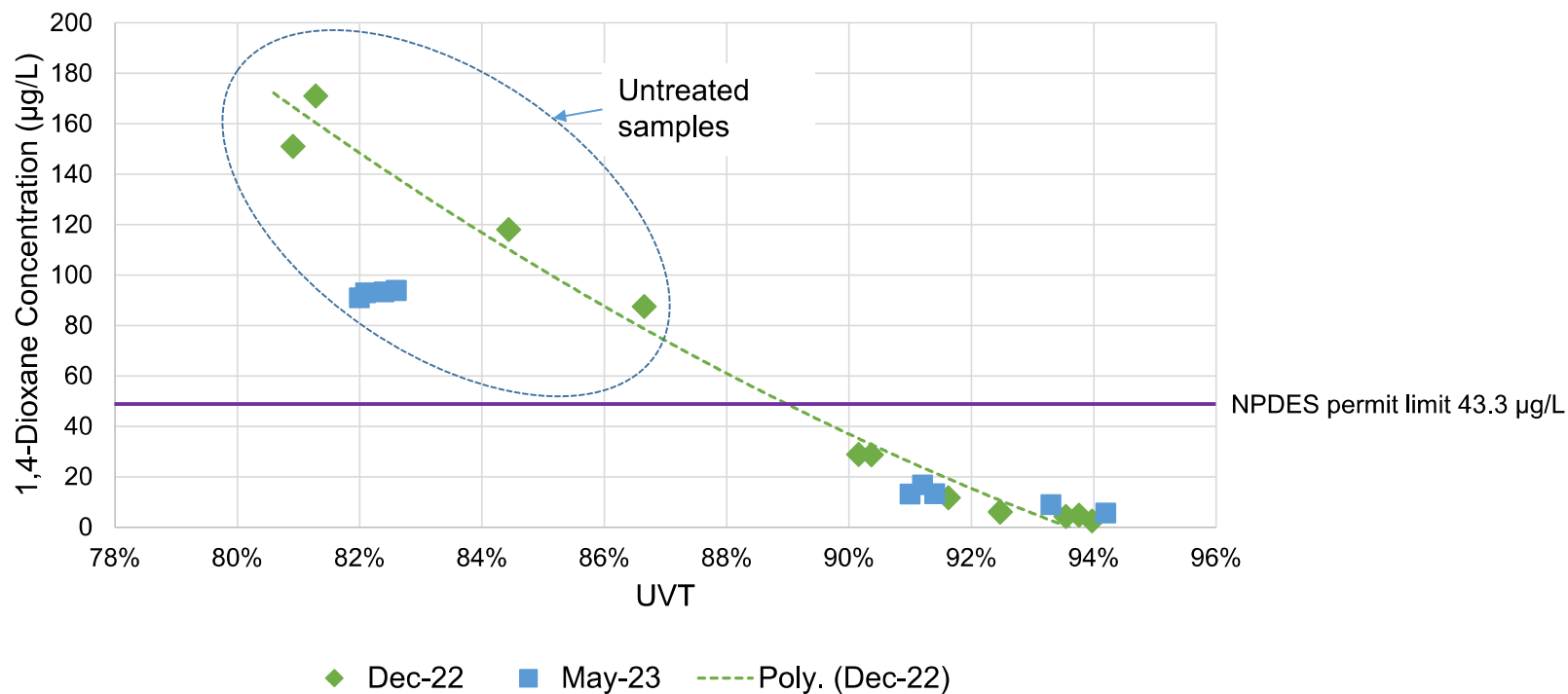


# UVT is correlated to 1,4-dioxane concentration



# UVT above 90% meets permit limit

# UVT above 92% indicates 1,4-dioxane is less than half the permit limit





# Conclusions

- Well designed and executed treatability studies provide reliable data for process selection and design development
- Ozone AOP can be lower cost than UV AOP depending on raw water quality parameters, particularly UVT
  - Low UVT means higher UV dose increasing capital and power costs
- UVT shows promise for process control and ozone dose optimization to meet 1,4-dioxane concentration targets



# Acknowledgements

- Brown and Caldwell Treatability Lab in Nashville, TN
- Brown and Caldwell Design and Startup Team
- Facility Operations Staff





# Thank you. Questions?

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**Brown** AND  
**Caldwell**