Effluent organic matter transformation achieved by 222 nm emission from KrCl* excimer lamps

Emma Payne
Prof. Karl Linden
University of Colorado Boulder
March 17, 2024

ACS SPRING 2024

University of Colorado Boulder

1

Outline

1. Introduction KrCl* excimer lamps
2. Project description and methods
3. Results
   a. Bulk water
   b. Size exclusion chromatography

University of Colorado Boulder 1

2

Outline

1. Introduction KrCl* excimer lamps
2. Project description and methods
3. Results
   a. Bulk water
   b. Size exclusion chromatography

University of Colorado Boulder 2

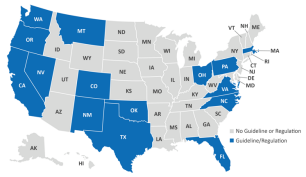
3

THE DENVER POST — Opinion Columnists | Opinion: Recycled water isn't gross; it is...

OPINION › OPINION COLUMNISTS › Opinion, Opinion Columnist

Opinion: Recycled water isn't gross; it is necessary

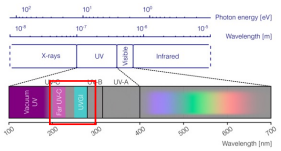
States with Potable Water Reuse Regulations or Guidelines



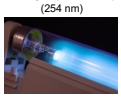
UV advanced oxidation often used for micropollutant abatement in water reuse

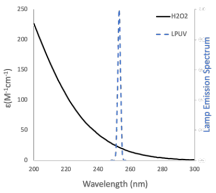
University of Colorado Boulder 3

4



Mercury vapor UV lamp
(254 nm)



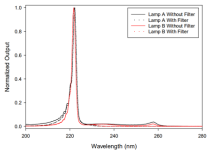


Common UV/AOP = 254 nm (LPUV) + H_2O_2

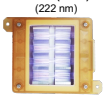
- High UV fluences
- Only 10% of H_2O_2 consumed
  → Costs for dosing & quenching

University of Colorado Boulder 4

5



Krypton chloride (KrCl*) excimer
(222 nm)



KrCl* Excimer (222 nm)	Conventional LPUV (254 nm)
Mercury free	Contains harmful mercury
Instant on	Requires warm up times
Wide operating temperature	Temperature affects efficiency
Safe for skin and eyes	Harmful for skin and eyes

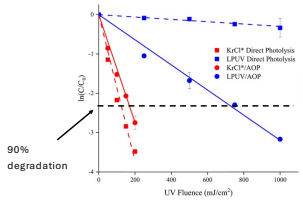
KrCl*/H_2O_2 led to 4x greater •OH generation than LPUV/H_2O_2

University of Colorado Boulder 5

Payne, E.M. et al. (2022). Environ. Sci. Tech. Lett.

6

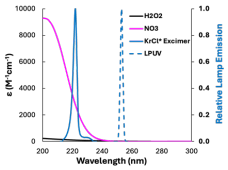
Carbamazepine



90% degradation

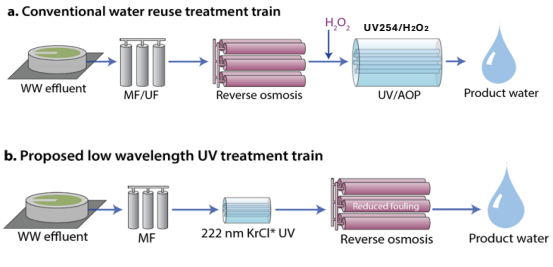
In secondary wastewater effluent,

- UV222 led to greater contaminant degradation than UV254/H_2O_2
- Degradation from **UV222 alone comparable to UV222/H_2O_2** & greater than UV254/H_2O_2



Liu, B., et al (2023). *Environ. Sci. Tech.*

7



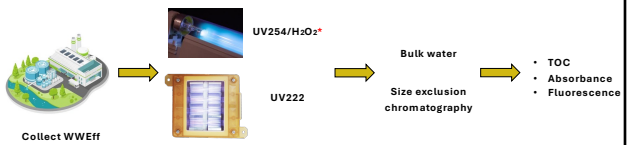
8

Outline

1. Introduction KrCl* excimer lamps
2. Project description and methods
3. Results
   a. Bulk water
   b. Size exclusion chromatography

9

Methods



Collect WWEff
- Conventional
- IPR

Collimated beam UV exposures

UV254/H_2O_2*

UV222

Bulk water

Size exclusion chromatography

- **TOC**
- **Absorbance**
- **Fluorescence**

*$[H_2O_2]$ determined such that $[\bullet OH]_{ss}$ is equal for UV222 and UV254/H_2O_2

10

Outline

1. Introduction KrCl* excimer lamps
2. Project description and methods
3. Results
   a. Bulk water
   b. Size exclusion chromatography

11

Wastewater Effluents

	Conventional	IPR
TOC (ppm)	7.71	3.00
Nitrate (mg-N/L)	6.64	2.18
UVT (%)	71.9	89.1
Alkalinity (mg-$CaCO_3$/L)	98	174
	Activated sludge (De)nitrification Secondary clarification 0.45 micron filtered	Riverbank filtration Aquifer recharge Softening

12

TOC

Conventional

Fluence (mJ cm^{-2})	UV222	UV254/H_2O_2
0	7.71	7.71
40	7.81	
125	7.5	
250	7.35	7.76
500	7.1	7.64
1000		7.56

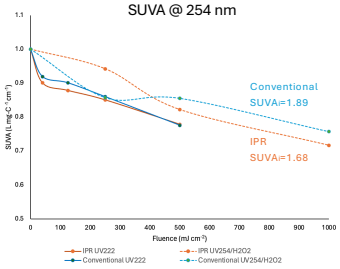
Indirect Potable Reuse

Fluence (mJ cm^{-2})	UV222	UV254/H_2O_2
0	3.00	3.00
40	3.14	
125	2.97	
250	2.91	2.81
500	2.85	2.93
1000		2.82

5-8% mineralization achieved by UV222 fluence of 500 mJ cm^{-2}, compared to 1-2% from UV254/H_2O_2

13

Absorbance

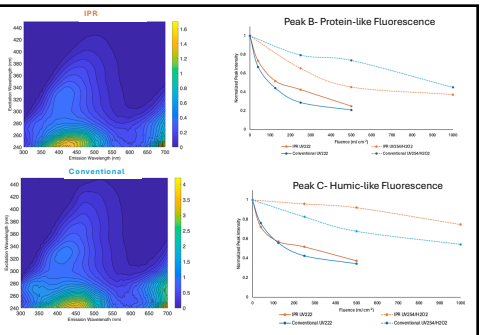


UV222 decreases SUVA more than UV254/H_2O_2

14

Fluorescence

UV222 selectively degrades fluorophores



15

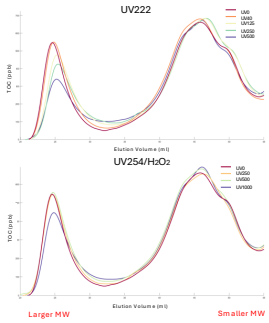
Outline

1. Introduction KrCl* excimer lamps
2. Project description and methods
3. Results
   a. Bulk water
   b. Size exclusion chromatography

16

Conventional Wastewater- TOC

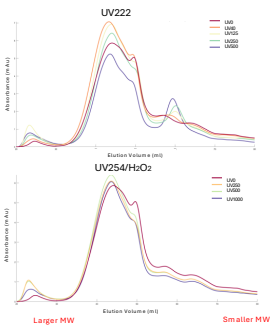
- **Large molecular weight peak decreases significantly** under UV222
  - Shift towards smaller MW at intermediate fluences
  - Mineralization evident at highest fluence



17

Absorbance at 280 nm

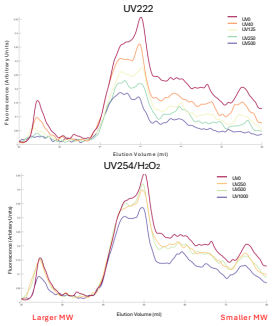
- **Absorbance increases** in large and medium molecular weight fraction for both UV222 & UV254/H_2O_2
  - Changes are **larger under UV222,** potentially implicating reactive nitrogen species



18

Fluorescence at ex280 nm

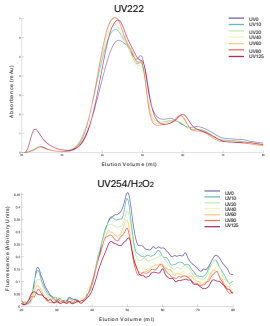
- **Fluorescence monotonically decreases with fluence** in all size fractions
  - Decrease larger for UV222



19

Zooming in on low fluences…

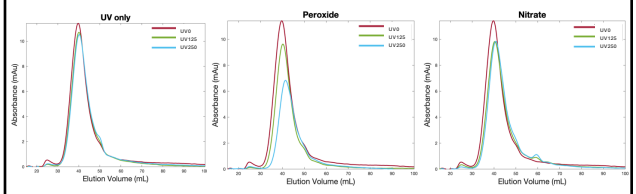
- Absorbance increases until fluence between 80 and 125 mJ cm^{-2}
- Still, fluorescence uniformly decreases



20

Mississippi River NOM UV222 – Absorbance at 280 nm

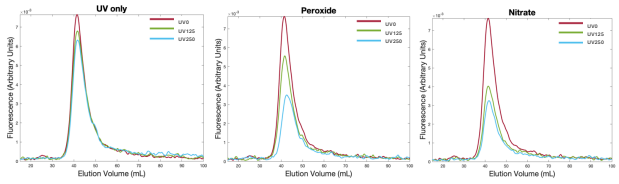
•OH generation: 2.4 mg-N/L = 9 ppm H_2O_2



Irradiation in presence of peroxide leads to greater decrease in absorbance than nitrate

21

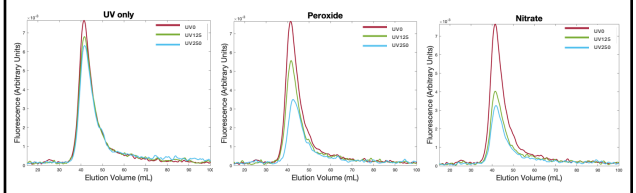
Mississippi River NOM UV222 – Fluorescence at ex280



Nitrate-sensitized photolysis leads to comparable or greater reduction in fluorescence

22

Mississippi River NOM UV222 – Fluorescence at ex280



Nitrate-sens …**nce**

Consistent with hypothesis of inorganic nitrogen incorporating into organic matter

23

Takeaways

- UV222 direct photolysis significantly degrades EfOM and alters EfOM character
- UV222 mineralizes 5-8% of TOC and shifts DOM towards smaller molecular weight fraction, even more than UV254/H_2O_2
- UV222 significantly degrades large molecular weight fraction of TOC and selectively degrades fluorophores

24

Implications and Future Work

- DOM isolate and model compound experiments for intermediate transformation product formation
- Complete analysis with additional wastewaters
- Post-UV/AOP chlorination and DBP formation
- Downstream reverse osmosis membrane fouling

25

Research Team and Acknowledgments

Karl Linden | Anthony Straub | Blair Hanson | Akash Bhat | Trisha Nickerson | Ben Jordan | Emma Langelan

Daniel McCurry

Other support from:

- City of Boulder Utilities
- Aurora Water
- Orange County Water District
- Produced Water Recycle, LLC.
- Dupont

Funding agency:

Emma.Payne@colorado.edu

26