UV 222 nm Emission from KrCl* Excimer Lamps Greatly Improves Advanced Oxidation Performance in Water Treatment

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WATER QUALITY Technology Conference
Dallas, Texas | November 5–9

Environmental Engineering
UNIVERSITY OF COLORADO BOULDER

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Outline

- Intro to UV Advanced Oxidation Processes (UV/AOP)
- KrCl* excimer lamp for UV/AOP
  - Direct photolysis + radical generation
  - Effect of background matrix
  - Transformation products
- Future research directions

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UV Water Treatment

UV Disinfection

- Cryptosporidium
- Giardia
- No disinfection byproducts

UV Advanced Oxidation

- NDMA
- 1,4-dioxane
- Pharmaceuticals & endocrine disrupting compounds
- Agricultural chemicals

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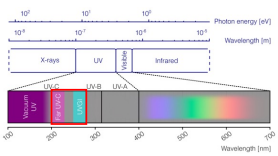
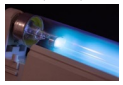
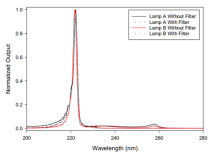
UV Sources



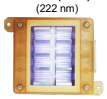
Mercury vapor UV lamp
(254 nm)





Germicidal UV LEDs
(250-400 nm)

Krypton chloride (KrCl*) excimer
(222 nm)



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What are KrCl* excimer lamps?

KrCl* Excimer (222 nm)	Conventional LPUV (254 nm)

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Mercury free	Contains harmful mercury

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Instant on	Requires warm up times

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Instant on	Requires warm up times
Wide operating temperature	Temperature affects efficiency

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What are KrCl* excimer lamps?

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
Safer for skin and eyes	Harmful for skin and eyes

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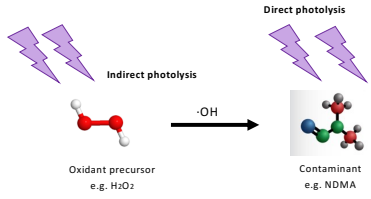
UV advanced oxidation (UV/AOP)



- Molar absorptivity
- Quantum yield (ϕ)

↓

UV/AOP efficiency

f(wavelength)

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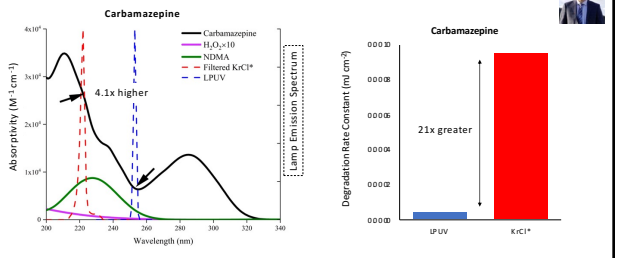
Direct Photolysis: Absorptivity and ϕ higher at 222 nm



ϕ(222) **14x greater** than ϕ(254)

Method: DI water, collimated beam apparatus (Bolton & Linden 2003), HPLC-UV

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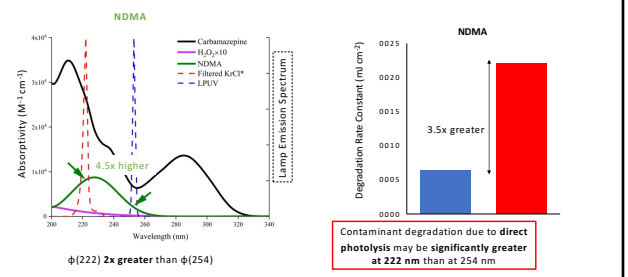
Direct Photolysis: Absorptivity and ϕ higher at 222 nm



ϕ(222) **2x greater** than ϕ(254)

Contaminant degradation due to **direct photolysis** may be **significantly greater at 222 nm** than at 254 nm

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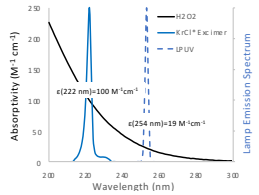
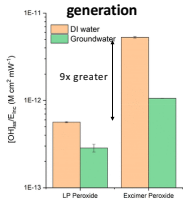
AOP: Absorptivity of radical promoter higher at 222 nm

H_2O_2 absorbs light **5x more at 222 nm**…



… leading to **more efficient ·OH generation**



Method: pCBA •OH probe, collimated beam (Vinge et al., 2020)

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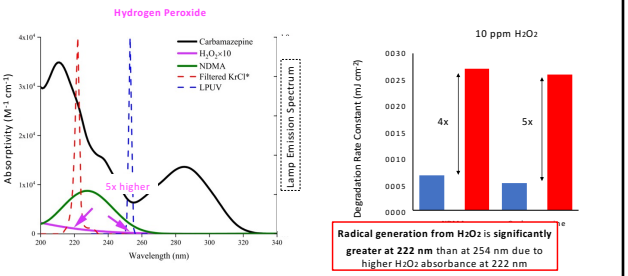
AOP: Absorptivity of radical promoter higher at 222 nm



Radical generation from H_2O_2 is significantly greater at 222 nm than at 254 nm due to higher H_2O_2 absorbance at 222 nm

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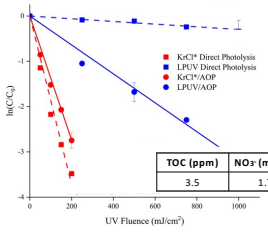
Radical generation from background water matrix

Carbamazepine degradation in **secondary effluent (SE)**



TOC (ppm)	NO_3^- (mg-N/L)	UVT(222)
3.5	1.75	37.4%

- "Direct photolysis" in SE was **19.6x greater** than in deionized water
- Adding 10 ppm H_2O_2 had no additional benefit on degradation under KrCl*

Under 222 nm irradiation, the **background water matrix** can efficiently **generate radicals**

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Radical generation from background water matrix

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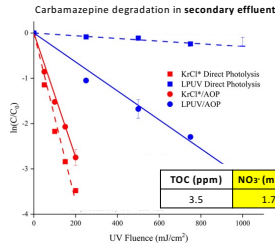

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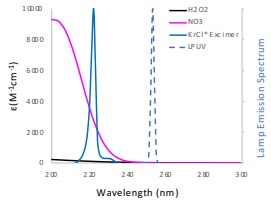
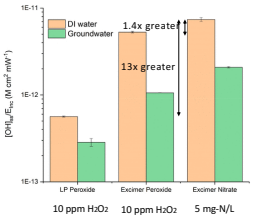


$$NO_3^- + h\nu \rightarrow \cdot OH$$

Nitrate photolysis at 222 nm **effectively generates ·OH**



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

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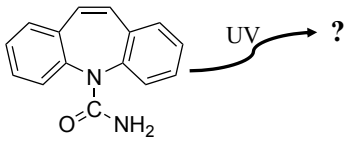
Transformation products during 222 nm degradation

Carbamazepine



- High resolution mass spectrometry
- Detection of analytes to the nearest 0.001 atomic mass units

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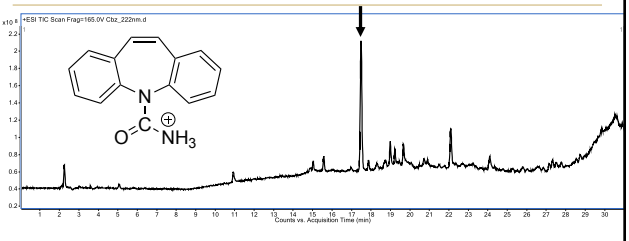
Carbamazepine parent compound



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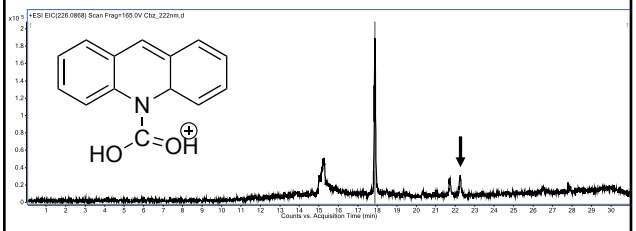
- OH replacing NH_2



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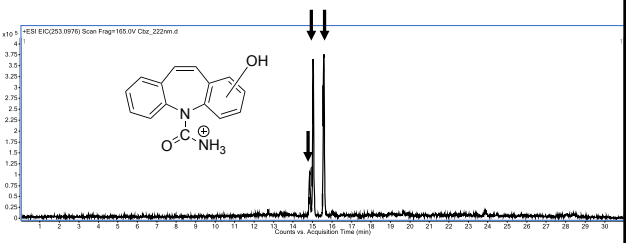
- OH hydroxylating aromatic ring



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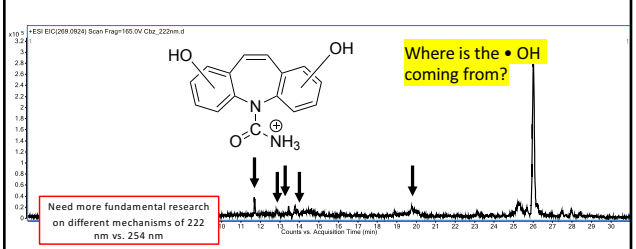

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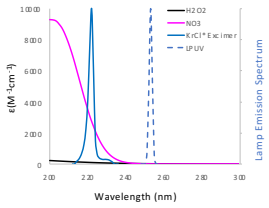
Future research directions: nitrite formation



$NO_3^- + h\nu \rightarrow \cdot OH$

$h\nu\downarrow$

$NO_2^- + \cdot OH$

- Regulated (MCL= 1 ppm as N)
- Scavenges hydroxyl radicals

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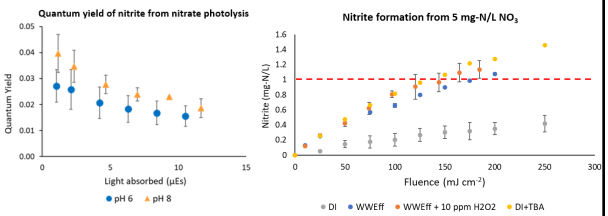
Future research directions: nitrite formation



Nitrite formed at 2-4% yield

•OH scavenging increases nitrite formation

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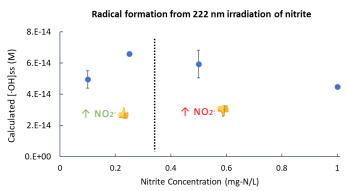
Future research directions: nitrite formation



$NO_3^- + h\nu \rightarrow \cdot OH$

$h\nu\downarrow$

$NO_2^- + \cdot OH$

$h\nu\downarrow$

$\cdot OH$

At low concentrations, increasing nitrite forms additional •OH, but at higher concentrations scavenging by nitrite negatively impacts •OH

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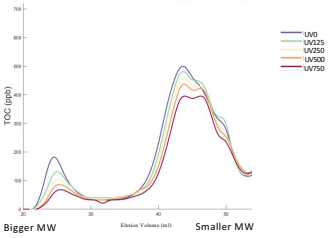
Future research directions: organic matter transformation



Bigger MW — Smaller MW

SEC with in-line TOC, UV and FLD detector

222 nm irradiation:

- Degrades large molecular weight fraction
- Decreases SUVA
- Transforms OM **significantly more than 254 nm irradiation**

WED02 session
8:30 am Wednesday

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Take Home Messages

- 222 nm irradiation from KrCl* excimer lamps generates •OH from H_2O_2 **more efficiently than conventional LPUV**
- Contaminant **direct photolysis may be greater** at 222 nm than 254 nm
- **Radical generation from background water matrix** can be as or more effective than from added H_2O_2
- Fundamental photochemistry at 222 nm is largely unknown

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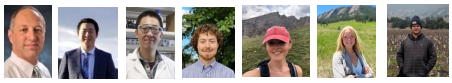
Acknowledgments



Karl Linden — Bryan Liu — Ben Ma — Ben Jordan — Emma Langelan — Lauren Mullen — Blair Hanson

Funding agency: NSF

Other support from: College of Engineering & Applied Science, USHIO

Linden Lab Group

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References

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