Assessing Downstream Potential for Attenuation of Microconstituents in River Systems Receiving Moderate Wastewater Inputs

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A Brief Roadmap

- Treated municipal effluent as a source of organic matter
- Photoreactivity of effluent organic matter
- Implications for river systems

Thanks to:
Laleen Bodhipaksha, Mykel Mendes, Matt Quaranta, Sharon Scott, Taylor Simmons, Charlie Sharpless (Mary Washington University)

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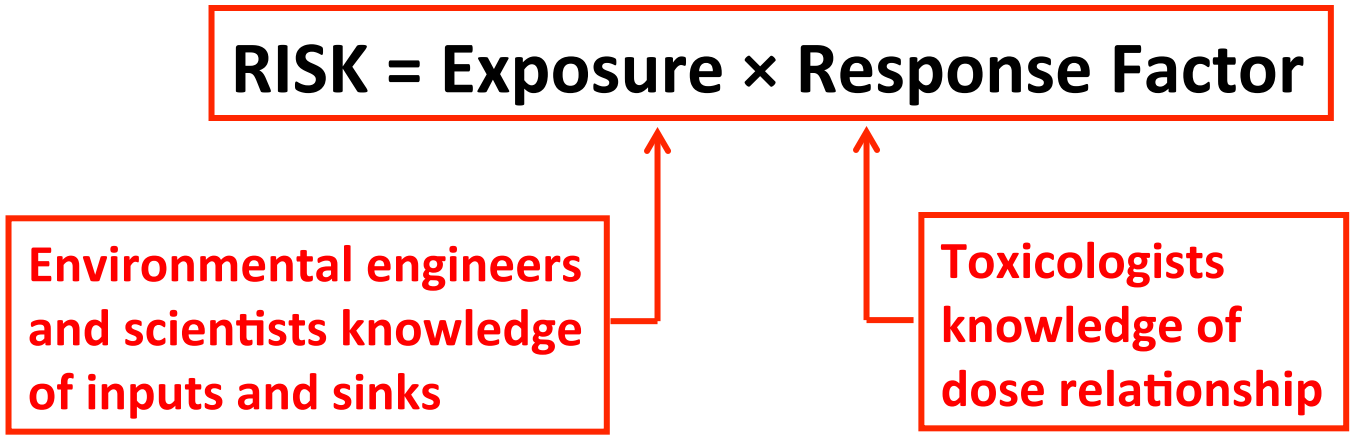
Risk Framework for Microconstituents

- Risk calculations allow quantitative ranking of hazards



- Survey studies have documented variable occurrence

Fluoxetine: 1%; 12 ng/L **Triclosan: 58%; 140 – 2300 ng/L**

Kolpin et al. 2002

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What is Known of Downstream Fate?

- **Few methodical fate studies undertaken for pharmaceuticals yield wide range in pathways and lifetimes**

Compound	Syst. Type	Process & $t_{1/2}$ (h)
Ibuprofen	River – Lin	Photolysis – 15 (lab) Biodegr'n – 5.4
	River - Fono	Photolysis – 150 Biodegr'n – 400 (lab)
Naproxen	River – Lin	Photolysis – 1.8 Sorption – 1.2
	River – Fono	Photolysis – 140 Biodegr'n – 400 (lab)
	L. Greifensee	Overall – 340, no mech.
Gemfibrozil	River – Lin	Biodegr'n – 5.4
	River - Fono	Photolysis – 554 Biodegr'n – 330 (lab)

Lin et al. 2006; Fono et al. 2006; Morrall et al. 2004; Tixier et al. 2003; Golet et al. 2002

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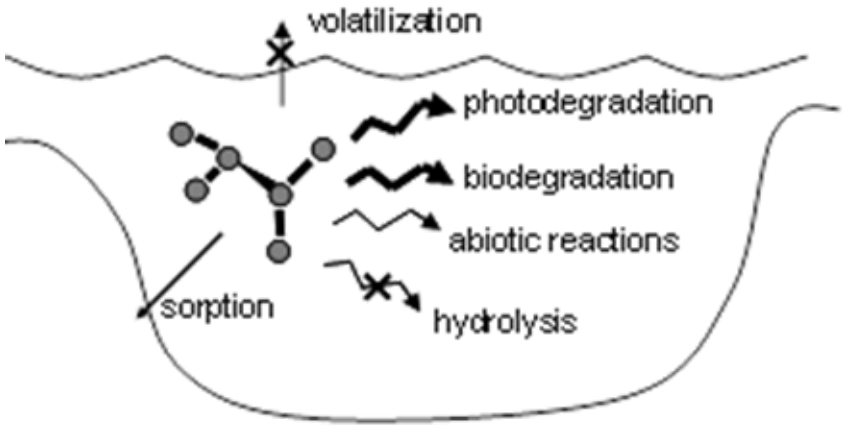
Key Environmental System Parameters

- **Micropollutant degradation via photolysis and biological pathways affected by environmental system parameters.**



- **20 (avg) – 60 (7Q10) % of NPDES discharges have < 1/10 dilution**
  - **→ What processes in systems with moderate effluent inputs?**
  - **→ What role for organic matter in enhancing degradation?**

Brooks et al. 2006

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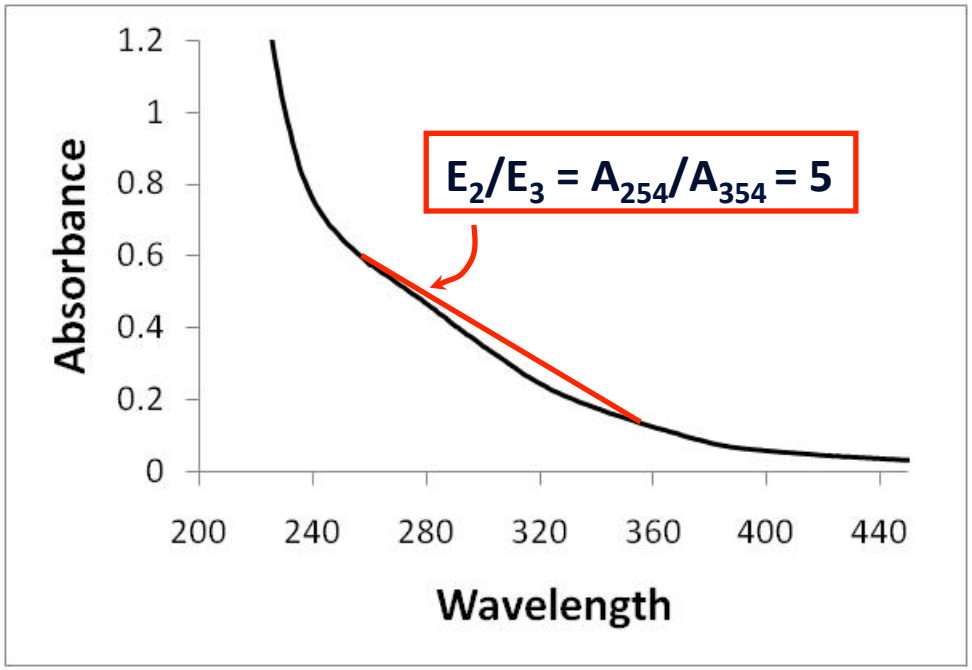
Focus – Role of Organic Matter in Photolysis

- **Interacting substructures direct the formation of reactive species produced by solar excitation**

DOM + sunlight → ^{3}DOM*, $^1O_2$, OH• → react with micropollutants



Terrestrial: low E_2/E_3 → **Microbial: high E_2/E_3**

incr. ^{3}DOM*, $^1O_2$

Quaranta et al., Wat Res, 2012; Darymple et al. ES&T 2010

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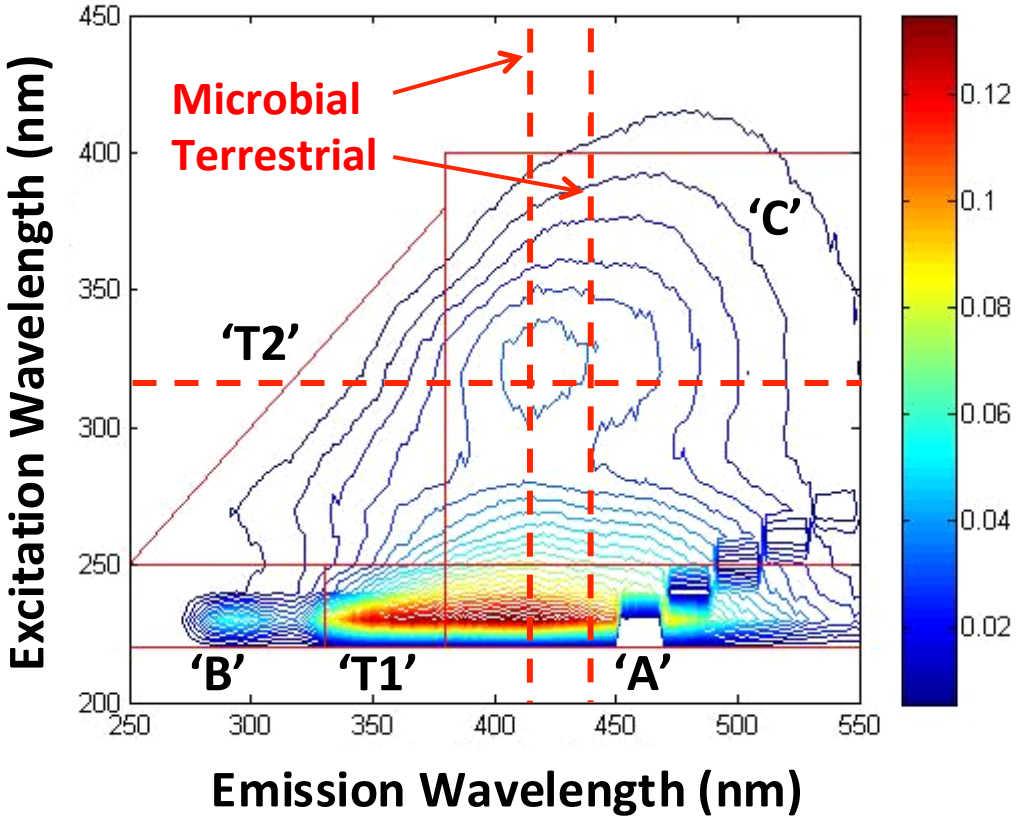
Effluent Organic Matter Characterization

- **Effluent organic matter shares characteristics with natural organic matter of microbial origin, incl. size, aromaticity**



- **Studies of aquatic photochemistry based on terrestrial sources**

Quaranta et al., Wat Res, 2012

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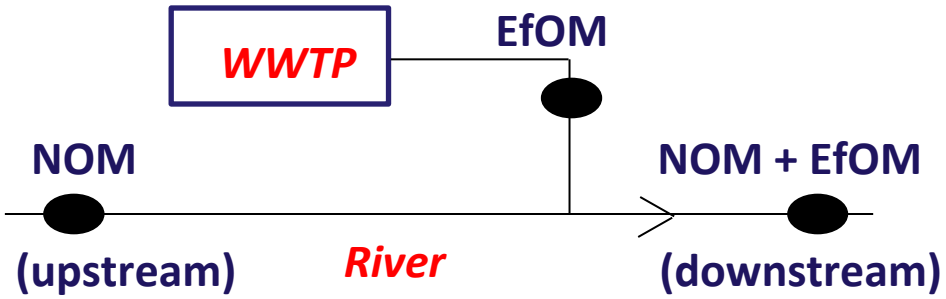
Effluent Organic Matter Photochemistry

- **Laboratory photoreactor studies using whole water samples to measure reactant production ($^1O_2$, ^{3}DOM*, OH•)**

Field sampling:



Hockanum River, CT (Hock) - urban (22% v/v effluent)
EFL Miami River, OH (Miami)- farm (11%)
Pomperaug River, CT (Pomp)- forest (6%)

Lab analysis:

$$\text{Quantum Yield} = \frac{\text{Molecules of reactant produced}}{\text{Photons of light absorbed}}$$

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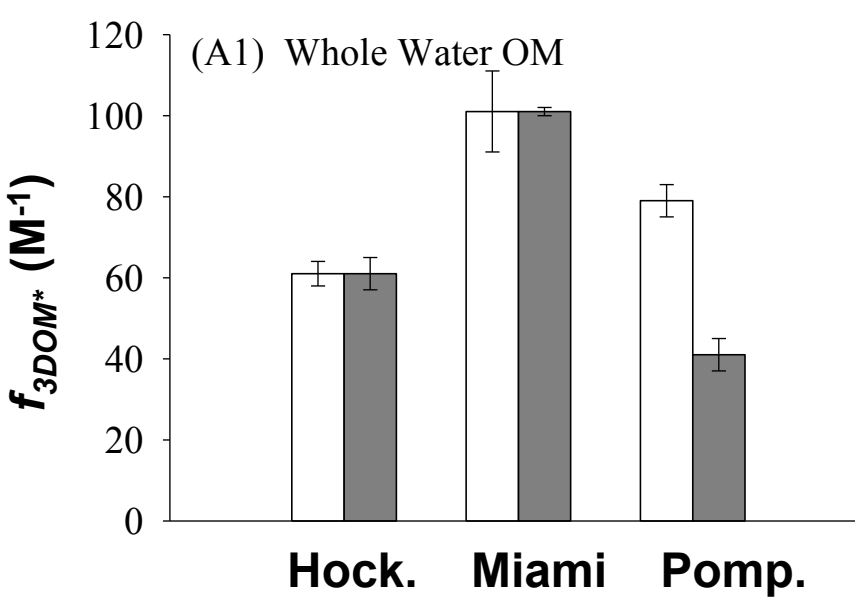
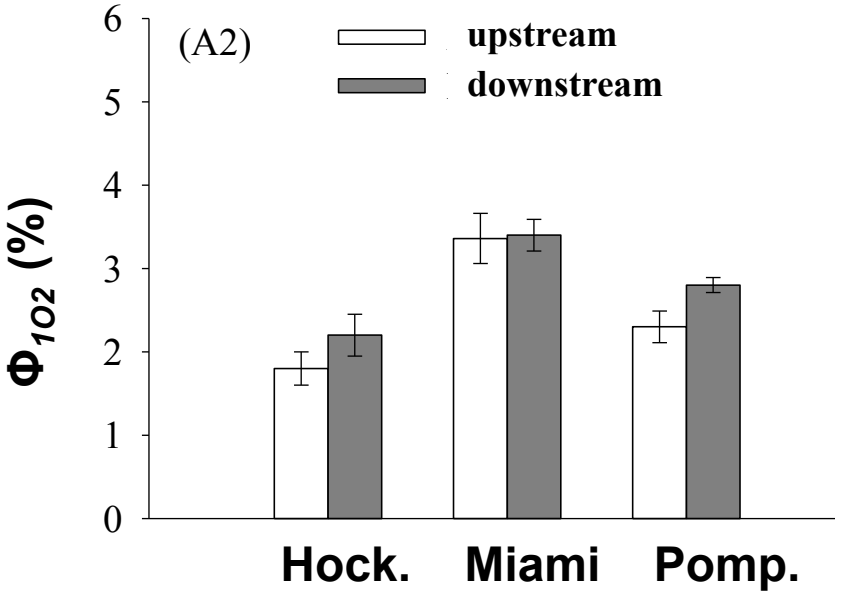
Downstream Reactive Species Yields

- **Rivers with moderate effluent contributions show little difference in ^{3}DOM* (f_{TMP}) and $^1O_2$ (Φ_{1O2}) yields**





Effluent: 22% 11% 6%

Bodhipaksha et al. *in review*

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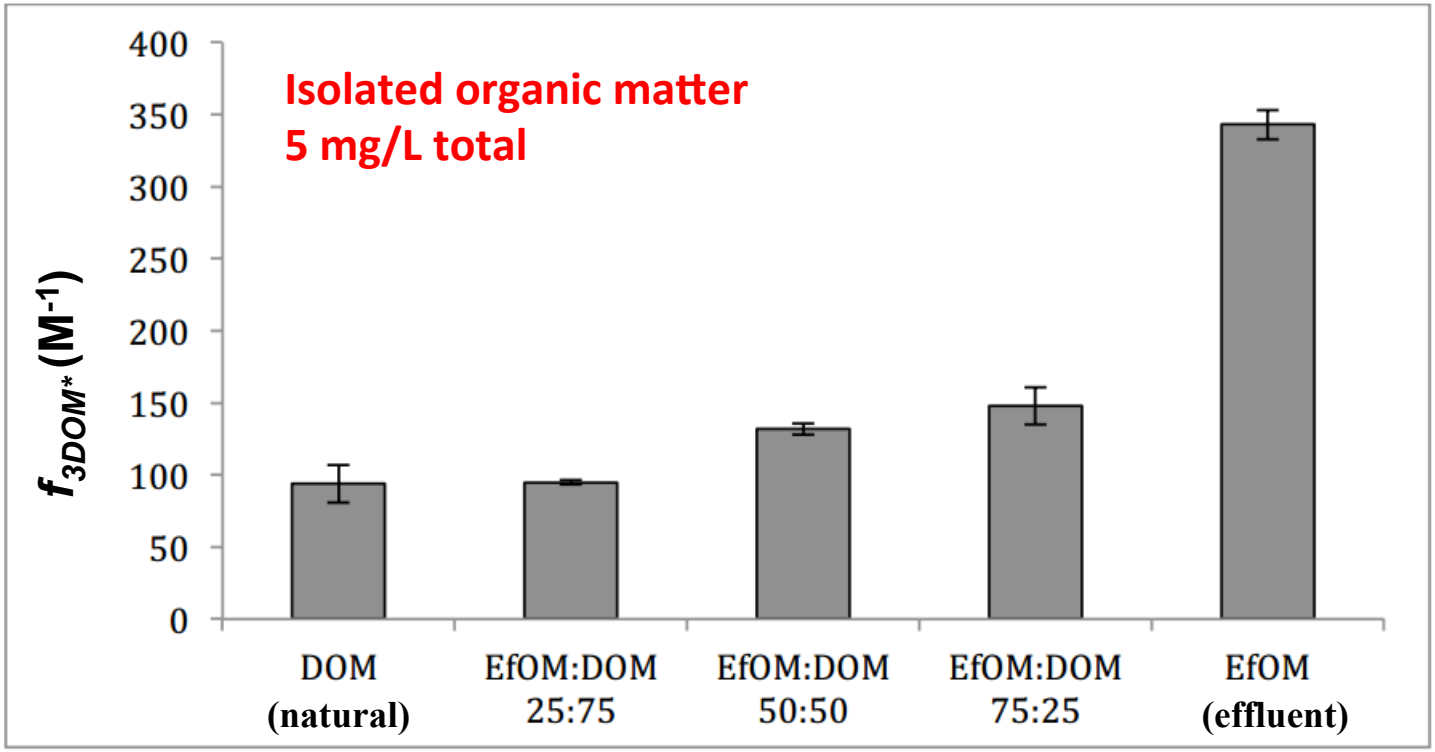
Theoretical Effluent Discharges

- **Reactive species production is proportional to percent of light absorption by organic matter from mixed sources**



incr. fraction effluent organic matter

Bodhipaksha et al. *in review*

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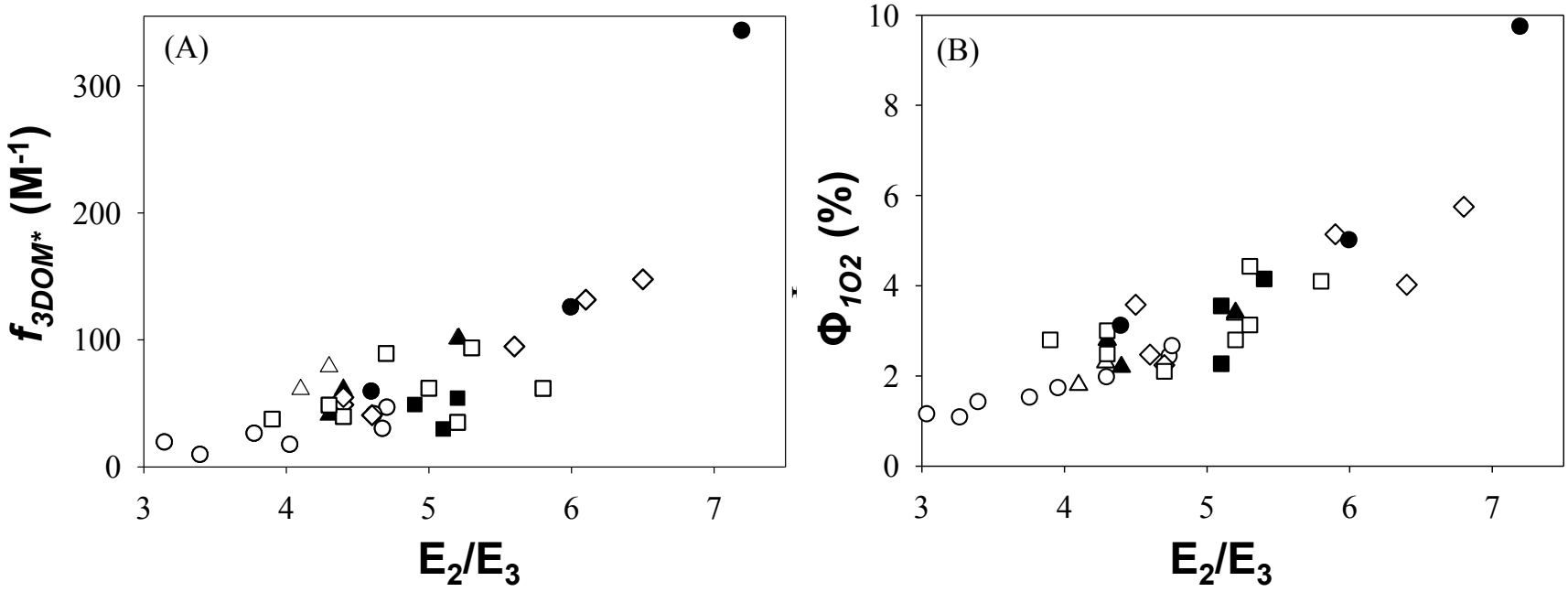
Reactivity Prediction from Optical Characteristics

- ^{3}DOM* and $^1O_2$ yields correlated with E_2/E_3 ratio, extending relationship for reference humic substances



- Potential for E_2/E_3 ratio to serve as predictor of reactive species production in effluent-receiving waters

Bodhipaksha et al. *in review*

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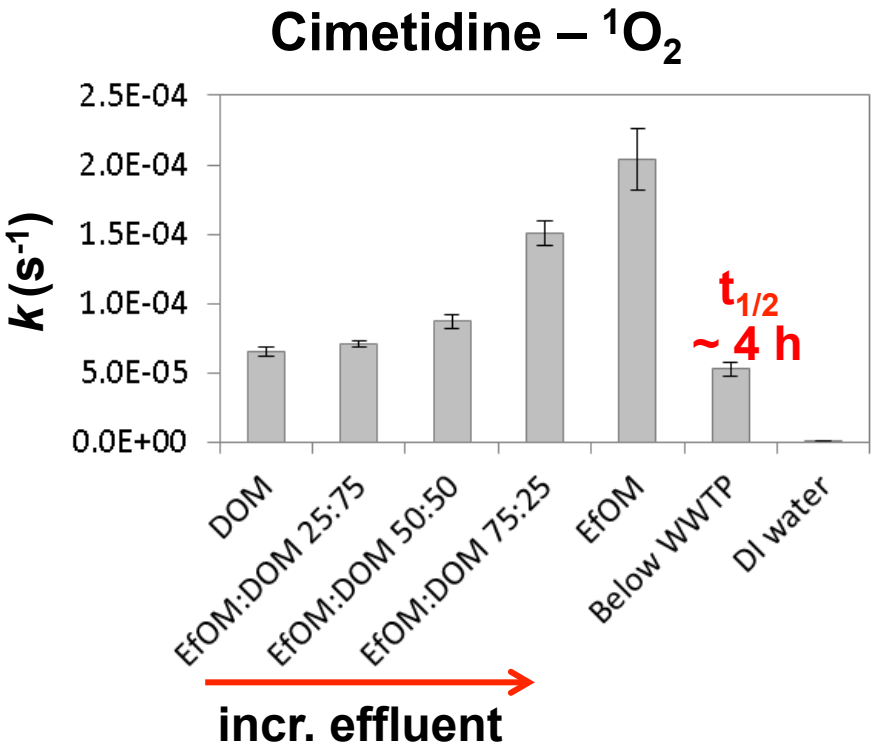
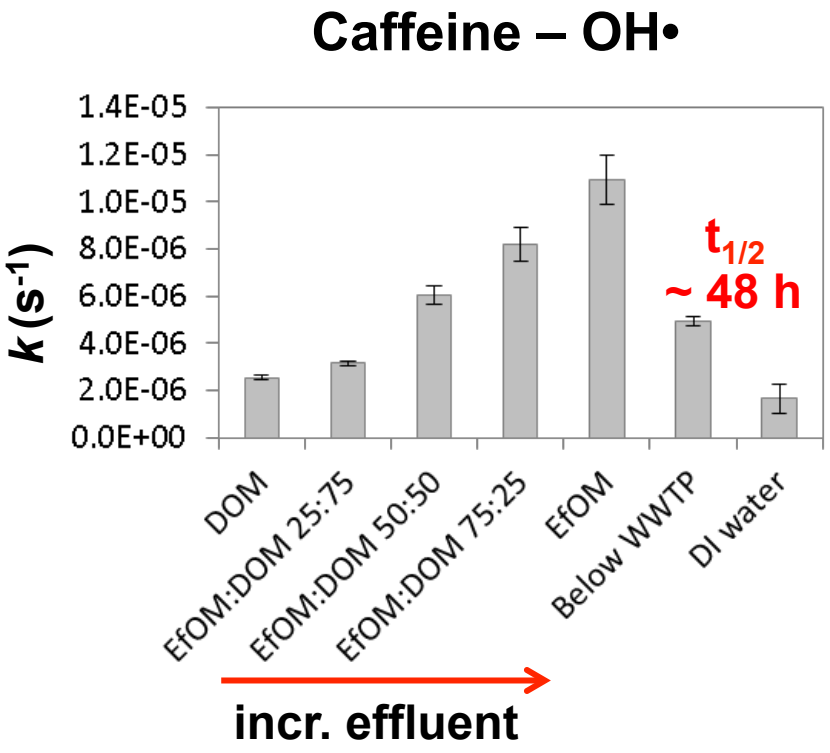
Validation of Indirect Photochemical Degradation

- **Pharmaceutical compounds with known degradation pathways show rates to be enhanced with photoreactivity of organic matter.**





Bodhipaksha et al. *in prep*

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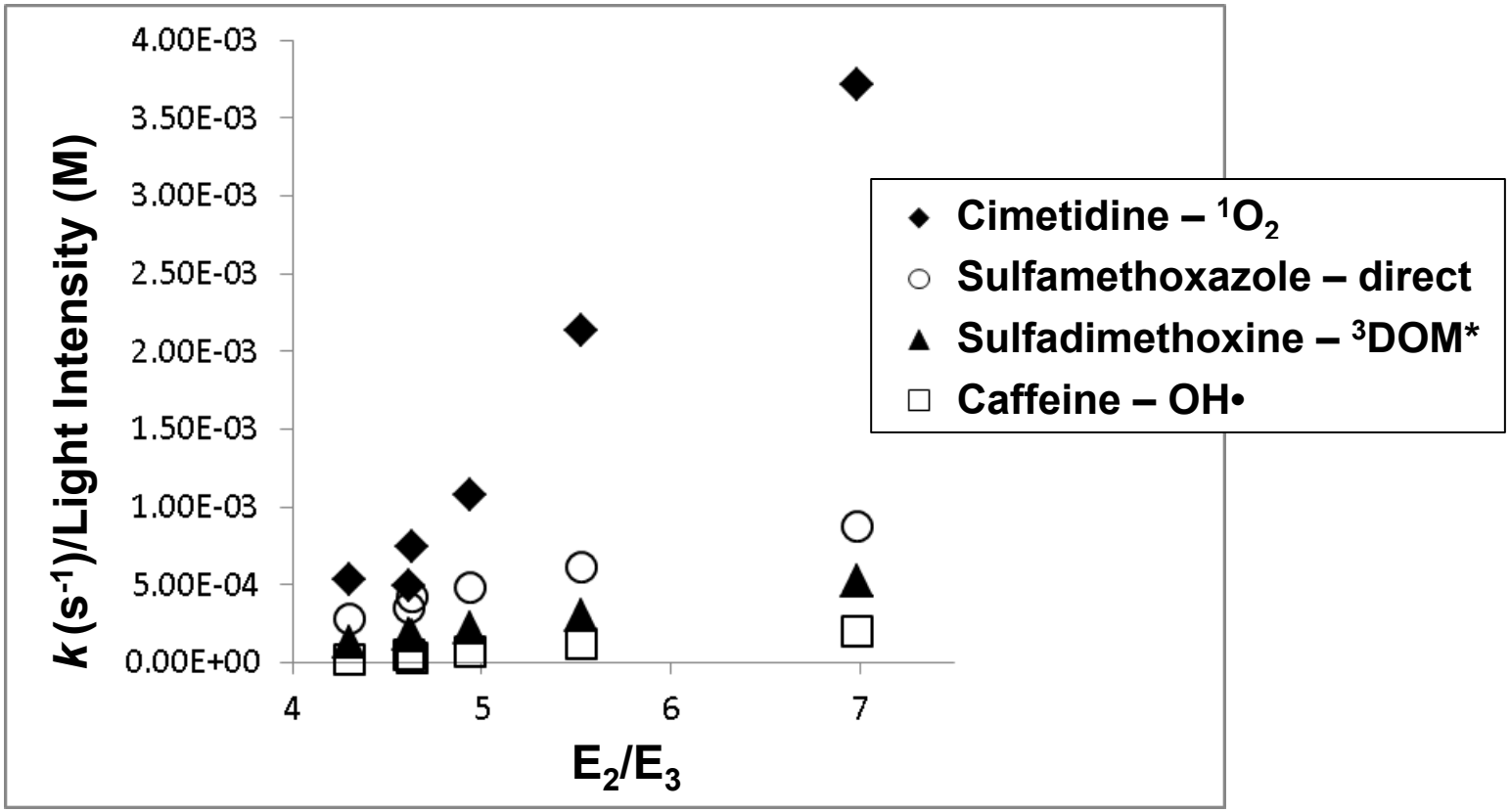
Photodegradation Correlated with Optical Properties

- Indirect photodegradation rates are correlated with E_2/E_3 ratios.



Bodhipaksha et al. *in prep*

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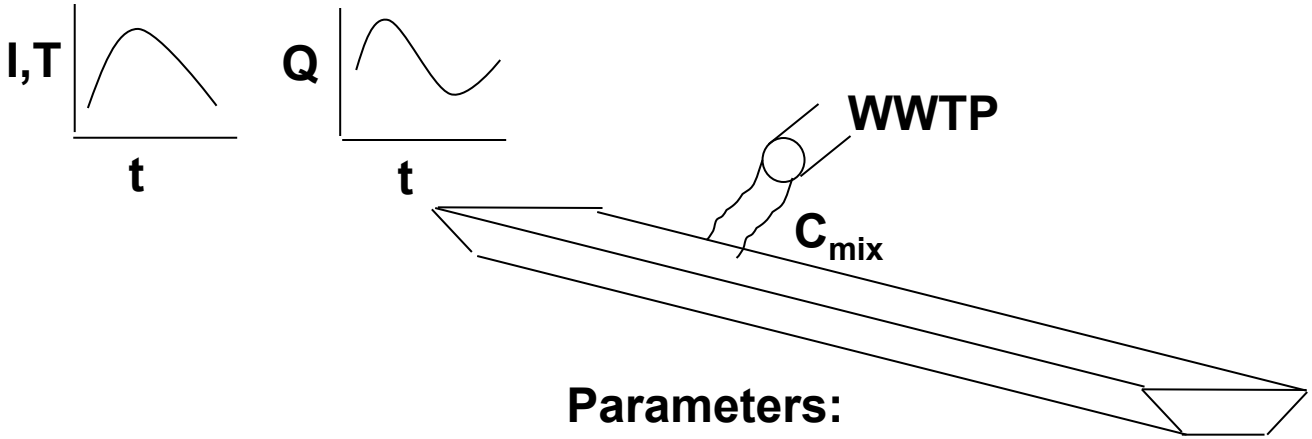
Integrated River Assessment

- Simulate downstream compound concentrations over seasonal hydrologic, temperature and light intensity cycles

Inputs:



Parameters:
h, abs, E2/E3

Output:

$$C_{out} = C_{mix} * \exp(-k_{deg} * t)$$

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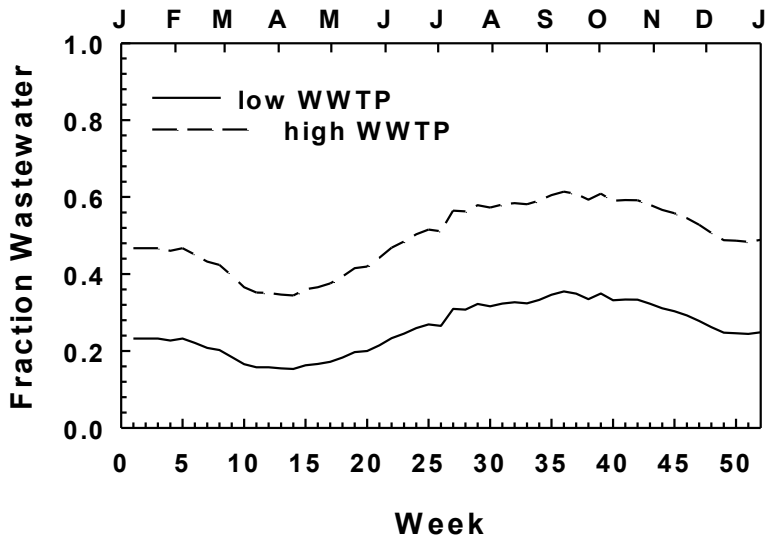
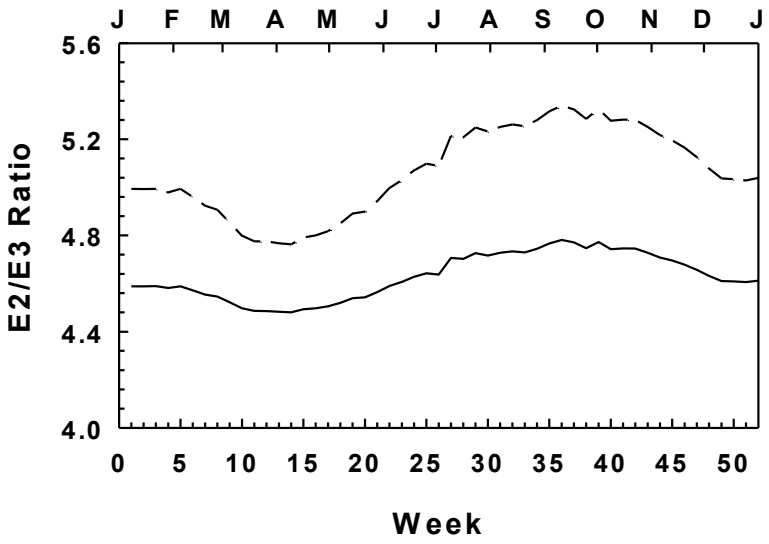
Seasonal Variation in Optical Characteristics

- Increasing effluent discharge ↑ water depth and ↓ travel time.





MacKay et al. *unpublished*

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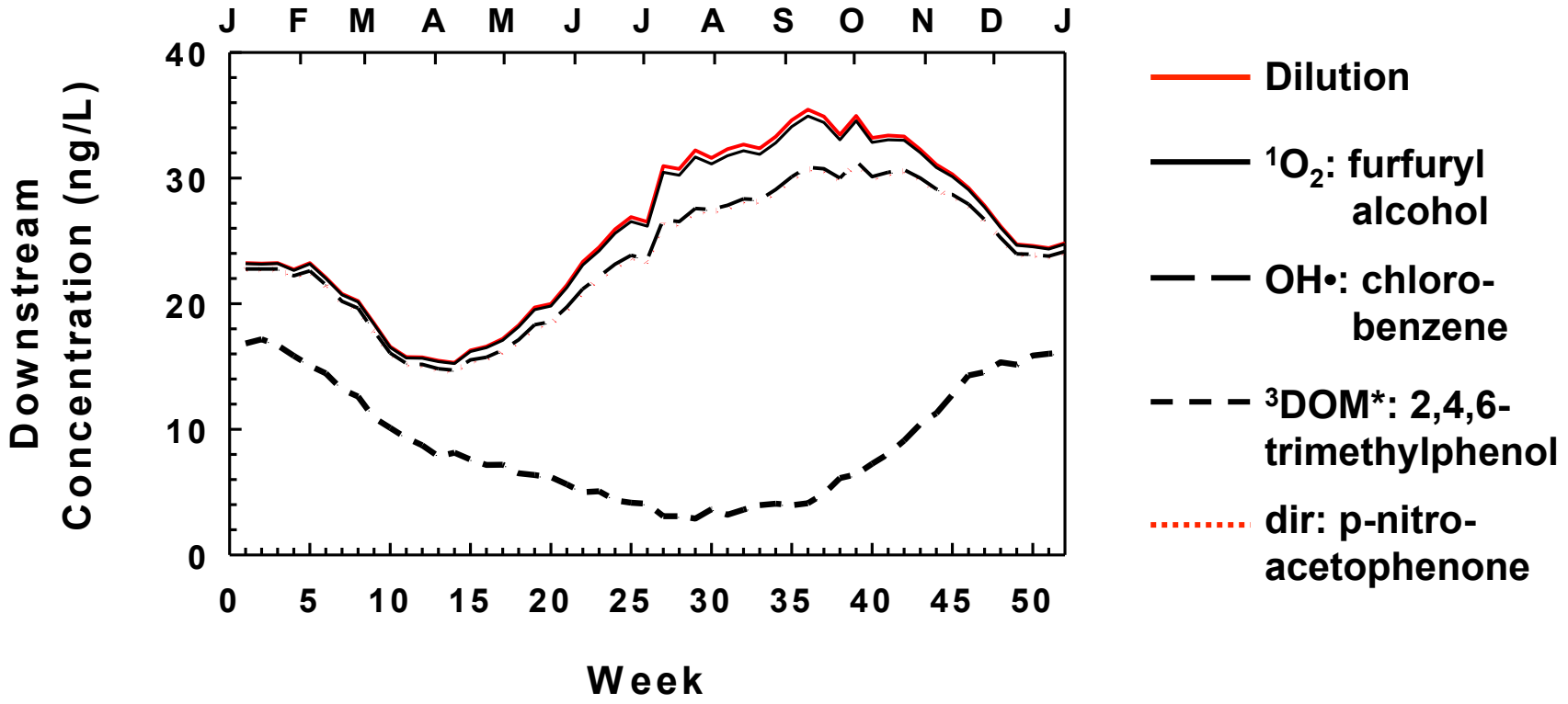
Downstream Concentration Attenuation

- **Dilution is an important processes in concentration reduction.**

C_{WWTP} = 100 ng/L; low Q_{WWTP}; avg travel time of 1 d



MacKay et al. *unpublished*

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Environmental Significance

- EfOM optical properties are similar to NOM from microbial sources.
- Effluent contributions have negligible influence on reactive species photoproduction in rivers with moderate WWTP discharges
- EfOM and mixture photoreactivity predictable from easily measured E2/E3 ratio
- Important to report dilution ratio from field sampling campaigns
- Continued simulations to assess importance of indirect photolysis on downstream removal of micropollutants

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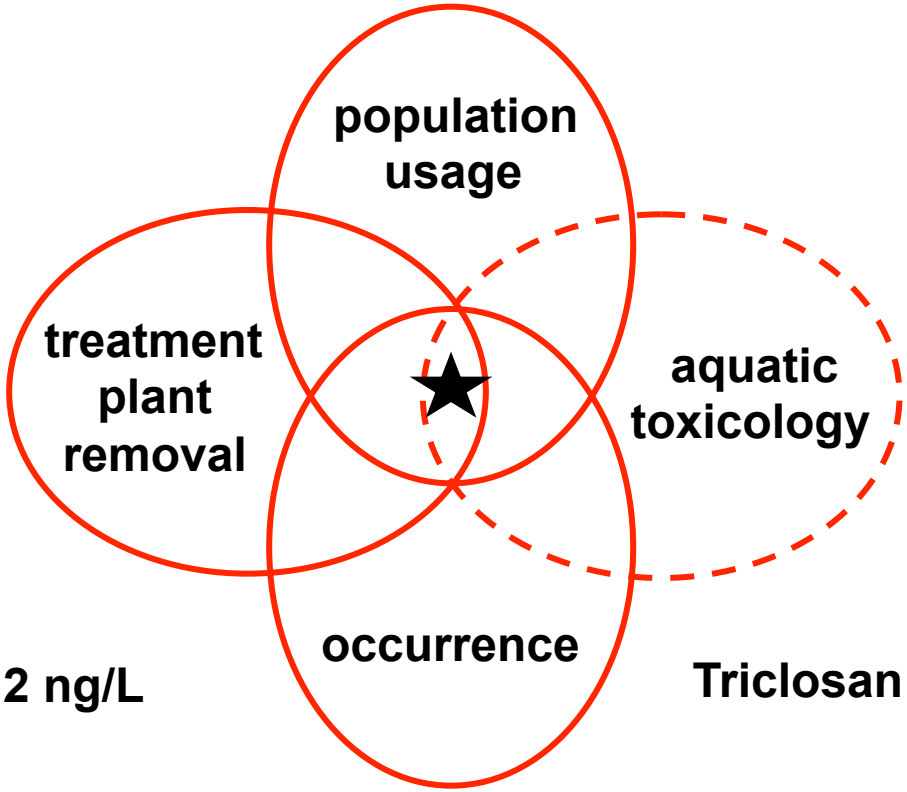
Sources of Wastewater-Derived Microconstituents

- Survey studies have documented variable occurrence



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Triclosan: 58%, 140 – 2300 ng/L

- What happens downstream from survey sample point?

Kolpin et al., ES&T, 2002

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