Singlet Oxygen Kinetics for Trace Organic Transformation in Wastewater Effluent

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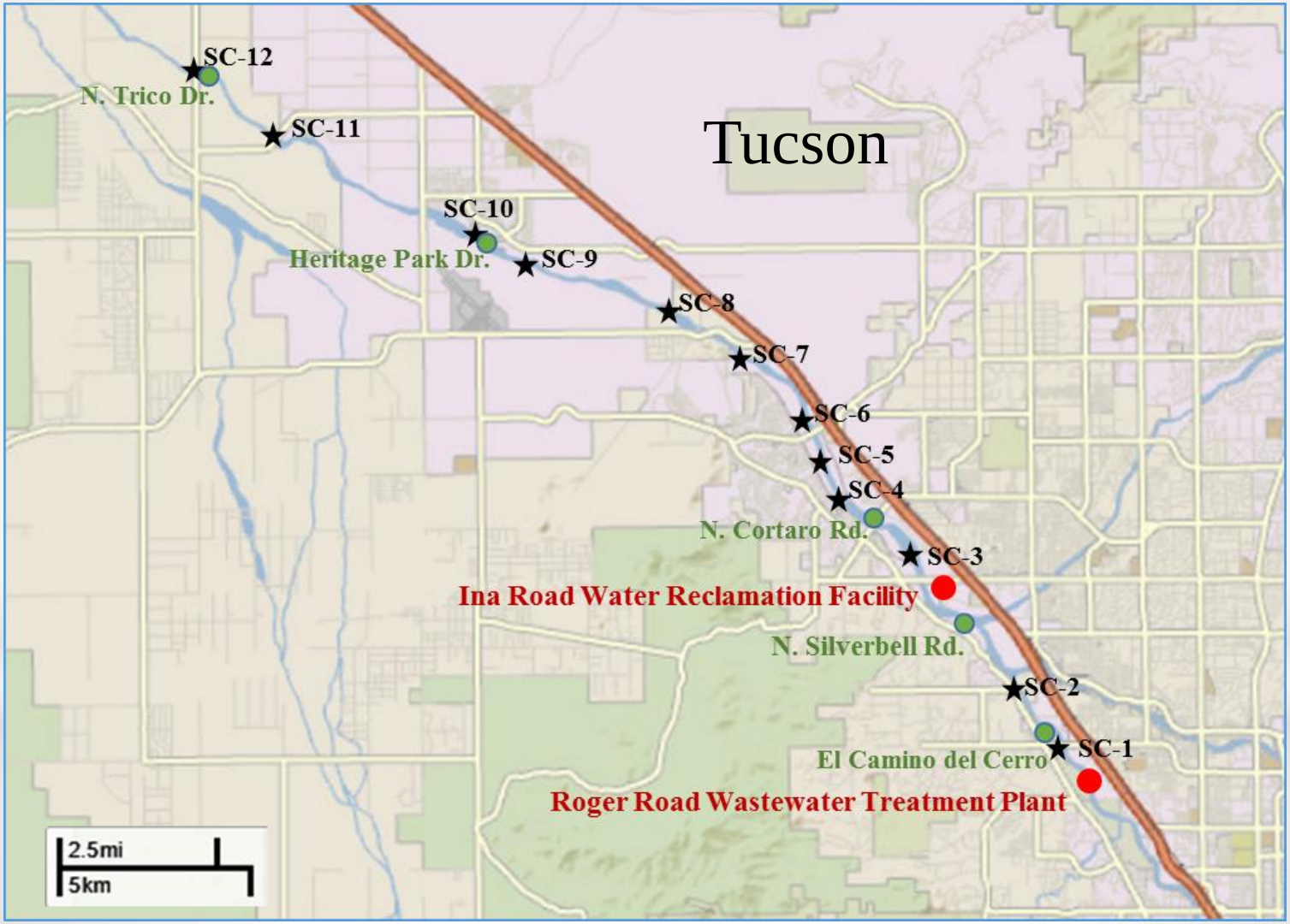
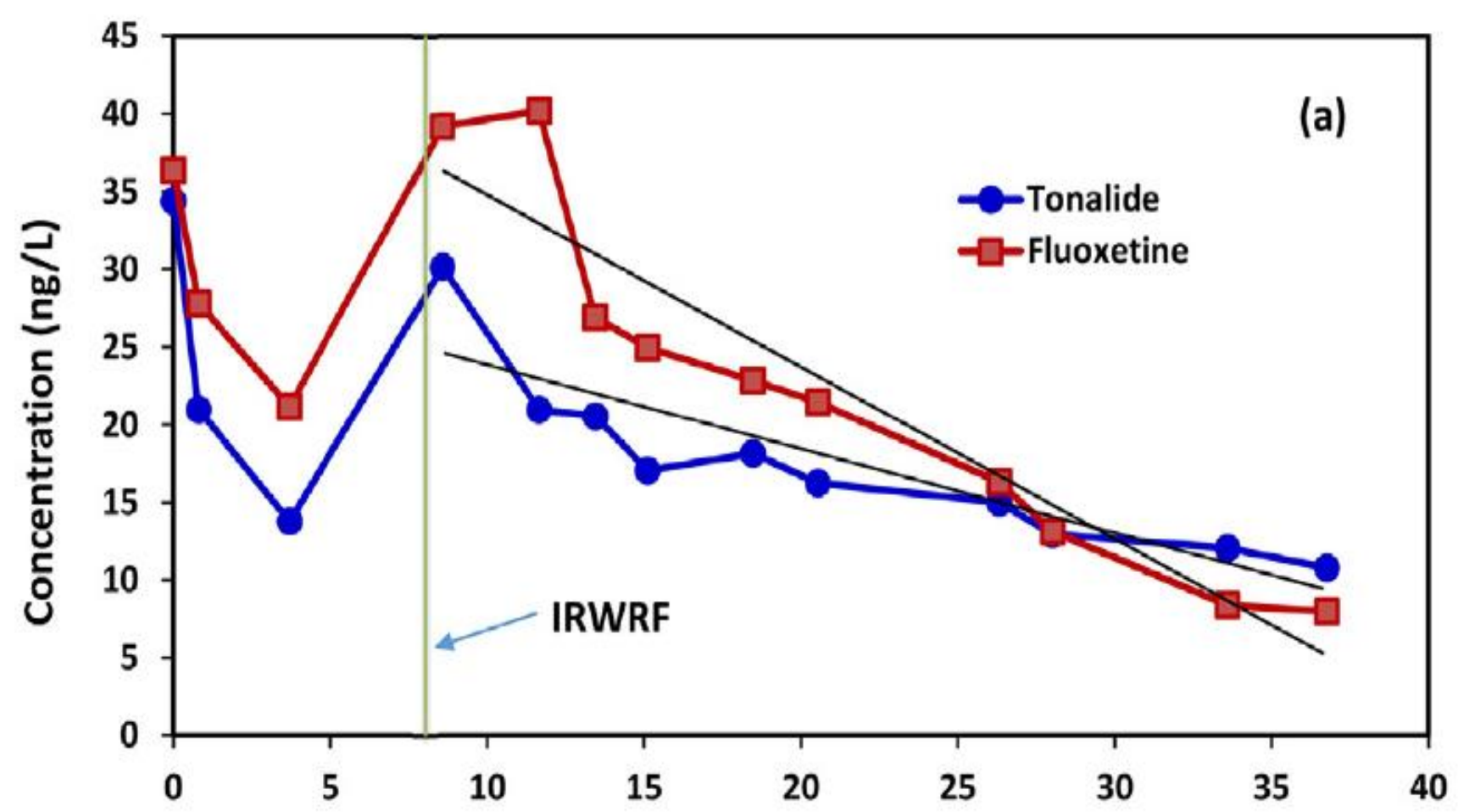
Rationale

- Trace organic compounds (TOrCs) with potential health and ecological effects (e.g. pharmaceuticals, endocrine disruptors) must be removed for reuse of treated wastewater
- Preliminary studies in the Santa Cruz River showed that some important TOrCs are attenuated with distance form treatment plant outfall
- Research shows that the mechanism responsible is reaction with singlet oxygen produced when photosensitizers in the wastewater effluent react with sunlight

The Santa Cruz River in Tucson, Arizona (wastewater-dependent stream)

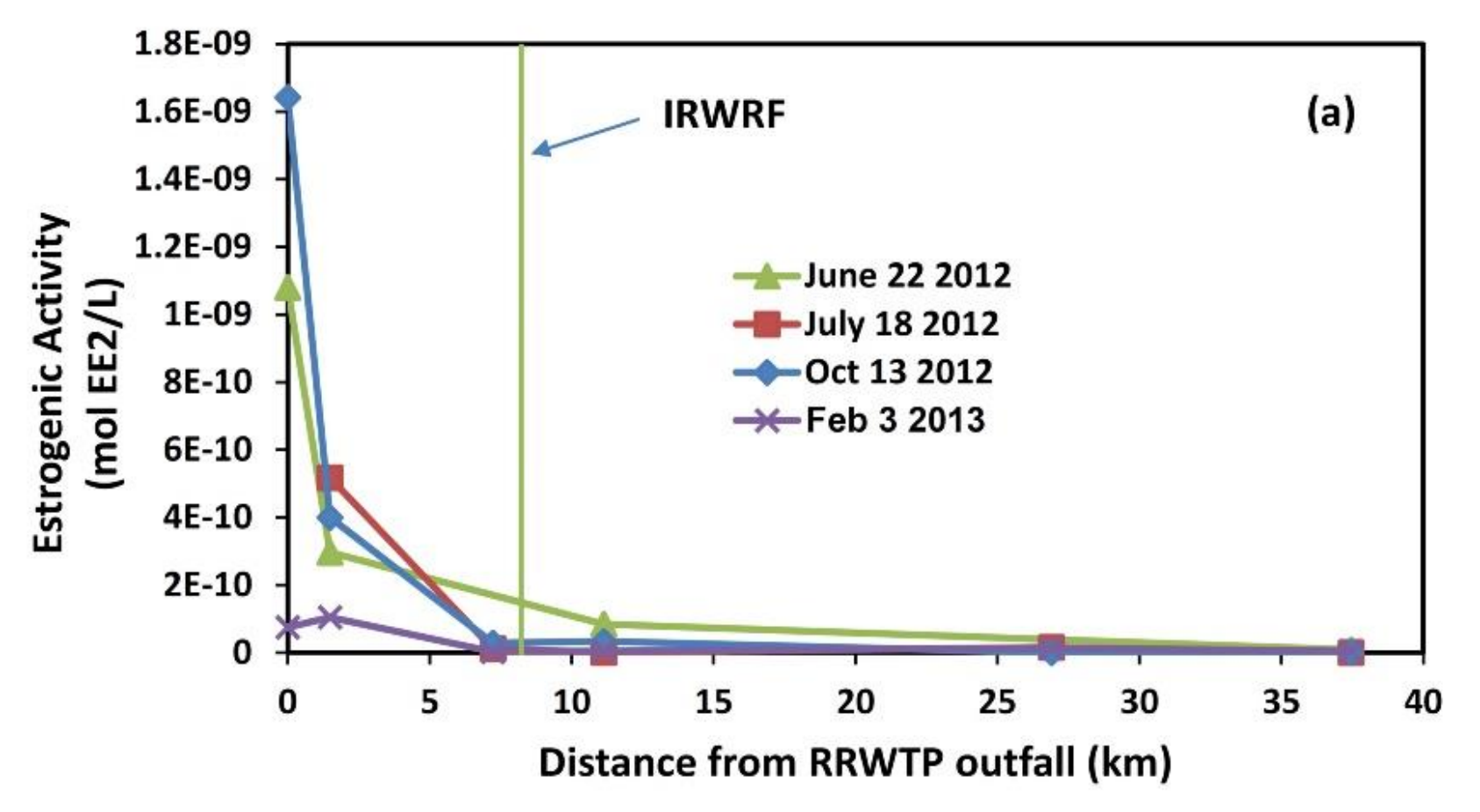


Attenuation of TOrCs in the Santa Cruz River



Fluoxetine (Prozac): Antidepressant
Tonalide: Fragrance

Attenuation of Estrogenic Activity in the SCR



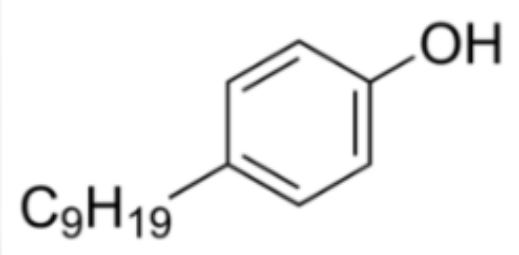
Possible mechanisms: Sediment sorption, biodegradation, photolysis

Solar Photolysis

Indirect solar photolysis plays a role in attenuation of TOrCs (estrogenic compounds in particular).

Model system to investigate mechanism:

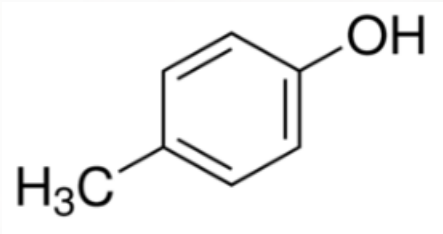
Alkylphenols



Nonylphenol (NP)

$k_{NP + *OH} = 1.30 \times 10^{10}\ M^{-1}s^{-1}$

Widespread endocrine disrupter

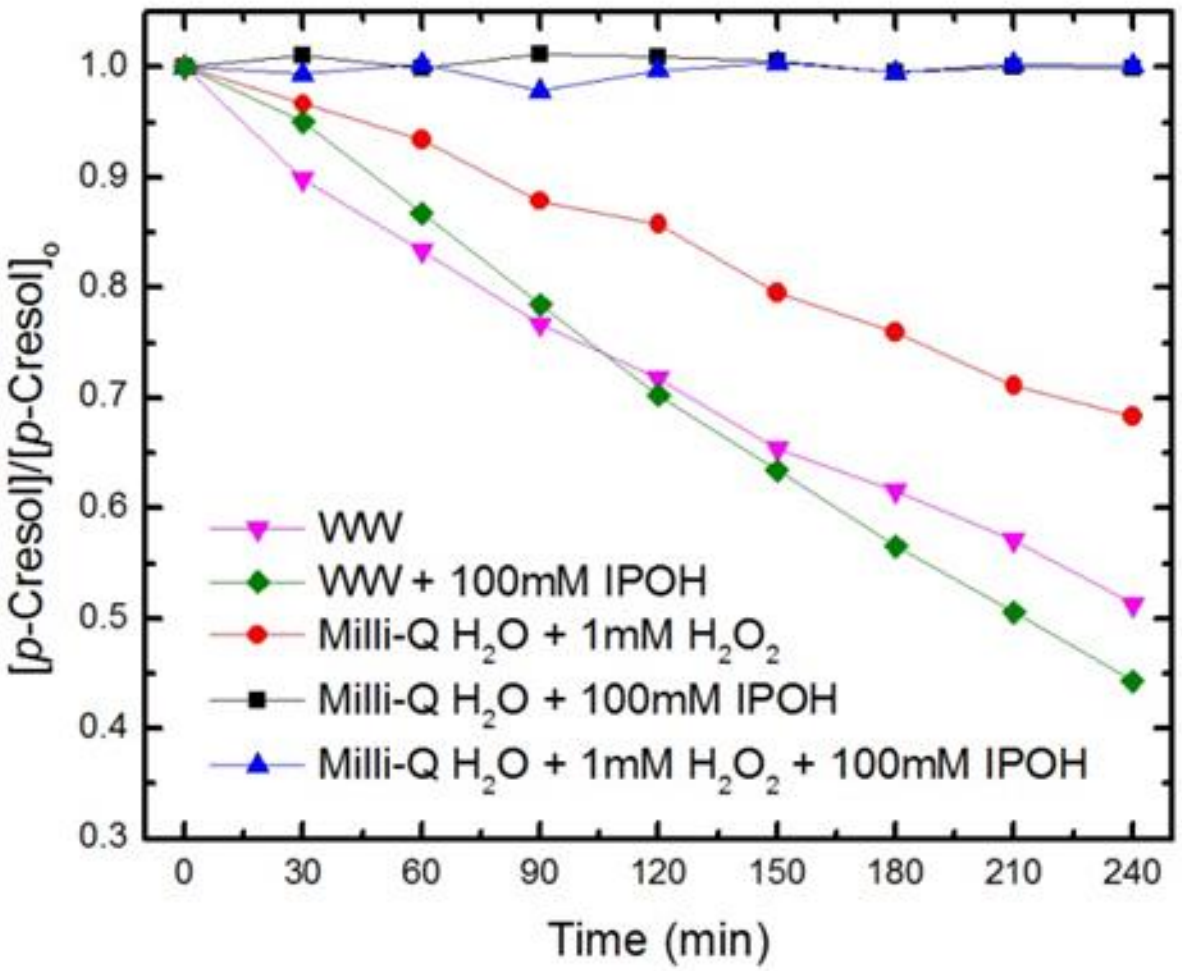


p-Cresol (PC)

$k_{PC + *OH} = 1.20 \times 10^{10}\ M^{-1}s^{-1}$

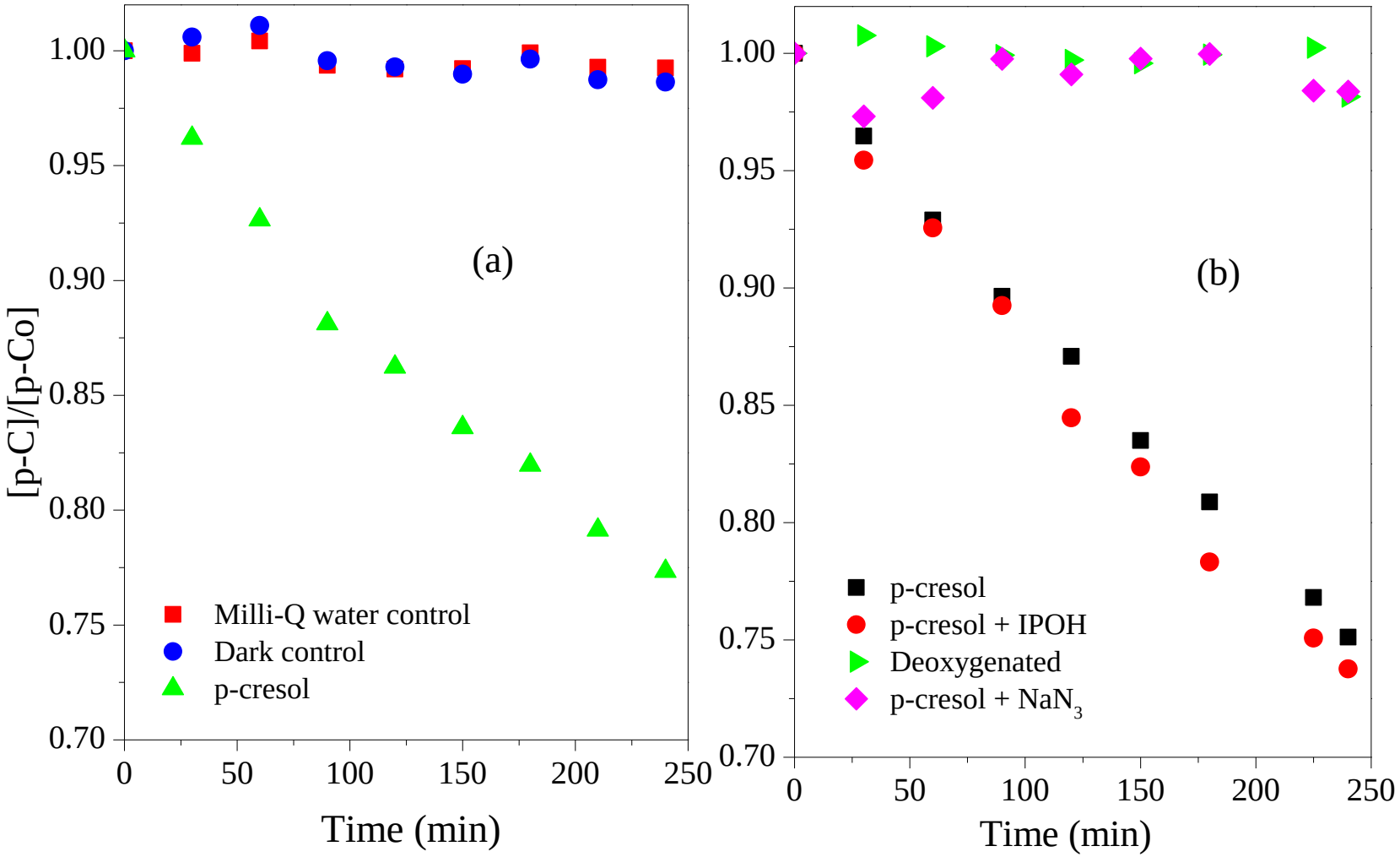
Model compound

Solar indirect photolysis of p-cresol

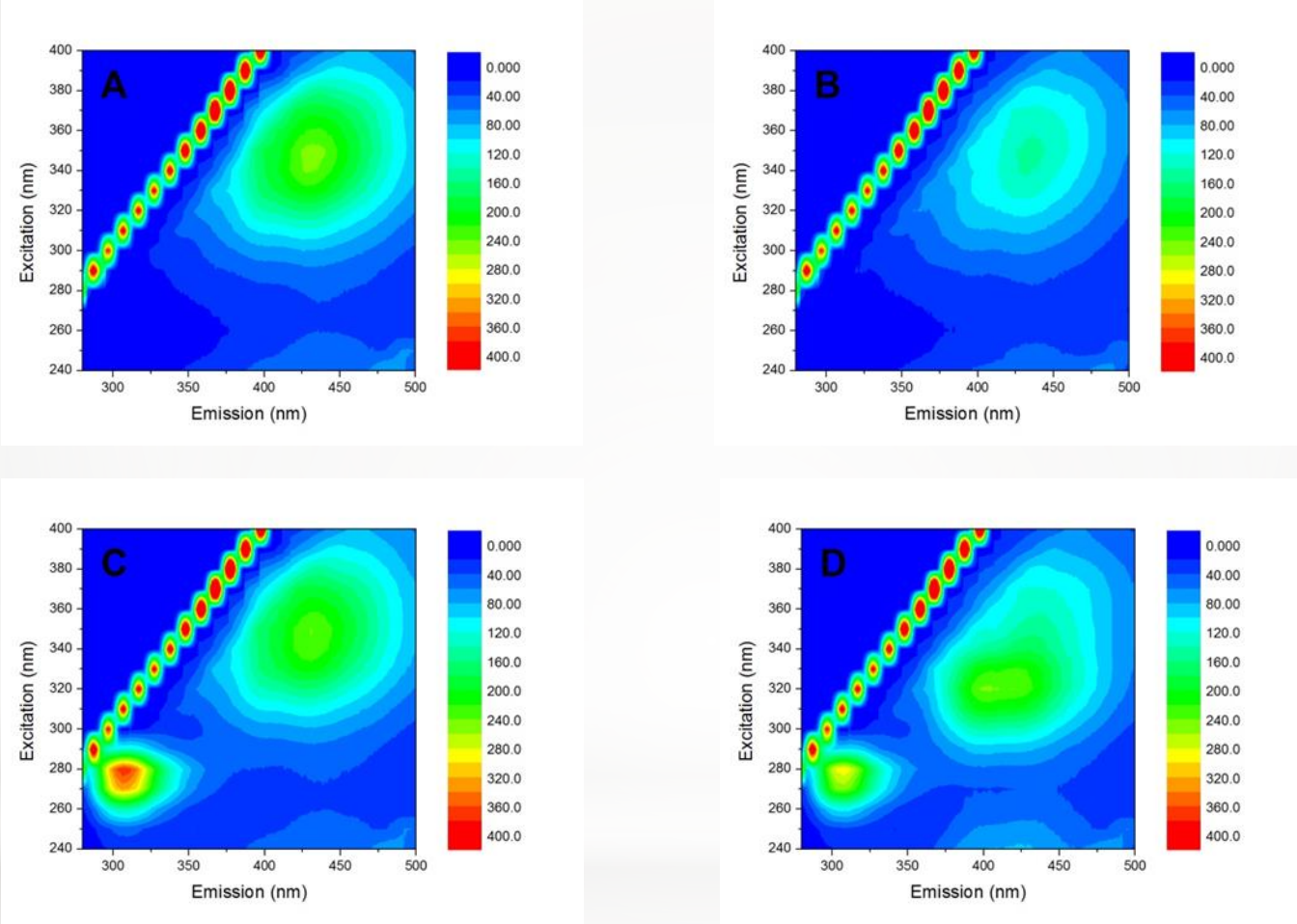


Initial p-c concentration: 50 μM

UVA (300-400 nm) indirect photolysis of p-cresol



Changes in the Wastewater Matrix During Solar Photolysis



Fluorescence intensity (EEM) plots of wastewater samples before (A) and after (B) 4 hours of sunlight without *p*-cresol, and before (C) and after (D) 4 hours of sunlight with $[p\text{-cresol}]_o$ = 50 μM.

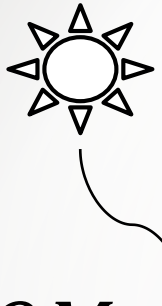
Summary of Observations on Solar Light Attenuation of TOrCs

1. Requires: Solar light, wastewater and dissolved oxygen
2. It is not caused by direct photolysis
3. It is not caused by formation of hydroxyl radicals

Hypothesis:

Compounds in effluent organic matter (EfOM) are excited to a triplet state by solar light and the excited molecules react with dissolved oxygen to form singlet oxygen, a powerful oxidizer

Mechanism

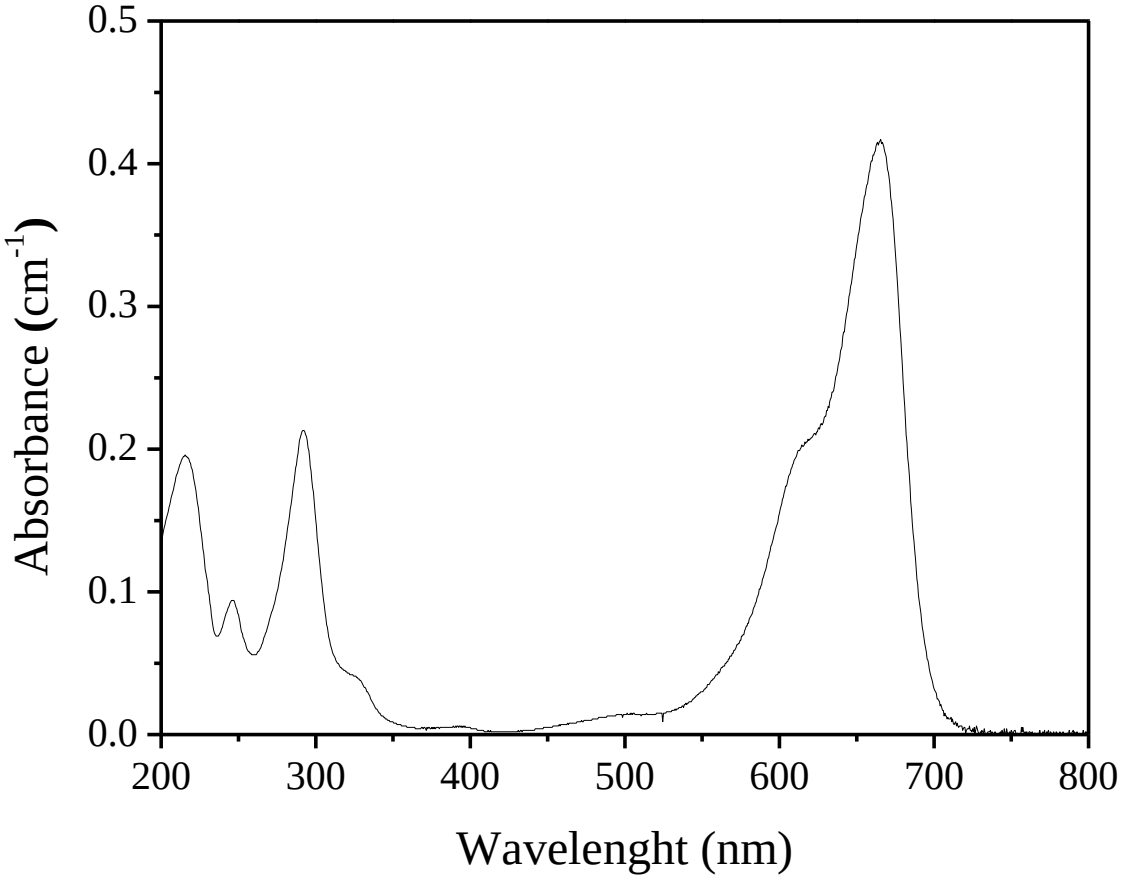


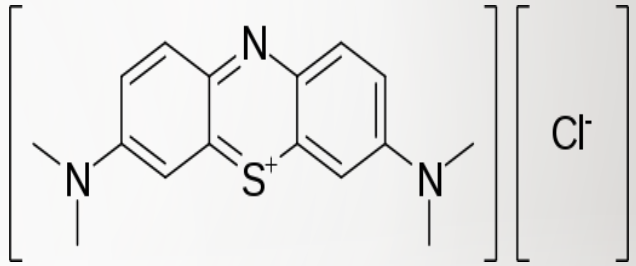
$$EfOM \rightarrow {}^{1}EfOM^{*} \rightarrow {}^{3}EfOM^{*} + O_2 \rightarrow {}^{1}O_2$$

$$^{1}O_2 + TOrC \rightarrow products$$

EfOM: Photosensitizer in wastewater effluent

Validation of the mechanism using a model photosensitizer: methylene blue (MB)

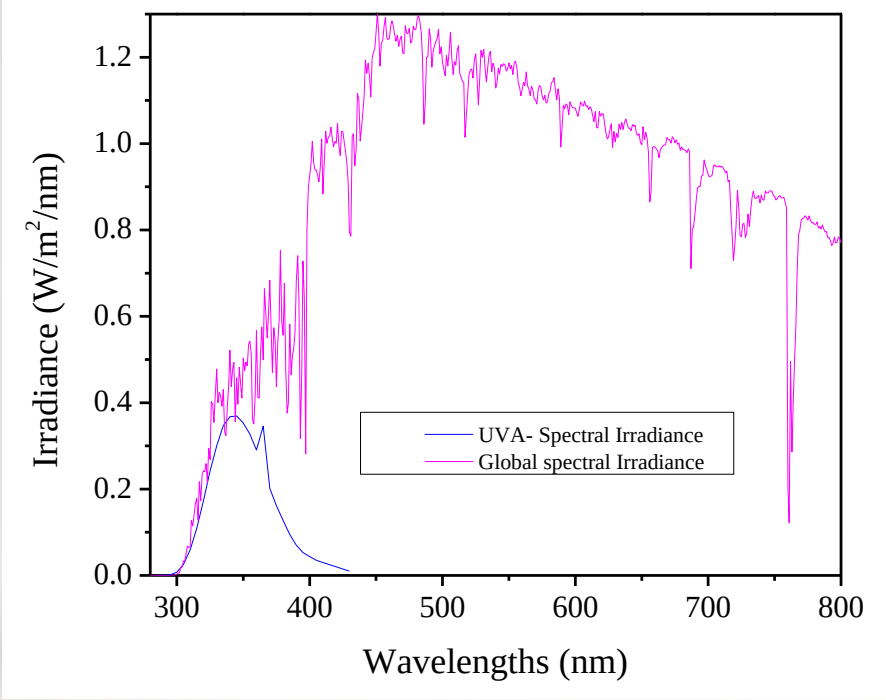




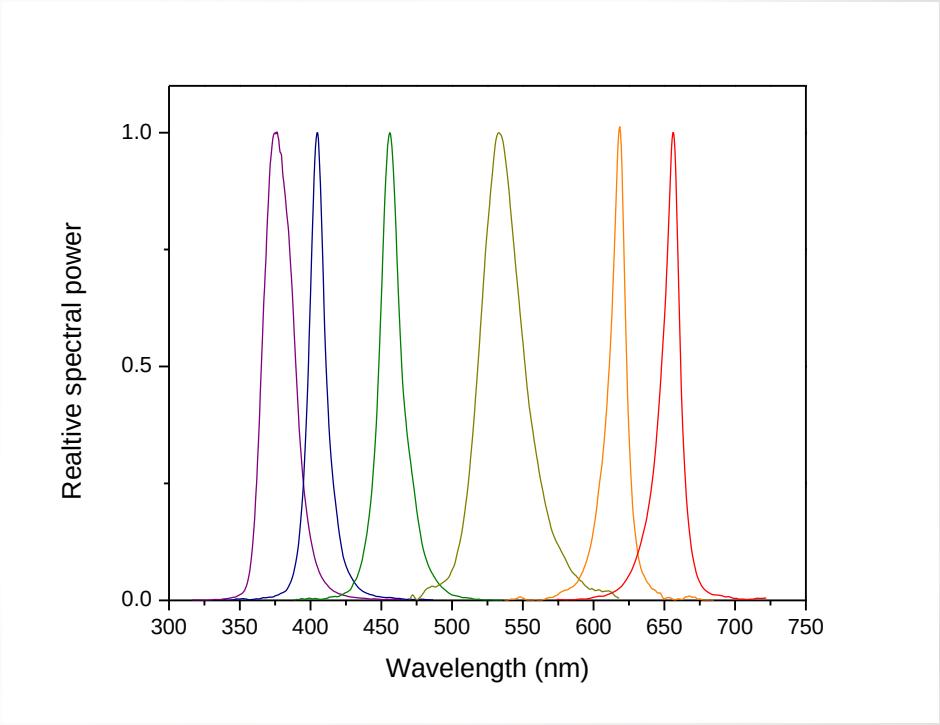
Targets (TOrCs): Furfuryl alcohol (FFA), p-cresol (p-c)

Light Sources Used in Experiments

UVA/sunlight



Light Emitting Diodes (LEDs)



A predictive kinetic model was developed to simulate target destruction in a batch reactor by singlet oxygen produced from the light excitation of MB

Kinetic model

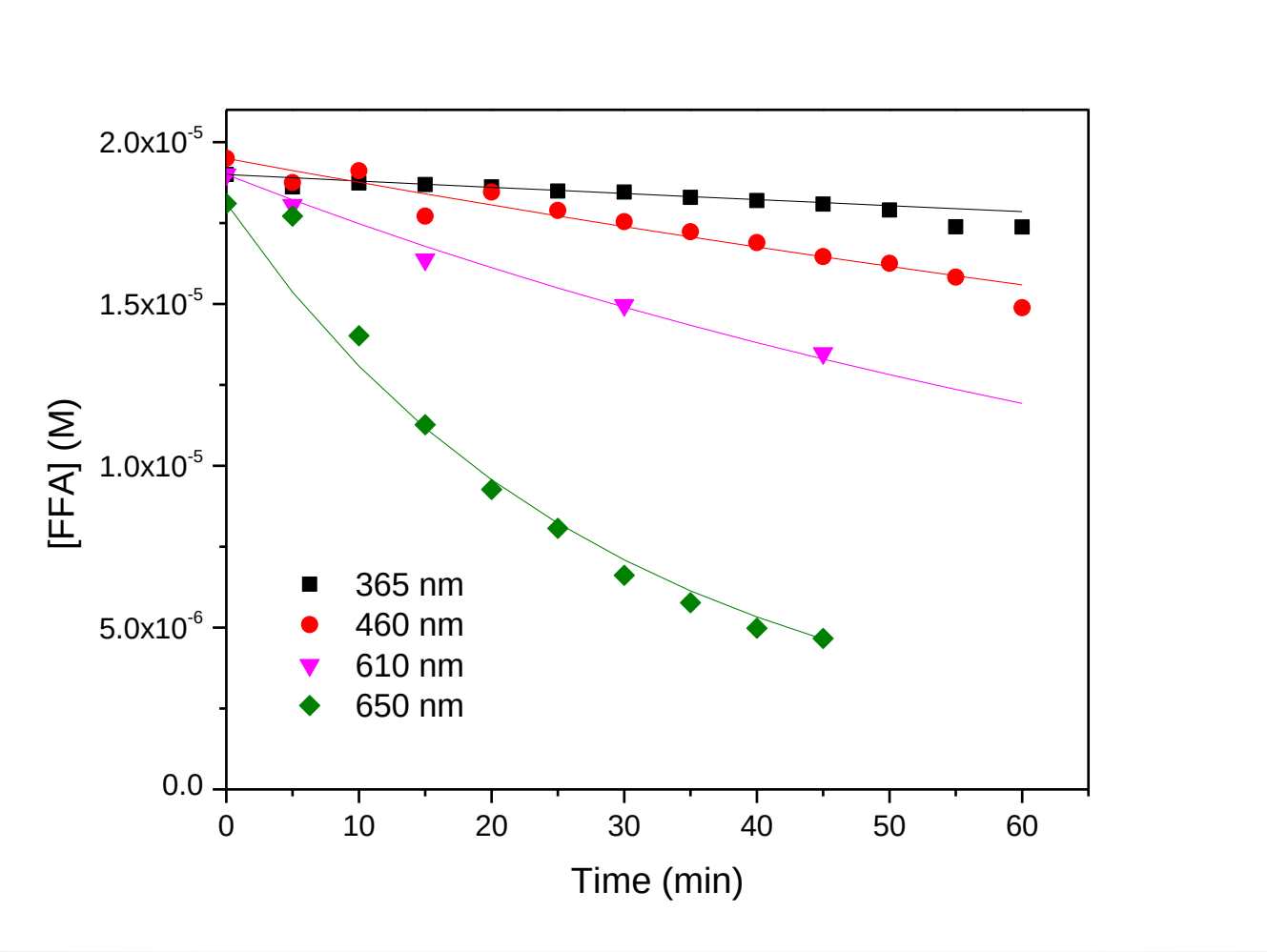
Photo-degradation of FFA by $^1O_2$ using MB as photosensitizer

$MB + hv \rightarrow MB^{\bullet} \rightarrow {}^3MB^{\bullet}$	ϕ_{MB^*} = wavelength dependent
${}^3MB^{\bullet} + O_2(aq) \rightarrow {}^1O_2 + MB$	$k_1 = 2.0\times10^9\ M^{-1}s^{-1}$
${}^1O_2 + FFA \rightarrow product$	$k_2 = 1.2\times10^8\ M^{-1}s^{-1}$
${}^1O_2 \rightarrow O_2(aq)$	$k_3 = 2.54\times10^4\ s^{-1}$

$$\phi = \frac{moles\ of\ compound\ that\ react}{moles\ of\ photons\ absorbed\ by\ compound\ at\ fixed\ wavelength}$$

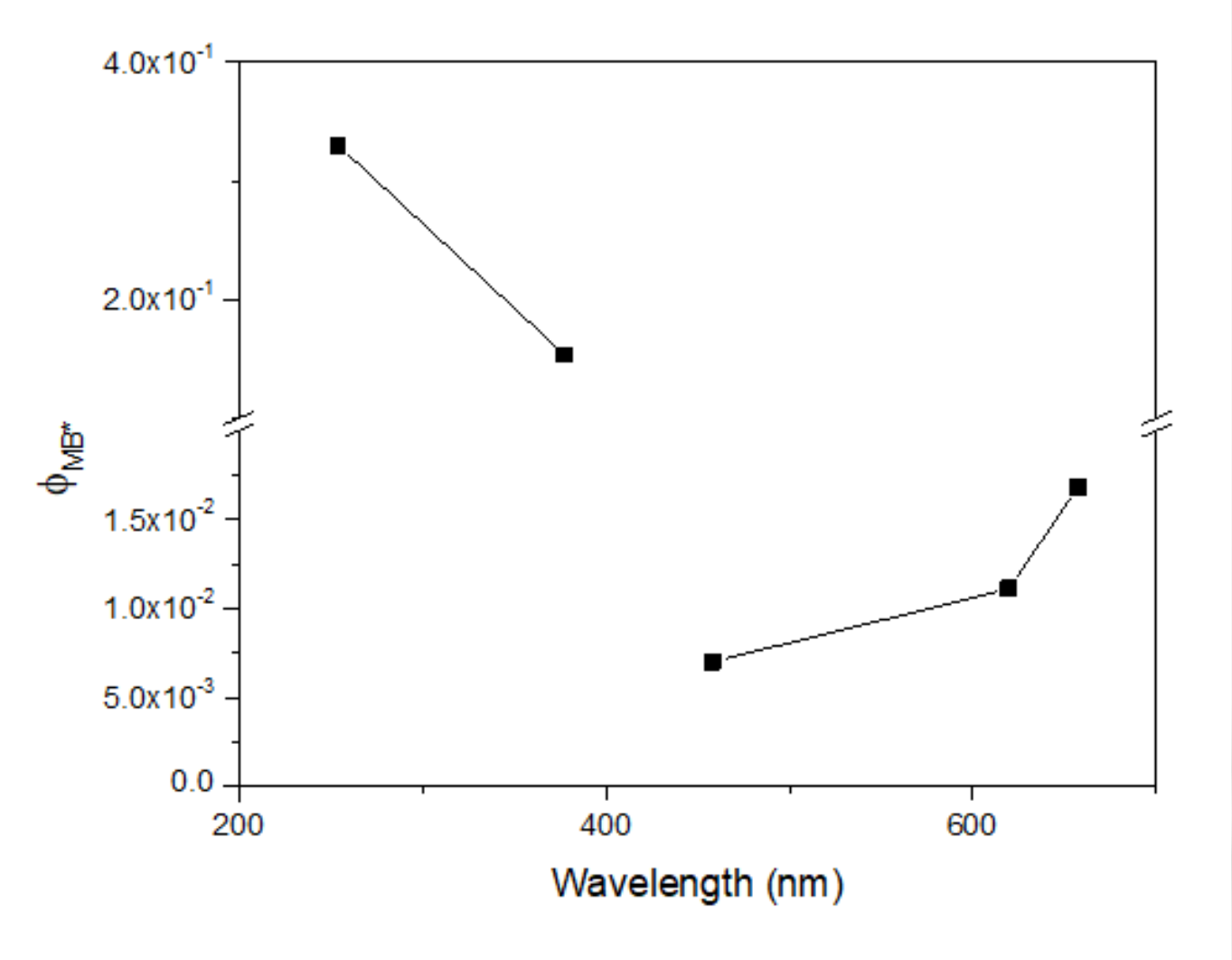
(quantum yield)

Degradation of FFA by Singlet Oxygen Produced from MB Using LEDs



Solid lines: Model predictions, adjustable parameter: MB quantum yield

Quantum Yield of MB for Production of Singlet Oxygen



Quantum yield: Moles of MB transformed to triplet state per mole of photon absorbed

If the model is correct

It should predict degradation of any compound with a known rate constant with singlet oxygen

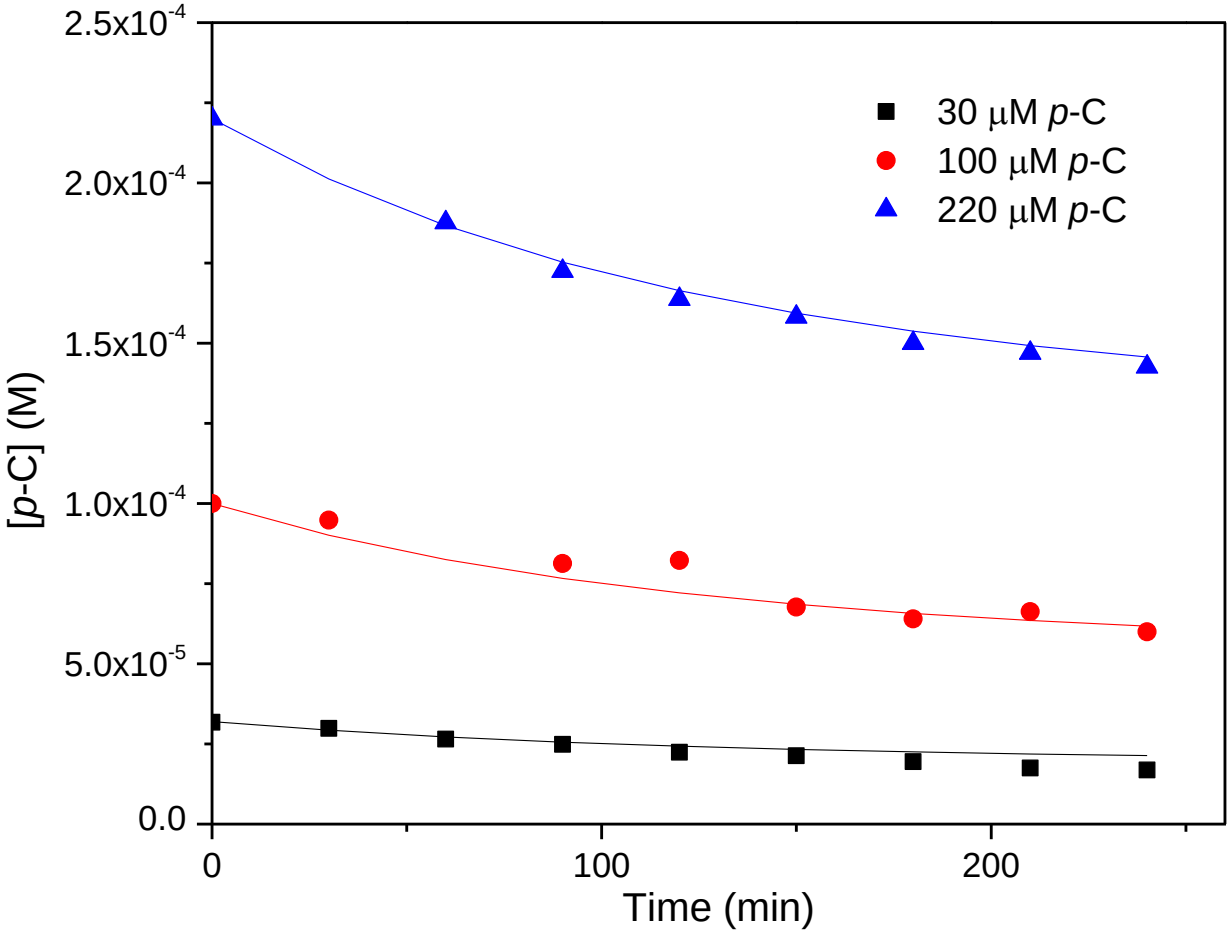
Model extended to *p*-cresol under sunlight

* Sunlight irradiance
* *p*-cresol rate constants

Photo-degradation of p-cresol by $^1O_2$ with MB as sensitizer

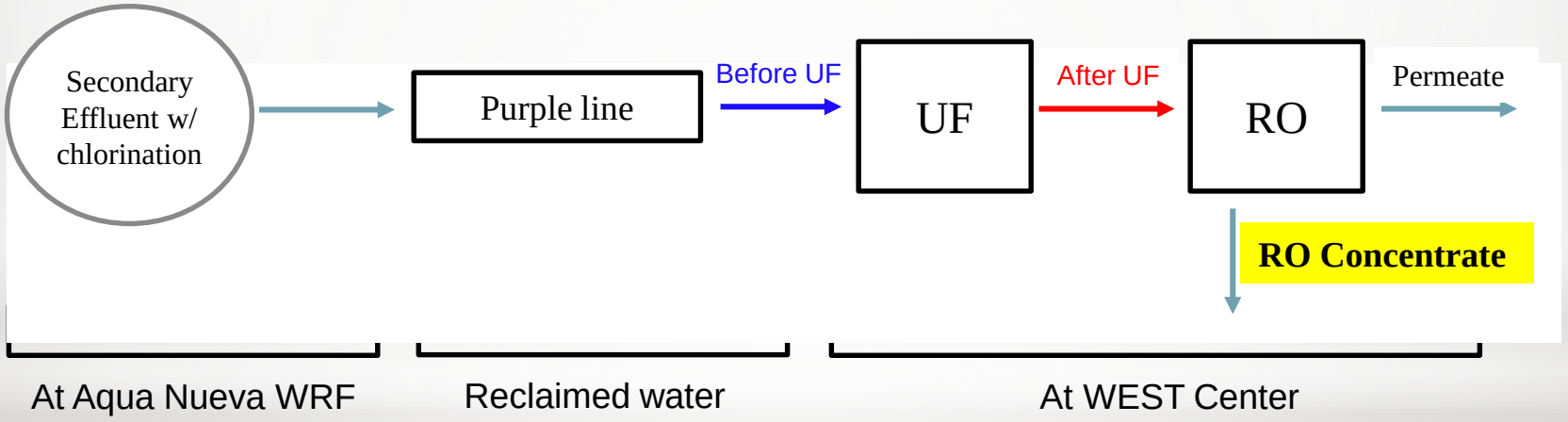
p-C + $^1O_2$ → products	$k_5 = 1.2\times10^7\ M^{-1}s^{-1}$
p-C_ion + $^1O_2$ → products	$k_6 = 3.7\times10^8\ M^{-1}s^{-1}$
p-C → p-C_ion + H^+	pK_a = 10.26 (at 25 °C)

Photo-degradation of *p*-cresol with MB (5 μM) under sunlight

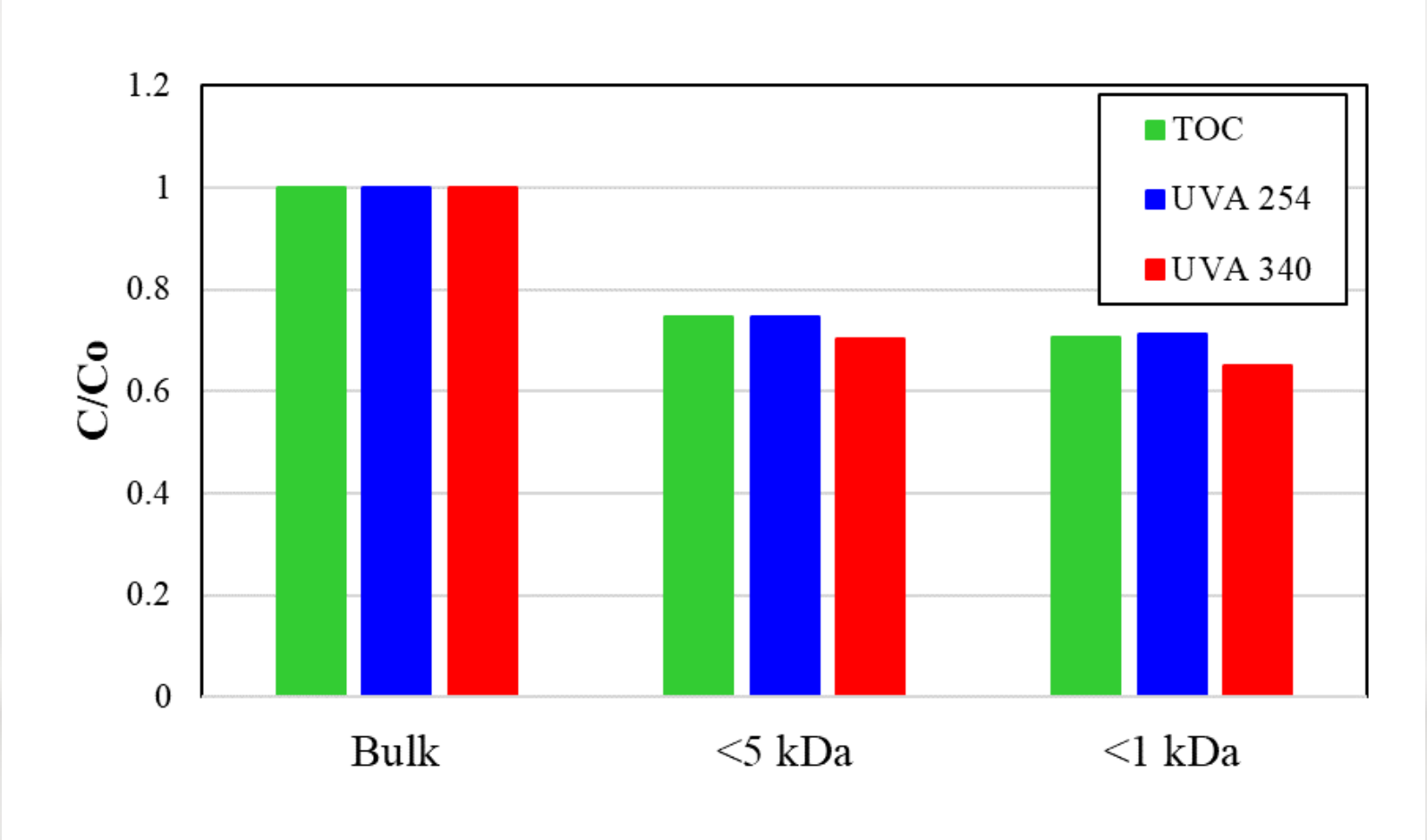


Experiments with wastewater effluent

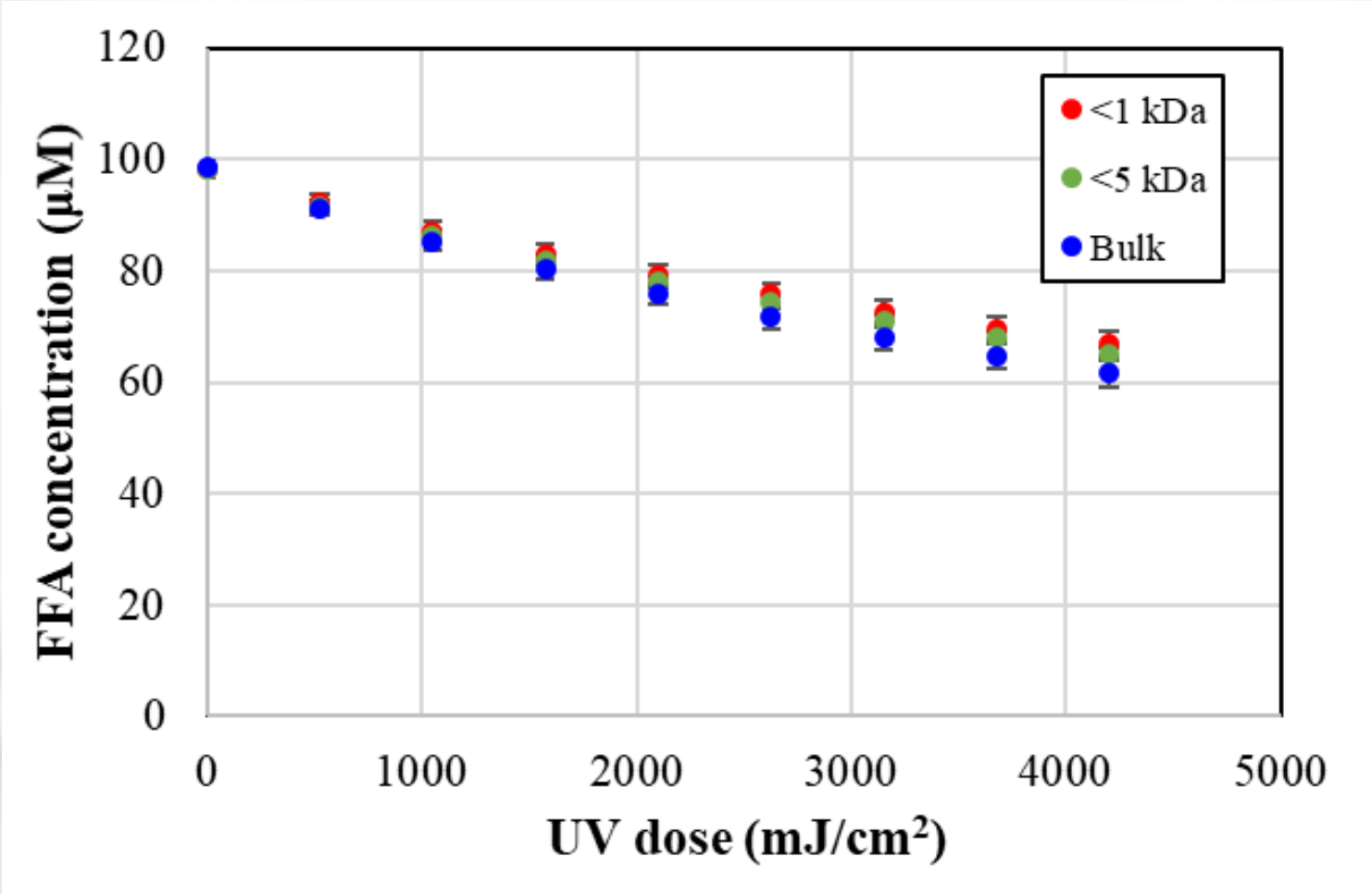
Reverse osmosis concentrate from wastewater effluent was selected to increase photosensitizing activity



Fractionation of RO concentrate by molecular weight



Degradation of FFA by fractionated RO concentrate



Conclusions

Photosensitizers in wastewater effluent produce singlet oxygen when exposed to solar light, thus attenuating trace organics

Production of singlet oxygen from photosensitizers can be represented by a simple kinetic model based on the quantum yield for excitation to the triplet state

Preliminary experiments indicate:

1. Photosensitizers in wastewater effluent have molecular weight lower than 1 kDa
2. Photosensitizers are hydrophilic
3. Wavelengths in the range 450-550 induce significant photosensitizing activity