

Modeling the photochemical removal of pharmaceutical compounds in planted constructed wetlands

**Angel Cortez Ramirez; Marty King;
Claire Ingvoldsen; Margarita Otero-Diaz;
Tesfayohanes Yacob**

**Environmental Resources Engineering, School of Engineering,
California State Polytechnic University, Humboldt**

> Introduction: PPCPs

- Pharmaceutical and personal care products (PPCPs) that end up in water systems pose environmental, and health risk.
- Most wastewater treatment plants lack the money and technology to specifically target these compounds using advanced treatment to achieve high level of removal.
- Research work has explored the use of post-polishing of conventional wastewater treatment effluent using various types of constructed wetlands to provide removal beyond conventional removal of PPCPs.



Figure 1: Pharmaceutical and personal care products (PPCPs)

<https://www.ysi.com/ysi-blog/water-blogged-blog/2018/12/pharmaceuticals-personal-care-products-water-treatment>

> Introduction: Constructed Wetlands

- Constructed wetlands combine multiple mechanisms to transform and remove PPCPs.
 - Direct and *indirect photolysis*
 - Biological removal
 - Adsorption based removal
 - Plant uptake (in case of planted wetlands)

> Photo-chemical transformation pathways

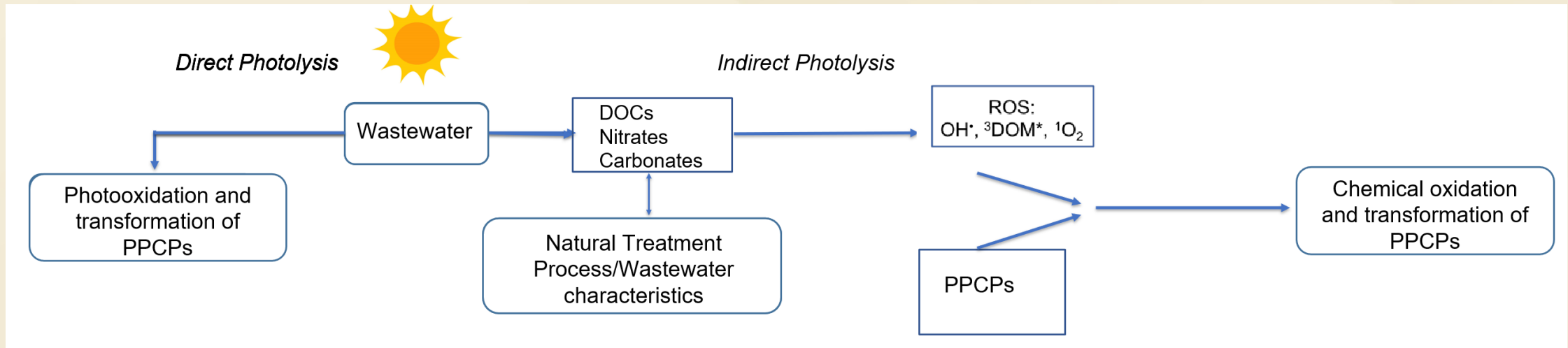


Figure 2: Schematics depicting photochemical based processes in constructed wetlands

> Modeling Aspects to Consider

| PPCPs Compound Specific | Wastewater Quality Changes | Reactive Oxygen Species Formation | Transport Aspects |
|---|---|---|------------------------------|
| Quantum Yields | DOC composition and concentration | Reaction between photosensitizers and photons | Hydraulic residence time |
| Molar absorption coefficient | Nutrient fluctuations | Depth of light penetration | Dispersion Parameters |
| pKa | Temperature Impacts | Available area | |
| Reaction constants with ROS species | Growth season impacts – from plants | Altitude and longitude | |
| Reaction rate with photons | pH | Season | |

> Arcata Wastewater Treatment Facility

- For this presentation we focus on the DOC transformation happening within the treatment train as that helps us identify the unique role of planted constructed wetlands
 - Determine how the DOC transformation affects the indirect ROS generation focusing on hydroxyl radicals

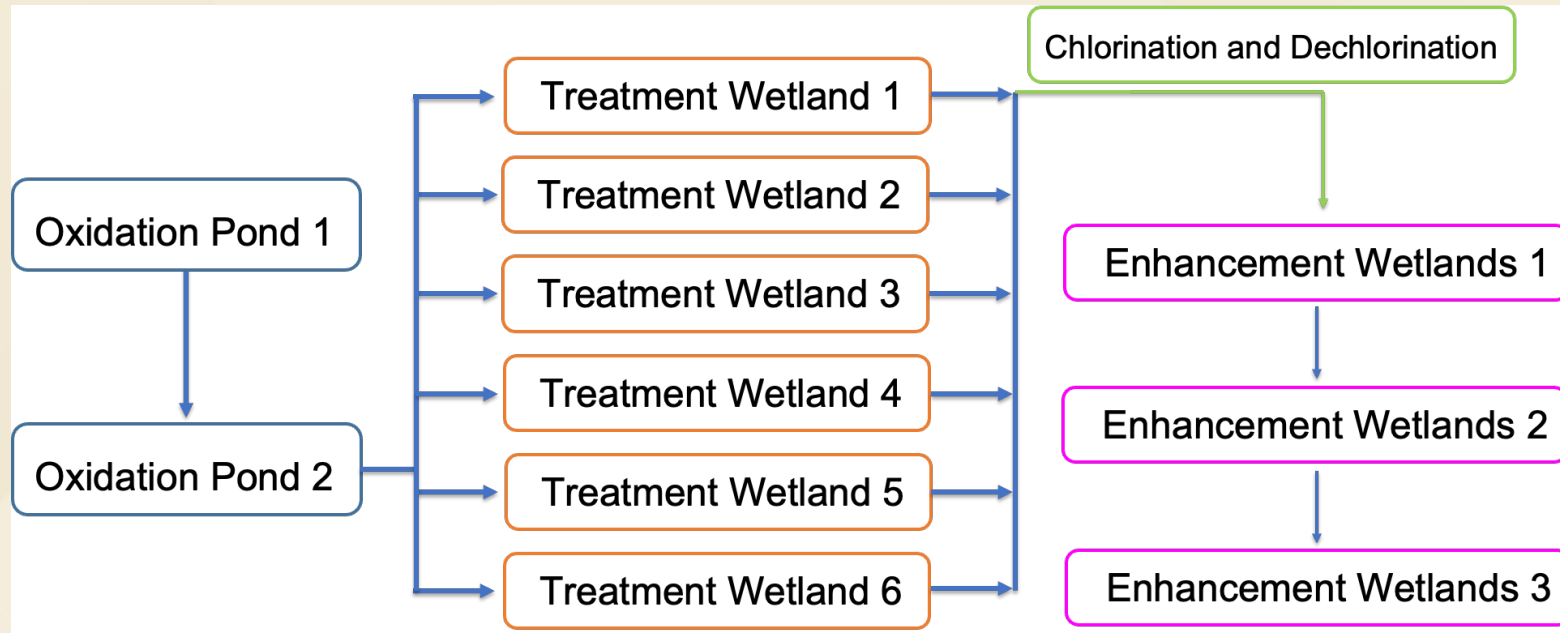


Figure 3: Wastewater flow path through the AWWTF

➤ Site Details

- Oxidation pond effluent (OX 4-2)
- Treatment wetland effluent (TW 8-2)
- Chlorination effluent/Enhancement wetland influent (EW 11 influent)
- Enhancement wetland effluents (EW 12, EW 14, and EW 15)

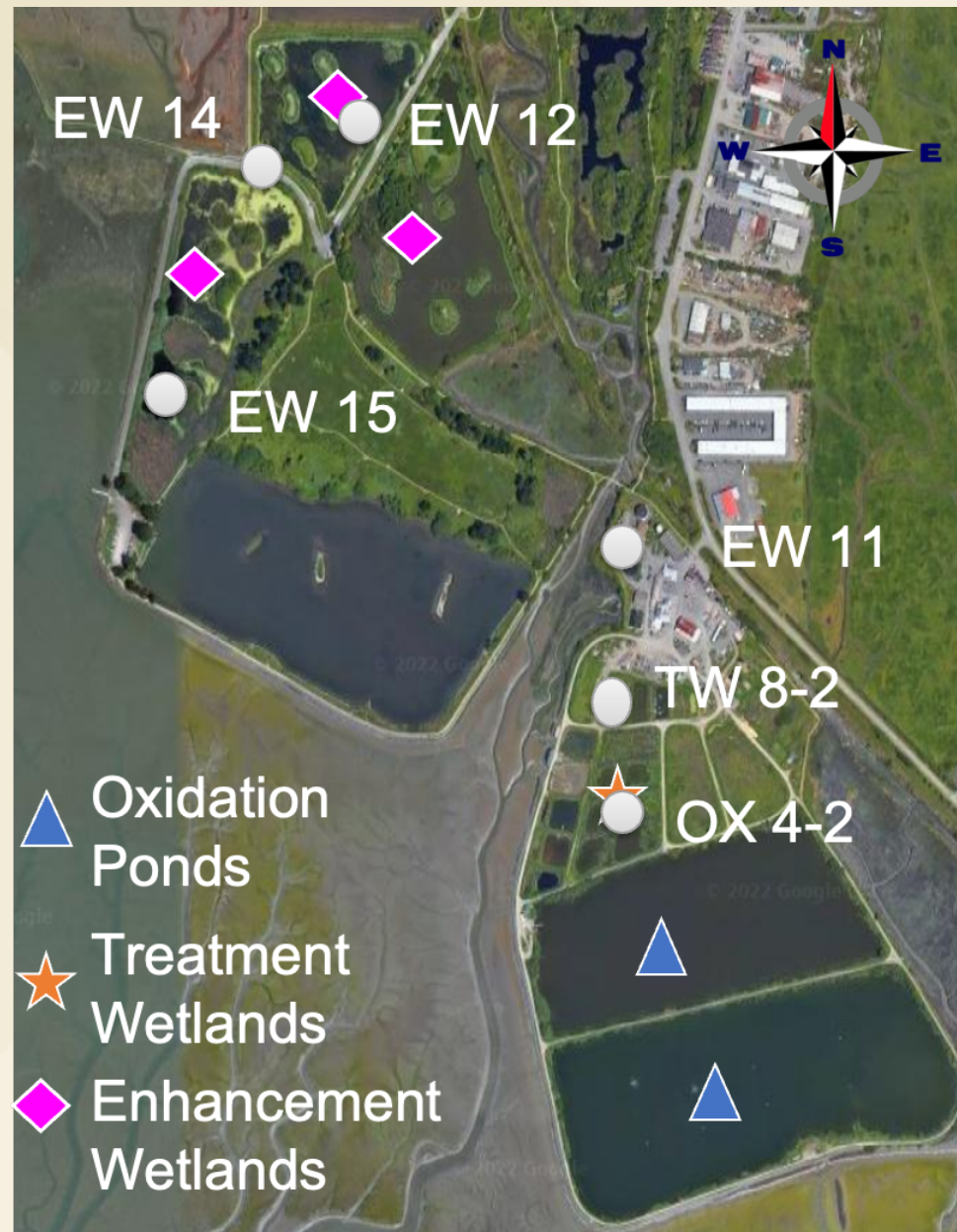


Figure 4: Satellite photo of AWWTF with sampling locations

> Some results

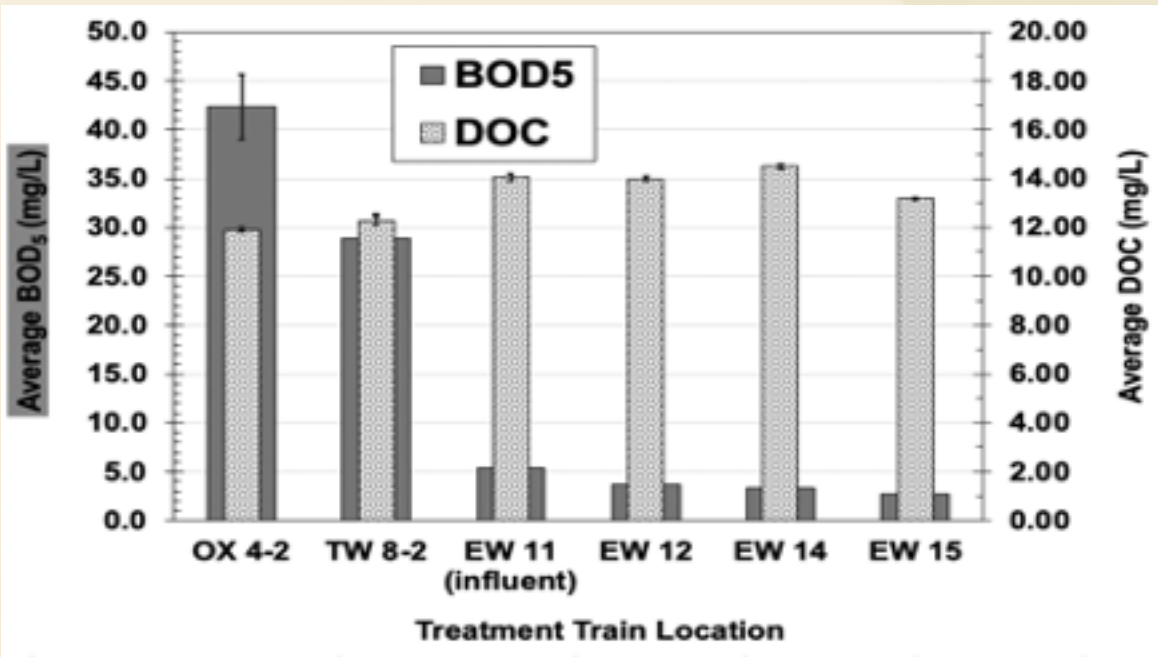


Figure 5: BOD₅ and DOC concentrations throughout the AWWTF

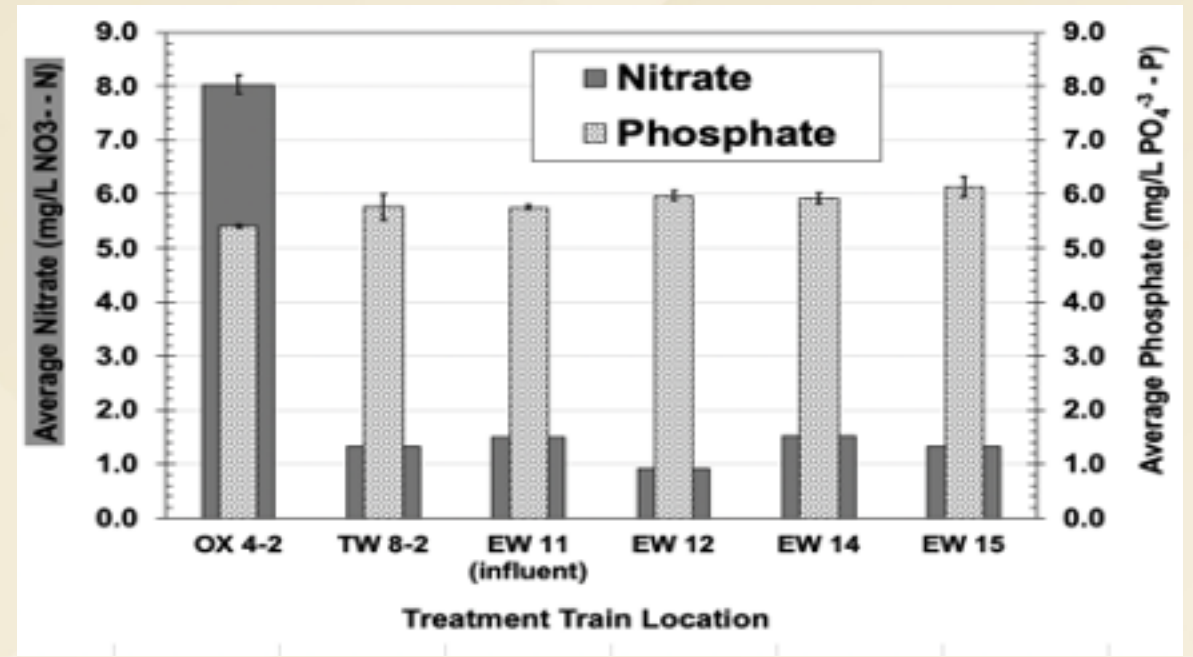


Figure 6: Dissolved nitrate and phosphate concentrations throughout the AWWTF

> Some Results

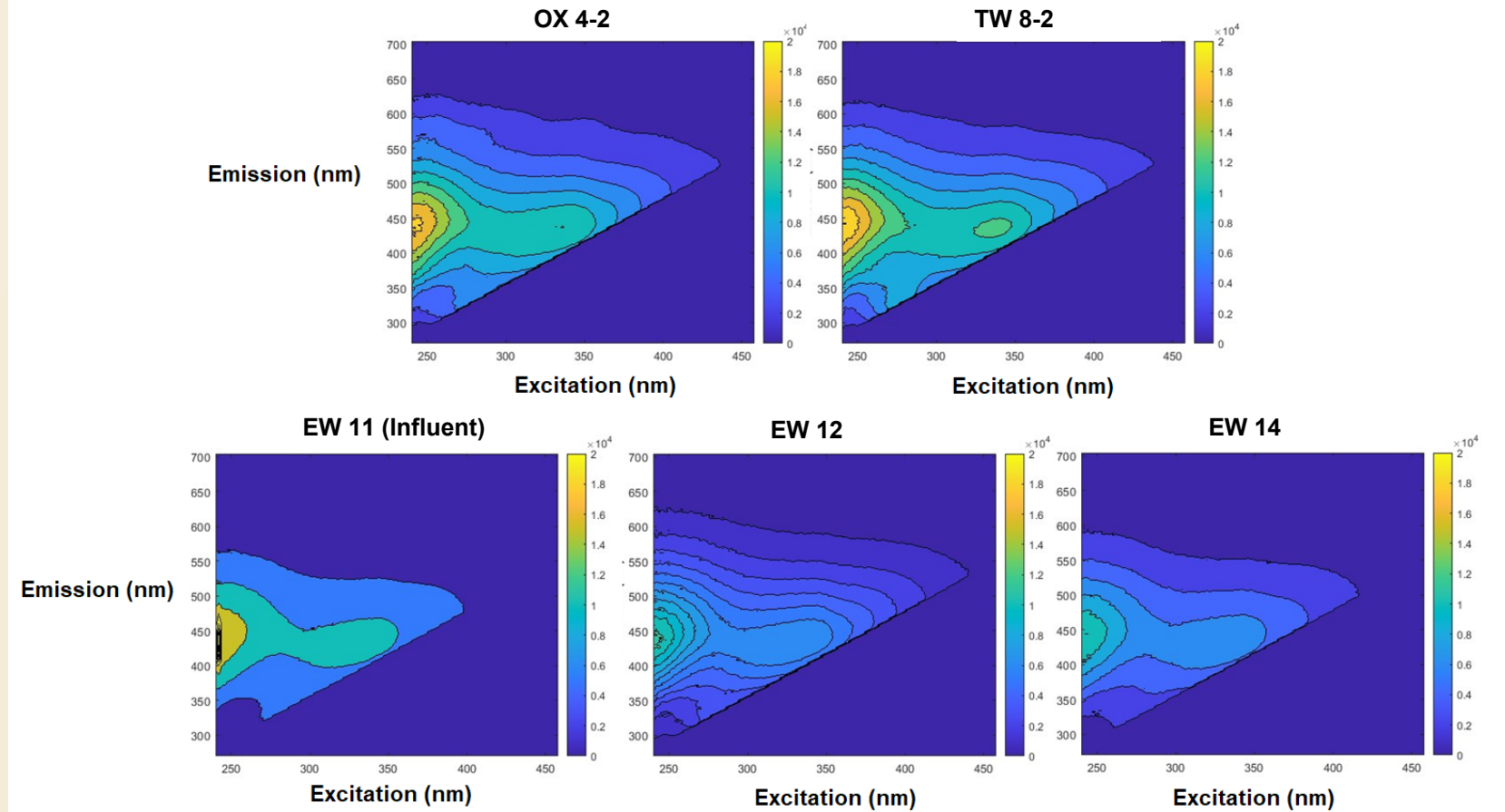


Figure 7: EEMS throughout the AWWTF. Z axis (color bar) is intensity in cps



> Some Results



- We saw an interesting effect of the treatment wetland on the hydroxyl radical formation
- Method details in Marty King's Poster

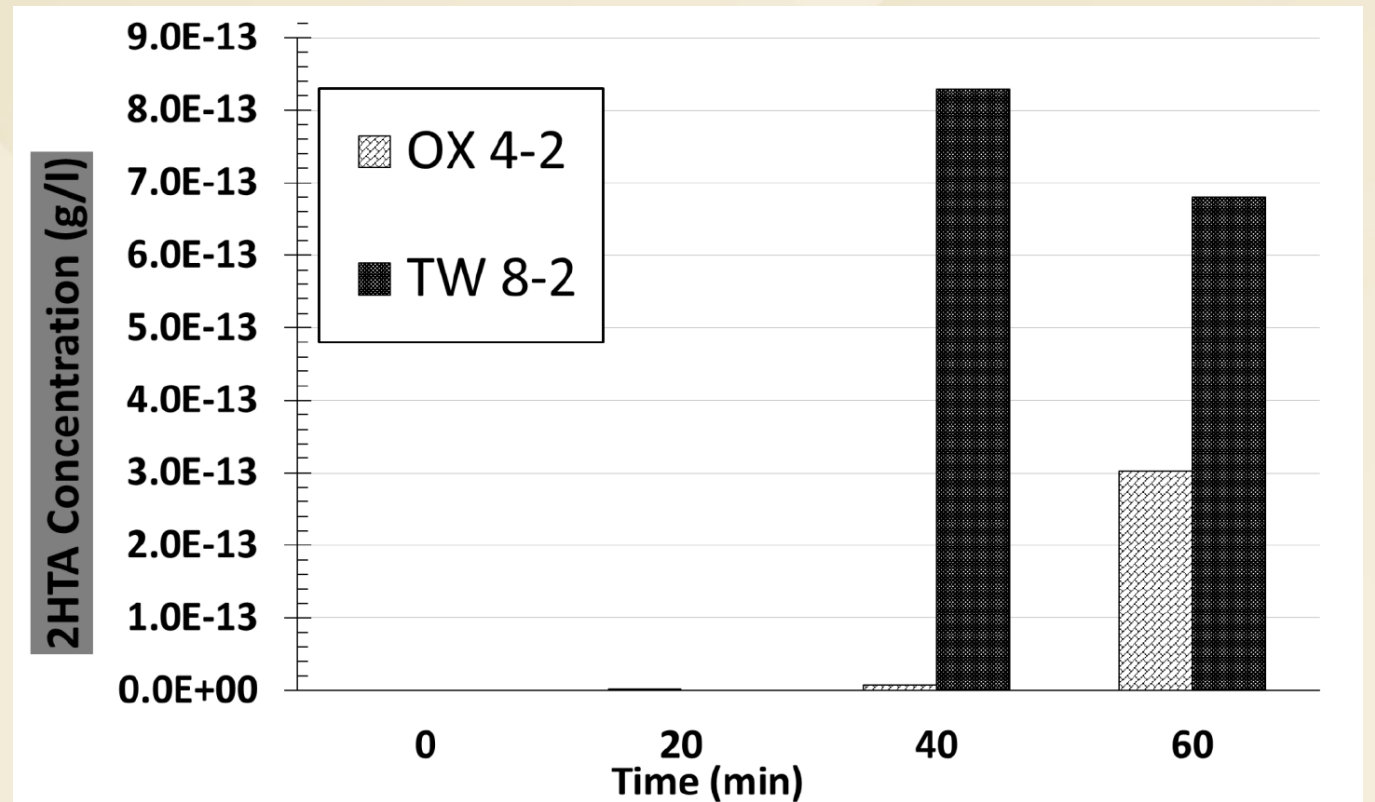


Figure 8: 2HTA concentrations of Oxidation Ponds (OX 4-2) and Treatment Wetlands (TW 8-2), taken at 20 min intervals during solar simulator experiment

› Organization of Research

Claire Ingvaldsen

- DOC Characterization and Modeling Using Fluorescence

Angel Cortez Ramirez

- Water quality analysis and process modeling

Marty King

- ROS formation experiments

Acknowledgements and Questions



H.

> Acknowledgements

- We recognize the land that is the focus of our research and the institutions that housed this project are located on the present and ancestral Homeland and unceded territory of the Wiyot Tribe. Tribes and Nations in Humboldt County include Hupa, Karuk, Mattole, Tolowa, Wailaki, Wiyot, Yurok. Donation to the Wiyot Tribe honor tax:
<http://www.honortax.org/index.html>
- Indian Natural Resources Science & Engineering Program
- NSF LSAMP (grant number HRD-1826490, NSF Native FEWS (grant number HRD 2120001)
- Yacob Startup Fund (Cal Poly Humboldt)
- AMRI is Arcata Marsh Research Institute, City of Arcata's Wastewater Treatment Plant,
<https://arcatamarsh.wordpress.com/>
- Dr. Matthew Hurst: Provided training and access to Shimadzu TOC Analyzer
- Dr. Jorge Monteiro: Provided training and access to the Edinburgh FS5 Spectrofluorometer
- Brandon Wilcox: Helped with the development of HPLC methodology and provided training
- Colin Wingfield: Provided Laboratory training in both Water Quality testing and safety
- Michelle Dostal: Logistical Assistance
- Schatz Energy Research Center Elizabeth Van Skike & Kayleigh Vincent-Welling: Provided training and assistance on Oriell® Sol3ATM CLASS AAA Solar Simulator



Indian Natural Resources
INRSEP
Science & Engineering Program



> References:

Chen, Wen, et al. "Fluorescence excitation– emission matrix regional integration to quantify spectra for dissolved organic matter." *Environmental science & technology* 37.24 (2003): 5701-5710.

Environmental Services Department, Andre, et al.. (2020). *Arcata Wastewater Treatment Facility Upgrades Project - PROPOSED MITIGATED NEGATIVE DECLARATION AND INITIAL STUDY*, City of Arcata, Arcata, CA.

Kadlec, R. H., and Wallace, S. (2009). *Treatment wetlands*. CRC Press, Boca Raton, FL.

Sardana, A., Cottrell, B., Soulsby, D., and Aziz, T. N. (2019). "Dissolved organic matter processing and photoreactivity in a wastewater treatment constructed wetland." *Science of The Total Environment*, 648, 923–934.

Silverman, Andrea I., David L. Sedlak, and Kara L. Nelson. "Simplified process to determine rate constants for sunlight-mediated removal of trace organic and microbial contaminants in unit process open-water treatment wetlands." *Environmental Engineering Science* 36.1 (2019): 43-59.

Timko, S. A. (2016). "Photochemistry of dissolved organic matter: Reactivity and application in constructed treatment wetlands." *eScholarship, University of California*, <<https://escholarship.org/uc/item/81j9d1ws>> (Jul. 23, 2022).

Zhang, D., Yan, S., and Song, W. (2014). "Photochemically induced formation of reactive oxygen species (ROS) from effluent organic matter." *Environmental Science & Technology*, 48(21), 12645–12653.

Zhou, Z., Guo, L., and Osburn, C. L. (2015). "Fluorescence Ems and PARAFAC techniques in the analysis of petroleum components in The water column." *Springer Protocols Handbooks*, 179–200.





- Dr. Margarita Otero-Diaz:
margarita.otero-diaz@humboldt.edu



- Dr. Tesfayohanes Yacob:
yacob@humboldt.edu

