Identification and Quantification of ·OH Formation Potential in Constructed Wetlands Treating Wastewater for the Removal of Pharmaceuticals

CSU Water Conference 2023 - Monterey Bay, Ca

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Introduction

There are no federal mandatory regulations for the removal of pharmaceuticals and personal care products (PPCPs) in wastewater. PPCPs are prevalent in wastewater and have adverse effects on the environment. Constructed wetlands allow for interaction between sunlight and dissolved organic carbon (DOC), causing photochemical reactions and formation of reactive oxygen species (ROS) which degrade PPCPs. As the wastewater undergoes wetlands treatment, DOC transforms through biological and photochemical processes. The type of DOC present affects the ROS formation potential. ***The objective of this project is to characterize DOC and determine the ·OH formation potential within the Arcata Wastewater Treatment Facility (AWWTF).***

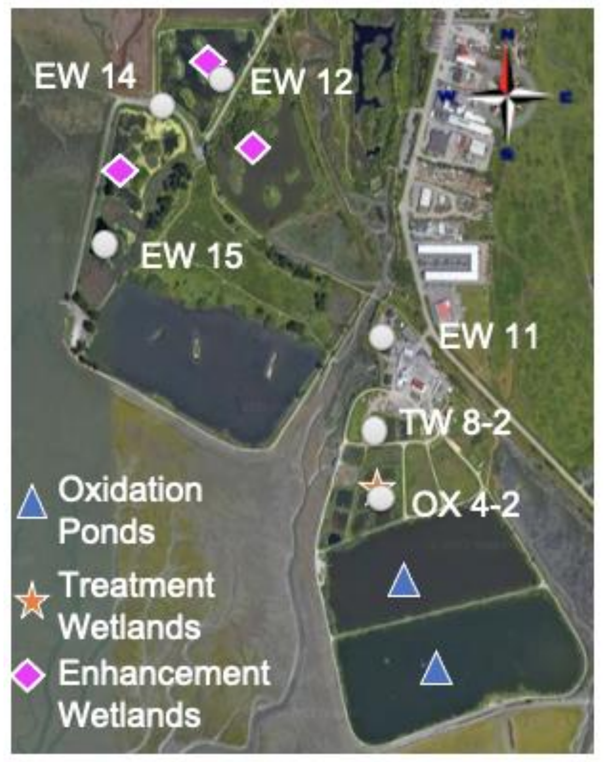

Figure 1. AWWTF sampling locations

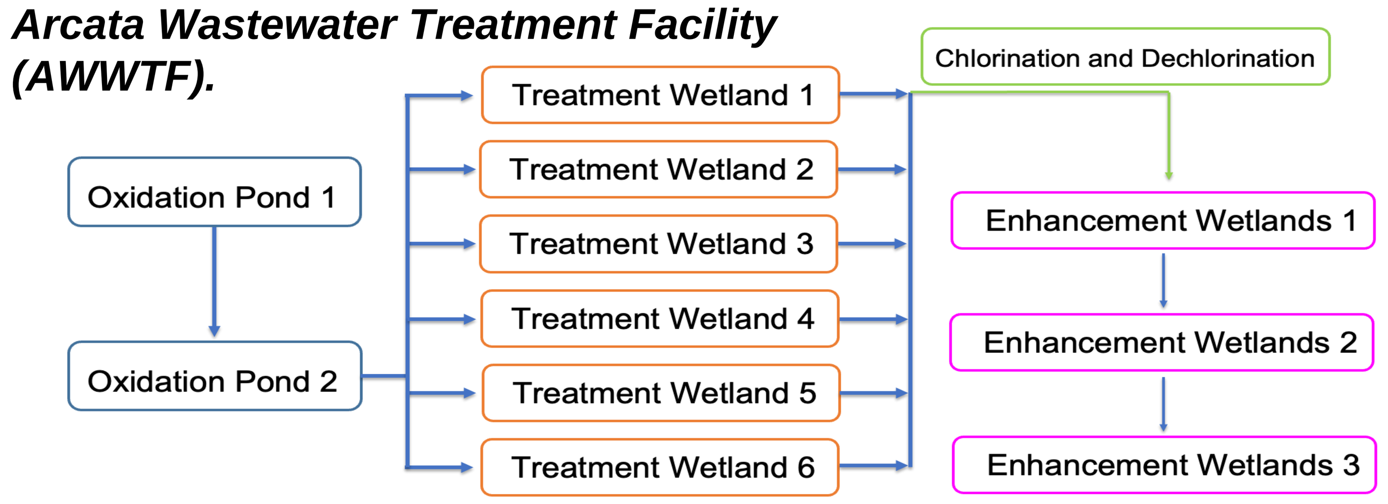

Figure 2. Wastewater flow path through the AWWTF

Water Quality Methods

- Samples analyzed within 24 hour of collection
- Samples were filtered with 1.2 µm glass fiber filters and the dissolved fraction was analyzed
- Typical water quality parameters analyzed:
  - DOC - Shimadzu TOC Analyzer
  - BOD_5 - Standards Methods 5210B
  - pH - Standards Methods 9040C

Emission & Excitation Matrix Spectra Methods

Samples were diluted to have a maximum absorbance of 0.1 AU using Agilent UV VIS Spectrophotometer. Samples were within a pH range of 6.76-7.45. Fluorescence of the samples were analyzed using an Edinburgh FS5 Spectrofluorometer with excitation wavelength from 240 nm to 458 nm using increments of 2 nm. Emissions spectra began 30 nm above each excitation wavelength and ended at 704 nm in increments of 1 nm. Fluorescence data analyzed using MATLAB to create an Excitation and Emission Matrix Spectra (EEMs). Rayleigh and Raman scattering were removed by comparing with deionized water's fluorescence (Zhou et al. 2015). Edinburgh FS5 Spectrofluorometer performed automatic spectral corrections for the instruments lamp and inner filter effects. Contour plots for samples were created from corrected data to characterize fluorescence peaks (Chen et al. 2003).

Dissolved Organic Carbon and Photolysis

Photodegradation of PPCPs occur through photolysis directly and indirectly. Indirect photolysis results when photosensitizers (e.g., DOCs and nitrates) react with photons to produce ROS like hydroxyl radical, •OH (Fig. 3). •OH formation potential is dependent on type of DOC present. Throughout AWWTF, DOC transforms due to natural treatment processes affecting •OH formation potential. DOC characteristics can be estimated and used to predict •OH formation potential and quantify removal of PPCPs through indirect photolysis. Fluorescence as means of characterizing wastewater's DOC is essential in understanding and creating an accurate indirect photolysis treatment model as DOCs are a complex mix of distinct chemical groups.

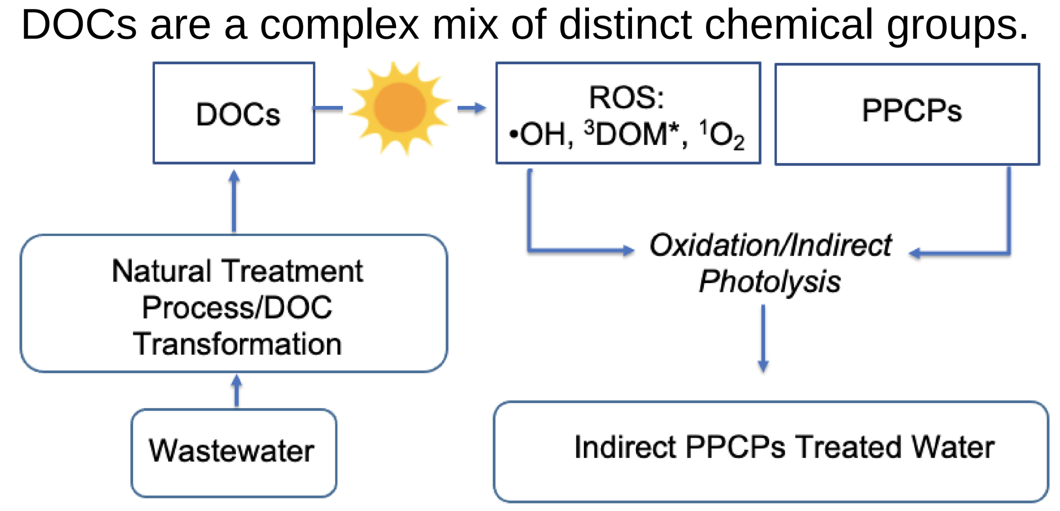

Figure 3. photochemical removal of PPCPs in natural treatment systems

·OH formation experimental Methods

To quantify production of •OH, WW samples spiked with Terephthalic Acid (TA) and irradiated at 1000 W/m² by Oriel® Sol3ATM CLASS AAA Solar Simulator (Fig. 4). TA is a probe compound that reacts with •OH making 2HTA (2-Hydroxy Terephthalic Acid).

$$TA + \cdot OH \rightarrow 2HTA$$

25 mL solutions (60 µmol/L TA) were well mixed with stir plate and sampled at 20-minute intervals over one-hour trials. Samples were analyzed using High-Performance Liquid Chromatograph (Agilent HPLC 1100) to measure product concentration of 2HTA to quantify •OH produced by interactions of DOC and light (Fig. 4).

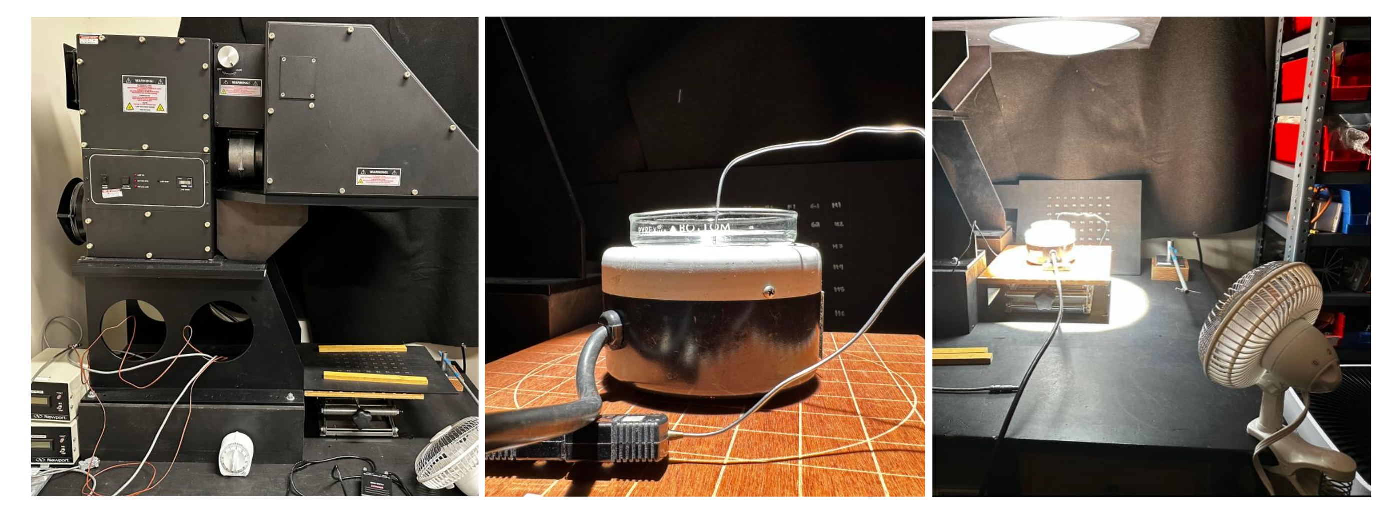

Figure 4. Solar simulator experimental setup with fan for temperature stability

Results and Discussion

Water quality results show BOD_5 decreased throughout the AWWTF (Fig. 5). The largest decrease was observed between TW 8-2 and EW 11, directly after chlorination. DOC increased after TW 8-2 and then fluctuated by less than 1 mg/L. Fluorescence analysis show shifting fluorescence signatures throughout the AWWTF indicating a transformation of DOC throughout the treatment process (Fig. 6). Oxidation pond effluent (OX 4-2) had a fulvic acid-like peak and a small humic acid-like region. Treatment wetland effluent (TW 8-2) had increase in fulvic acid-like peak area as well as humic acid-like peak area *and* photon intensity.

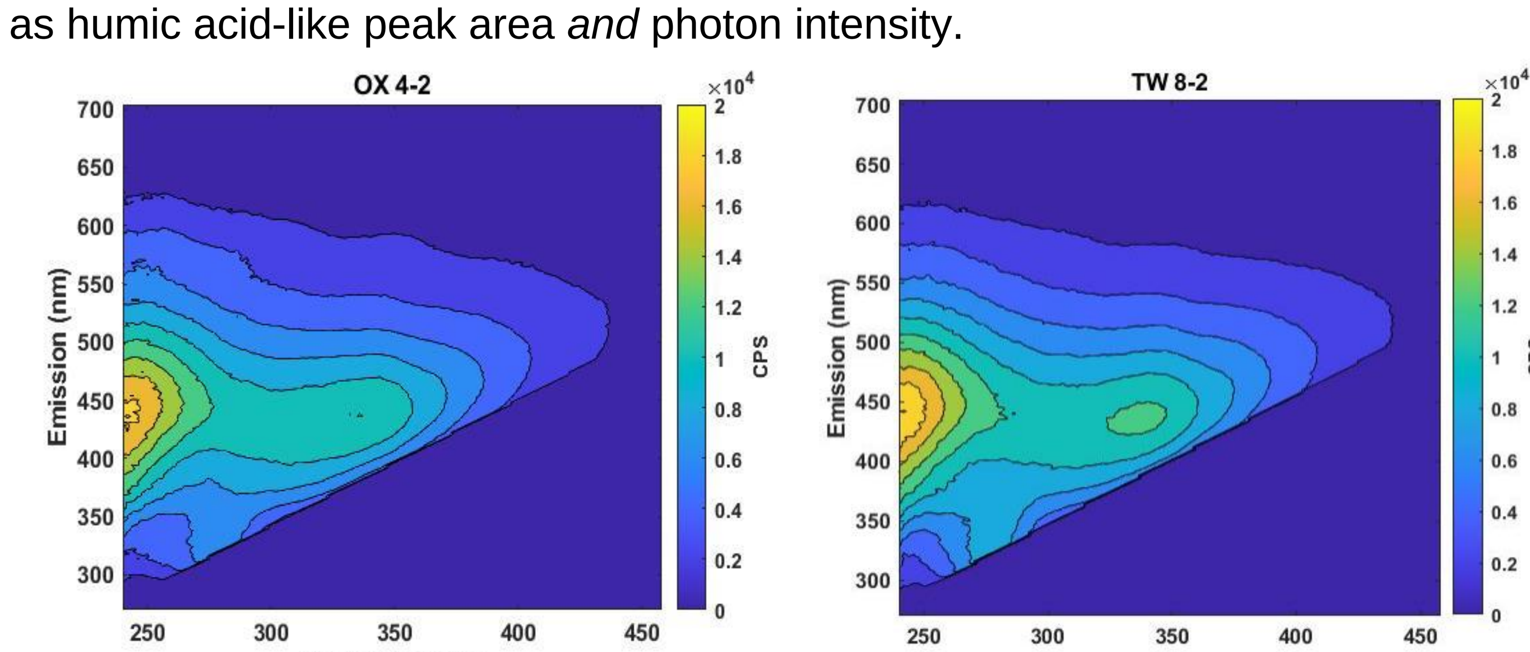

Figure 6. Excitation and emission matrix spectra (EEMs) for Oxidation Ponds (OX 4-2) and Treatment Wetlands (TW 8-2)

The first solar simulator run resulted in an increased 2HTA production at 40th minute in the treatment wetland effluent (TW 8-2) (compared to the 0- and 20-minute samples) (Fig. 7). This preliminary 2HTA data indicates that the TW effluent had more •OH formation rates compared to the Ox pond effluent. Temperature stability methods were developed to minimize sample temperatures fluctuating and possibly affecting reaction rates. A small desktop fan, placed 46 cm away and blowing at max setting at the petri dish was able to keep sample temperature change within a standard deviation of 0.2 ºC over the course of 4 one-hour trial runs.

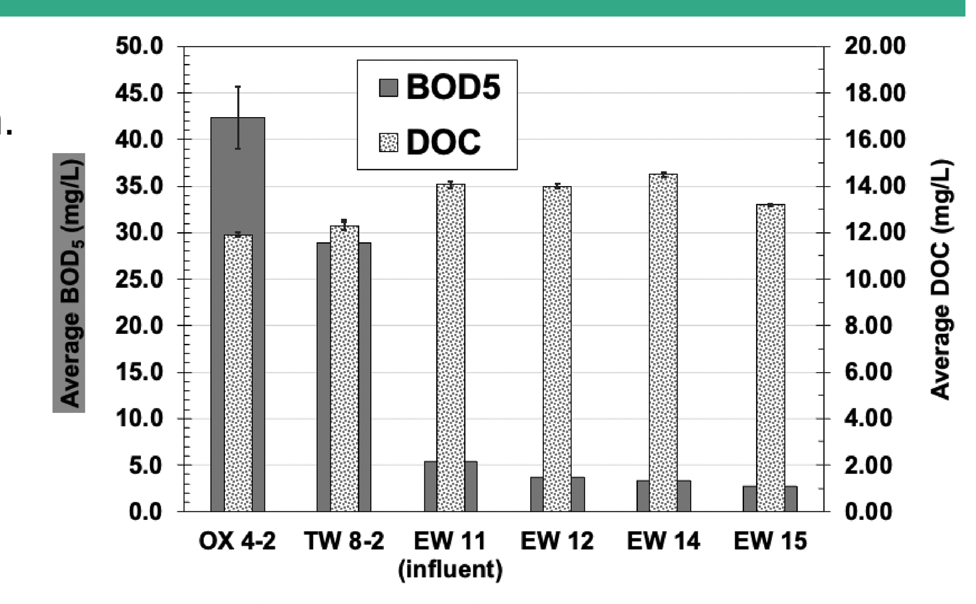

Figure 5. BOD_5 and DOC concentrations throughout AWWTF

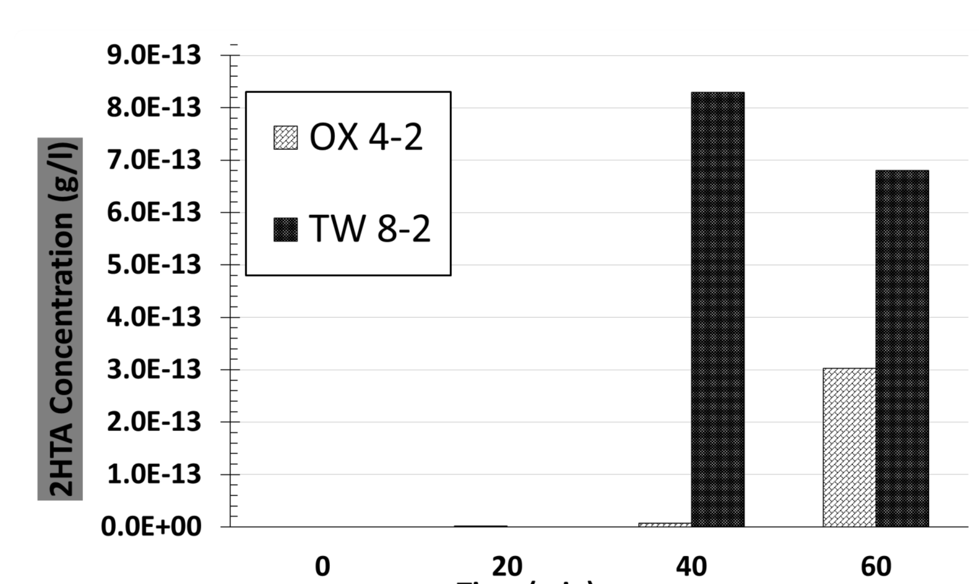

Figure 7. 2HTA concentrations of Oxidation Ponds (OX 4-2) and Treatment Wetlands (TW 8-2), taken at 20 min intervals during solar simulator experiment

Conclusions

Throughout the AWWTF treatment process, the wastewater's BOD_5 has an overall reduction; however, there is minimal change in the DOC concentration. Results indicate increase in area and intensity of humic like and fulvic acid like peaks in TW-8 compared to OX-4. Humic acid-like compounds have been shown to reduce •OH formation (Sardana et al. 2019). Fulvic acid-like compounds have been shown to enhance the production of •OH. 2HTA concentrations indicate that fulvic benefit of •OH formation potential outweighs humic inhibition in the treatment wetland. Fluorescence results helped to relate composition of DOC to the ROS formation potential of constructed wetland wastewater treatment at AWWTF.

Future Work

- Investigate the characterization of DOC throughout each season
- •OH formation potential experiments on more sample locations within treatment train
- Finalize PARAFAC model to quantify EEMs results and correlate DOC to ROS formation

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
- NSF LSAMP (grant number HRD-1826490, NSF Native FEWS (grant number HRD 2120001), NSF Geoscience Alliance (grant number EAR 2039341).
- 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

References

Cal Poly Humboldt.