Electronic Supporting Information:

Photodegradation of pharmaceutical compounds in partially nitritated wastewater during UV irradiation

*Priya I. Hora, Paige J. Novak, and William A. Arnold**

Department of Civil, Environmental, and Geo- Engineering, University of Minnesota – Twin Cities, 500 Pillsbury Drive SE, Minneapolis, Minnesota 55455, United States

*****Corresponding author. Phone: 612-625-8582; Fax: 612-626-7750; email: arnol032@umn.edu

8 pages, 6 tables, and 1 figure

Table S1: Target Pharmaceuticals Used in the Study

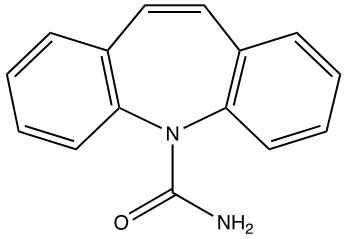
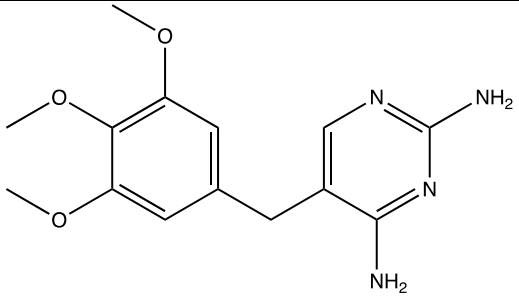
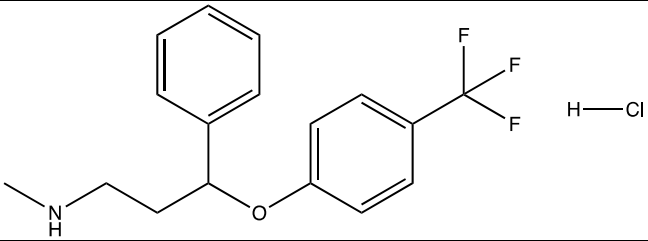
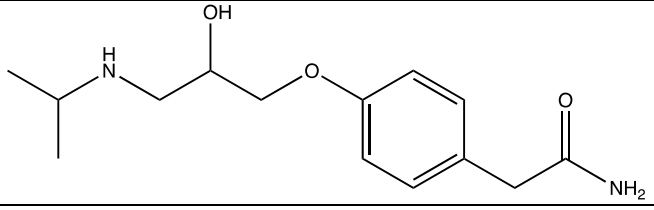
Compound	Therapeutic Class	Molecular Structure
Carbamazepine	Anticonvulsant	
Trimethoprim	Antibiotic	
Fluoxetine Hydrochloride	Antidepressant	
Atenolol	beta-blocker	

Table S2: Water quality parameters of the effluent used in photochemical study

Water Quality Parameter	Method	Effluent[a]
Nitrite (NO_2^- mg-N/L)	Metrohm ion chromatograph	0.0146
Nitrate (NO_3^- mg-N/L)	Metrohm ion chromatograph	9.311
Ammonia (NH_3 mg-N/L)	Hach colorimetric test kit	7
Dissolved organic carbon (DOC mg-C/L)	Shimadzu TOC-L analyzer	4.151
Dissolved inorganic carbon (DIC mg-C/L)	Shimadzu TOC-L analyzer	46.27
pH	Thermo Orion pH meter	7.5

[a]Before experiments, amended with $NaNO_2$ and $(NH_4)_2SO_4$ to achieve ~20 mg-N/L each of NO_2^- and NH_4^+.

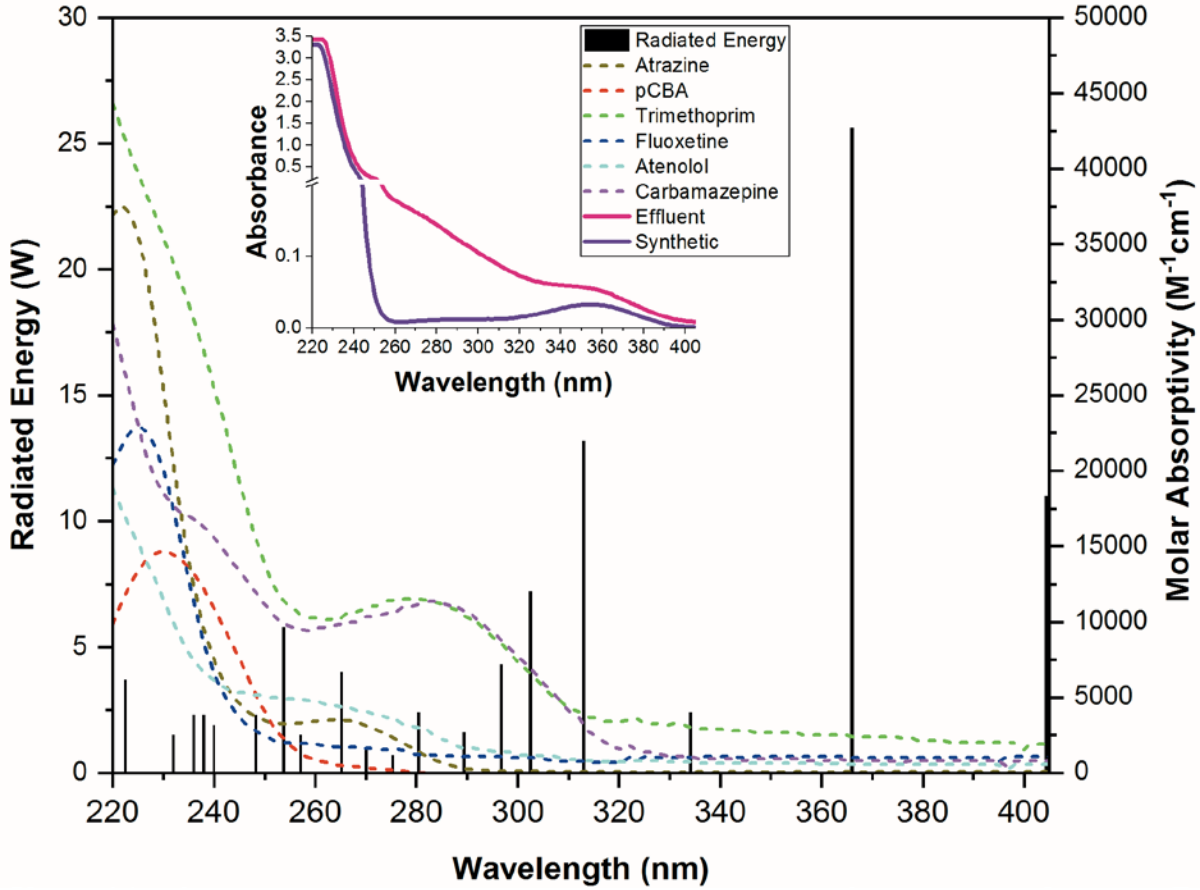


Figure S1: Molar absorptivity of pharmaceuticals, probe, and actinometer on a per wavelength basis (right y-axis); radiated energy in watts of mercury vapor lamp per lamp centerlines (left y-axis); absorption spectra of matrices (inset).

Analytical Methods:

Table S3: RP-HPLC Methods for Pharmaceuticals, Probe, and Actinometer

Compound	Column[a]	Mobile Phase (v:v)	Injection V (µL)	Flow Rate (mL/min)	Detector λ (nm)
para-Cholorobenzoic acid	Eclipse XDB-C18 (4.6x150 mm, 3.5 µm)	45% Acetonitrile 55% Phosphate Buffer (10mM; pH3; 10% ACN)	40	1.0	238
Atenolol	Eclipse XDB-C18 (4.6x150 mm, 5.0 µm)	5% Acetonitrile 95% 0.1% (v/v) phosphoric acid	90	1.0	224
Carbamazepine	Eclipse XDB-C18 (4.6x150 mm, 3.5 µm)	65% Acetonitrile 35% Phosphate Buffer (10mM; pH3; 10% ACN)	50	1.0	290
Trimethoprim	Eclipse XDB-C18 (4.6x150 mm, 3.5 µm)	90% Acetonitrile 10% Phosphate Buffer (10mM; pH3; 10% ACN)	100	1.0	274
Fluoxetine	Eclipse XDB-C18 (4.6x150 mm, 3.5 µm)	65% Acetonitrile 35% Phosphate Buffer (10mM; pH3; 10% ACN)	40	1.0	230
Atrazine	Supelco Discovery RP-Amide C16 (15 cmx4.6 mm, 5 µm)	50% Acetonitrile 50% 0.1% (v/v) phosphoric acid	35	1.0	220

[a]Columns were at room temperature (~20 °C) except for atenolol (maintained at 30 °C)

Total N-Nitrosamine (TONO) Analysis

TONO analysis followed the method of Kulshrestha et al.[1] All samples were diluted to 200 mL (4-fold dilution) and quenched with 2 g/L of sulfamic acid overnight (to prevent nitrite interference) prior to solid phase extraction (SPE). Tandem SPE (activated carbon and Oasis HLB) was performed and the extracts combined and concentrated on a rotary evaporator and via N_2 blow down to concentrate the final samples to 1 mL in methanol. The limit of quantification (LOQ) for the original samples was 10 ng/L as nitrosodimethylamine (NDMA). A lab blank control and positive control were also performed for quality assurance. The final concentration is an average of two measurements and the standard deviations were calculated.

Table S4a: Pseudo-first-order reaction rate constants for direct photolysis controls (k_{dir}) and experiments with synthetic matrix (k_{sw}) and amended effluent (k_{eff}) for $\lambda \geq 280$ nm [a]

Compound	k_{dir} (min^{-1})	k_{sw} (min^{-1})	k_{eff} (min^{-1})
Carbamazepine	$5.31\pm0.39\times10^{-4}$	$5.28\pm0.26\times10^{-3}$	$5.34\pm0.50\times10^{-3}$
Trimethoprim	$8.38\pm2.34\times10^{-4}$	$5.62\pm0.13\times10^{-3}$	$5.17\pm0.26\times10^{-3}$
Fluoxetine	$1.43\pm0.10\times10^{-3}$	$5.84\pm0.47\times10^{-3}$	$7.07\pm0.29\times10^{-3}$
Atenolol	$6.84\pm0.66\times10^{-4}$	$5.23\pm0.68\times10^{-3}$	$7.50\pm0.31\times10^{-3}$
pCBA	$2.01\pm0.18\times10^{-4}$	$2.75\pm0.08\times10^{-3}$	$2.81\pm0.09\times10^{-3}$

[a]Errors are 95% confidence intervals.

Table S4b: Pseudo-first-order reaction rate constants for direct photolysis controls (k_{dir}) and experiments with synthetic matrix (k_{sw}) and amended effluent (k_{eff}) $\lambda \geq 220$ nm [a]

Compound	k_{dir} (min^{-1})	k_{sw} (min^{-1})	k_{eff} (min^{-1})
Carbamazepine	$1.08\pm0.02\times10^{-2}$	$1.40\pm0.04\times10^{-2}$	$1.37\pm0.01\times10^{-2}$
Trimethoprim	$3.78\pm0.22\times10^{-2}$	$1.23\pm0.08\times10^{-2}$	$1.20\pm0.10\times10^{-2}$
Fluoxetine	N/A	N/A	N/A
Atenolol	$1.39\pm0.21\times10^{-2}$	$1.10\pm0.23\times10^{-2}$	$1.93\pm0.03\times10^{-2}$
pCBA	$4.72\pm0.14\times10^{-2}$	$1.64\pm0.05\times10^{-2}$	$1.48\pm0.03\times10^{-2}$

[a]Errors are 95% confidence intervals.

Screening Factors:

Screening factors (S_{i_j}) were calculated following McCabe and Arnold and Karpuzcu, et al.[2,3] as the ratio of light absorption rates (R_a) in pharmaceutical or probe (species *i*) solutions with and without screening species (*j*) present (i.e., comparing the rate of light absorption of compound in buffer versus effluent) over a range of wavelengths λ. The screening factors help to attribute differences in observed photolysis rates to: 1) physical screening due to absorption of light otherwise available for direct photolysis by the matrix; or, 2) other reduction or enhancement reactions.

$$R_{a,i} = \sum_{\lambda} \frac{W_{\lambda}(1-10^{-a_{i\lambda}z})}{z} \quad (1)$$

$$R_{a,i\_j} = \sum_{\lambda} \frac{W_{\lambda}(1-10^{-(a_{i_\lambda}+a_{j_\lambda})z})}{z} \frac{a_{i_\lambda}}{a_{i_\lambda}+a_{j_\lambda}} \quad (2)$$

$$S_{i\_j} = \frac{R_{a,i\_j}}{R_{a,i}} \quad (3)$$

Where W_{λ} $(mEi\ cm^{-2}s^{-1})$ is the spectral photon fluence rate derived from actinometry, $z = 1.12\ cm$ [4] is the effective light path length in the 13x100 mm quartz test tubes accounting for reflection and refraction, $a_{\lambda}(cm^{-1})$ is the light attenuation coefficient (measured absorbance in a quartz cuvette with path length 1 cm)). Values for S_{i_j} are between 0 and 1, with 0 indicating no light is absorbed by species *i* (i.e., all light absorbed by screening species *j*), and 1 indicating no light is screened by species *j*. Tabulated screening factors are presented below in Table S5.

Pseudo-first-order rate constants for direct photolysis in buffer in the λ≥220 nm experiments were corrected by multiplying by the respective S_{i_j} as illustrated in equation 4.

$$k'_{direct,corrected} = k'_{direct} \times S_{i\_j} \quad (4)$$

Table S5: Light Screening Correction Factors

Compound	$S_{i,j,nit}$	$S_{i,j,eff}$
Carbamazepine	0.735	0.625
Trimethoprim	0.665	0.563
Fluoxetine	0.480	0.405
Atenolol	0.628	0.525
pCBA	0.464	0.376

References

1 P. Kulshrestha, K. C. McKinstry, B. O. Fernandez, M. Feelisch and W. A. Mitch, Application of an optimized total N -nitrosamine (TONO) assay to pools: Placing N -nitrosodimethylamine (NDMA) determinations into perspective, *Environ. Sci. Technol.*, 2010, **44**, 3369–3375.

2 M. E. Karpuzcu, A. J. McCabe and W. A. Arnold, Phototransformation of pesticides in prairie potholes: effect of dissolved organic matter in triplet-induced oxidation, *Environ. Sci. Process. Impacts*, 2016, **18**, 237–245.

3 A. J. McCabe and W. A. Arnold, Reactivity of Triplet Excited States of Dissolved Natural Organic Matter in Stormflow from Mixed-Use Watersheds, *Environ. Sci. Technol.*, 2017, **51**, 9718–9728.

4 A. Leifer, *The Kinetics of Environmental Aquatic Photochemistry: Theory and Practice*, American Chemical Society, Washington, DC, 1988.