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UV Degradation Kinetics and Modeling of Pharmaceutical Compounds in Laboratory Grade and Surface Water via Direct and Indirect Photolysis at 254 nm

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Direct and indirect photolysis of pharmaceutically active compounds (PhACs) was investigated in laboratory-grade water (LGW) and a local surface water using a low-pressure ultraviolet batch reactor. The PhACs selected in this study belong to different therapeutic classes and are known to occur in environmental samples. Fundamental photolysis and advanced oxidation process parameters obtained in LGW (such as the decadic molar absorption coefficient, quantum yield, and degradation rate constants) are reported and discussed. These parameters, together with the incident photon irradiance, solution depth, and solution absorbance were used to develop UV and UV/H_2O_2 photolysis models that were compared with experimental results obtained in the surface water. The model predicted the experimental UV photolysis removals well but underestimated the UV/H_2O_2 photolysis results. These models were used to discuss the effects of optical path length and H_2O_2 concentration on the UV-based rate constant predictions.

Introduction

The occurrence of different classes of pharmaceutically active compounds (PhACs) have been reported by several authors in sediments as well as sewage, surface water, groundwater, and drinking water (*1*−*3*). Of special concern are those PhACs that have been found to resist water and wastewater treatment and have, as a consequence, been detected in drinking water, and these include analgesics, antibiotics, antiepileptics, blood lipid regulators, and contrast media agents.

Ultraviolet (UV) disinfection of wastewater and drinking water is generally accomplished using low-pressure (LP) mercury lamps that emit, primarily, monochromatic light at 254 nm (*4*). Due to its disinfection effectiveness against a wide range of waterborne pathogens, UV is widely used for drinking water disinfection in Europe and currently gaining importance in the U.S. (*4*−*6*). As a disinfection barrier UV does not produce any of the regulated disinfection byproducts (DBPs) and by meeting part of the overall disinfectant demand, it will reduce the chlorine dose needed for final disinfection which, in turn, will decrease the concentrations of halogenated DBPs formed (*7*).

In addition to its disinfection effectiveness, UV can also degrade organic compounds by direct photolysis of photolabile compounds as a consequence of light absorption, or by indirect photolysis using hydrogen peroxide (H_2O_2), an advanced oxidation process (AOP), which will lead to the formation of highly reactive, unselective, and short-lived hydroxyl radicals ($^{\bullet}OH$). In surface water (SW), indirect photolysis may also occur without addition of UV/H_2O_2, by the production of oxidants such as $^{\bullet}OH$ during UV photolysis of SW components such as dissolved organic matter (DOM) (*8*).

Few degradation studies of PhACs by LP/UV light and AOP treatment exist. Vogna et al. (*9*) found that the negligible LP/UV photolysis of the anti-epileptic drug carbamazepine was enhanced when using the UV/H_2O_2 AOP. Huber et al. (*10*) used competition kinetics to determine the second-order rate constants for the reaction of several PhACs including carbamazepine with $^{\bullet}OH$ and these varied from 3.3 to 9.8 × 10^9 $M^{-1}s^{-1}$. Competition kinetics was also used by Packer et al. (*11*) to find the $^{\bullet}OH$ rate constants of naproxen, clofibric acid, and ibuprofen.

PhACs that belong to different therapeutic classes were selected in this study (Supporting Information (SI) Table 1) due to their high usage in the U.S. and Europe and their reported occurrence in the aquatic environment (*1*−*3*). These were naproxen and ketoprofen (analgesics), carbamazepine (antiepileptic), clofibric acid (the active metabolite of the lipid regulator clofibrate), ciprofloxacin (antibiotic), and iohexol (X-ray contrast medium).

The goal of this study was to examine the potential effectiveness of UV and UV/AOP as drinking water remediation technologies for PhACs most commonly found in surface waters some of which have distinctly different chemical structures. The specific objectives were to determine fundamental photolysis parameters in LGW for all targeted PhACs and, for a subset (naproxen, carbamazepine, clofibric acid, and iohexol), evaluate their removal from SW during UV and UV/H_2O_2 photolysis experiments. Photolysis models have been tested mainly in synthetic water matrices which facilitates the predictions since the exact composition of the water matrix is known (*8*, *12*, *13*). To our knowledge, no studies have been conducted to test the validity of the UV photolysis model for explaining experimental photodegradation in SW, and only one study tested the accuracy of the model for LP/UV/H_2O_2 photolysis predictions for bisphenol A in SW (*12*).

Materials and Methods

Reagents. All PhACs except iohexol were purchased as solids of the highest grade commercially available (Sigma-Aldrich, St. Louis, MO). Iohexol was obtained from the Department of Radiology at the University of North Carolina (UNC) Hospital (Chapel Hill, NC). Stock solutions of the PhACs were prepared in LGW and diluted as required. LGW was produced by a Park International water deionization system with activated carbon filtration supplied by Pure Water Solutions (Hillsborough, NC). Bovine liver catalase was obtained from Sigma-Aldrich (one unit decomposed 1 μmole of H_2O_2). All the other reagents used were analytical grade. The SW, a blend of water from Lake Michie and the Little River Reservoir (with temperature 21 °C, pH 7, 2.5 NTU, 25 mg$CaCO_3$/L total

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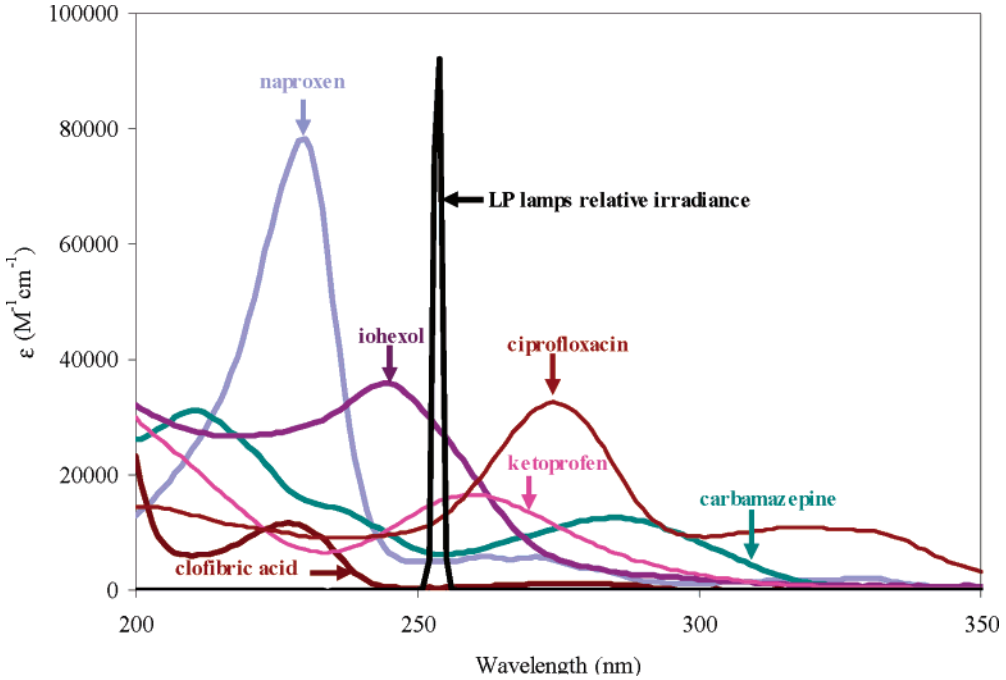

FIGURE 1. Decadic molar absorption coefficient (ϵ) of the selected PhACs (*y*-axis) overlaid with the relative irradiance of LP/UV lamps.

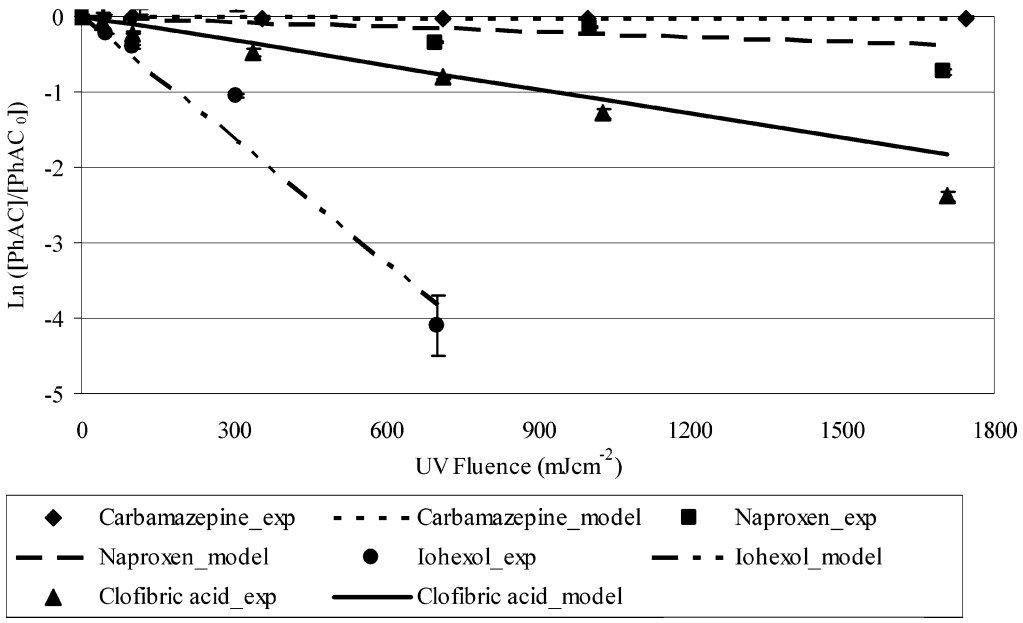

FIGURE 2. LP experimental (exp) and model UV photolysis results obtained for carbamazepine, clofibric acid, iohexol, and naproxen in SW.

alkalinity, and 4.2 mgC/L dissolved organic carbon), was collected at the influent to the Brown Water Treatment Plant (Durham, NC), transported immediately to the UNC laboratory in a cooler at 4 °C, and upon arrival filtered using Waters nylon filters (0.45 μm, 47 mm; Waters Corporation, Milford, MA).

Analytical Methods. Reverse-phase high performance liquid chromatography (HPLC) with photodiode array (PDA) detection was used for the analysis of *para*-chlorobenzoic acid (pCBA) and all PhACs except iohexol and ciprofloxacin. Liquid chromatography−tandem mass spectrometry (LC/MS−MS) was used for iohexol and ciprofloxacin analysis in positive ion mode using a 1200 L triple stage quadrupole mass spectrometer with an electrospray ionization interface (Varian, Walnut Creek, CA).

The absorbance of the LGW and SW samples spiked with each of the selected PhACs was measured (between 200 and 400 nm) using a Cary 100 bio-spectrophotometer (Varian, Houston, TX).

The H_2O_2 residual was determined using a method described by Klassen et al. (*14*). Additional details on the analytical methods followed are provided as Supporting Information.

UV Photolysis Experiments. The photodegradation experiments were conducted using a bench-scale UV quasi-collimated beam setup housed with four 15 W LP germicidal lamps (ozone-free, General Electric no. G15T8). The PhACs-spiked water samples were placed in an open Petri dish under a manual shutter beneath the UV sources (SI Figure 1) (*13*).

Irradiance measurements were obtained by placing a calibrated radiometer (IL1700 SEL240/W, International Light, Newburyport, MA) at the height of the water level in the Petri dish to obtain the incident irradiance. The UV fluence was calculated as the incident irradiance which varied between

TABLE 1. LP/UV and LP/UV/H_2O_2 Photolysis Rate Constants Obtained in Laboratory Grade Water (LGW) and Surface Water (SW)[a], (a) Fluence-based and (b) Time-Based

(a) Fluence-Based Rate Constants ($\times 10^{-3}$ cm^2mJ^{-1})

	LGW		SW	
	0 mg/L H_2O_2	10 mg/L H_2O_2	0 mg/L H_2O_2	10 mg/L H_2O_2
carbamazepine	0.02 (0.01) $R^2 = 0.226$	10.9 (0.36) $R^2 = 0.993$	0.03 (0.02) $R^2 = 0.201$	2.70 (0.06) $R^2 = 0.994$
naproxen	0.20 (0.02) $R^2 = 0.918$	11.9 (0.24) $R^2 = 0.998$	0.50 (0.06) $R^2 = 0.826$	3.00 (0.05) $R^2 = 0.998$
clofibric acid	1.10 (0.04) $R^2 = 0.983$	13.3 (0.58) $R^2 = 0.989$	1.30 (0.05) $R^2 = 0.985$	1.70 (0.25) $R^2 = 0.881$
iohexol	5.50 (0.14) $R^2 = 0.995$	7.70 (0.35) $R^2 = 0.984$	5.80 (0.46) $R^2 = 0.953$	6.40 (0.38) $R^2 = 0.972$
ciprofloxacin	0.60 (0.16) $R^2 = 0.591$	nd	nd	nd
ketoprofen	17.8 (4.93) $R^2 = 0.766$	nd	nd	nd

(b) Time-Based Rate Constants (min^{-1})

	LGW		SW	
	0 mg/L H_2O_2	10 mg/L H_2O_2	0 mg/L H_2O_2	10 mg/L H_2O_2
carbamazepine	1.30×10^{-3} (7.20×10^{-4}) $R^2 = 0.226$	1.34 (4.44×10^{-2}) $R^2 = 0.993$	2.20×10^{-3} (1.27×10^{-3}) $R^2 = 0.201$ [1.40×10^{-3}]	0.22 (5.27×10^{-3}) $R^2 = 0.994$ [0.12]
naproxen	1.65×10^{-2} (1.43×10^{-3}) $R^2 = 0.918$	1.24 (2.54×10^{-2}) $R^2 = 0.998$	3.39×10^{-2} (4.48×10^{-3}) $R^2 = 0.826$ [1.68×10^{-2}]	0.24 (3.74×10^{-3}) $R^2 = 0.998$ [0.19]
clofibric acid	0.07 (2.61×10^{-3}) $R^2 = 0.983$	1.19 (5.14×10^{-2}) $R^2 = 0.989$	0.10 (3.65×10^{-3}) $R^2 = 0.985$ [0.08]	0.14 (2.07×10^{-2}) $R^2 = 0.881$ [0.19]
iohexol	0.26 (6.86×10^{-3}) $R^2 = 0.995$	0.41 (2.44×10^{-2}) $R^2 = 0.984$	0.35 (2.72×10^{-2}) $R^2 = 0.953$ [0.33]	0.41 (2.42×10^{-2}) $R^2 = 0.972$ [0.39]
ciprofloxacin	0.04 (1.09×10^{-2}) $R^2 = 0.591$	nd	nd	nd
ketoprofen	1.28 (3.54×10^{-1}) $R^2 = 0.766$	nd	nd	nd

[a] Standard errors of the correlation coefficient (R^2) are given in parenthesis; SW time-based model rate constants results are given in square brackets; nd, not determined

1.1 and 2.1 $mWcm^{-2}$ corrected for the water absorbance and path length, multiplied by the exposure time (*13*). A small stir bar was placed inside the Petri dish to ensure homogeneous UV exposure.

LP/UV photolysis of LGW solutions containing individual PhACs was evaluated at UV fluences of approximately 0, 40, 100, 300, 700, 1000, 1700 $mJcm^{-2}$ to determine the PhAC fluence- and time-based rate constants and the quantum yields of the compounds. These tests were then repeated in SW to compare the removals obtained and to challenge the UV photolysis models introduced by Schwarzenbach et al. (*8*), previously modified to model the UV and UV/H_2O_2 photolysis of N-nitrosodimethylamine (*13*) and used to predict photolysis of endocrine disrupting compounds (*12*). The solutions were prepared by spiking 100 mL aliquots of either the LGW or SW with an initial concentration of a single PhAC (1−3 μM) and exposing the solution to the different UV fluences described above. After the exposure time generating the required fluence, 100 μL was pipetted into an amber autosampler vial and the vials were stored at 4 °C up to 12 h prior to duplicate analysis of the parent compound.

UV/H_2O_2 Photolysis Experiments. The AOP photodegradation experiments were conducted in LGW and SW, as described above for the UV photolysis experiments, with the addition of 10 mg/L H_2O_2 to the sample prior to UV exposure. 1 mL samples were taken at different exposure times and placed in amber vials containing 200 μg/L catalase to quench any residual H_2O_2 prior to analysis.

A competition kinetics approach was used to determine the oxidation rate constants between the PhACs and $^{\bullet}OH$ using pCBA as a reference compound (*15*). Experiments were conducted by spiking H_2O_2 (30 mg/L) into a Petri dish containing pCBA (0.5 μM) and the individual PhAC (1−3 μM) in LGW and exposing the sample to LP/UV light. This experiment was conducted using a higher H_2O_2 concentration (30 mg/L) to ensure that H_2O_2 was present in excess and that efficient $^{\bullet}OH$ production was achieved with LP/UV photolysis. In order to control for LP direct UV photolysis of pCBA, this experiment was also conducted without adding H_2O_2 and the PhACs. The time-based UV photolysis rate constants obtained for pCBA and the PhACs in LGW were subtracted from the UV/H_2O_2 photolysis rate constants to obtain the intrinsic $^{\bullet}OH$ rate constant.

The lower UV fluence values (40 and 100 $mJcm^{-2}$) encompass the range of typical disinfection practices and the concentration of H_2O_2 (10 mg/L) selected in this study represents the upper end of values employed for UV-based oxidation during drinking water treatment (*16*).

Results and Discussion

UV Photolysis. For a compound to be photolabile it needs to have the capacity to absorb photons of the incident light. The decadic molar absorption coefficient ($\epsilon(\lambda)$) measures the probability that a compound will absorb light at a certain wavelength (λ) and was determined by measuring the absorbance (a), within the 200−400 nm range, of solutions spiked with each of the PhACs at concentrations ranging from 0.1 to 10 μM ([PhAC]) using a 1 cm path length (z):

$$a = \epsilon(\lambda) \times [\text{PhAC}] \times z \quad (1)$$

Figure 1 shows the decadic molar absorption coefficient (ϵ) for each PhAC at different wavelengths overlaid with the relative irradiance of the LP lamps used. The $\epsilon(\lambda_{254\ nm})$ obtained were 400 $M^{-1}cm^{-1}$ for clofibric acid, 4900 $M^{-1}cm^{-1}$ for naproxen, 6070 $M^{-1}cm^{-1}$ for carbamazepine, 12 400 $M^{-1}cm^{-1}$ for ciprofloxacin, 15 450 $M^{-1}cm^{-1}$ for ketoprofen, and 27 620 $M^{-1}cm^{-1}$ for iohexol. The value obtained in this study for carbamazepine agrees very well with the value reported by Vogna et al. (6025 $M^{-1}cm^{-1}$) (*9*).

The results show that even though iohexol and ketoprofen absorb light at the 254 nm wavelength emitted by LP lamps, naproxen, clofibric acid, and carbamazepine absorb light mainly at lower wavelengths (in the range of 200−240 nm) and present absorbance minima at approximately 250 nm. Degradation of these compounds by LP/UV photolysis was, therefore, not expected to be high, and indeed at the water treatment UV fluence of 40 $mJcm^{-2}$, naproxen and carbamazepine concentrations after UV exposure were not distin-

TABLE 2. LP Specific Rate of Light Absorption (K_s), Quantum Yield (ϕ), and Second-order Reaction Rate Constant of •OH with the Selected PhACs (R^2=1) in LGW; ϕ and $K_{OH/PhAC}$, Standard Errors Given in Parenthesis

compound	K_s (λ = 254 nm) (einstein mol^{-1} s^{-1})	Φ (mol einstein^{-1})	slope ln(PhAC/PhAC$_0$) vs ln(pCBA/pCBA$_0$)	$K_{OH/PhAC}$ ($\times$ 10^9 M^{-1} s^{-1})
carbamazepine	0.0366	0.0006 (0.89×10^{-4})	1.17	5.85 (0.09)
naproxen	0.0297	0.0093 (0.27×10^{-3})	1.72	8.61 (0.002)
clofibric acid	0.0022	0.5390 (0.94×10^{-1})	1.14	5.72 (0.02)
iohexol	0.1095	0.0403 (0.96×10^{-4})	0.76	3.81 (0.07)
ciprofloxacin	0.0701	0.0103 (0.37×10^{-3})	1.24	6.22 (0.001)
ketoprofen	0.0904	0.2364 (0.72×10^{-2})	1.08	5.38 (0.07)

guishable from their initial concentrations (SI Figure 2). Using an extremely high LP/UV fluence of 1700 mJcm^{-2}, the degradation of carbamazepine by UV photolysis was still less than 5% although naproxen concentration was reduced by approximately 50%. On the other hand, clofibric acid concentration was reduced by 91 ± 0.6% and iohexol to levels below detection. The resistance of carbamazepine to degradation by LP/UV photolysis is consistent with the findings of Vogna et al. (*9*). Even though ketoprofen and ciprofloxacin degradation was not tested in SW, their degradation in LGW using a UV fluence of 40 mJcm^{-2} was 80 and 48%, respectively. These results were expected since, as illustrated in Figure 1, ketoprofen absorbs $UV_{254\ nm}$ radiation better than ciprofloxacin. In SW, the degradation of these compounds could either decrease, due to the competition of DOM for the UV light, or increase due to an indirect production of •OH from reaction of the UV light with DOM.

The degradation kinetics of the PhACs by LP/UV photolysis were modeled according to eqs 2 and 3 (*8*, *13*):

$$-\frac{d[\mathrm{PhAC}]}{dt} = k'_d[\mathrm{PhAC}] = K_s(\lambda_{254\mathrm{nm}})\phi_{254\mathrm{nm}}[\mathrm{PhAC}] \quad (2)$$

with

$$K_s(\lambda_{254\mathrm{nm}}) = \frac{E^o{}_p(\lambda_{254\mathrm{nm}})\epsilon(\lambda_{254\mathrm{nm}})[1 - 10^{-a(\lambda 254\mathrm{nm})z}]}{a(\lambda_{254\mathrm{nm}})z} \quad (3)$$

where k'_d represents the time-based pseudo-first-order rate constant for the individual PhAC by LP photolysis in LGW. The fluence and time-based rate constants obtained are presented in Table 1. $K_s(\lambda)$ represents the specific rate of light absorption by the compound, $E^o{}_p(\lambda)$ the incident photon irradiance, $\epsilon(\lambda)$ the decadic molar absorption coefficient (described above), $a(\lambda)$ the solution absorbance, z the solution depth in the Petri dish (3.1 cm), and ϕ the quantum yield.

The extremely low R^2 values obtained for carbamazepine UV photolysis in LGW and SW were expected due to the negligible removal of the compound. On the other hand, the lower explained variation obtained for ketoprofen and ciprofloxacin (compared to the other PhACs that were degraded to some extent) may be due to experimental problems with the instruments' response for these particular analytes. However, when the fluence-based rate constants obtained for ketoprofen and ciprofloxacin were retested on different days, similar values ($k'_{d,\mathrm{ketoprofen}} = 20.9 \times 10^{-3}$ cm^{2}mJ^{-1}; $k'_{d,\mathrm{ciprofloxacin}} = 0.8 \times 10^{-3}$ cm^{2}mJ^{-1}) to those reported in Table 1a were obtained, showing that the results obtained are consistent despite the low calibration sensitivity. It is important to note that the high rate constants reported for ketoprofen were obtained using only the experimental results obtained between 0 and 100 mJcm^{-2} since the compound seemed to re-form or degrade into a byproduct that elutes at the same time as the parent compound in the HPLC chromatogram at UV fluences higher than 300 mJcm^{-2}.

The two main parameters that influence the direct photolysis of a compound are the decadic molar absorption coefficient (shown in Figure 1) and the quantum yield. The quantum yield (ϕ) for degradation of each PhAC represents the ratio between the total number of molecules of the compound degraded to the total number of photons absorbed by the solution due to the compound's presence. This parameter is shown in Table 2 and was experimentally determined as the ratio between the pseudo-first-order rate constant (k'_d) and the specific rate of light absorbed by the compound at 254 nm (K_s) as described in eq 2. Even though clofibric acid shows an absorbance minimum at this wavelength with ϵ below that for naproxen and carbamazepine, its higher quantum yield explains why it can be removed from SW to a greater extent than either of those compounds (Table 1).

The quantum yield value obtained for the PhACs was used together with the specific rate of light absorption determined in the SW experiments to model the time- and UV fluence-based rate constants in the SW. The experimental and model UV photolysis results obtained in the SW are compared in Figure 2 and the rate constants obtained are shown in Table 1 (with the model results given in square brackets). In Figure 2, the average of duplicate experimental results is represented by the symbols and the error bars show the two duplicate values measured; the plotted lines represent the model results obtained using the UV photolysis eqs 2 and 3 described earlier.

Figure 2 shows that pseudo-first-order kinetics explains the experimental results obtained and that the experimental and model results agree well. The model can, therefore, be used to predict the extent of removal expected for these compounds under other experimental conditions. As expected, due to the absorbance spectra of the compounds and the quantum yield, iohexol showed higher removals than clofibric acid, while naproxen and carbamazepine show negligible removals from the SW. The slight underestimation of the model rate constants compared to the experimental results may be because of the raw water contribution to indirect photolysis conditions not accounted for in the UV model.

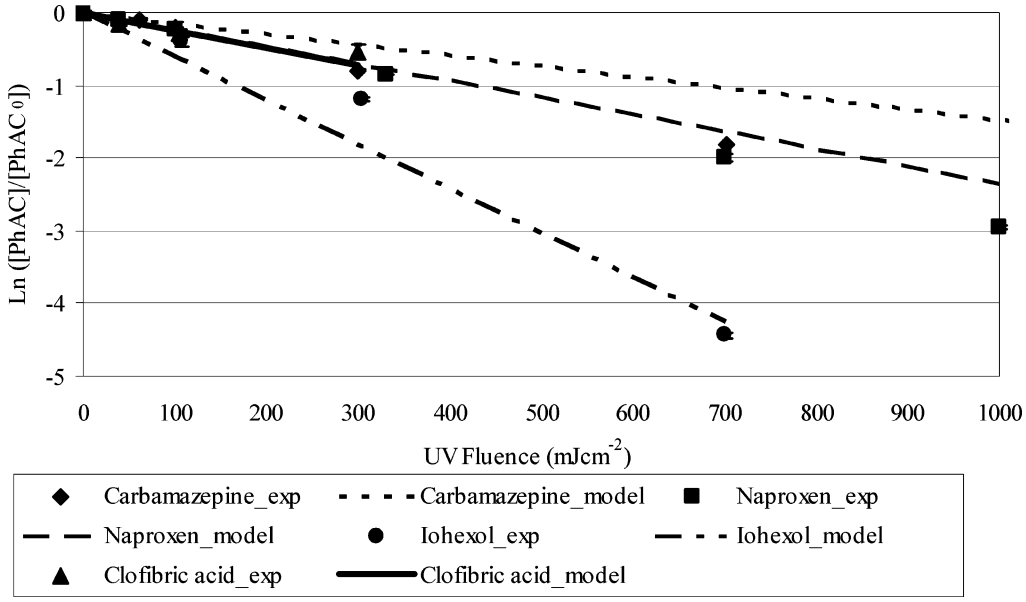

FIGURE 3. LP experimental (exp) and model UV/H_2O_2 oxidation (with addition of 10 mg/L H_2O_2) results obtained for carbamazepine, clofibric acid, iohexol, and naproxen in SW.

UV/H_2O_2 Photolysis. Considerably higher removals of carbamazepine and naproxen were obtained in the SW when 10 mg/L of H_2O_2 was added, due to the production of the highly reactive •OH (SI Figure 2). Even though the removals obtained by UV/H_2O_2 photolysis for all PhACs were less than 20% of the initial concentration at the lower UV fluence (40 mJcm^{-2}), all the compounds were reduced to levels below detection by UV/H_2O_2 photolysis at the higher UV fluence tested (1700 mJcm^{-2}). Nevertheless, the generation of •OH in SW does not appreciably enhance the degradation of clofibric acid and iohexol, perhaps because they have already been effectively degraded by direct photolysis. This is not the first time that •OH chemistry has proved ineffective in attempts to degrade chemical pollutants. Data presented by Sharpless and Linden (*13*) also showed the negligible benefit of UV/H_2O_2 in aiding the degradation of NDMA, but again this was mainly a result of the very effective direct photolysis decay.

In the presence of H_2O_2, the overall degradation of PhACs will be a function of UV and UV/H_2O_2 photolysis, and the process can be modeled using eqs 4−7 (*8*, *13*):

$$-\frac{d[\mathrm{PhAC}]}{dt} = (k'_d + k'_i)[\mathrm{PhAC}] \tag{4}$$

with k'_i being the pseudo-first-order initial rate constant for indirect photolysis. This constant is a function of the second-order reaction rate constant ($k_{OH/PhAC}$), determined experimentally using pCBA as a probe compound, and the steady-state concentration of •OH ($[OH]_{ss}$):

$$k'_i = k_{\mathrm{OH/PhAC}}[\mathrm{OH}]_{ss} \tag{5}$$

$[OH]_{ss}$ is a function of the quantum yield for photolysis of H_2O_2 into two •OH (Φ_{OH}), the sum of the pseudo-first-order rates of reaction of •OH with scavengers ($k_{OH/S}$; e.g. HCO_3^-, CO_3^{2-}, DOC, H_2O_2), and all the other parameters described above in the UV photolysis expressions:

$$[^{\bullet}\mathrm{OH}]_{ss} = \frac{k_{a,\mathrm{H_2O_2}}(\lambda_{254\mathrm{nm}})\phi_{\mathrm{OH}}(\lambda_{254\mathrm{nm}})[\mathrm{H_2O_2}]}{\sum_i k_{\mathrm{OH/S}}[S]_i} \tag{6}$$

$$K_{a,\mathrm{H_2O_2}}(\lambda_{254\mathrm{nm}}) = \frac{E^o{}_p(\lambda_{254\mathrm{nm}})\epsilon_{\mathrm{H_2O_2}}(\lambda_{254\mathrm{nm}})[1 - 10^{-(a(\lambda 254\mathrm{nm}) + \epsilon_{\mathrm{H_2O_2}}(\lambda 254\mathrm{nm})[\mathrm{H_2O_2}])z}]}{(a(\lambda_{254\mathrm{nm}}) + \epsilon_{\mathrm{H_2O_2}}(\lambda_{254\mathrm{nm}})[\mathrm{H_2O_2}])z} \tag{7}$$

The rate constants for the reaction between •OH and the various scavengers were taken as:

$k_{OH/HCO3^-} = 8.5 \times 10^6$ Lmol^{-1}s^{-1} (*17*), $k_{OH/CO3^{2-}} = 3.9 \times 10^8$ Lmol^{-1}s^{-1} (*17*), $k_{OH/DOC} = 2.5 \times 10^4$ Lmg^{-1}s^{-1} (*18*), and $k_{OH/H2O2} = 2.7 \times 10^7$ Lmol^{-1}s^{-1} (*17*). The DOC concentration of the filtered SW was 4.2 mg/L C, the H_2O_2 concentration was determined in each experiment (*14*), and bicarbonate and carbonate concentrations were calculated according to eq 8 using the alkalinity (Alk) and pH values of the filtered SW:

$$\mathrm{Alk} = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{OH^-}] - [\mathrm{H^+}] = (\alpha_1 + 2\alpha_2) \times [\mathrm{TOTCO_3}] + [\mathrm{OH^-}] - [\mathrm{H^+}] \tag{8}$$

At pH 7, the distribution coefficients of the carbonate species, α_1 and α_2, at 25 °C are 0.817 and 3.82×10^{-4}, respectively (calculated using the acidity constants (*19*) $k_{a1} = 10^{-6.35}$ and $k_{a2} = 10^{-10.33}$). Accordingly, the bicarbonate and carbonate concentrations of the filtered SW were calculated as 5×10^{-4} M and 2×10^{-7} M, respectively, after determination of the total carbonate concentration ($[TOTCO_3] = 6 \times 10^{-4}$ M).

The second-order rate constants for reaction of the PhACs with •OH were determined by competition kinetics using pCBA as a reference compound (*10*), assuming a first-order kinetic dependence on each PhAC and pCBA, and that the two reactions proceed independently in parallel.

The second-order rate constants ($k_{OH/PhAC}$) can, therefore, be determined as the slope of a plot of ln([PhAC]/[PhAC$_0$]) vs ln([pCBA]/[pCBA$_0$]), assuming the very fast reaction rate

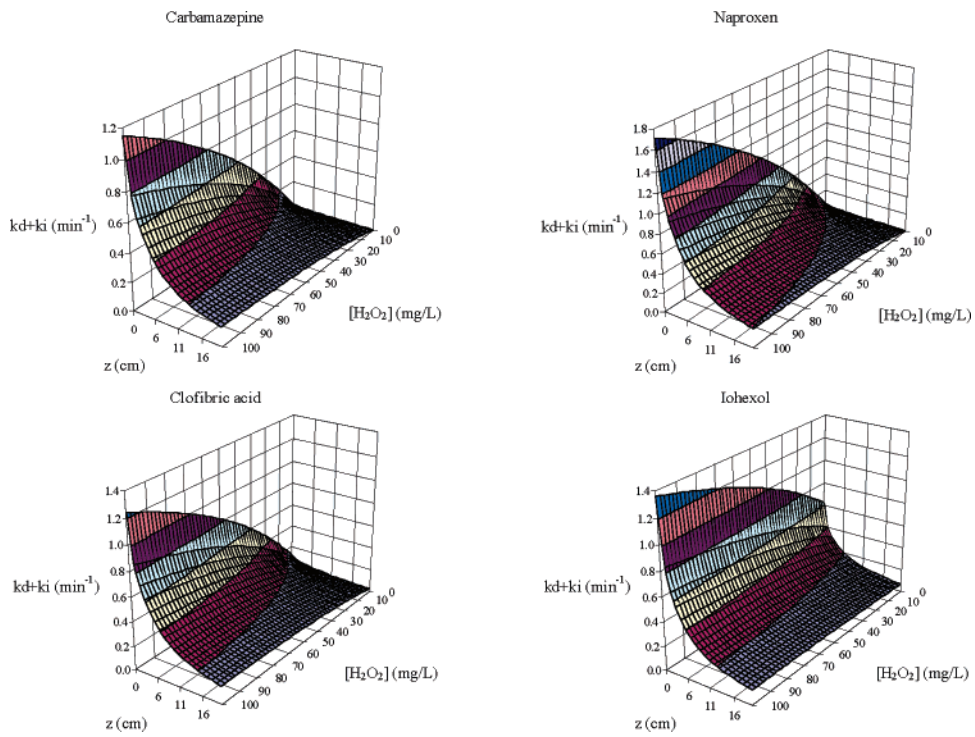

FIGURE 4. Modeled overall photolysis time-based rate constant ($k_d + k_i$) of PhACs in SW as a function of hydrogen peroxide concentration ([H_2O_2]) and solution depth (z).

between •OH and pCBA of 5×10^9 $M^{-1}s^{-1}$ (*20*):

$$\ln\left(\frac{[\mathrm{PhAC}]}{[\mathrm{PhAC}_0]}\right) = \ln\left(\frac{[\mathrm{pCBA}]}{[\mathrm{pCBA}_0]}\right)\frac{k_{\mathrm{OH/PhAC}}}{k_{\mathrm{OH/pCBA}}} \tag{9}$$

Before conducting the UV/H_2O_2 photolysis experiments, the UV photolysis of pCBA was tested without addition of H_2O_2. The results ($k'_d = 1.90 \times 10^{-2}$ min^{-1}; standard error = 4.85×10^{-3} min^{-1}) show that little degradation of this compound can be expected by UV photolysis because even at the very high UV fluence of approximately 1700 $mJcm^{-2}$ only about 20% of the compound was removed from LGW.

The LGW time-based UV photolysis rate constants obtained for each PhAC (Table 1b) and pCBA (described above) were subtracted from the overall UV/H_2O_2 photolysis experimental time-based rate constants obtained for each PhAC and pCBA, to account for the degradation of these compounds by UV photolysis. Table 2 summarizes the relative slope values from the LP/UV/H_2O_2 photolysis depletion of the selected PhACs and pCBA and the experimentally determined second-order rate constants (with the corresponding standard errors) obtained using eq 9.

Second-order rate constants for reactions of organic compounds with •OH typically vary between 10^6 and 10^{10} $M^{-1}s^{-1}$ and have been reported in the literature (*8*). The selected PhACs can therefore be considered to be fast-reacting compounds. The experimental rate constants obtained in this study agree well with values reported in the literature for carbamazepine (5.8×10^9 $M^{-1}s^{-1}$ in our study compared to 8.8×10^9 $M^{-1}s^{-1}$ in the study conducted by Huber et al. (*10*)) and seven other PhACs that varied between 3.3 and 9.8 $\times 10^9$ $M^{-1}s^{-1}$. Very similar rate constants were also obtained for iohexol in our study (3.81×10^9 $M^{-1}s^{-1}$) and iopromide in the Huber et al. study (*10*) (3.3×10^9 $M^{-1}s^{-1}$). These rate constants were expected to be similar since iopromide (also an X-ray contrast media agent) has a very similar structure to iohexol. Packer et al. (*11*) also reported rate constants for naproxen (9.6×10^9 $M^{-1}s^{-1}$) and clofibric acid (4.7×10^9 $M^{-1}s^{-1}$) that were similar to the values obtained in our study.

Figure 3 illustrates the experimental (symbols) and model (lines) UV/H_2O_2 photolysis results obtained for the loss of the parent PhAC from the SW. The experimental and model fluence- and time-based rate constants obtained in the SW as a result of UV/H_2O_2 photolysis are presented in Table 1 (model results given in square brackets were calculated using eqs 4−9 described earlier) alongside the results of the previously discussed UV photolysis experiments. At 1700 $mJcm^{-2}$ the residual PhAC parent compound was below detection and cannot, therefore, be shown in Figure 3.

The model results underestimated the experimental removals obtained for carbamazepine, although the reasons behind this were not known. A slight underestimation of the model results was also reported in SW for bisphenol A, which like carbamazepine, is also a fast-reacting compound with •OH (*12*). One possible explanation for the model underestimation could be the influence of physical processes not accounted for by the model such as photosensitization induced by NOM, although this was not identified with the other contaminants tested.

The UV fluences needed to achieve 50, 90, and 99% removals of the contaminants by UV and UV/H_2O_2 (using 10 mg/L of H_2O_2) photolysis in SW, can be calculated using the experimental UV and UV/H_2O_2 photolysis fluence-based rate constants (Table 1a). Even though, as previously noted, no significant improvements are seen when using the UV peroxide AOP for iohexol and clofibric acid, the use of 10 mg/L H_2O_2 decreased considerably the UV fluence needed to remove carbamazepine and naproxen from SW (SI Table 2). UV photolysis at a fluence of 100 $mJcm^{-2}$ on a contaminated SW will probably degrade less carbamazepine, naproxen, ciprofloxacin, and clofibric acid than iohexol and ketoprofen. Using the same UV fluence in the presence of 10 mg/L of H_2O_2 is expected to enhance the degradation of carbamazepine and naproxen.

While the results indicate that some of the contaminants studied can be removed to some degree at UV fluence levels near that used for disinfection (40−140 mJ/cm^{-2}) (*16*), to achieve broad UV-based destruction of chemical contaminants it is clear that higher fluence levels (above 500 mJcm^{-2}) such as those used for NDMA removal (*13*) will be required, and addition of H_2O_2 will assist this degradation in some cases.

Future studies should address whether the use of higher UV fluences and AOPs that could degrade a wide variety of organic compounds are economically feasible and competitive when compared to the use of other treatment processes (such as ozonation and membranes). This comparison should take into consideration the possibility of byproduct formation during photolysis, ozonation, and the use of AOPs, and how to deal with membrane rejection concentrate.

Model Predictions of UV and UV/H_2O_2 Rate Constants: H_2O_2 and Solution Depth Effects. The UV and UV/H_2O_2 photolysis models described in this paper (eqs 1−9) were used to predict changes in the overall UV-based rate constant as a function of solution depth and H_2O_2 concentration (Figure 4).

When H_2O_2 was added to the SW, the overall rate constant increased at the same solution depth with increasing H_2O_2 concentrations, and the increase was more noteworthy for the compounds that reacted faster with $^{\bullet}$OH such as naproxen, carbamazepine, and clofibric acid (Figure 4). This change is, therefore, lower for iohexol due to its slower reaction with $^{\bullet}$OH (Table 2). For all the compounds, the expected increase in the overall rate constants as a function of H_2O_2 concentration is slightly attenuated at high H_2O_2 levels, probably due to the scavenging of light by H_2O_2 (*13*) and the $^{\bullet}$OH scavenging by H_2O_2. However, using LP lamps this attenuation is lower because H_2O_2 absorbs light more strongly at wavelengths below 250 nm and, therefore, is not very effective in absorbing the emitted LP light at the applied peroxide concentrations (<15 mg/L). With increased solution depth, water quality will attenuate the light absorbed by peroxide and, therefore, affect $^{\bullet}$OH production, decreasing the overall removal rate constants.

The batch reactions carried out in this study indicate that the H_2O_2 concentration, optical path length, and SW matrix are very important UV reactor design considerations. However, it should be emphasized that these experiments were conducted in a batch reactor on a bench-scale, and hence, the irradiance measurement is less complex than in a full-scale UV reactor where there will be multiple light sources. In full-scale UV reactors, the fluence rate distribution, hydraulics, and reactor design also need to be taken into consideration for reactor optimization.

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Supporting Information Available

Additional figures, tables, and method details are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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