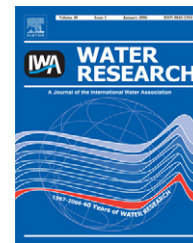


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Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water

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ABSTRACT

A medium-pressure (MP) ultraviolet (UV) system was used to investigate the UV photolysis and UV/H₂O₂ oxidation of pharmaceutically active compounds (PhACs) that belong to different therapeutic classes and were found to occur in the aquatic environment. The results obtained in laboratory-grade water (LGW) and surface water (SW) were compared with low-pressure (LP) results reported previously. Overall, MP lamps proved to be more efficient to maximize the bench-scale degradation of the selected group of compounds (ketoprofen, naproxen, carbamazepine, ciprofloxacin, clofibric acid, and iohexol) by both UV photolysis and UV/H₂O₂ oxidation. Fundamental direct and indirect photolysis parameters obtained in LGW are reported and used to model the MP-UV photolysis and MP-UV/H₂O₂ oxidation of the pharmaceuticals in SW, predicting the experimental results very well.

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1. Introduction

Due to their extensive use in developed countries, pharmaceutically active compounds (PhACs) belonging to a variety of therapeutic classes occur in different aquatic environments (Costanzo et al., 2005; Heberer, 2002; Kolpin et al., 2002; Öllers et al., 2001; Putschew et al., 2001; Stackelberg et al., 2004; Ternes, 1998; Ye et al., 2007). The selected sub-set of PhACs under study herein were ketoprofen and naproxen (analgesics), carbamazepine (anti-epileptic agent), ciprofloxacin (antibiotic), clofibric acid (metabolite of the lipid regulator clofibrate), and iohexol (X-ray contrast agent). The chemical structure and maximum reported occurrence levels in the aquatic environment are given in the Supplementary data section as SD Table 1.

Low-pressure (LP) mercury lamps that emit quasi-monochromatic ultraviolet (UV) light at 253.7 nm are conventionally used in UV disinfection (Openländer, 2003). Because few degradation studies of PhACs by UV light and advanced oxidation process (AOP) treatment have been conducted to date, LP bench-scale experiments were conducted previously to test whether the selected PhACs could be effectively degraded in drinking water treatment plants (Pereira et al., 2007). The bench-scale results obtained showed that some of the contaminants (such as ketoprofen and ciprofloxacin) were removed surprisingly well by LP-UV photolysis at UV fluences of 100 mJ/cm², while others were also removed by LP-UV photolysis and the UV/H₂O₂ AOP, albeit to a lesser extent. The negligible degradation of carbamazepine using LP-UV photolysis agrees well with previous findings by Vogna et al. (2004). The LP-UV/H₂O₂ oxidation experiments conducted also

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included indirect determination of the second-order reaction rate constants of the selected PhACs with OH radicals using *p*-chlorobenzoic acid (pCBA) as a probe compound as described by Elovitz and von Gunten (1999).

Medium-pressure (MP) polychromatic mercury lamps that emit a broadband spectrum from 205 to above 500 nm are also used in UV disinfection practice and for degradation of photolabile compounds. In the presence of hydrogen peroxide, MP-UV can be very effective in oxidizing a broad variety of organic compounds by the production of highly reactive and nonselective OH radicals. For example, MP photolysis and MP-UV/H₂O₂ oxidation have been shown to efficiently remove methyl *tert*-butyl ether from contaminated drinking water (Cater et al., 2000), *N*-nitrosodimethylamine from simulated drinking water (Sharpless and Linden, 2003), and endocrine-disrupting compounds from laboratory-grade water (LGW) (Rosenfeldt and Linden, 2004).

Even though LP mercury lamps have two to three times the germicidal efficiency of MP lamps, MP lamps have a much higher UV-C intensity per lamp and are a good choice for large UV disinfection units (Oppenländer, 2003) or where space is a constraint. Because of the higher intensity of the MP systems, fewer lamps need to be installed and MP reactors are, as a consequence, more compact than LP reactors.

This study monitored the degradation of the selected PhACs using an MP-UV source in a batch reactor. The PhACs were spiked into LGW and surface water (SW) and their photodegradation was monitored at different UV fluences in UV photolysis and UV/H₂O₂ oxidation experiments. Fundamental photolysis parameters as well as experimental and model UV and UV/H₂O₂ results are reported, discussed, and compared with the previous LP-UV results. The experimental parameters obtained were used to model systems under different experimental conditions, such as the level of hydrogen peroxide concentration added and the reactor path length.

2. Materials and methods

The reagents and analytical methods used to determine the PhAC concentration were described previously (Pereira et al., 2007).

In summary, all the PhACs except iohexol were obtained as neat solids from Sigma Aldrich (St. Louis, MO). Iohexol was obtained as a liquid stock solution (647.1 mg/mL) from the University of North Carolina Hospital (Chapel Hill, NC). Primary dilutions of the individual PhACs were prepared in LGW. Secondary dilutions on which UV treatment was practised were prepared in LGW and SW, with initial concentrations ranging from 1 to 3 μ M. The SW used (25 mg/L as CaCO₃ total alkalinity, pH 7, 4.2 mgC/L dissolved organic carbon (DOC), and 74% UV transmission) was collected at the Brown Water Treatment plant (Durham, NC), filtered using Waters (Waters Corporation, Milford, MA) nylon filters (0.45 μ m, 47 mm), and stored at 4 °C until use.

Reverse-phase high-pressure liquid chromatography (HPLC) with photo-diode array detection was used for the analysis of pCBA and all PhACs, except iohexol and ciprofloxacin that were analyzed using positive ionization by liquid

chromatography with tandem mass spectrometry detection (LC–MS/MS).

Decadic molar absorption coefficients (ϵ_λ) were determined by spiking each PhAC individually into LGW at levels ranging from 1 to 10 μ M, and the UV absorbance of the samples was measured (between 200 and 400 nm) using a Cary 100 biospectrophotometer (Varian, Houston, TX).

The MP-UV photolysis batch experiments were conducted at neutral pH and at room temperature, controlled with a cooling coil. The exposures were performed under a collimated beam apparatus (Calgon Carbon Corp, Pittsburgh, PA, modified by Duke University) using a 1 kW MP-UV lamp (Hanovia Co., Union, NJ), with the spiked water samples placed under an automated shutter in an open Petri dish containing a small stir bar to provide constant mixing to the 3.1 cm depth sample. Before and after exposing the spiked samples to UV light, a calibrated radiometer (IL1700 SEL240/W, International Light, Peabody, MA) was placed under the UV source at the same height as the water level in the Petri dish, to obtain incident irradiance measurements. The UV fluence was calculated as the incident irradiance from 200 to 300 nm, corrected for the water absorbance at each wavelength and path length, multiplied by the exposure time (Bolton and Linden, 2003; Linden and Darby, 1997). MP-UV photolysis of the individual PhACs was followed in LGW at UV fluences of approximately 0, 40, 100, 300, 700, 1000, and 1700 mJ/cm². Each desired UV fluence was divided by the average irradiance over 200–300 nm, to calculate the time needed to achieve that specific UV fluence. In the UV/H₂O₂ oxidation batch experiments, 10 mg/L of hydrogen peroxide was added to the LGW samples containing individual PhACs. The hydrogen peroxide residual was determined using a method described by Klassen et al. (1994). After exposure, catalase was used to quench the residual hydrogen peroxide.

For a subset of PhACs selected (carbamazepine, naproxen, clofibric acid, and iohexol), the experiments conducted in LGW were repeated in SW to compare their removals and to validate the photolysis model.

3. Results and discussion

3.1. MP-UV photolysis

Fig. 1 shows the PhAC decadic molar absorption coefficient (ϵ) of the targeted PhACs measured in LGW overlaid with the normalized emission spectrum of the LP and MP-UV lamps at neutral pH.

Because the decadic molar extinction coefficient (ϵ_λ) measures the probability that a compound will absorb light at a particular wavelength (Schwarzenbach et al., 1993), the results obtained suggest that MP lamps will probably be efficient at photodegrading the selected PhACs. The LP results reported previously (Pereira et al., 2007) show that, from all the selected compounds, iohexol presents the highest values for ϵ at 254 nm, which suggests that LP lamps, with monochromatic output at 254 nm, could be more efficient in degrading this compound than the other PhACs.

Using iohexol as an example, when the PhAC is spiked into SW (at 3 μ M), the natural organic components of the water

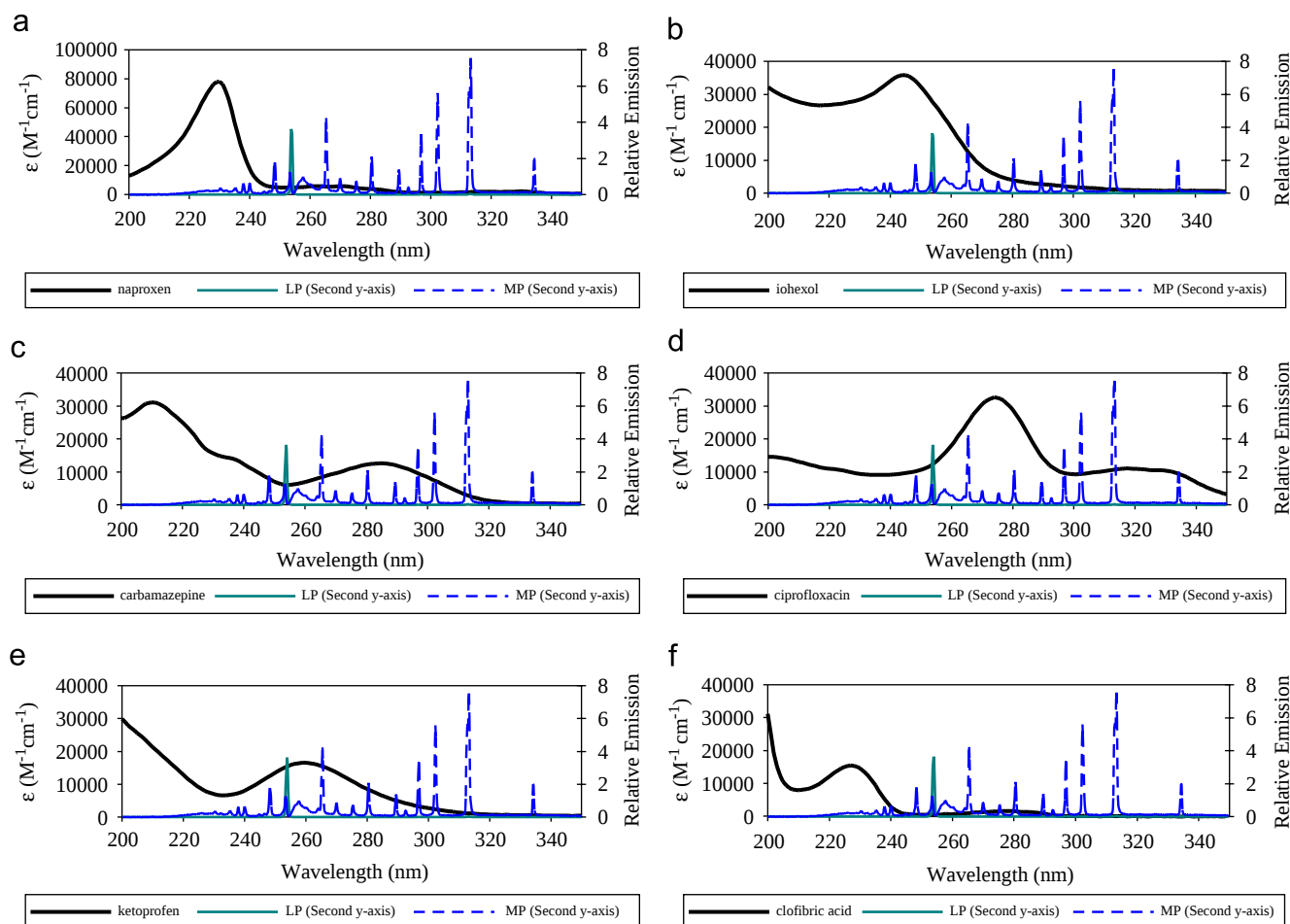


Fig. 1 – Decadic molar absorption coefficient of targeted PhACs (primary Y-axis) overlaid with the normalized emission spectrum of LP and MP/UV lamps for (a) naproxen, (b) iohexol, (c) carbamazepine, (d) ciprofloxacin, (e) ketoprofen, and (f) clofibric acid.

will compete for the MP-UV light especially at wavelengths below 230 nm (as can be seen in the supplementary data section as SD, Fig. 1). This screening effect will be most noticeable for compounds that absorb light mainly at wavelengths lower than 250 nm such as iohexol, naproxen, clofibric acid and carbamazepine. Fig. 2 illustrates the MP-UV photolysis and UV/H₂O₂ oxidation results in SW obtained at UV fluences of 40 and 100 mJ/cm² with results compared with those reported previously for LP-UV.

At 100 mJ/cm², naproxen's negligible removal by LP-UV photolysis increased to approximately 36% with MP lamps, while the removal of clofibric acid increased from approximately 19% using the LP system to 50% using MP lamps. Note that removal of carbamazepine by UV photolysis from SW using both types of lamps at these UV fluences was minor (with MP rates being slightly faster than LP rates) and ciprofloxacin photodegradation was not tested in SW.

Fig. 3 and Table 1 show the experimental fluence and time-based rate constants for the targeted PhACs obtained using an MP system in LGW and SW. The results show that, in most cases, the SW matrix competition for UV light reduces the UV photolysis rate constants only very slightly.

Iohexol and ketoprofen, for which the decadic molar absorption coefficient overlaid with the emission spectra of both LP and MP lamps (Fig. 1), differ in their degradation results. While ketoprofen can be degraded in LGW more efficiently using MP lamps instead of LP lamps ($k_{f,MP} = 0.0205$ and $k_{f,LP} = 0.0178$ cm²/mJ), for iohexol LP lamps are more efficient than MP lamps at degrading this compound from SW ($k_{f,MP} = 0.0031$ and $k_{f,LP} = 0.0058$ cm²/mJ) and LGW ($k_{f,MP} = 0.0024$ and $k_{f,LP} = 0.0055$ cm²/mJ).

Even though at UV fluence levels of 100 mJ/cm² (Fig. 2b) the difference between using LP and MP lamps to degrade iohexol in SW is lower than 9%, the use of MP lamps increased the degradation of clofibric acid and naproxen by more than 30%.

3.2. MP-UV photolysis modeling

The PhAC degradation kinetics by MP-UV photolysis was modeled using the following expressions (Schwarzenbach et al., 1993; Sharpless and Linden, 2003):

$$-\frac{d[\text{PhAC}]}{dt} = k'_d[\text{PhAC}] = \left(\sum_{\lambda=200}^{300} K_s(\lambda) \right) \phi[\text{PhAC}] \quad (1)$$

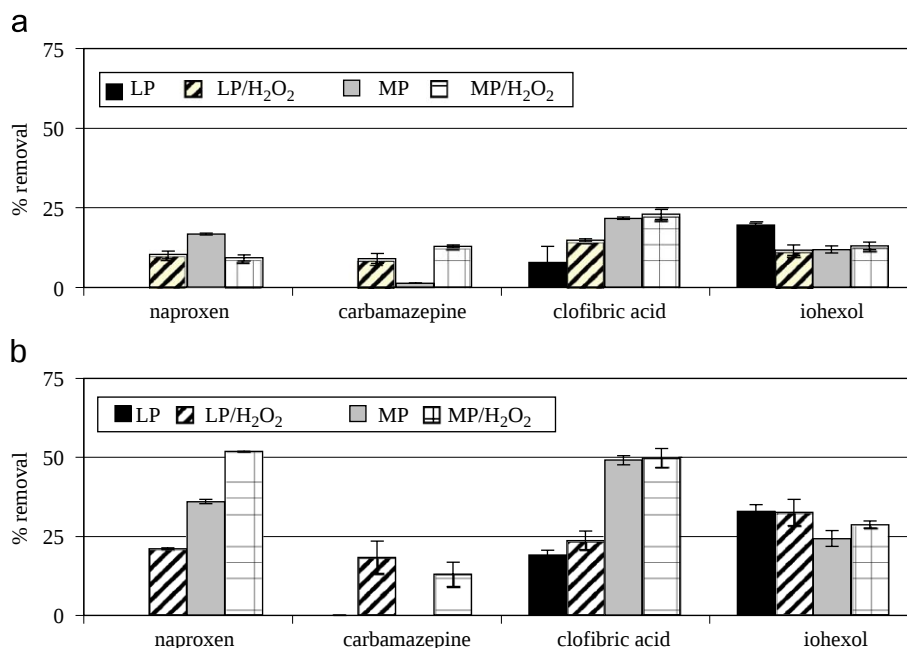


Fig. 2 – PhAC removal from surface water by UV photolysis and UV/H₂O₂ oxidation using LP and MP lamps at (a) 40 and (b) 100 mJ/cm².

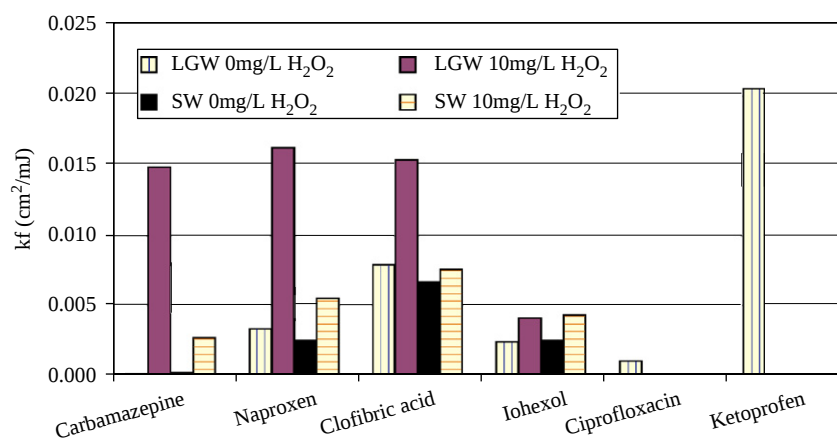


Fig. 3 – Fluence-based rate constants (k_f) obtained by MP-UV photolysis and UV/H₂O₂ oxidation in laboratory-grade water (LGW) and surface water (SW).

with

$$K_s(\lambda) = \frac{E_p^0(\lambda)\epsilon(\lambda)[1 - 10^{-a(\lambda)z}]}{a(\lambda)z} \quad (2)$$

For MP-UV photolysis, k'_d represents the time-based LGW pseudo-first-order rate constant (Table 1), $K_s(\lambda)$ the specific rate of light absorption by the compound, $E_p^0(\lambda)$ the incident photon irradiance, $\epsilon(\lambda)$ the decadic molar absorption coefficient, $a(\lambda)$ the solution absorbance, z the solution depth in the Petri dish (3.1 cm), and ϕ the observed quantum yield. Since MP lamps emit polychromatic light, all the parameters described in these equations as wavelength dependent were experimentally obtained between 200 and 300 nm, and the overall specific rate of light absorption was calculated as the sum of all values obtained in this wavelength range.

Table 2 shows the specific rate of light absorption and observed quantum yield values obtained in LGW for all the PhACs using LP (at 253.7 nm) and MP (at 200–300 nm) systems.

The quantum yield values represent the ratio between the total number of molecules of the compound transformed per total number of photons absorbed by the solution due to the compound's presence (Schwarzenbach et al., 1993). Despite its relatively high absorbance, the extremely low quantum yield observed for carbamazepine is responsible for this compound's low probability of being degraded using UV photolysis. The quantum yield values for all the selected PhACs except iohexol were higher using the polychromatic MP system.

The experimentally determined photolysis parameters were used to model the time and UV fluence-based rate

Table 1 – Fluence (k_f) and time-based rate constants (k_t) obtained by MP-UV photolysis and UV/H₂O₂ oxidation in laboratory-grade water (LGW) and surface water (SW); coefficient standard errors given in parentheses; model SW k_f and k_t results given in square brackets

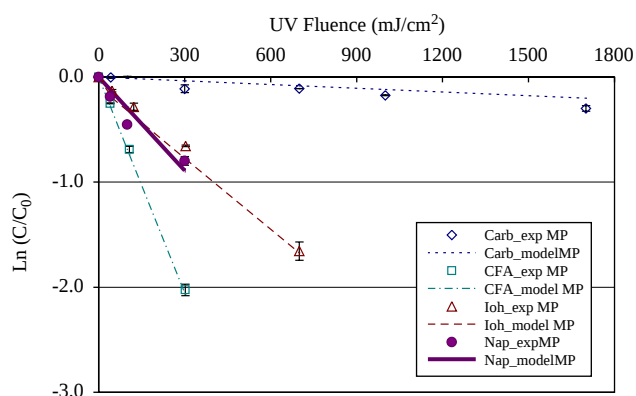
	LGW		SW	
	0 mg/L H ₂ O ₂	10 mg/L H ₂ O ₂	0 mg/L H ₂ O ₂	10 mg/L H ₂ O ₂
k_f (units as $\times 10^{-3}$ cm ² /mJ)				
Carbamazepine	0.1 (6.3×10^{-6}) $R^2 = 0.968$	14.9 (2.4×10^{-4}) $R^2 = 0.999$	0.2 (1.5×10^{-5}) [0.1]	2.7 (4.9×10^{-5}) [2.7]
Naproxen	3.3 (4.9×10^{-5}) $R^2 = 0.998$	16.3 (6.0×10^{-4}) $R^2 = 0.994$	2.5 (2.7×10^{-4}) $R^2 = 0.932$ [3.0]	5.5 (4.1×10^{-4}) $R^2 = 0.968$ [5.3]
Clofibric acid	7.9 (2.9×10^{-4}) $R^2 = 0.992$	15.4 (4.5×10^{-4}) $R^2 = 0.997$	6.7 (1.2×10^{-4}) $R^2 = 0.998$ [6.9]	7.6 (2.6×10^{-4}) $R^2 = 0.995$ [9.4]
Iohexol	2.4 (7.7×10^{-5}) $R^2 = 0.990$	4.1 (5.5×10^{-5}) $R^2 = 0.998$	3.1 (2.8×10^{-4}) $R^2 = 0.932$ [2.3]	4.3 (2.7×10^{-4}) $R^2 = 0.960$ [3.1]
Ciprofloxacin	1.0 (1.8×10^{-4}) $R^2 = 0.713$	nd	nd	nd
Ketoprofen	20.5 (3.8×10^{-3}) $R^2 = 0.877$	nd	nd	Nd
k_t (units as $\times 10^{-1}$ min ⁻¹)				
Carbamazepine	0.2 (0.8×10^{-3}) $R^2 = 0.968$	26.6 (4.4×10^{-2}) $R^2 = 0.999$	0.1 (9.5×10^{-4}) $R^2 = 0.919$ [0.1]	1.7 (3.1×10^{-3}) $R^2 = 0.997$ [1.7]
Naproxen	4.2 (6.3×10^{-3}) $R^2 = 0.998$	29.9 (1.1×10^{-1}) $R^2 = 0.994$	1.6 (1.7×10^{-2}) $R^2 = 0.932$ [1.8]	6.7 (4.9×10^{-2}) $R^2 = 0.968$ [6.5]
Clofibric acid	10.0 (3.6×10^{-2}) $R^2 = 0.992$	28.6 (8.3×10^{-2}) $R^2 = 0.997$	4.3 (7.7×10^{-3}) $R^2 = 0.998$ [4.4]	9.5 (3.2×10^{-2}) $R^2 = 0.995$ [11.6]
Iohexol	2.5 (8.3×10^{-3}) $R^2 = 0.990$	6.4 (8.5×10^{-3}) $R^2 = 0.998$	1.7 (1.5×10^{-2}) $R^2 = 0.932$ [1.3]	4.6 (2.9×10^{-2}) $R^2 = 0.960$ [3.4]
Ciprofloxacin	1.4 (2.5×10^{-2}) $R^2 = 0.713$	nd	nd	nd
Ketoprofen	26.5 (4.9×10^{-1}) $R^2 = 0.877$	nd	nd	nd
nd—not determined.				

constants in the SW experiments. The model rate constants obtained are shown in square brackets in Table 1 and were used to obtain the model MP-UV photolysis results repre-

sented by the lines in Fig. 4. In Fig. 4, the average of duplicate MP-UV photolysis results obtained in a single collimated beam experiment is represented by the symbols, while the

Table 2 – Specific rate of light absorption (K_s) and observed quantum yield (ϕ); LP results previously reported by Pereira et al. (2007); observed quantum yield standard errors given in parentheses

Compound	K_s (λ) (einstein mol ⁻¹ s ⁻¹)		ϕ (moleinstein ⁻¹)	
	LP	MP	LP	MP
Carbamazepine	0.0366	0.1145	0.0006 (0.89×10^{-4})	0.0023 (0.10×10^{-4})
Naproxen	0.0297	0.1271	0.0093 (0.27×10^{-3})	0.0556 (0.64×10^{-4})
Clofibric acid	0.0022	0.0218	0.5390 (0.94×10^{-1})	0.7678 (0.13×10^{-1})
Iohexol	0.1095	0.1425	0.0403 (0.96×10^{-4})	0.0295 (0.68×10^{-4})
Ciprofloxacin	0.0701	0.1903	0.0103 (0.37×10^{-3})	0.0119 (0.11×10^{-3})
Ketoprofen	0.0904	0.1166	0.2364 (0.72×10^{-2})	0.3786 (0.61×10^{-2})

**Fig. 4 – MP/UV photolysis experimental (exp) and model results obtained in surface water for carbamazepine (Carb), clofibric acid (CFA), iohexol (Ioh), and naproxen (Nap).**

bars show the actual values obtained in the duplicate samples.

As expected, the quantum yield and decadic molar absorption coefficients used in the model predicted the compounds' relative removal rates very well. Clofibric acid showed the highest and carbamazepine the lowest removal rates, while naproxen and iohexol were found to have similar removals in SW. Differences in matrix absorbance did not have an impact on the SW model predictions.

3.3. MP-UV/H₂O₂ oxidation

The production of highly reactive hydroxyl radicals when 10 mg/L of hydrogen peroxide was subject to a UV fluence of 100 mJ/cm² increased the degradation of carbamazepine and naproxen in SW considerably (Fig. 2b). Specifically, the negligible removal of carbamazepine by UV photolysis at this UV fluence increased to 13% by UV/H₂O₂ oxidation, whereas naproxen's removal increased from 36% to 52%. For all the PhACs spiked individually into a given matrix, the UV/H₂O₂ fluence-based rate constants obtained were higher than the UV photolysis rate constants (Table 1). However, the removal of

iohexol and clofibric acid at low UV fluences (40 and 100 mJ/cm² shown in Fig. 2) did not increase considerably using UV/H₂O₂ oxidation. Fig. 2 also illustrates that at 100 mJ/cm², up to 50% UV/H₂O₂ photodegradation of the compounds can be obtained in the SW matrix tested, while at 900 mJ/cm² greater than 90% removal could be obtained (as can be seen in Table 3 below) for some of the chemicals.

The large difference between UV/H₂O₂ decay rate constants in LGW and SW, compared with the negligible difference in UV photolysis rate constants (shown in Fig. 3 and Table 1), can be explained by a combination of competition by the natural organic matter (NOM) in SW for the UV light, and by NOM scavenging of the OH radicals produced by the UV/AOP.

Table 3 shows the MP-UV fluences needed to achieve 50%, 90%, and 99% degradation of the compounds by UV photolysis and UV/H₂O₂ oxidation in SW using the experimental rate constants presented in Table 1. Table 3 also shows, in parentheses, the UV fluences needed to achieve the same degradation using LP lamps as reported in our previous study (Pereira et al., 2007).

The bench-scale results obtained show that, parallel to the conclusions for UV photolysis, MP lamps also appear to be the best option to achieve degradation of the selected group of compounds by the UV/H₂O₂ AOP. Using UV/H₂O₂ oxidation will lower the UV fluences needed to achieve a target percent removal, specifically for carbamazepine and naproxen.

3.4. MP-UV/H₂O₂ oxidation modeling

In the presence of hydrogen peroxide, the overall degradation of PhACs will be contributed to by both UV photolysis and UV/H₂O₂ oxidation (Schwarzenbach et al., 1993; Sharpless and Linden, 2003):

$$-\frac{d[\text{PhAC}]}{dt} = (k'_d + k'_i)[\text{PhAC}], \quad (3)$$

with k'_i being the pseudo-first-order rate constant for UV/H₂O₂ oxidation that is a function of the second-order reaction rate constant ($k_{\text{OH/PhAC}}$) determined experimentally using

Table 3 – Comparison between the UV fluences (mJ/cm²) needed to achieve 50%, 90%, and 99% removal of the PhACs in surface and laboratory-grade water (LGW) using LP and MP-UV photolysis and UV/H₂O₂ oxidation; LP results from Pereira et al. (2007) given in parentheses

	50% removal		90% removal		99% removal	
	0 mg/L H ₂ O ₂	10 mg/L H ₂ O ₂	0 mg/L H ₂ O ₂	10 mg/L H ₂ O ₂	0 mg/L H ₂ O ₂	10 mg/L H ₂ O ₂
Carbamazepine	3466 (23,105)	257 (257)	11,513 (76,753)	853 (853)	23,026 (153,506)	1706 (1706)
Naproxen	277 (1386)	126 (231)	921 (4605)	419 (768)	1842 (9210)	837 (1535)
Clofibric acid	103 (533)	91 (408)	344 (1771)	303 (1354)	687 (3542)	606 (2709)
Iohexol	277 (120)	161 (108)	921 (397)	535 (360)	1842 (784)	1071 (720)
Ciprofloxacin ^a	693 (1155)	nd	2303 (3838)	nd	4605 (7675)	nd
Ketoprofen ^a	34 (39)	nd	112 (129)	nd	225 (259)	nd

nd—not determined.
^a Determined in LGW.

pCBA as a competition kinetics probe compound (Pereira et al., 2007) and the steady-state concentration of OH radicals ($[\bullet\text{OH}]_{ss}$):

$$k'_i = k_{\text{OH}/\text{PhAC}} [\bullet\text{OH}]_{ss} \quad (4)$$

$[\bullet\text{OH}]_{ss}$ is a function of the quantum yield for photolysis of H₂O₂ into two OH radicals (ϕ_{OH}), the sum of the second-order rates of reaction of OH with scavengers ($k_{\text{OH}/S}$; e.g. HCO₃⁻, CO₃²⁻, DOC, and H₂O₂), and all the other parameters described above in the UV photolysis equations:

$$[\bullet\text{OH}]_{ss} = \frac{\sum_i K_{a,\text{H}_2\text{O}_2}(\lambda) \phi_{\text{OH}}(\lambda) [\text{H}_2\text{O}_2]}{\sum_i k_{\text{OH}/S}[\text{S}]_i} \quad (5)$$

$$K_{a,\text{H}_2\text{O}_2}(\lambda) = \frac{E_p^0(\lambda) \varepsilon_{\text{H}_2\text{O}_2}(\lambda) [1 - 10^{-(a(\lambda) + \varepsilon_{\text{H}_2\text{O}_2}(\lambda) [\text{H}_2\text{O}_2])z}]}{(a(\lambda) + \varepsilon_{\text{H}_2\text{O}_2}(\lambda) [\text{H}_2\text{O}_2])z} \quad (6)$$

The second-order rates of reaction of OH radicals with scavengers were taken as $k_{\text{OH}/\text{HCO}_3^-} = 8.5 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988), $k_{\text{OH}/\text{CO}_3^{2-}} = 3.9 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988), $k_{\text{OH}/\text{DOC}} = 2.5 \times 10^4 \text{ L mg}^{-1} \text{ s}^{-1}$ (Larson and Zepp, 1988), and $k_{\text{OH}/\text{H}_2\text{O}_2} = 2.7 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988). The DOC concentration of the filtered SW was 4.2 mg/LC, the bicarbonate and carbonate concentrations were calculated using the SW alkalinity and pH values as discussed previously (Pereira et al., 2007), and the hydrogen peroxide concentration added (10 mg/L) was experimentally verified (Klassen et al., 1994).

Fig. 5 and Table 1 show the UV/H₂O₂ oxidation experimental and model results obtained in SW. In Fig. 5, the average of duplicate experimental results obtained in a single collimated beam experiment is represented by the symbols, the bars represent the two duplicate values obtained, and the lines represent the model results obtained using Eqs. (3)–(6).

Even though this model underestimated the experimental results when used to predict the removals of carbamazepine

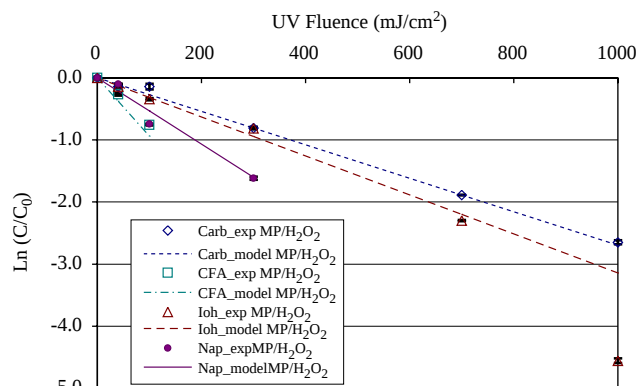


Fig. 5 – UV/H₂O₂ oxidation (10 mg/L H₂O₂) MP experimental (exp) and model results obtained in SW for carbamazepine (Carb), clofibric acid (CFA), iohexol (Ioh), and naproxen (Nap).

and naproxen using LP lamps, the agreement was excellent for MP-UV/H₂O₂ oxidation. The MP-UV photolysis and UV/H₂O₂ oxidation models were, therefore, further used to predict the overall rate constants for these compounds under different experimental conditions (Fig. 6) by changing the path length (z) and the hydrogen peroxide concentration added ($[\text{H}_2\text{O}_2]$). As discussed by Sharpless and Linden (2003), depending on the type of lamps used, there should be a concentration of H₂O₂ that corresponds to the maximum enhancement of the degradation rate constants. This is because photolysis of H₂O₂ will produce OH radicals that can enhance the degradation of PhACs, but H₂O₂ will also scavenge light that would otherwise be available to degrade the compounds. The effect of different optical path lengths was also evaluated because in actual UV reactors the path length will often be higher than in the Petri dish used in the experimental setup and therefore UV

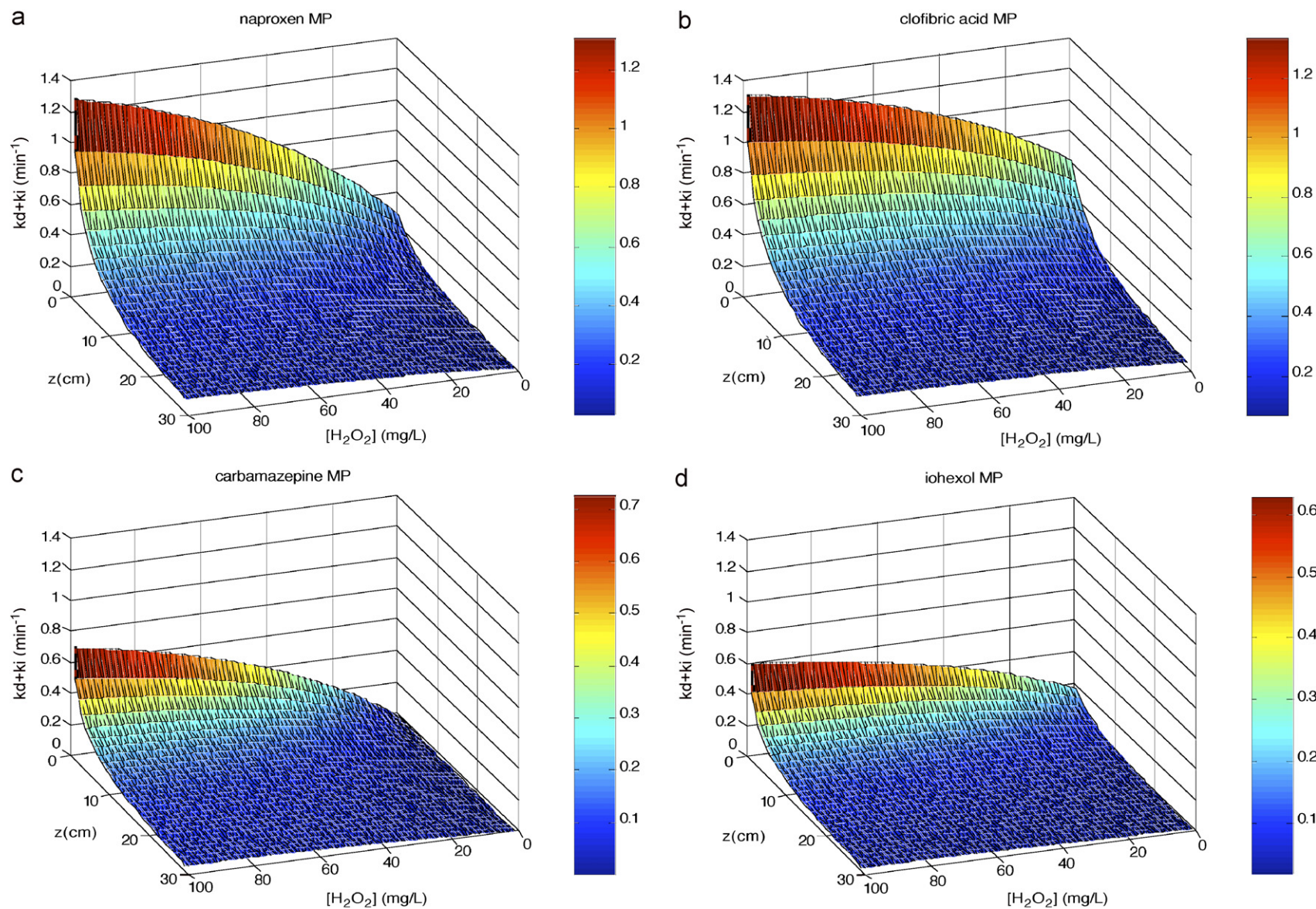


Fig. 6 – MP overall time-based rate constants ($k_d + k_i$) of naproxen (a), clofibric acid (b), carbamazepine (c), and iohexol (d) as a function of path length (z) and hydrogen peroxide concentration ($[\text{H}_2\text{O}_2]$).

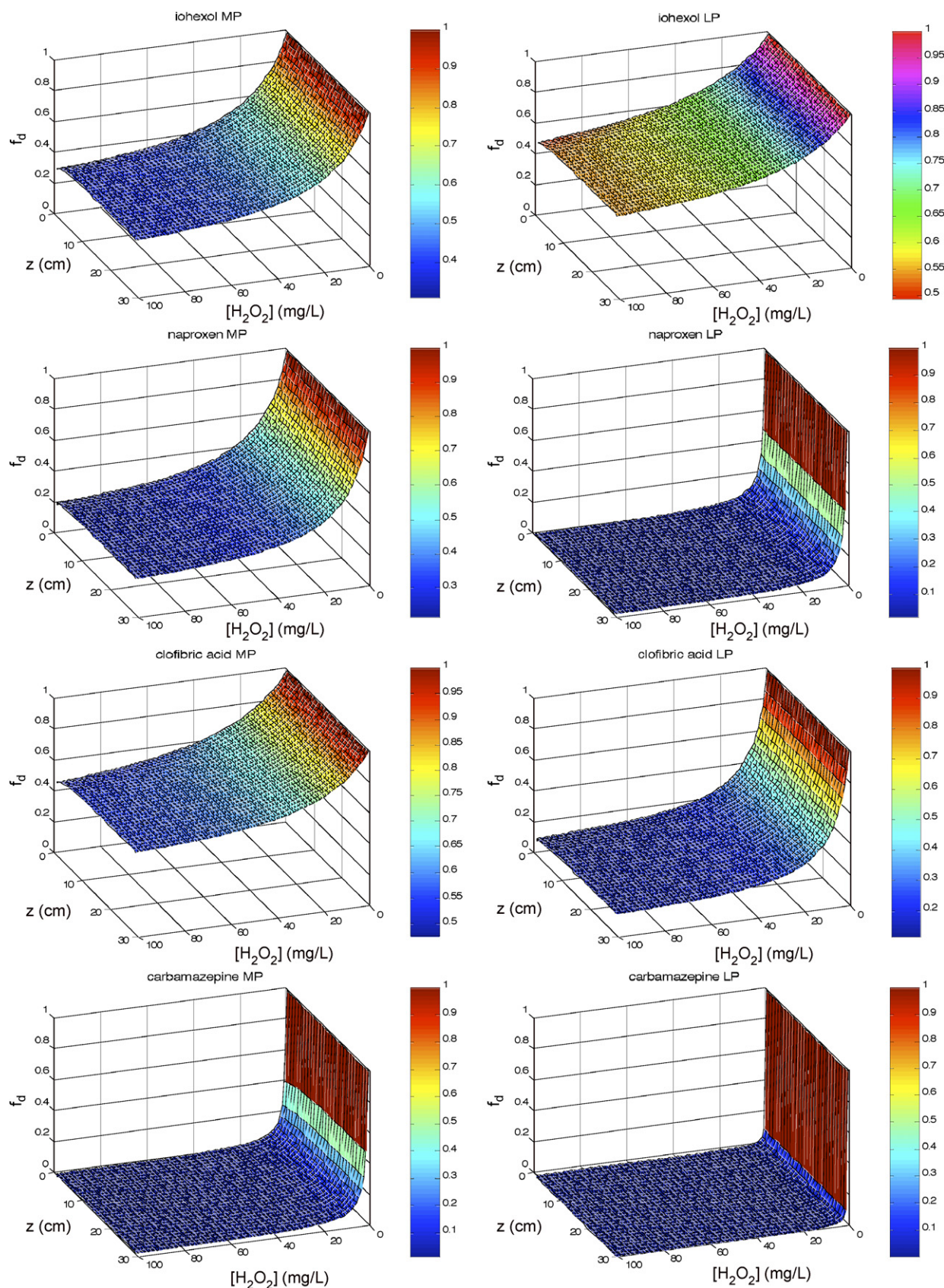


Fig. 7 – Surface water modeling of the LP and MP/UV photolysis fraction ($f_d = k'_d/(k'_d + k'_i)$).

absorption by hydrogen peroxide and the general water matrix will be more significant.

The modeling results (Fig. 6) show that, as expected, the overall rate constant increases with an increase in the hydrogen peroxide concentration and a decrease in path length. As observed previously (Sharpless and Linden, 2003), the expected increase in the overall rate constants as a function of hydrogen peroxide concentration is slightly attenuated at high H_2O_2 levels probably due to the scavenging of light by H_2O_2 and H_2O_2 scavenging of the OH radicals generated. The higher overall rate constants obtained by naproxen and clofibric acid can be explained by their higher quantum yield and second-order OH radical reaction rate constants (Pereira et al., 2007). In addition, the higher value of the second-order reaction rate constant of OH radicals with naproxen explains the more pronounced increase in the overall removal of this compound with the increase in H_2O_2 concentration in solution. The use of increased levels of H_2O_2 in UV treatment would need to be balanced with the cost of H_2O_2 use.

Fig. 7 presents the UV photolysis fraction using MP and LP lamps that allows a comparison of the relative importance of UV and UV/ H_2O_2 processes for the degradation of the selected PhACs under different experimental conditions.

The UV photolysis fraction (f_d) for each compound was obtained as the ratio of the UV photolysis rate constant (k_d') to the overall combined (UV and UV/ H_2O_2) rate constant ($k_d' + k_i'$). As discussed earlier, UV photolysis using MP lamps is more effective at achieving degradation of most of the targeted PhACs than LP lamps. Using LP, the sharpest relative decreases in UV photolysis (as measured by f_d) with an increase of the H_2O_2 concentration were obtained for carbamazepine and naproxen due to these compounds' low LP quantum yields. Even though the LP quantum yield for iohexol is lower than clofibric acid, a steeper UV photolysis decrease with increasing OH radical production was observed for clofibric acid most likely due to its higher second-order OH radical reaction rate constant. The extremely low UV photolysis obtained for carbamazepine using both LP and MP lamps shows that OH radical production is the main pathway for the degradation of this compound.

These results can be used by treatment plants that currently employ UV treatment to optimize their processes and can also be used to compare the relative efficiency of UV or UV/ H_2O_2 processes with the use of ozone or other AOP processes. However, when trying to implement these findings for full-scale UV facilities, it is important to emphasize that the compounds tested in this study are not necessarily representative of all the possible compounds that may be present in an actual water treatment plant intake, and that factors such as water quality, fluence rate distribution, hydraulics, reactor design, and electrical energy need to be taken into consideration when making treatment decisions or choosing between LP or MP-UV systems.

4. Conclusions

The use of low- and medium-pressure (MP) mercury lamps was evaluated for UV and UV/ H_2O_2 treatment of ketoprofen,

naproxen, carbamazepine, ciprofloxacin, clofibric acid, and iohexol. Overall, in the laboratory-scale experiments conducted, MP lamps proved to be more effective at maximizing the degradation of the selected group of compounds by both UV and UV/ H_2O_2 processes when compared with LP. UV photolysis and UV/ H_2O_2 oxidation modeling predicted the experimental results obtained very well for the MP system tested. Using LP lamps the highest removal rate was obtained by iohexol followed by clofibric acid, naproxen, and carbamazepine, while with MP lamps clofibric acid showed the highest removal rate followed by iohexol, naproxen, and carbamazepine. Removal of carbamazepine from SW using UV photolysis is not likely to be feasible due to its low quantum yield (0.6×10^{-3} and 2.3×10^{-3} mole einstein $^{-1}$ using LP and MP lamps, respectively), while UV/ H_2O_2 oxidation will increase the degradation of carbamazepine and naproxen considerably in SW. As an example, at the UV fluence of 100 mJ/cm 2 the MP removal of carbamazepine will increase from negligible to 13%, while the removal of naproxen will increase from 36% to 52%. The UV/ H_2O_2 oxidation fluence-based rate constants obtained using LP and MP lamps varied between $1.7 \times 10^{-3} \leq k_{f,LP/H_2O_2,SW} \leq 6.4 \times 10^{-3}$ and $2.7 \times 10^{-3} \leq k_{f,MP/H_2O_2,SW} \leq 7.6 \times 10^{-3}$ cm 2 /mJ, respectively. Interestingly, the levels of UV fluence capable of achieving reasonable degradation of some of these compounds are similar to those that would be applied for UV disinfection.

The UV photolysis and UV/ H_2O_2 oxidation models were also used to predict the degradation of the compounds under different experimental conditions. In general, the rate constants increase with decreased light source path length and increased hydrogen peroxide concentration, although at high concentrations the increase of the overall degradation rate constants is slightly attenuated due to the screening of UV light and OH radical scavenging.

These findings have implications for wastewater and drinking water treatment and show that a wide range of pharmaceutically active compounds (PhACs) can be degraded by the use of UV photolysis and UV/ H_2O_2 oxidation.

As a final consideration, UV photolysis of naproxen using UV lamps was accompanied by production of at least two photolysis by-products, since two peaks with different retention times were detected in the high-pressure liquid chromatography (HPLC) chromatograms of the degraded parent compound (not reported). Further studies should be conducted to identify these by-products. No by-products of the other PhACs were identified in HPLC chromatograms, suggesting that if these are formed, their structures will differ considerably from the parent compound and they will therefore absorb UV light at different wavelengths. If instead of being mineralized, some PhACs are transformed during photolysis, then the by-product identities and their potential environmental and human health impacts need to be studied.

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Appendix A. Supplementary Material

The online version of this article contains additional supplementary data. Please visit [doi:10.1016/j.watres.2007.05.056](https://doi.org/10.1016/j.watres.2007.05.056).

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