A Bench-scale Evaluation of the Removal of Selected Pharmaceuticals and Personal Care Products by UV and UV/H_2O_2 in Drinking Water Treatment

by

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A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Civil Engineering

Waterloo, Ontario, Canada, 2006

AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

A bench-scale study of the degradation of four selected pharmaceuticals and personal care products (PPCPs) was carried out using UV and UV/H_2O_2 treatment employing low pressure (LP) and medium pressure (MP) lamps. The target substances included the pharmaceutical compounds ibuprofen, naproxen, and gemfibrozil, along with the bactericide triclosan. There were four main objectives of the study, as follows: to evaluate the removal of the target compounds using UV irradiation alone and UV/H_2O_2, to determine the reaction kinetics for direct and indirect photolysis of each selected compound, to determine the influence of major water quality parameters on the efficacy of treatment, and to compare the applied UV and UV/H_2O_2 doses to those that have been found to be effective for disinfection and removal of taste and odour compounds, respectively.

For initial ultra-pure water experiments the target compounds were spiked at concentrations of approximately 250 µg/L (~1 µM). In latter ultra-pure water experiments and in the partially-treated water experiments, the selected PPCPs were spiked at a lower range (c~500-1000 ng/L), which is more representative of reported environmental concentrations. In an ultra-pure water matrix, a high LP fluence of 1000 mJ/cm^2 caused only triclosan to substantially degrade. Furthermore, with LP-UV/H_2O_2 only triclosan and naproxen had average percent removals above 60% at a typical disinfection fluence of 40 mJ/cm^2 with 100 mg/L H_2O_2. Complete degradation of all four compounds in ultra-pure water was achieved with very high fluences (compared to those used for UV disinfection) with MP-UV alone (at or above 1000 mJ/cm^2) or with relatively high fluences for MP-UV/H_2O_2 (200-300 mJ/cm^2) with 10 mg/L H_2O_2. Overall, when compared at similar applied fluences, the MP lamp was much more effective than the LP lamp. Furthermore, the addition of H_2O_2 typically increased removal rates, in some cases substantially, through formation and subsequent reaction of the PPCP with the •OH radical.

When target substances were treated all together in an ultra-pure water solution, removals were lower than when they were treated independently at the same individual concentrations (~250 µg/L) this may simply have been the result of a higher total contaminant concentration in solution, which lessened the availability of the •OH radical and incident UV irradiation for degradation of all compounds. On the other hand, removals were improved when the combined target compounds were present at a lower individual concentration range (~750 ng/L), which suggests that removals may be

concentration driven, with reduced matrix effects seen at lower overall contaminant concentrations. Furthermore, during the partially-treated water experiments, variability in treatment performance was observed with differing water quality; however, it was not evident which specific quality parameters influenced treatment effectiveness. On the other hand, substantial and sometimes complete, degradation of the target compounds was still seen in the partially-treated water with high MP-UV/H_2O_2 doses (e.g. 300 mJ/cm^2 + 10 mg/L H_2O_2 and 500 + 10 mg/L H_2O_2).

For the kinetic experiments, compounds were spiked individually in ultra-pure water (c~250 µg/L = ~1µM). The photolysis of the target compounds during treatment was assumed to be a pseudo-first-order reaction. Kinetic parameters were determined for both direct and indirect photolysis for both lamps. The calculated rate constants confirmed the importance of •OH radicals for degradation of these compounds, especially for ibuprofen and gemfibrozil. For ibuprofen and gemfibrozil, direct photolysis rate constants could not be determined for LP-UV because very little degradation was seen at the fluences tested. LP-UV direct phototlysis rate constants for naproxen and triclosan were 0.0002 and 0.0033 cm^2/mJ, respectively. Overall rate constants describing degradation of the four compounds due to LP-UV/H_2O_2 ranged from 0.0049 to 0.0124 cm^2/mJ. All four compounds had fluence-based reaction rate constants for MP-UV indirect photolysis of approximately 0.01 cm^2/mJ, while MP-UV direct photolysis rate constants ranged between 0.0007-0.007 cm^2/mJ, with ibuprofen having the lowest and triclosan the highest.

The overall trends were similar to those seen by other researchers for the removal of taste and odour compounds. For example, fluences required for substantial removal were much higher than typical disinfection doses, the MP lamp was more effective than the LP lamp (when compared solely on a fluence-basis), and the addition of H_2O_2 improved removals.

On the whole, UV/H_2O_2 appears to be a very promising technology for the removal of these selected PPCPs during drinking water treatment, and is likely to be equally effective for other, similar contaminants.

Acknowledgements

I would like to express my sincerest gratitude to Dr. Sigrid Peldszus for her willingness to share her exceptional knowledge, for her patience, and for her leadership on this project. I would also like to offer my sincerest thanks to Dr. Peter M. Huck for giving me this opportunity and for his expert guidance throughout.

Additionally, I would like to thank Dr. William B. Anderson for his valuable advice and support. I would also like to acknowledge indispensable scientific contributions from Zirui (Ray) Yu and Scott Gray. Financial support for this work was provided by the NSERC Chair in Water Treatment and its partners; I would like to thank the undisclosed partner that provided access to a full-scale drinking water treatment plant for sampling during a portion of this work.

My deepest gratitude to my family, especially to my parents, Gary Crosina and Bonnie Daudlin, and my brother, Brent Crosina, for their unwavering love and enthusiasm. Many thanks to my close friends and fellow grad students: Laura Jones, Erika Klyszejko, Blythe Reiha, Ryan Browne, Evan Jones, Evan Wilson, and Jeff DeLoyde (to name a few) for all of their shared laughter and support. Warmest thanks also to Bridget Schmidt, Shalene Wright, and Heather Doidge for sustaining invaluable friendships from near and far. Finally, with much love, immeasurable thanks to Rod Locke.

Dedication

I would like to dedicate this work to my grandparents: Roy Crosina, Shirley Crosina, Lucille Russell, and the late Elmer Russell, whose fine efforts have created opportunities that will continue to shape generations to come.

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Chapter 1
Problem Overview and Objectives

Pharmaceuticals and personal care products (PPCPs) have been increasingly recognized as environmental contaminants (Daughton and Ternes, 1999; Weigel et al., 2004). There are several potential sources and mechanisms through which these compounds reach the environment, including wastewater effluents, agricultural runoffs, and septic system bed leaching. Consequently, such compounds have been found to be present in surface waters, ground waters, and treated waters (e.g. Kolpin et al., 2002; Sosiak and Hebben, 2005; Stackelberg et al., 2004; Zühlke et al., 2004). In many cases drinking water standards or lifetime health advisories do not yet exist for these substances, making it difficult to assess the need for removal of these compounds during treatment. If such standards did exist, they would be based only on the exposure studies with individual substances. A few researchers have evaluated the potential risks of exposure to individual pharmaceuticals at environmental concentrations, including drinking water as an exposure pathway, and have determined that there is no risk to humans (e.g. Schwab et al., 2005; Web et al., 2003). On the other hand, it is presently unclear whether there would be increased toxic effects or synergistic effects through exposure to multiple compounds, even at very low levels (Stackelberg et al., 2004). A recent study by Pomati et al. (2006) demonstrated that a mixture of pharmaceuticals at typical environmental levels (ng/L range) can lead to physiological and morphological effects on human embryonic cells. This study emphasizes the need for further studies to evaluate the long-term risks and to characterize potential interactions between pharmaceutically active ingredients present in the environment (Pomati et al., 2006).

Risk assessments are further complicated by a lack of fate and transport data since it is uncommon practice to routinely monitor for most PPCPs in water sources or finished water (Stackelberg et al., 2004). Effective analytical technology, if available, has only recently been developed (Kolpin et al., 2002) and would involve high costs if used on a routine basis. It is likely that with increased urbanization and further degradation of water supplies, contamination of source waters with PPCPs will only increase; therefore, in anticipation of relevant toxicology data, it is imperative that the water treatment industry moves forward to investigate the removal of PPCPs for which standards may exist in the future. The results can then be applied as necessary to improve drinking water quality. It is also important to have such knowledge to share with the public. Several media outlets have recently pointed out the potential risks posed by PPCPs present in the environment (e.g. CBC, 2006). As public awareness increases there is likely to be greater pressure on academia and utilities to provide some sort of response - either through relevant toxicology studies or by taking proven actions to minimize any threats.

Following that reasoning, this research set out to fill in some of the knowledge gaps surrounding the treatment of PPCPs under drinking water conditions. More specifically, this thesis paper details an investigation of the removal of select pharmaceutical compounds and one personal care product using UV irradiation alone and an advanced oxidation process

(AOP), specifically UV with hydrogen peroxide (UV/H_2O_2). This investigation addressed the following objectives:

i. To evaluate the removal of the target compounds using UV irradiation alone and UV in combination with hydrogen peroxide.

ii. To determine the reaction kinetics for direct and indirect photolysis of each selected compound.

iii. To determine the influence of major water quality parameters on the efficacy of UV and UV/H_2O_2 treatments, where the primary objective was to assess the feasibility of using UV/H_2O_2 to eliminate pharmaceutical compounds from a local drinking water source (i.e. Grand River water).

iv. To compare the applied UV/H_2O_2 doses to those that have been found to be effective for removal of taste and odour compounds, such as geosmin and MIB. In addition, UV levels required for the AOP will be compared to UV dosages conventionally applied for disinfection.

The target compounds for this study were selected based on three main criteria: a lack of relevant published data pertaining to removal of these compounds with UV/H_2O_2; that they

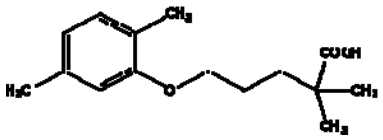
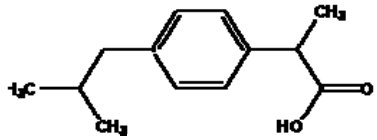
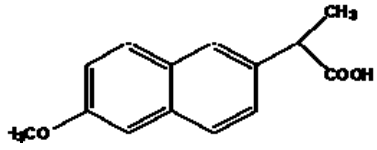
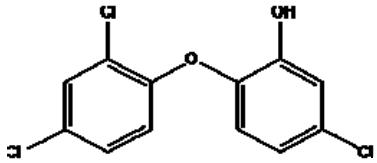
have been detected in the Grand River (Kormos et al., 2006; Yu et al., 2006), a source of drinking water for some urban areas in Southern Ontario; and that they can be analyzed for using GC/MS (the equipment available in our laboratory) with detection limits suitable for drinking water.

The list of compounds that met all of these criteria consists of three pharmaceutically active compounds (PhACs) and one personal care product (PCP):

- ibuprofen
- naproxen
- gemfibrozil
- triclosan

Naproxen and ibuprofen are both anti-inflammatory drugs. Gemfibrozil is a lipid-regulating prescription drug. Triclosan is an antibacterial agent found in personal care products such as soap, mouthwash, and toothpaste. Table 1.1 outlines the chemical properties of these four PPCPs.

Table 1.1: Chemical formulas, molecular weights, and structures of selected compounds (Source: Yu et al., 2005)

Compound	CAS No.	Chemical Formula	Molecular Weight	Structure
Gemfibrozil	25812-30-0	$C_{15}H_{22}O_3$	250.337	
Ibuprofen	15687-27-1	$C_{13}H_{18}O_2$	206.284	
Naproxen	22204-53-1	$C_{14}H_{14}O_3$	230.2628	
Triclosan	3380-34-5	$C_{12}H_7Cl_3O_2$	289.5451	

This thesis is organized into eight chapters. Following the two introductory chapters, Chapter 3 is dedicated to outlining the approach and methods that were employed. Subsequent discussion chapters are arranged according to three experimental objectives: Chapter 4 outlines the results of the exploratory experiments, Chapter 5 discusses application to partially-treated water, and Chapter 6 details the kinetics studies. Prior to the concluding

chapter, Chapter 7 is dedicated to summarizing the work and its relevance to the water treatment industry.

Chapter 2
Background and Literature Review

This section provides some background information on advanced oxidation processes (AOPs). As well, it includes an overview of relevant published research pertaining to the removal of PPCPs.

2.1 Advanced Oxidation Processes

During oxidation of organic contaminants, the ultimate goal is to produce simple, relatively harmless inorganic molecules (Parsons, 2004). Advanced oxidation processes are characterized by their production of the hydroxyl radical (•OH), a very strong oxidant, in sufficiently high concentrations to affect water quality (Glaze et al., 1990). The symbol • represents the radical center, a single unpaired electron (Parsons and Williams, 2004).

The hydroxyl radical can be generated through several different processes, all referred to as AOPs. Many of them employ treatment processes that are becoming more commonplace, such as ultraviolet irradiation (UV) and ozone (O_3). Examples include the following: ultraviolet irradiation combined with ozone (UV/O_3); ozone combined with hydrogen peroxide (O_3/H_2O_2), often referred to as Peroxone; and UV combined with titanium dioxide (UV/TiO_2). This research involved the investigation of another one of these treatments: ultraviolet irradiation combined with hydrogen peroxide (UV/H_2O_2), studied at bench-scale.

2.1.1 UV with Hydrogen Peroxide

The advanced oxidation process combining UV with hydrogen peroxide (H_2O_2) generates the hydroxyl radical by direct photolysis, or cleavage, of the hydrogen peroxide molecules (Parsons and Williams, 2004). This process has been widely studied and applied in both drinking water and wastewater applications (Tuhkanen, 2004). Nonetheless, predicting oxidation performance requires knowledge of several factors: identities and concentrations of the contaminants, both the organic and inorganic matrix of the water including radical scavengers, identities and concentrations of the oxidants in the system, the rate constant for oxidation by each oxidant at a specific site in a molecule, and the kinetic rate law for each process (Tuhkanen, 2004). That said, UV/H_2O_2 can potentially be applied to drinking water for the purpose of removing micro- and macro-pollutants (Tuhkanen, 2004).

One benefit of this process is that hydrogen peroxide is an inexpensive, readily available chemical (Glaze et al., 1987). Hydroxyl radical generation through photolysis of H_2O_2 is a direct process with a quantum yield of two hydroxyl radicals formed per photon absorbed as follows (Glaze et al., 1987; Tuhkanen, 2004):

$$H_2O_2 + \text{photon} \rightarrow {}^{\bullet}OH + {}^{\bullet}OH$$

Unfortunately, in reality this process is not as efficient as it may seem. Even though hydrogen peroxide exhibits a peak UV absorbance at about 220 nm (Tuhkanen, 2004), it has

a very low molar extinction coefficient, meaning that in order to generate a sufficient level of •OH radicals, there must be a relatively high concentration of hydrogen peroxide present, which may not be acceptable in drinking water treatment scenarios (Glaze et al., 1987). In accordance, Tuhkanen (2004) states that because of its low UV absorption coefficient, hydrogen peroxide must be present at quite high concentrations in order to generate sufficient hydroxyl radicals; on the other hand, at excessively high concentrations, surplus hydrogen peroxide molecules can react with or scavenge the hydroxyl radicals, thereby reducing oxidation efficiency (Tuhkanen, 2004). Consequently, it is important to strike a balance between hydroxyl radical generation and scavenging in order to optimize the required concentration of hydrogen peroxide. Optimization may also be desirable in terms of finding the lowest effective dose, thereby reducing the hydrogen peroxide residual that has to be removed during subsequent treatment steps.

Relevant UV/H_2O_2 studies cite a wide range of hydrogen peroxide concentrations suitable for AOP studies. For example, 1.0 M H_2O_2 (34 000 mg/L) was used for clofibric acid treatment with UV/H_2O_2 (Andreozzi et al., 2003) and 0.01 M H_2O_2 (340 mg/L) was used for diclofenac treatment with UV/H_2O_2 (Ravina et al., 2002). Similarly, Vogna et al. (2004a) tested 0.1 to 1.0 M H_2O_2 (3400 mg/L to 34 000 mg/L) for diclofenac treatment with UV/H_2O_2 and 5.0 mM H_2O_2 (170 mg/L) for carbamazepine treatment (Vogna et al., 2004b). All of these hydrogen peroxide concentrations were quite high because the investigations were focused on assessing the formation of intermediate compounds at bench-scale. Other researchers have looked at a lower range (e.g.2-15 mg/L), which is more representative of the hydrogen

peroxide doses that might be applied during full-scale drinking water treatment (e.g. Steckley et al., 2006; Mysore et al., 2006, Swaim et al., 2006). For example, Rosenfeldt and Linden (2004) found that 15 mg/L H_2O_2 gave the best results during UV/H_2O_2 degradation of bisphenol A, ethinyl estradiol, and estradiol. Furthermore, during advanced oxidation of select pharmaceuticals, Pereira (2005) used 10 mg/L H_2O_2.

During the UV/H_2O_2 process, elimination of organic compounds may result from two processes: direct photolysis resulting from UV irradiation, as well as hydroxyl radical attack (Tuhkanen, 2004), often referred to as indirect photolysis. Low pressure (LP) mercury vapour lamps with a 254 nm peak emission are most commonly used in this AOP with hydrogen peroxide absorbing maximum UV at wavelengths of about 220 nm (Tuhkanen, 2004). On the other hand, a large dissociation energy (213 kJ/mol) is required to produce hydroxyl radicals from hydrogen peroxide by cleaving the O-O bond; therefore, useful radical yields may require short wave UV energy with wavelengths between 200-280 nm (Wang et al., 2000), which are part of the broader emission spectra produced by a medium pressure (MP) UV lamp.

2.2 Challenges Associated with AOPs

The challenges that may be encountered when implementing an advanced oxidation process range from water quality issues to economical considerations. Several factors must be considered when deciding whether to use an AOP: the physico-chemical properties and concentration of the contaminants of concern, particularly the reaction rate constants with

hydroxyl radicals; the presence of radical scavengers or compounds that absorb UV; the required degree of removal; the cost; the efficiency of alternative processes; and the expected by-products (Suty et al., 2004).

The presence of •OH radical scavengers can strongly affect the efficiency of an AOP; this is particularly relevant for natural waters (Huber et al., 2003). Scavengers present in solution may hinder the rate of contaminant oxidation by reacting with the OH radicals; such scavengers include inorganic carbon species, i.e. bicarbonate and carbonate (Tuhkanen, 2004). When the hydroxyl radicals are scavenged by bicarbonate or carbonate ions, the products may be carbonate ion radicals that in turn may react with the organic compounds; however, these new radicals are more selective and have lower rate constants species (Tuhkanen, 2004). On the other hand, bicarbonate and carbonate do not adsorb UV light, they simply react readily with hydroxyl radicals (Wang et al., 2000), and thus they do not compete for UV irradiation during UV-based AOPs.

For all UV processes, feasibility is greatly influenced by the costs associated with electrical energy requirements. The electrical energy per order (E_{EO}) represents the energy required to reduce a contaminant concentration by a factor of ten (Huck et al. 1996). This parameter may be used to assess the economic feasibility of UV-AOPs and for comparing alternative UV options; however, this parameter is contaminant and water specific since it will depend on several water quality parameters, most notably the presence of radical scavengers (Huck

et al., 1996). Furthermore, E_{EO} values will be specific to a given set-up, hydrogen peroxide dose, and power level, making it difficult to draw comparisons between different studies (Cotton and Collins, 2006). On the other hand, this is a useful parameter to use during assessment since electrical efficiency will be inversely related to the E_{EO} value (Cotton and Collins, 2006). One interesting note is that E_{EO} values tend to decrease, i.e. electrical efficiency increases, with increasing hydrogen peroxide dose (Cotton and Collins, 2006).

Storage of hydrogen peroxide also warrants consideration. The rate of H_2O_2 self-decomposition to water and oxygen is strongly influenced by pH, specifically, it occurs at high pH values (Chu, 2001). Therefore, hydrogen peroxide is generally stored at pH of 5 to prevent self-decomposition. Otherwise, the use of a degraded hydrogen peroxide solution would prevent the formation of hydroxyl radicals; instead oxygen would be present, which is a much poorer oxidant (Chu, 2001). Photo-decay rates of hydrogen peroxide are also found to vary with pH; in general a higher pH will result in higher H_2O_2 decay rates and thus higher production rates for OH radicals (Chu, 2001). So the storage pH should be lower than the pH of the treated water.

2.3 Related Published Research

As discussed in Chapter 1, pharmaceuticals and personal care products (PPCPs) may enter the source waters through wastewater effluents, as well as via other pathways. These compounds are generally present at trace levels but are nonetheless of concern and in some cases have been detected in finished water, suggesting a resistance to conventional treatment.

Some studies suggest that UV irradiation may be useful for the removal of some PPCPs. For example, there have been a few investigations of the photolysis of triclosan in both in the environment and in laboratory settings. The results of these studies all show that this anti-bacterial agent found in several personal care products is readily photolyzed (Lindstrom et al., 2002; Tixier et al., 2002) although intermediates such as 2,8-dichlorodibenzo-*p*-dioxin may be formed (Latch et al., 2003). It should be noted that one of the transformations products of triclosan, methyl triclosan, has been found to be resistant to photodegradation and persistent in the environment (Lindstrom et al., 2002) with some degree of bioaccumulation observed in fish (Balmer et al., 2004). In a similar study, Packer et al. (2003) investigated the degradation of four pharmaceutical compounds: naproxen, diclofenac, and ibuprofen (all anti-inflammatory drugs), as well as clofibric acid (a lipid lowering agent) in the environment by photolysis due to sunlight exposure. They determined that direct photolysis by sunlight was an important and rapid degradation pathway for naproxen and diclofenac, but less so for clofibric acid. For ibuprofen, it seemed that indirect photolysis was required for degradation (Packer et al., 2003). For the cases where direct photolysis is an important degradation pathway in the environment, then it is likely that UV irradiation will be an effective way to degrade these PPCPs during drinking water treatment.

Advanced oxidation processes are a promising technology to deal with several organic contaminants, such as taste and odour compounds (e.g. Rosenfeldt et al., 2005), present at trace levels and may also be effective for the removal of PPCPs. In the event that complete mineralization does not occur, the parent compounds may still be sufficiently transformed

through oxidation that there is a reduction in the intended pharmaceutical effects (Huber et al., 2003). On the other hand, the resulting transformations may not be sufficient to reduce pharmaceutical effects and may in fact lead to toxic by-products (Huber et al., 2003). For example, acridine, a mutagenic compound, has been found to be an important intermediate during the advanced oxidation of carbamazepine (an anti-epileptic drug) with UV/H_2O_2 (Vogna et al, 2004b). This highlights the importance of mineralizing parent compounds during oxidation in order to ensure complete degradation and thus mitigation of toxic effects.

2.3.1 Investigations into PPCP removal with AOPs

Several bench-scale studies have been carried out to investigate the removal of pharmaceuticals using advanced oxidation. This section summarizes the most relevant studies published to-date.

Huber et al. (2003) carried out an investigation of the degradation kinetics of several pharmaceutical compounds treated with ozone and advanced oxidation; however the rate constants determined are time-based constants and are thus water and set-up specific. However, the selected compounds were found to react two to three times faster with hydroxyl radicals than several other micropollutants (e.g. MtBE, PCE, TCE, atrazine) suggesting that during water treatment, pharmaceuticals may be more efficiently removed during AOPs than other trace contaminants of concern (Huber et al., 2003).

Andreozzi et al. (2003) found that ozonating an aqueous solution of clofibric acid (1.5 mM), a lipid lowering agent, resulted in a 34.0% mineralization after 20 min and 49.1% mineralization after 60 min. These results can be contrasted with a parallel AOP study in which UV/H_2O_2 treatment resulted in nearly complete removal of clofibric acid after 60 min, though a poor degree of mineralization was achieved (Andreozzi et al., 2003). Clofibric acid is a chlorinated compounds and in both cases sufficient initial chlorine content was released as chloride to infer that no hazardous chlorinated intermediates were formed. The pH value was shown to affect the kinetic constants for ozonation but not for •OH radical attack during UV/H_2O_2 (Andreozzi et al., 2003).

Zwiener and Frimmel (2000) also investigated the removal of clofibric acid, as well as ibuprofen and diclofenac (anti-inflammatory agents). They compared conventional ozonation with O_3/H_2O_2 for the removal of these compounds from drinking water. Of the three, diclofenac was the only compound readily degraded with an ozone dose of 1 mg/L, which is evidence supporting the selective nature of ozone (Zwiener and Frimmel, 2000). The AOP process was applied to both distilled and river water solutions and at best, the compounds were degraded to 2.1%, 0.6%, and 0.1% of their initial concentration for clofibric acid, ibuprofen, and diclofenac, respectively. The river water required higher oxidant doses to overcome radical scavenging, but no degradation products could be detected (Zwiener and Frimmel, 2000). Vogna et al. (2004a) also found that both ozonation and advanced oxidation were effective methods for the reduction of diclofenac in aqueous solutions. They found that the degree of mineralization was 32% and 39% for ozone and UV/H_2O_2, respectively, after a

90 minute contact time (Vogna et al, 2004a). For diclofenac, direct photolysis was also found to be an important reaction pathway, although mineralization was not achieved with UV alone (Vogna et al., 2004a). The study by Huber et al. (2003) confirms that the direct photolysis pathway dominates during UV/H_2O_2 treatment of diclofenac.

Another study by Vogna et al. (2004b) carried out a detailed investigation into the removal of the anti-epileptic drug carbamazepine using UV/H_2O_2. While only slow degradation occurred in the presence of sunlight, UV/H_2O_2 was found to be an efficient treatment method (Vogna et al., 2004b). Although, as mentioned earlier, there was some concern regarding the formation of acridine intermediates (Vogna et al., 2004b). Unfortunately, UV fluences were not given in many of these studies, so it is difficult to accurately make comparisons.

Shemer et al. (2006) compared the removals of the antibacterial drug Metronidazole via UV, UV/H_2O_2, Fe^{2+}/H_2O_2 (Fenton), and UV/Fe^{2+}/H_2O_2 (photo-Fenton). Less than 15% removal was achieved using UV alone, with the MP lamp slightly out-performing the LP lamp. Degradation was faster through the addition of 25 mg/L of hydrogen peroxide; more specifically degradation rates were improved by a factor of 16 and 56 for the LP and MP lamps, respectively (Shemer et al., 2006). Notably, increasing the hydrogen peroxide concentration to 50 mg/L only lead to a slight increase in degradation rates (Shemer et al., 2006). MP-UV/H_2O_2 with a fluence of 250 mJ/cm^2 resulted in 65% degradation of Metronidazole compared to 60% for LP-UV/H_2O_2 at the same fluence (Shemer et al., 2006).

Some pharmaceutically active compounds, such as synthetic hormones from birth control, fall into the category of endocrine disrupting compounds (EDCs). In a study by Rosenfeldt and Linden (2004), the EDCs bisphenol A, ethinyl estradiol, and estradiol were treated with UV irradiation alone, and then UV/H_2O_2. In all cases, the AOP proved to be more effective at degrading these compounds than UV photolysis (Rosenfeldt and Linden, 2004).

In association with the AWWA Research Foundation, the Nevada Water Authority carried out an extensive study of the removal of EDCs and PhACs using several different conventional and advanced treatment processes, including UV/H_2O_2 (Snyder, 2006). They found removals better than 75%, often even complete removal, for several of these compounds, including triclosan. The results were determined using 750 mJ/cm^2 of UV with 5 mg/L of H_2O_2 and overall were very comparable to results from treatment with O_3/H_2O_2 (2.6 mg/L ozone with 0.5 mg/L H_2O_2). In contrast, they measured a range of removals for compounds spiked into natural waters at levels of 100-300 ng/L and treated with 40 mJ/cm^2 of MP-UV. For example, triclosan, naproxen and ibuprofen showed removals of approximately 65%, 25%, and 10%, respectively. During an earlier part of the same study, a range of EDCs and PPCPs were found to undergo substantial degradation with ozone alone, with marginally higher removals achieved by applying O_3/H_2O_2 (Westerhoff et al., 2004).

For her doctoral thesis, Vanessa Pereira (2005) investigated the removal of several pharmaceutical compounds: ketoprofen (analgesic), naproxen (analgesic), carbamazepine

(anti-epileptic), ciprofloxacin (antibiotic), clofibric acid (lipid regulator), and iohexol (x-ray contrast media) with both LP and MP UV irradiation and UV/H_2O_2. Furthermore, she calculated kinetic parameters for both direct and indirect photolysis of the compounds in ultra-pure water. As determined by fluence-based rate constants for the LP lamp, iohexol was the most readily degraded, followed by clofibric acid, naproxen, and carbamazepine (Pereira, 2005). For the MP lamp, the removal rate of clofibric acid was highest, followed by naproxen and iohexol, and then carbamazepine (Pereira, 2005). A comparison of MP direct photolysis rate constants determined in ultra-pure water and surface water showed a very slight difference. This was expected considering that although the water matrices were different, the calculation of the UV fluence takes into account the absorbance of the water (Pereira, 2005).

Pereira (2005) observed negligible degradation of naproxen and carbamazepine following LP-UV at 40 mJ/cm^2 applied to surface water. While some improvement was seen, the addition of hydrogen peroxide (10 mg/L) at this fluence still only resulted in removals less than 20% for all four compounds. A much higher LP-UV fluence of 1700 mJ/cm^2 resulted in less than 5% removal of carbamazepine, but naproxen removal were about 50%. On the other hand, at this same fluence, clofibric acid was degraded to 90% and iohexol was degraded to a level below the method detection limit. No significant difference was observed for these two compounds when hydrogen peroxide was added. At 1700 mJ/cm^2, LP-UV/H_2O_2 considerably improved removals for naproxen and carbamazepine, with final concentrations all below detection limits. Similar trends for these two compounds were

observed for the MP lamp. More specifically, treatment of the four selected compounds with 10 mg/L H_2O_2 at MP fluences of 100 mJ/cm^2 and 900 mJ/cm^2 resulted in as much as 50% and 90% degradation, respectively. Interestingly, iohexol was more efficiently degraded with the LP lamp than the MP lamp, which is likely to do the absorbance spectra for this compound (Pereira, 2005). Overall, Pereira found that the MP lamp was more effective at degrading the selected compounds, with the exception of iohexol.

The results of all of these studies indicate that AOPs, particularly UV-based AOPs, are a promising treatment method for the removal of pharmaceuticals and personal care products. Moreover, this literature review suggests that AOPs are more efficient than conventional oxidation or photolysis alone. From this review, it can be concluded that some of the important factors to consider in future studies are water quality parameters, particularly radical scavengers, as well as lamp type, UV fluence and hydrogen peroxide dose.

Chapter 3
Approach, Material, and Methods

This section is divided according to the three types of experiments that were performed, for each of which there is a subsequent chapter discussing the results. The design, set-up, and methods that were used are outlined as they pertain to each of these groups of experiments: ultra-pure water experiments, partially-treated water experiments, and kinetics experiments. In many cases, the emphasis is on deviations from previously described set-ups or methods.

There were three types of exploratory experiments carried out in ultra-pure water: *Preliminary*, *Competition*, and *Linking* experiments. The first category of experiments was aimed at evaluating the degradation of the compounds individually. The remaining two types of experiments examined degradation of the compounds together in solution, at a high and then at a low concentration range. Ibuprofen, naproxen, gemfibrozil, and triclosan were purchased as solids from Sigma-Aldrich (Oakville, ON). For all of the experiments, stock solutions were made by dissolving the individual compounds into ultra-pure water. Avoiding the use of a solvent eliminated possible interference and competition effects that may have otherwise occurred.

3.1 Approach for Exploratory Experiments

For the *Preliminary* experiments, the target PPCPs were studied independently in order to prevent possible competition effects. Samples were made by spiking the target compounds

into ultra-pure water at concentrations around 250 µg/L (approximately 1 µM). This concentration range is higher than those observed in the environment but provided for use of a smaller sample size (100 mL) for irradiation, which was beneficial for both experimental and analytical reasons.

The subsequent two sets of ultra-pure water experiments examined the target compounds in combination. The first set of experiments was named *Competition* experiments because the intent was to determine whether there was any apparent competition amongst the four target PPCPS during either photolysis or oxidation. It was anticipated that some of the compounds may react preferentially and thus the treatment effects for the other compounds would be diminished. These experiments were done under many of the same treatment conditions as the Preliminary experiments, the only difference being that the compounds were spiked all together in solution. The concentrations for each compound were the same as in the Preliminary experiments (approximately 250 µg/L each).

The third set of exploratory experiments was titled the *Linking* experiments. Again, the objective was to assess the removal of all four compounds in combination, but this time at a lower concentration range of 450-1500 ng/L. These experiments were later used to compare removals in ultra-pure water to experiments done using partially treated water, which were also done this lower concentration range, more representative of levels that have been measured in the environment. In order to maintain appropriate method detection limits

(MDLs), this lower concentration range required that a larger sample volume (500 mL) be irradiated and the sample processing procedure be altered.

3.1.1 Experimental Set-up and Sample Processing

This section outlines the laboratory set-up and sample processing steps.

3.1.1.1 Apparatus and UV Fluence

A collimated beam apparatus (Calgon Carbon Corp, Pittsburgh, PA) was used to carry out the irradiations (Figure 3.1). Depending on the required volume, samples were placed in 7.6 cm (for 100 mL samples) or 12.5 cm (for 500 mL samples) diameter Pyrex crystallizing dishes (Fisher Scientific, Ottawa, ON) situated on a vertically adjustable platform that supported a stir plate. The samples were centered directly below the collimating tube and gently stirred. Exposure times were determined using a spreadsheet outlined by Bolton and Linden (2003) and made available by the International Ultraviolet Association (IUVA, 2005).

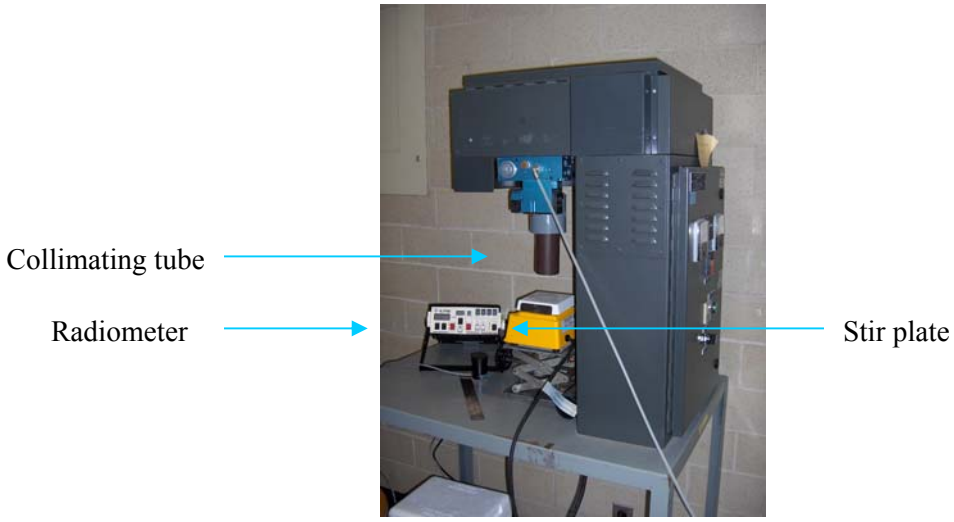


Figure 3.1: Collimated beam apparatus

Fluence or UV dose (mJ/cm^2) was obtained from the fluence rate (mW/cm^2) and the exposure time (s) (Bolton and Linden, 2003). Measurements used to determine fluence included the following: the inner diameter of the dish, the sample volume (and thus sample depth), radiometer readings on a horizontal plane extending beyond the boundaries of the dish, the absorption coefficient for the relevant irradiation wavelengths (i.e. 200-300 nm for the medium pressure lamp), which is sample specific, and the distance from center of lamp to sample surface. For all experiments, the distance from the lamp to the sample surface was set at 36 cm.

UV doses typically applied for disinfection during drinking water treatment were tested. These dosages are typically in the range of 16 to 40 mJ/cm^2 according to Zimmer et al. (2003). Similarly, the Ontario Ministry of the Environment (MOE, 2006) states 40 mJ/cm^2

as the minimum germicidal UV fluence required for primary disinfection of ground water. Pereira (2005) cites 40 and 100 mJ/cm^2 as being a typical UV doses for drinking water disinfection; she incorporated these fluences into her evaluation of direct photolysis of selected pharmaceuticals. The previously mentioned fluences are all within the range required for inactivation of pathogens, such as *Cryptosporidium* and *Giardia*, and viruses put forth by Malley et al. (2004) as well as in a draft Ultraviolet Disinfection Guidance Manual (US EPA, 2003). Comparable dosages to these were applied during this research; UV fluences of 40 mJ/cm^2 and 170 mJ/cm^2 were tested during the *Preliminary* experiments. For the *Competition* and *Linking* experiments, 40 mJ/cm^2 was applied as the lower fluence. A fluence of 300 mJ/cm^2 was also tested during the *Linking* experiments. While a considerably higher fluence of 1000 mJ/cm^2 was applied during the *Preliminary* and *Competition* experiments, as well as 4175 mJ/cm^2 during the *Preliminary* experiments. These higher fluences are all in a range comparable to UV fluences applied in relevant UV/H_2O_2 studies. For example, UV fluences up to 1700 mJ/cm^2 were used in a relevant study by Pereira (2005), while Rosenfeldt and Linden (2004) reportedly used a UV fluence of 1000 mJ/cm^2.

For this work, UV fluence was calculated using germicidal dose calculations. Germicidal fluence takes into account the absorbance spectra of DNA. Alternatively, un-weighted fluence could be calculated and would result in a shorter required exposure time, more relevant for non-biological reactions. The use of a germicidal dose allows for a more straight-forward comparison with other research and with industry where disinfection is the

primary concern. For reference, germicidal fluences of 40 and 1000 mJ/cm^2 were calculated to be equivalent to unweighted fluences of 50 and 1325 mJ/cm^2, respectively.

Both low pressure (LP) and medium pressure (MP) UV lamps were tested and compared based solely on applied fluence. The key difference between the two lamps is their emission spectra: LP lamps primarily emit at 254 nm, while MP lamps emit at various wavelengths between 200-600 nm (Stefan, 2004). The MP lamp used was a 1 kW mercury lamp (#6806A444, Hanovia, Union, NJ). A 12 W LP lamp was used (#101049, Atlantic Ultraviolet, Hauppauge, NY). In general, a longer exposure time was required with the LP lamp than the MP lamp to achieve the same fluences. Thus, for practical reasons, the LP lamp was usually used to test a smaller range of experimental conditions than the MP lamp.

In all instances, experiments were conducted with UV irradiation alone (no H_2O_2 addition) so that the results could be compared to the UV/H_2O_2 experimental results and used to differentiate between degradation due to photolysis alone and oxidation with the •OH radical.

3.1.1.2 Hydrogen Peroxide Addition and Quenching

During these studies, hydrogen peroxide (30%, Sigma-Aldrich, Oakville, ON) was dosed at 10 and/or 100 mg/L for the lower fluences and at 100 and/or 1000 mg/L for the higher fluences. Although these doses are higher than those that would be used in full-scale practice, they were based on relevant published studies (outlined in Chapter 2) and were

chosen for initial experiments to enhance the likelihood of observing a difference between the two treatment processes. Hydrogen peroxide measurements were carried out before and after irradiation following the I_3^- spectrophotometric method as outlined by Klassen et al. (1994). In all cases, minimal, if any, degradation of H_2O_2 was observed.

Liu et al. (2003) cite the importance of quenching the remaining hydrogen peroxide following UV/H_2O_2 treatment in order to reduce subsequent chlorine demand. Catalase provides a quick, effective means for quenching residual H_2O_2, even at high concentrations (Liu et al., 2003). It was important to quench the residual H_2O_2 during this bench-scale work in order to halt any ongoing reactions. This ensured that the measured concentrations accurately reflected the levels present immediately following irradiation. Therefore, in the experiments where hydrogen peroxide was added, 0.5 mL of a 4 g/L catalase (from bovine liver; Sigma-Aldrich, Oakville, ON) solution was added to each sample following irradiation.

3.1.1.3 Sample Processing

Samples for the *Preliminary* and *Competition* experiments were processed in duplicate as follows. A 20 mL aliquot was acidified to a pH of about 2 using hydrochloric acid, and then mecoprop-d^3 (EQ Laboratories, Atlanta, GA) was added as a surrogate at a concentration of 2 μM prior to extraction. Liquid-liquid extraction was performed by adding 8 mL of methyl-*t*-butyl ether (MtBE; GC grade; VWR, Mississauga, ON) followed by vigorous shaking for 10 minutes. Samples were then allowed to stand to provide for phase separation (~15 minutes) and in some cases due to time constraints, they were allowed to sit overnight at 4°C.

Following phase separation, 5 mL of organic phase was removed from each sample for analysis. The MtBE solution was gently blown off using nitrogen gas and then the samples were derivatized at 60ºC for 90 minutes after adding 200 µL of MTBSTFA (Sigma-Aldrich, Oakville, ON), following the method put forth by Yu et al. (2006). A flow chart is included in Appendix A that briefly outlines the sample processing steps.

Analyses were carried out using gas chromatography and mass spectroscopy (GC/MS). A fused-silica column (DB 1701, 30 m x 0.25 mm x 0.25 µm) was used in the GC/MS system consisting of an HP 5890, an MD 5791, and an HP 7673 auto-sampler (Agilent Technologies, Santa Clara, CA). GC/MS analysis was carried out in select ion mode (SIM) with the method and temperature program put forth by Yu et al. (2006). Some of the pertinent analytical parameters are included in Appendix A. If analysis could not be carried out immediately then derivatized samples were stored in a freezer (below -5°C) for up to three days.

Samples for the Linking experiments required a slightly different processing procedure due to the lower concentration range of the target compounds. The full volume of the 500 mL samples was acidified to a pH of about 2 using hydrochloric acid, and again, 0.5 mL of mecoprop-d^3 was added as a surrogate, this time at a concentration of 140 ng/L. Solid-phase extraction was then carried out as outlined by Yu et al. (2006) using Oasis HLB 60 mg extraction cartridges (Waters Corporation, Massachusetts, USA). If necessary, extraction

cartridges were stored in the freezer (below -5°C) overnight. Samples were subsequently eluted from the extraction cartridges with 6 mL of a 50:50 v/v acetone and ethyl acetate mixture, gently blown off using nitrogen gas, and derivatized as described earlier in this section. Again, analyses were carried out using gas chromatography and mass spectroscopy (GC/MS) in select ion mode (SIM) according to Yu et al. (2006).

3.1.2 Quality Control and Assurance

Several measures were taken to ensure and control the quality of the results. This included several sets of control experiments. One set of control experiments was carried out using H_2O_2 addition alone (no irradiation) and it was determined that the resulting degradation of target compounds was negligible. A second control experiment involved the processing of two types of samples from a stock solution (~2 μM): some taken directly from the volumetric flasks in which they were mixed and others transferred to and from a Pyrex crystallizing dish where they were stirred. The results were compared and it was determined that there was negligible loss (usually between 0.5-6%) attributable to transfer to and from the dish or due to stirring. The final set of control experiments involved a comparison of standards to which catalase was added to those that did not receive any catalase. For the most part, the differences between quantified results were less than 10% and as low as 0.02%. From these, it was determined that there was negligible loss of the target compounds due to catalase addition.

A minimum of two replicates was carried out for each compound or compound mixture at each set of treatment conditions and in addition, samples were analyzed in duplicate when liquid-liquid extraction was used. In accordance with Bolton and Linden (2003), samples were exposed to the different test UV fluences in a random order, with the replicates also randomly separated; however, each lamp type was tested in turn. For the *Linking* experiments, duplicate irradiations were conducted at each set of experimental conditions, but only single analysis could be performed since the entire irradiated sample volume was required for analysis in order to achieve a suitable detection limit with the solid-phase extraction.

Blank samples consisting of ultra-pure water were processed alongside the other samples. Quality control standards were also processed in parallel, which were made in ultra-pure water and spiked with a known concentration of target compounds. The stock solution for the standards was made using acetone or methanol as a solvent. The inclusion of standards ensured for quality assurance when samples were stored overnight following extraction.

A surrogate (mecoprop-d^3) was added to all samples, standards, and blanks during processing. The surrogate response curves were later used to normalize the data collected from the GC/MS. This normalization accounts for variability in processing and analysis.

For the liquid-liquid extraction-derivatization procedure, the method detection limit was determined to be <0.04 μM (<11 μg/L) for all four compounds, using the procedure (1030 C) outlined in Standard Methods (APHA et al., 2005). Analysis of standard solutions generally resulted in recoveries between 80-120%. For the *Linking* experiments, which were conducted at the lower concentration range and required solid-phase extraction, MDLs were determined to be <18 ng/L (<0.08 nM). In this case, recoveries were determined to be between 77 and 139%, with average recoveries for each compound between 90 and 110%.

3.2 Approach for Partially Treated Water Experiments

The second type of experiments that were carried out utilized partially treated water. This water was collected from a local drinking water treatment plant that has the Grand River in Southern Ontario as its intake source. Water was collected from a point in the treatment train at which AOP is being considered for implementation: following sedimentation and flocculation, but prior to filtration and chlorination.

Samples were collected under three seasonal conditions: winter, spring run-off, and summer. The aim was to test the treatment of UV and UV/H_2O_2 for removal of the target compounds in waters with different characteristics. The objective of these experiments was to ascertain the influence of various water quality parameters on the efficacy of the two treatments. As with the exploratory experiments, control experiments were conducted with UV irradiation alone (no H_2O_2 addition) in order to differentiate between degradation due to photolysis alone and oxidation with the OH radical.

3.2.1 Experimental Set-up and Sample Processing

The same collimated beam apparatus was utilized for the partially treated water experiments (Figure 3.1). As well, 500 mL samples were placed in the same larger capacity Pyrex crystallizing dishes as for the *Linking* experiments. Again, this allowed for a lower PPCP concentration range to be examined within the limitations of the analytical method. All four target compounds were spiked into the partially treated water at concentrations between 500-1000 ng/L, which is more representative, although on the high end, of reported environmental levels (e.g. Kolpin et al., 2002; Sosiak and Hebben, 2005).

For the partially treated water experiments, after quenching of the hydrogen peroxide and surrogate addition, samples were pre-filtered using 0.45 μm hydrophilic mixed cellulose ester membrane filters (Pall Corporation; VWR, Mississauga, ON) and a vacuum apparatus. Previous studies showed that losses due to pre-filtration were negligible (Yu et al., 2006). Samples were then processed in the same manner as described for the *Linking* experiment samples, as previously outlined in Section 3.1.1.3.

Two replicate irradiations were conducted at each set of experimental conditions, but only single analysis could be performed since all of the irradiated sample volume was required for analysis in order to achieve a suitable detection limit with the solid-phase extraction. As with the exploratory experiments, analyses were carried out using gas chromatography and mass spectroscopy (GC/MS) in select ion mode (SIM) according to Yu et al. (2006).

Both LP and MP lamps were tested to treat the partially treated water. For practical reasons pertaining to required exposure times, the experiments with the LP lamp were limited to a fluence of 40 mJ/cm^2 in combination with 0, 3, and 10 mg/L of H_2O_2 (higher fluences would have required exposure times up to several hours long). Three fluences were tested with the MP lamp: 40, 100, and 300 mJ/cm^2, each in combination with 0, 3, and 10 mg/L of H_2O_2. These lower hydrogen peroxide doses are more representative of what would be applied at full-scale (as discussed in Chapter 2), as opposed to the higher doses applied during the exploratory experiments.

Several water quality parameters were measured: pH, total organic carbon (TOC), nitrate, turbidity, UV absorbance, and alkalinity. Measurements were performed using Standard Methods (APHA et al., 2005); specifically, the following procedure numbers were used: 4500-H^+ (pH), 5310 C (TOC), 4500-NO_2^- B (nitrate), 2130 (turbidity), 5910 B (UV absorbance), and 2320 (alkalinity). These parameters may give an indication of the presence of substances in the water that are known to scavenge hydroxyl radicals or compete for UV irradiation. As well, UV absorbance can be converted to UV transmittance, which is an important parameter to consider during design and implementation of UV systems (Cotton and Collins, 2006; US EPA, 2003).

3.2.2 Quality Control and Assurance

Several steps were taken to control and assure the quality of the experiments. Blank samples consisting of un-spiked sample water were processed alongside the other samples. These

background samples indicated any detectable concentrations of these target compounds present in the water present prior to spiking; however, any background levels were included as part of the initial concentrations used to calculate percent removals.

Experimental sets were replicated in order to achieve a minimum of two data points under each set of conditions. In accordance with Bolton and Linden (2003), samples were exposed to the different UV fluences in a random order, with the replicates also randomly separated. However, each lamp type was tested in turn.

As with the exploratory experiments, a surrogate (mecoprop-d^3) was added to all samples, standards, and blanks during processing. The surrogate response curves were later used to normalize the data collected from the GC/MS. This normalization accounts for variability in processing and instrumental analysis of the samples. Method detection limits (MDLs) were determined for the partially treated water as outlined in Standard Methods. For the partially-treated water experiments, MDLs were higher than for ultra-pure water, presumably due to the water matrix; they were in the range between 35-125 ng/L (0.17-0.43 nM).

Experiments were conducted as soon as possible after sample collection in order to maintain consistent water quality parameters. Water sampled from the treatment plant was stored in the fridge at 4°C between experiments for up to one week. Solvent-free spiking was done the same day as treatment and was carried out in batches of 3 to 4 L of sampled water, which

was then vigorously mixed for about an hour in order to dissolve the compounds and to achieve a uniform concentration.

3.3 Approach for Kinetics Experiments

The final set of experiments carried out was aimed to collect data with which to estimate the kinetic parameters associated with direct and indirect photolysis for the degradation of the select compounds. Experiments were carried out at a range of fluences for both the MP and LP lamps, with and without hydrogen peroxide addition.

The MP lamp was tested at the following fluences: 40, 100, 170, 300, 400, 500, 600, 1000, 4175 mJ/cm^2. The same fluences up to 500 mJ/cm^2 were repeated during the experiments with hydrogen peroxide addition. Due to the considerably longer exposure times, the LP lamp was tested at a fewer number of fluences: 40, 100, and 300. The hydrogen peroxide dose used during the AOP experiments with both lamps was 10 mg/L.

3.3.1 Experimental Set-up and Sample Processing

The set-up and processing for these experiments is almost identical to the *Preliminary* experiments. The compounds were studied independently, in ultra-pure water solutions at the same concentration range (~ 2 μM) used for the *Preliminary* experiments. Correspondingly, samples were processed and analyzed using the same liquid-liquid extraction and derivatization procedure outlined for the *Preliminary* and *Competition* experiments.

3.3.2 Quality Control and Assurance

As with the *Preliminary* and *Competition* experiments, blanks and standards were processed alongside all samples.

Chapter 4
Ultra-pure Water Experiments

This chapter outlines the results of the exploratory ultra-pure water experiments, which were the starting point for the overall investigation. Detailed results for these experiments are included in Appendix B.

4.1 Compound Absorbance Spectra

Throughout this work, an HP 8453 UV-visible spectrophotometer (Agilent Technologies, Santa Clara, CA) was used to determine the UV absorbance spectra of the sample solutions, correcting for the background absorbance of the water matrix. For ease of comparison, the absorbance spectrum for each compound in solution was measured at a high concentration range prior to starting the experiments (Figure 4.1); the shapes of the absorbance curves are still relevant for lower concentration ranges. It should be pointed out that the ibuprofen and gemfibrozil curves overlap in Figure 4.1, making them difficult to distinguish.

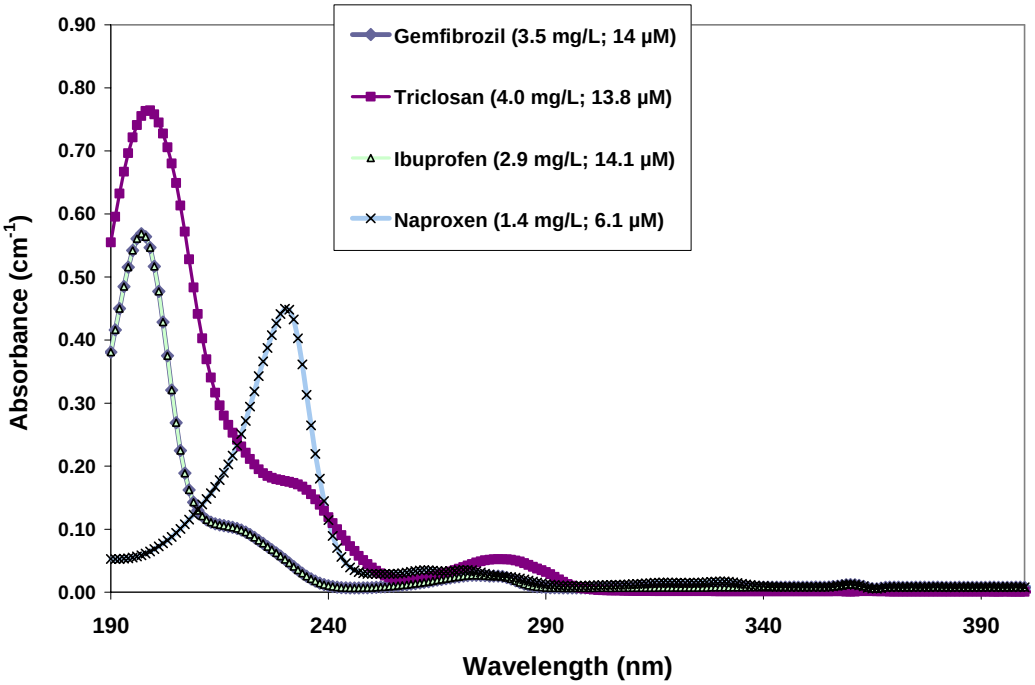


Figure 4.1: Absorbance spectra for target compounds

These absorbance plots were then overlaid with the spectral output of the two lamp types: the medium pressure lamp and the low pressure lamp (Stefan and Bolton, 2002) as shown in Figure 4.2. Some predictions could then be made based on the comparison between lamp output and compound absorbance. In order for compounds to undergo photolysis, one condition is that they must absorb UV irradiation at the wavelength(s) emitted, although other factors such as compound structure, also play a role. Due to the low absorbance of irradiation at the 254 nm wavelength by all four compounds, it was expected that they would all undergo minimal photolysis when exposed to low-pressure UV irradiation. All of the compounds had a slightly higher absorbance in the 270-290 nm range and absorbance

maxima below 240 nm, which suggested that medium pressure UV irradiation would be more effective at inducing photolysis (when lamp performance was compared at the same fluence). It should be noted that although the MP lamp emits at wavelengths above 300 nm, it is wavelengths between 200-300 nm that are usually of interest (and used for fluence calculations) for drinking water treatment since they are in the germicidal range (Bolton, 2000).

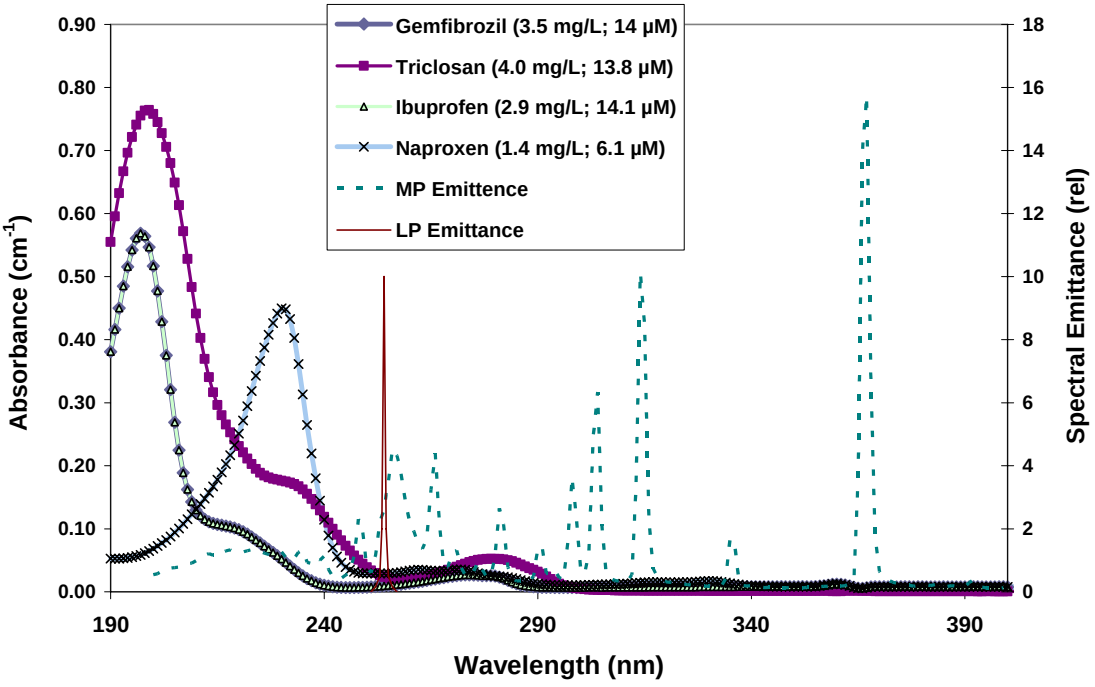


Figure 4.2: Compound absorbance plots with MP and LP lamp emission spectra

4.2 Preliminary Experiments

The *Preliminary* experiments served to determine whether there was any degradation of the compounds resulting from either UV treatment alone or UV/H_2O_2. These experiments were carried out in what was considered to be a best-case scenario: the compounds were studied independently and in an ultra-pure water matrix. As detailed in Chapter 3, the compounds were spiked at a concentration of approximately 250 µg/L and were processed using liquid-liquid extraction followed by derivatization and GC/MS analysis.

The *Preliminary* results using LP UV irradiation alone at a typical disinfection fluence of 40 mJ/cm^2 resulted in little or no removal for any of the compounds (Figure 4.3). The highest percent removal observed with LP-UV was for triclosan. It was expected that triclosan and naproxen would be susceptible to photolysis based on some results in the literature that were outlined in Chapter 2 (e.g. Packer et al., 2003; Pereira, 2005; Tixier et al., 2002). The results from a typical AOP fluence were notably better than those using a typical disinfection fluence. A higher applied LP-UV fluence of 1000 mJ/cm^2 improved removal for naproxen and triclosan to 25% and 80%, respectively, confirming that these two compounds are susceptible to photolysis (Figure 4.3). In contrast, gemfibrozil was not readily degraded with UV alone. Unfortunately, the integrity of both ibuprofen samples was compromised during processing and so percent removals are not available for this compound at 1000 mJ/cm^2 (as indicated on the graph). It appears that production of the •OH radical led to the partial removal of these two compounds (between 25-55%) following an LP-fluence of 40 mJ/cm^2

with the addition of 100 mg/L of H_2O_2. Additions of hydrogen peroxide also lead to considerable improvement in the removals of naproxen and triclosan.

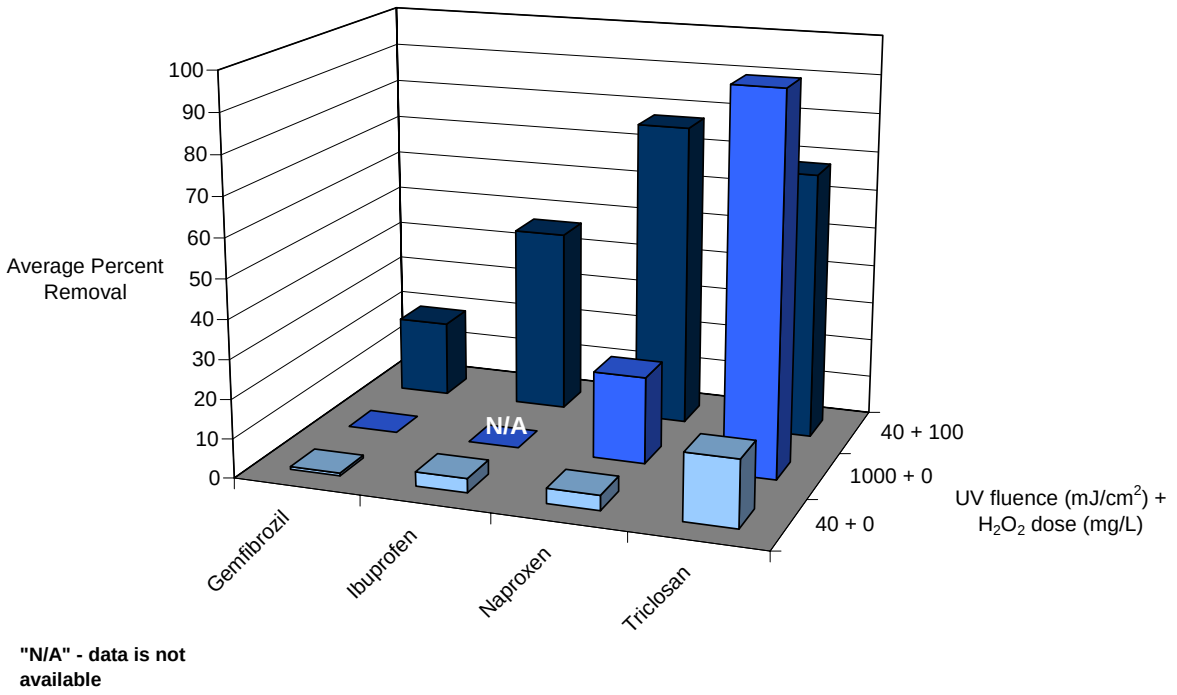


Figure 4.3: Preliminary results using the LP UV lamp

Irradiation with the MP lamp resulted in higher removals than with the LP lamp, even at low fluences (Figure 4.4). This was expected based on the broader emission spectrum of the MP lamp. In accordance, gemfibrozil and ibuprofen were less resistant to photolysis when MP-UV was applied. Once again, at higher fluences, improved removals were seen using the MP lamp, with some degradation observed for ibuprofen and gemfibrozil and nearly complete

degradation of naproxen and triclosan at 1000 mJ/cm^2. All compounds underwent more than 98% degradation with an MP-UV fluence of more than 4000 mJ/cm^2.

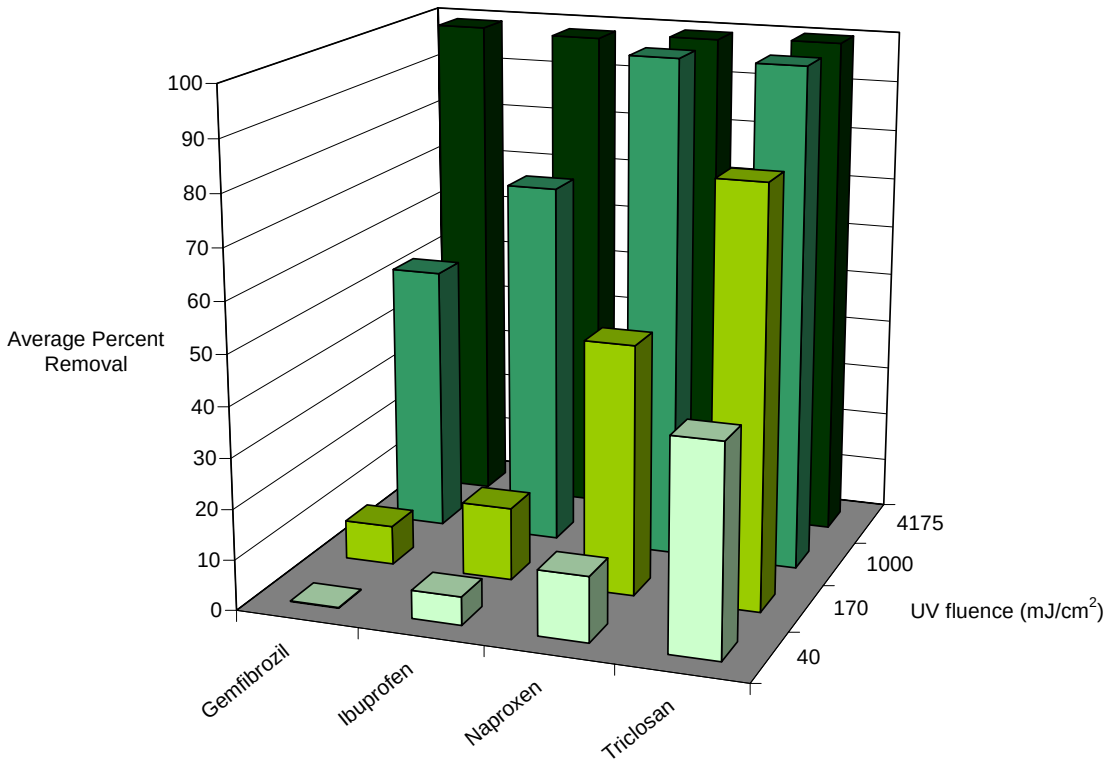


Figure 4.4: Preliminary irradiation results using the MP UV lamp

The addition of hydrogen peroxide improved the degradation results for all compounds at all fluences (Figure 4.5). At the lower fluences, in the range typical for disinfection, removals of all compounds were at least 40% with the addition of 100 mg/L of hydrogen peroxide. Furthermore, a H_2O_2 dose of 1000 mg/L at 1000 mJ/cm^2 and 4175 mJ/cm^2 resulted in more than 99% removal of all four compounds. As mentioned in Chapter 3, degradation of the

target compounds was negligible during control experiments using hydrogen peroxide addition alone (no irradiation). Consequently, improved degradation during irradiation in the presence of H_2O_2 is due to the formation of •OH radicals.

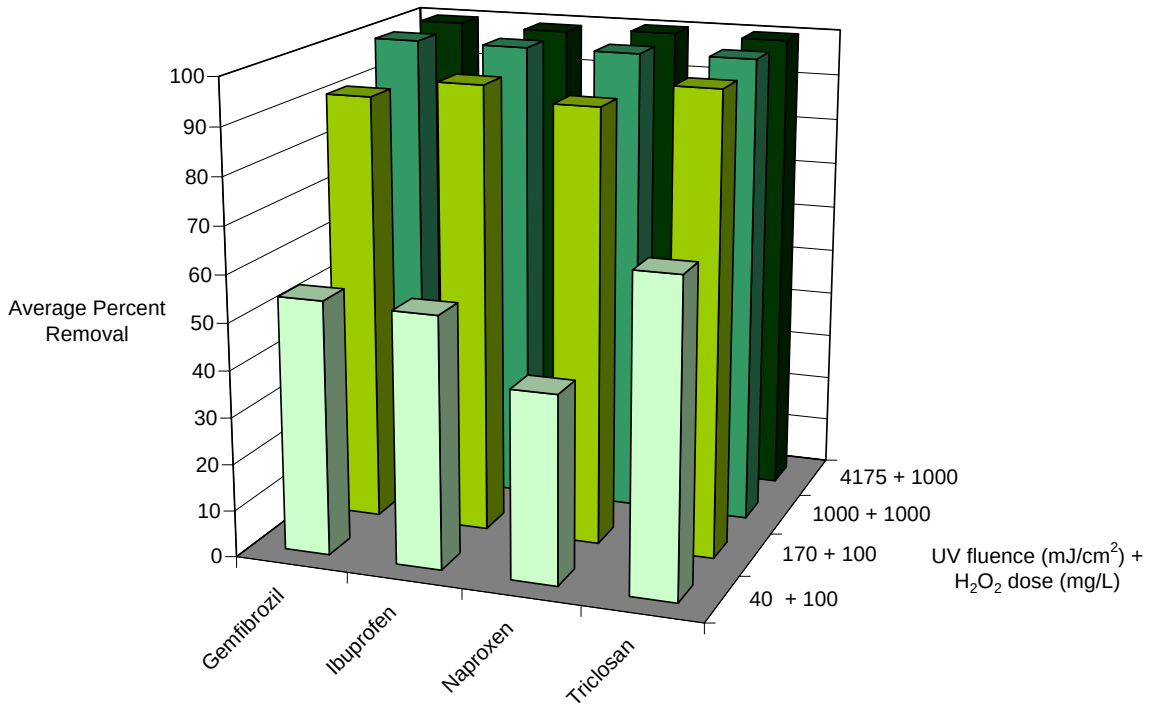


Figure 4.5: Preliminary AOP results using the MP UV lamp

Standard deviations could not be shown on these graphs, but were generally low (often less than 5%) and are provided in Appendix B.

To summarize, the results of these *Preliminary* experiments showed that when compared at the same fluences, the MP lamp was more effective than the LP lamp at degrading the target compounds, a trend that was particularly true for ibuprofen and gemfibrozil. On the other hand, with both lamps, the addition of hydrogen peroxide improved removals for all four compounds. In fact, almost 90% removal of these compounds was achieved at an MP-UV fluence of only 170 mJ/cm^2 plus 100 mg/L of H_2O_2, as opposed to the higher fluences of 1000 or 4175 mJ/cm^2 required for UV alone.

4.3 Competition Experiments

The *Competition* experiments were carried out at a few of the same treatment levels as the *Preliminary* experiments. The goal was to ascertain whether having all of the target compounds present in solution (as may be the case in real waters) had any impact on treatment efficiency as opposed to when they were alone in solution. These experiments were carried out at the same individual concentration range (~250 μg/L) as the *Preliminary* experiments and again in an ultra-pure water matrix; the difference being that all four compounds were spiked together in solution. It should be noted that although individual compounds were at the same concentration as in the *Preliminary* experiments, the total contaminant concentration was higher (~1000 μg/L).

The results show that the compounds that were determined to be less susceptible to photolysis during the *Preliminary* experiments, namely gemfibrozil and ibuprofen, exhibited lower removals when in combination than during individual irradiations (Figure 4.6). In fact,

the average percent removal for ibuprofen was fifty-three percentage points less than during the *Preliminary* experiments. This suggests that naproxen and triclosan out compete gemfibrozil and ibuprofen for photons, perhaps due to faster reaction rates. The same trend was seen for both the LP and MP lamps, but was most evident at the higher MP-fluence. The remainder of the results is included in Appendix B.

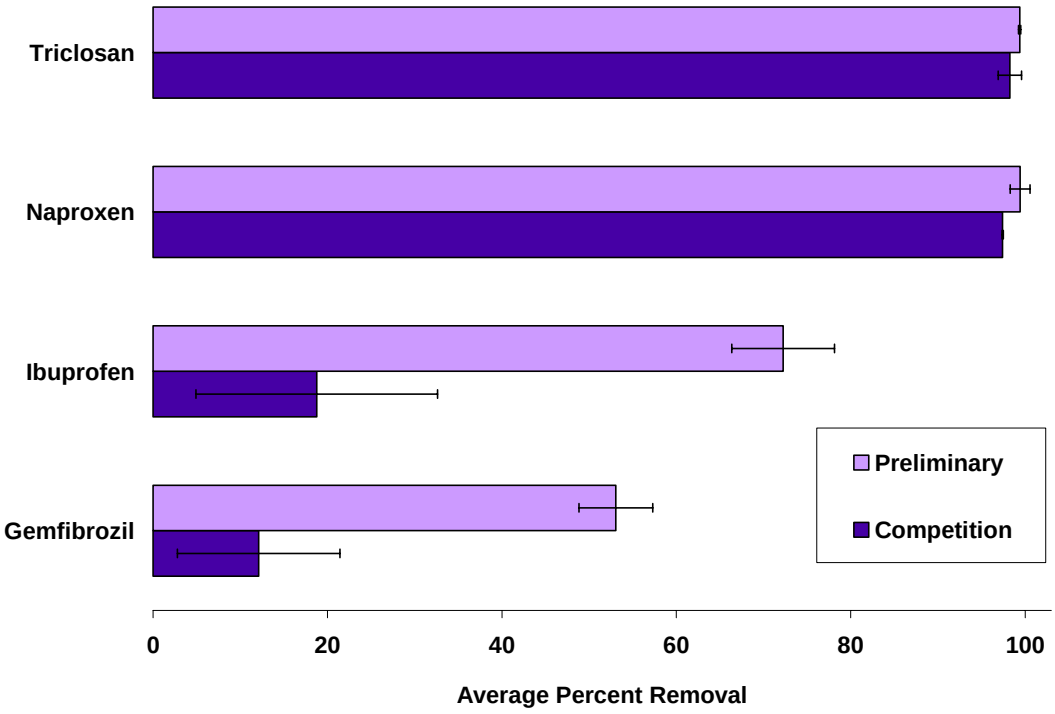


Figure 4.6: Comparison of removals following an MP-UV fluence of 1000 mJ/cm^2

Similar reductions in treatment efficiency were seen for the UV/H_2O_2 process at a low UV fluence of 40 mJ/cm^2. Triclosan, naproxen, and ibuprofen exhibited less degradation when they were in solution with the other target compounds compared to when they were alone in solution (Figure 4.7). This decreased treatment efficiency was most obvious at the lower

fluence, with removals as much as fourty-eight percentage points lower than in the mixed solution. The exception is the result for gemfibrozil, which exhibited more degradation (about fourteen percentage points higher) during the *Competition* experiment with the LP lamp at a fluence of 40 mJ/cm^2 with 100 mg/L of H_2O_2 added. This inconsistent result may be a result of analytical error. Alternatively, it may be explained by the behaviour of gemfibrozil under these specific conditions, which is not yet understood and may pertain to differences in its compound structure when compared to the other target PPCPs.

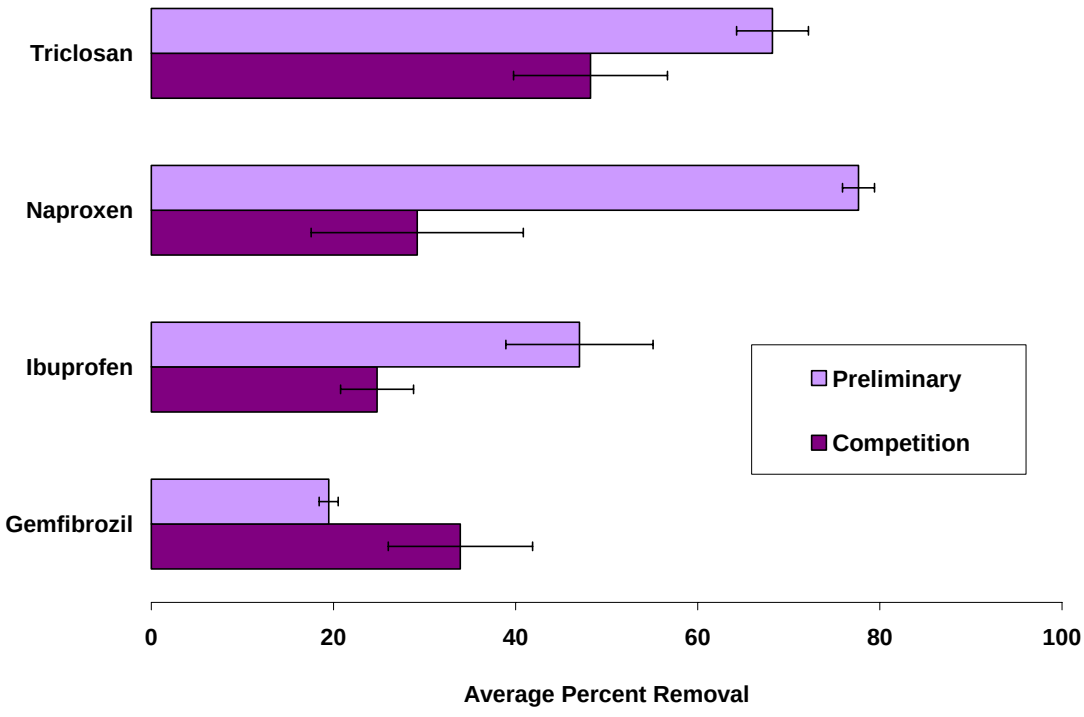


Figure 4.7: Comparison of removals following an LP-UV fluence of 40 mJ/cm^2 with 100 mg/L of H_2O_2 added

The same trend was also seen for the UV/H_2O_2 process employing the MP lamp, although with less pronounced differences, the greatest being for ibuprofen for which degradation was fourty-four percentage points less than during *Preliminary* experiments (Figure 4.8). In this case the trend for gemfibrozil was more consistent with the other three compounds.

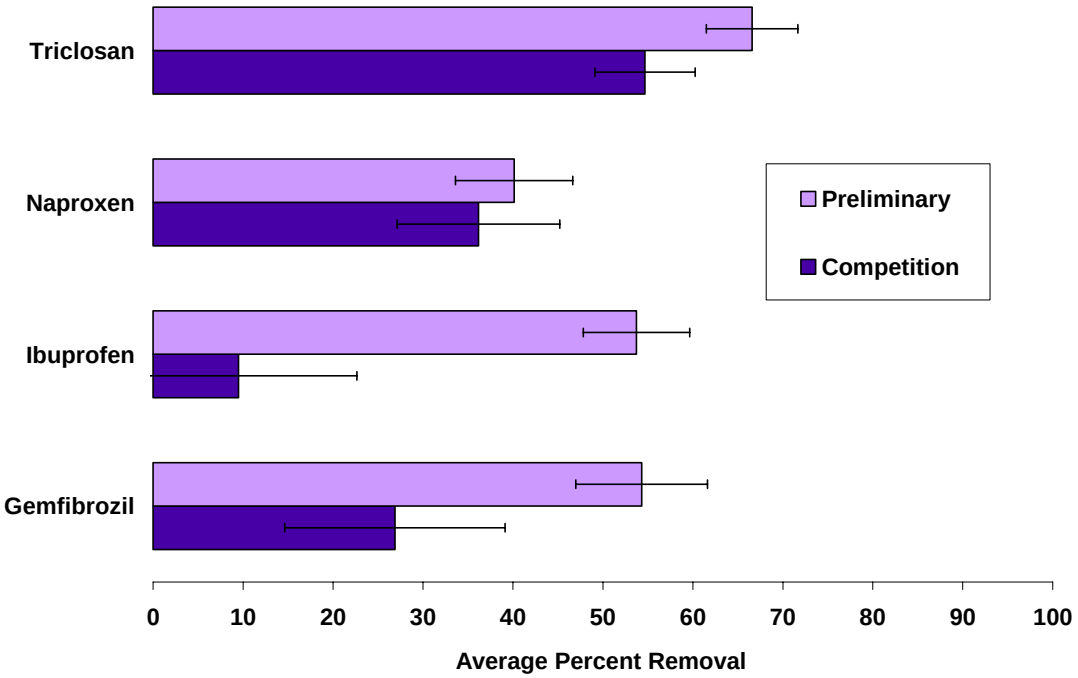


Figure 4.8: Comparison of removals following an MP-UV fluence of 40 mJ/cm^2 with 100 mg/L of H_2O_2 added

The removals for the *Preliminary* and *Competition* experiments at high fluences and high hydrogen peroxide doses were comparable; in both cases the average removals approached 100% (Figure 4.9). This implies that sufficient hydroxyl radicals were formed to nearly completely degrade the target compounds. When contrasted with the differences between

results at low fluences, this suggests that competition for the •OH radical may lead to limiting reactions, thereby reducing the degradation of certain compounds when it is in short supply.

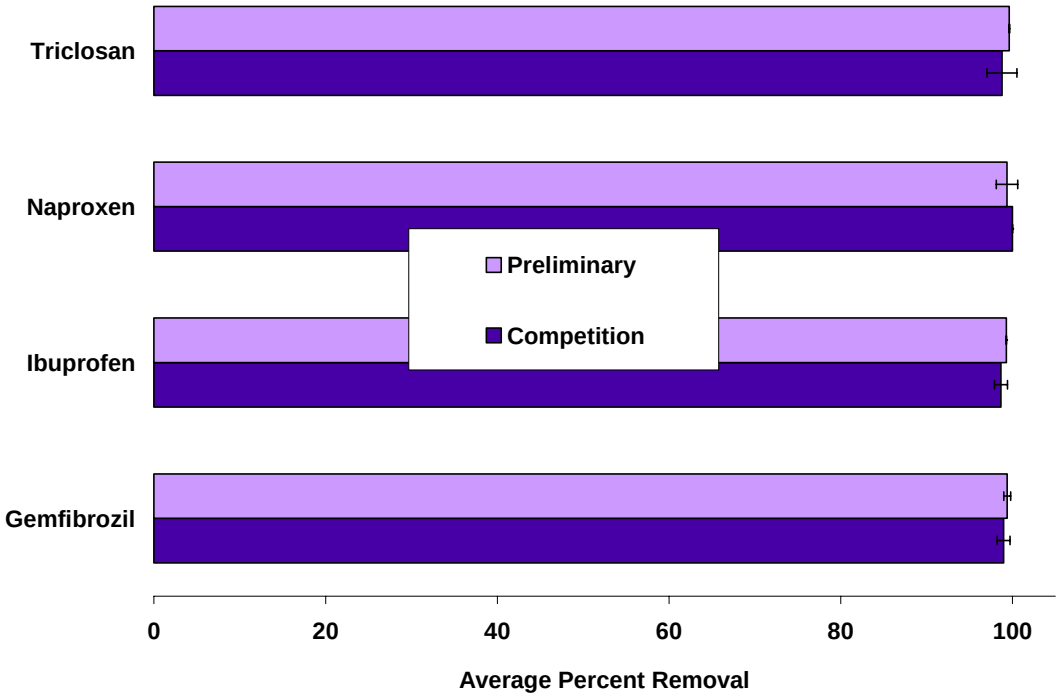


Figure 4.9: Comparison of removals following an MP-UV fluence of 1000 mJ/cm^2 with 1000 mg/L of H_2O_2 added

Additional *Competition* results are included in the Appendix B. Overall these results show that removals of the target compounds may be reduced when other compounds able to undergo photolysis or react with the hydroxyl radical are also present in solution. Such hindered degradation may apply to compounds that are less susceptible to photolysis or to

cases where there is an insufficient concentration of •OH radicals to completely degrade all compounds. These lower removals may also be explained by the higher total contaminant concentration present in the *Competition* experiments compared to the *Preliminary* independent experiments. When examining the removal of one particular compound, the role of the other target contaminants present in solution may be analogous to an interfering water matrix. If that is the case, the availability of •OH radicals may be an important factor determining degradation. Similarly, UV absorbance by the other contaminants may present some sort of matrix effect not adequately accounted for in the fluence calculation, thereby inhibiting photolysis of the other compounds.

4.4 Linking Experiments

The *Linking* experiments were carried out to determine if competition effects were still observed and if the same overall trends were seen when the target compounds were present at lower concentrations. As outlined in Chapter 3, during the *Linking* experiments the target PPCPs were spiked at concentrations between 450 -1500 ng/L, as opposed to the higher range (~250 μg/L) at which the *Preliminary* and *Competition* experiments were carried out. This lower concentration range is more representative of the levels at which these compounds have been detected in the environment. These experiments were also used to make a link (thus their name) between the ultra-pure water experiments and the partially-treated water experiments, which were all conducted using the same contaminant concentration range. A secondary objective of the *Linking* experiments was to ascertain

whether the hydrogen peroxide dose influenced the UV/H_2O_2 results, which was done by testing two different hydrogen peroxide doses at the lower fluence of 40 mJ/cm^2.

The low pressure lamp was tested at one fluence using three hydrogen peroxide levels: 0, 10, and 100 mg/L. As expected, the results showed a significant improvement in percent removals with the addition of hydrogen peroxide (Figure 4.10); however, there was no obvious difference between the two levels of hydrogen peroxide and in practise concentrations higher than 10 mg/L would rarely be applied.

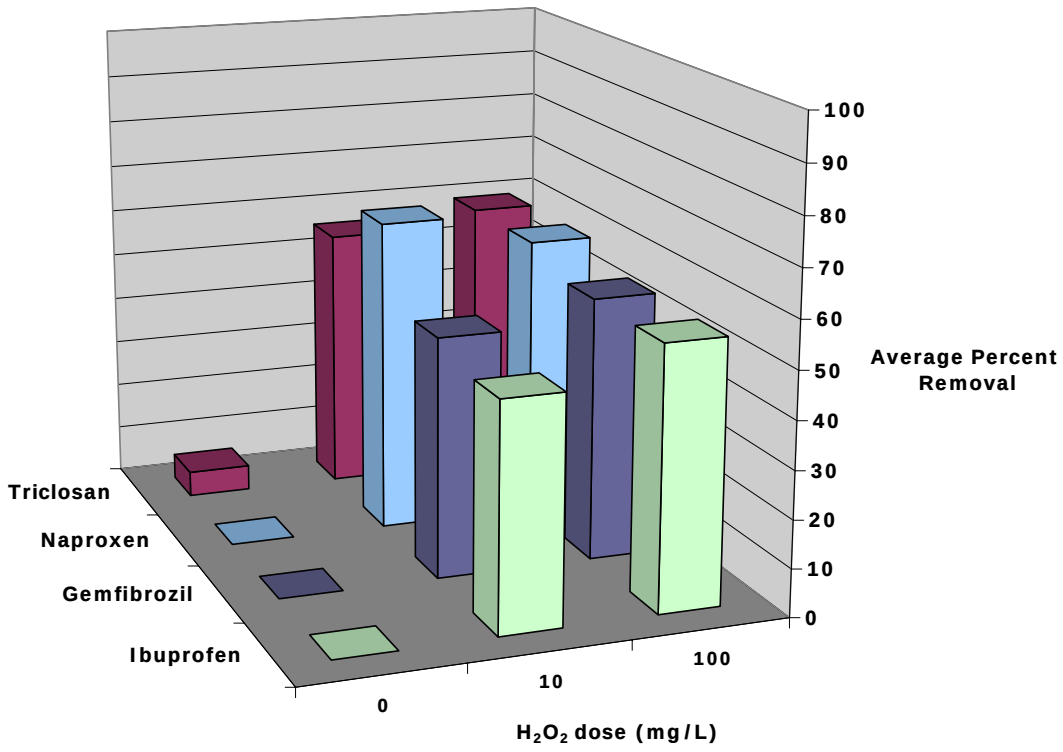


Figure 4.10: Linking experiments with LP lamp at a fluence of 40 mJ/cm^2

The MP lamp was tested at two UV fluences and again, in both cases, the addition of hydrogen peroxide led to improved degradation of the target compounds (Figure 4.11). All four target compounds were at least 97% degraded with a UV fluence of 300 mJ/cm^2 and 10 mg/L of hydrogen peroxide added.

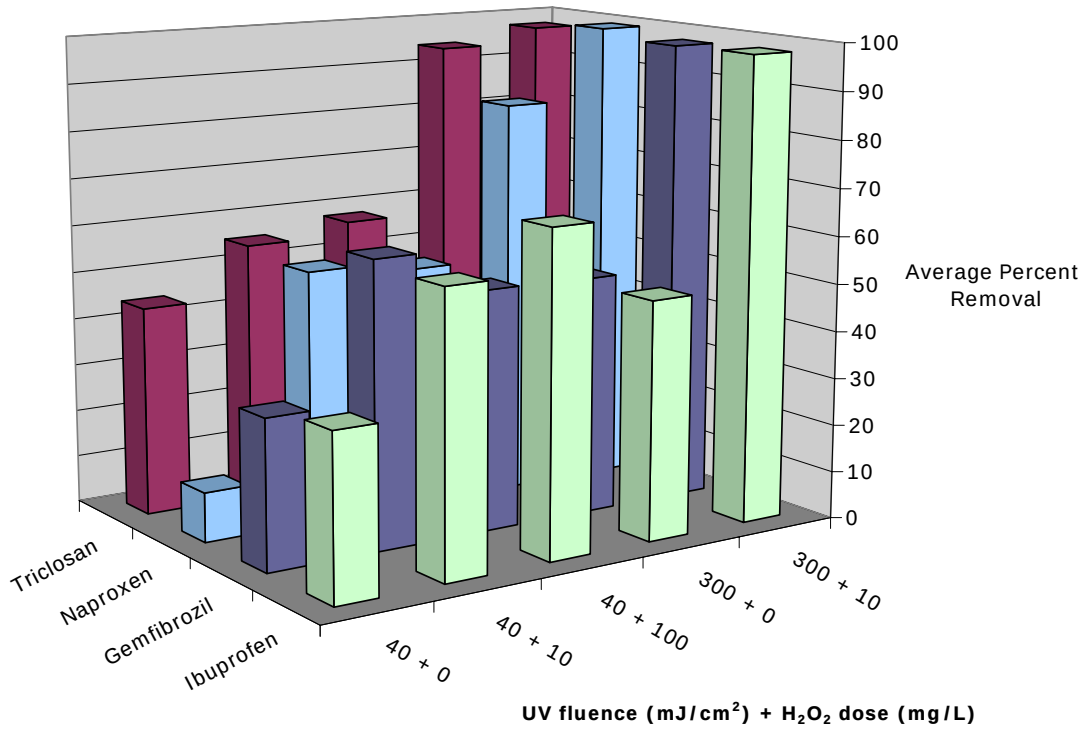


Figure 4.11: Linking experiments carried out with MP lamp

These results can be weighed against the other ultra-pure water experiments. At a low LP fluence of 40 mJ/cm^2, the *Linking* experiments appear to elicit similar results as the *Preliminary* and *Competition* experiments (Figure 4.12). Comparable trends were also seen

for the MP lamp, although removals of ibuprofen and gemfibrozil were improved at the lower concentration range of the *Linking* experiments (Figure 4.13). The error bars on these figures represent one standard deviation above and below the average percent removals (calculated using two replicate irradiations for the *Linking* experiments).

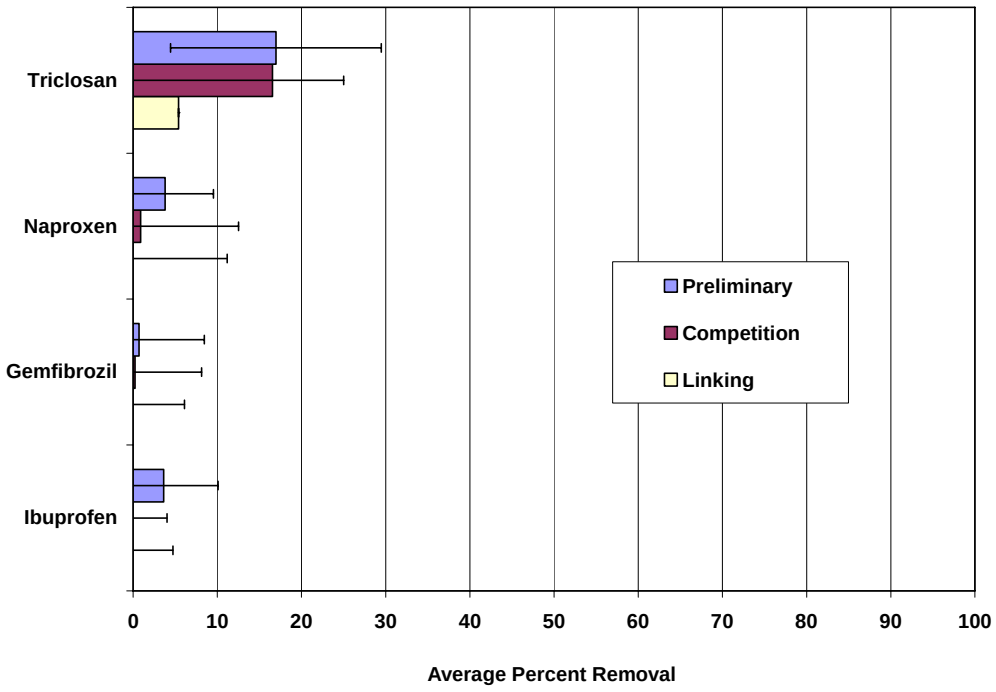


Figure 4.12: Linking experiments with LP lamp at 40 mJ/cm^2

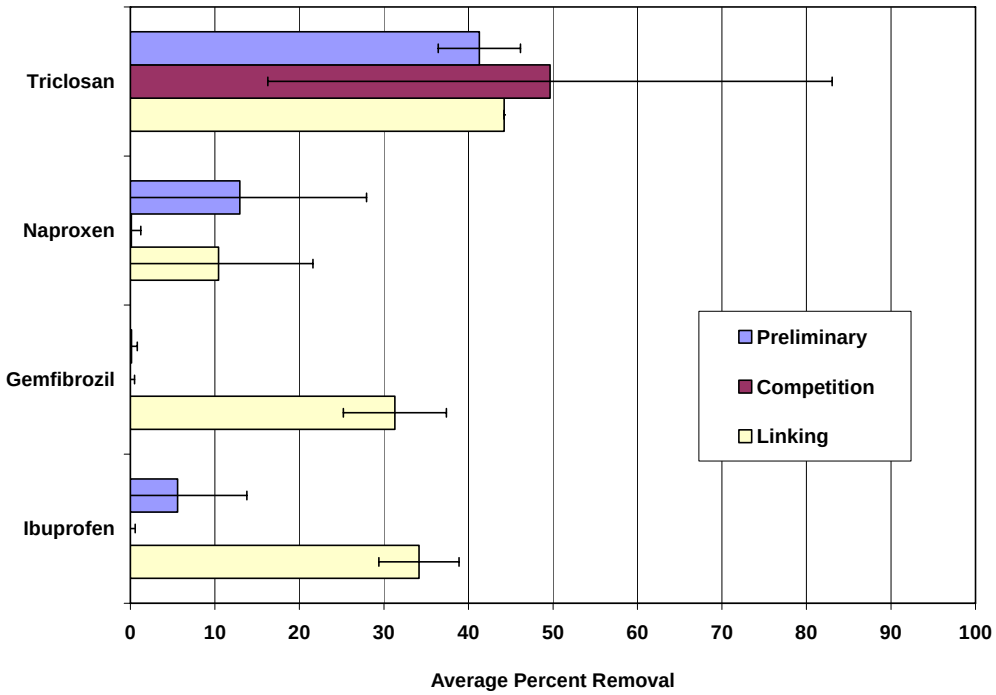


Figure 4.13: Linking experiments with MP lamp at 40 mJ/cm^2

A comparison of the UV/H_2O_2 results shows a similar contrast between the three experimental sets (Figure 4.14). Even at the low fluence, the average percent removal for all compounds was better for the *Linking* experiments than the *Competition* experiments. This is likely due to the fact that the concentration of target compounds was much lower and thus required less treatment to remove the same or a higher percentage of the initial concentration. Furthermore, the overall contaminant concentration was lower in the *Linking* experiments which meant that any matrix effects that may have existed in the *Competition* effects would be lessened, while •OH radical availability would likely be increased. For ibuprofen and gemfibrozil, the two compounds that are less susceptible to photolysis, the *Linking*

experiments employing the LP lamp achieved removals as much as thirty percentage points higher than the *Competition* experiments. Again for gemfibrozil and ibuprofen, the results of the *Linking* experiments were also better than the *Preliminary* experiments during which the compounds were alone in solution (albeit at a higher concentration). It should be noted that the *Linking* results in Figure 4.14 are representative of only one sample because the second sample was unintentionally over-exposed to the UV light (resulting in a fluence of 44 mJ/cm^2) and is not included in this comparison; however, it is interesting to note that at a fluence of 44 mJ/cm^2, removals were about ten percentage points higher than at 40 mJ/cm^2, which still corroborates the trend of higher removals at this lower concentration range.

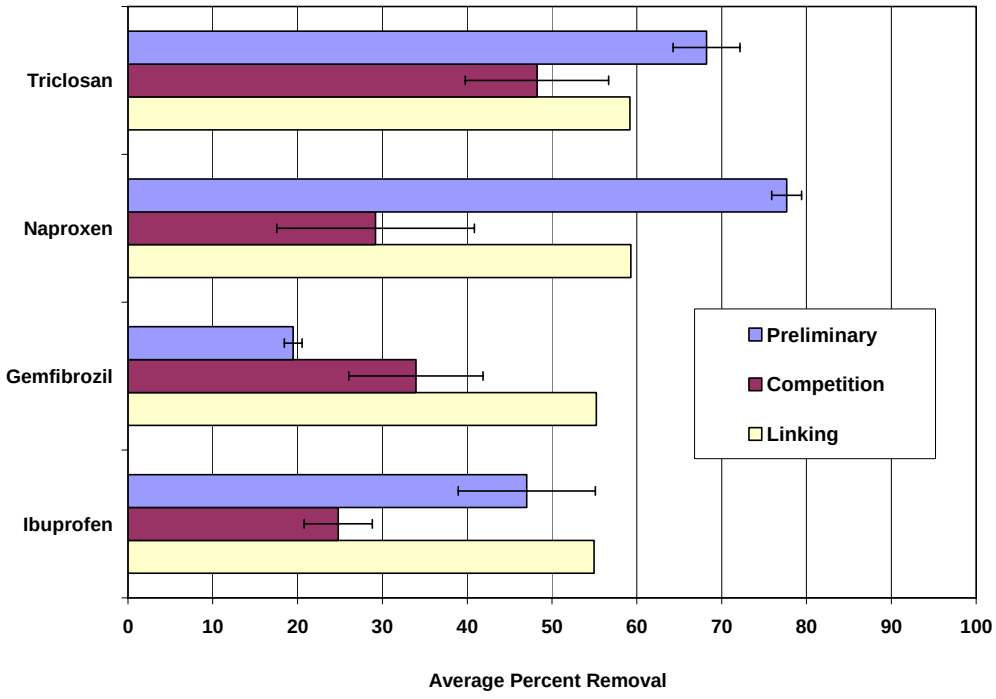


Figure 4.14: Linking experiments with LP lamp at 40 mJ/cm^2 + 100 mg/L H_2O_2

Similar contrasts between the *Competition* and *Linking* experiments can be made for the results from the medium pressure lamp with hydrogen peroxide addition where *Linking* experiments resulted in removals as much as fifty-eight percentage points higher than during the *Competition* experiments. Again, the improved removals at the lower concentration range were most evident for gemfibrozil and ibuprofen (Figure 4.15). The removals for the *Linking* experiments are more similar to those seen during the *Preliminary* experiments under these treatment conditions.

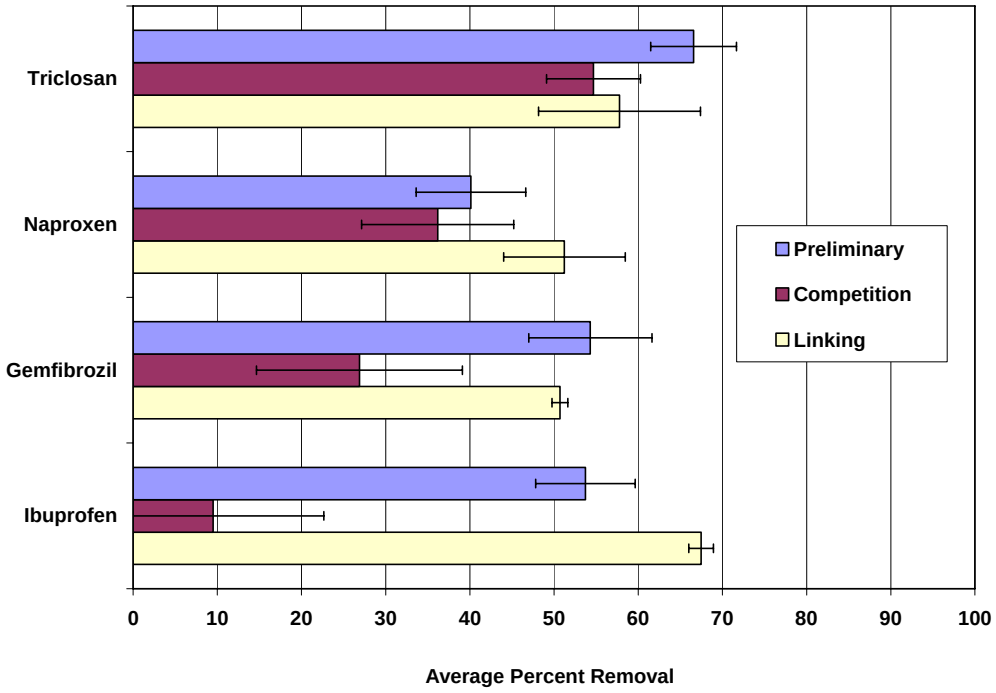


Figure 4.15: Linking experiments with MP lamp at 40 mJ/cm^2 + 100 mg/L H_2O_2

Overall, the results of the *Linking* experiments suggest that the efficiency of UV/H_2O_2 may be concentration-driven, with improved removals achieved when the contaminants are

present at lower levels and the overall concentration of organic compounds in solution is lower. The same may be true for UV irradiation alone, although it was only evident for the two compounds less susceptible to photolysis (i.e. ibuprofen and gemfibrozil) and only with the MP lamp.

A summary of the results presented throughout this chapter can be found in Chapter 7, Section 7.1.

Chapter 5
Partially-treated Water Experiments

For the experiments using partially treated water, samples were collected from a water treatment plant for which the source is the Grand River, Ontario. The sampling point was a location in the treatment train at which the plant operator was considering implementing an AOP; that is to say, following the flocculation and sedimentation step. The sampled water was neither filtered nor chlorinated. More often though, UV and UV-based AOPs are implemented post-filtration; therefore, this earlier sampling location provided a sort of worst-case scenario with respect to water quality. Sampling events occurred during three seasons: winter, spring run-off, and summer. Several water quality parameters were measured: pH, TOC, nitrate, turbidity, UV absorbance, and alkalinity. These parameters give an indication of the presence of substances in the water that may scavenge hydroxyl radicals or compete for UV irradiation. Water quality measurements are presented in Table 5.1.

Table 5.1: Water quality measurements for the three partially-treated waters

	Winter	Spring Run-off	Summer
pH	7.4	7.3	7.6
turbidity (NTU)	0.55	0.59	0.25
TOC (mg/L)	4.07	5.33	4.75
alkalinity (mg/L as $CaCO_3$)	204	152	138
nitrate (mg/L) (NO_3-N)	0.4	1.6	2.0

One noteworthy difference between the three seasonal waters is alkalinity; the winter water contained 204 mg/L as $CaCO_3$ while the spring run-off and summer water contained 152 and 138 mg/L as $CaCO_3$, respectively. Alkalinity is of concern because of its hydroxyl radical scavenging properties. Conversely, the spring and summer waters contained higher nitrate levels than the winter water. Nitrate is known to readily absorb UV irradiation and thus may compete for photons; however, the presence of nitrate should be compensated for in the measured absorbance of the water matrix, which is used to determine the exposure time required to achieve a specific fluence. The TOC measurements differed slightly but were in the range of 4 to 5 ppm. It should also be noted that, even though the total amount present did not vary appreciably, the character of the TOC may have changed between the three seasons (and this might have an effect on treatment). Although the TOC was measured during this study, it was not characterised. In addition, it should be considered that during full-scale application of such treatment, the water temperature may influence results, but

during these experiments sampled water was refrigerated and then allowed to approach room temperature before experiments were conducted; therefore, temperature effects were not evaluated. The results for the partially treated water were compared to experiments that used ultra-pure water spiked with a mix of target compounds at the same concentration range of 1000 ng/L.

The UV absorbance for all three waters was converted to UV transmittance (T_λ) at wavelength λ using the following equation as outlined by Bolton (2001):

$$T_\lambda = 10^{-A_\lambda}$$

Percent transmittance ($\%T_\lambda$) is then simply the transmittance multiplied by 100%. The results are shown in Figure 5.1. The transmittances for all three waters are very comparable, with slightly lower transmittance seen for the summer water between 240-290 nm. For comparison purposes, the transmittance of ultra-pure water spiked with the same concentration of target compounds is also shown in Figure 5.1.

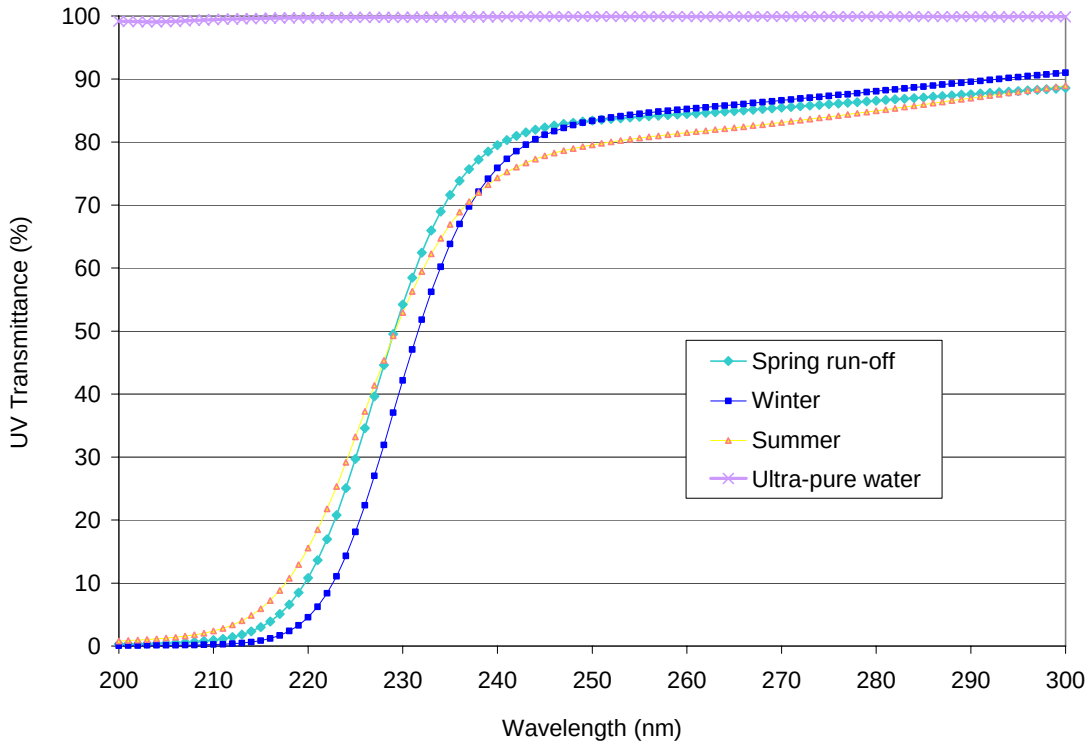


Figure 5.1: Percent UV Transmittance for partially treated waters

5.1 Results for the Low-pressure UV

The LP lamp was used at a low fluence (i.e. 40 mJ/cm^2) for experiments with all three waters. Higher LP fluences were not tested for a few reasons: removals during the ultra-pure water experiments were generally low, much lower than with the MP lamp; with the available set-up, high LP fluences required very long exposure times (up to several hours), which were not very realistic for the time-frame of the experiments; as well, the practicality of high LP fluences for full-scale applications will greatly depend on the number of lamps and the configuration available. For the LP experiments that were conducted, tests were carried out with and without hydrogen peroxide. As detailed in Section 3.2.1, replicate

irradiations were done for each set of experimental conditions, but only single analysis could be carried out for each since the full sample volume was required for processing.

For the winter and spring water, two H_2O_2 doses were tested: 3 mg/L and 10 mg/L. There were no observed differences between treatments with these doses, so only the higher dose was tested for the summer water. It is important to note that the measured H_2O_2 doses for the summer water experiments were between 7 and 8 mg/L. Although the intended dose was 10 mg/L, it may be that the hydrogen peroxide solution had degraded and a lower concentration was actually dosed. Similarly, for the spring water, the measured doses were usually closer to 9 mg/L than 10 mg/L. However, since little difference was seen between H_2O_2 doses of 3 and 10 mg/L for the winter water or between 3 and 9 mg/L for the spring run-off water, it is expected that the results for H_2O_2 doses between 8 and 10 mg/L within the context of these experiments should be very comparable. As well, minimal, if any, degradation of the H_2O_2 was observed when measurements were taken before and after irradiation, which suggests that H_2O_2 was not the limiting factor for the reactions. On the other hand, there is likely an optimum H_2O_2 dose, which will be water and fluence specific as discussed in Chapter 2, but determining the optimum dosages was beyond the scope of this work.

The results for the LP lamp showed minimal, if any, removals with 40 mJ/cm^2 irradiation for all three sampled waters. Low, yet comparable removals were observed for all three seasonal waters at a fluence of 40 mJ/cm^2 (Figures 5.2, 5.3, and 5.4).

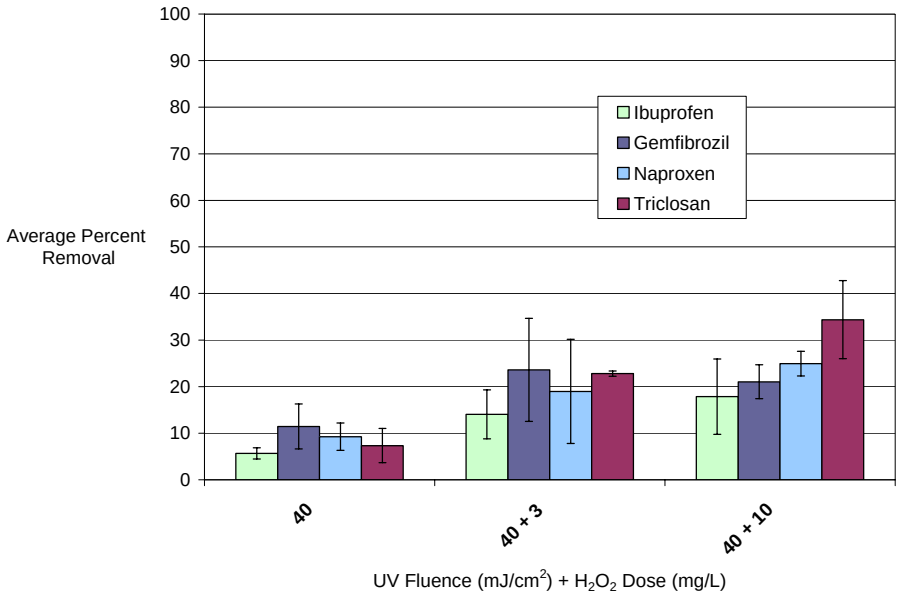


Figure 5.2: Average percent removal of target compounds spiked into partially treated winter water and subjected to LP-UV and LP-UV/H_2O_2

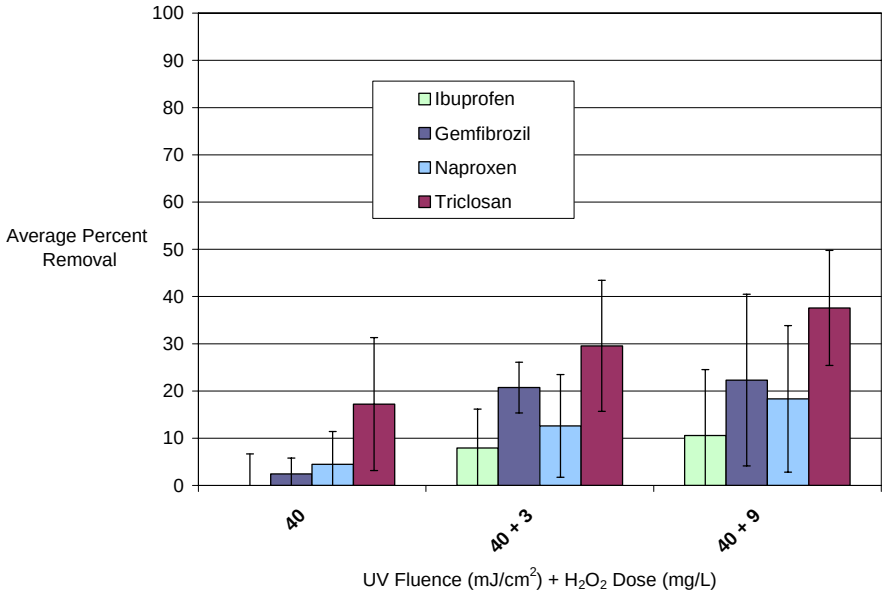


Figure 5.3: Average percent removal of target compounds spiked into partially treated spring run-off water and subjected to LP-UV and LP-UV/H_2O_2

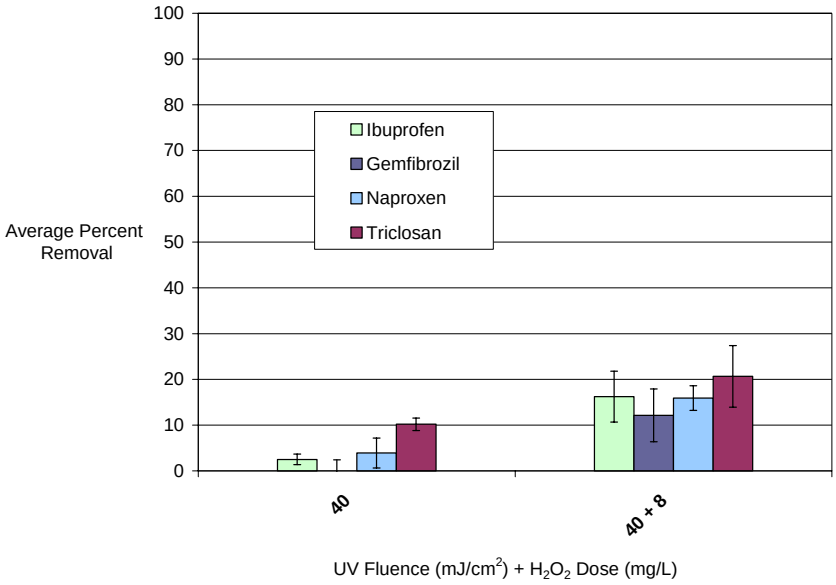


Figure 5.4: Average percent removal of target compounds spiked into partially treated summer water and subjected to LP-UV and LP-UV/H_2O_2

The error bars shown on Figure 5.2, as well as other graphs in this chapter, show one standard deviation above or below the average percent removal for the two replicate samples. At this fluence of 40 mJcm^2, the addition of hydrogen peroxide consistently improved removals for ibuprofen and gemfibrozil by about ten percentage points. For ibuprofen and naproxen, average removals were highest for the winter water. Average removals for gemfibrozil and triclosan were highest in the spring water, with comparable removals seen in the winter water, but lower removals seen in the summer water. An evaluation of water quality parameters shows that the winter water had the lowest levels of TOC and nitrate. On the other hand, the winter water had the highest alkalinity while summer water had the highest nitrate level. The contrasting results may be related to one or more of these water

quality parameters, but further investigation would be required for confirmation. It should also be mentioned that the large error bars (representative of standard deviations) suggest that the differences may not be statistically significant, but again, additional experiments would be required for confirmation.

As expected after the results of the exploratory experiments, triclosan consistently underwent the most degradation of the four compounds spiked. That said, given that removals were largely below 30%, these results confirm that the LP lamp is not effective at removing any of these compounds at a typical disinfection dose, even with the addition of hydrogen peroxide at reasonable doses. They also suggest that water quality may affect the treatment effectiveness.

5.2 Results for Medium-pressure UV

The medium-pressure lamp was employed to test a range of fluences, as high as 500 mJ/cm^2, for treatment of the three sampled waters. To reiterate, at 40 mJ/cm^2, hydrogen peroxide was tested at two doses: 3 and 10 mg/L, for the winter and spring waters, but no remarkable difference was observed between the two sets of results, and thus only the 10 mg/L dose was applied to the summer water. As with the LP experiments, in some cases sample measurements indicated that the H_2O_2 dose was slightly less than intended.

5.2.1 Winter Sampling Conditions

For the winter water, the MP lamp led to measurable degradation of all four compounds, even at the low fluence of 40 mJ/cm^2 (Figure 5.5). Figure 5.5 also shows the results for 100 mJ/cm^2. At the lowest fluence, the results for naproxen are similar to the results for gemfibrozil and ibuprofen. On the other hand, naproxen removals were as much as twenty percentage points greater than ibuprofen and gemfibrozil removals at 100 mJ/cm^2, which is in agreement with the results from Chapter 4 showing that naproxen is more susceptible to photolysis than the other two. Similarly, as expected, triclosan underwent the most degradation, with removals above 85%. For all four compounds, the addition of hydrogen peroxide at a fluence of 40 mJ/cm^2 did not lead to improved removals. It is possible that under these particular matrix conditions this low MP-fluence was insufficient to produce a sufficient level of hydroxyl radicals to cause perceptible oxidation of the target compounds, either because hydroxyl radical formation was somehow impeded or hydroxyl radicals were at first scavenged.. The benefits of adding H_2O_2 were not seen until the higher fluences (100 and 300 mJ/cm^2) were applied, at which point removals were especially enhanced for ibuprofen and gemfibrozil, when compared to UV alone (Figures 5.5 and 5.6). It should be noted that in some cases one or more sample data sets had to be rejected (and are not included in this thesis), often due to problems with surrogate addition (thereby preventing accurate normalization of the data), and so standard deviations could not be calculated. In addition, when both data sets were below the MDL, standard deviations were not calculated. In such instances, error bars are not shown on the graphs.

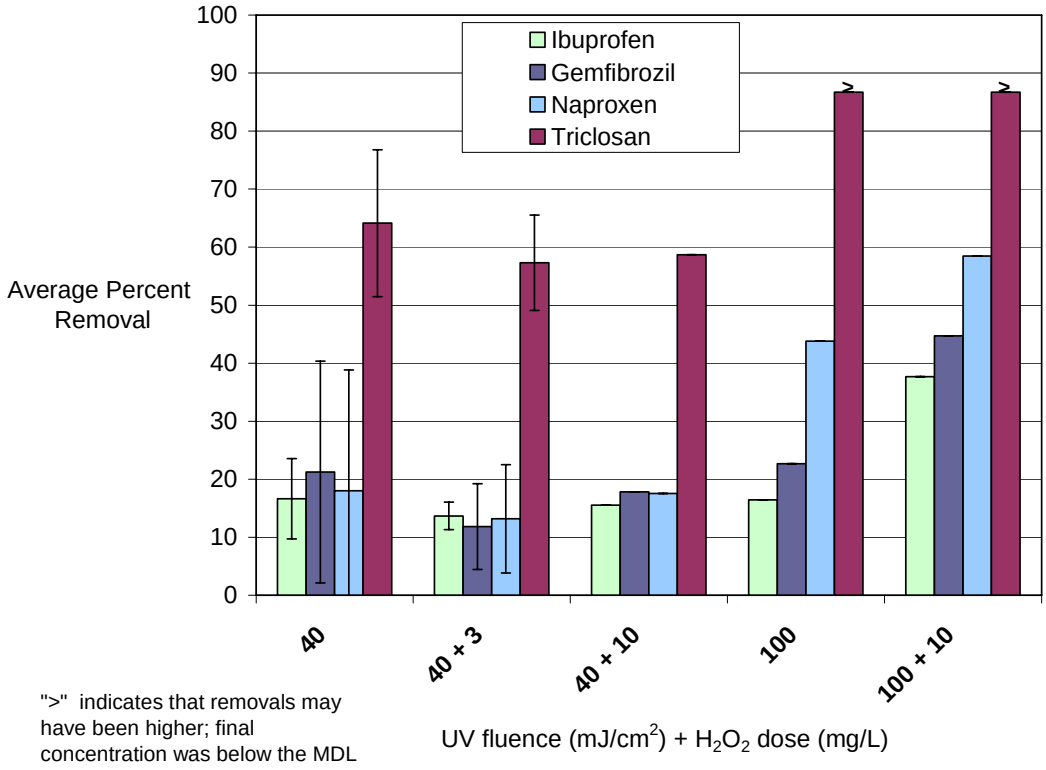


Figure 5.5: Average percent removal of target compounds spiked into partially treated winter water and subjected to MP-UV and MP-UV/H_2O_2 at fluences of 40 and 100 mJ/cm^2

A fluence of 300 mJ/cm^2 with the addition of 10 mg/L of H_2O_2 resulted in removals between 46 and 82% for ibuprofen, gemfibrozil, and naproxen (Figure 5.6). The removal for triclosan was 84% or possibly even better since the final concentration was below the method detection limit.

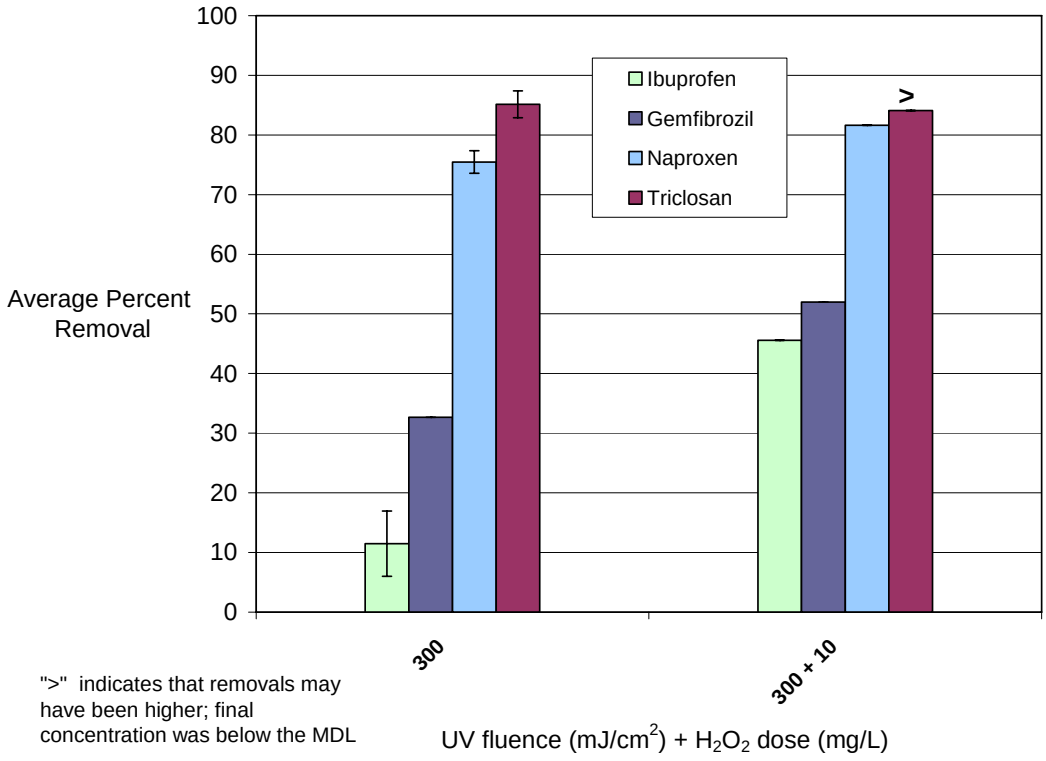


Figure 5.6: Average percent removal of target compounds spiked into partially treated winter water and subjected to MP-UV and MP-UV/H_2O_2 at a fluence of 300 mJ/cm^2

Overall, these results confirm that UV fluences higher than those typically used for disinfection are required to cause substantial degradation of these compounds. Furthermore, the MP UV was more effective than LP UV, which is in agreement with the findings presented in Chapter 4 as well as several results presented by other researchers (e.g. Pereira, 2005; Shemer et al., 2006) as discussed in Chapter 2. In contrast, however, the addition of H_2O_2 only appreciably improved removal in combination with the higher fluences.

5.2.2 Spring Sampling Conditions

The MP results for the spring water are very comparable to those for the winter water. The complete results for the spring water are presented in Appendix C (Figure C.1).

As shown in Figure 5.7, the percent removals of triclosan observed in the spring run-off water were very comparable to those in the winter water.

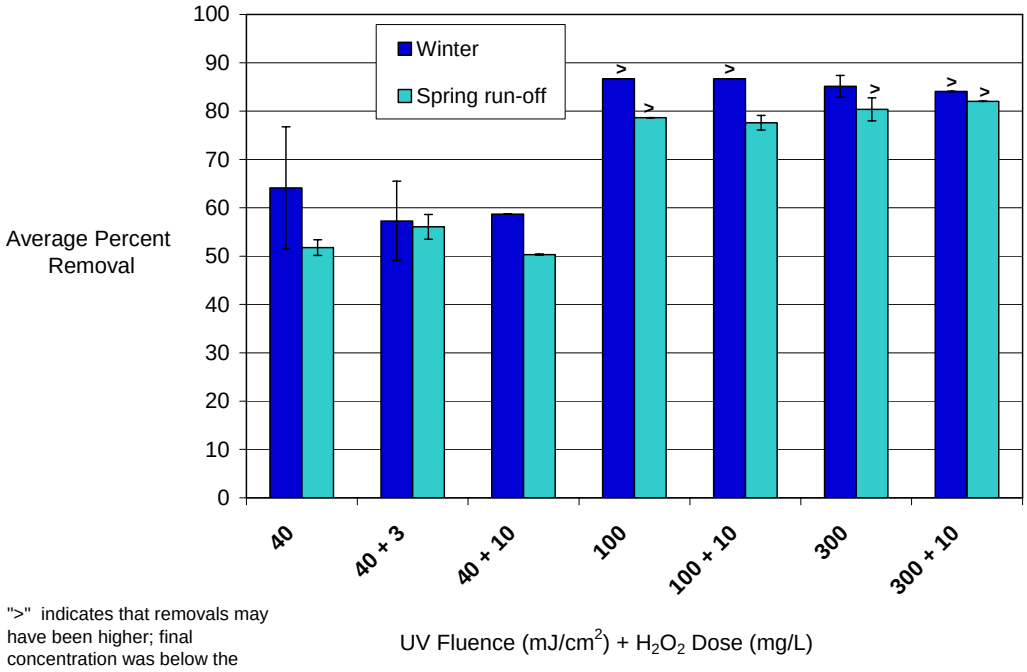


Figure 5.7: Average percent removal of triclosan spiked into partially treated winter and spring water and subjected to MP-UV and MP-UV/H_2O_2

The removals for naproxen and gemfibrozil also compared well with the winter water results, although with more variability (Appendix C, Figures C.2 and C.3). On the other hand, for

ibuprofen, removals with UV alone were consistently lower in the spring run-off water, as illustrated by Figure 5.8. This may be due to one or more water quality parameters, such as turbidity, TOC, and nitrate concentration, all of which were slightly higher in the spring run-off water. Since the UV transmittance for the two waters is very similar, it may be that something in the water matrix is competing for UV irradiation or scavenging hydroxyl radicals; however, the competition for UV should be accounted for when the absorbance of the water is factored into the calculation of the exposure times required to achieve a specific fluence. Moreover, the ibuprofen results for UV alone are not as expected since subsequently higher UV fluences did not produce equal or greater percent removals.

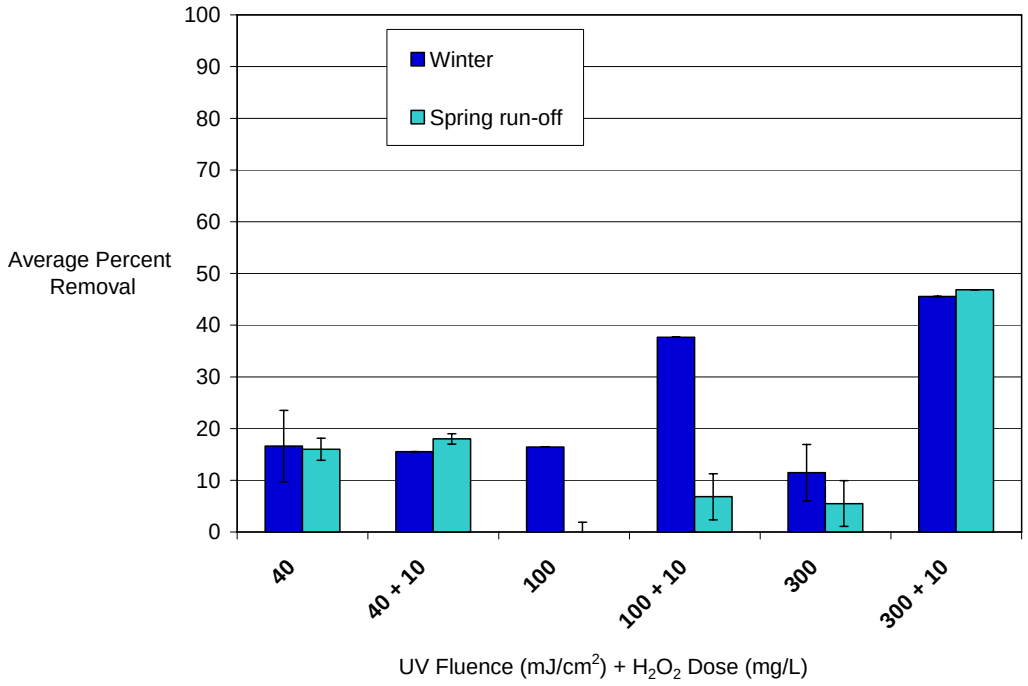


Figure 5.8: Average percent removal of ibuprofen spiked into partially treated winter and spring water and subjected to MP-UV and UV/H_2O_2

An attempt was made to run standards using the matrix water in order to calculate recoveries; however, for several reasons (e.g. unable to accurately correct for background concentrations), the recoveries were not meaningful and it is not appropriate to look to them for explanation. If proper recoveries had been carried out, the results may have shown that the discrepancies in these spring water results are due in part to analytical error. Moreover, there may be analytical errors that are specific to this water matrix. It is possible however, that such error would at least partially cancel out during calculation of the percent changes. This point will be discussed further in the context of the summer water.

There is no consistent difference between waters for the UV/H_2O_2 results, as exhibited in Figure 5.8. It would be expected that the AOP results might be less affected by water quality than the UV results if the affecting substances in the water matrix were competing for UV, rather than scavenging hydroxyl radicals.

5.2.3 Summer Sampling Conditions

For the partially treated water sampled during the summer conditions, the same experimental conditions were applied, with the exception of 40 mJ/cm^2 with 3 mg/L of H_2O_2, which was not tested for this water. As mentioned previously, this set was eliminated because no difference was seen between hydrogen peroxide doses at this low fluence for the winter and spring run-off waters. Two additional experimental conditions were added to the set: 500 mJ/cm^2 and 500 mJ/cm^2 + 10 mg/L of H_2O_2. Since only triclosan had been degraded to levels below the MDL during experiments with the winter and spring run-off waters it was decided

to test a higher fluence to see if the other three compounds would be further degraded. The complete set of results for the summer water are presented in Appendix C (Figure C.4).

The results for the summer water were somewhat different than expected. As shown in Figure 5.9 for ibuprofen, the removals at points where a UV fluence of 40 mJ/cm^2 was applied are higher for the summer water than was seen for the other two waters. Furthermore, the results for ibuprofen do not necessarily follow any of the trends established thus far. More specifically, the removals seen with 40 mJ/cm^2, 40 mJ/cm^2 + 8 mg/L H_2O_2, and 100 mJ/cm^2 are much higher than expected, especially when compared with the results of UV alone at higher fluences.

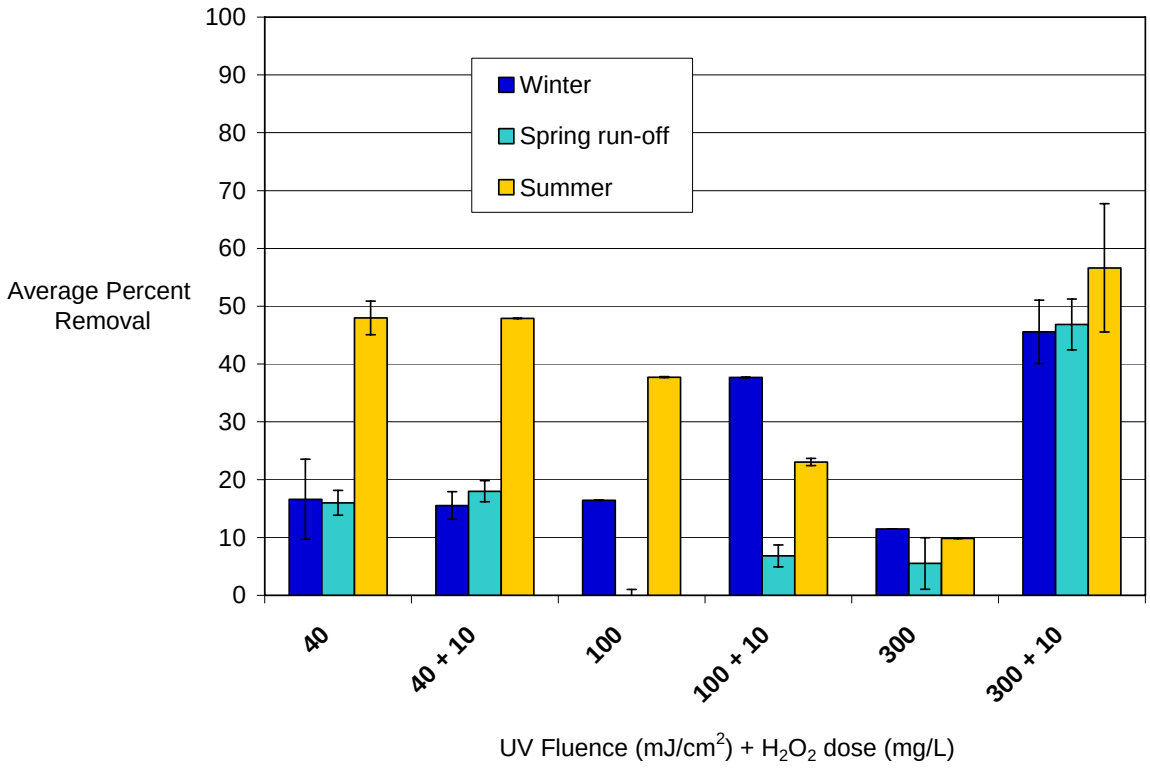


Figure 5.9: Average percent removal of ibuprofen spiked into partially treated winter, spring run-off, and summer water and subjected to MP-UV and UV/H_2O_2

The results for gemfibrozil were also not as anticipated (Figure 5.10). In almost all cases, removals in the summer water were lower than had been seen in the winter and spring waters. As with ibuprofen, contrary to expectation, removals with higher fluences of UV alone did not yield higher removals.

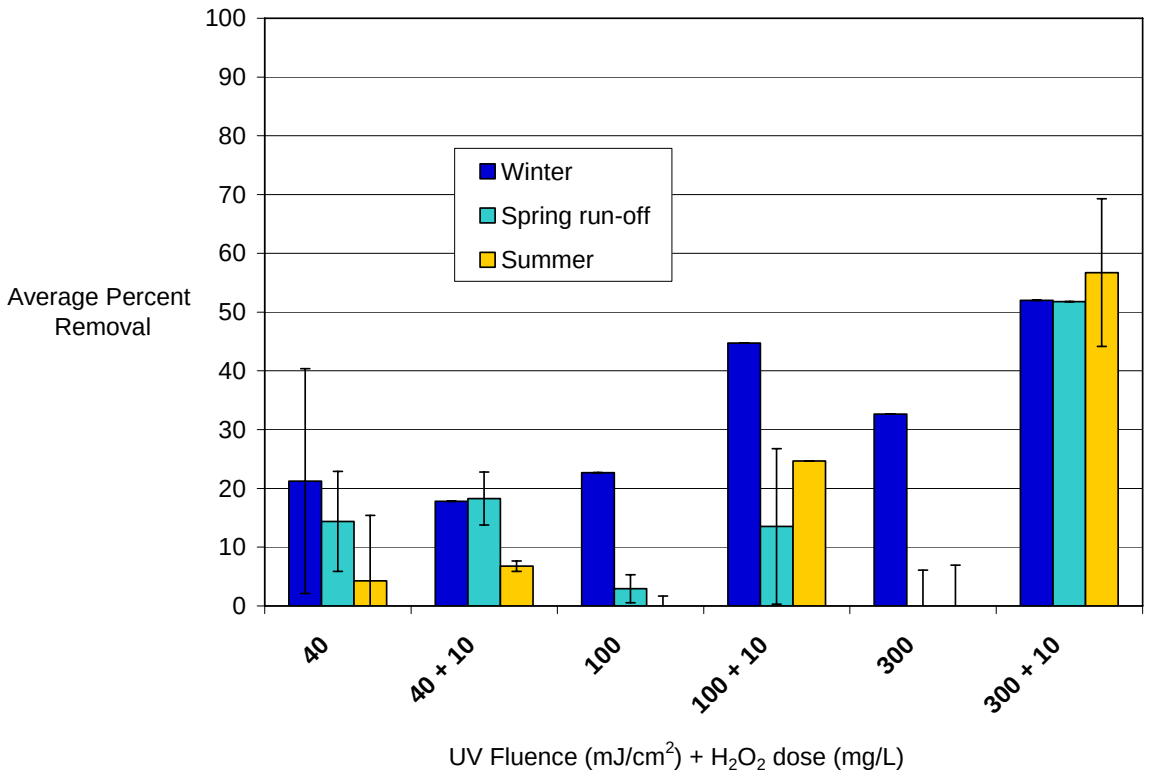


Figure 5.10: Average percent removal of gemfibrozil spiked into partially treated winter, spring run-off, and summer water and subjected to MP-UV and UV/H_2O_2

On the other hand, the summer water results for naproxen and triclosan are very comparable to those seen for the other two waters. The naproxen results are representative of this and are shown in Figure 5.11; the results for triclosan are included in Appendix C.

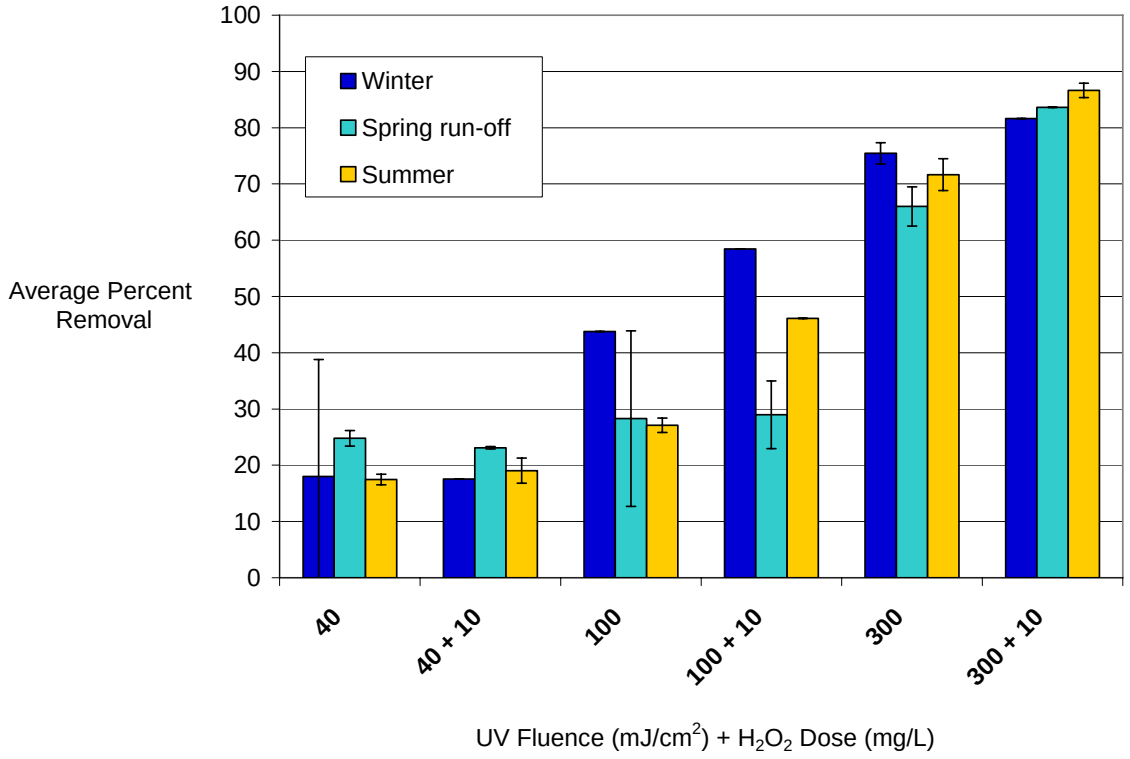


Figure 5.11: Average percent removal of naproxen spiked into partially treated winter, spring run-off, and summer water and subjected to MP-UV and UV/H_2O_2

One explanation for the summer results for ibuprofen and gemfibrozil may lie in analytical error caused by the water matrix. During these experiments, quality control standards made in ultra-pure water were run alongside the samples. The recoveries for these standards were considered to be quite good: most were within the range of 75-110%, with overall average recoveries between 97-103% for the four compounds. On the other hand, the few recovery standards run in the summer matrix water elicited a broader range of recoveries; however,

accurate corrections for the background concentrations could not be made, and so these recoveries are not meaningful and it is not appropriate to include them as part of this discussion. If recoveries had been carried out properly, they may have shown that something in the water matrix was interfering with the analytical process. Such interference would justify the high standard deviations that were sometimes seen during these experiments. Furthermore, they may have, at least in part, explained the unexpected results for ibuprofen and gemfibrozil. That said, a closer comparison of the summer water results for just the two highest fluences does illustrate the anticipated trend: that a higher fluence leads to further removals and improves the effectiveness of the AOP (Figure 5.12).

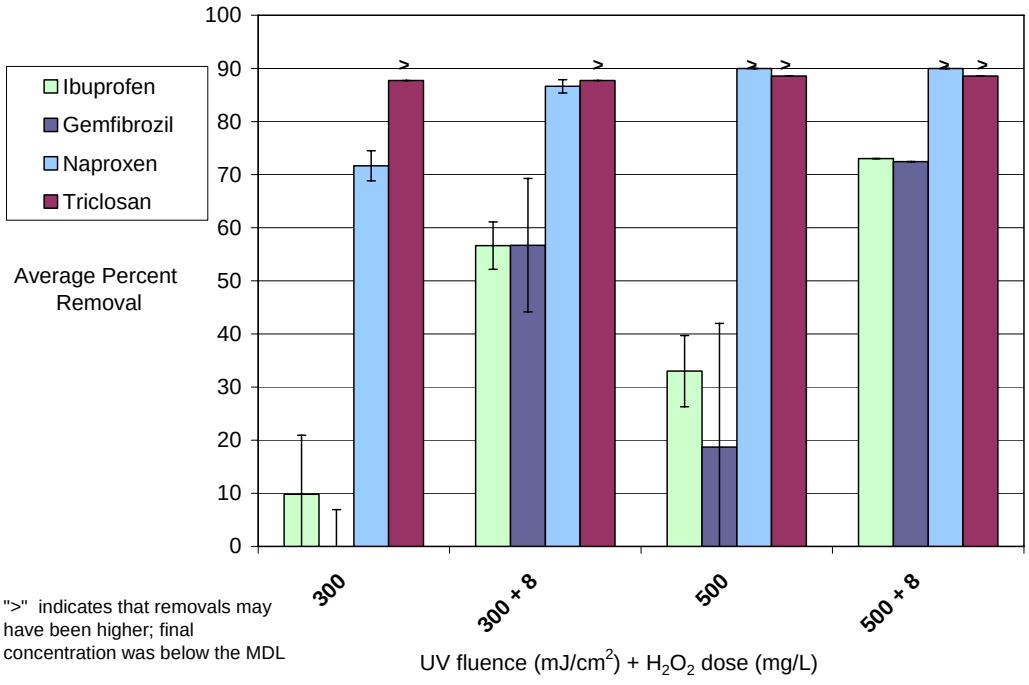


Figure 5.12: Average percent removal of target compounds spiked into partially treated summer water and subjected to MP-UV and MP-UV/H_2O_2 at high fluences

As well, the additional applied fluence of 500 mJ/cm^2 had the desired effect of degrading at least one additional compound, in this case naproxen, to levels approaching or below the MDL.

5.3 Comparison with Ultra-pure Water Results

A portion of the results of the partially treated water experiments can be compared with the experiments that were carried out by spiking ultra-pure water in the same low concentration range (around 1000 ng/L) under the same treatment conditions (the results of which were presented in their entirety in Chapter 4 as the *Linking* experiments).

For both the partially-treated water and the ultra-pure water, minimal, if any, removal of the target compounds was observed following an LP fluence of 40 mJ/cm^2. On the other hand, the addition of hydrogen peroxide at this low LP fluence led to improved removals. This is true for all four types of water, although the removals in the partially-treated water were still lower than for the ultra-pure water (Figure 5.13). It is probable that the partially-treated water had radical-scavenging substances present, which would have inhibited the oxidation of the target compounds. It is also possible that not as many radicals were formed in the first place due to the lower UV transmittance of the partially-treated waters.

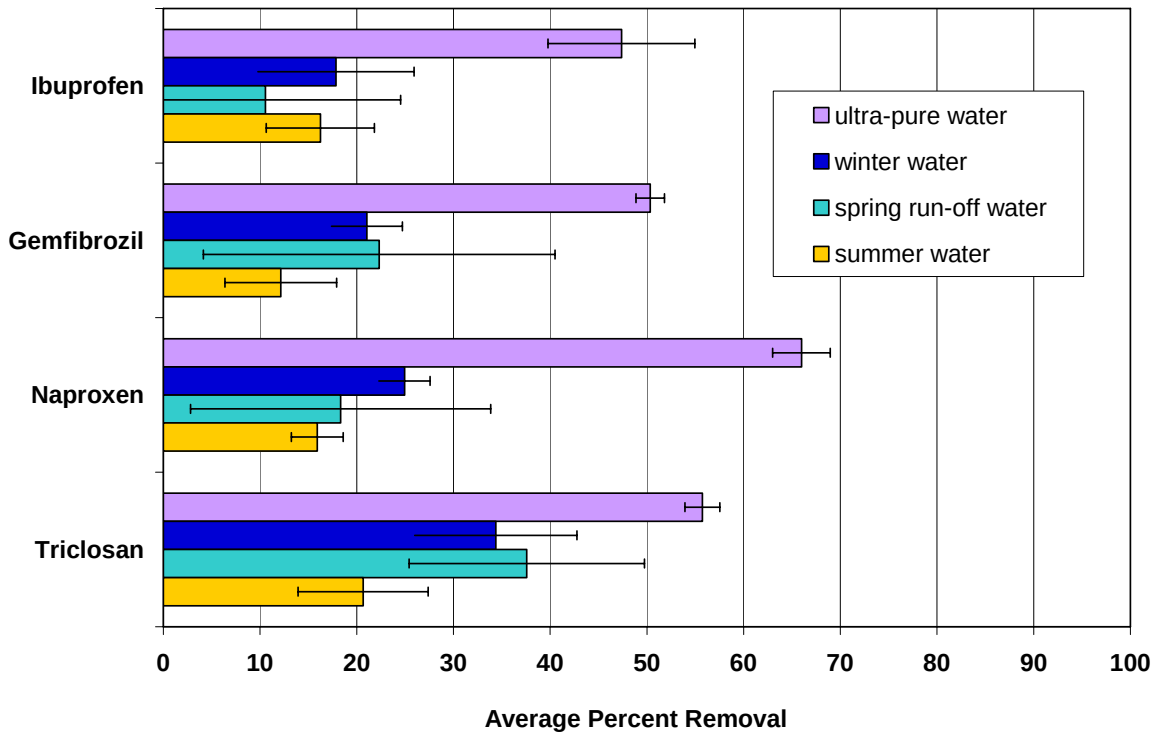


Figure 5.13: Average percent removal of target compounds spiked into four different waters; subjected to LP-UV at 40 mJ/cm2 + 10 mg/L H_20_2

The low removals seen at 40 mJ/cm^2 with the MP lamp in the partially-treated water were generally comparable with those seen in the ultra-pure water (Figure 5.14). At this low MP fluence the effect of water quality is not obvious. This may be due to the high standard deviations of the measured contaminant concentrations. It is also possible that the UV degraded substances naturally present in the partially treated water to form hydroxyl radicals, which in turn reacted with the target compounds. This would explain the instances when higher removals were seen in one or more of the partially-treated waters than in the ultra-pure water.

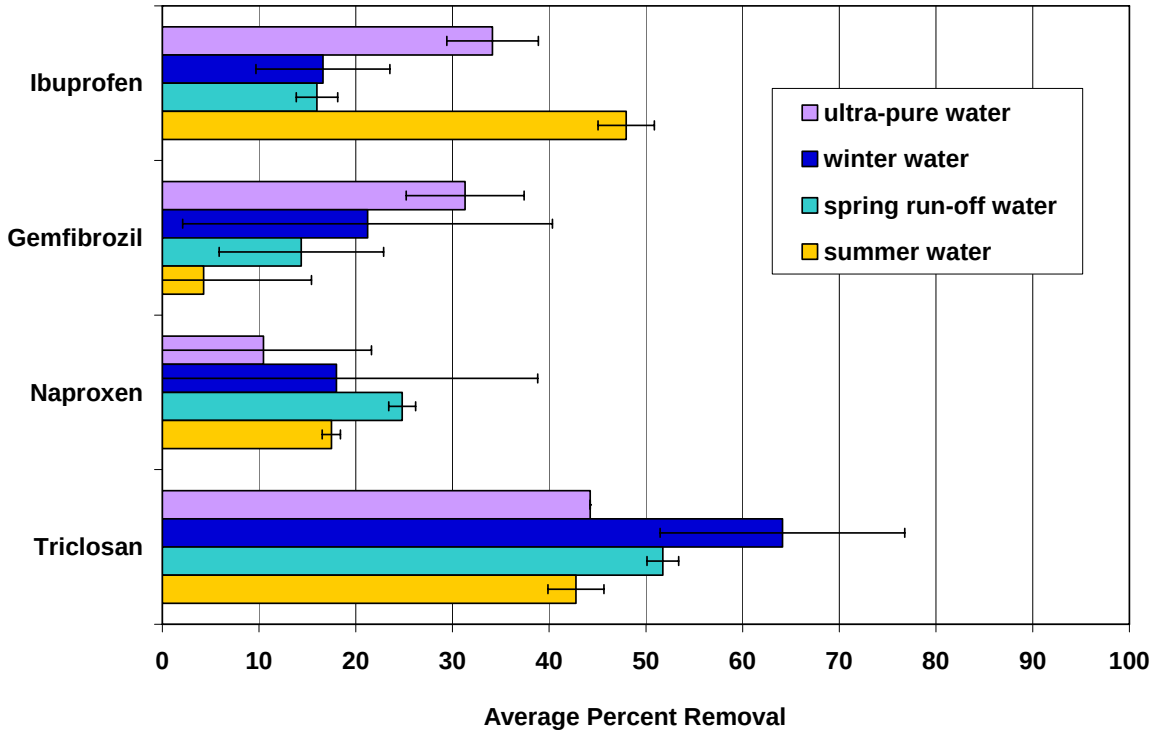


Figure 5.14: Average percent removal of target compounds spiked into four different waters; subjected to MP-UV at 40 mJ/cm^2

On the other hand, the addition of hydrogen peroxide to the partially-treated water did not lead to obvious improvements in the percent removals at low MP fluences, and removals were again lower than had been seen in ultra-pure water (Figure 5.15). It is possible that the lower MP fluences were inadequate to produce sufficient hydroxyl radicals under the matrix conditions of the partially-treated water.

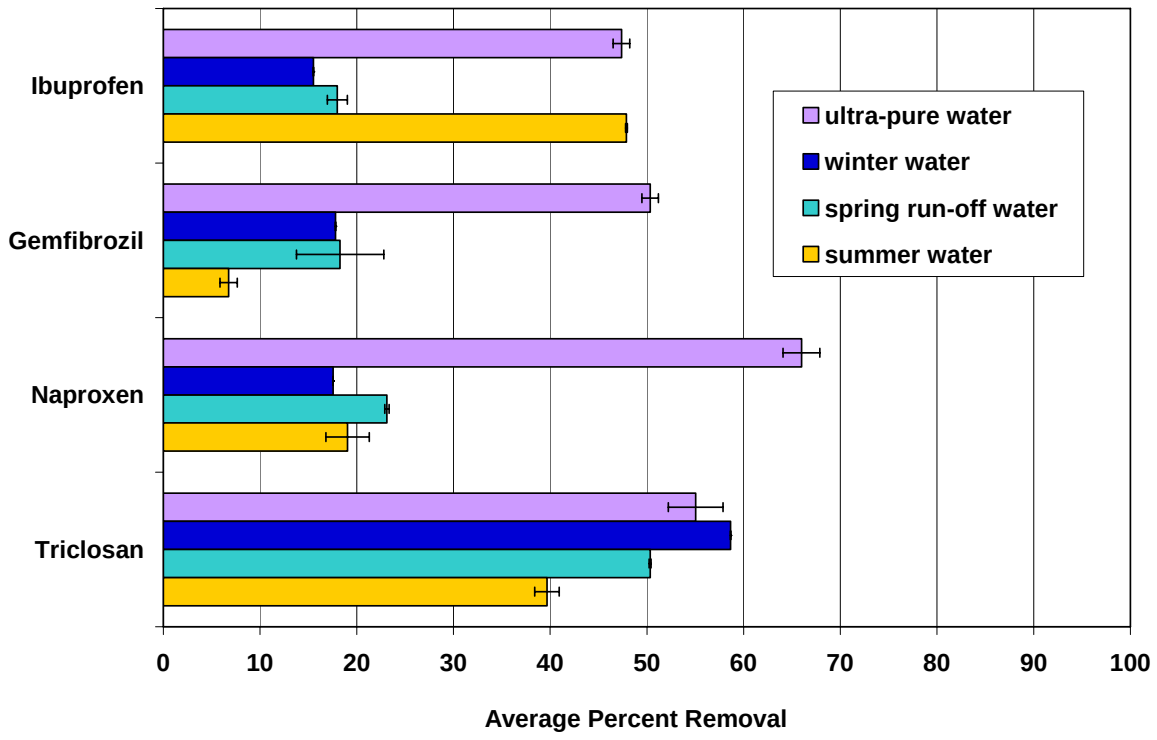


Figure 5.15: Average percent removal of target compounds spiked into four different waters; subjected to MP-UV at 40 mJ/cm^2 + 10 mg/L H_20_2

Figure 5.16 shows the results for all four waters with an applied fluence of 300 mJ/cm^2. This comparison shows that water quality had a greater impact on the removals of ibuprofen and gemfibrozil, compounds that seem to be less susceptible to photolysis.

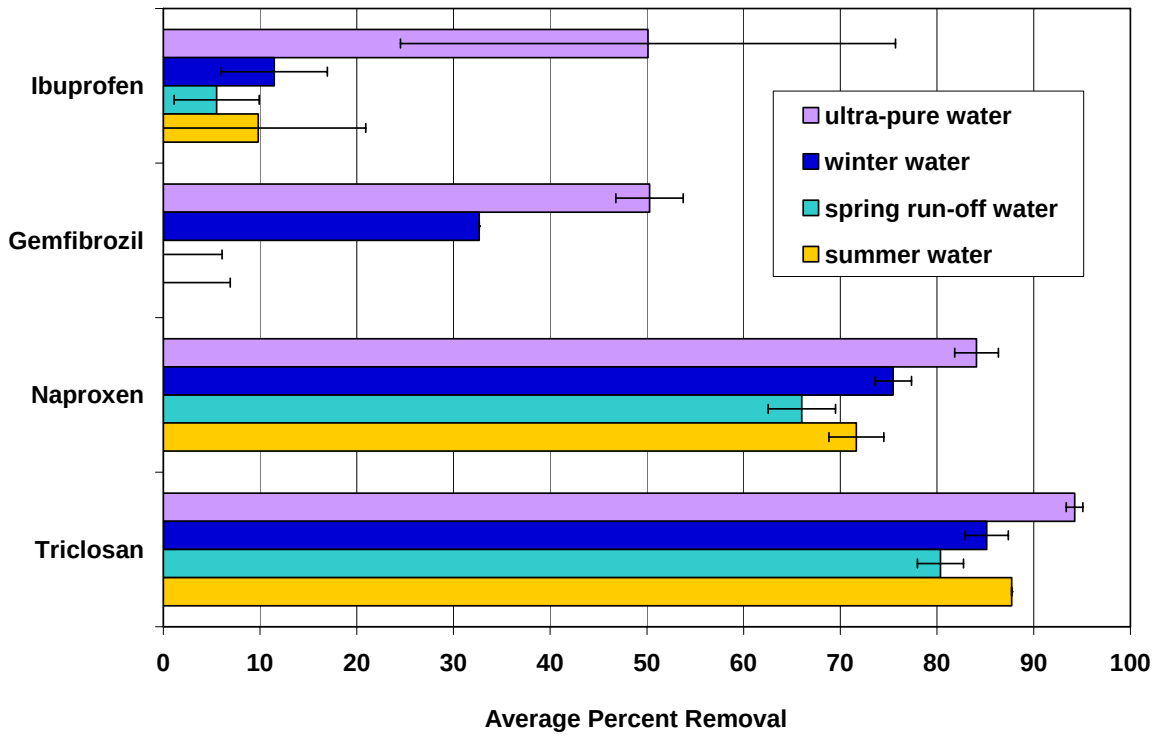


Figure 5.16: Average percent removal of target compounds spiked into four different waters; subjected to MP-UV at 300 mJ/cm^2

At a fluence of 300 mJ/cm^2 with 10 mg/L of hydrogen peroxide, it appears that the differences in water quality have less of an impact on the removals than for UV alone at that fluence, particularly for ibuprofen and gemfibrozil, the two compounds shown to be least susceptible to photolysis (Figure 5.17). For ibuprofen and gemfibrozil, the results in the three partially treated waters are comparable, although removals are less than those seen in the ultra-pure water. On the other hand, removals of naproxen and triclosan are quite comparable in all four waters. This shows that the water quality is more likely to impact the

removals of compounds that are less susceptible to photolysis, which in turn points to the hydroxyl radical scavenging substances likely present in the partially treated waters.

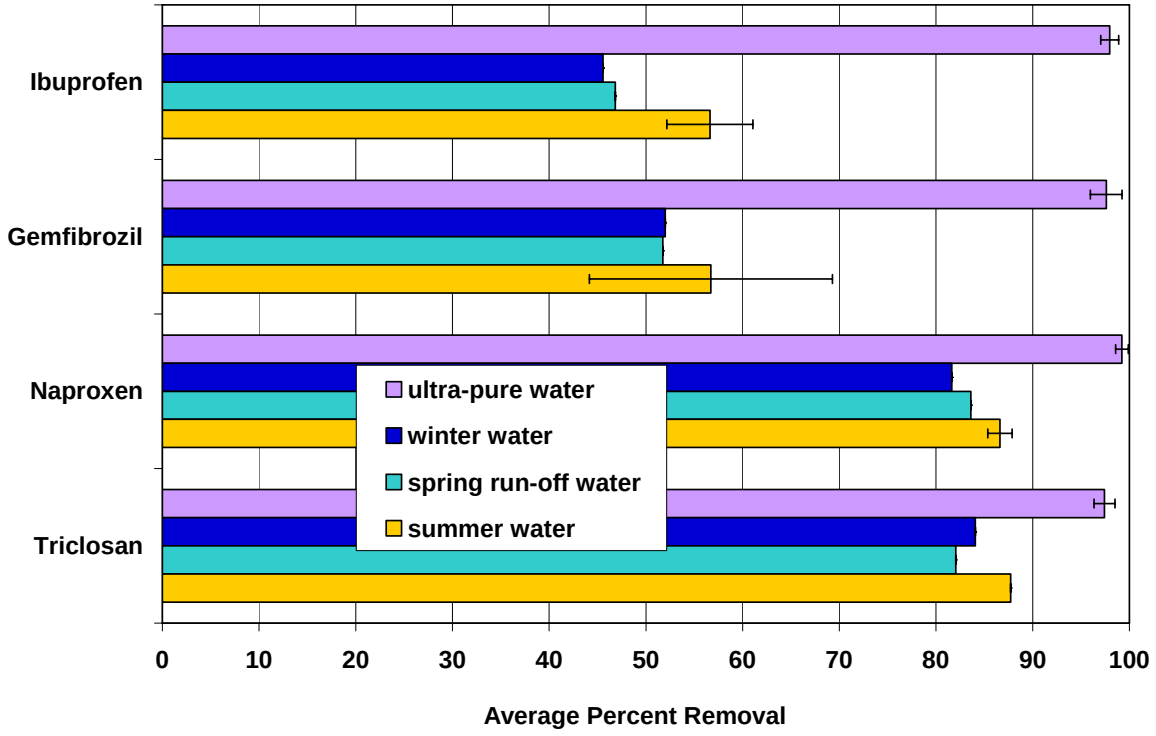


Figure 5.17: Average percent removal of target compounds spiked into four different waters; subjected to MP-UV at 300 mJ/cm^2 + 10 mg/L H_20_2

Overall, the removals in partially-treated water were lower than in ultra-pure water, as would be expected due to hydroxyl radical scavenging and reduced UV transmittance.

An overall summary of the partially-treated water results is provided in Chapter 7, Section 7.2.

Chapter 6
Kinetics Study

Experiments were carried out to obtain estimates of kinetic parameters describing the degradation of the target compounds. These estimates were calculated from the results of experiments involving single irradiations carried out at a range of fluences. Each compound was examined independently. The target concentration of the prepared solutions was 1 μM; actual initial concentrations were measured and found to be between 0.5 and 2.0 μM, with variability attributed to the difficulty of dissolving these compounds in ultra-pure water without the use of a solvent. Duplicate analyses were then carried out on each of the irradiated samples using the liquid-liquid extraction and derivatization process described in Chapter 3. As with the previous experiments, both the LP and MP lamps were employed, with and without hydrogen peroxide addition (at 10 mg/L). Further details of the method and approach for these experiments are outlined in Chapter 3.

To reiterate, during UV/H_2O_2 treatment, substances can be degraded by both direct photolysis due to the UV irradiation, and indirect photolysis due to reactions with the OH radicals that are produced. Both of these degradation pathways are reflected in the calculated kinetic parameters, more specifically by two different reaction rate constants. The photolysis of the target compounds during treatment was assumed to be a pseudo-first-order reaction (Pereira, 2005; Sharpless and Linden, 2003), which was later confirmed by the experimental

results. Therefore, the following differential and linearized forms of the first-order rate equations apply (Sawyer et al., 1994):

$$r = -d[C]/dt = k'[C]$$

$$\ln([C]/[C_o]) = -k't$$

According to Sharpless and Linden (2003), the overall rate constant for UV/H_2O_2 treatment will be the sum of two rate constants as follows:

$$k' = k_d' + k_i'$$

where k' is the pseudo-first-order rate constant (s^{-1}) observed during UV/H_2O_2 treatment**,** k_d' is the direct photolysis pseudo-first-order rate constant (s^{-1}) and k_i' is the indirect photolysis pseudo-first-order rate constant (s^{-1}). For our purposes, k_d' can be determined experimentally from direct photolysis experiments, that is, when UV irradiation was applied but no hydrogen peroxide was added. The calculation of k_i' then simply entails the subtraction of k_d' from k', which is also determined experimentally, in this case during experiments with hydrogen peroxide addition.

Alternatively, fluence-based rate constants can be determined. Since time-based rate constants rely on the exposure times required to achieve a specific fluence, they will be dependent on all of the same factors that go into calculating that exposure time; therefore, they will be specific to a particular set-up, lamp, water matrix, and volume of treated water. On the other hand, fluence-based rate constants should be the same for different set-ups and waters, as long as fluence is calculated accurately and consistently between labs. The equation incorporating a fluence-based rate constant would be as follows:

$$\ln (C/C_o) = -k*(\text{UV fluence})$$

The units for k would then be the inverse of those for fluence, in this case cm^2/mJ. This rate constant can be experimentally determined as the absolute value of the slope (assuming a negative slope) of a plot of UV fluence versus $\ln(C/C_o)$. Such fluence-based rate constants were determined during these experiments.

The results presented in this chapter for naproxen will be compared to results found by Pereira (2005), who, as mentioned in Chapter 2, carried out similar experiments for naproxen, as well as other pharmaceutical compounds not included in this study. It is important to note, however, that she used a different analytical method, which may explain slight discrepancies between the results. As well, she used a different treatment set-up, although theoretically this should not contribute to differences in reported values.

6.1 Direct Photolysis Kinetics for LP- UV

Plotting the results from experiments with the LP lamp and carrying out linear regression provides estimates for k_d'. The results from each duplicate analysis are shown, as opposed to averages. Additional points were included from the exploratory experiments. More specifically, the LP-UV results at 1000 mJ/cm^2 from those initial experiments were included rather than repeating what would have been identical experiments.

The LP-UV results for ibuprofen and gemfibrozil are shown in Figure 6.1. Unfortunately, the LP results at 1000 mJ/cm^2 were not available for ibuprofen, as the integrity of both samples was compromised during processing. Over the range of fluences tested, less than 10% removal was measured for both of these compounds. Linear regression resulted in low R-squared values, which indicated that there was no true trend at these fluences for the LP lamp. Further to that point, the slope of the trend lines would have been extremely small.

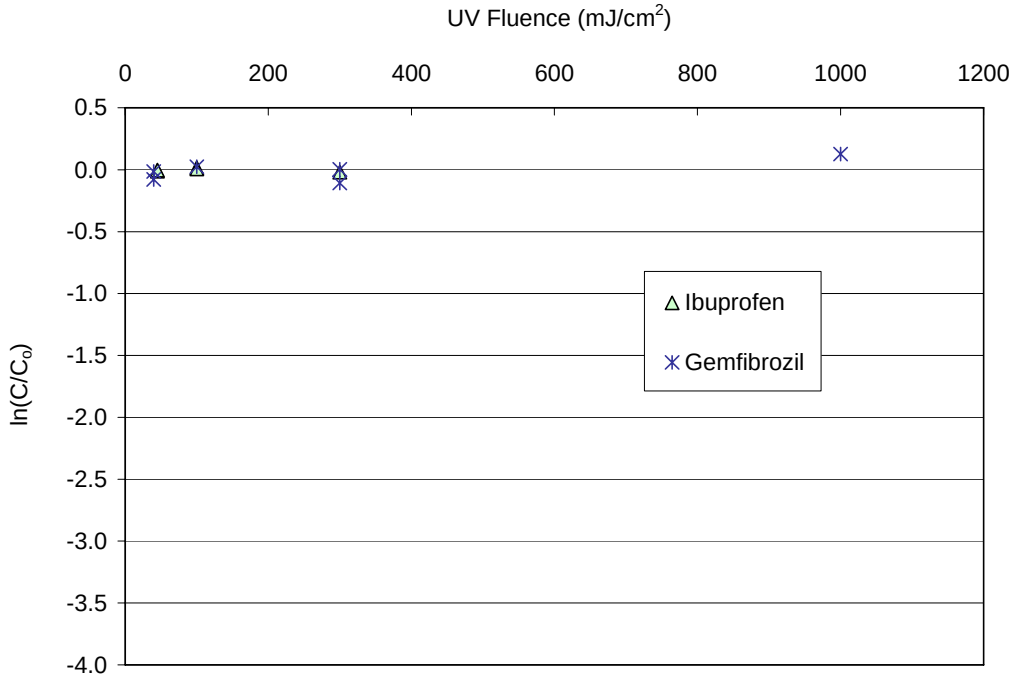


Figure 6.1: Results of kinetics experiments for ibuprofen and gemfibrozil using LP-UV at a range of fluences

Removals for the other two compounds were higher, particularly for triclosan (Figure 6.2). The estimated fluence-based rate constants (k_d') for naproxen and triclosan are 0.0002 and 0.0033 cm^2/mJ, respectively (Figure 6.2). This value for naproxen is in agreement with results presented by Pereira (2005), who also calculated a value of 0.0002 cm^2/mJ. Although adding the 1000 mJ/cm^2 point from the earlier ultra-pure water experiments to the naproxen plot did not change the value for k_d', it improved the R-squared value (from 0.7007 to 0.9268), showing that the 1000 mJ/cm^2 point is consistent with the other data.

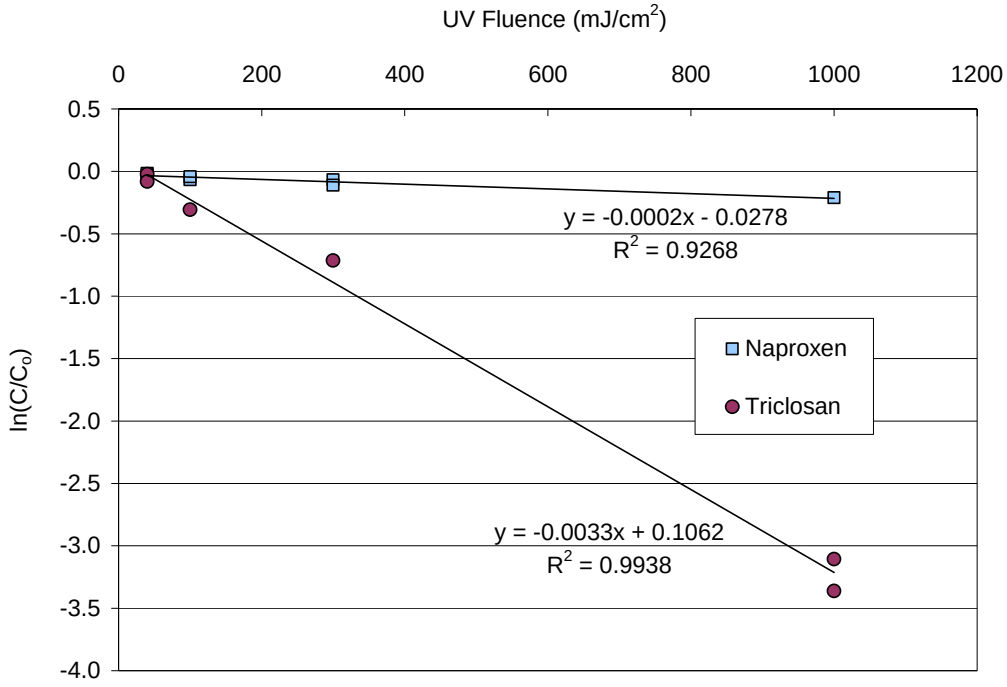


Figure 6.2: Results of kinetics experiments for naproxen and triclosan using LP-UV at a range of fluences

Of all four compounds, triclosan had the highest rate constant by one order of magnitude. This is in agreement with the earlier findings that triclosan is more readily and rapidly degraded by LP-UV than the other target PPCPs.

6.2 Indirect Photolysis Kinetics for LP-UV/H_2O_2

This section describes the results from experiments using the LP lamp at a range of fluences with 10 mg/L of H_2O_2 added. Carrying out linear regression on the results provided estimates for k', the overall reaction rate constant for the LP-UV/H_2O_2 process. Again,

single irradiations were carried out at each fluence and the results from each duplicate analysis are shown, as opposed to averages.

Figure 6.3 shows the results for ibuprofen and gemfibrozil. As expected, the addition of hydrogen peroxide improved removals, particularly at the higher fluence of 300 mJ/cm^2. There was no improvement in the removal of ibuprofen at the two lower fluences, perhaps because these levels were inadequate to produce a sufficient hydroxyl radical concentration. This lag in removal contributes to the slightly lower R-squared value and positive intercept for the linear fit. A similar, although less pronounced effect, was seen for gemfibrozil. In theory, a positive intercept suggests that the target compounds are actually formed at low fluences, which is implausible in this scenario since the target compound is the only substance present, as opposed to in the environment, where conjugate forms may be present (Andrews, 2006). This trend of an apparent lag-phase may suggest one or both of the following: that there is a threshold fluence required to achieve •OH radical formation from H_2O_2, or that there is a threshold fluence necessary before •OH radicals are formed in sufficiently high concentrations to cause measurable levels of oxidation. In some water matrices it may also be possible that at low fluences one or more water quality parameters interfere with •OH radical attack either by inhibiting formation or by scavenging them, although that would not apply in this case since ultra-pure water was used. If any of this reasoning holds true, then it is likely that first order kinetics only apply at and above the threshold fluence. Additional data points would be required to ascertain such a threshold.

Interestingly, utilizing the gathered data, ibuprofen has the lowest k' value of all four compounds at 0.0056 cm^2/mJ, while at 0.0124 cm^2/mJ, gemfibrozil has the highest.

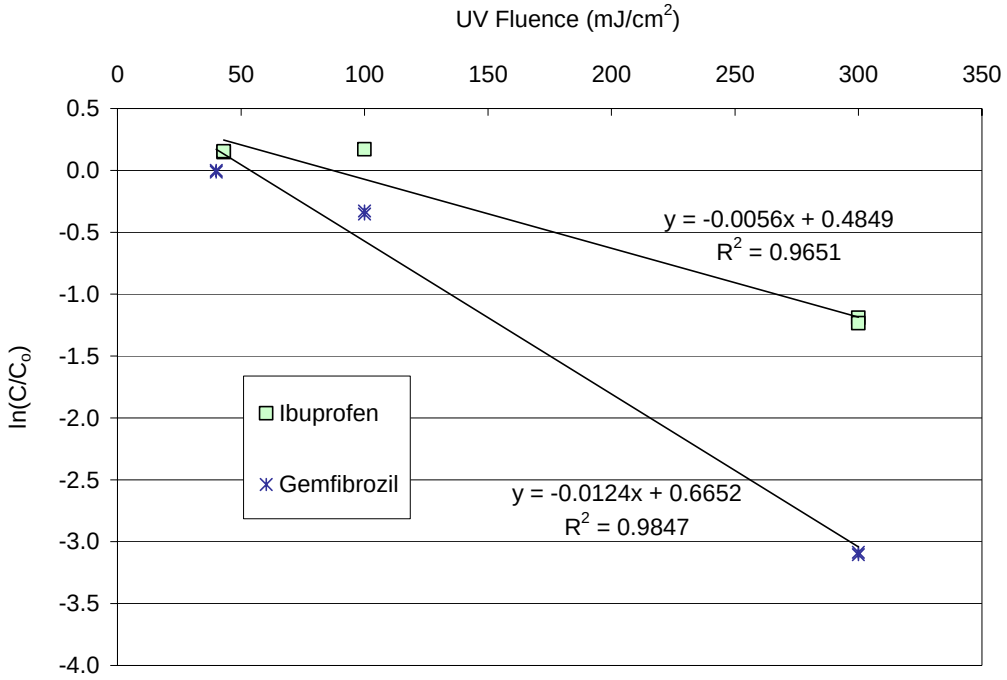


Figure 6.3: Results of kinetics experiments for ibuprofen and gemfibrozil using LP-UV at a range of fluences with addition of 10 mg/L H_2O_2

The results for naproxen and triclosan (Figure 6.4) also showed improved removals with hydrogen peroxide addition, most markedly for naproxen. The value for k' taken from the plot for naproxen is 0.0078 cm^2/mJ. This is in the same range as the fluence-based rate constant of 0.0119 cm^2/mJ presented by Pereira (2005) for naproxen under the same treatment conditions (i.e. also LP-UV with 10 mg/L H_2O_2).

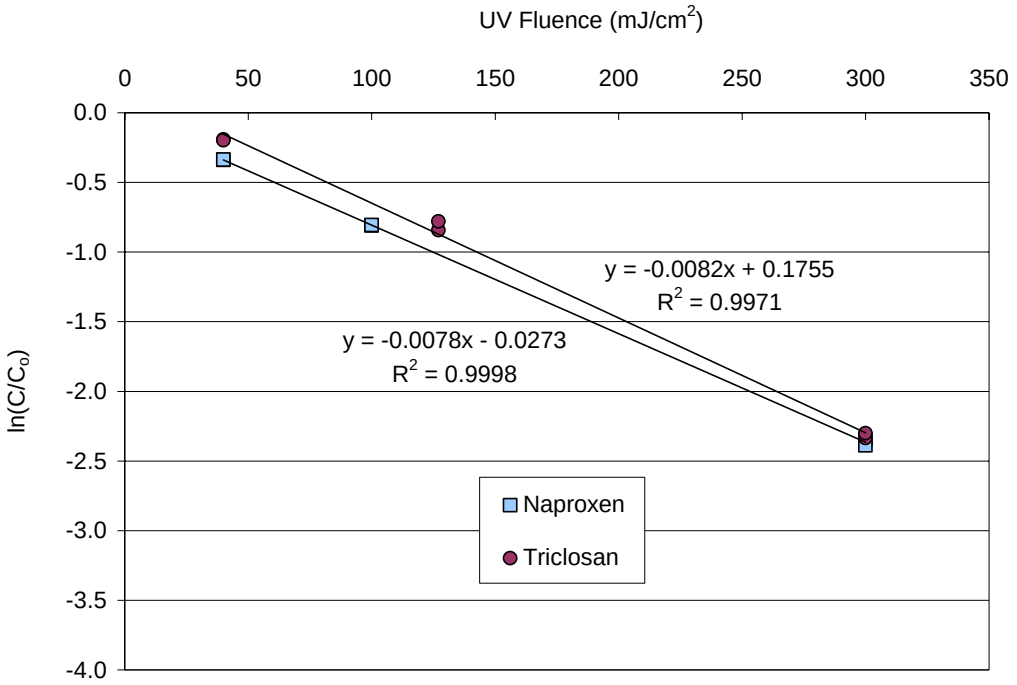


Figure 6.4: Results of kinetics experiments for naproxen and triclosan using LP-UV at a range of fluences with addition of 10 mg/L H_2O_2

The rate constants attributed to reaction with the hydroxyl radical (k_i') were calculated by subtracting the k_d'values determined in section 6.1 from the k' values determined in this section (Table 6.1). It is interesting to note that gemfibrozil has the highest rate constant for indirect photolysis, suggesting that it reacts most readily with the hydroxyl radical. Also noteworthy is that the direct and indirect rate constants for triclosan are comparable, while the indirect rate constant for naproxen is more than one order of magnitude higher than the direct rate constant. This indicates that although the overall rate constants (k') are almost

identical for naproxen and triclosan, the two reaction pathways contribute to a different proportion of the degradation for each.

Table 6.1: Degradation rate constants for the target compounds with LP-UV

Compound	k_d' ($cm^2\ mJ^{-1}$)	k' ($cm^2\ mJ^{-1}$)	k_i' ($cm^2\ mJ^{-1}$)
Ibuprofen	N/A	0.0056	0.0056
Gemfibrozil	N/A	0.0124	0.0124
Naproxen	0.0002	0.0078	0.0076
Triclosan	0.0033	0.0082	0.0049

6.3 Direct Photolysis Kinetics for MP-UV

As with the LP lamp, plotting the results from experiments with the MP lamp and carrying out linear regression provided estimates for k_d'. Again, the results from duplicate analyses of the single irradiations are shown. For experiments with the MP lamp, observed removals often approached 100%, which was not the case with the LP lamp; therefore it was necessary to consider the method detection limit when employing the results to estimate MP-UV kinetic parameters. All results below the MDL were excluded from the kinetics plots; these results are indicated in tables included in Appendix D.

The results for ibuprofen and gemfibrozil are shown in Figure 6.5. As expected, removals were much higher than those seen with the LP lamp, which allowed for the determination of k_d' values.

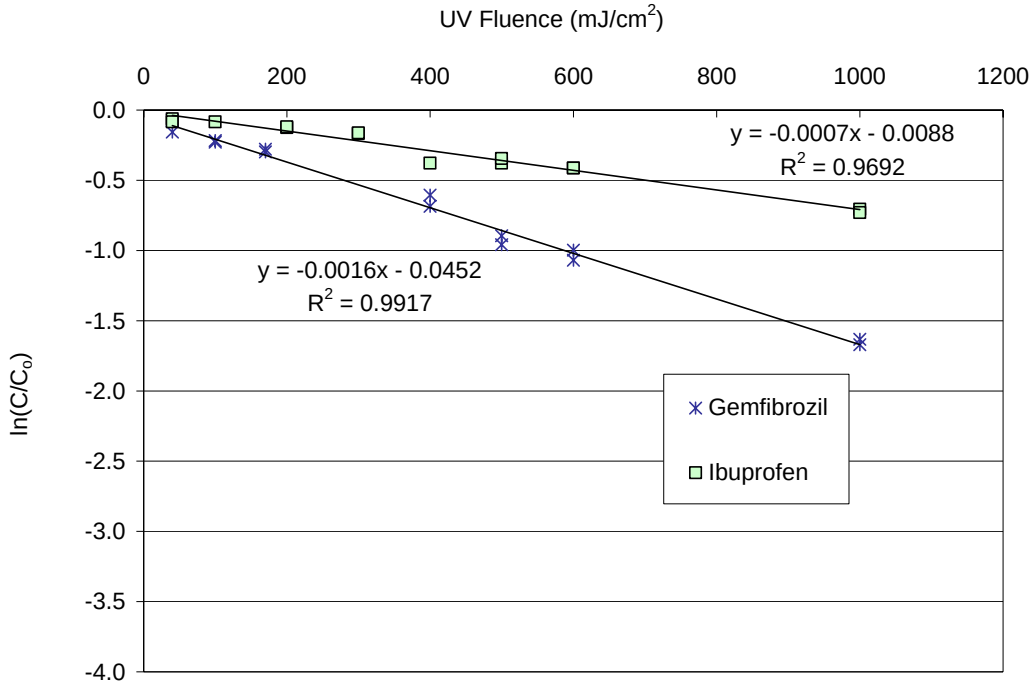


Figure 6.5: Results of kinetics experiments for ibuprofen and gemfibrozil using MP-UV at a range of fluences

For naproxen and triclosan, removals were even higher, resulting in the exclusion of results at the higher fluences when final concentrations were below the detection limits. There appears to be an outlier result for triclosan at 100 mJ/cm^2 that cannot be explained; it was a duplicate extraction and followed the same analytical process as the other sample taken at that fluence. With these results, poor R^2 values were obtained for both compounds. From the naproxen graph, it almost appears as if there are two separate linear trends, one for fluences below 500 mJ/cm^2 and one for fluences of 500 mJ/cm^2 and higher. This may be due to the fact that, the naproxen concentrations following irradiations of 500 and 600

mJ/cm^2 were only slightly above the MDL, as well, as the fact that the removals were very high and very close in value: 96 and 98% removal, respectively.

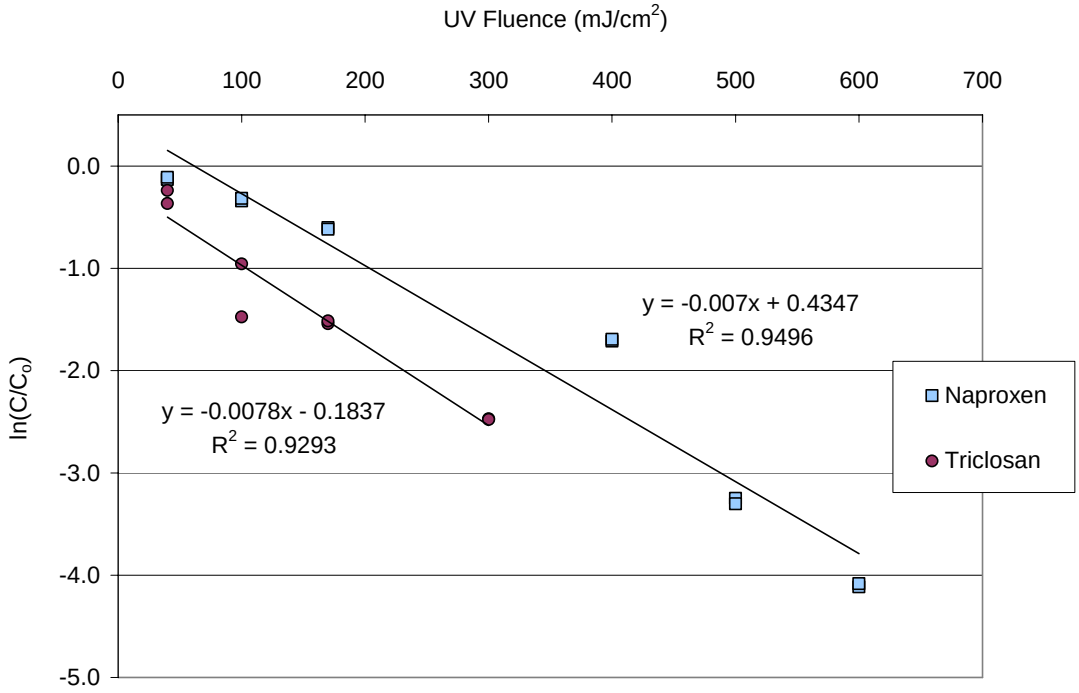


Figure 6.6: Results of kinetics experiments for naproxen and triclosan using MP-UV at a range of fluences

If the two points at 500 and 600 mJ/cm^2 for naproxen are removed from the plot, it leads to an improved R^2 value of 0.9965 and results in a k_d' value (0.0045 cm^2/mJ) that corresponds better with the expectation that naproxen removals are high, but generally lower than triclosan (Figure 6.7). As well, it reduces the value of the positive intercept, which, as discussed earlier, is improbable. Furthermore, the rate constant for naproxen is then closer to that put forth by Pereira's, which was 0.0033 cm^2 mJ^{-1}. It may be possible in this case that

for unknown reasons, first-order kinetics do not apply; however, further investigation would be required to properly assess that. On the other hand, inclusion of these higher points improved the R^2 value for triclosan and only slightly altered the k_d' value (to 0.0071, down from 0.0078); these points are shown as colourless to indicate that they are below the MDL (Figure 6.7). The k_d' values from these revised plots are the ones taken for further discussion and comparison.

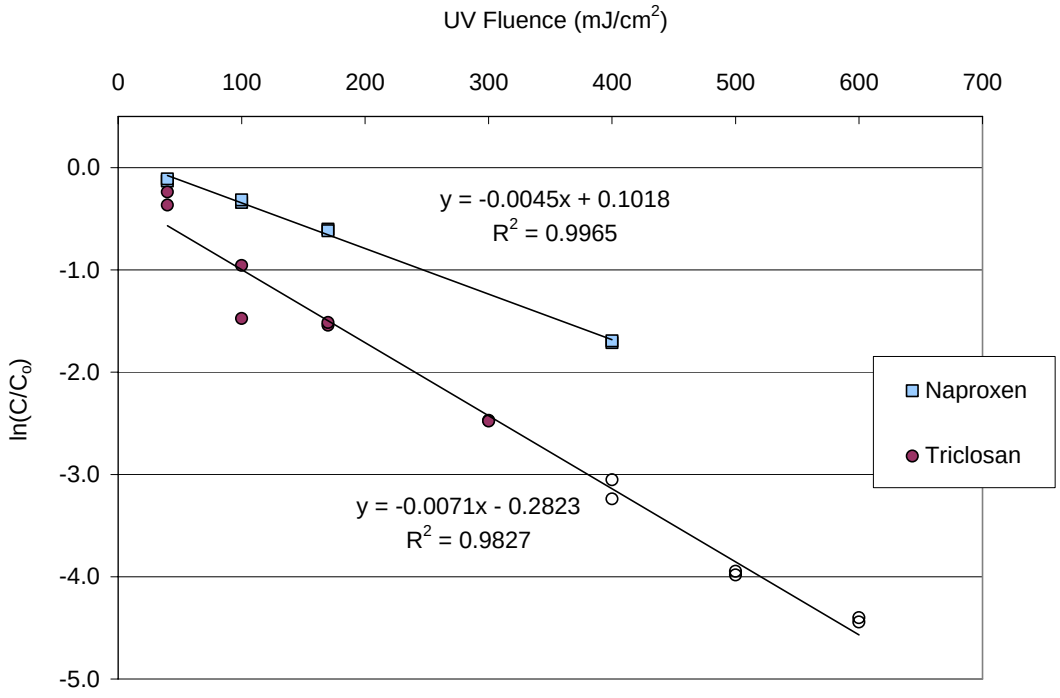


Figure 6.7: Results of kinetics experiments for naproxen and triclosan using MP-UV at a range of fluences, higher fluence results removed for naproxen

6.4 Indirect Photolysis Kinetics for MP-UV/H_2O_2

This section outlines the results found for MP-UV irradiation at a range of fluences with addition of 10 mg/L of H_2O_2. As before, the results from duplicate analyses of the single irradiations are shown, but all results below the MDL were excluded from the kinetics plots. For this reason, the results for fluences greater than 300 mJ/cm^2 were almost always excluded.

For all four compounds, very high R-squared values were achieved, indicating strong trends in the results. Ibuprofen exemplified the lowest degradation rate constant (Figure 6.8), which is in accordance with results seen previously where ibuprofen often experienced the lowest percent removals.

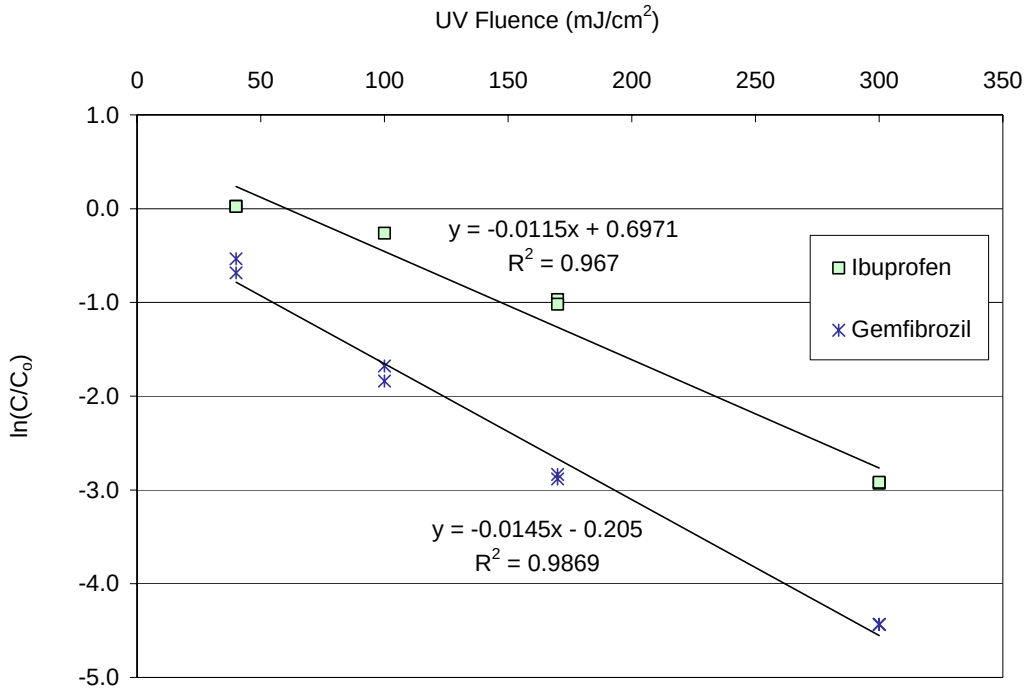


Figure 6.8: Results of kinetics experiments for ibuprofen and gemfibrozil using MP-UV at a range of fluences with the addition of 10 mg/L H_2O_2

The rate constant for gemfibrozil is 0.0204 cm^2/mJ, which is in the same range as the value of 0.0146 cm^2/mJ determined for naproxen (Figure 6.9). The latter compares very well with Pereira's value of 0.0163 cm^2/mJ. For triclosan, only the two lowest fluences resulted in concentrations above the MDL; however, the measured concentration following the 170 mJ/cm^2 irradiation was very close to the MDL. The inclusion of this point on the plot (shown as a lighter shade) corroborates the degradation trend, which, as expected, exemplifies a faster rate of removal for triclosan than for the other three compounds.

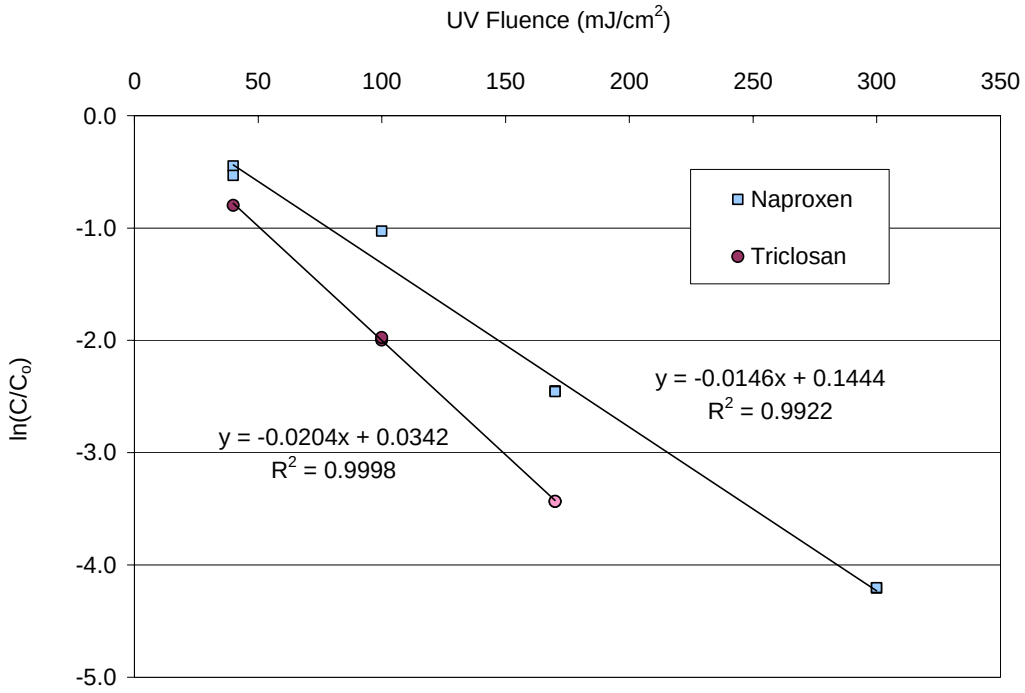


Figure 6.9: Results of kinetics experiments for naproxen and triclosan using MP-UV at a range of fluences with the addition of 10 mg/L H_2O_2

As with the LP lamp, the indirect rate constants can be calculated as the difference between k' and k_d'. The results for the MP lamp are summarized in Table 6.2. It is interesting to note that the indirect rate constants for all four compounds are essentially the same. This corresponds with the fact that the •OH radical is a non-selective oxidant and so the oxidation of each compound is likely controlled by access to •OH radicals; the fact that the reaction rates were essentially the same for each compound confirms that generation and transport of the •OH radicals was the same in each case, thereby highlighting the consistency in experimental conditions. It should be noted that such results were not seen for the LP lamp.

Again, this is likely due to the differing trends seen for ibuprofen and gemfibrozil, specifically the supposed lag-phase at lower LP fluences discussed previously. This difference between lamps may be attributed to the absorption maximum of H_2O_2 being at 200 nm (Tuhkanen, 2004), which is below the emission maximum (254 nm) of the LP lamp; therefore a higher LP-fluence than MP-fluence may be required to initiate the production of •OH radicals. Perhaps if additional data points were collected for the LP lamp and the k_i' values were re-evaluated, the LP findings may be similar to those for the MP lamp.

Table 6.2: Degradation rate constants for the target compounds with MP-UV

Compound	k_d' ($cm^2\ mJ^{-1}$)	k' ($cm^2\ mJ^{-1}$)	k_i' ($cm^2\ mJ^{-1}$)
Ibuprofen	0.0007	0.0115	0.0108
Gemfibrozil	0.0016	0.0145	0.0129
Naproxen	0.0045	0.0146	0.0101
Triclosan	0.0071	0.0204	0.0133

These kinetics results suggest that the differences in removal rates during MP-UV/H_2O_2 treatment can be attributed solely to the differences in direct photolysis rates. For ibuprofen and gemfibrozil, the majority of degradation is due to indirect photolysis. For naproxen, the indirect photolysis rate constant is approximately twice as high as the direct photolysis rate constant, while for triclosan, these values are more alike. This is similar to what was seen for the LP lamp.

6.5 Molar Absorption Coefficients

A comparison of the absorption coefficients for the target compounds may provide a partial explanation for the differences in direct photolysis rates, as well as for the differences observed between the MP and LP lamps.

According to Schwarzenbach et al. (2003), $\varepsilon_i(\lambda)$ is the decadic molar absorption coefficient, which is a "measure of the probability that the compound *i* absorbs light at a particular wavelength", specifically wavelength λ. The units for $\varepsilon_i(\lambda)$ are $M^{-1}cm^{-1}$ and it can be calculated from the absorbance of the solution as follows:

$$\varepsilon_i(\lambda) = A(\lambda)/ (C_i \bullet l)$$

Where $A(\lambda)$ is the absorbance of a solution containing compound *i*, which can be measured with a spectrophotometer; C_i is the concentration of compound *i* (mol/L) in the solution; and *l* is the path length of the light (cm), assumed to be the same as the spectrophotometer cell width (Schwarzenbach et al., 2003).

A 1 cm wide spectrophotometer cell, or cuvette, was used throughout this work when measuring absorbance. Figure 6.10 shows the decadic molar extinction coefficient determined for all four compound using measurements taken during the kinetics experiments.

As mentioned, the compounds were dissolved in ultra-pure water without the use of a solvent. Furthermore, absorbance values were corrected for a blank, which, in all instances, was ultra-pure water.

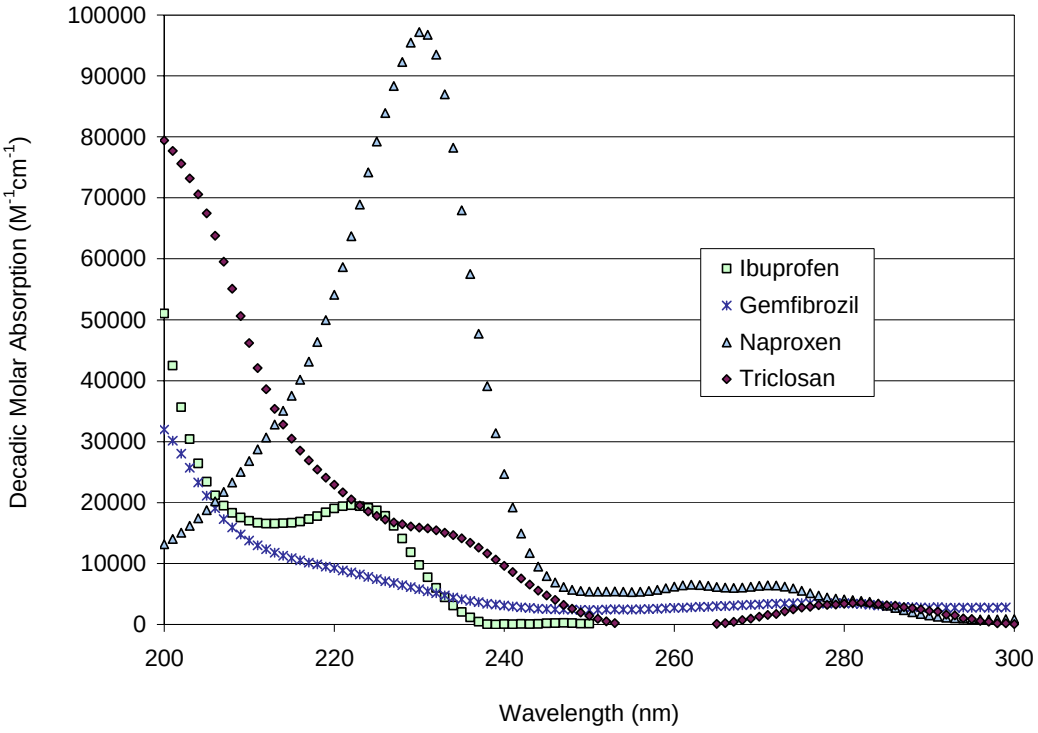


Figure 6.10: Calculated decadic molar absorption coefficients for the target compounds over a range of wavelengths

From this plot, it can be seen that naproxen and triclosan generally have higher decadic molar extinction coefficients over the 200-300 nm range. This suggests that they are more likely to absorb the UV light emitted from the MP lamp. This is in agreement with the results that

were seen during the kinetics experiments, more specifically, the higher k_d' values determined for these two compounds.

On the other hand, the decadic molar extinction coefficients around 254 nm do not help to explain the results seen for the LP lamp. From the plot alone, it would be expected that naproxen and gemfibrozil would have the highest k_d' values for the LP lamp, when in fact, triclosan had the highest k_d' value by one order of magnitude and a value for gemfibrozil could not even be determined. This suggests that a compound's susceptibility to photolysis involves additional factors and cannot be predicted solely from molar extinction coefficients.

An overall summary of the kinetics study is provided in Chapter 7, Section 7.3.

Chapter 7
Results Summary and Significance to the Industry

This chapter will serve to summarize the overall findings of this research while making connections between all of the experimental results. As well, this summary will draw further comparisons that accomplish the final objective set out at the beginning of this study, which was to compare the results of this study to typical disinfection processes as well as to AOP treatment that has been proven effective for the removal of taste and odour compounds. These items are directly related to the overall significance of this work to the drinking water treatment industry, which will also be discussed throughout this chapter.

7.1 Summary of Ultra-Pure Water Experiments

The first objective of this project was to simply evaluate the removal of the target PPCPs using UV irradiation alone and UV/ H_2O_2. These ultra-pure water experiments were outlined in detail in Chapter 4, with the method described in Chapter 3. The results of the *Preliminary* experiments, which examined the target compounds individually, clearly showed that at similar fluences, the MP lamp was much more effective than the LP lamp at removing these compounds; this same trend was consistently seen during all of the subsequent experiments.

When the compounds were studied independently in ultra-pure water, greater than 90% removal of naproxen and triclosan was achieved with a high MP-UV fluence of 1000

mJ/cm^2, results that were not seen for ibuprofen and gemfibrozil until the next highest fluence tested (i.e. 4175 mJ/cm^2). The addition of hydrogen peroxide substantially reduced the fluence required to achieve such high removals; in fact, all four compounds underwent more than 85% removal with just 170 mJ/cm^2 of MP-UV and the addition of 100 mg/L of H_2O_2. Throughout the ultra-pure water experiments, the addition of hydrogen peroxide typically increased removal rates, presumably through formation and subsequent reaction with the •OH radical.

The next set of ultra-pure water experiments were the *Competition* experiments, which examined removal of all four compounds spiked together in solution. Interestingly, ostensible competition effects were observed when target substances were treated in combination. This was indicated by lower removals than were seen during the *Preliminary* experiments in which compounds were studied independently. It is important to note, however, that the overall contaminant concentration was higher during the *Competition* experiments than during the *Preliminary* experiments. This may actually explain the lower removals observed for a given contaminant during the *Competition* experiments since the other contaminants in solution may have exerted matrix effects during treatment. In other words, if •OH radicals were not present in excess it may have presented a limiting factor, in which case lower removals of some compounds may be explained by differing reaction rates. Furthermore, reduction in photolysis could similarly be explained by matrix effects not adequately accounted for during the calculation of exposure times required to achieve a particular fluence (i.e. through sample absorbance).

The final set of exploratory experiments in ultra-pure water were tagged the *Linking* experiments. Similar to the *Competition* experiments, these evaluated the removal of all four target compounds together in solution; the difference was that these experiments utilized a lower concentration range of the compounds (~ 750 ng/L rather than ~250 µg/L). In general, the percent removals were higher than for the *Competition* experiments. Moreover, they were comparable and sometimes slightly better than the results seen during the *Preliminary* experiments, which were done at the same high individual contaminant concentration range as the *Competition* experiments (i.e. ~200 µg/L) but studied the compounds independently. The results of the *Linking* experiments in comparison to the earlier ultra-pure results suggest that percent removals of the target compounds may be concentration driven. It may be that when contaminant concentrations are higher, the availability of photons or •OH radicals becomes a limiting factor if one (or both) is no longer present in excess. On the other hand, it may be that removals during the *Competition* experiments were lower than the *Linking* experiments simply because the apparent matrix effects exerted on one compound by the other three were lessened. Furthermore, it is possible that increased removals were the result of greater availability of the •OH radical and UV irradiation.

7.2 Summary of Partially-treated Water Experiments

The second major objective of this study was to determine the influence of water quality parameters on the efficacy of UV irradiation and UV/H_2O_2. The corresponding experiments investigated the removal of the target compounds spiked into partially-treated water

experiments, as discussed in Chapter 5. These experiments utilized water sampled during three different seasons from a local drinking water treatment plant. Samples were taken at a point in the treatment train at which an AOP may be implemented: following the flocculation-sedimentation step but prior to filtration and chlorination. Several of the water quality parameters varied for the three seasonal waters tested; however, although some differences were seen, no clear trends were observed. In fact, in many cases, the results were somewhat comparable for all three waters. Although, a comparison to the ultra-pure water experiments carried out under the same conditions (i.e. the *Linking* experiments) showed that removals were generally lower in the partially-treated water, indicating that water quality does affect treatment performance. Another notable contrast with the ultra-pure water results was that for the partially-treated water, the benefits of adding hydrogen peroxide were often not seen until the higher MP-UV fluences of 100 or 300 mJ/cm^2. This suggests that one or more water quality parameters was either impeding the formation of •OH radicals or scavenging them; this interference then had to be overcome before •OH radicals were formed in sufficient levels to cause perceptible oxidation of the contaminants. Overall, the results from the partially-treated water experiments suggest that there will be variability in treatment performance with varying water quality and that the results are likely to be water specific. This in turn suggests that pilot-scale or bench-scale studies would be required in order to properly assess the potential of these treatments for the removal of PPCPs at full-scale.

7.3 Summary of Kinetics Study

The final sets of experiments were designed to achieve the third objective, which was to obtain estimates of kinetic parameters describing the degradation of the target compounds. These experiments were carried out in ultra-pure water at a range of fluences for both lamps, as discussed in Chapter 3, and the results were presented in Chapter 6. Fluence-based rate constants were determined for both direct photolysis (degradation resulting from UV irradiation) and indirect photolysis (degradation resulting from oxidation by the •OH radical). The kinetic parameters for naproxen compared well with those presented in a study by Pereira (2005), which recently became available. Markedly, the indirect photolysis rate constants for all four compounds were essentially the same (~ 0.01 cm^2/mJ), which corroborates the non-selective nature of the •OH radical mentioned in Chapter 2. On the other hand, the rate constants for direct photolysis differed between compounds. Triclosan had the highest direct photolysis rate constant, followed by naproxen, gemfibrozil, and then ibuprofen with the lowest. These results correspond well with those for both the ultra-pure water and partially-treated water experiments during which triclosan consistently underwent the highest percent removal with UV treatment alone, with naproxen removals usually slightly less. Furthermore, ibuprofen and gemfibrozil generally required very high UV fluences to be substantially removed by UV alone. Altogether the results clearly demonstrate that triclosan is the most susceptible to direct photolysis, while ibuprofen and gemfibrozil are somewhat resilient.

A comparison of direct and indirect photolysis rates determined for the MP lamp implies that the differing removal rates observed for the four compounds during UV/H_2O_2 treatment are attributable to the differences in direct photolysis rates. Based on the rate constants for ibuprofen and gemfibrozil, degradation is primarily due to indirect photolysis. In the case of naproxen, both processes are important but indirect photolysis is the dominant reaction. On the other hand, for degradation of triclosan, both direct and indirect photolysis are equally important. Similar results were seen for the LP lamp, although for LP-UV/H_2O_2 it appeared that there was a threshold fluence required before •OH radicals were present in sufficient concentrations to cause perceptible degradation of the target compounds. This lag-phase exhibited on the kinetics plots put into question the use of pseudo-first order kinetics to describe the entirety of the LP results. It may also explain why the calculated indirect rate constants were more varied amongst the target compounds than for the MP lamp results. Overall though, the calculated kinetic rate constants confirm the importance of •OH radical attack for the degradation of these PPCPs, especially for ibuprofen and gemfibrozil.

7.4 Comparison to Other Treatment Objectives

The final objective of this study was to compare the UV fluences found to be effective for removal of these PPCPs to those that have been conventionally applied for disinfection, as well as to those found to be of use (either alone or as part of AOPs) for removal of taste and odour compounds. As mentioned throughout, typical UV fluences applied for disinfection are around 40 mJ/cm^2. In all of the LP lamp experiments carried out during this study, removals at this low fluence were usually very low (20% or less) or were negligible

altogether. Removals at 40 mJ/cm^2 with the MP lamp were a bit higher, but still less than 50%, with the exception of triclosan, for which removals were still only as high as 64%. Given that the concentrations used in this research were generally within the range of expected environmental concentrations, these results imply that in order to achieve substantial removals of these compounds in practice, even if the water quality is very good, fluences much higher than are typically used for disinfection would be required.

The fluences that were found to substantially remove the selected PPCPs are comparable to those found to be effective in taste and odour studies. For example, Rosenfeldt et al. (2005) found that less than 20% of geosmin and methylisoborneol (MIB) were removed using an MP-UV fluence of 50 mJ/cm^2. On the other hand, MP-UV/H_2O_2 with a fluence of 1000 mJ/cm^2 removed more than 70% of geosmin and MIB (Rosenfeldt et al., 2005). There are other parallels for the removal of taste and odour compounds: at the same fluences, the MP lamp is generally more effective than the LP lamp; the addition of H_2O_2 markedly improves removals; and water quality will influence the treatment effectiveness (e.g Rosenfeldt et al., 2005; Gray and Andrews, 2006). These similarities suggest that the same treatment (i.e. MP-UV/H_2O_2) could likely be used to degrade a range of trace organics, including both persistent taste and odour-causing compounds and PPCPs.

Overall, it can be said that UV/H_2O_2, particularly when MP-UV is utilized, is a promising treatment for the removal of PPCPs, as it has been shown here to be effective for the removal

of ibuprofen, gemfibrozil, naproxen and triclosan, which are representative of several other PPCPs.

Chapter 8
Conclusions and Recommendations

This chapter summarizes the major findings of this study. As well, recommendations for further studies will be presented.

8.1 Major Findings

The major findings of this bench-scale study with respect to the removal of selected pharmaceuticals and personal care products (PPCPs) from both ultra-pure water and partially treated water from a drinking water treatment plant using UV alone and the advanced oxidation process UV/H_2O_2 are as follows:

- The MP lamp was much more effective than the LP lamp in all cases when similar fluences were applied; this was likely due to the broader emission spectra of the MP lamp.

- Addition of H_2O_2 typically increased removal rates, in some cases substantially, through formation and subsequent reaction of the PPCP with the •OH radical.

- Complete removal of all four compounds from ultra-pure water was achievable with very high fluences (compared to those used for UV disinfection) with MP-UV alone (at or above 1000 mJ/cm^2) or with relatively high fluences for MP-UV/H_2O_2 (200-300 mJ/cm^2) with 10 mg/L H_2O_2.

- In an ultra-pure water matrix, a high LP fluence of 1000 mJ/cm^2 caused only triclosan to substantially degrade; furthermore, only triclosan and naproxen had average percent removals above 60% with LP-UV/H_2O_2 at a typical disinfection fluence of 40 mJ/cm^2 with 100 mg/L H_2O_2.

- Removals were lower when target substances were treated in combination as opposed to independently; there was apparent competition for both UV absorbance and oxidation by the •OH radical; however, this may simply have been the result of a higher total contaminant concentration in solution, which may have led to simulated matrix effects that lessened the availability of the •OH radical and incident UV irradiation for degradation of all four compounds.

- Removals were improved when the combined target compounds were present at a lower individual concentration range (~750 ng/L, as opposed to ~250 µg/L), which suggests that removals may be concentration driven, with reduced matrix effects seen at lower overall contaminant concentrations.

- All four compounds had fluence-based reaction rate constants for MP-UV indirect photolysis of approximately 0.01 cm^2/mJ; MP-UV direct photolysis rate constants ranged between 0.0007-0.007 cm^2/mJ, with ibuprofen having the lowest and triclosan the highest; LP-UV direct photolysis rate constants could only be determined for naproxen and triclosan and were 0.0002 and 0.0033 cm^2/mJ, respectively; overall rate constants describing degradation of the four compounds due to LP-UV/H_2O_2 ranged from 0.0049 to 0.0124 cm^2/mJ.

- Kinetic parameters determined for both direct and indirect photolysis confirmed the importance of •OH radicals for degradation, especially for ibuprofen and gemfibrozil.

- Variability in treatment performance was observed with varying water quality; the parameters measured included pH, TOC, nitrate, alkalinity, turbidity, and UV transmittance; however, it was not evident which specific quality parameters influenced treatment effectiveness.

- The overall trends were similar to those seen for taste and odour compounds by other researchers; for example, fluences required for substantial removal were much higher than typical disinfection doses, the MP lamp was more effective than the LP lamp (when compared solely on a fluence-basis), and the addition of H_2O_2 improved removals.

Overall UV/H_2O_2 appears to be a very promising technology for the removal of these selected PPCPs during drinking water treatment.

8.2 Recommendations for Further Study

There are several areas of this research that could be further explored. One possibility is a more detailed investigation into the kinetics of the degradation reactions of the target compounds. More specifically, it would be useful to determine the second-order rate constants for the reactions with the •OH radicals, as done by other researchers for similar compounds (e.g. Pereira, 2005). In addition, it would be interesting to examine potential competition kinetics that result when the compounds are not alone in solution.

Perhaps even more important than further kinetics work would be an evaluation of the degree of mineralization that these compounds undergo during treatment. As mentioned in Chapter 2, with oxidation processes there exists the possibility of creating by-products or intermediate compounds if the contaminants are not completely mineralized during treatment. As demonstrated in related studies with PPCPs (e.g. Vogna et al., 2004b), there is the potential to form intermediates that are more toxic than the original pharmaceutical would be. On the other hand, relatively innocuous compounds may instead be formed. It would be valuable to know which is the case for these selected PPCPs during treatment with UV and UV/H_2O_2.

Also beneficial, especially for extrapolation to full-scale applications, would be a closer evaluation of the influence of water quality on treatment effectiveness. Such an investigation would be particularly useful if one or more parameters could be isolated as being the most important for consideration when assessing the suitability of UV or UV/H_2O_2 for a specific water containing these selected PPCPs.

There are other areas of research that would also benefit full-scale applications. For example, it would be useful to optimize the hydrogen peroxide dosages required during UV/H_2O_2. Finding the minimum useful hydrogen peroxide dose could potentially diminish the problem of having to remove residual hydrogen peroxide during subsequent steps in the treatment train. This in turn leads to the final recommendation, and that is to pursue novel

methods for quenching residual hydrogen peroxide. The catalase used during this and other bench-scale work is not appropriate for application in a full-scale treatment plant. The quenching methods that are currently considered for full-scale application include several chemical agents as well as granular activated carbon (GAC). It would be advantageous to have additional methods to remove the hydrogen peroxide, particularly methods that do not require both the addition and subsequent removal of yet another chemical.

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Appendix A

Sample Processing and Analysis

This appendix includes material relevant to Chapter 3.

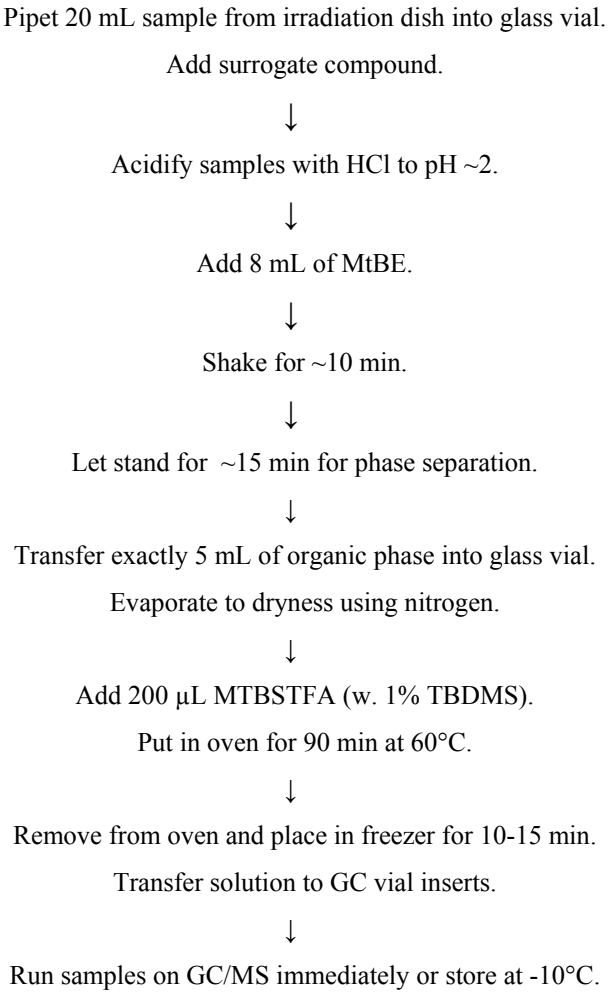

Figure A. 1: Sample processing flow chart for Preliminary experiments

Table A. 1: Parameters used for GC/MS Analysis

Compound Name	Retention Time (min)	Quantification Ion $(m/z)^3$	Qualification Ion(s) $(m/z)^3$
Ibuprofen	14.20	263	161
Mecoprop-d3	14.86	227	274
Gemfibrozil	19.45	243	307, 364
Naproxen	21.72	287	185
Triclosan	21.86	347	200

Table A. 2: GC/MS Operating Information

Column:	DB 1701 (30m x 0.25 mm x 0.25 μm)
Carrier Gas:	helium (1.2 mL/min)
Solvent Delay:	13.9 min
Injection Volume:	4 μL*
Temperature program:	3 min at 45°C, first ramp: 20°C/min to 200°C, 5 min at 200 °C second ramp: 10°C/min to 250°C, 5 min at 250°C third ramp: 5°C/min to 300°C, 5 min at 300°C

Notes:

* a smaller injection volume of 3 μL was used for the samples analyzed during the Kinetics Study

Appendix B

Data from Ultra-pure Water Experiments

This appendix includes the data presented in Chapter 4.

Table B. 1: Data for *Preliminary* experiments; target compounds were studied independently in an ultra-pure water matrix at a concentration of ~250 µg/L

Compound	Lamp Type	UV Fluence (mJ/cm^2)	H_2O_2 Dose (mg/L)	Average Percent Removal*	Standard Deviation*
Gemfibrozil	LP	40	0	0.7	7.8
		40	100	19.5	1.0
		1000	0	0.0	N/A
	MP	40	0	0.1	0.7
		40	100	54.3	7.3
		170	0	7.8	6.2
		170	100	91.5	6.0
		1000	0	53.1	4.2
		1000	1000	99.4	0.4
		4175	0	99.1	0.1
		4175	1000	99.7	0.6
Ibuprofen	LP	40	0	3.6	6.4
		40	100	47.0	8.1
		1000	0	0.0	N/A
	MP	40	0	5.6	8.2
		40	100	53.7	5.9
		170	0	14.5	4.6
		170	100	95.5	0.4
		1000	0	72.2	5.9
		1000	1000	99.3	0.0
		4175	0	98.3	0.5
		4175	1000	99.1	0.1

Naproxen	LP	40	0	3.8	5.7
		40	100	77.7	1.8
		1000	0	22.2	N/A
	MP	40	0	12.9	15.0
		40	100	40.1	6.5
		170	0	49.5	2.4
		170	100	92.5	1.4
		1000	0	99.4	1.1
		1000	1000	99.4	1.3
		4175	0	99.3	1.3
		4175	1000	100.0	0.0
Triclosan	LP	40	0	17.0	12.5
		40	100	68.2	3.9
		1000	0	96.0	0.7
	MP	40	0	41.3	4.9
		40	100	66.6	5.1
		170	0	82.3	0.8
		170	100	97.7	0.3
		1000	0	99.4	0.1
		1000	1000	99.6	0.0
		4175	0	99.9	0.2
		4175	1000	99.8	0.2

Notes:

N/A - not available
*** Calculated values are based on two replicate irradiations and duplicate analyses**

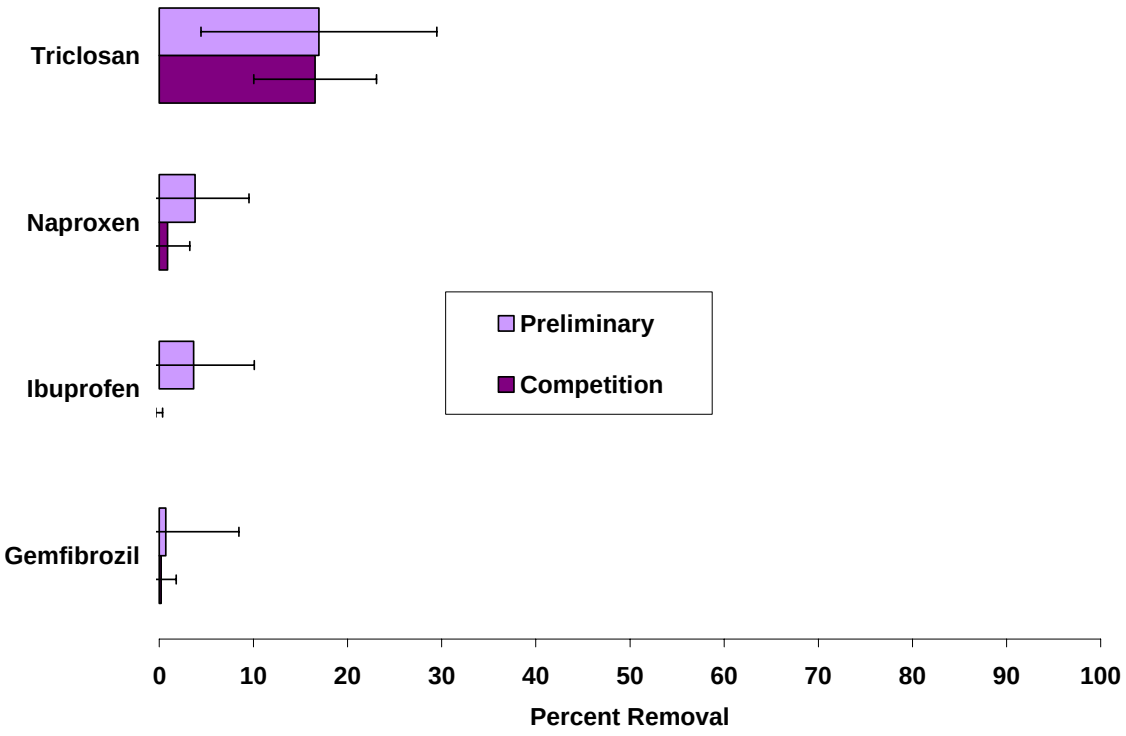

Figure B. 1: Comparison of *Preliminary* and *Competition* removals following an LP-UV fluence of 40 mJ/cm^2

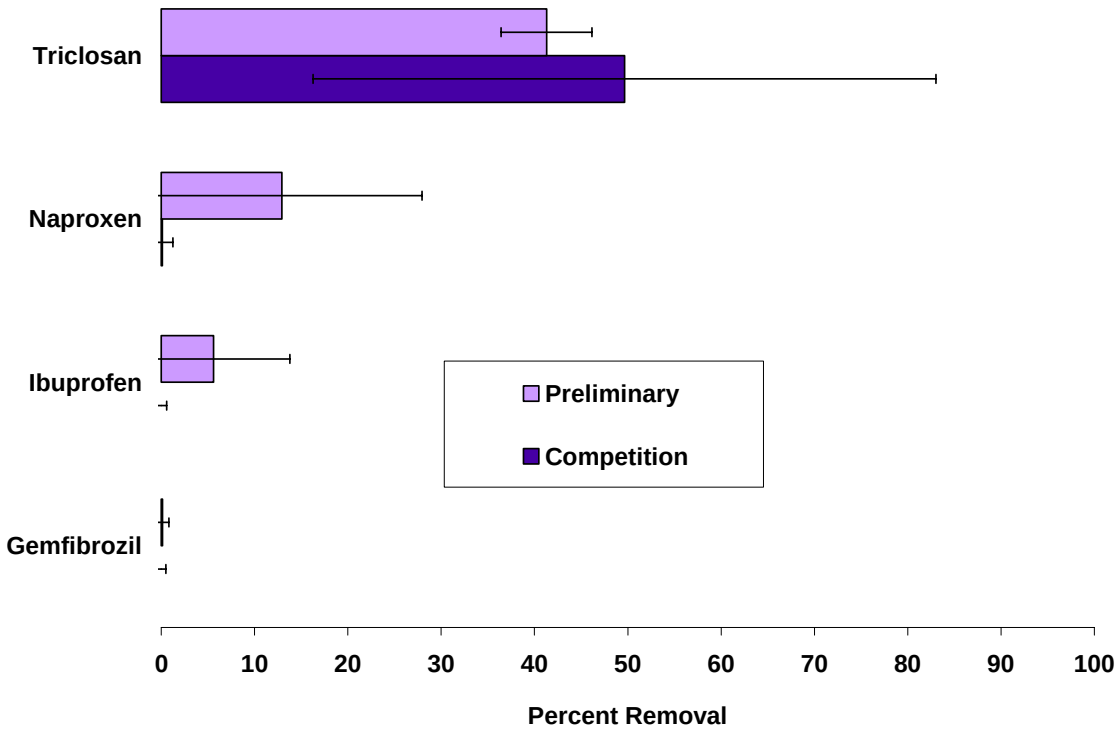

Figure B. 2: Comparison of *Preliminary* and *Competition* removals following an LP-UV fluence of 40 mJ/cm^2

Table B. 2: Data for *Competition* experiments; target compounds were spiked together in solution, each at a concentration of ~250 µg/L in an ultra-pure water matrix

Compound	Lamp Type	UV Fluence (mJ/cm^2)	H_20_2 Dose (mg/L)	Average Percent Removal*	Standard Deviation*
Gemfibrozil	LP	40	0	0.2	1.6
		40	100	33.9	7.9
	MP	40	0	0.0	0.5
		40	100	26.9	12.2
		1000	0	12.1	9.3
		1000	1000	99.0	0.8
Ibuprofen	LP	40	0	0.0	0.4
		40	100	24.8	4.0
	MP	40	0	0.0	0.6
		40	100	9.5	13.2
		1000	0	18.8	13.8
		1000	1000	98.7	0.8
Naproxen	LP	40	0	0.9	2.4
		40	100	29.2	11.6
	MP	40	0	0.1	1.1
		40	100	36.2	9.0
		1000	0	97.4	0.1
		1000	1000	100.0	0.0
Triclosan	LP	40	0	16.6	6.5
		40	100	48.2	8.4
	MP	40	0	49.7	33.4
		40	100	54.7	5.6
		1000	0	98.2	1.3
		1000	1000	98.8	1.7

Notes:

N/A - not available
*** Calculated values are based on two replicate irradiations and duplicate analyses**

Table B. 3: Data for *Linking* experiments; target compounds were spiked together in solution, each at a concentration of ~750 ng/L in an ultra-pure water

Compound	Lamp Type	UV Fluence (mJ/cm^2)	H_20_2 Dose (mg/L)	Average Percent Removal*	Standard Deviation*
Ibuprofen	LP	40	0	0.0	13.4
		40	10	47.4	7.6
		40	100	55.0	N/A
	MP	40	0	34.1	4.7
		40	10	58.6	0.9
		40	100	67.5	1.5
		300	0	50.1	25.6
		300	10	98.0	0.9
Gemfibrozil	LP	40	0	0.0	8.0
		40	10	50.3	1.5
		40	100	55.2	N/A
	MP	40	0	31.3	6.1
		40	10	59.9	0.9
		40	100	50.7	0.9
		300	0	50.3	3.5
		300	10	97.6	1.6
Naproxen	LP	40	0	0.0	13.2
		40	10	66.0	3.0
		40	100	59.3	N/A
	MP	40	0	10.4	11.2
		40	10	53.3	1.9
		40	100	51.2	7.2
		300	0	84.1	2.3
		300	10	99.2	0.7
Triclosan	LP	40	0	5.4	7.2
		40	10	55.7	1.8
		40	100	59.2	N/A
	MP	40	0	44.2	0.0
		40	10	55.0	2.8
		40	100	57.8	9.6
		300	0	94.2	0.9
		300	10	97.4	1.1

Notes:

N/A - not available
*** Calculated values are based on two replicate irradiations and single analysis**

Appendix C

Data and Additional Graphs from Partially-treated Water Experiments

This appendix includes the data and additional graphs pertaining to Chapter 5.

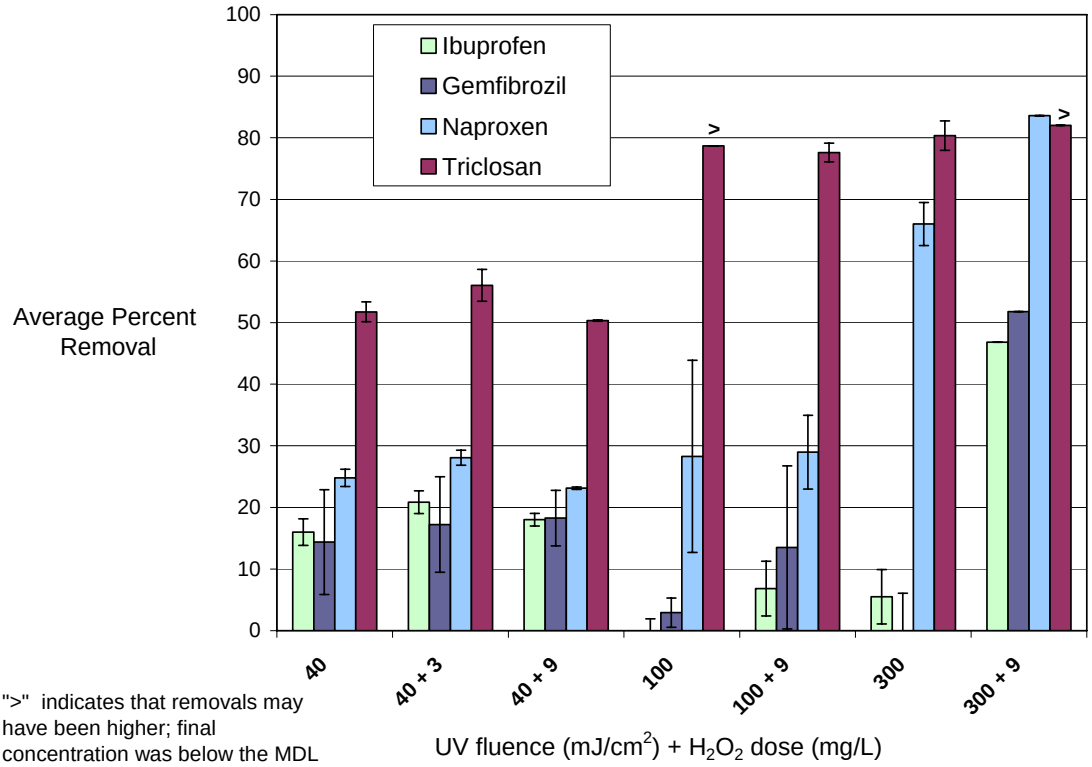

Figure C. 1: Average percent removal of target compounds spiked into partially treated spring water and subjected to MP-UV and MP-UV/H_2O_2 at fluences of 40, 100, and 300 mJ/cm^2

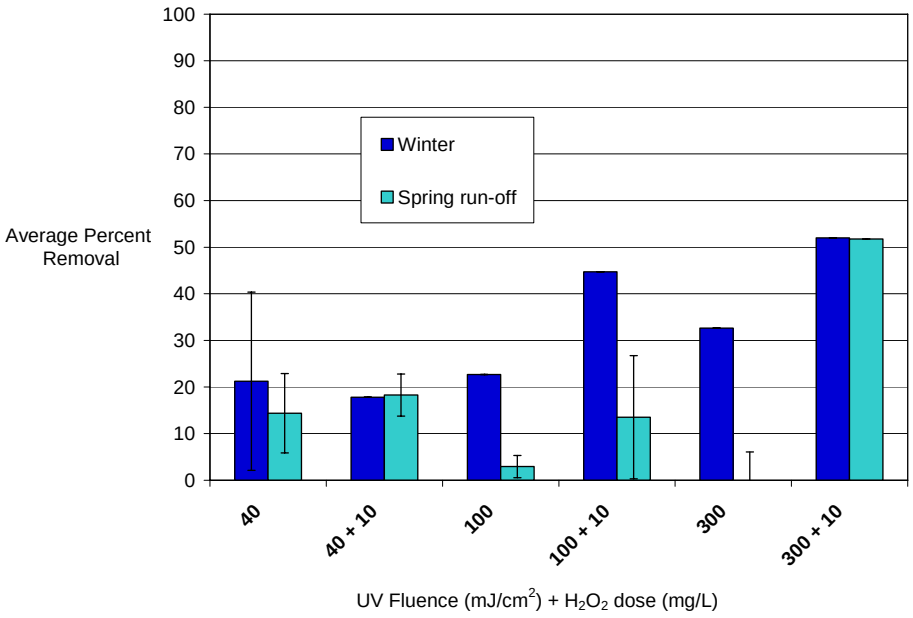

Figure C. 2: Average percent removal of gemfibrozil spiked into partially treated winter and spring water and subjected to MP-UV and MP-UV/H_2O_2

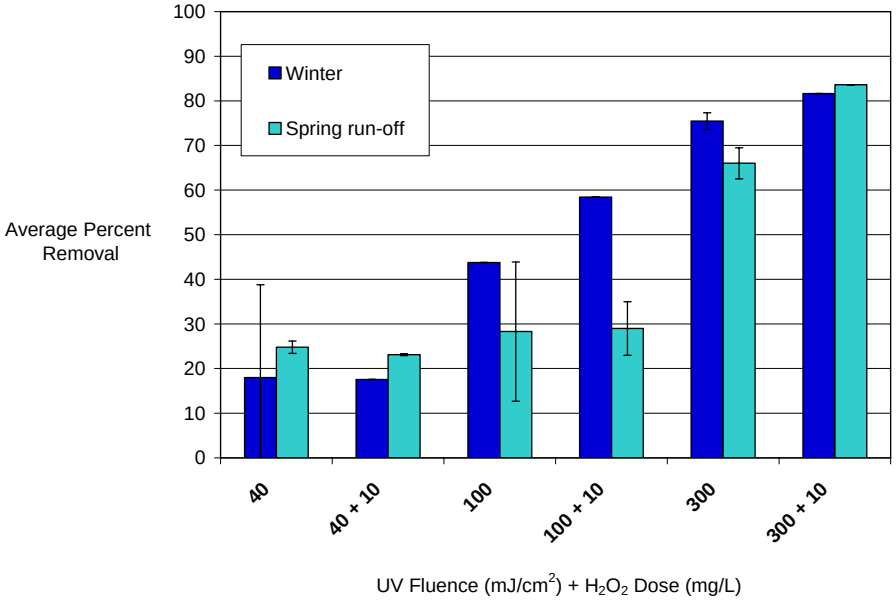

Figure C. 3: Average percent removal of naproxen spiked into partially treated winter and spring water and subjected to MP-UV and MP-UV/H_2O_2

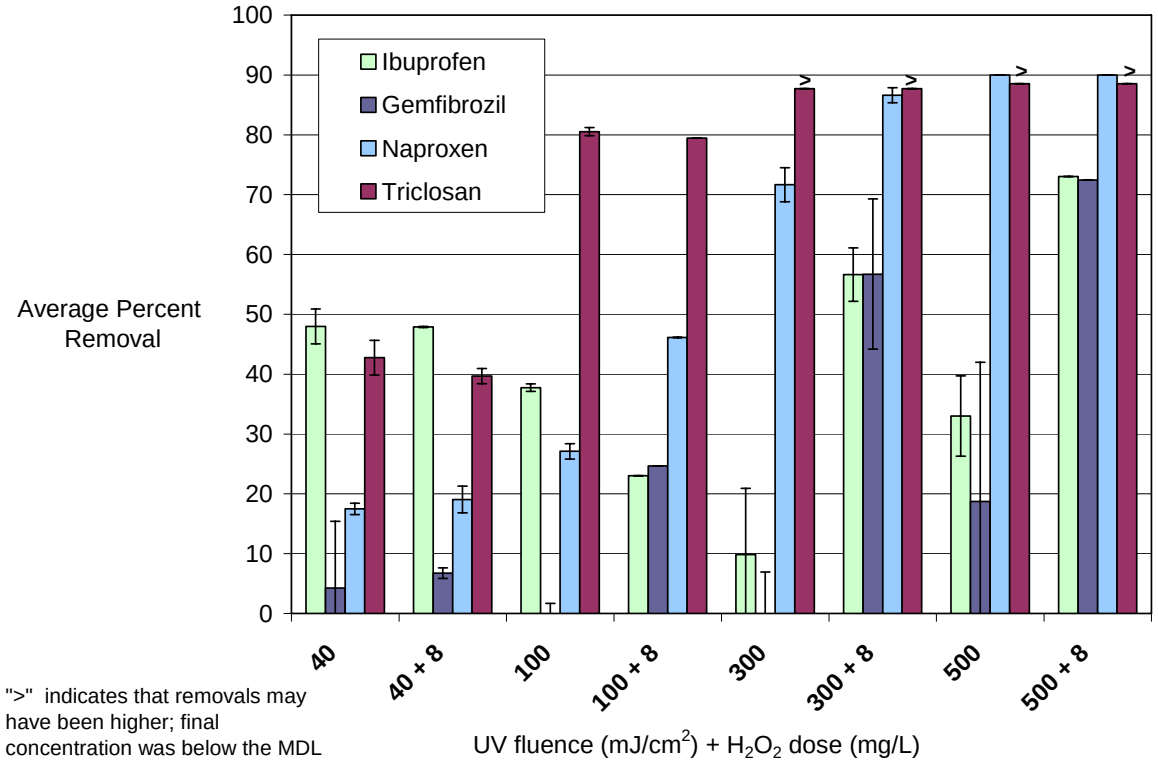

Figure C. 4: Average percent removal of target compounds spiked into partially treated summer water and subjected to MP-UV and MP-UV/H_2O_2 at fluences of 40, 100, 300 and 500 mJ/cm^2

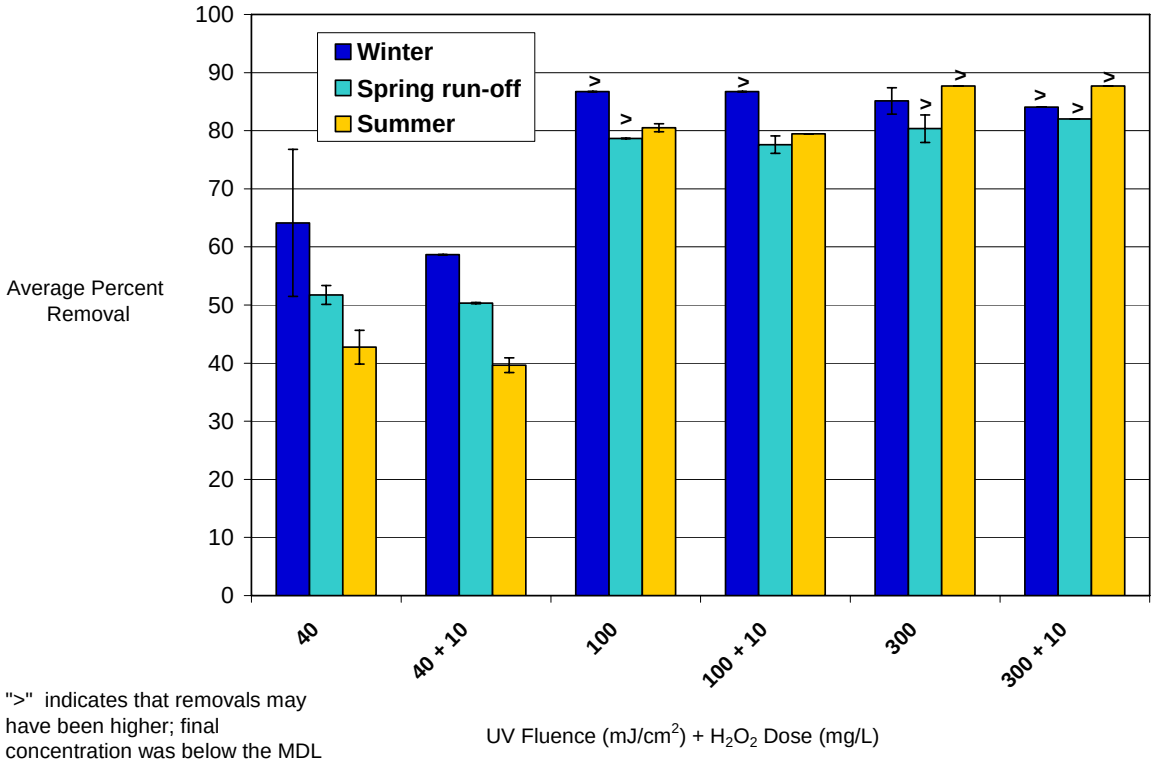

Figure C. 5:Average percent removal of triclosan spiked into partially treated winter, spring run-off, and summer water and subjected to MP-UV and UV/H_2O_2

Table C. 1: Ibuprofen and gemfibrozil data for partially-treated water experiments; target compounds were spiked together into sampled water, each at a concentration of ~750 ng/L; three seasonal waters tested

Compound	Lamp Type	UV Fluence (mJ/cm^2)	H_20_2 Dose (mg/L) [2]	Winter Water		Spring Run-off Water		Summer Water	
				Average Percent Removal[1]	Standard Deviation[1]	Average Percent Removal[1]	Standard Deviation[1]	Average Percent Removal[1]	Standard Deviation[1]
Ibuprofen	LP	40	0	5.7	1.2	0.0	6.7	2.5	1.2
		40	3	14.0	5.3	7.9	8.3	N/A	N/A
		40	10	17.9	8.1	10.6	14.0	16.2	5.6
	MP	40	0	16.6	6.9	16.0	2.1	48.0	2.9
		40	3	13.7	2.4	20.8	1.8	N/A	N/A
		40	10	15.5	0.0	18.0	1.0	47.9	0.1
		100	0	16.4	0.0	0.0	1.9	37.7	0.6
		100	10	37.7	0.0	6.8	4.4	23.0	0.0
		300	0	11.5	5.5	5.5	4.4	9.8	11.1
		300	10	45.6	0.0	46.8	0.0	56.6	4.5
		500	0	N/A	N/A	N/A	N/A	33.0	6.7
		500	10	N/A	N/A	N/A	N/A	73.0	0.0
Gemfibrozil	LP	40	0	11.5	4.8	2.4	3.4	0.0	2.4
		40	3	23.6	11.1	20.7	5.4	N/A	N/A
		40	10	21.1	3.7	22.3	18.2	12.1	5.8
	MP	40	0	21.2	19.1	14.4	8.5	4.3	11.2
		40	3	11.9	7.4	17.2	7.7	N/A	N/A
		40	10	17.8	0.0	18.3	4.5	6.8	0.9
		100	0	22.7	0.0	2.9	2.4	0.0	1.7
		100	10	44.7	0.0	13.5	13.2	24.7	0.0
		300	0	32.7	0.0	0.0	6.1	0.0	6.9
		300	10	52.0	0.0	51.8	0.0	56.7	12.6
		500	0	N/A	N/A	N/A	N/A	18.7	23.3
		500	10	N/A	N/A	N/A	N/A	72.4	0.0

Notes:

N/A - not available

1 - Calculated values are based on two replicate irradiations and single analysis

2 - These are the intended H_2O_2 doses; random H_2O_2 measurements were taken and as described in the text of Chapter 5, some deviations were seen; more specifically the measured doses were as follows: Winter samples were between 8.9-9.8 mg/L , Spring samples were between 8.5-9.7 mg/L, and Summer samples were between 7.0-8.2 mg/L

Table C. 2: Naproxen and triclosan data for partially-treated water experiments; target compounds were spiked together into sampled water, each at a concentration of ~750 ng/L; three seasonal waters tested

Compound	Lamp Type	UV Fluence (mJ/cm^2)	H_20_2 Dose (mg/L)	Winter Water		Spring Run-off Water		Summer Water	
				Average Percent Removal[1]	Standard Deviation[1]	Average Percent Removal[1]	Standard Deviation[1]	Average Percent Removal[1]	Standard Deviation[1]
Naproxen	LP	40	0	9.3	2.9	4.5	6.9	3.9	3.3
		40	3	19.0	11.2	12.6	10.9	N/A	N/A
		40	10	24.9	2.6	18.3	15.5	15.9	2.7
	MP	40	0	18.0	20.8	24.8	1.4	17.5	0.9
		40	3	13.2	9.3	28.1	1.2	N/A	N/A
		40	10	17.5	0.0	23.1	0.2	19.0	2.2
		100	0	43.8	0.0	28.3	15.6	27.1	1.3
		100	10	58.4	0.0	29.0	6.0	46.1	0.0
		300	0	75.5	1.9	66.0	3.5	71.7	2.8
		300	10	81.6	0.0	83.6	0.0	86.6	1.3
		500	0	N/A	N/A	N/A	N/A	**90.0**	0.0
		500	10	N/A	N/A	N/A	N/A	**90.0**	0.0
Triclosan	LP	40	0	7.4	3.7	17.2	14.1	10.2	1.4
		40	3	22.8	0.6	29.6	13.9	N/A	N/A
		40	10	34.4	8.4	37.6	12.2	20.7	6.7
	MP	40	0	64.1	12.6	51.8	1.6	42.8	2.9
		40	3	57.3	8.2	56.0	2.6	N/A	N/A
		40	10	58.7	0.0	50.3	0.1	39.7	1.3
		100	0	**86.7**	0.0	**78.7**	0.0	80.5	0.7
		100	10	**86.7**	0.0	77.6	1.5	79.5	0.0
		300	0	85.1	2.2	**80.4**	2.4	**87.7**	0.0
		300	10	**84.1**	0.0	**82.0**	0.0	**87.7**	0.0
		500	0	N/A	N/A	N/A	N/A	**88.6**	0.0
		500	10	N/A	N/A	N/A	N/A	**88.6**	0.0

Notes:

N/A - not available

1 - Calculated values are based on two replicate irradiations and single analysis

2 - These are the intended H_2O_2 doses; random H_2O_2 measurements were taken and as described in the text of Chapter 5, some deviations were seen; more specifically the measured doses were as follows: Winter samples were between 8.9-9.8 mg/L , Spring samples were between 8.5-9.7 mg/L, and Summer samples were between 7.0-8.2 mg/L

Appendix D

Data from Kinetics Study

Table D. 1: MP direct photolysis data for ibuprofen; spiked at ~250 µg/L in an ultra-pure water matrix; single irradiations and duplicate analyses were carried out

Compound	Lamp Type	UV Fluence (mJ/cm^2)	C/Co	ln(C/Co)
Ibuprofen	MP	40	0.940	-0.06
			0.920	-0.08
		100	0.920	-0.08
			N/A	N/A
		200	0.882	-0.13
			0.887	-0.12
		300	0.846	-0.17
			0.850	-0.16
		400	0.685	-0.38
			N/A	N/A
		500	0.686	-0.38
			0.708	-0.34
		600	0.662	-0.41
			0.662	-0.41
		1000	0.494	-0.71
			0.482	-0.73
		4175	**0.025**	**-3.68**
			0.026	**-3.66**

Notes:

N/A - not available

Bold - values shown in bold indicate that samples were below the method detection limit (MDL) of 0.0258 µM (5.33 µg/L)

Table D. 2: MP direct photolysis data for gemfibrozil; spiked at ~250 µg/L in an ultra-pure water matrix; single irradiations and duplicate analyses were carried out

Compound	Lamp Type	UV Fluence (mJ/cm^2)	C/Co	ln(C/Co)
Gemfibrozil	MP	40	0.930	-0.07
			0.855	-0.16
		100	0.805	-0.22
			0.796	-0.23
		170	0.756	-0.28
			0.742	-0.30
		300	N/A	N/A
			N/A	N/A
		400	0.504	-0.69
			0.546	-0.61
		500	0.384	-0.96
			0.408	-0.90
		600	0.344	-1.07
			0.369	-1.00
		1000	0.195	-1.63
			0.188	-1.67
		4175	N/A	N/A
			0.012	**-4.44**

Notes:

N/A - not available

Bold - values shown in bold indicate that samples were below the method detection limit (MDL) of 0.0304 µM (7.60 µg/L)

Table D. 3: MP direct photolysis data for naproxen; spiked at ~250 µg/L in an ultra-pure water matrix; single irradiations and duplicate analyses were carried out

Compound	Lamp Type	UV Fluence (mJ/cm^2)	C/Co	ln(C/Co)
Naproxen	MP	40	0.877	-0.131
			0.896	-0.110
		100	0.711	-0.341
			0.730	-0.315
		170	0.548	-0.601
			0.539	-0.617
		400	0.181	-1.711
			0.184	-1.694
		500	0.039	-3.248
			0.037	-3.301
		600	0.016	-4.114
			0.017	-4.084
		1000	**0.000**	N/A
			0.000	N/A

Notes:

N/A - not available
Bold - values shown in bold indicate that samples were below the method detection limit (MDL) of 0.0164 µM (3.79 µg/L)

Table D. 4: MP direct photolysis data for triclosan; spiked at ~250 µg/L in an ultra-pure water matrix; single irradiations and duplicate analyses were carried out

Compound	Lamp Type	UV Fluence (mJ/cm^2)	C/Co	ln(C/Co)
Triclosan	MP	40	0.694	-0.37
		40	0.789	-0.24
		100	0.384	-0.96
		100	0.229	-1.47
		170	0.214	-1.54
		170	0.220	-1.51
		300	0.085	-2.47
		300	0.084	-2.48
		400	**0.039**	**-3.24**
		400	**0.047**	**-3.05**
		500	**0.019**	**-3.98**
		500	**0.019**	**-3.95**
		600	**0.012**	**-4.44**
		600	**0.012**	**-4.40**
		1000	**0.006**	**-5.13**
		1000	**0.006**	**-5.17**
		4825	**0.004**	**-5.60**
		4825	**0.004**	**-5.60**

Notes:

N/A - not available

Bold - values shown in bold indicate that samples were below the method detection limit (MDL) of 0.0357 µM (10.33 µg/L)

Table D. 5: MP indirect photolysis data for ibuprofen; spiked at ~250 µg/L in an ultra-pure water matrix; single irradiations and duplicate analyses were carried out

Compound	Lamp Type	UV Fluence (mJ/cm^2)	H_2O_2 Dose (mg/L)	C/Co	ln(C/Co)
Ibuprofen	MP	40	10	1.026	0.03
				1.023	0.02
		100	10	0.770	-0.26
				N/A	N/A
		170	10	0.380	-0.97
				0.361	-1.02
		300	10	0.053	-2.93
				0.054	-2.92
		400	10	**0.019**	**-3.95**
				0.018	**-3.99**
		500	10	**0.008**	**-4.80**
				0.008	**-4.79**

Notes:

N/A - not available

Bold - values shown in bold indicate that samples were below the method detection limit (MDL) of 0.0258 µM (5.33 µg/L)

Table D. 6: MP indirect photolysis data for gemfibrozil; spiked at ~250 µg/L in an ultra-pure water matrix; single irradiations and duplicate analyses were carried out

Compound	Lamp Type	UV Fluence (mJ/cm^2)	H_2O_2 Dose (mg/L)	C/Co	ln(C/Co)
Gemfibrozil	MP	40	10	0.586	-0.53
				0.504	-0.69
		100	10	0.187	-1.68
				0.159	-1.84
		170	10	0.059	-2.84
				0.056	-2.88
		300	10	0.012	-4.43
				0.012	-4.44
		400	10	**0.009**	**-4.67**
				0.010	**-4.57**
		500	10	N/A	N/A
				0.009	**-4.66**

Notes:

N/A - not available

Bold - values shown in bold indicate that samples were below the method detection limit (MDL) of 0.0304 µM (7.60 µg/L)

Table D. 7: MP indirect photolysis data for naproxen; spiked at ~250 µg/L in an ultra-pure water matrix; single irradiations and duplicate analyses were carried out

Compound	Lamp Type	UV Fluence (mJ/cm^2)	H_2O_2 Dose (mg/L)	C/Co	ln(C/Co)
Naproxen	MP	40	10	0.640	-0.45
				0.588	-0.53
		100	10	0.358	-1.03
				N/A	N/A
		170	10	0.086	-2.45
				0.086	-2.46
		300	10	0.015	-4.21
				0.015	-4.20
		400	10	0.010	-4.58
				0.012	-4.44
		500	10	N/A	N/A
				0.000	**N/A**
		600	10	**0.000**	**N/A**
				0.000	**N/A**
		1000	10	**0.000**	**N/A**
				0.000	**N/A**

Notes:

N/A - not available
Bold - values shown in bold indicate that samples were below the method detection limit (MDL) of 0.0164 µM (3.79 µg/L)

Table D. 8: MP indirect photolysis data for triclosan; spiked at ~250 µg/L in an ultra-pure water matrix; single irradiations and duplicate analyses were carried out

Compound	Lamp Type	UV Fluence (mJ/cm^2)	H_2O_2 Dose (mg/L)	C/Co	ln(C/Co)
Triclosan	MP	40	10	N/A	N/A
				0.451	-0.80
		100	10	0.136	-2.00
				0.139	-1.97
		170	10	**0.032**	**-3.44**
				0.032	**-3.43**
		300	10	**0.006**	**-5.07**
				0.004	**-5.41**
		400	10	**0.016**	**-4.13**
				0.013	**-4.31**
		500	10	**0.005**	**-5.21**
				0.006	**-5.16**

Notes:

N/A - not available

Bold - values shown in bold indicate that samples were below the method detection limit (MDL) of 0.0357 µM (10.33 µg/L)

Table D. 9: Direct photolysis data for the LP lamp; compounds studied independently; each spiked at ~250 µg/L in an ultra-pure water matrix; single irradiations and duplicate analyses were carried out

Compound	Lamp Type	UV Fluence (mJ/cm^2)	H_2O_2 Dose (mg/L)	C/Co	ln(C/Co)
Ibuprofen	LP	45	0	0.989	-0.01
				0.996	-0.004
		100	0	1.015	0.015
				1.007	0.007
		300	0	0.981	-0.019
				N/A	N/A
Gemfibrozil	LP	40	0	0.985	-0.015
				0.924	-0.079
		100	0	N/A	N/A
				1.025	0.024
		300	0	1.002	0.002
				0.898	-0.108
		1000	0	1.135	0.127
Naproxen	LP	40	0	0.970	-0.030
				0.985	-0.015
		100	0	0.934	-0.068
				0.958	-0.043
		300	0	0.934	-0.068
				0.894	-0.112
		1000	0	0.809	-0.212
Triclosan	LP	40	0	0.978	-0.022
				0.921	-0.082
		100	0	N/A	N/A
				0.736	-0.307
		300	0	N/A	N/A
				0.489	-0.715
		1000	0	0.045	-3.107
				0.035	-3.362

Notes:

N/A - not available

Table D. 10: Indirect photolysis data for the LP lamp; compounds studied independently; each spiked at ~250 µg/L in an ultra-pure water matrix; single irradiations and duplicate analyses were carried out

Compound	Lamp Type	UV Fluence (mJ/cm^2)	H_2O_2 Dose (mg/L)	C/Co	ln(C/Co)
Ibuprofen	LP	43	10	1.159	0.148
			10	1.167	0.155
		100	10	1.185	0.170
			10	N/A	N/A
		300	10	0.304	-1.190
			10	0.291	-1.235
Gemfibrozil	LP	100	10	0.721	-0.327
			10	0.703	-0.353
		40	10	0.987	-0.013
			10	1.000	0.000
		300	10	0.045	-3.106
			10	0.046	-3.086
Naproxen	LP	40	10	0.712	-0.339
			10	0.714	-0.336
		100	10	0.445	-0.810
			10	0.447	-0.806
		300	10	0.096	-2.343
			10	0.092	-2.387
Triclosan	LP	40	10	0.825	-0.192
			10	0.821	-0.197
		127	10	0.431	-0.842
			10	0.458	-0.780
		300	10	0.097	-2.335
			10	0.100	-2.301

Notes:

N/A - not available