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The Role of Nitrate in Ultraviolet Photolysis of Free Chlorine

by

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B.A., Austin College 2008

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This thesis entitled:

The Role of Nitrate in Ultraviolet Photolysis of Free Chlorine

written by Traci L. Brooks

has been approved for the

Department of Civil, Environmental, and Architectural Engineering

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November 28, 2011

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

ABSTRACT

Traci L. Brooks (M.S. Environmental Engineering)

The Role of Nitrate in Ultraviolet Photolysis of Free Chlorine

Directed by Karl Linden and Aaron Dotson

Although chlorine in water can be beneficial for disinfection, it is also a nuisance chemical for some industries such as microchip processing, pharmaceuticals manufacturing, and beverage companies. For these industrial processes, there is a need to dechlorinate the water using non-chemical based methods. Ultraviolet light (UV) can be used for both disinfection purposes and for chemical removal in municipal and industrial water supplies. The degradation of chlorine has been known to occur under both low-pressure (LP) and medium-pressure (MP) UV. When dissolved organic matter and other compounds such as nitrate are present in the water, enhanced degradation of chlorine occurs. The mechanisms associated with the enhanced chlorine degradation rates, primarily through the photolysis of chlorine and nitrate, were studied. The pH and related chlorine speciation was an important factor when examining the reactions taking place. Polychromatic light from MP UV sources was found to be much more effective at removing free chlorine when nitrate was present, with the fastest decay rates occurring at basic pH. Enhanced degradation of chlorine with nitrate present resulted from nitrite formation and radical production during the photolysis of nitrate with light below 240 nm. Nitrite reacts quickly with both chlorine and hydroxyl radicals, but these reactions are strongly dependent on the pH. These finding provide insight into the use of UV light in the ultrapure water industry.

ACKNOWLEDGMENTS

I would first like to thank my advisor, Karl Linden, for his patience and support during this research. I owe a great deal of thanks to Aaron Dotson for all of his insight, encouragement, and support in the lab and while working to appreciate all of the chemistry involved in this research. I am very grateful for the support and help from all the members and friends of the Linden Lab group who helped to encourage and support me. I would also like to thank all of my family and friends for all of their love and support over the years. I could not have done this without you.

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CHAPTER 1: INTRODUCTION

Chlorine is a strong oxidant that is used in a majority of water treatment systems for disinfection or pre-oxidation. In drinking water distribution systems, a residual left in the distribution system acts as an important secondary disinfectant but can be problematic when this water is used for industrial purposes. These industrial activities include microchip processing, pharmaceuticals manufacturing, and beverage companies. The residual chlorine can interfere with these processes by damaging reverse osmosis (RO) membranes used in ultra pure water production, creating undesirable chemical reactions, and taste and odor problems in beverage production (Shipe, 2003; McClean, 2007). As an alternative to adding chemical quenching agents, like sodium metabisulfite and sodium bisulfite (White, 2010; Rajagopalan, 2006) for dechlorination, ultraviolet (UV) light can be used as a non-chemical method for chlorine destruction.

Photolysis of free chlorine (HOCl and OCl-, pKa = 7.5) occurs where the emission spectrum of the UV light overlaps with the absorption spectrum of the chlorine species and applied at such an intensity to result in a photochemical response. Figure 1 presents the associated UV lamp emission spectra (low pressure monochromatic output and medium pressure polychromatic output from lamps used in the Linden Laboratory) and the molar absorptivity of free chlorine. The difference in overlap between the free chlorine species and UV lamp types suggest that different photolysis rates will occur.

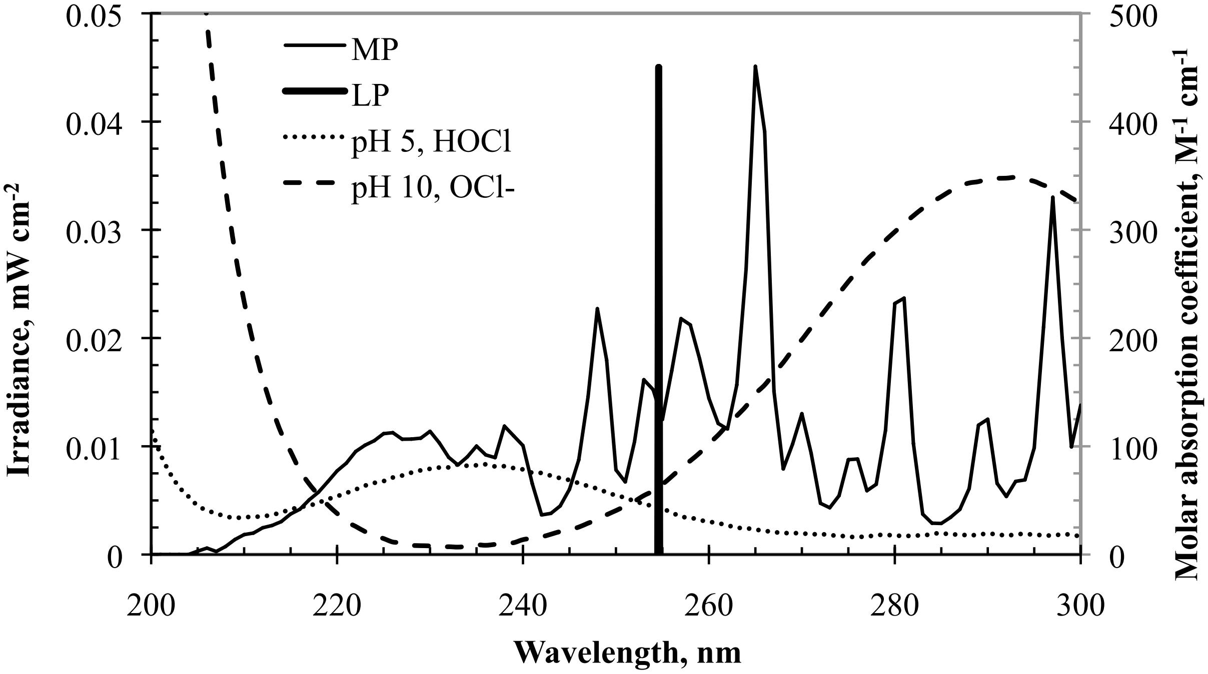

Figure 1. Medium-pressure and low-pressure lamp emission spectra and the molar absorption of chlorine species HOCl and OCl-

The effects of water quality, including pH and the presence of photosensitizing compounds such as nitrate, can play a role in the decay rate of chlorine. The pH does not affect the molar absorption spectra of nitrate (Figure 2). The photolysis of nitrate forms nitrite and hydroxyl radicals (·OH). It has been shown that nitrite and the subsequent radical formation from the photolysis of nitrate interact with chlorine causing degradation (Feng et al., 2007; Lister and Rosenblum, 1961; Pendlebury and Smith, 1973).

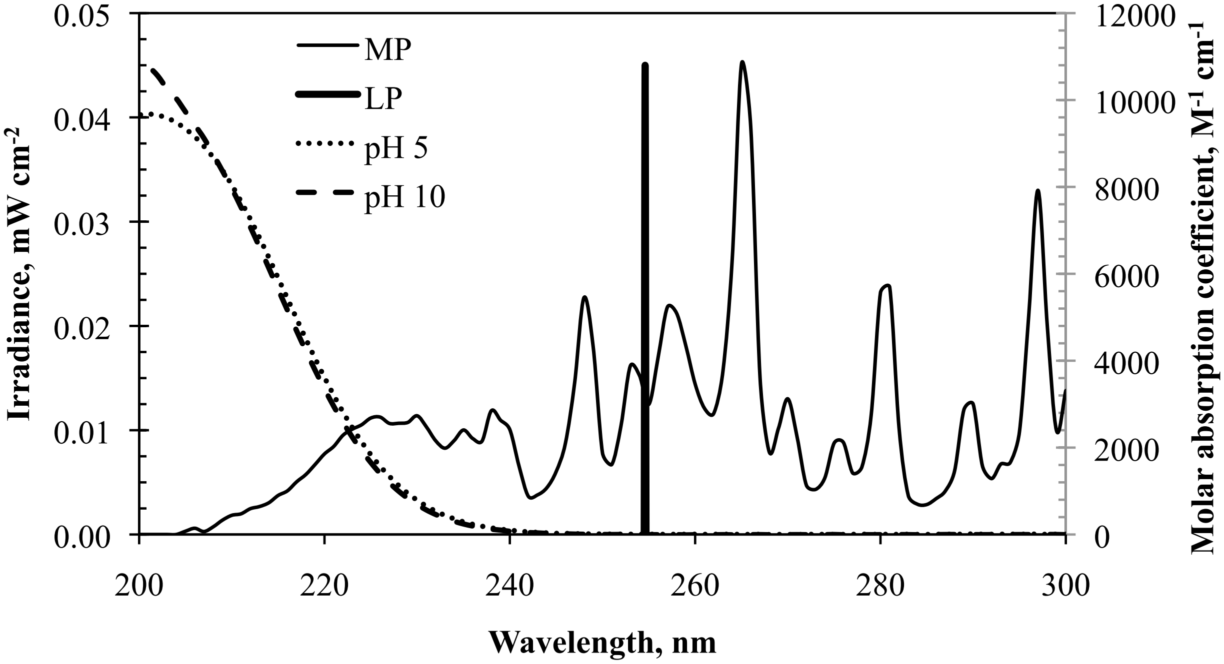

Figure 2. Medium-pressure and low-pressure lamp emission spectra and molar absorption coefficients of nitrate at pH 5 and 10

1.1 Photochemistry

The use of UV for disinfection during drinking water treatment has been studied for over a century (Linden and Rosenfeldt, 2011). The UV wavelength range in the electromagnetic spectrum extends from 100-400 nm with a generally recognized germicidal wavelength range extending from 200-280 nm, which is characterized as the UV-C range. The amount of energy emitted from UV is dependent on wavelength and described with Planck's Law of Radiation,

$$u = \frac{hc}{\lambda} \tag{1}$$

where u is the energy of a photon (J), h is Planck's constant (6.6261×10^{-34} J s), c is the speed of light (2.9979×10^{8} m s^{-1}), and λ is the wavelength (m).

The high energy of UV light in the germicidal range can cause damage to DNA and produce photochemical reactions in chemicals that absorb the light. The resulting transformation of the absorbing species are dependent on the first law of photochemistry, which states that only the photons absorbed by the system can produce a photochemical change. The attenuation of UV light occurs when it passes through water and is described through the Beer-Lambert law,

$$A = \log\frac{I_0}{I} = \varepsilon lc \tag{2}$$

where A is the absorbance, I_0 is the initial intensity of light entering the water, I is the intensity of light leaving the water, ε is the molar absorption coefficient (M^{-1} cm^{-1}), l is the path length (cm), and c is the molar concentration of the absorbing constituents (M). The absorbance is related to the UV transmittance (UVT) of the water, the amount of light passing through the water over a known path length,

$$\%UVT = 100 \times 10^{-A} \tag{3}$$

When determining the molar absorption coefficient of chlorine (Figure 1), the absorbance was measured from a known concentration at single wavelength intervals. The absorption spectra for HOCl peaks around 235 nm and OCl^- peaks around 292 nm. The most light is absorbed at these wavelengths.

The quantum yield is used to determine the efficiency of UV by establishing a value for the number of moles of product formed or reactant removed per mole of photon absorbed, represented by Φ. A quantum yield of 1 means that each photon absorbed is causing a photochemical change, while a quantum yield greater than one means that reaction with photoproducts are likely occurring and the decay is not solely a result of direct photolysis.

1.2 Photolysis of Chlorine

The molar absorption coefficients of free chlorine at a given wavelength are given in Figure 1. Free chlorine used for disinfection is present in two major species, hypochlorous acid (HOCl) and hypochlorite ion (OCl^-). The relative concentrations of these two species in a water sample is pH dependent, illustrated graphically in Figure 3 and chemically in Equations 4 and 5 as follows:

$$\left\{HOCl\right\} \leftrightarrow \left\{OCl^-\right\} + \left\{H^+\right\} \quad \textbf{(4)}$$

$$Ka = \frac{\left\{OCl^-\right\}\left\{H^+\right\}}{\left\{HOCl\right\}} = 10^{-7.5} \quad \textbf{(5)}$$

At pH 7.5, an equal amount of each species, HOCl and OCl^-, is present. At pH < 6, HOCl is the dominant species, and at pH > 9, OCl^- is the governing species.

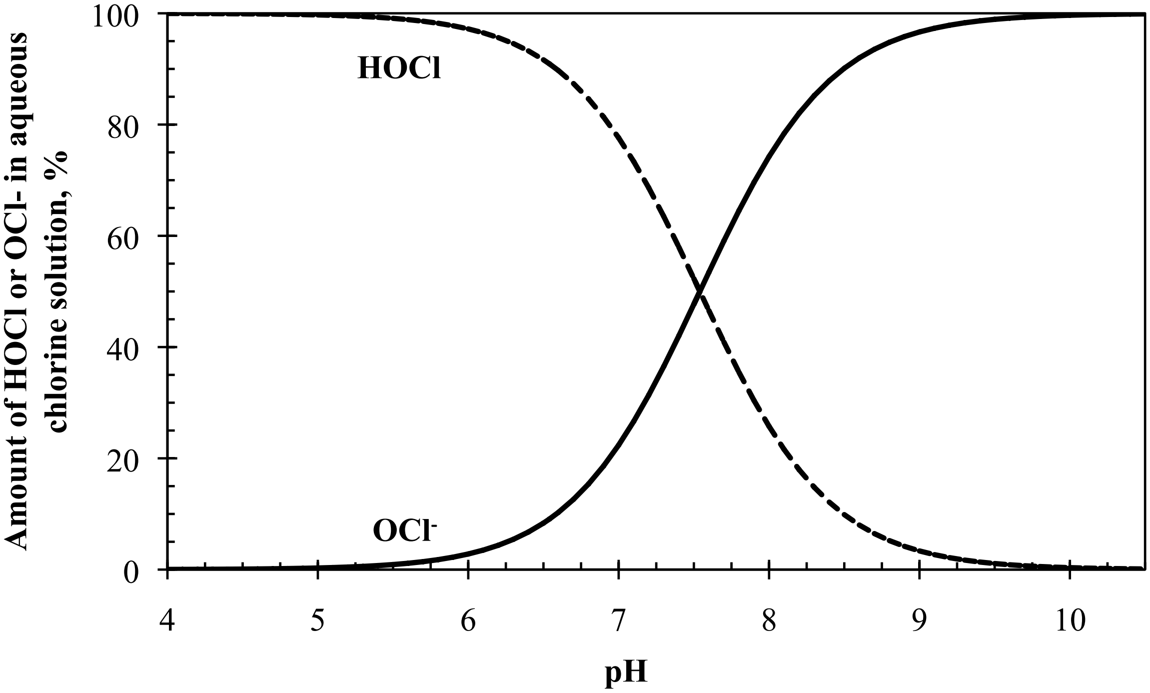

Figure 3. Chlorine speciation as a function of pH

The UV photolysis of free chlorine has been previously examined under a variety of conditions and photolysis mechanisms have been published. The basis of photolysis of the two free chlorine species, HOCl and OCl^- was examined by Feng et al. (2007) using a low-pressure UV lamp at 254 nm. The absorption peaks for HOCl and OCl^- were found to be 236 nm and 292 nm, respectively, with absorption coefficients of 101 $M^{-1}cm^{-1}$ for HOCl and 365 $M^{-1}cm^{-1}$ for OCl^- at these wavelengths. The molar absorption coefficients of HOCl and OCl^- at 254 nm are 59 and 66 $M^{-1}cm^{-1}$, respectively. Additionally, Nowell and Hoigne (1992a) found the molar absorption coefficients at 254 nm to be 121 $M^{-1}cm^{-1}$ and 155 $M^{-1}cm^{-1}$ for HOCl and OCl^-. Comparatively, the molar absorption coefficients in this study for HOCl and OCl^- at 254 nm were found to be 45 and 59 $M^{-1}cm^{-1}$, respectively. The absorption coefficient, at a peak of 236 nm, for HOCl was found to be 83 $M^{-1}cm^{-1}$. At a peak of 293 nm for OCl^-, the absorption coefficient was found to be 348 $M^{-1}cm^{-1}$. In the discussed studies, OCl^- was determined to have a greater absorption coefficient at 254 nm and a great absorption at the peak wavelength. Nowell and Hoigne (1992b) used a low-pressure mercury lamp emitting at 255 nm for UV irradiation, which might explain the higher absorption coefficients.

Feng and colleagues (2007) examined the quantum yields of HOCl and OCl^- in deionized water to determine the effect of direct photolysis. Laboratory water was chosen over natural water because the dissolved organic matter and other water quality parameters affect the quantum yield and subsequent chlorine decay due to the formation of radicals. The quantum yield at 253.7 nm of HOCl was found to be 1.0 ± 0.1 mol Es^{-1} as long as the concentration was not greater than 71 mg L^{-1}, suggesting other photochemical factors are contributing to chlorine decay. The quantum yield at 253.7 nm for OCl^- was found to be independent of the concentration at 0.9 mol Es^{-1}. Watts and Linden (2007), also using deionized water, found the quantum yield at

254 nm for HOCl to be 1.5 mol Es^{-1} and 1.3-1.7 mol Es^{-1} for mixed solutions of HOCl and OCl^- between pH 7 and 8.

In addition to photolysing HOCl and OCl^- to chloride and oxygen radicals (·Cl and $·O^-$), hydroxyl radical (·OH) production has been observed and quantified by both Nowell and Hoigne (1992b) and Watts and Linden (2007). Hydroxyl radical production is of interest due to the non-selective effects on chlorine and other constituents in the water. Nowell and Hoigne examined the ·OH production during exposure to UV light at 255 nm. It was found to have an ·OH yield of 0.85 mol Es^{-1} for HOCl and 0.12 mol Es^{-1} for OCl^-, resulting in more ·OH production from HOCl than OCl^-. Looking at the production and scavenging rates of ·OH by chlorine during both LP and MP UV photolysis, Watts and Linden (2007) found that HOCl had a ·OH production rate of 1.4 mol Es^{-1} and small scavenging rate of 8.46×10^4 $M^{-1}s^{-1}$. Compared to that of H_2O_2, which has ·OH production yields and scavenging rates of 1 mol Es^{-1} and 2.7×10^7 M^{-1} s^{-1}, HOCl was more efficient at producing ·OH than H_2O_2 which is commonly used in advanced oxidation processes where formation of ·OH is the primary process goal.

Ormeci et al. (2005) looked empirically at how free chlorine would impact UV dose delivery in deionized, treated, and source water under both low-pressure (LP) monochromatic UV and medium-pressure (MP) polychromatic UV. It was found that in deionized water, chlorine decayed faster under low-pressure while both treated and surface water had a faster decay under MP UV. Ormeci's research suggested that background water quality played a large role in the rate of chlorine decay. Dark samples with no exposure to UV light were performed to determine if any underlying reactions or volatilization of chlorine were occurring. It was found that there was some chlorine loss in all water samples with the most occurring in the source water and a very minimal amount in the deionized water samples. This illustrated that other chemical constituents present in the aqueous solution, such as TOC can have an effect on the chlorine decay rate. The fluence-based decay rates for chlorine, with initial chlorine concentration of 4-5 mg L^{-1}, under low-pressure lamps were 1.2×10^{-3} cm^2mJ^{-1} (DI), 3.8×10^{-3} cm^2mJ^{-1} (treated), and 6.8×10^{-3} cm^2mJ^{-1} (source). Decay rates under medium-pressure UV were 9.0×10^{-4} cm^2mJ^{-1} (DI), 5.6×10^{-3} cm^2mJ^{-1} (treated), and 8.4×10^{-4} cm^2mJ^{-1} (source). Comparatively, Feng et al. (2007), using LP UV, found the decay rate of HOCl to be 2.85×10^{-4} cm^2 mJ^{-1} and 2.86×10^{-4} cm^2 mJ^{-1} for OCl^- at high concentration of chlorine, 71 mg L^{-1}. The difference between Ormeci's and Feng's results might be a result of the water qualities used in the respective experiments. The deionized water used in Ormeci's experiments has a pH of 8 and a TOC of 0.25 mg L^{-1} while Feng examined deionized water containing only chlorine at pH 5 and 10.

1.3 Photolysis of Nitrate and Nitrite

The molar absorption coefficients of nitrate are presented in Figure 2. The photolysis of nitrate is important to consider when looking at the effects of UV systems. For instance, it is known that nitrite and OH radicals are formed during photolysis of nitrate under medium-pressure (Sharpless et al., 2003) and low-pressure mercury arc UV (Mark et al., 1996).

The photochemistry of nitrate and nitrite is complicated and involves many reactions between different types of radicals ($\cdot OH$, $NO\cdot$, $\cdot NO_2$, $\cdot O^-$, and $ONOO\cdot$) and intermediate reactions as will be discussed below. Mack and Bolton (1999) give an extensive review of much of the known photochemistry for nitrate and nitrite in aqueous solutions including many pathways that are possible and others that are possible but less likely. The reactions and rate constants for many of the reactions are compiled in Table 1.

Mark et al. (1996) also examined the photochemistry of nitrate in aqueous solution using a low-pressure mercury lamp emitting at 254 nm with the 185 nm emission absorbed by a quartz sleeve. The quantum yield of nitrite was found to be both pH and dose-dependent. The quantum yield was 0.01 at acidic pH and 0.1 at pH 10, with these values decreasing as the fluence increased. This rise in quantum yield is due to the partial conversion of peroxynitrite ($ONOO^-$) to nitrite (Reactions 14 and 16 in Table 1). $ONOO^-$ and its weak acid HOONO (peroxynitrous acid) were found to be important intermediates of nitrate photolysis

$$\{HOONO\} \leftrightarrow \{ONOO^-\} + \{H^+\} \tag{6}$$

$$Ka = \frac{\{ONOO^-\}\{H^+\}}{\{HONOO\}} = 10^{-6.8} \tag{7}$$

Additionally, $ONOO^-$ is much more stable at more basic pH and acts as a buffer for nitrite by reacting with ·OH. This results in accumulation of nitrite in more basic systems while the nitrite reacts with ·OH in more acidic systems because $ONOO^-$ is less stable (Mark et al., 1996; Sharpless and Linden, 2001). It has also been found that when constituents, such as H_2O_2, are present in the system that have a higher ·OH scavenging rate than nitrite, the concentration of nitrite increases (Sharpless et al., 2003). It can, therefore, be determined that the concentration of nitrite is dependent upon the pH of the water and other constituents present in the water.

1.4 Reactions between Chlorine and Nitrite

A summary of the principal reactions involving UV light, chlorine, nitrate and nitrite is presented in Table 1. Free chlorine has the potential to oxidize nitrite to nitrate (Reactions 25-27) when the two compounds are combined. The reaction between chlorine and nitrite is pH dependent and results in end products comprised of nitrate, chloride, and hydrogen ions (Dlyamandoglu et al., 1990). All of the reactions involved with chlorine and nitrite are pH dependent including the few intermediate reactions that include the NO_2Cl and N_2O_4 (Reactions 28-31). The formation of NO_2Cl was found to be significantly slower at higher pH (Cachaza et al, 1976). Additionally, Reactions 24 and 25 are the rate limiting, intermediate steps of the reactions between chlorine and nitrite (Lahoutifard et al., 2003). In a study examining the control of nitrite concentrations with chlorine in the drinking water system, chlorine was found to be effective at removing nitrite at neutral pH with 98% nitrite oxidation. However, at pH 10 only 30% of nitrite was oxidized (Yang and Cheng, 2007). These reactions are also present in Table 1.

Table 1. The major reactions during the photolysis of chlorine, nitrate, nitrite, and the reactions between chlorine and nitrite

Reaction Number	Reaction	k or ϕ	Reference
1	$HOCl + hv \rightarrow \cdot OH + \cdot Cl$	1.0	Feng et. al. (2007)
2	$\cdot OH + HOCl \rightarrow H_2O + \cdot OCl$	8.46×10^4 $M^{-1}s^{-1}$	Watts and Linden (2007)
3	$OCl^- + H_2O \leftrightarrow HOCl + OH^-$	-	Margerum et. al. (1994)
4	$OCl^- + hv \rightarrow \cdot O^- + \cdot Cl$	0.9	Feng et. al. (2007)
5	$\cdot O^- + H_2O \rightarrow \cdot OH + OH^-$		Feng et. al. (2007)
6	$OCl^- + \cdot OH \rightarrow \cdot OCl + OH^-$	8.8×10^9 $M^{-1}s^{-1}$	Feng et. al. (2007)
7	$NO_3^- + hv \rightarrow NO_2^{\cdot} + O^{\cdot -}$	0.09	Mark et. al. (1996); Mack and Bolton (1999)
8	$NO_2^{\cdot} + O^{\cdot -} + H_2O \rightarrow \cdot OH + OH^-$	-	Mark et. al. (1996); Mack and Bolton (1999)
9	$NO_3^- + hv \rightarrow ONOO^-$	0.1	Mark et. al. (1996)
10	$NO_3^- + hv + H^+ \rightarrow \cdot NO_2 + \cdot OH$	0.1	Sharpless et. al. (2003)
11	$\cdot OH + \cdot NO_2 \rightarrow HOONO$	1.3×10^9 $M^{-1}s^{-1}$	Mack and Bolton (1999)
12	$HOONO \rightarrow NO_3^- + H^+$	4.0×10^5 $M^{-1}s^{-1}$	Sharpless and Linden (2001)
13	$\cdot OH + ONOO^- \rightarrow \cdot ONOO + OH^-$	5.0×10^9 $M^{-1}s^{-1}$	Mark et. al. (1996); Mack and Bolton (1999); Coddington et. al. (1999)
14	$\cdot NO + \cdot NO_2 + H_2O \rightarrow 2NO_2^- + 2H^+$	-	Mark et. al. (1996)
15	$\cdot NO_2 + \cdot ONOO + H_2O \rightarrow 2NO_3^- + 2H^+$	-	Mark et. al. (1996); Mack and Bolton (1999)
16	$NO_2^- + hv \rightarrow \left[NO_2^-\right]^*$	-	Mack and Bolton (1999)
17	$\left[NO_2^-\right]^* \rightarrow \cdot NO + O^{\cdot -}$	-	Mack and Bolton (1999)
18	$O^{\cdot -} + H_2O \rightarrow \cdot OH + OH^-$	1.7×10^6 $M^{-1}s^{-1}$	Mack and Bolton (1999)
19	$NO_2^- + \cdot OH \rightarrow \cdot NO_2 + OH^-$	1.0×10^{10} $M^{-1}s^{-1}$	Mack and Bolton (1999)
20	$\cdot NO + \cdot NO_2 \rightarrow N_2O_3$	1.1×10^9 $M^{-1}s^{-1}$	Mack and Bolton (1999)
21	$N_2O_3 + H_2O \rightarrow 2H^+ + 2NO_2^-$	5.3×10^2 $M^{-1}s^{-1}$	Mack and Bolton (1999)
22	$N_2O_3 + \cdot ONOO \rightarrow NO_2^- + 2 \cdot NO_2$	-	
23	$NO_2^- + OCl^- \rightarrow NO_3^- + Cl^-$	-	Lister and Rosenblum (1961)
24	$NO_2^- + HOCl \rightarrow NO_3^- + Cl^- + H^+$	-	Margerum et. al. (1994)
25	$NO_3^- + HOCl \rightarrow NO_2Cl + OH^-$	4.4×10^4 $M^{-1}s^{-1}$	Margerum et. al. (1994)

CHAPTER 2: RESEARCH GOALS

This research determined the degradation rates of free chlorine by LP and MP UV, and the role of nitrate on the decay rate of free chlorine. Laboratory experiments were performed in model and natural waters in a manner to probe specific hypotheses. Based on results from a set of experiments that looked at the chlorine decay in a water from Portland and laboratory water, it was found that chlorine decayed much faster in the water from Portland. It was thought that hydroxyl radicals and nitrate had a major role in this enhanced degradation. The differences in the decay of chlorine, the role of nitrate and hydroxyl radicals in these reactions will be discussed.

CHAPTER 3: EXPERIMENTAL METHODS

3.1 Water Quality

This study examined the degradation of chlorine in model waters and natural water. Model waters were prepared fresh in the laboratory prior to each experiment. A potassium phosphate buffer (50 mM) was used to control the pH of model waters. A mixture of 1 M monobasic potassium phosphate (KH_2PO_4) and 1 M dibasic potassium phosphate (K_2HPO_4) from was used to prepare water with a pH of 7.0 ± 0.5. To achieve a pH of 10, dibasic potassium phosphate and sodium hydroxide (NaOH) mixed at appropriate ratios and monobasic potassium phosphate only was used to achieve a pH of 5. Selectively buffering the pH allowed hypochlorous acid (HOCl) at pH 5 or hypochlorite (OCl^-) at pH 10 to exist as the dominant species in model waters. The pH and temperature of the samples were monitored using a Beckman ϕ340 pH/Temperature Meter (Beckman Instruments Inc., Fullerton, CA) before and after irradiation. A chlorine stock was prepared from aqueous sodium hypochlorite, NaOCl (6%), from J.T. Baker (Phillipsburg, NJ). The initial concentration of chlorine for all experiments was 2.82×10^{-5} M (2 mg L^{-1}). The initial concentrations of nitrate evaluated were 1.61×10^{-5} M to 4.84×10^{-5} M (1-3 mg-N L^{-1}).

The natural water was collected tap water from Portland, Oregon intended for use in a microchip production facility. The water quality for the Portland water samples is presented in Table 2.

Table 2. Water Quality Parameters for Portland Water, as received.

Parameter	Units	Sample
pH		7.7-7.9
Chloride	mg/L	5.1-5.3
Nitrate	mg-N/L	0.695
Nitrite	mg-N/L	BDL
Ammonia	mg-N/L	0.007
TOC	mg/L	0.94
Alkalinity	mg-$CaCo_3$/L	48.8
Conductivity	µS/cm	0.115
Free Chlorine	mg-Cl_2/L	0.82-0.87

3.2 Ultraviolet Irradiation

Bench-scale collimated beam systems were used to perform ultraviolet irradiation. The samples were continuously stirred in a 12.5 cm diameter dish containing 450 mL of sample at a depth of 3.7 cm. The low-pressure (LP) system used was equipped with four Sankyo Denki G15T8 15 W low-pressure UV lamps emitting at the monochromatic wavelength of 253.7 nm. The medium-pressure UV system was a Calgon Carbon Corporation Inc. (Pittsburgh, PA) designed collimated beam system with a single 1kW polychromatic MP lamp. The irradiance was measured before each test using a calibrated IL 1700 radiometer with a SED 240 detector and W diffuser (International Light, Peabody, MA). The incident irradiance maintained during all experiments was 1.0 mW cm^{-2}. A Varian Cary 100 Bio UV-Visible Spectrophotometer (Agilent, Foster City, CA) was used to measure UV absorbance. The UV fluence was calculated based on Bolton and Linden (2003) using Beer's Law while accounting for surface reflection, sample depth, UV transmittance, and petri factor. For MP UV a sensor factor and germicidal factor were also incorporated to account for the polychromatic UV wavelength, 200-300 nm emission.

3.3 Chemical Analysis

The concentration of chlorine was evaluated at several time points during irradiation using a Hach DR 5000 spectrophotometer (Loveland, CO) and employing the DPD (N, D-diethyl-p-phenylenediamine) method (Hach Methods 8021). The chlorine detection limit for free chlorine was 0.03 mg-Cl L^{-1}. Nitrate was measured using Ion Chromatography, Dionex model DX-500 with conductivity detector CD20 and pump GP40 (Sunnyvale, CA). The Hach Nitrogen, nitrite, LR, NitriVer 3 Reagent was used to measure the concentrations of nitrite. An ·OH radical scavenger, 10 μM t-butanol (Sigma-Aldrich, St. Louis, MO) was used. The temperature of the samples was controlled during irradiation using copper coils attached to a recalculating chiller. All experiments were run in triplicate to allow for statistical analysis.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Low Pressure UV

4.1.1 Photolysis of Chlorine

Deionized water was buffered to pH 5, 7, and 10 prior to being spiked with 2 mg L^{-1} of free chlorine and exposed to LP UV. There was a difference between the decay rates of chlorine at the difference pH, with HOCl having a slightly higher decay rate than OCl^- (Figure 4). The decay rates of free chlorine under LP UV were 3.89×10^{-4}, 3.07×10^{-4}, and 2.85×10^{-4} cm^2 mJ^{-1} for pH 5, 7, and 10, respectively. The error bars represent one standard deviation of uncertainty.

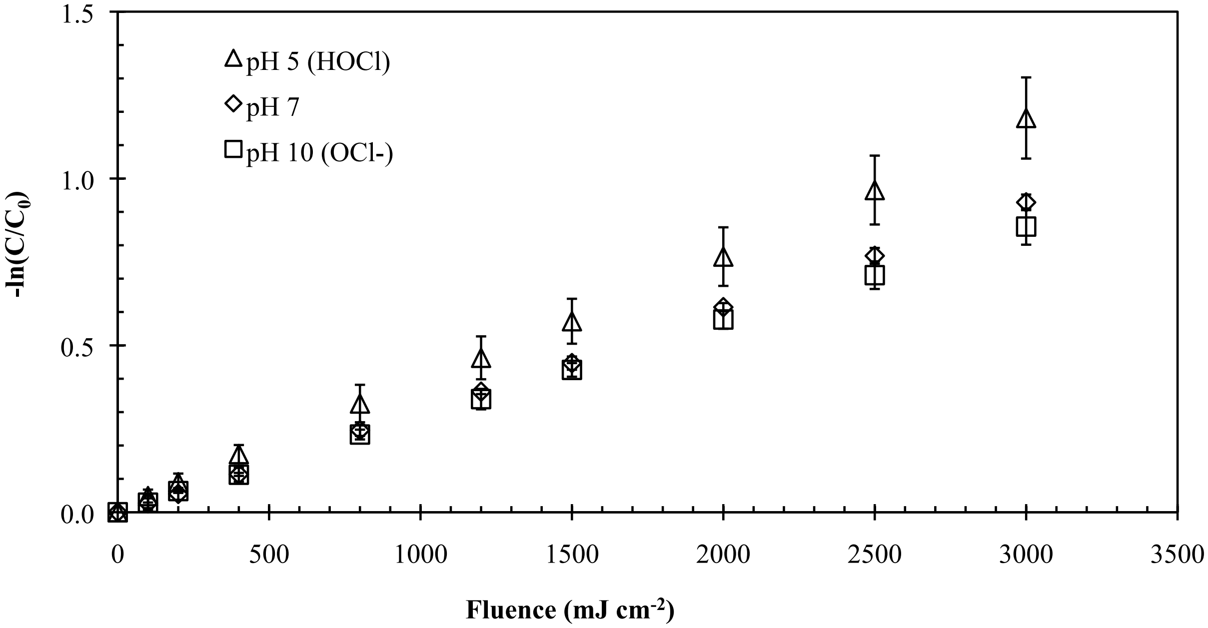

Figure 4. Decay of chlorine under LP UV in nitrate free water

The rates of LP UV decay of free chlorine were less than MP UV decay rates. This was a result of the difference between monochromatic emission spectra at 253.7 nm and the absorption coefficients of HOCl at 236 nm and OCl^- at 292 nm. The chlorine decay rate of HOCl is slightly higher than the rate of OCl^- with 69,1% removal of HOCl and 57.5 % removal of OCl^-. This is likely due to the slightly lower quantum yield of OCl^- (0.9 mol Es^{-1}) compared to HOCl (1.0 mol Es^{-1}).

4.1.2 Photolysis of Nitrate

There was negligible formation of nitrite during photolysis with LP UV (0.008-0.01 mg-N/L) when the initial concentration of nitrate was approximately 3 mg-N/L. As a result of the slow decay rate and minimal nitrite formation, experiments evaluating at the combined photolysis and reaction of chlorine and nitrate in LP UV were not explored.

4.2 Medium Pressure UV

4.2.1 Photolysis of Chlorine

MP UV enhanced the degradation rate of free chlorine in comparison to LP UV. This enhanced degradation was due to the increased molar absorption coefficient of both HOCl (peak at 292 nm and below 220nm) and OCl^- (peak at 235 nm and below 200 nm) resulting in more photons being absorbed by the free chlorine (Figure 1). The decay of chlorine was first examined in model water with no nitrate added, under MP UV irradiation. An ·OH radical scavenger, t-butanol, was added to evaluate the possible role of ·OH in the decay of chlorine.

The reactions occurring during the photolysis of chlorine begin with the HOCl (a weak acid) and OCl^- (the conjugate base). When HOCl undergoes photolysis radicals are formed that can then react with HOCl to form water and chloride radical (Reactions 1-2). When OCl^- undergoes photolysis, radicals are also formed, eventually leading to the formation of ·OH (Reactions 4-5). When ·OH react with OCl^-, hydroxide is formed (Reaction 6).

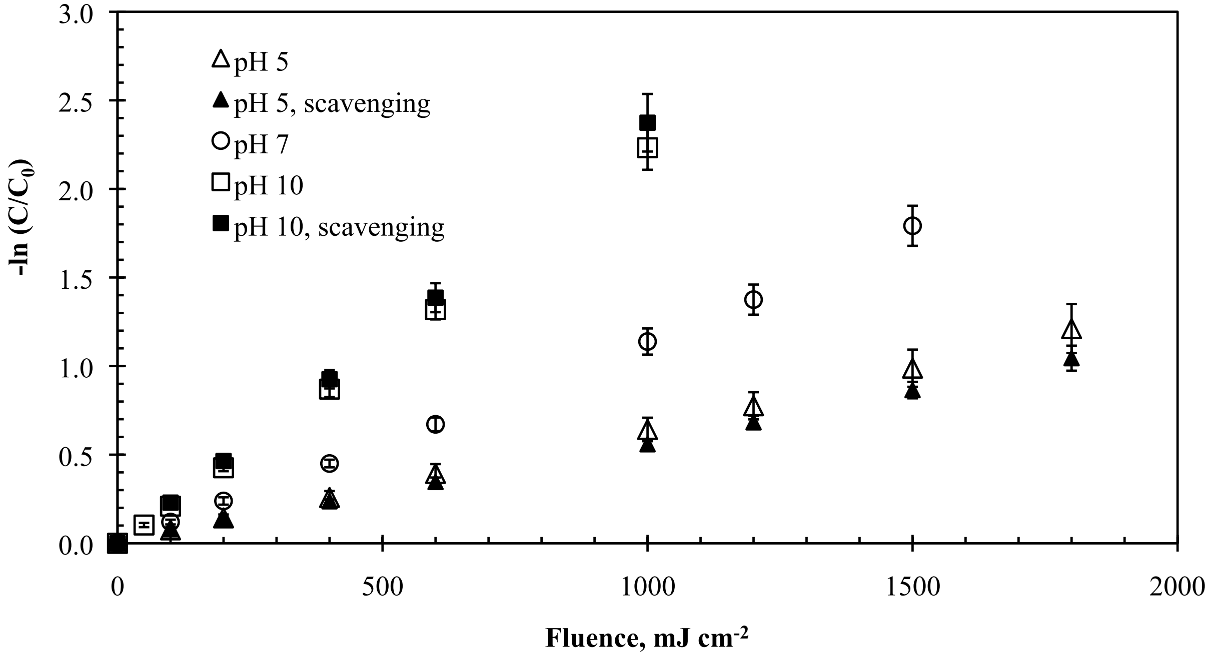

Figure 5. Decay of free chlorine under MP UV in nitrate free water

There was a much faster decay of chlorine at higher pH than at lower pH with 89.2% removal during photolysis of OCl^- and 70.0% removal for HOCl. The decay of chlorine (Figure 5) was observed both with and without the ·OH radical scavenger t-butanol. The presence of t-butanol did not impact the decay rate of chlorine suggesting that ·OH radicals do not play a major role in the decay of chlorine under conditions of under conditions of nitrate free water. Other radicals (·OCl and ·Cl) are formed during the photolysis and subsequent chain reaction of both HOCl and OCl^-. At pH 10, these radicals do not initiate any chain reactions because the quantum yield is independent of the concentration. At pH 5, however, there is the possibility that these radicals contribute to further reactions to decay HOCl.

The results from the samples with chlorine suggest that ·OH reaction with both chlorine species is insignificant since the slight differences seen in the decay rates are within standard error. Therefore, when only chlorine is present in the water, the decay rates are controlled by direct photolysis rather than reaction with radicals.

4.2.2 Photolysis of Nitrate/Nitrite

Medium pressure UV photolysis had a much greater impact on nitrate and nitrite reactions than LP UV. The molar absorption coefficients for nitrate at both pH 5 and 10 greatly increases below 220 nm (Figure 2), illustrating why nitrate photolysis is exhibited with MP UV and not LP UV, as there is not much absorption at 253.7 nm. The overlap between the lamp emission spectra and molar absorptivity of nitrate show that absorbance occurs below 220 nm.

Two concentrations, 1 and 3 mg L^{-1} were studied to examine nitrate and nitrite reactions during photolysis both in clean water and in the presence of chlorine (Section 4.2.3). The nitrate concentration for both 1 mg L^{-1} and 3 mg L^{-1} demonstrated some decay during the UV exposures (Figure 6a and b). The greatest decrease in nitrate concentration was seen at pH 10 when the $\cdot OH$ radical scavenger t-butanol was not added to the system. The maximum decrease in nitrate concentration of 60% occurred at 1 mg L^{-1} and 20% decrease occurred at 3 mg L^{-1}, showing that nitrate decay is not dependent on concentration. The greater nitrate removal at pH 10 is likely a result of the intermediate compound of nitrate photolysis, $ONOO^-$, being more stable at more basic pH (Mark et al., 1996). When looking at the corresponding nitrite formation (Figure 7a and 7b), the greatest formation of nitrite also occurs at pH 10 when t-butanol is absent from the system. When t-butanol is present at pH 10, there is 20-24.5% decay in nitrate, suggesting that some nitrate reformation is occurring through the presence of other radical activity via Reaction 15.

The nitrate concentration at pH 5 has very little decay (0-9%) both when the ·OH radical scavenger is present and absent. The decay is also independent of the concentration. The smaller amount of nitrate removal in more acidic water when t-butanol is absent from the water can be explained by Reactions 13 and 15 where peroxynitrite is re-oxidized by ·OH and forms back into nitrate (Mark et al., 1996).

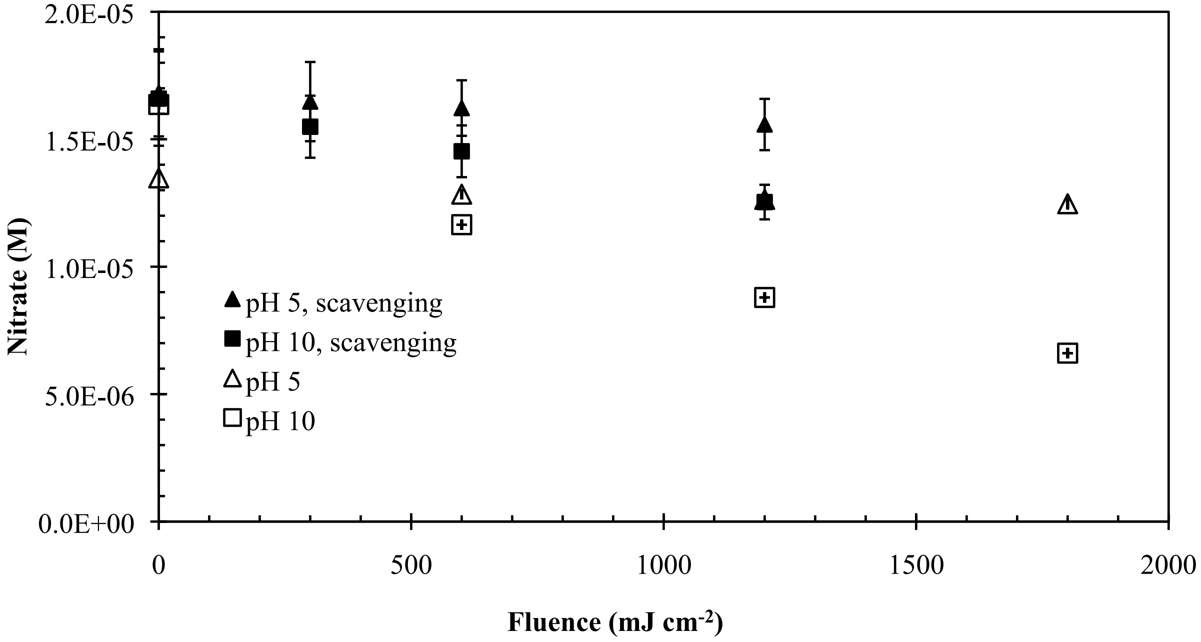

Figure 6a. Medium pressure photolysis of nitrate with an initial concentration of 1 mg-N/L

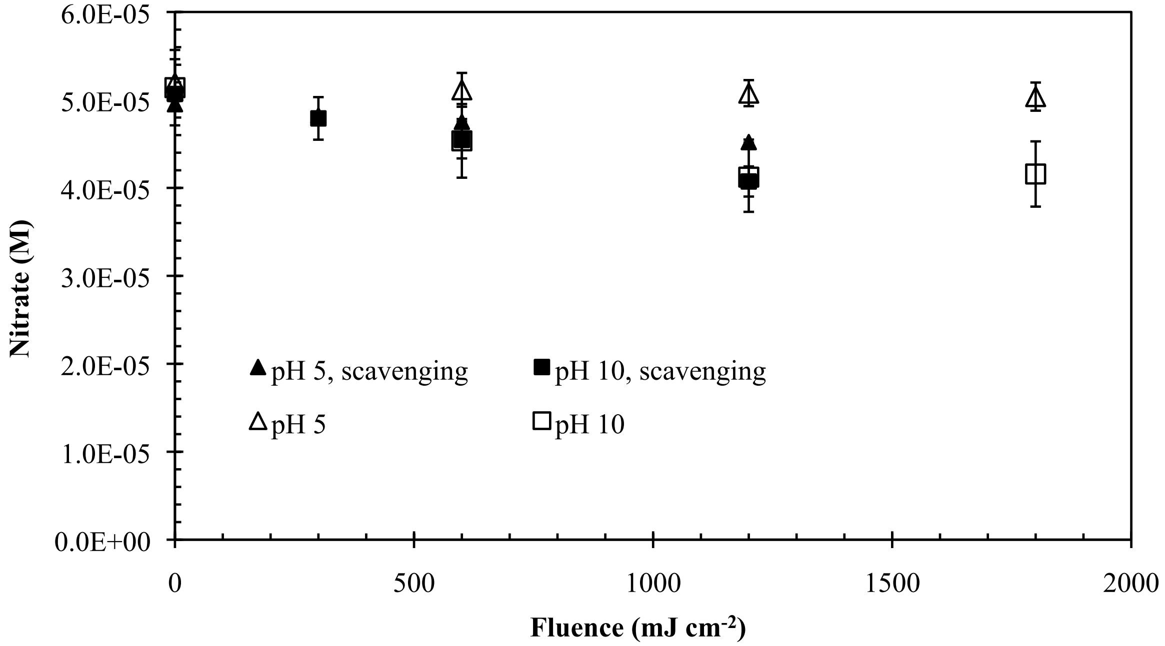

Figure 6b. Medium pressure photolysis of nitrate with an initial concentration of 3 mg-N/L

The formation of nitrite during the photolysis of nitrate is directly related to amount of nitrate that is decayed (Figure 7a and b). There is a difference between the rate of formation of nitrite low and high pH, with the greatest rate of formation being observed at pH 10. This directly correlates to the greatest amount of nitrate removal. The presence of ·OH in the system was evident from the differences in formation of nitrite, especially at lower pH. When ·OH are formed during the photolysis of nitrate at pH 5, the amount of nitrite formed was less than when the radical scavenger was present suggesting that nitrite is an efficient ·OH scavenger with a rate constant of 1.0×10^{10} $M^{-1}s^{-1}$ (Reaction 19) as suggested by Sharpless and colleagues. This occurs at low pH due to the decreased stability of $ONOO^-$ as previously discussed. The opposite seems to be true for nitrite formation at pH 10 where the water without t-butanol had the greatest formation suggesting that $ONOO^-$ protects the nitrite concentration from decay by acting as a radical scavenger (Mack and Bolton, 1999). The experimentally determined rates of nitrite formation are detailed in Table 3.

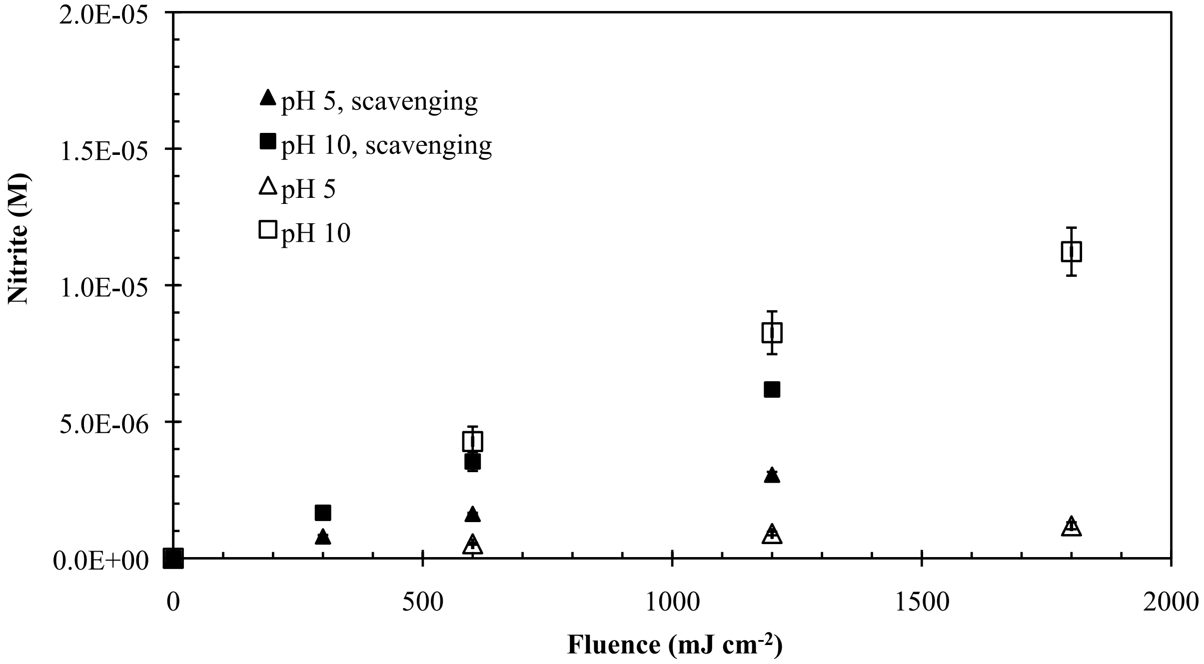

Figure 7a. The formation of nitrite during MP UV from an initial nitrate concentration of 1 mg L^{-1}

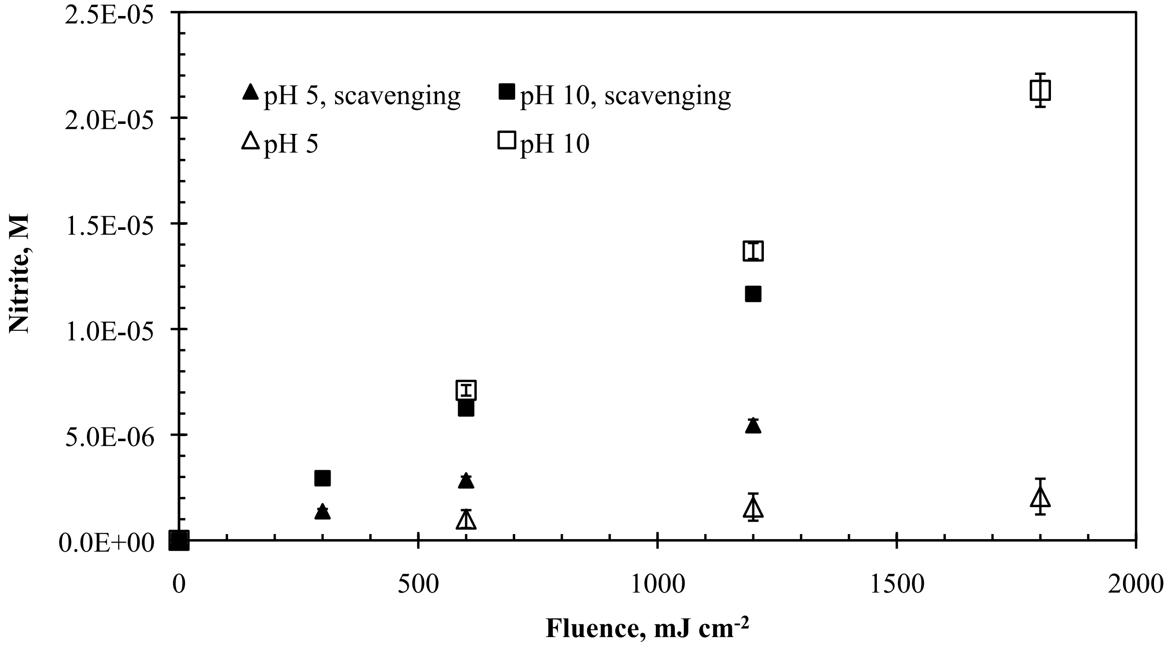

Figure 7b. The formation of nitrite during MP UV from an initial nitrate concentration of 3 mg L^{-1}

The photochemistry of nitrate and nitrite is complex and the main reactions thought to occur are discussed below. Mack and Bolton (1999) created an integrated scheme (Figure 8) of the primary photoprocesses and consequent reactions during photolysis of nitrate. While the main result of the photolysis of nitrate is the formation of nitrite and the reformation of nitrate many intermediate reactions also occur. When nitrate undergoes photolysis, several radicals including $\cdot OH$, $\cdot NO_2$, and $\cdot O^-$ form (Reactions 7, 8, and 10). When $\cdot OH$ and $\cdot NO_2$ react, peroxynitrous acid (HOONO) is formed (Reaction 11), which leads to the reformation of nitrate (Reaction 12). Additionally, peroxynitrite ($ONOO^-$) is formed during nitrate photolysis (Reaction 9). When peroxynitrite reacts with $\cdot OH$ and $\cdot NO_2$, $ONOO^-$ decomposition takes place (Reactions 13 and 15), which also leads to nitrate reformation. One reason for this restoration of nitrate is that second order reactions are occurring, indicated by the fact that "in the absence of an oxidizable additive, the nitrite quantum yield falls with increasing fluence rate" (Mark et al., 1996). These reactions were also found to be pH dependent with $ONOO^-$ being more stable at basic pH (Mark et al., 1996; Sharpless and Linden, 2001).

Table 3. The rates of formation of nitrite during MP UV

	Experiment	**Rate of Formation ($M\ cm^2\ mJ^{-1}$)**	**R^2**
1 mg/L	pH 5	7.80×10^{-10}	0.973
	pH 5, scavenging	2.59×10^{-9}	0.998
	pH 10	6.93×10^{-9}	1.00
	pH 10, scavenging	5.31×10^{-9}	0.992
3 mg/L	pH 5	1.38×10^{-9}	0.967
	pH 5, scavenging	4.58×10^{-9}	0.999
	pH 10	1.15×10^{-8}	0.999
	pH 10, scavenging	9.86×10^{-9}	0.998

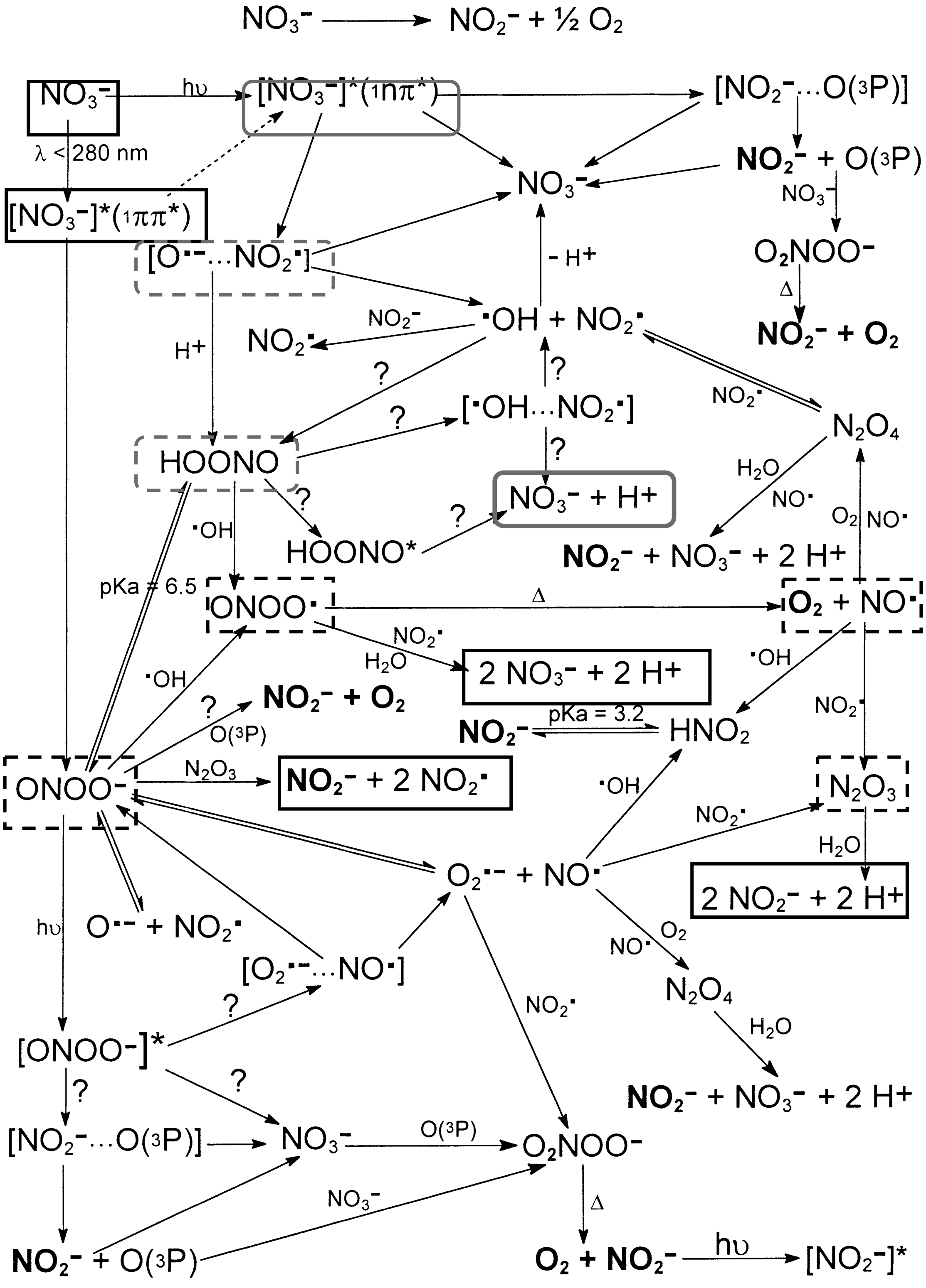

Figure 8. Scheme of potential reaction occurring during photolysis of nitrate (Mack and Bolton, 1999). The boxed routes are the pathways thought to occur based on the literature and the experimental results.

The nitrite formed during photolysis of nitrate is governed by the reactions with compounds formed during the subsequent photolysis of nitrite. During the photolysis of nitrite, ·NO and $·O^-$ form, and $·O^-$ quickly reacts with water developing into ·OH (Reactions 16-18). Nitrite quickly reacts with ·OH (Reaction 19) removing it from the system. Dinitrogen trioxide (N_2O_3) is formed when ·NO and $·NO_2$ react (Reaction 20). When N_2O_3 reacts with both water and ·ONOO in separate reactions, nitrite is formed (Reactions 21 and 22). Although the reaction rate for Reaction 22 is unknown, it has been suggested as a competing reaction with Reaction 21 when the pH is greater than 6 (Goldstein et al. 1998; Mack and Bolton 1999). Nitrite also forms during reactions between ·NO, $·NO_2$, and water (Reaction 14). Many of the possible reactions that are based primarily on the photolysis of nitrate are highlighted in the nitrate photolysis scheme (Figure 8)

4.2.3 Reactions between Chlorine and Nitrate/Nitrite

The reactions during the combined photolysis of chlorine, nitrate, and nitrite under MP UV were studied in model water. In order to initially determine the interactions that might occur between chlorine and nitrite formed during nitrate photolysis, chlorine and nitrite were combined stoichiometrically preceding any photolysis experiments. It was found that nitrite reacts quickly with HOCl with about a 5:1 chorine to nitrite molar ratio. The reaction of nitrite and OCl^-, however, was much slower and inconsequential. Reactions 23-25 are most likely to be occurring.

In the presence of nitrate, an enhanced degradation rate of chlorine was observed for both high and low pH (Figure 9a and b) during photolysis. Additionally, the effect of ·OH scavenging on the system is notable, especially at more acidic pH when HOCl is the dominant species. There is an exponential increase in the decay rate of chlorine when the ·OH scavenger was present (Figure 9b). The same exponential increases in chlorine decay were seen when the initial concentration of nitrate was 1 mg L^{-1} and the decay rates of chlorine for both nitrate concentrations were similar (Table 4).

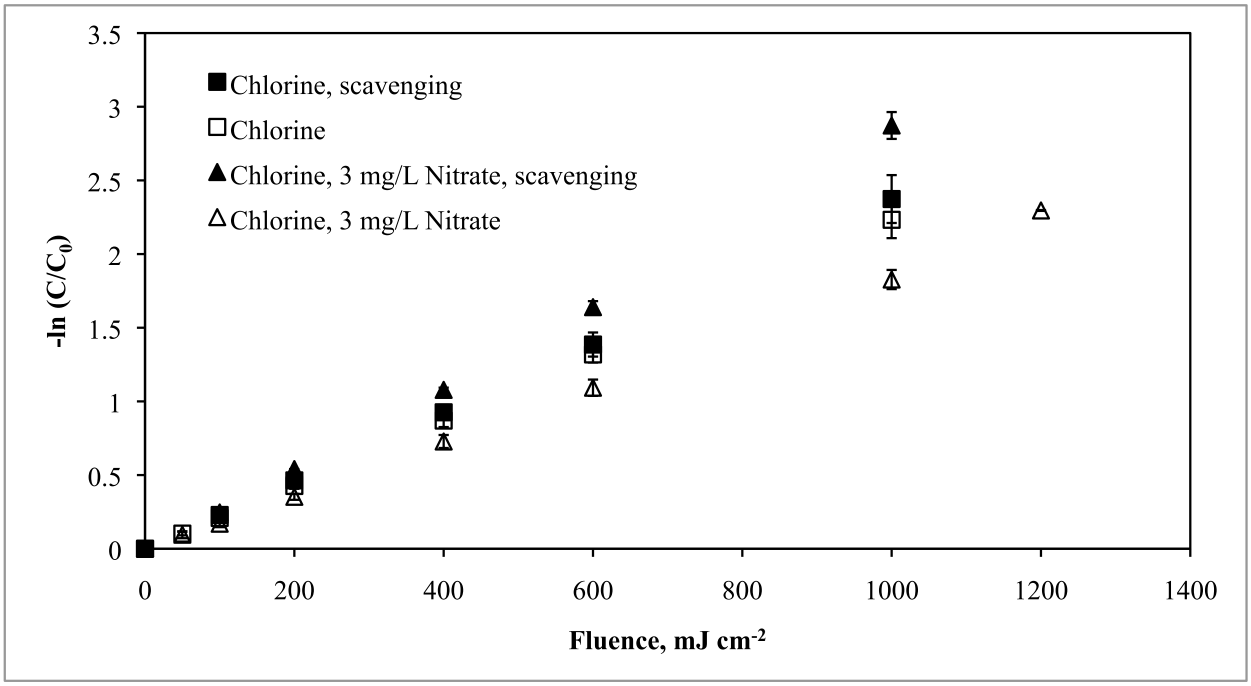

Figure 9a. The decay of OCl^- at pH 10 comparing the rates when an initial concentration of 3 mg L^{-1} of nitrate is present in the sample and when OCl^- is alone

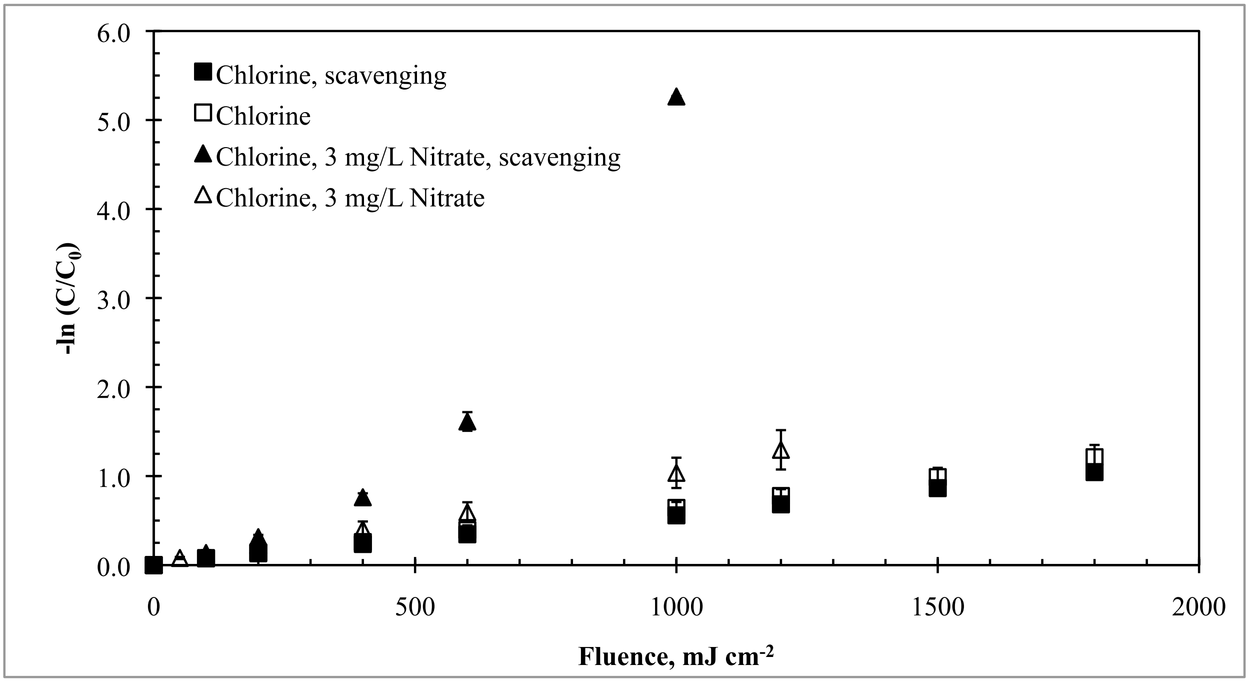

Figure 9b. The degradation of HOCl at pH 5, comparing rates when an initial concentration of 3 mg L^{-1} nitrate is present in the system and when HOCl is alone.

The presence of nitrate in the system has a considerably different effect at HOCl at pH 5 than OCl^- at pH 10 based on chlorine speciation and the stability of intermediate reactions during the photolysis of nitrate at higher pH. The degradation rates of chlorine at pH 10 did not significantly vary either when nitrate was added to the system or when the ·OH were formed during photolysis of chlorine and nitrate. This was consistent with previous results that ·OH scavenging at higher pH by nitrate, nitrite, or chlorine is negligible as a result of ·OH interacting with other compounds formed during photolysis ($ONOO^-$ or other radicals).

When ·OH scavenger t-butanol was present, the chlorine decay increased exponentially at pH 5. This was likely a result of the nitrite concentration increasing in the system instead of nitrite playing a role of scavenging the ·OH created during photolysis of nitrate and chlorine. When the concentration of nitrite increases, HOCl would quickly decrease by the Reactions 25-

29. In this situation the decay of chlorine was affected by the nitrite present (formed from the nitrate photolysis) in the system in addition to other radical reactions such as $\cdot NO$ and $\cdot NO_2$ (Reaction 20).

The concentration of nitrate during the photolysis of chlorine and nitrate did not change at pH 5 due to oxidation of nitrite back to nitrate by HOCl, as was expected from the results of nitrate photolysis (Section 4.2.2) and the interactions between nitrite and HOCl. The nitrate concentration did decrease at pH 10 due to the formation of nitrite that was only measurable at pH 10 due to the slow reaction with OCl^-. The nitrite formation (Figure 10) was unaffected by the chlorine in system at pH 10. It should be noted that nitrite formation was slightly higher when the radical scavenger was absent from the system.

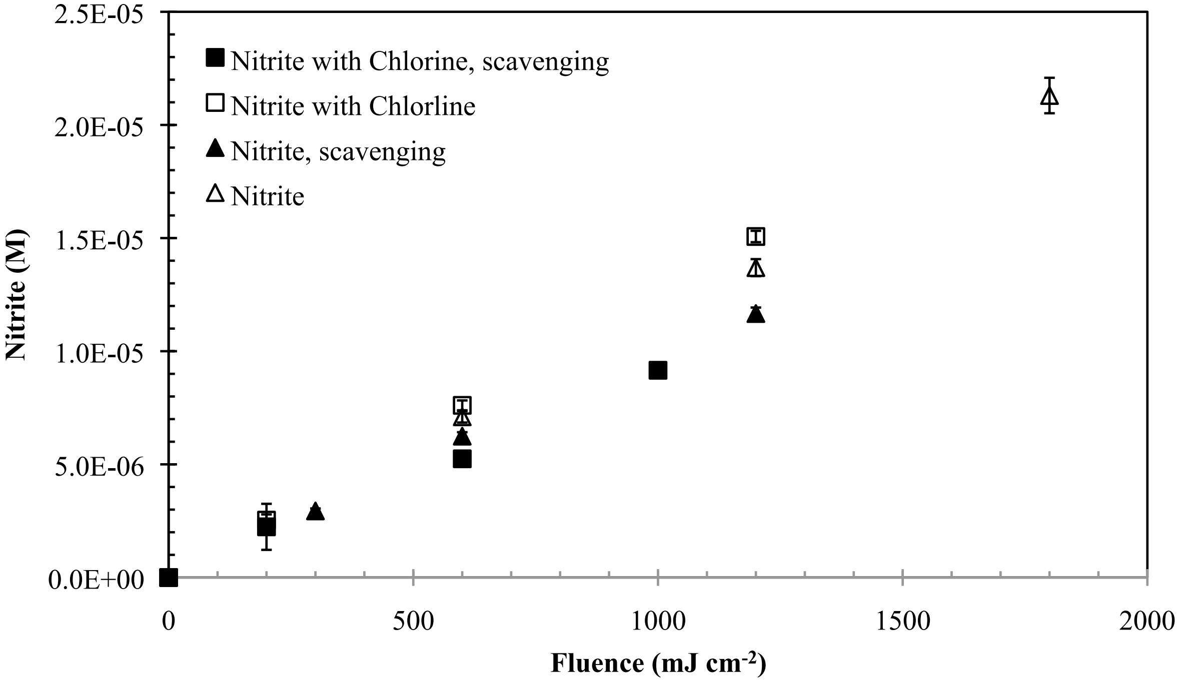

Figure 10. Nitrite formation with chlorine present and absent from the system from an initial nitrate concentration of 3 mg L^{-1}.

4.2.4 Natural Waters

To examine the fundamentals of the role of water quality in the decay of chlorine under UV irradiation in a natural water, tap water from Portland, Oregon was utilized to study the decay rate of chlorine under MP UV. The water from Portland had a pH between 7.7-7.9, a nitrate concentration of 0.695 mg-N L^{-1}, no detectable nitrite concentration, and 0.942 mg L^{-1} TOC. When compared to the chlorine degradation rates in model water when both chlorine and nitrate (at pH 5 and 10) are present and chlorine at pH 7 is alone with other constituents absent from the system, the decay rate of chlorine in the natural water is still significantly greater (Figure 11). This suggests that other reactions are likely occurring. Possible reactions include, chlorine reaction with dissolved organics and the possibility of chlorine-nitrite reactions if the ·OH are scavenged by another constituent in the water.

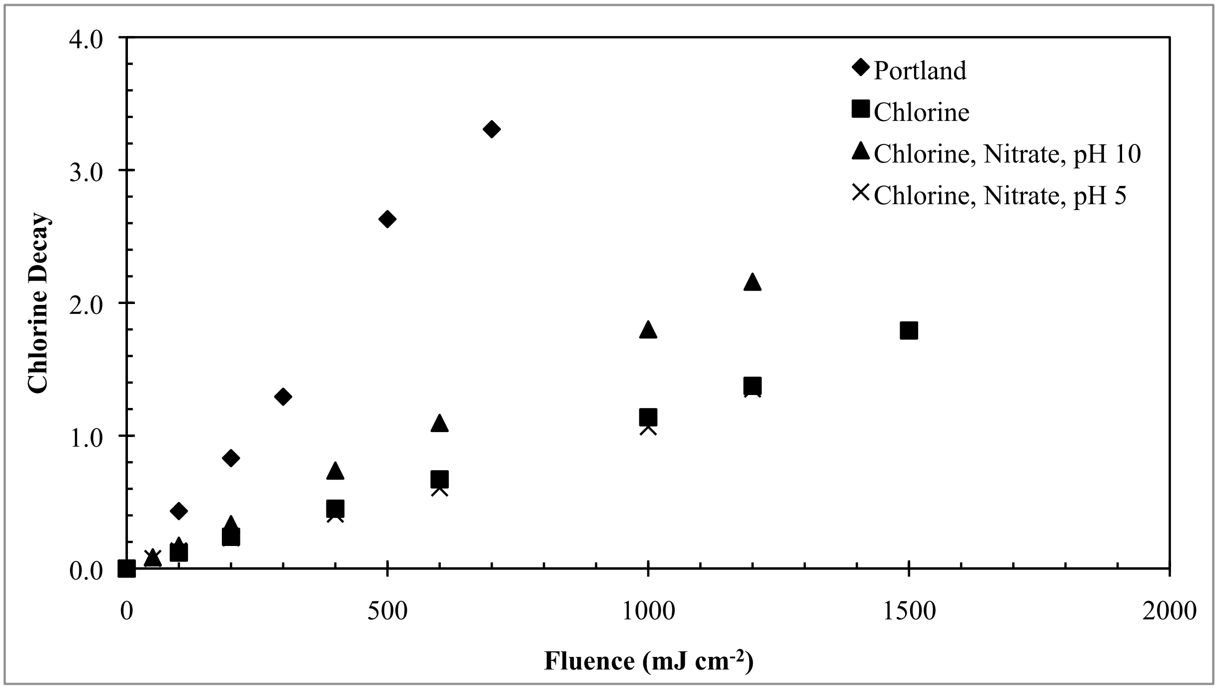

Figure 11. The degradation rates of chlorine in natural water, chlorine with 1 mg L^{-1} of nitrate at pH 5 and 10, and chlorine with other constituents absent from the system at pH 7.

The chlorine decay rates are compared in Table 4. Use of low pressure UV resulted in the lowest rate constants, while basic pH under medium pressure resulted in some of the highest rate constants. The Portland water had the highest first order reaction rate and the reactions between chlorine and nitrite at pH 5 resulted in an exponential increase in chlorine decay, although the rate constant given looks at the initial rate of chlorine degradation.

Table 4. The chlorine decay rates with varying concentrations of nitrate under MP and LP UV.

	Experiment	**Chlorine decay rate constant (cm^2 mJ^{-1})**
Chlorine, no nitrate	pH 5	6.60×10^{-4}
	pH 5, scavenging	5.75×10^{-4}
	pH 10	2.21×10^{-3}
	pH 10, scavenging	2.35×10^{-3}
	pH 7	1.16×10^{-3}
Chlorine with 1 mg L^{-1} nitrate	pH 5	1.09×10^{-3}
	pH 5, scavenging	*1.41×10^{-3}
	pH 10	1.80×10^{-3}
	pH 10, scavenging	3.06×10^{-3}
Chlorine with 3 mg L^{-1} nitrate	pH 5	1.05×10^{-3}
	pH 5, scavenging	*1.81×10^{-3}
	pH 10	1.87×10^{-3}
	pH 10, scavenging	2.82×10^{-3}
LP	pH 5	3.89×10^{-4}
	pH 7	3.07×10^{-4}
	pH 10	2.85×10^{-4}
MP	Portland	4.80×10^{-3}

*The rate constant at pH 5 with nitrate and scavenging shows only the initial rate. The rate increases with increasing fluence.

CHAPTER 5: CONCLUSIONS

MP UV was much more effective at photolyzing chlorine than LP UV as a result of the emission of MP and LP UV and the absorbance spectra of chlorine species. The degradation of chlorine occurs much faster at basic pH (OCl^-) through direct photolysis than acidic pH (HOCl). While hydroxyl radicals are produced during photolysis, free chlorine does not scavenge these radicals promoting free chorine decay. Nitrite, however, was a very effective radical scavenger and radical reactions play a key role in how nitrite effects the degradation of chlorine.

The decay of chlorine in natural waters is complex as several different reactions are likely occurring. The enhancement of chlorine decay in natural waters was much greater than could be explained by the presence of nitrate and subsequent formation of nitrite during photolysis. In order to fully understand the reactions taking place, a more in depth study is needed. Knowing details about the different mechanisms that enhance the degradation of chlorine can help to make the dechlorination process more efficient for industrial purposes. This research could also benefit drinking water treatment by giving insight into the limit of chlorine addition if added upstream of UV disinfection.

It is important to note that the UV fluences tested in this study were well outside typical disinfection ranges. However, when UV is used for the removal of emerging contaminants of concern, such as NDMA, much higher UV doses are applied, 1000 mJ cm^{-2} (Sedlak and Kavanaugh, 2006). Additionally, due to the high UV fluences used, the economic viability as a pretreatment option for some industrial water consumers would need to be examined. Other forms of chlorine removal may be more cost effective than the use of high UV dose. A few of these effective technologies include granular activated carbon (GAC) or ion exchange.

CHATER 6: BIBLIOGRAPHY

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