MONOCHLORAMINE ADVANCED OXIDATION FOR REMOVAL OF TRACE ORGANICS IN WASTEWATER

by

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As members of the Master's Committee, we certify that we have read the thesis prepared by Aaron Ben, titled *MONOCHLORAMINE ADVANCED OXIDATION FOR REMOVAL OF TRACE ORGANICS IN WASTEWATER* and recommend that it be accepted as fulfilling the dissertation requirement for the Master's Degree.

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Aaron Casey Ben

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2 NOMENCLATURE

TRC	Total Residual Chlorine
FC	Free Chlorine
MC	Monochloramine
DC	Dichloramine
PC	*p*-cresol
WW	Wastewater
WWTP	Wastewater Treatment Plant
AOP	Advanced Oxidation Processes
EP	Emerging Pollutants
UV	Ultra Violet
RO	Reverse Osmosis
TOC	Total Organic Carbon
NDMA	N-Nitrosodimethylamine
DPD	N, N-Diethyl-p-Phenylenediamine
FAS	Ferrous Ammonium Sulfate
CT	Contact Time
NP	*p*-Nonylphenol

3 ABSTRACT

Monochloramine and free chlorine are both common disinfectants and candidates for Advanced Oxidation Processes (AOP). Results from this study show that free chlorine in the form of HOCl and OCl- has faster degradation kinetics for emerging pollutants. Unfortunately, free chlorine only becomes stable after chlorine demand is satisfied. Monochloramine on the other hand, forms instantaneously upon the addition of chlorine in the presence of ammonia and is a relatively stable compound. Advanced Oxidation Processes using UV 254 light with monochloramine has not been thoroughly investigated. In this study, monochloramine AOP is used to degrade *p*-cresol to illustrate its oxidative effectiveness. Monochloramine AOP is then compared to chlorine AOP; Chlorine AOP can achieve 90% *p*-cresol degradation after 15 minutes while monochloramine AOP degraded approximately 65% p-cresol after 15 minutes; both results operated at concentrations of 100 µM oxidant, under UV 254 light with an incident irradiance of 10.38 W/m^2 , with an initial *p*-cresol concentration of 10 µM, and using deionized water buffered with 10 mM phosphate buffer at pH 7. The viability of Monochloramine AOP in wastewater is tested in this study; unfortunately, monochloramine AOP only achieves 10% *p*-cresol reduction in 15 minutes under UV 254 irradiation for wastewater experiments. Lastly, breakpoint curves are generated while under 15 minutes of UV 254 irradiation to directly compare how the molar ratio of Cl_2:NH_3 affects AOP degradation of *p*-cresol.

4 INTRODUCTION

As necessary as oil is to an automobile, potable water is equally necessary to the well-being of mankind. Water resources should be preserved, requiring a new perspective on water use. One of the ways of becoming water smart is to reclaim water for human consumption from Wastewater Treatment Plant (WWTP) effluent. Advanced Oxidation Processes (AOPs) can play an important role in water reclamation. AOP is the process of producing highly reactive radical species to degrade Emerging Pollutant (EP) concentrations in aqueous solutions. There are multiple types of AOPs, but they all can inactivate a multitude of toxic chemicals such as estrogenic compounds, antiviral compounds, antibiotics, and herbicides (Lado Ribeiro et al., 2019). Water reuse via AOP has been gaining attention lately due to the economic and environmental benefits. From an economic standpoint, wastewater can be seen as a "misplaced resource" (Capocelli et al., 2019), so it is currently underutilized.

Besides waster reuse, another important factor for AOP research is minimization of trace organic compounds released into the environment. One particular compound of interest is *p*-nonylphenol (NP), an EP within the past 10 years that is also an endocrine disruptor that can interfere with the hormonal systems of wildlife; however, photocatalytic oxidation has the potential to completely mineralize NP (Priac et al., 2017) or in other words AOP can completely transform EPs to CO_2 and H_2O as final products. NP and alkylphenol ethoxylates are commonly found in WWTP influent or in natural water resources due to their continuous release into the environment (Acir et al., 2018). The purpose of this study is to characterize trace organic degradation by AOP, specifically Monochloramine AOP compared to Chlorine AOP; characterizing such kinetics allows researchers to better understand the Monochloramine AOP process so that this knowledge can then be utilized in industrial applications.

Monochloramine (MC) AOP and Chlorine AOP are compared side by side in ammoniacal waters and wastewater effluent for WWTP application, the only difference between Free Chlorine (FC) and monochloramine formation is the ammonia content present in the water. For this study, *p*-cresol was chosen as the surrogate for NP due to its similar chemical properties, less toxicity, and ease of use. Chlorine AOP has been relatively new in the AOP field, even more so for

Monochloramine AOP as the many research papers on the topic regarding its AOP potential have been within the last couple of years.

Although water reuse via AOP can be seen as a potential solution to over exploitation of natural water resources, AOP is not without consequences. Note that products from an EP parent compound can be more or less toxic as the parent compound (Sharma et al., 2018). As it may be, the goal of AOP technologies is to provide unselective radicals that mineralize the parent compounds into carbon dioxide and water as the final products (Lado Ribeiro et al., 2019) thereby eliminating the toxic and harmful effects that the trace organics might impose on the environment.

4.1 BACKGROUND

Advanced Oxidation Processes may be classified as chemical, electro-chemical, sono-chemical and photochemical processes each generating hydroxyl radicals in a different way (Teodosiu et al., 2018). Ultraviolet light (UV) based AOPs include UV/H_2O_2, $UV/O3$, UV/PDS, and UV/Cl_2 as established processes with emphasis on UV/H_2O_2 and UV/Cl_2 although chlorine as the oxidizer is relatively new and usually done only on lab-scale systems (Miklos et al., 2018).

There are several advantages of Chlorine AOP: it has been reported to be more effective than the UV/H_2O_2 process for some micro-pollutants; additionally it may be the more cost effective AOP process due to the easy retrofitting of existing disinfection processes into the UV/Chlorine AOP (Zhu et al., 2018), note that this would also apply to retrofitting for monochloramine AOP. Chlorine is the most widely used disinfectant for municipal wastewater (EPA, 2013), thus most WWTPs have the infrastructure for chlorine injection, processing, storage, etc. The usage of combined chlorine (Monochloramine, Dichloramine, & Trichloramine) has increased since the discovery that it produces much less Disinfection By Products (DBPs) (Yang et al., 2018) than chlorine, and most WWTPs try to minimize the release of harmful DPBs into the environment. As of 2014 it was discovered that about one in four utilities in the US are using combined chlorine for disinfection due to its advantages of chlorine disinfection (Critten et al., 2014).

Interestingly, UV/Chloramine AOP may be occurring de facto at WWTPs due to their usage of chloramine disinfection which includes a contact time of 40 minutes with exposure to UV rays from sunlight. Relative turbidity of their wastewater may be preventing irradiation of deeper waters, but at the surface chloramine may be reacting to form radicals, thus performing indirect photolysis in addition to direct photolysis of organic compounds. The idea of UV/Chloramine AOP is relatively new and its effectiveness at degrading p-cresol should be investigated.

Chlorine AOP may have its benefits, but a disadvantage of UV/Chlorine is it is heavily pH dependent. Free Chlorine (FC) has a pKa is 7.53 meaning that at neutral pH a solution would consist of mostly hypochlorous acid (HOCl) but at pH of 8 the solution would consist of mostly hypochlorite ion (OCl⁻). Chlorine AOP is favorable for low pH waters such as reverse osmosis permeate (Miklos et al., 2018) where HOCl species dominate, and low pH is also favorable for free chlorine disinfection since HOCl exhibits faster disinfection kinetics than OCl⁻ (Crittenden et al., 2014).

4.2   CHLORINE DEMAND

To have Free Chlorine in water (HOCl and OCl⁻), the chlorine demand must first be met. Chlorine demand comes from a multitude of reactions including reactions with ammonia, organic matter, and organic nitrogen in the water samples. Chlorine demand is represented by the difference between the amount of chlorine added and the amount of total chlorine remaining at the end of the contact period (Davis, 2010). Other definitions include the Total Residual Chlorine (TRC), which includes free and combined chlorine both of which have oxidative properties unlike the chloride ion. Before free chlorine appears in wastewater, chlorine species will usually exist as inorganic or organic chloramines.

$$\text{Free Chlorine} = HOCl + OCl^-$$

$$\text{Inorganic Combined Chlorine} = NH_2Cl + NHCl_2 + NCl_3$$
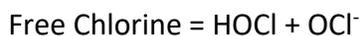
Total Residual Chlorine = Free Chlorine + Inorganic Combined Chlorine + Organic Combined Chlorine

4.3 BREAKPOINT CHEMISTRY

Total chlorine may exist as free chlorine (also known as Free Available Chlorine) (Cl_2, $HOCl$, and OCl^-), as combined chlorine with organic matter, and as inorganic chloramines (NH_2Cl, $NHCl_2$, and NCl_3). The dominant chlorine species in water samples is highly dependent on the pH, and on the ratio of Chlorine to Ammonia ($Cl_2:NH_3$) in the water samples. Formation of combined chlorine is shown below. Note that the sum of monochloramine, dichloramine and trichloramine form the total combined chlorine (Crittenden et al., 2014).

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \text{ (Monochloramine Formation)}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \text{ (Dichloramine Formation)}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \text{ (Trichloramine Formation)}$$
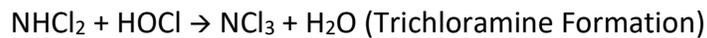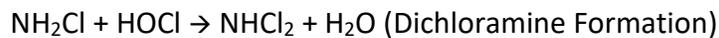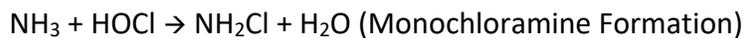
Breakpoint is defined as the point where the total oxidative chlorine (free and combined chlorine) is nonexistent, where chloramine residuals decline to a minimum value after some time of equilibration (Davis, 2010). Free and combined chlorine species do not include the chloride (Cl^-) ion which has no oxidative potential. Breakpoint occurs at a $Cl_2:NH_3$ molar ratio of 1.5, after breakpoint free chlorine is the only oxidative chlorine species existing (Crittenden et al., 2014).

Increasing chlorine dosage within water with a fixed amount of ammonia initially present causes total chlorine residual to increase until the molar ratio of chlorine to ammonia approaches 1 (Crittenden et al., 2014) as seen in Zone A of Figure 1.
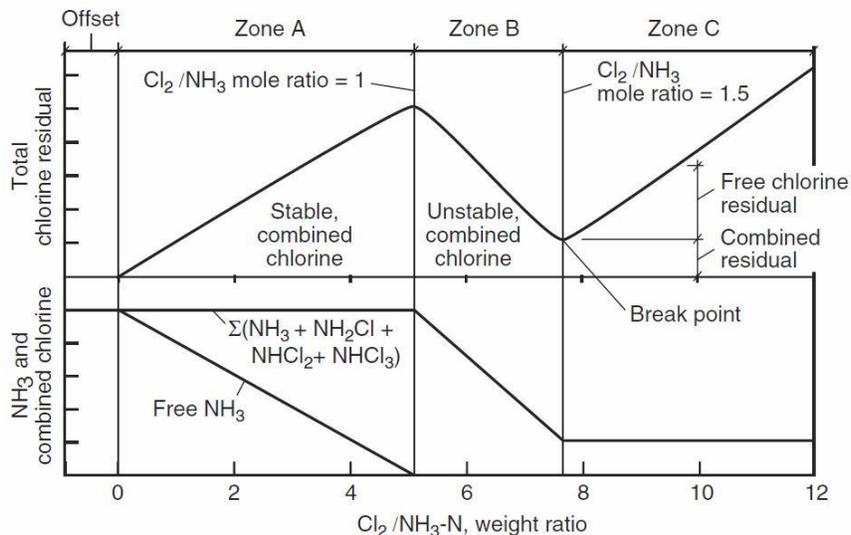
Figure 1 Chlorine Break Point Chemistry - Figure from (Crittenden et al., 2014)

When a molar ratio of 1 is reached, gasses will form along with a strong odor. These gasses are attributed to N_2 gas in Zone B; in this region, hypochlorous acid can oxidize ammonia to nitrogen gas and nitrate ion, resulting in the complete loss of chlorine residual (Crittenden et al., 2014). In addition to N_2 gas formation, products may also include H_2O, Cl^-, H^+, NO_3^- and other unidentified reaction products (Chen & Jensen, 2006).

$$3HOCl + 2NH_3 \rightarrow N_2(g) + 3H_2O + 3HCl \text{ (Nitrogen Gas Formation)}$$
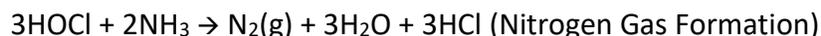
Beyond the breakpoint at a $Cl_2:NH_3$ molar ratio of approximately 1.5, the free chlorine added in stays relatively stable within the water along with a lesser concentration of combined chlorine in the form of monochloramine, dichloramine, and trichloramine (Crittenden et al., 2014). For the purposes of chloramination and chloramination AOP, zone A is the desired range where monochloramine is the dominant species. Monochloramine is the only chloramine present in Zone A at pH 8, but significant amounts of dichloramine can be present at pH 6 (Crittenden et al., 2014). Note that in the offset region of figure 1, reduction of readily oxidizable substances such as Fe(II), Mn(II), and H_2S occurs rapidly, within a fraction of a second (Crittenden et al., 2014) when properly mixed.

Dissolved organic nitrogen compounds in wastewater are very important because their presence affects the breakpoint chemistry by shifting the breakpoint to the right as seen with

glycine's effect on breakpoint chlorination (Hui et al., 2013). It was found that using simply the sum of organic-N with NH_3-N is not sufficient as a chlorination dosing control parameter for a target residual chlorine due to the different stoichiometric reaction ratios of ammonia and glycine with chlorine (Hui et al., 2013), this would complicate things when a target residual of free chlorine needs to be achieved. Furthermore, the second order kinetics for the chlorination of neutral amines to organic chloramines are 10-100 times faster than the reactions for monochloramine formation; Second Order reaction rate constants for the chlorination of neutral amines into organic chloramines are in the range of 10^7-10^8 $M^{-1}s^{-1}$, compared to $3.07x10^6$ $M^{-1}s^{-1}$ for NH_2Cl formation (Hui et al., 2013). These organic chloramines continue to react with chlorine causing a greater chlorine demand, but these organic chloramines are also found to have little or no microbicidal activity and are ineffective in the disinfection process (Hui et al., 2013), it is unclear what kind of effect these organic chloramines have on the AOP process for removing trace organics.

4.4   DISINFECTION WITH FREE & COMBINED CHLORINE

Chloramines have been commonly used as a disinfectant to prevent algae growth for the reverse osmosis (RO) process, and chloramines permeate through the RO membranes with the permeate stream (Chuang et al., 2017). Following most RO systems is AOP via UV/Hydrogen Peroxide, although with the chloramines still present, some treatment trains are de facto performing UV/Chloramine AOP (Chuang et al., 2017).

With the benefits that chloramination can provide over chlorination, inorganic and organic chloramines in general have little to no inactivation potential against microorganisms (Shang et al., 2000). Also, in most natural ammoniacal waters especially WW, nitrogen exists as organic-N compounds, a much less studied field in chlorination (Shang et al., 2000).

Chloramines may yield lower amounts of DBPs compared to free chlorine disinfection of wastewater; however the presence of chloramines has also lead to the investigation of its effect on the regeneration of N-Nitroso-dimethylamine (NDMA), a carcinogen, after the AOP process due to the interaction of dichloramine and NDMA precursors; the same study found

that reducing the time between pH adjustment for coagulation following AOP & RO treatment will reduce this effect (Selbes et al., 2018). Additionally, irradiation of chlorine causes the formation of a Cl radical, and with Cl radical based reactions it may be possible to form chlorate, perchlorate and halogenated DBPs (Miklos et al., 2018) during Chlorine AOP and Chloramine AOP.

The Tres Rios WWTP in Tucson, AZ operates at pH 7-7.4 (roughly 7 in the winter, and 7.4 in the summer), with suspended solids around 3 ppm. They utilize existing ammonia in the Wastewater (WW) and add FC to create chloramines. At pH's above 7, they add chlorine at levels that produce mostly monochloramine. If ammonia drops to below 1 ppm, they supplement secondary effluent with digester centrate for its ammonia content.

In 2007, research was conducted on the role of chloramination versus chlorination in ammoniacal shower grey waters. The findings of this report indicate monochloramine is relatively more chemically stable when compared to free chlorine (March & Gual, 2007). The paper goes on to conclude that chlorination doses greater than the chlorine demand where FC can finally exist, represents a waste of chlorinating agent (March & Gual, 2007). Free chlorine has a higher disinfection strength than combined chlorine, but chlorination can produce unpleasant taste and odor in drinking water (March & Gual, 2007). Another benefit of disinfection with monochloramine is its reduction in NDMA formation from NDMA precursors (Selbes et al., 2018).

Results from a different study shown in Figure 2 indicate that with natural shower greywater, monochloramine has relatively little change in concentration from 15 minutes to 2 hours before the peak. The graph also shows how unstable free chlorine after the breakpoint can be over the same time span.

Wastewater treatment plants have been recognizing the true potential of chloramines and have been known to implement chloramination into their treatment trains. An example of this is the Tres Rios WWTP located in Tucson, Arizona. Tres Rios artificially maintains an ammonia concentration of at least 5 mg/L-N while applying chlorine for disinfection at a 1:1 molar ratio
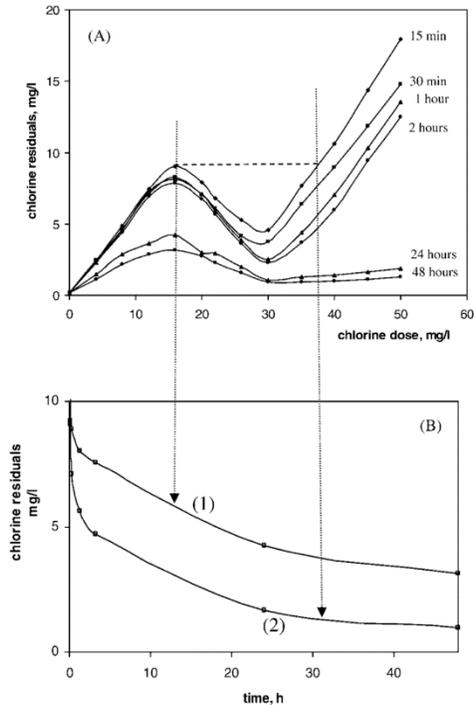
Figure 2 (a) Evolution of chlorination curves with contact time and (b) Residual chlorine decay for two initial chlorination dosages: (1) 16 mg Cl2/L, and (2) 37 mg Cl2/L (obtained by interpolation) - Figure from (March & Gual, 2007)

$Cl_2:NH_3$. Secondary effluent ammonia concentrations at Tres Rios have been seen to be much lower than the 5 mg/L NH_3-N, at about 0.68 mg/L-N total chlorine demand. It is common practice at Tres Rios to supplement secondary effluent with digester centrate, a stream high in ammonia content, into the secondary effluent to maintain the 5 mg/L-N ammonia concentration before adding sodium hypochlorite for disinfection. At another WWTP, Agua Nueva in Tucson, chloramination occurs where the company maintains a 1.2 mg/L NH_3-N and applies a 1.5 mg/L Cl_2 dosage for a $Cl_2:NH_3$ molar ratio of 0.25 (mass ratio of 1.25).

4.5 PHOTOLYSIS OF FREE CHLORINE & MONOCHLORAMINE

Direct photolysis of free chlorine and monochloramine reactions to produce free radicals are shown below (Chuang et al., 2017).

$$HOCl + h\nu \rightarrow \ ^{\cdot}OH + \ ^{\cdot}Cl$$

$$OCl^- + h\nu \rightarrow \ ^{\cdot}O^- + \ ^{\cdot}Cl$$

$$NH_2Cl + h\nu \rightarrow {}^{\cdot}NH_2 + {}^{\cdot}Cl$$
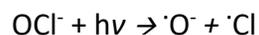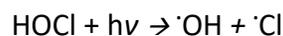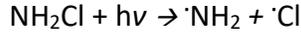
It is important to know that molar absorptivity refers to a molecules ability to absorb photons from a light source although the molecule does not always react to form radicals; the fraction of photons that react to produce radicals depends on the fraction of photons absorbed that create radical species. High molar absorptivity and high quantum yield (ϕ) are qualities of the better AOP mechanism.

Recent research has reported quantum yields for the radical generation by the UV photolysis at 254 nm of HOCl, OCl⁻, and NH$_2$Cl to be 0.62, 0.55, and 0.20 mol/Ein respectively; NH$_2$Cl quantum yields from other research have been between 0.26 - 0.62 mol/Ein (Chuang et al., 2017). In a comparison of UV/Monochloramine, UV/Chlorine, and UV/Hydrogen Peroxide it was found that the performance of UV/Hydrogen Peroxide and UV/Monochloramine AOPs were comparable at pH 5.5 – 8.3, but at pH 5.5 where RO operates, the UV/Chlorine AOP was more efficient (Chuang et al., 2017). Additionally, at a higher pH the UV/Monochloramine and UV/Hydrogen peroxide performed better than UV/Chlorine AOP (Chuang et al., 2017). Remember that at a pH greater than 8, free chlorine is predominantly as the OCl⁻ ion, and combined chlorine is predominantly monochloramine as seen in figure 3. The molar absorptivities at 254 nm have been reported to be much higher for monochloramine than for hypochlorous acid and hypochlorite ion, the values of which are 371, 62, and 60 M⁻¹cm⁻¹ respectively (Chuang et al., 2017).
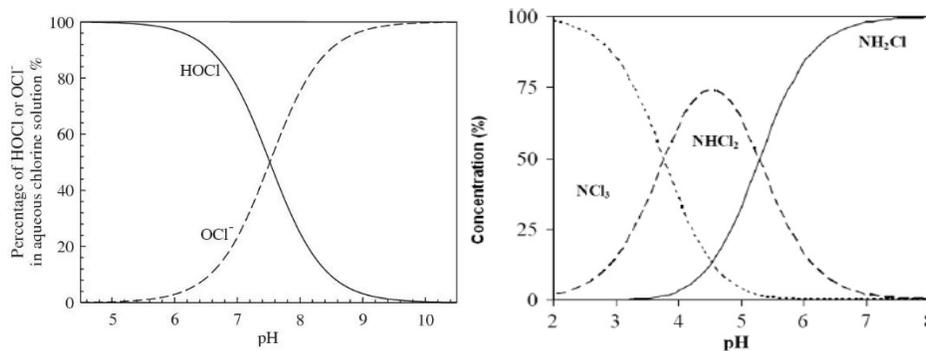
Figure 3 Free and Combined Chlorine Speciation dependence on pH (pKa = 7.5) Figures from (Feng et al., 2007) (Left Image) & Kinani et al., 2012 (Right image)
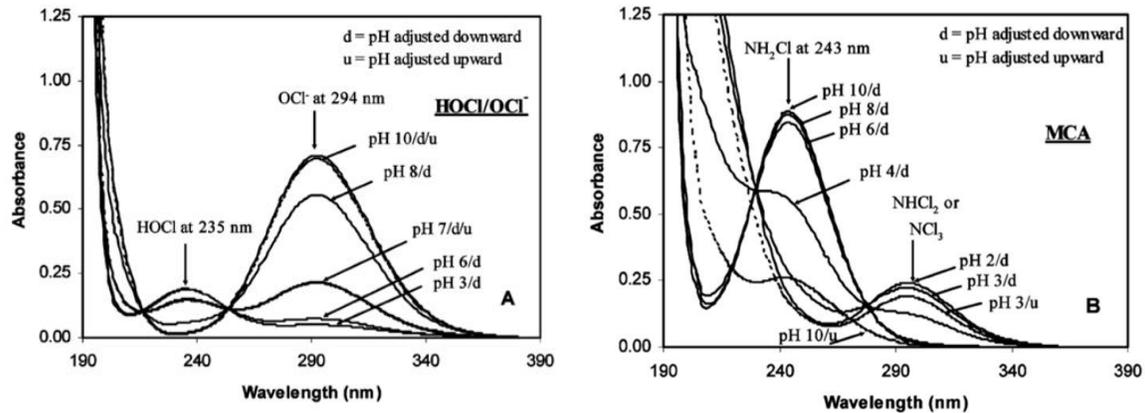
Figure 4 UV Spectra as a function of pH of Free Chlorine and Combined Chlorine at mM Figures from (Qiang &
Adams, 2004)

5 MONOCHLORAMINE AOP

5.1 MATERIALS & METHODS

5.1.1 Phosphate Buffer

A phosphate buffer was utilized for all reactors and calibration curves set at pH 7 using 10 mM
total phosphate by adding in 252 mg Potassium Phosphate Monobasic (KH_2PO_4), and 163 mg
Sodium Phosphate Dibasic (Na_2HPO_4) into 300 mL. These amounts were calculated via the
Henderson Hasselback equation, yet the final pH was always about 0.25 pH units lower than
desired therefore dilute Sodium Hydroxide (NaOH) was titrated into the solution to reach a pH
of 7.

5.1.2 Free Chlorine & Monochloramine Characterization via DPD Colorimetric Method

Note that there is no ideal way to measure free and combined chlorine, yet there are some
established methods such as the iodometric, DPD, and amperometric methods. However, the
standard analytical methods for chloramines, such as EPA Methods 4500-Cl B, C, D, E, F, G, H, &
I, cannot differentiate organic combined chlorines from inorganic combined chlorines [Marta et
al., 1989].

Free chlorine and monochloramine were measured via reactions with DPD (N, N-diethyl-p-
phenylenediamine) to form the Wurster dye chemical product as seen in figure 5. The Wurster

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dye has a two-peaked absorption spectrum; all absorbance data was taken at a 515 nm wavelength in a UV-1800 Shimadzu Spectrophotometer. The Free Chlorine calibration curve can be seen in figure 6. The Monochloramine calibration curve can be seen in figure 7.

Use of DPD (N,N-Diethyl-*p*-Phenylenediamine) is a colorimetric method that is a well-established technique in chlorine analysis (Harp, 2002). DPD provides the color, and potassium iodide acts as a catalyst to allow the combined chlorine to form color as outlined in the Standard Methods (Franson et al., 2005).

Another essential tool is the amperometric method which is an electrochemical technique that measures the change in current resulting from chemical reactions occurring. Note that the amperometric sensor method does not use the same methodology as the laboratory amperometric titration apparatus as seen in Standard Methods 4500-Cl D. However, considering the robustness of DPD, and due to common usage in on-line process testing (HACH, 2009), DPD methods were the choice of analysis for chlorine. In general, residual disinfectant monitors utilizing the colorimetric measurement method showed better performance than those employing amperometric/polarographic methods (Malkov & Visser, 2011). A magenta color is formed as oxidative species oxidize DPD into the Wurster dye (Primary oxidation product at near neutral pH but there is another colorless Imine that is formed). The Wurster dye can be measured photometrically at wavelength 515 nm to correlate absorbance to the corresponding chlorine concentration. The downside to DPD though is that it does not differentiate between inorganic and organic combined chlorine, this is important to understand when organic-N is present during chlorination.

Sulfuric acid (H_2SO_4) was utilized to lower the pH to retard DPD instability. Disodium ethylenediamine tetraacetate (Na_2EDTA) is also utilized to retard DPD deterioration due to atmospheric oxidation.
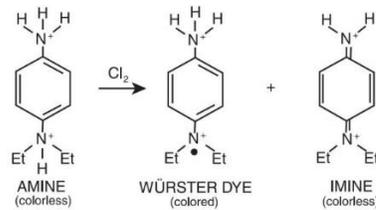
Figure 5 DPD - Chlorine Reaction Products; Figure from (Harp, 2002)

y = 0.0052x + 0.0234
R² = 0.9968
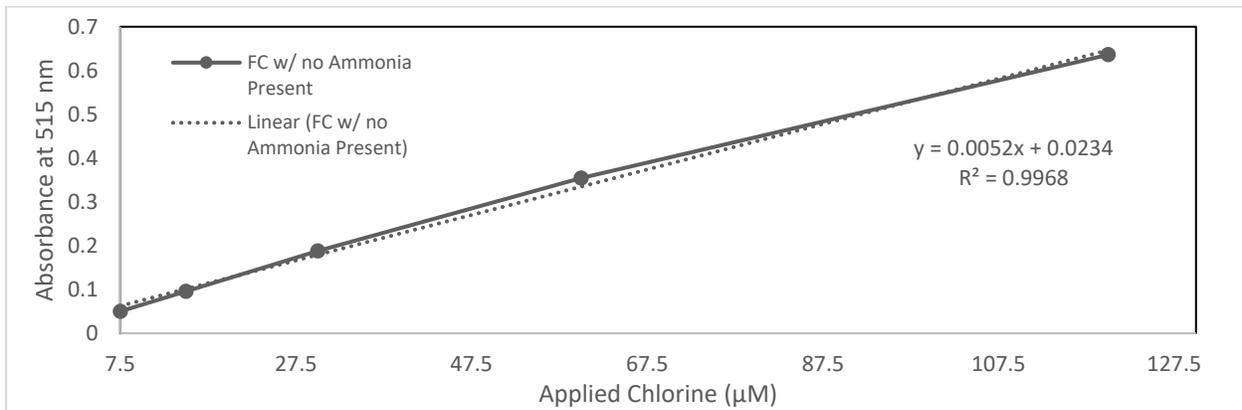
Figure 6 Free Chlorine Calibration Curve, 0 mg/L NH$_3$-N, pH 7

y = 0.0052x + 0.0081
R² = 0.9983
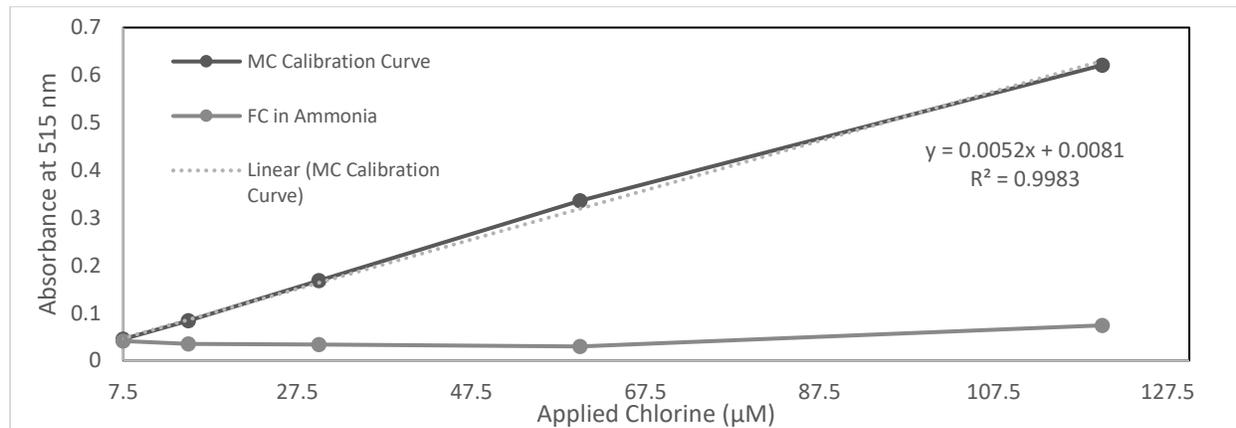
Figure 7 Monochloramine Calibration Curve, 5 mg/L NH$_3$-N, pH 7

5.1.3   DPD Ferrous Titrimetric Method to determine Free Chlorine, Monochloramine & Dichloramine

A 10 mL titration Class A straight bore burette was utilized with 0.05 mL graduation intervals (Kimble, 10-mL Burette w/ PTFE Stopcock). Titrations were performed using a stir bar and stirred in place using a 500 mL Erlenmeyer Flask. A plastic dropper was utilized to add the necessary drops of KI stock solution as required by Standards Method 4500-Cl F.

The titrimetric method has reproducibility for total chlorine or TRC, however there is a noticeable difference when comparing experimental monochloramine speciation to dichloramine speciation. After a repeat experiment (Chen et al., 2006), at pH 7, phosphate buffered solution, and with a 15-minute contact time the titrimetric method showed more monochloramine present compared to the Amperometric Titration method from Standard Methods 4500-Cl D.

An advantage of the DPD/FAS titrimetric method over the amperometric titrimetric method is that DPD methods are less susceptible to temperature, and pH. Both methods though have NCl_3 as an interference. High NCl_3 concentrations would contribute to either the free chlorine or dichloramine for the Amperometric titration method. Monochloramine can also intrude into the free chlorine fraction, and dichloramine can interfere in the monochloramine fraction.

5.1.4 P-Cresol Analysis

The target compound, p-cresol, was analyzed via fluorescence spectroscopy. Sodium thiosulfate was utilized as a quencher of free chlorine to prevent further degradation of PC by FC. An Excitation Emission Matrix (EEM) was created utilizing a LS 55 Fluorescence Spectrometer, not comparable to the LS3, that measured fluorescence of PC. A common issue with this method is the inner filter effect where shorter fluorescence waves get reabsorbed by other molecules resulting in a distorted measured spectrum, thus each sample's absorbance spectrum was analyzed and corrected for this. Each subsequent sample for PC was analyzed first with a UV-Vis 1800 from Shimadzu, the fluorescence spectrometer, then the data was analyzed in MATLAB to calculate the area under the curve between 300 and 337. The emission and excitation ranges were from 250 to 397 nm, and 240 to 320 nm respectively during fluorescence.
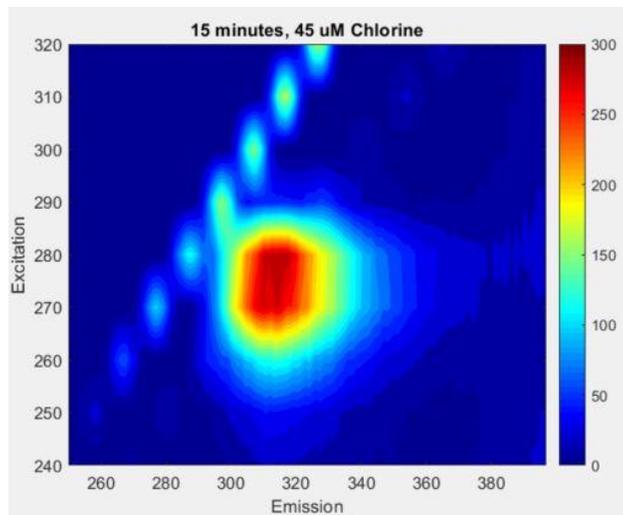
Figure 8 Example of an EEM generated via Fluorescence Spectroscopy

5.1.5   Ammonia, Monochloramine & p-cresol Stock Solutions

All ammonia stock solutions were prepared in volumetric flasks, utilizing the appropriate amount of ammonium chloride (Lot #BCBW7397 from Sigma Aldrich). Each stock solution of free ammonia was prepared before each experiment session and were unbuffered but maintained a neutral pH. Ammonium chloride in its solid form is a very easy compound to deal with at room temperature compared with PC. To achieve a concentration of 5 mg/L NH_3-N, 0.5 mL of a stock solution was injected into the 300 mL reactor; the ammonia stock solution consisted of 573.12 mg NH_4Cl in 50 mL.

A monochloramine stock solution was created by adding in 200.6 mg NH 4Cl, adjusting the pH to above 8 with NaOH, then adding in 4.18 mL NaOCl, and finally making up to 50 mL. This allowed 0.5 mL injections to achieve 100 μM NH_2Cl concentrations within a 300 mL reactor. The molar ratio of the stock solution was 0.8 Cl_2:NH_3 (mass ratio of 4.05 Cl_2:NH_3).

P-cresol stock solutions were prepared the day before and were allowed to mix overnight using a 99+% pure from Acros Organics (Lot # A0376826). A stock solution of 10 mM was the goal, however PC in the solid form can be difficult to work with and tends to stick to the weighing tray, perhaps a side effect of the chemicals high hygroscopicity. As a way around this, a mass of PC was weighed quickly to prevent sticking, and immediately mixed with 10 mL of DI water.

This mass varied between sessions but was recorded and the correct injection volume was calculated for each PC stock solution. By injecting the proper amount of stock solution into the reactor, the appropriate reactor PC concentration was achieved. Initial mass of PC into the 10 mL stock solution ranged from 10 mg to 20 mg, as a result the injection amounts ranged from 320 – 160 μL.

5.1.6   Free Chlorine AOP Procedure

All chemicals were reagent grade and used without further purification. The sodium hypochlorite (NaOCl) solution (Product # 239305 Lot # SHBH4120V @ Sigma Aldrich) Certificate of Analysis provides a concentration of 4.64% available chlorine as determined by a sodium thiosulfate titration. Note that the bottle indicates a 4-4.99% available chlorine solution. This solution was used for all experimentation and was swapped out on a monthly basis. The concentration value is based on a weight/weight (w/w) basis of available chlorine as Cl_2, note that the solution has a density of 1.097 g/mL. For example, to achieve a 100 μM Cl_2 (7.09 mg/L as Cl_2) concentration within a 300 mL reactor would require a 41.79 μL injection from the 4.64% Cl_2 stock solution. Stoichiometrically, one mole of Cl_2 is the same as one mole of HOCl as shown by the reaction below. Also, one mole of NH_2Cl is the same as one mole of Cl_2 based on the reactions below. NaOCl directly dissociates itself into HOCl, which has acid-base chemistry with OCl^-.

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

$$NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^-$$

$$HOCl \longleftrightarrow OCl^- + H^+$$
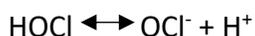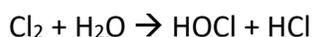
Free chlorine is injected into a 300 mL mixed batch reactor immediately prior to UV exposure. Initial free chlorine and *p*-cresol samples were taken as a baseline. All reactors were covered in two layers of black film (Black 80 Gauge Stretch Film, Part # 66538752 from MSC Industrial) for the purpose of extinguishing stray light. For all experiments other than in wastewater, Milli-Q water (resistivity > 18.0 MΩ·cm) was used.

5.1.7   Monochloramine AOP Procedure

In the experimental portion of this study two approaches for monochloramine formation were taken. One method consisted of ammonia and *p*-cresol coming to equilibrium in a well-mixed batch reactor for a couple minutes, then sodium hypochlorite was injected in the appropriate quantity at a Cl_2:NH_3 molar ratio < 0.4. This sort of process where hypochlorite solution is injected last best mimics what occurs at WWTPs at the disinfection portion of the treatment train, and thus was the method of choice for all experimental breakpoint curves. For the 1 mg/L NH_3-N in the reactor, dosages of applied chlorine ranged from 0 to 8 mg/L as Cl_2 (0 to 112.83 µM Cl_2) to characterize the combined chlorine range prior to breakpoint. The convention of using mass per volume concentrations stems from WWTP applications, where this form of annotation is much more common than molar concentrations. The method of "as Cl_2" or "as N" was utilized to standardize chlorine and nitrogen containing compounds.

For breakpoint curve analytics the DPD/FAS (N, N-diethyl-p-phenylenediamine / Ferrous Ammonium Sulfate) method was utilized to distinguish between FC, monochloramine, and dichloramine as outlined by Standard Methods (Franson et al., 2005). This method was chosen for its ability to provide a full scope of what was happening with free and combined chlorine speciation as a function of the Cl_2:NH_3 ratio. Note however, that for the experimental breakpoint curve where chlorine is kept constant and ammonia is the variable, only total chlorine was measured via the colorimetric method.

For kinetic experiments where the rate of PC degradation with varying monochloramine was the goal, a well-mixed batch reactor was allowed to mix for 2 minutes with 5 mg/L NH_3-N, and some pre-set amount of sodium hypochlorite. Equilibrium of combined chlorine is reached within that time, before PC was added to the solution. Dosages of monochloramine ranged from 0 – 100 µM NH_2Cl, all Total Residual Chlorine (TRC) was assumed to be as monochloramine.

For kinetic experiments, a colorimetric method was utilized to determine TRC, which was assumed to be all as monochloramine using a small enough Cl_2:NH_3 molar ratio of 0.3 and below.

All reactors were covered on the sides with two layers of black film for the purpose of extinguishing stray light. Between samples, sodium thiosulfate was utilized as a quencher of free and combined chlorine.

5.1.8   Dark Chlorination & Chloramination Procedure

All dark chlorination experiments were similar to the AOP procedure with the absence of UV radiation. Batch reactors were still well mixed and were covered with foil during the experimental contact time. These reactors were also covered with two layers of black film to prevent possible stray light reactions.

5.1.9   Wastewater Experimentation & Chlorine Demand

Wastewater was gathered from the Tres Rios WWTP Secondary Clarifier, before chlorination disinfection and before centrate supplementation for chloramination. The wastewater was then filtered using a 0.7 μm vacuum filtration apparatus to remove solids. Mixing of wastewater was kept to a minimum; too much mixing over an hour or so caused precipitation of unknown solids. Wastewater samples were gathered the morning of experimentation, kept in an amber bottle that was filled to the top.

Chlorine demand must be overcome before free chlorine begins to appear in wastewater, even then free chlorine will continue to react with species present in wastewater and can be seen to degrade over time. Interestingly, free chlorine in DI water alone will begin to slightly degrade with time as well. The procedure for chlorine demand consisted of repeated injection of a specified preset volume of sodium hypochlorite, then an immediate free chlorine check was performed using the DPD colorimetric method. The time to complete the chlorine demand check took approximately 6 minutes, which means that between each injection the free chlorine is allowed to react with the WW while some free chlorine in WW degraded slowly with time.

5.1.10   Wastewater Breakpoint Curves

Breakpoint curves were conducted on pure water samples and wastewater samples using sodium hypochlorite. Phosphate buffer was utilized to maintain a pH of 7. A chlorine contact

time of 15 minutes for both DI water and wastewater was established before aliquots were drawn. All samples were kept in the dark during chlorination to prevent photolysis reactions. As stated, chlorine residual was measured in accordance to Standard Methods 4500-Cl F (DPD Ferrous Titrimetric Method).

For kinetic experiments, the DPD colorimetric method was utilized to get TRC, which again was assumed to be monochloramine for all reactions with a Cl_2:NH_3 molar ratio of 0.3 or less.

6   RESULTS AND DISCUSSION

For UV 254 irradiation experiments, the average fluence rate was found to be 2.21 E-05 Ein/m^{2}s (10.38 W/m^2) obtained from known *p*-cresol direct photolysis kinetics given that ϕ_{254} = 0.034 mol-Ein^{-1} and ε_{254} = 340 M^{-1}cm^{-1} for *p*-cresol. Area of the water surface of the reactor was 96.77 cm^2, while the total liquid volume was 300 mL and the UV path length (i.e. depth of liquid) was approximately 3.1 cm. Direct photolysis of PC (the only absorber of light) in DI water allowed us to back calculate I_0 (Ein/cm^2/s) from the k_{obs} using the following direct photolysis equation assuming minimal light absorbance and a collimated beam.

$$k_{obs} = -2.303 * \phi_{PC} * I_0 * \varepsilon_{PC}$$

In this study, experimental breakpoints at pH 7 indicate a free chlorine residual at a molar ratio of 1.5 begin to appear after 15 minutes, but the point of minimum chloramine residuals (breakpoint) occurs at around a 1.8 Cl_2:NH_3 molar ratio for dark chlorination and AOP at pH 7. Breakpoint slightly shifts to higher ratios when pH is decreased.

We can see almost instantaneous MC formation in figure 9 that stays constant at approximately 96-98% speciation of total chlorine when mixing sodium hypochlorite into ammoniacal waters at a Cl_2:NH_3 molar ratio less than 0.4. However, when analyzing the same experimental set up in wastewater, some free chlorine residual shows up with the DPD colorimetric method, this

may be due to organic chloramines interacting with DPD and not necessarily due to free chlorine, as with DI water monochloramine similarly forms within a minute.
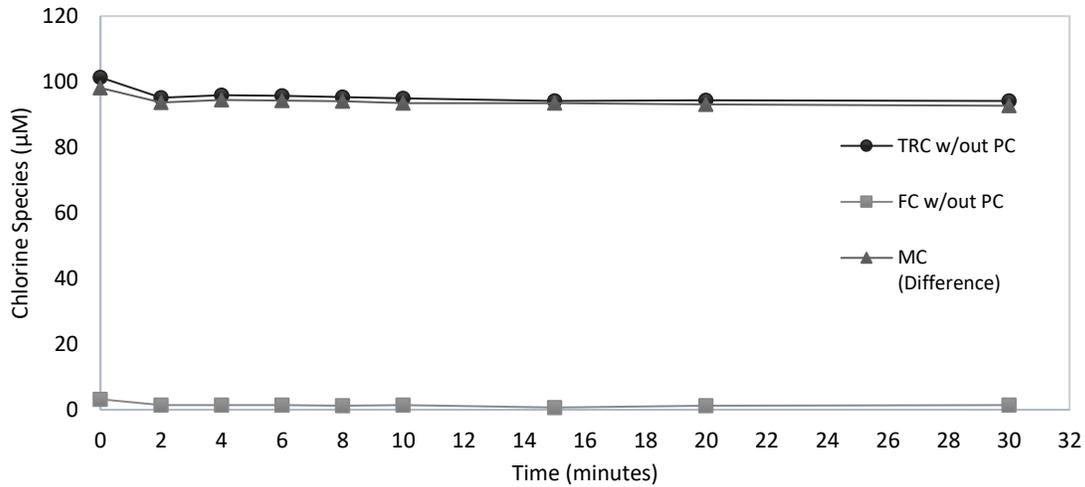

Figure 9 Monochloramine Formation in DI Water kinetics, pH 7, 100 μM Cl₂, 5 mg/L NH₃-N

Regarding wastewater experiments, 5 mg/L NH_3-N was added on top of to the chlorine demand that is already in the wastewater. By performing the chlorine demand check, we can see that there is approximately a preexisting 0.68 mg/L as Nitrogen demand in the WW, the components of which include organic nitrogen.

As seen in figure 10, it took 36 μM of applied chlorine for free chlorine to get breakthrough of free chlorine in the solution. The non-linearity of the free chlorine portion after breakpoint can be attributed to the degradation of free chlorine with other wastewater species in the water that do not react as instantaneous as chlorine demanding species. It took 36 μM of applied chlorine before breakpoint which suggests a 0.68 mg/L chlorine demand as N, assuming breakpoint occurs at a Cl_2:NH_3 molar ratio of 1.5 as seen in literature (Davis, 2010). However, in Davis' case, it is not clear if ammonia was the only item present in breakpoint chlorination.

Breakpoint chemistry agreed well previous literature for DI water and wastewater alike. The calculated breakpoints for DI water occurred at 2, and 1.8 for waters with 5 mg/L NH_3-N at pH 6.75 and pH 7 respectively. These values were estimated to be slightly higher than the 1.5 value of breakpoint from literature, however the point of free chlorine presence in this study

did occur at a $Cl_2:NH_3$ molar ratio much closer to 1.5, at about 1.55. The point of breakpoint and free chlorine appearance after 15 minutes are not the same as seen in the curves.
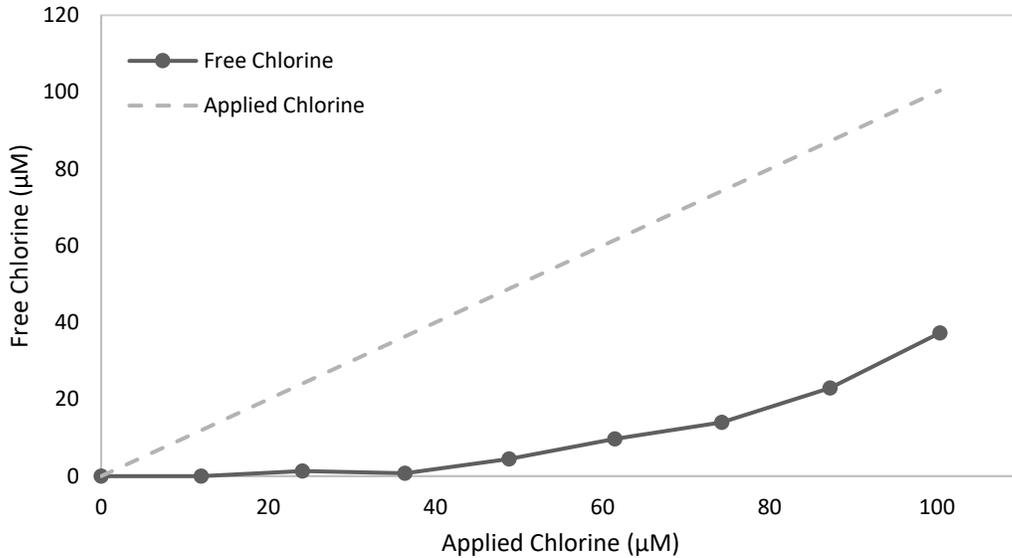

Figure 10 Instantaneous Chlorine Demand Check, pH 7, FC begins to appear at 36.4 µM Applied Chlorine suggesting a chlorine demand of 0.68 mg/L as N

Figure 11 shows three different breakpoint curves during this study where the DPD/FAS titrimetric method was used to analyze chlorine speciation. The first breakpoint curve is in DI water to compare with previous literature data, the data matched well with the previous data, shift in the breakpoint and TRC peak to the left may be a result of the slight pH difference, pH 6.75 for this experimental curve versus pH 7 from literature. TRC, or total chlorine species, data may match well but it is obvious that there is a clear difference in monochloramine speciation detection and dichloramine detection due to the difference of methods. This breakpoint curve was created in the dark at pH 6.75, with 5 mg/L NH_3-N in equilibrium with the water before chlorine addition; as a reminder, TRC is the total chorine species, MC is monochloramine, DC is dichloramine, and FC is free chlorine.
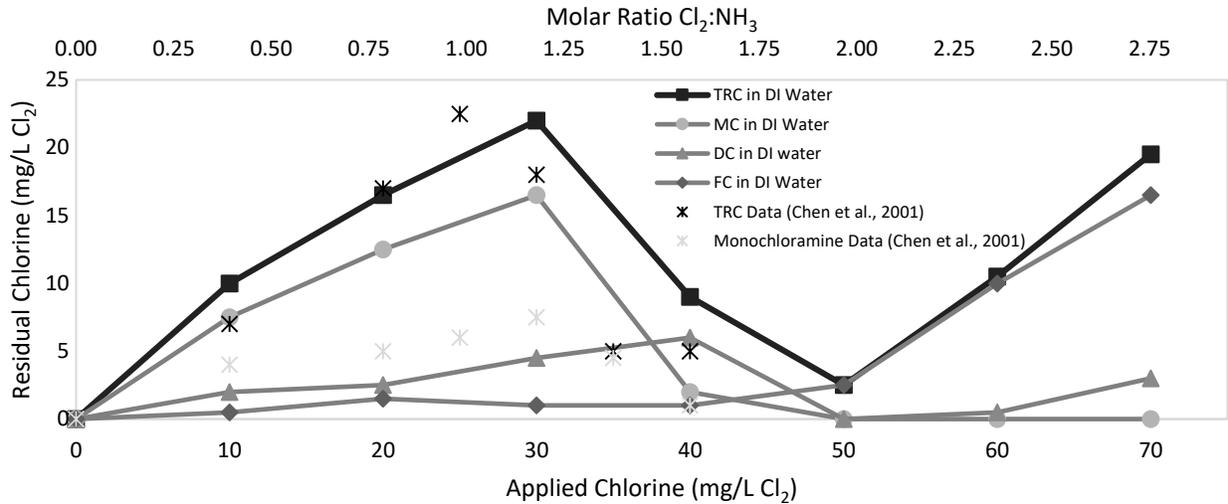
Figure 11 Breakpoint Chemistry in Pure water compared to another source, (Chen & Jensen, 2006) *, pH 6.75 , 5 mg/L NH₃-N, 15 minute contact time, DPD/FAS Titrimetric Method*

The next breakpoint curve shown in figure 12 shown below was created to show the degradation of chloramines under UV254 irradiation versus in the dark after a 15-minute contact time. The rate of disappearance of inorganic combined chlorines is obvious compared to that without light, indicating that along the breakpoint curve, when monochloramine is present, photolysis reactions occur. Interestingly, at a ratio of 1.35 or so we see that dichloramine becomes the dominant species, and dark chlorination degradation exceeds the rate of degradation by photolysis. When free chlorine becomes present at a molar ratio of 1.6, we see that photolysis becomes the dominant method of chlorine degradation again.
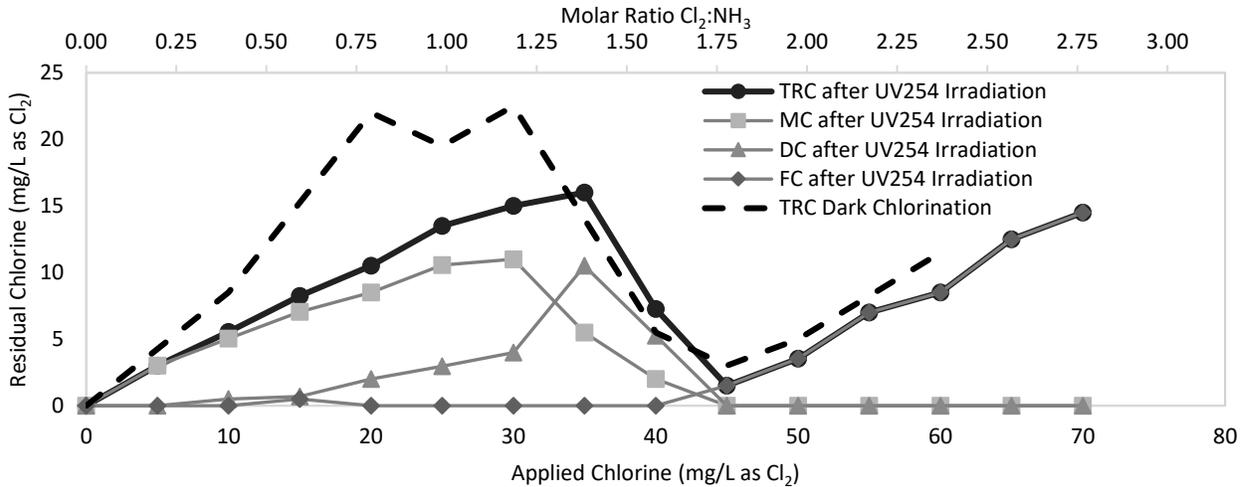
Figure 12 Breakpoint Chemistry in Wastewater pH 7, 5 mg/L NH$_3$-N, 15-minute contact time, DPD/FAS Titrimetric Method

For the last breakpoint curve shown in figure 13, the idea was to see chlorine speciation in DI water and compare to secondary effluent wastewater prepared as explained Methods. Chlorine was applied in similar dosages and we can see the formation of identical DPD reactants from zero to a molar ratio of about 0.5. Note though that DPD is known to react with organic chloramines that shows up as monochloramine, so it is unclear if the DPD reactant shown is in fact inorganic or organic chloramines. It is also important to note that the peak of wastewater TRC is shifted to the right and is relatively higher in chlorine concentration than the DI breakpoint curve. The shift is due to small amounts of chlorine demand already present in the wastewater during the 5 mg/L ammonia addition, putting the total chlorine demand around roughly 5.68 mg/L NH$_3$-N with the combination of ammonia stock solution.

The peak in the wastewater breakpoint curve is simply due to the 0.68 as N difference in chlorine demand. Again, the chlorine demanding species consist of a multitude of things, including organic-N which react with chlorine, though it is not known if resulting organic chloramines participate in the AOP process. Reaction with DPD would indicate some oxidative potential.
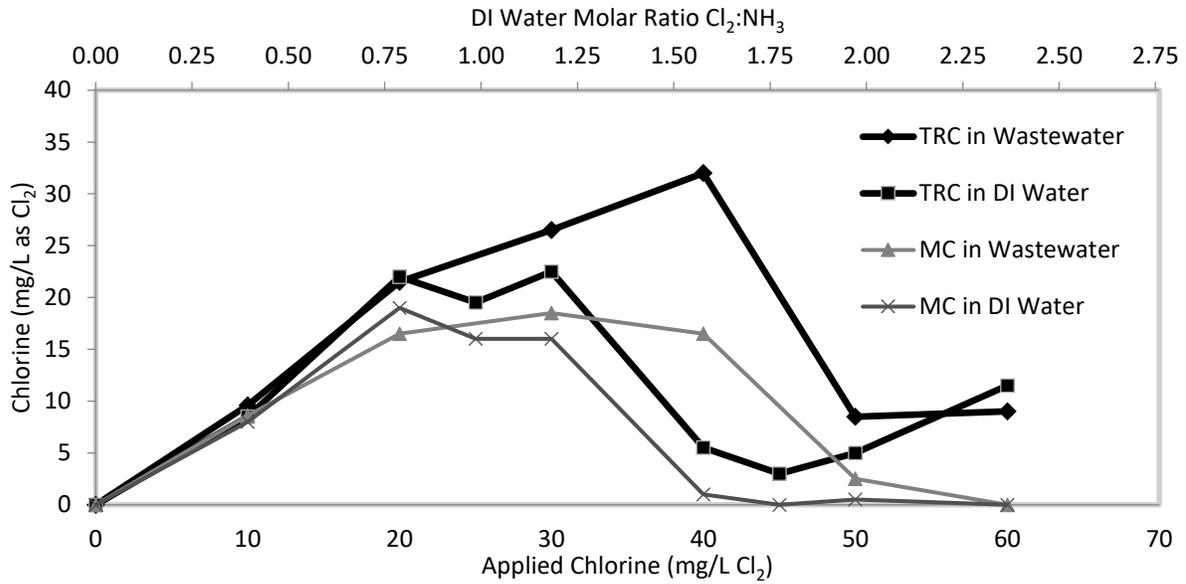
Figure 13 Comparison of DI Water to Wastewater Breakpoint, 5 mg/L NH₃-N & ~ 5.68 mg/L NH₃-N Respectively

Figure 14 shows the degradation of PC by monochloramine AOP. This was performed with the formation of monochloramine before introduction of PC, the idea was to not have HOCl contribute to the AOP process and at a molar ratio of < 0.3 Cl_2:NH_3, all combined chlorine was as monochloramine. We can see a PC degradation of approximately 80% after 30 minutes in DI Water from Monochloramine AOP.

Figure 14 Monochloramine AOP to degrade p-cresol under UV 254, pH 7, 5 mg/L NH$_3$-N, [PC]$_0$ = 10 μM

In wastewater, PC degradation is only around 20% after 30 minutes as shown in figure 15; this plot involved two method for MC formation, the preformation of monochloramine (K$_{eq}$ NH$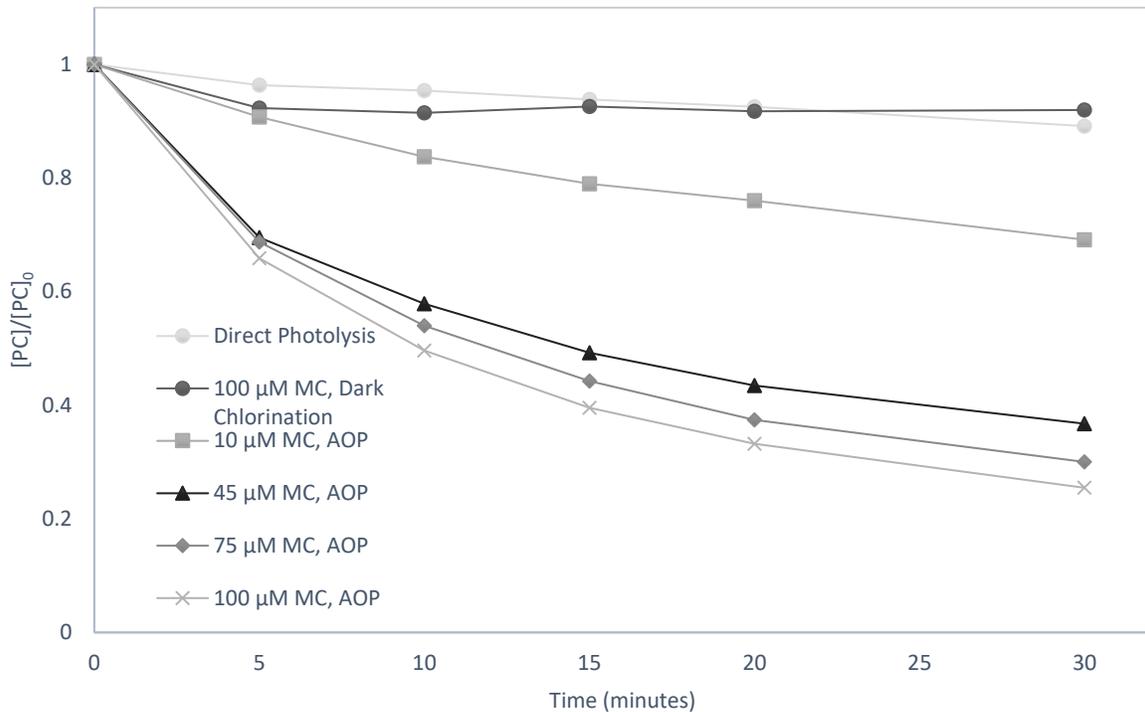_4$Cl from NH$_3$ and HOCl is 1.97E08) before PC injection and direct chlorine injection into WW with 5 mg/L NH$_3$ supplemented and approximately 0.68 mg/L-N preexisting nitrogenous mixture. Organic chloramines will form at a faster rate than that of inorganic chloramines, thus in the WW reactors there exists a combination of organic and inorganic chloramines for the sodium hypochlorite spike. With a large enough dosage of ammonia, ammonia to organic N mass ratio was about 7.35, effect of organic chloramines on the AOP process was mitigated. The oxidation potential of organic chloramines is not fully understood, yet the data shows that PC degradation is less efficient in wastewater despite the MC formation method. Either way, both methods for Monochloramine AOP with monochloramine provided better PC degradation than direct photolysis and direct chlorination alone.
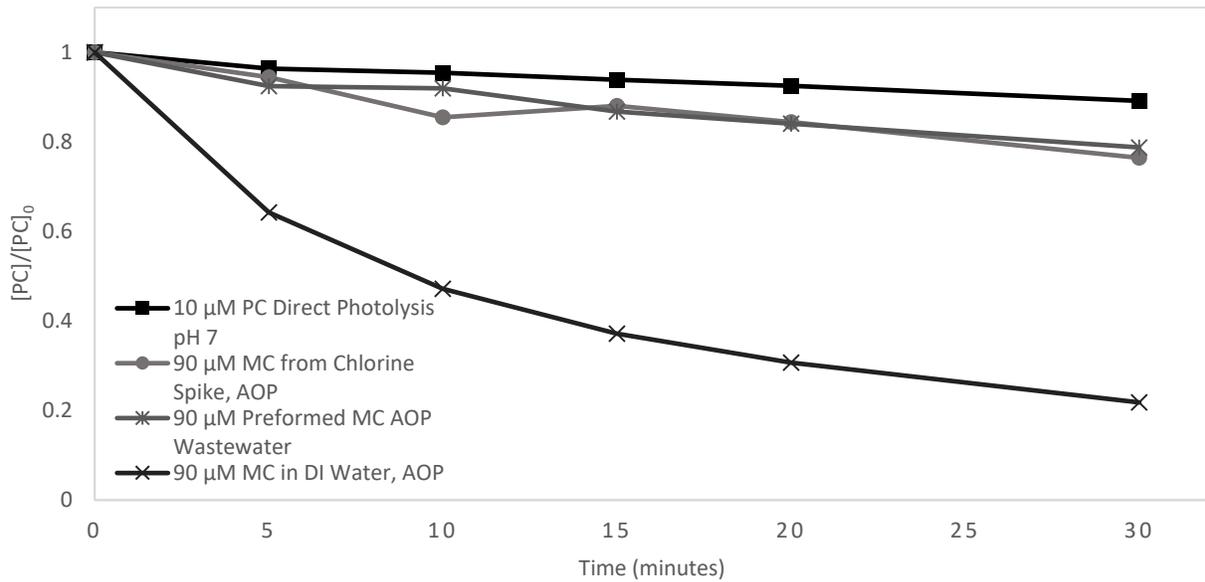
Figure 15 MC Formation Comparison PC degradation DI water vs Wastewater, pH 7, 5 mg/L NH$_3$-N, [PC]$_0$ = 10 µM

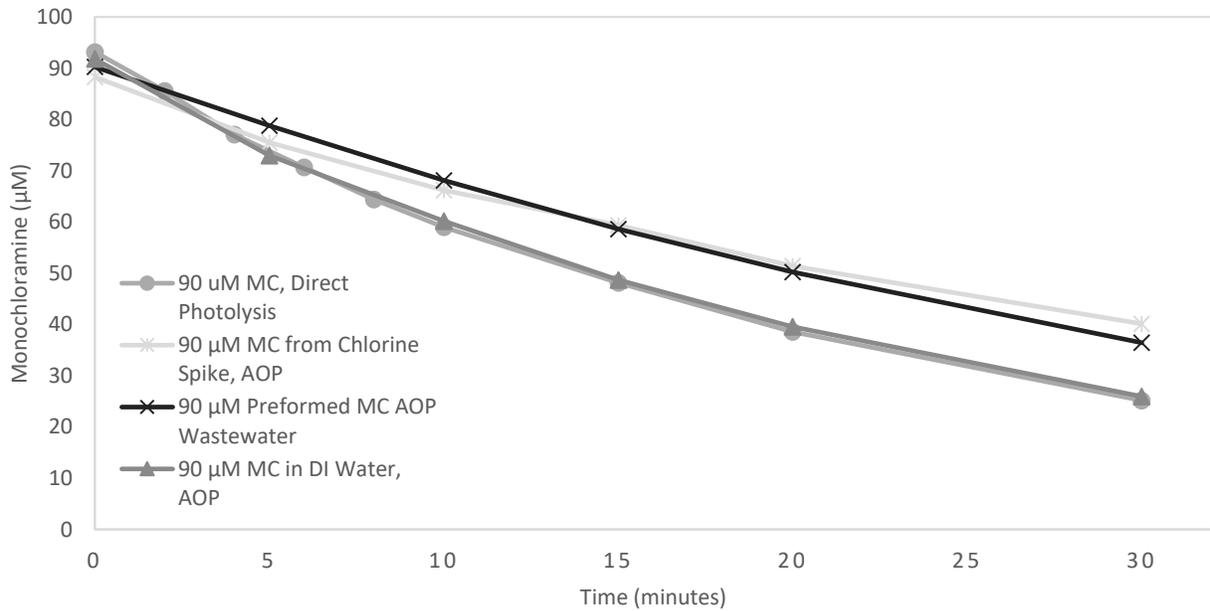*Figure 16 Monochloramine Formation Comparison in Wastewater & DI Water, AOP, pH 7, [PC]$_0$ = 10 µM*

Monochloramine kinetics shown in figures 17 and 18 show a relatively similar degradation under UV 254 at different initial preformed monochloramine concentrations, this could be a result of the high molar absorptivity of monochloramine which is much higher than that of hypochlorous acid and hypochlorite ion (371, 62, and 60 $M^{-1}cm^{-1}$ respectively (Chuang et al., 2017)), though it is known that it's quantum yield of monochloramine is relatively low compared to hypochlorous acid and hypochlorite ion (0.2, 0.62, and 0.55 mol/Ein respectively (Chuang et al., 2017)). An interesting find was that monochloramine degradation was the same under UV 254 with or without *p*-cresol present.

Breakpoint chemistry allows the formation of different combined species, though for chloramination and chloramine AOP the target chlorine species would be monochloramine due to the potential of less harmful byproducts. Direct photolysis of monochloramine outputs the NH_2 and Cl radical species, and its known that the Cl radical species is more selective than OH radical species; in fact Cl radical reacts more with electron rich contaminants such as phenol, toluene, aniline, dimethylaniline, dimethoxybenzene, and hexamethylbenzene; additionally high bicarbonate concentrations in real water samples significantly reduce the contribution of Cl radical (Fang et al., 2014). Dark chlorination of PC with monochloramine does not lead to significant PC degradation.
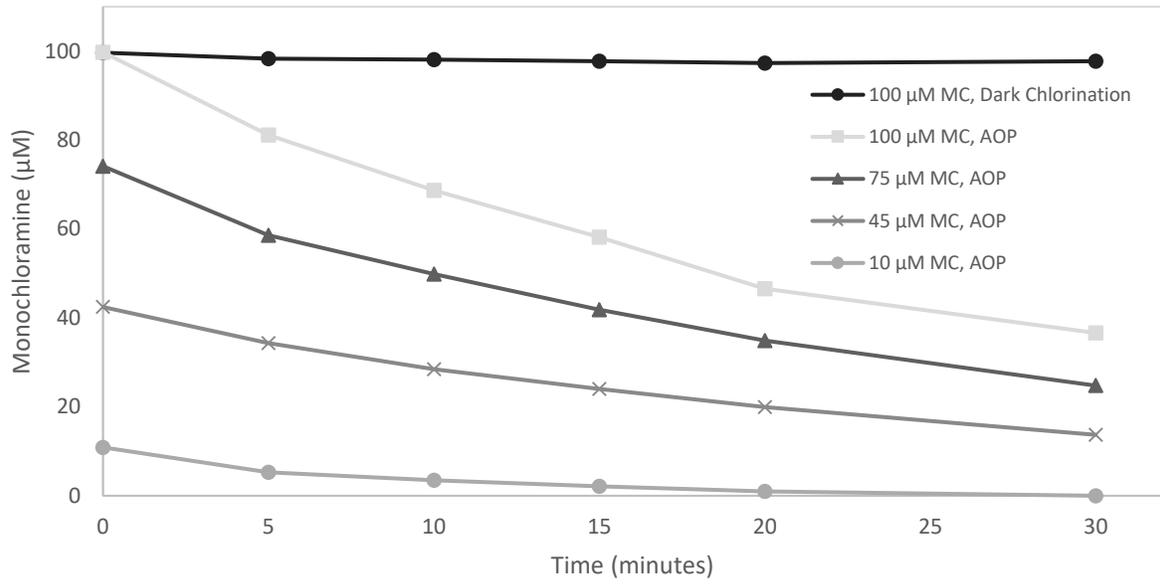
Figure 17 Monochloramine Degradation in DI Water via AOP, pH 7, 5 mg/L NH$_3$-N, [PC]$_0$ = 10 μM
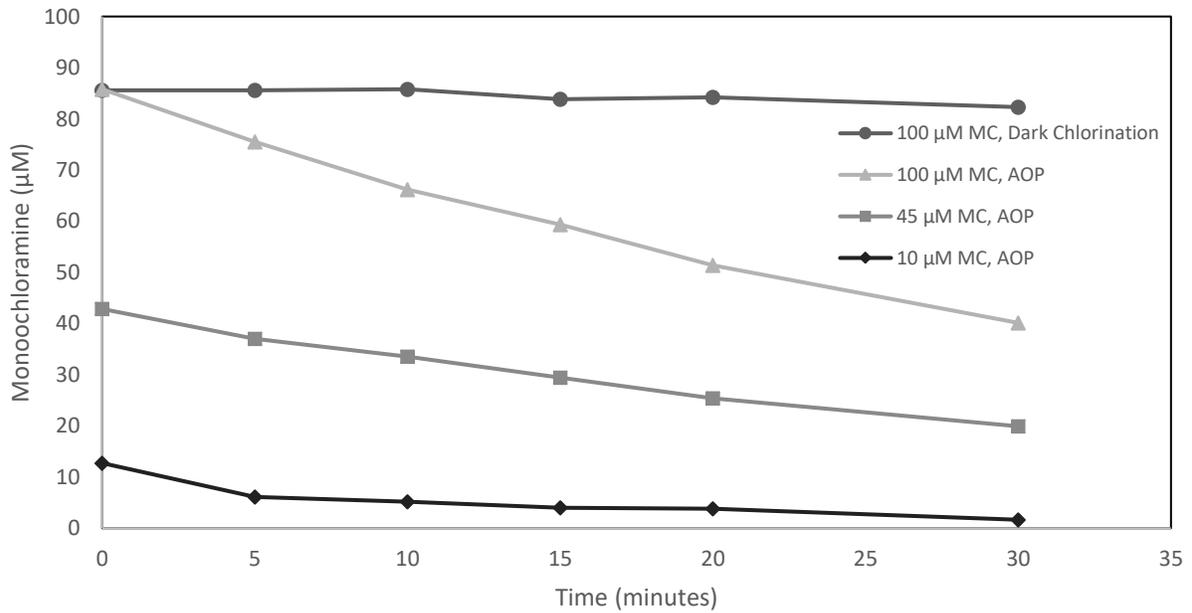
Figure 18 Monochloramine Degradation in Wastewater via AOP, pH 7, ~ 5.68 mg/L NH$_3$-N, [PC]$_0$ = 10 μM

Comparing the chlorine degradation side by side from figures 16 and 18 (see figure 19) except for the 10 μM, we can see that degradation is relatively the same but differs per medium AOP is conducted in. We can see that there is only a slight degradation in monochloramine from varying concentrations of MC in DI water, and the same goes for wastewater. This may be due to the high molar absorptivity of monochloramine which allows its degradation to be consistent and only dependent on the flux of photons that are allowed to reach it, meaning that turbidity and other absorbing molecules may be the reason we see the decrease in consumption from DI water to wastewater since wastewater components are also absorbing a fraction of light at 254 nm.

Figure 19 Comparison of Monochloramine AOP Degradation in DI water vs Wastewater and Dark Chlorination at pH 7, [PC]$_0$ = 10 μM

Comparing Monochloramine AOP to FC AOP in figure 20, we can clearly see that FC AOP has faster degradation rates of PC, which was to be expected. Know that for FC to first be present, the chlorine demand must first be met for free chlorine to leave a residual.
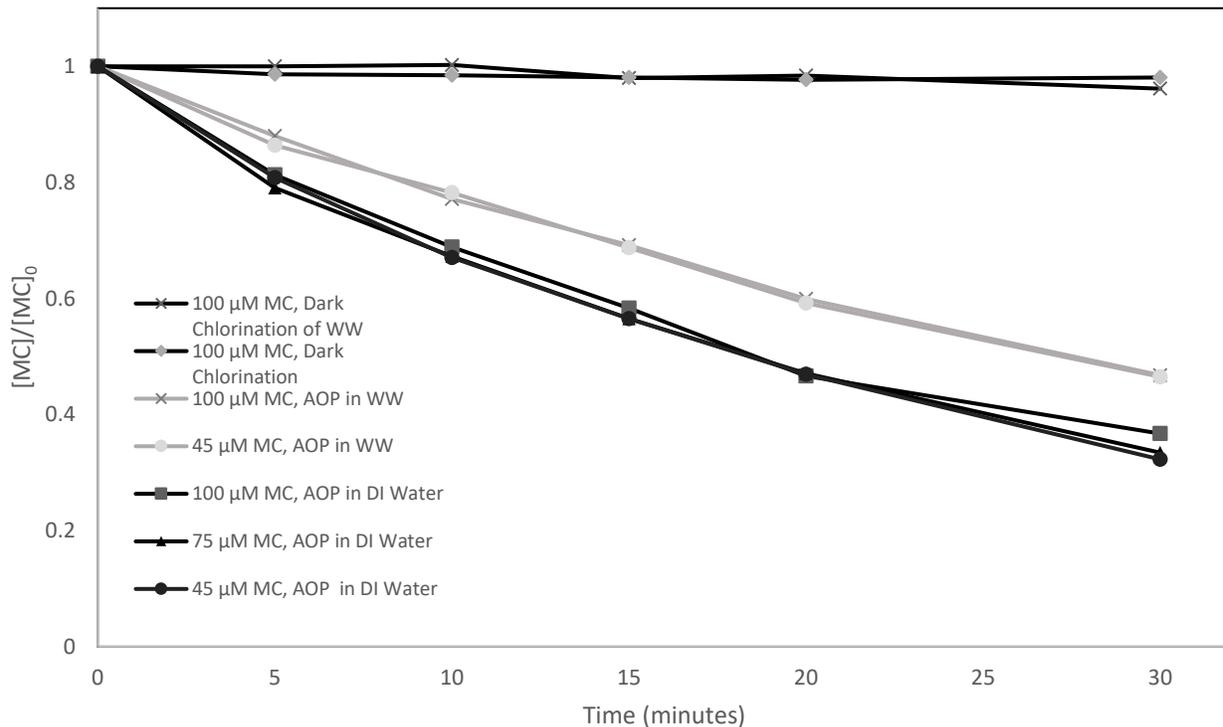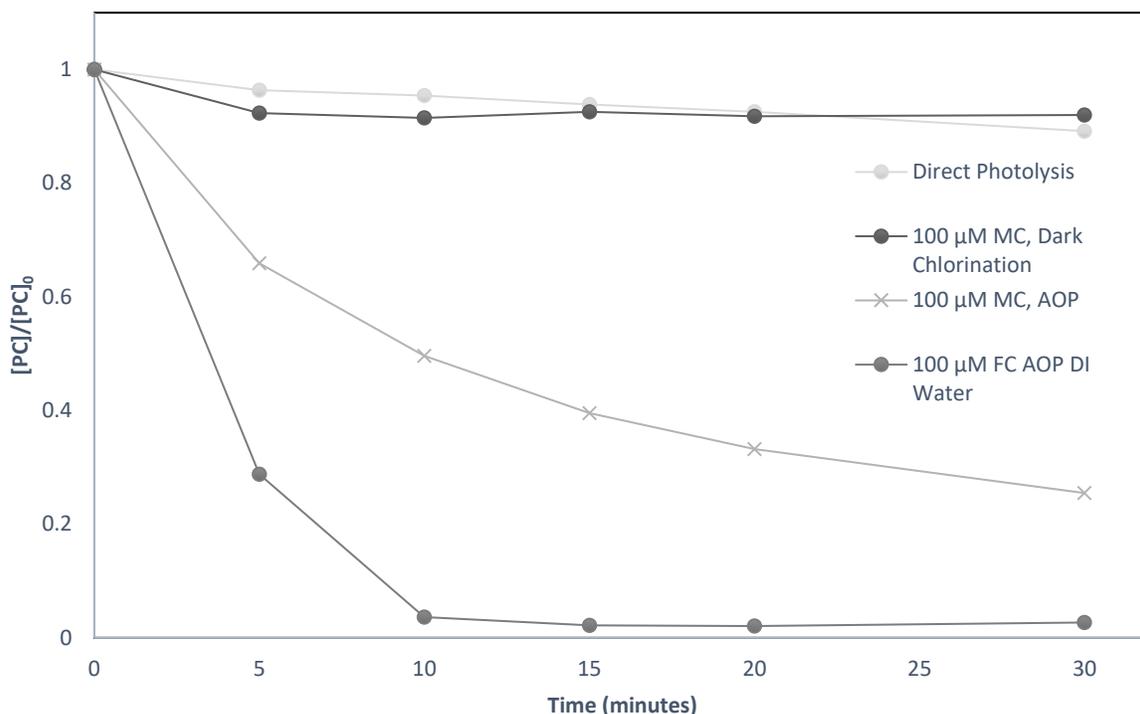

Figure 20 Monochloramine vs Chlorine AOP kinetics, pH 7, 5 mg/L NH$_3$-N, [PC]$_0$ = 10 μM

Breakpoint chemistry as seen in figure 21 below shows that there is a high correlation between monochloramine formation and PC degradation after 15 minutes under UV254, we can even see that PC degradation can be almost 90% in one case at a Cl$_2$:NH$_3$ molar ratio near breakpoint; in reality WWTPs would not operate at this molar ratio due to the presence of dichloramine at this range. Two other points need to be made about this plot, one is to know that the method for this data set involved equilibrium of ammonia and PC in the water, then injection of chlorine to mimic real world applications where trace organics are already present in wastewater before chlorine is introduced via chlorination or chloramination. The other point to be made is that chlorine in general is increasing which is why we see more PC degradation as we move to the left of the curve, thus in the next plot the goal was to keep chlorine constant rather than keep ammonia constant.
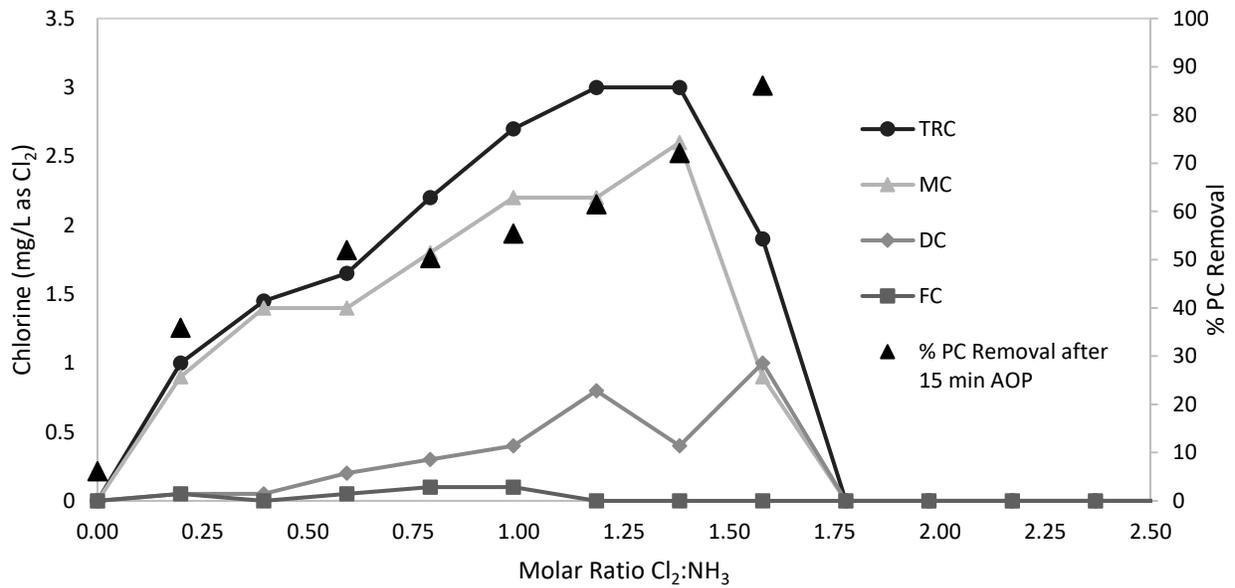
Figure 21 Percent p-cresol removal along the Breakpoint Curve of Monochloramine, pH 7, [PC]$_0$ = 10 μM

As stated, a better way to understand the Cl$_2$:NH$_3$ molar ratio effect on AOP's ability to degrade PC was to keep chlorine constant but change ammonia concentrations, this was achieved by adding the same amount of free chlorine into each reactor to achieve a total chlorine concentration of 100 μM, each with differing amounts of ammonia. This data can be seen in figure 22. The procedure consisted of equilibrating different amounts of ammonia in DI water first, then allowing chlorine to interact with the ammonia for 1 minute before PC addition (this is enough time for total chlorine to degrade by roughly 50% into N$_2$ and other products near the breakpoint!). The point of PC injection and exposure to UV 254 was taken as the time zero, given that the ammonia and chlorine had 1 minute to equilibrate. Note that the point at zero is direct photolysis. Also, breakpoint occurs at a molar ratio of approximately 2.3, much different than the previous molar ratio breakpoints of 1.75, the reason being is not fully clear. Also notice that free chlorine of 100 μM is not fully achieved since breakpoint chlorination products have stripped out the chlorine to form non-oxidative byproducts.

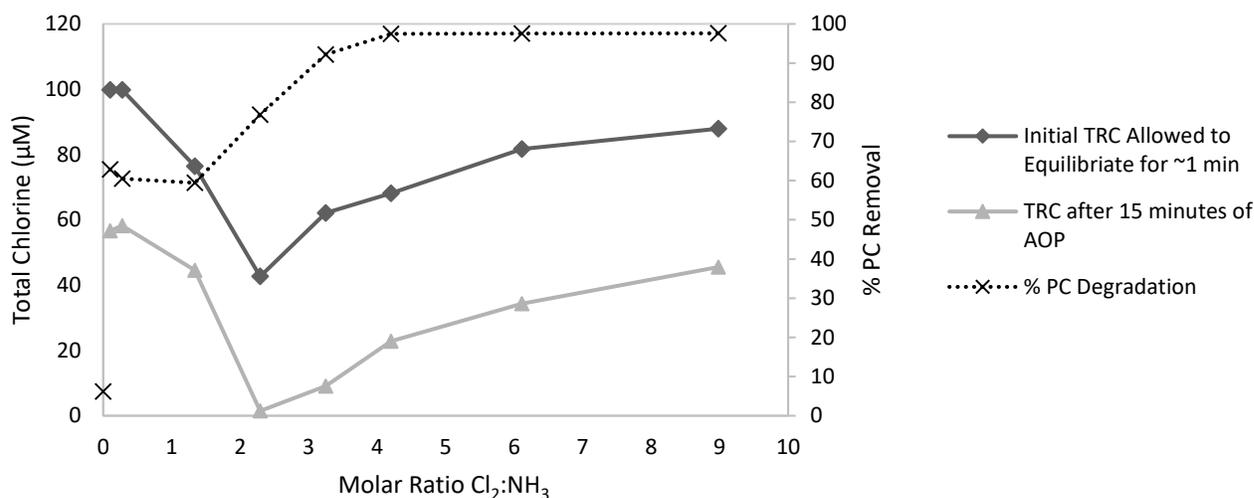*Figure 22 Breakpoint Chlorination AOP keeping chlorine constant but changing NH_3 to get different $Cl_2:NH_3$ molar ratios at pH 7, and 15 minutes of UV254 Irradiation, $[PC]_0 = 10 \mu M$*

7 CONCLUSIONS

Free chlorine AOP will remain the more powerful oxidizing process to degrade *p*-cresol, however the use of free chlorine has its downsides such as pH dependence, relative instability, and the need to first overcome chlorine demand. Monochloramine AOP in general is relatively new, and this study has shown that it has potential to degrade PC. We can see this clearly in the kinetic experiments where PC degradation via monochloramine AOP approaches 80% after 15 minutes for a meager 100 µM dose. Monochloramine AOP degradation of *p*-cresol was found to be extremely higher than disinfection and direct photolysis alone, perhaps monochloramine usage in industry has not yet been fully achieved.

In real world applications where chlorine is injected into wastewater matrices (which would include *p*-cresol in equilibrium) the degradation of PC is not the main priority. This may be due to several reasons, including chlorine's interaction with chlorine demanding species such as organic nitrogen, thus forming a relatively small amount of inorganic chloramines that contribute to the AOP process. This theory was checked using a preformed monochloramine stock solution and the results indicate that there is no difference between preformation of

monochloramine before injection into wastewater, and chlorine injection into wastewater with a high amount of ammonia present. It could be because of the 5 mg/L NH_3-N addition to wastewater before chlorine injection, free chlorine saw more ammonia in solution therefore reacting with mostly ammonia to form inorganic chloramine which we know can perform AOP. More testing should be performed to see the impact of organic nitrogen present in wastewater on the AOP process for monochloramine. Either way, performance of monochloramine AOP was much less efficient in wastewater.

In the case of spiking chlorine in waters with PC and ammonia in equilibrium, there is a high degradation of PC just after 15 minutes of irradiation, almost 90% degradation near the breakpoint, though WWTPs maintain a Cl_2:NH_3 molar ratio of 0.25 to 1 to minimize DBP formation. This high degradation rate may be due to the sheer amount of chlorine, thus in another set of experiments the chlorine dosage was kept constant while the ammonia content was changed. This method was a much better way to analyze PC degradation potential along the breakpoint curve, and as expected free chlorine AOP was the great process. It was great to see too that Monochloramine AOP had degraded a fair amount of *p*-cresol as well.

Monochloramine's high molar absorptivity allows it to decay at relatively the same rate depending on which solution the AOP process is occurring in. For example, in DI water, we could see that the normalized decay rate was the same for different concentrations of initial monochloramine, with or without *p*-cresol present. This decay rate was different from AOP in wastewater, however the rate of decay was the same in wastewater for varying initial concentrations of chloramine for AOP too.

8 FUTURE WORK

There are multiple forms of creating monochloramine for the purpose of AOP, one case can be preformation of monochloramine, then spiking with PC under UV254 to compare degradation rates along different ratios on the breakpoint curve. Another method is to create stock monochloramine then inject this into the water matrix, these variations can be further studied as to see which method of monochloramine formation works best for PC degradation, while also knowing that in industrial practices, chlorine is injected into a water matrix filled with organic nitrogen and ammonia alike. The difference between the two methods arise when there is organic nitrogen present in the water.

It is unclear on how organic chloramines react under UV254, and it is unclear if they contribute to degradation of PC under UV254, a number of organic nitrogen compounds exist in the wastewater matrix and each may have varying interactions with free chlorine and therefore the organic combined chlorine species could be further investigated. The items to investigate include the reversibility of inorganic chloramine to organic chloramine. However, it may also be the case that inorganic chloramines have relatively stable formation and undergo AOP without converting first to organic chloramines.

Effects of organic-N compounds (e.g. glycine, cysteine, asparagine, uracil, cytosine, and guanine) are unknown since these also interact with Free Chlorine and have the potential to yield false positives in the monochloramine and dichloramine reading of the DPD/FAS titrimetric method. Two other methods have been discussed in this study and they have the potential to differentiate between inorganic and organic chloramines. For example, using the DPD colorimetric and Salicylate Spectrophotometric Method in parallel would allow the researcher to quantify the amount of organic species formed during the chlorine injection step.

Degradation of hydrogen peroxide under UV254 promotes OH radical formation that contribute to the mineralization of p-cresol by addition of OH to the molecule then undergoing a continuous degradation. In the case of monochloramine a Cl radical is formed, and it is unclear if a Cl radical is combining with PC forming chlorinated product intermediates. These

intermediates may or may not have increased toxicity compared to PC, and this is something to investigate.

The effects of pH are unclear for monochloramine AOP, however this study performed experiments at neutral pH to mimic real life applications. Monochloramine is the dominant species at higher pH's, so it can be hypothesized that we would see the same PC degradation between pH 6 and pH 10. At lower pH's where dichloramine begins to form, it is unclear if this compound contributes to the AOP process or has negative effects, this should be investigated as well.

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