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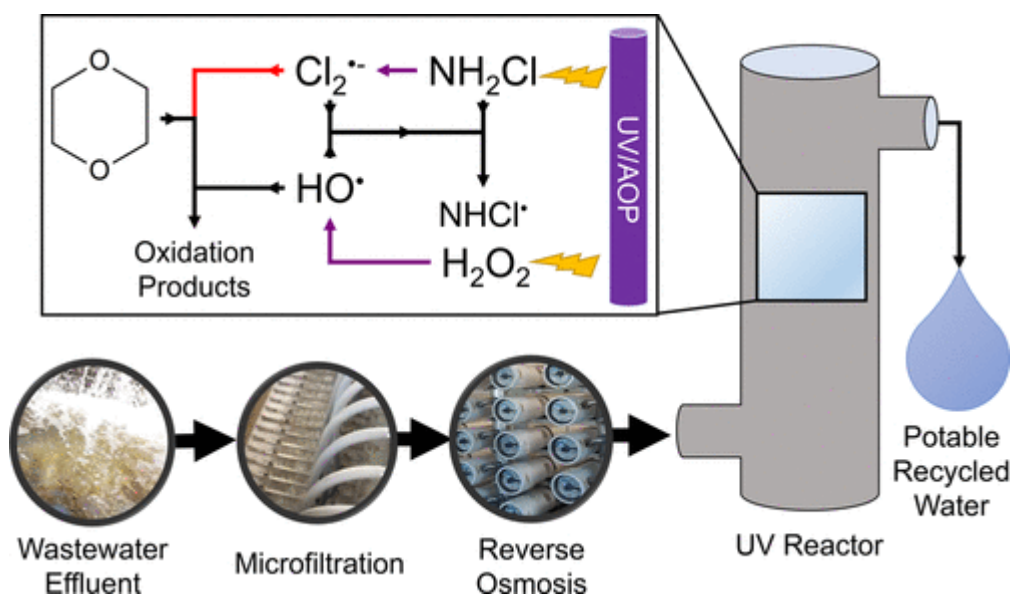
## Photolysis of Mono- and Dichloramines in UV/Hydrogen Peroxide: Effects on 1,4-Dioxane Removal and Relevance in Water Reuse

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### Abstract

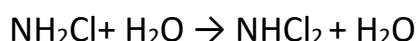
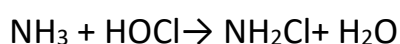
Growing demands and increasing scarcity of fresh water resources necessitate potable water reuse, which has been implemented with the aid of UV-based advanced oxidation processes (UV/AOPs) that remove potentially hazardous trace organic contaminants from reclaimed water. During the potable reuse treatment process, chloramines are added to prevent membrane fouling that are carried over to the UV/AOP, where hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is commonly added. However, the impact of chloramines on the photolysis of  $\text{H}_2\text{O}_2$  and the overall performance of the UV/AOP remains unknown. This study investigated the impacts of the photochemistry of monochloramine ( $\text{NH}_2\text{Cl}$ ) and dichloramine ( $\text{NHCl}_2$ ) associated with the photolysis of  $\text{H}_2\text{O}_2$  on the degradation of 1,4-dioxane (1,4-D), a trace organic contaminant ubiquitous in recycled water. Results indicated that  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  alone functioned as oxidants upon UV photolysis, which produced  $\text{HO}\cdot$  and  $\text{Cl}_2\cdot-$  as the two primary oxidative radicals. The speciation of chloramines did not have a significant impact on the degradation kinetics. The inclusion of monochloramine in UV/ $\text{H}_2\text{O}_2$  greatly decreased 1,4-D removal efficiency.  $\text{HO}\cdot$  was the major radical in the mixed  $\text{H}_2\text{O}_2$ /chloramine system. Results from this study suggest that recognizing the existence of chloramines in UV/ $\text{H}_2\text{O}_2$  systems is important for predicting UV/AOP performance in the treatment train of potable reuse.

### Graphical Abstract



## Introduction

Potable reuse has become increasingly important to alleviate water shortage in drought stricken regions. (1,2) Water reuse treatment trains rely on a sequence of processes which remove microbiological, inorganic and trace organic contaminants from wastewater effluent that may have adverse health effects. (3–5) Specifically, microfiltration (MF) or ultrafiltration (UF) are used to remove bacteria and colloidal particles from the wastewater effluent, reverse osmosis (RO) for salt rejection, and they are commonly followed by a UV-based advanced oxidation process (UV/AOP) for disinfection and removal of trace contaminants. (2) To prevent MF and RO membrane biofouling, chloramines are typically introduced in the feedwater, through the addition of chlorine which reacts with ammonia present in the wastewater effluent:  $\text{NH}_3 + \text{HOCl} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$



Typically, both monochloramine (NH<sub>2</sub>Cl) and dichloramine (NHCl<sub>2</sub>) are generated in the feedwater, with their speciation depending on solution pH, and ratio between free chlorine and ammonia. (6–8) NH<sub>2</sub>Cl has a greater disinfection efficiency than NHCl<sub>2</sub> and is the preferred antifouling species. (9) More importantly, because both chloramines are small and neutral, they easily diffuse through RO membranes and carry over to the UV/AOP step.

Meanwhile, RO membranes do not efficiently remove small and neutrally charged trace organic contaminants including 1,4-dioxane (1,4-D), which is widely present in municipal wastewater (10) due to its use as an industrial stabilizer of chlorinated solvents and presence in personal care products. (11,12) 1,4-D is classified as a 2B carcinogen, (13) and thus, the State of California requires the demonstration of a minimum of 0.5-log removal of 1,4-D during AOP for potable reuse and established a 1 ng/L notification level. (14,15) Because 1,4-D is not subject to direct photolysis, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is typically added during UV treatment, where the

photolysis of  $\text{H}_2\text{O}_2$  at 254 nm produces highly reactive hydroxyl radicals ( $\text{HO}\cdot$ ) that degrade 1,4-D and other trace organic contaminants. (16–18)

Chloramine species have high molar absorptivity coefficients relative to  $\text{H}_2\text{O}_2$ , i.e., 388 and  $142 \text{ M}^{-1}\text{cm}^{-1}$  for  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  at 254 nm, respectively, compared to  $18.8 \text{ M}^{-1}\text{cm}^{-1}$  for  $\text{H}_2\text{O}_2$ . Chloramines are photolyzed to produce unique radicals including  $\text{NH}_2\cdot$ ,  $\text{NHCl}\cdot$ , and  $\text{Cl}\cdot$  with differing quantum yields, 0.54 for  $\text{NH}_2\text{Cl}$  and 0.82 for  $\text{NHCl}_2$ . (19,20) The amino radical ( $\text{NH}_2\cdot$ ) reacts with phenol and compounds with primary amine functional groups, while  $\text{NHCl}\cdot$  is relatively nonreactive. (21,22) Chlorine atom ( $\text{Cl}\cdot$ ) reacts with a diffusion limited rate constant with aromatic compounds and also reacts with chloride to form chlorine dimer ( $\text{Cl}_2\cdot^-$ ), which reacts with water to form  $\text{HO}\cdot$  or decays to form chloride. (23–25) The photolysis of  $\text{NH}_2\text{Cl}$  has also been recently found to degrade 1,4-D via the generation of  $\text{Cl}_2\cdot^-$  and  $\text{HO}\cdot$ . (26,27) The photochemistry of trichloramine ( $\text{NCl}_3$ ) has previously been used to remove it from swimming pool water. (28)

Current literature on the photochemistry associated with UV/AOPs implemented for potable reuse considers pure and single oxidant systems (e.g., UV/ $\text{H}_2\text{O}_2$  or UV/ $\text{NH}_2\text{Cl}$ ) but does not consider the de facto coexistence and simultaneous photolysis of chloramines and  $\text{H}_2\text{O}_2$  during UV/AOP. Although chloramines can react with  $\text{H}_2\text{O}_2$  without UV irradiation over the course of hours, (29) the impact of chloramines on UV/ $\text{H}_2\text{O}_2$  with respect to the removal of trace organic contaminants remains unknown. It is likely that a unique set of chain reactions controls radical generation and treatment efficiency. Therefore, the objectives of this study were to evaluate the efficacy of UV/chloramine, especially the impact of chloramine speciation (i.e.,  $\text{NH}_2\text{Cl}$  vs.  $\text{NHCl}_2$ ) on 1,4-D removal, and examine the impacts of coexisting chloramines on the photochemistry of  $\text{H}_2\text{O}_2$ .

## Materials and Methods

All chemicals were of ACS or reagent grade. A majority of experiments were prepared in deionized (DI) water ( $18.2 \text{ M}\Omega\cdot\text{cm}$ , Millipore), and in some experiments real RO permeate from a water reuse treatment facility was used. A 5% NaOCl solution (Arcos Organics) was standardized by  $\text{KMnO}_4$  method prior to use. (30) A 50 mM  $\text{NH}_2\text{Cl}$  stock solution was prepared daily by titrating 30 mM  $(\text{NH}_4)_2\text{SO}_4$  with 50 mM NaOCl at a N-to- $\text{Cl}_2$  molar ratio of 1.2. The  $(\text{NH}_4)_2\text{SO}_4$  solution was buffered at pH 8.8 using 4 mM borate. The final  $\text{NH}_2\text{Cl}$  stock solution had a pH of 8.8 and was equilibrated for at least 1 h. prior to use. A 25 mM  $\text{NHCl}_2$  stock solution was prepared by lowering the pH of the  $\text{NH}_2\text{Cl}$  solution below 5.5 using  $\text{HClO}_4$  and equilibrating for 10 min. The concentrations of chloramine stock solutions were confirmed by standard DPD method. (30)

To start an experiment, DI water was purged with  $\text{N}_2$  gas for 20 min to lower dissolved  $\text{O}_2$  and inorganic carbon levels similar to those observed in RO permeate. This was followed by the addition of 250  $\mu\text{M}$  1,4-D and radical probe compounds (20  $\mu\text{M}$  nitrobenzene and 10  $\mu\text{M}$  benzoic acid). Chloramines and  $\text{H}_2\text{O}_2$  were then added in their specified concentrations as required. The concentrations of 1,4-D and oxidants were higher than those in RO permeate to provide useful insight into

reaction kinetics and radical chemistry. (26) In the single chloramine systems (UV/NH<sub>2</sub>Cl or UV/NHCl<sub>2</sub>), the concentration of NH<sub>2</sub>Cl and NHCl<sub>2</sub> was varied between 0.2 and 6 mM with a fixed concentration of 1,4-D (250 μM), resulting in a molar ratio of chloramine-to-1,4-D between 0.8 and 24. In experiments to study the impact of mixed oxidants, stock solutions of NH<sub>2</sub>Cl, NHCl<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> were made separately, and working solutions were prepared prior to UV irradiation. Mixtures of chloramines were found to be stable for the duration of the experiments. All experiments were conducted at pH 5.8 which is typical for reverse osmosis permeate and maintained with 40 mM phosphate buffer at 20 °C which was maintained by air circulation in the reaction chamber.

The prepared solution was dispensed into sealed 8 mL quartz reaction tubes placed in a carousel UV reactor (Ace Glass) equipped with a low-pressure Hg lamp (Ultra Sun Technologies). Samples were taken at 5 min intervals under UV irradiation for a total of 25 min (UV dosage ≈ 3500 mJ/cm<sup>2</sup>). Upon removal from the UV reactor, chloramine and H<sub>2</sub>O<sub>2</sub> concentrations were immediately measured by DPD and KI methods, respectively. (31) In preparation for organic analysis, the residual oxidants in the remaining sample were quenched with 5.5 mM thiosulfate. Concentrations of probe compounds and 1,4-D were quantified by HPLC-UV (Text S1 of the Supporting Information, SI). A competition kinetic method (32) was used to calculate steady-state radical concentrations (Text S2). In brief, the experimentally measured pseudo first-order degradation kinetics of probe compounds and the literature reported second-order rate constants of reactions between probe compounds and radicals were used to calculate the steady-state radical concentrations. In all cases, the addition of probe compounds consumed a negligible fraction of radicals and did not interfere with 1,4-D degradation. Probe compounds and 1,4-D were found not to directly photolyze in control experiments.

Nitrogen product analysis from chloramine decay was carried out by a combination of methods. Total nitrogen was measured by a TOC analyzer equipped with a nitrogen detector (OI Analytical Aurora 1030). Ammonia was measured by the standard phenate method. (33) Nitrate was determined using the salicylic acid method, (34) and nitrite was determined using the sulfanilamide method. (30) Organic nitrogen was determined by subtracting nitrate, nitrite, and ammonia from total nitrogen. Gaseous nitrogen formation was calculated by subtracting the initial total nitrogen from total dissolved nitrogen measured after exposure to 3500 mJ/cm<sup>2</sup>.

## Results and Discussion

### Photochemistry of NH<sub>2</sub>Cl and NHCl<sub>2</sub>

In this study, we first examined the capability of NH<sub>2</sub>Cl and NHCl<sub>2</sub> to remove 1,4-D under UV photolytic conditions analogous to the treatment of RO permeate at a wastewater recycling facility. The rate of 1,4-D removal under NH<sub>2</sub>Cl photolysis was approximately 60–80% higher than with NHCl<sub>2</sub> when the chloramine dosage was less than 2 mM. At concentrations less than 4 mM, NH<sub>2</sub>Cl was more efficient at removing 1,4-D than NHCl<sub>2</sub> and reached the maximal rate at 2 mM compared to 4 mM for NHCl<sub>2</sub> (Figure 1A). NH<sub>2</sub>Cl has a greater molar absorptivity coefficient at 254

nm, but a lower quantum yield (0.54 vs 0.82) than  $\text{NHCl}_2$ . (20) The combined effects led to similar photolysis rates between  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  at 2 mM (Figure S1). However, the effective yield of reactive radicals from the photolysis of  $\text{NH}_2\text{Cl}$  was higher than  $\text{NHCl}_2$  at a chloramine dosage less than 2 mM.

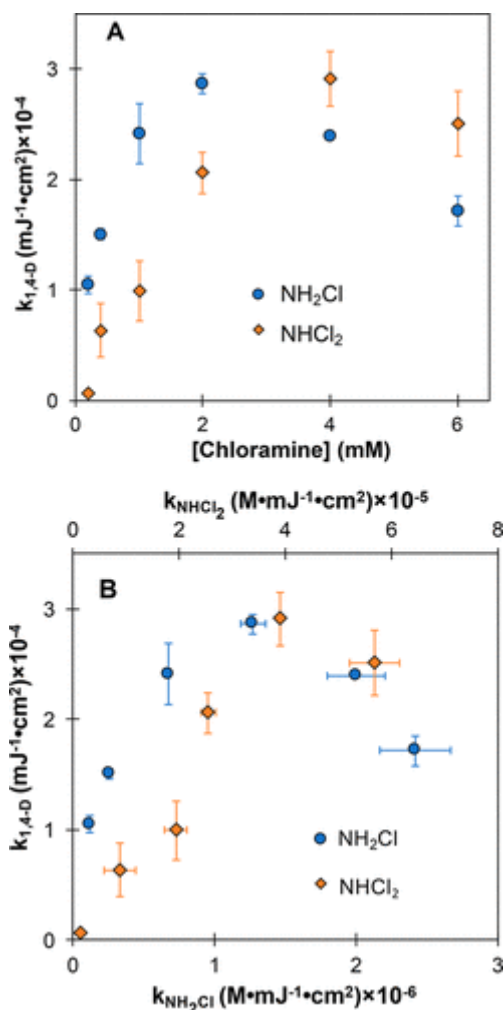
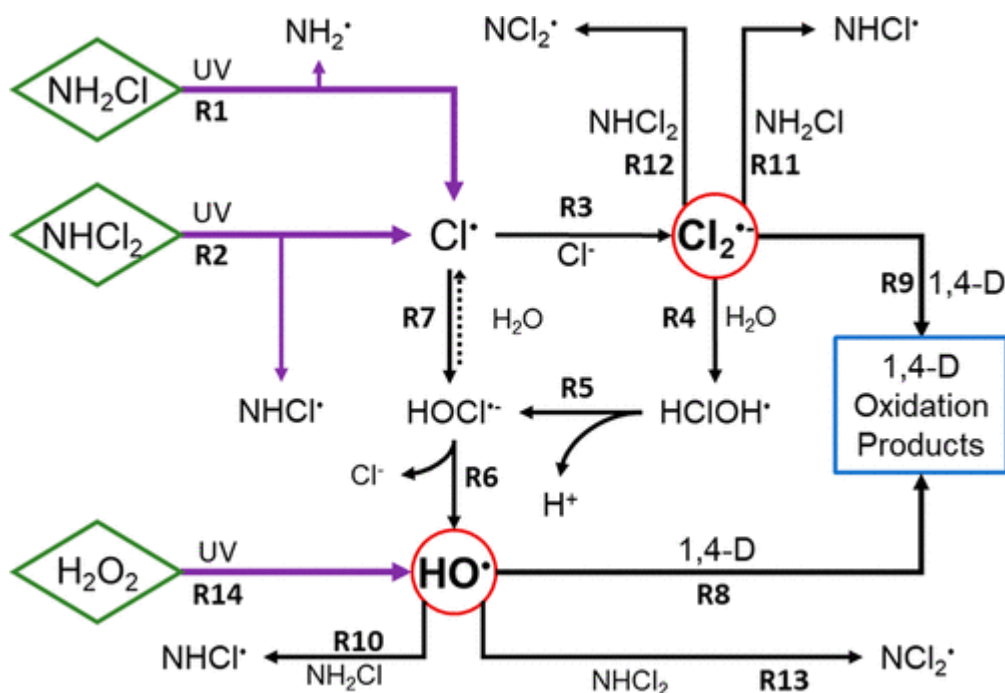


Figure 1. Degradation of 1,4-dioxane in UV photolysis of chloramine. (A) The removal rate constant of 1,4-dioxane vs the dosage of chloramine. (B) The correlation between 1,4-dioxane removal rate constant and chloramine photolysis rates. pH = 5.8, [1,4-dioxane] = 250  $\mu\text{M}$ , [chloramine] = 0.2–6 mM,  $[\text{NB}]_0 = 20 \mu\text{M}$ ,  $[\text{BA}]_0 = 10 \mu\text{M}$ ,  $\text{TOTPO}_4 = 40 \text{ mM}$ .

Upon UV photolysis, both  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  generate  $\text{Cl}\cdot$  in addition to the formation of  $\text{NH}_2\cdot$  and  $\text{NHCl}\cdot$ , respectively (Scheme 1, R1–R2). The majority of  $\text{Cl}\cdot$  reacts with residual chloride present in the chloramine solution and forms  $\text{Cl}_2\cdot^-$  (Scheme 1, R3), with only 0.05% and 1% of  $\text{Cl}\cdot$  reacting with 1,4-D and BA, respectively. Therefore, essentially all reactive chlorine species is generalized as  $\text{Cl}_2\cdot^-$ . Chloride is present at an equal molar concentration to chloramine due to the hydrolysis of aqueous  $\text{Cl}_2$  to form hypochlorous acid during the preparation of chloramines:





Scheme 1. Photolysis of Monochloramine, Dichloramine, And Hydrogen Peroxide in a Mixed System with Respect to 1,4-Dioxane Removal

$\text{Cl}\cdot$  and  $\text{Cl}_2\cdot^-$  undergo further hydrolysis to form  $\text{HO}\cdot$  (Scheme 1, R4–R7). (35) Both  $\text{Cl}_2\cdot^-$  and  $\text{HO}\cdot$  are major contributors to 1,4-D removal (Scheme 1, R8–R9), resulting in an increase in the 1,4-D degradation rate constant with increasing chloramine dosage with chloramine concentrations lower than 1 and 2 mM for  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$ , respectively (Figure 1A).

As the chloramine dosage increased beyond the optimal level, the scavenging of  $\text{Cl}_2\cdot^-$  and  $\text{HO}\cdot$  by  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  (Scheme 1, R10–R13) competed against the rate of radical production, resulting in a decline in 1,4-D removal efficiency (Figure 1A). Furthermore, the UV fluence normalized rate constant of 1,4-D degradation exhibited a bell-shape correlation with the photolysis rate of  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$ , respectively (Figure 1B), revealing a radical promoting regime at lower chloramine photolysis rates, and a radical scavenging regime at higher chloramine photolysis rates. At the maximal 1,4-D removal rate constants,  $\text{NH}_2\text{Cl}$  reacted with 52% of  $\text{HO}\cdot$  and 96% of  $\text{Cl}_2\cdot^-$ , and  $\text{NHCl}_2$  reacted with 53% of  $\text{HO}\cdot$  and 95% of  $\text{Cl}_2\cdot^-$ . As the chloramines exceed their optimal concentrations, a greater percentage of  $\text{HO}\cdot$  and  $\text{Cl}_2\cdot^-$  reacted with chloramines instead of 1,4-D (Texts S3–S4 and Figures S2–S3 in SI).

Radical distributions obtained with probe compounds confirmed that  $\text{HO}\cdot$  was the major reactive radical contributing to 1,4-D degradation through chloramine photolysis, followed by  $\text{Cl}_2\cdot^-$  (Figure 2). However, the contribution of  $\text{Cl}_2\cdot^-$  to 1,4-D degradation was greater with  $\text{NHCl}_2$  photolysis than with  $\text{NH}_2\text{Cl}$  photolysis at concentrations greater than 2 mM.  $\text{NH}_2\text{Cl}$  reacts with  $\text{Cl}_2\cdot^-$  approximately 2.6 times faster than  $\text{NHCl}_2$  (Scheme 1, R11,  $1.14 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  vs R12,  $4.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ), (36) leading to a greater steady-state concentration of  $\text{Cl}_2\cdot^-$  in the  $\text{NHCl}_2$  system.

The net effect is an increased  $\text{Cl}_2^{\cdot-}$  contribution to 1,4-D removal in the  $\text{HCl}_2$  system as well as a shift in the optimal chloramine concentration.

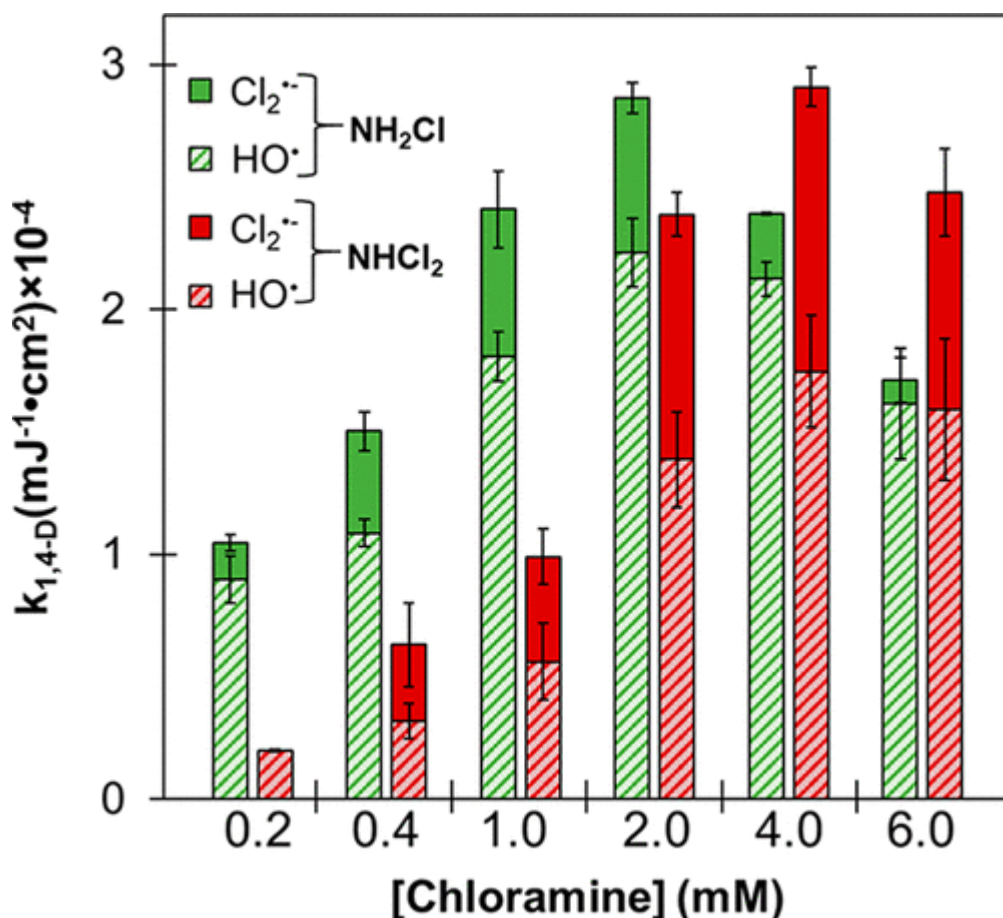


Figure 2. Contributions of reactive radicals to 1,4-dioxane degradation in UV photolysis of  $\text{NH}_2\text{Cl}$  or  $\text{NHCl}_2$ . Contributions based on steady-state concentrations of radicals derived from the competition kinetic method. Error bars relate to radical distribution and not to 1,4-dioxane removal rate constant. [1,4-dioxane] = 250  $\mu\text{M}$  and  $\text{pH} = 5.8$ .

### Impacts of Chloramine Speciation

The impacts of the relative percentage of  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  in the chloramine mixture on the efficiency of 1,4-D degradation under UV photolysis were investigated. The 1,4-D removal rate constant increased by 37% as the  $\text{NH}_2\text{Cl}$ -to- $\text{NHCl}_2$  ratio increased (solid bars in [Figure 3](#)). The percentage contribution of radicals to 1,4-D degradation remained unchanged regardless of the chloramine composition, averaging at 70% from  $\text{HO}\cdot$  and 30% from  $\text{Cl}_2^{\cdot-}$ . The photolysis of a mixture of  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  behaves as a gradient between the two species, where the photolysis of one species does not aid the photolysis of the other (solid bars in [Figure 3](#)). However, the observed rate constants of 1,4-D degradation were lower than the calculated theoretical values without considering radical scavenging effects (striped bars in [Figure 3](#)), suggesting that the simultaneous photolysis of  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  resulted in a scavenging effect on reactive radical generation. The

theoretical values were calculated based on photon absorption and radical contributions from both  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  (calculations in [Text S5](#) of [SI](#)).

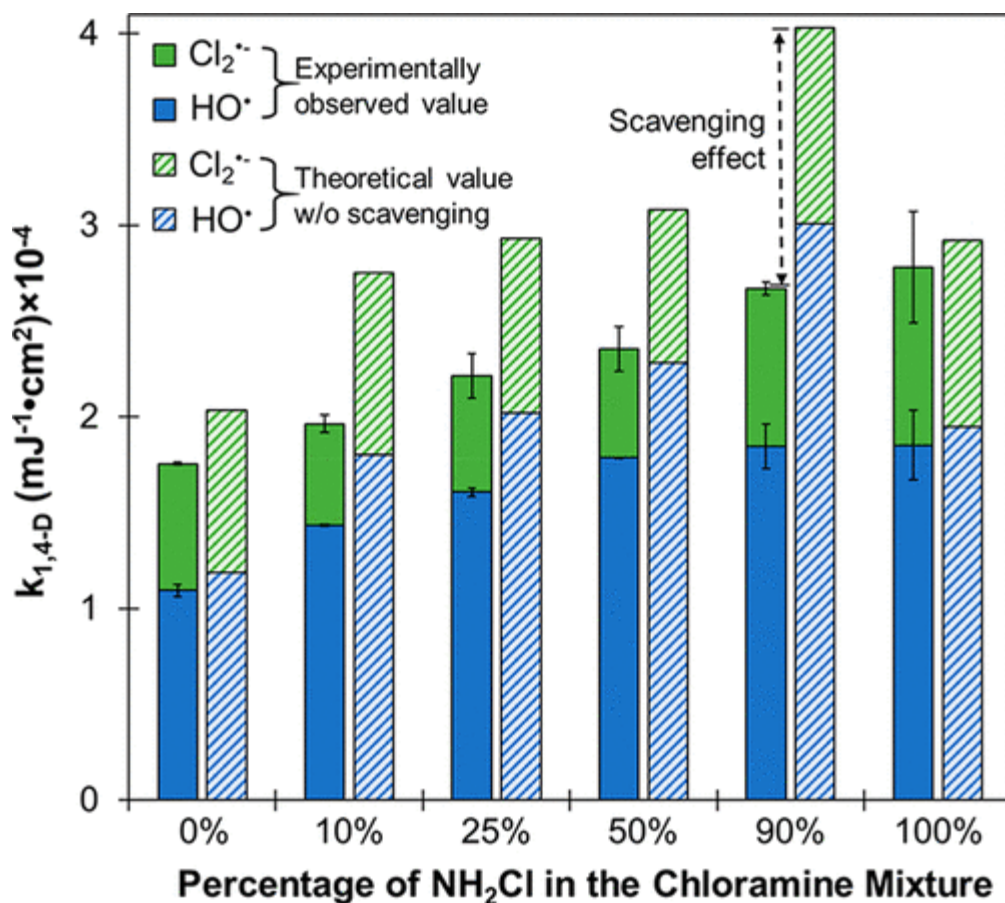


Figure 3. Degradation of 1,4-dioxane in a mixed chloramine system, the contribution of the primary oxidative radicals and the calculated contribution of the individual chloramines. Percentage of  $\text{NH}_2\text{Cl}$  refers to the percentage of total chloramine that exists as  $\text{NH}_2\text{Cl}$ . [Total chloramine] = 2 mM, pH = 5.8,  $\text{TOTPO}_4$  = 40 mM, [1,4-dioxane] = 250  $\mu\text{M}$ , [NB] = 20  $\mu\text{M}$ , and [BA] = 10  $\mu\text{M}$ .

In the  $\text{NH}_2\text{Cl}/\text{NHCl}_2$  mixture, the experimentally observed 1,4-D removal rate constants were between 30% and 50% lower than the theoretical rate constants not accounting for radical scavenging effects (Figure 3). The reactive radicals (i.e.,  $\text{HO}\cdot$  and  $\text{Cl}_2^{\cdot-}$ ) were scavenged by the respective chloramines and account for the difference ([Scheme 1](#), R10–R13). For example, with 50%  $\text{NH}_2\text{Cl}$  in the mixture,  $\text{NH}_2\text{Cl}$  scavenged 30%  $\text{HO}\cdot$  and 68% of  $\text{Cl}_2^{\cdot-}$ , and  $\text{NHCl}_2$  scavenged 15% of  $\text{HO}\cdot$  and 26% of  $\text{Cl}_2^{\cdot-}$ . With 90%  $\text{NH}_2\text{Cl}$  in the mixture,  $\text{NH}_2\text{Cl}$  scavenged 48% of  $\text{HO}\cdot$  and 92% of  $\text{Cl}_2^{\cdot-}$ , while  $\text{NHCl}_2$  scavenged a negligible percentage of radicals (Figure S4, detailed calculations in [Texts S6–S7](#) of [SI](#)).

Furthermore, the kinetics of 1,4-D removal was positively correlated with the  $\text{NH}_2\text{Cl}$  photolysis rate and negatively correlated with the  $\text{NHCl}_2$  photolysis rate (Figure S5A). This is because  $\text{NHCl}_2$  is less effective at lower concentrations, as demonstrated previously, and absorbs less light.  $\text{NH}_2\text{Cl}$  has a higher molar absorptivity coefficient at 254 nm than  $\text{NHCl}_2$ , forming more active radical species as the photolysis rate increases. The total chloramine concentration in the mixture



was held constant at 2 mM. Therefore, the optimum concentration for  $\text{NH}_2\text{Cl}$  existed initially and increases in  $\text{NHCl}_2$  were below the optimum concentration for  $\text{NHCl}_2$ . Increases in  $\text{NHCl}_2$  photolysis rate in the mixture led to a decline in overall radical production. Related to this, the rate of chloramine photolysis positively correlated with chloramine concentration (Figure S5B). When the proportion of the mixture that is  $\text{NH}_2\text{Cl}$  or  $\text{NHCl}_2$  increased, the UV light absorbed by either component increased (Figure S6), leading to a higher photolysis rate.

## Impacts of $\text{NH}_2\text{Cl}$ Photolysis on UV/ $\text{H}_2\text{O}_2$

The impact of  $\text{NH}_2\text{Cl}$  during the UV photolysis of  $\text{H}_2\text{O}_2$  and associated 1,4-D removal was subsequently investigated. Results showed that the presence of  $\text{NH}_2\text{Cl}$  dramatically decreased the removal rate constant of 1,4-D (solid bars in Figure 4A). Compared to conditions without  $\text{NH}_2\text{Cl}$ , the addition of 0.2 mM  $\text{NH}_2\text{Cl}$  to 2 mM  $\text{H}_2\text{O}_2$  resulted in a 24% decrease in the 1,4-D removal rate constant under UV photolysis. As additional  $\text{NH}_2\text{Cl}$  up to 2 mM was added, the overall 1,4-D removal rate constant continued to drop, reaching a minimum at only 37% of the rate constant of  $\text{H}_2\text{O}_2$  alone. As the  $\text{NH}_2\text{Cl}$  concentration increased, the difference between the experimental and theoretical values, in absence of scavenging, increased up to 70%, with the experimental values much lower than theoretical predictions (solid bars vs striped bars in Figure 4A).

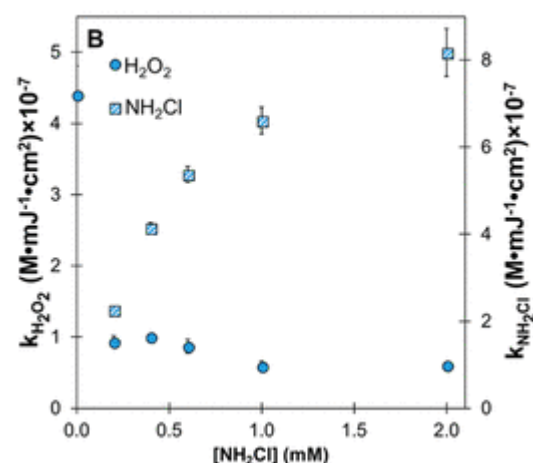
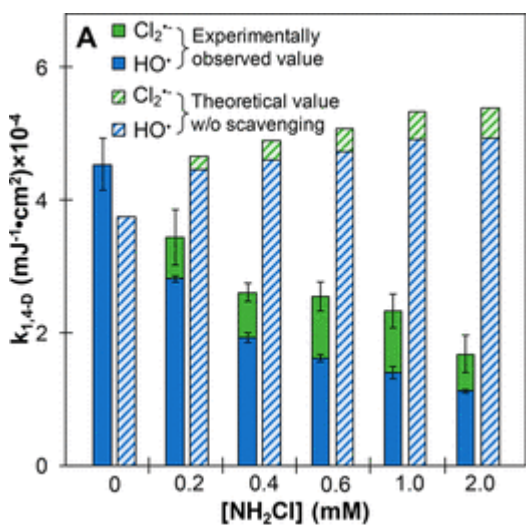


Figure 4. Impact of  $\text{NH}_2\text{Cl}$  that coexists with  $\text{H}_2\text{O}_2$  on the degradation of 1,4-dioxane and oxidant consumption under UV photolysis. (A) 1,4-D degradation rate constant and (B) oxidant photolysis rates. The concentration of  $\text{H}_2\text{O}_2$  was fixed at 2 mM in the mixture,  $[\text{1,4-dioxane}] = 25 \mu\text{M}$ ,  $[\text{Cl}^-] = 2 \text{ mM}$ , and  $\text{pH} = 5.8$ .

These results suggest that radical scavenging occurred with the inclusion of even a low concentration of  $\text{NH}_2\text{Cl}$  with  $\text{H}_2\text{O}_2$  during UV photolysis. Two factors contributed to this trend. First, the coexistence of  $\text{NH}_2\text{Cl}$  with  $\text{H}_2\text{O}_2$  dramatically reduced the  $\text{HO}\cdot$  steady-state concentration. For example, a 75% decrease in the  $\text{HO}\cdot$  contribution was observed when  $\text{NH}_2\text{Cl}$  was increased from 0 to 2 mM (solid bars in [Figure 4A](#)). The decrease in  $\text{HO}\cdot$  is due to scavenging by  $\text{NH}_2\text{Cl}$  (R10 in [Scheme 1](#)), which generates  $\text{NHCl}\cdot$  that is not reactive with 1,4-D. Specifically,  $\text{NH}_2\text{Cl}$  reacted with 51% of the  $\text{HO}\cdot$ , with 39% left to react with 1,4-D ([Text S8](#)). The percentage of  $\text{HO}\cdot$  reacting with 1,4-D decreased as  $\text{NH}_2\text{Cl}$  concentration increased ([Figure S7](#)). Conversely, the  $\text{Cl}_2^{\cdot-}$  contribution to degradation increased from 18% at 0.2 mM  $\text{NH}_2\text{Cl}$  to 33% at 2 mM (solid bars in [Figure 4A](#)), which resulted from enhanced  $\text{NH}_2\text{Cl}$  photolysis. However, the majority of  $\text{Cl}_2^{\cdot-}$  generated (i.e., 95% at 2 mM  $\text{NH}_2\text{Cl}$ ) was scavenged by  $\text{NH}_2\text{Cl}$  ([Text S9](#), [Figure S8](#)).

Second, photon screening associated with the presence of  $\text{NH}_2\text{Cl}$  significantly impacted the AOP. With the coexistence of 0.2 mM  $\text{NH}_2\text{Cl}$  and 2 mM  $\text{H}_2\text{O}_2$ , the percentage of UV light absorbed by  $\text{H}_2\text{O}_2$  decreased by 67% compared to  $\text{H}_2\text{O}_2$  alone, vastly reducing the photolysis rate of  $\text{H}_2\text{O}_2$  and the production of  $\text{HO}\cdot$  ([Figure S9](#)). As the  $\text{NH}_2\text{Cl}$  concentration increased further, UV-light absorption by  $\text{NH}_2\text{Cl}$  increased, increasing the photolysis rate and production of  $\text{NH}_2\cdot$  and  $\text{Cl}\cdot$  ([Figure 4B](#)). As a result, a net loss of oxidative radical production was observed instead of promoting increased 1,4-D degradation.

### Impacts of $\text{NHCl}_2$ Photolysis on UV/ $\text{H}_2\text{O}_2$

The presence of  $\text{NHCl}_2$  during  $\text{H}_2\text{O}_2$  photolysis had an insignificant impact on the 1,4-D degradation rate, in comparison to  $\text{NH}_2\text{Cl}$ . For example, compared to  $\text{H}_2\text{O}_2$  alone, the presence of 0.2 mM  $\text{NHCl}_2$  in conjunction with 2 mM  $\text{H}_2\text{O}_2$  photolysis reduced the removal rate constant of 1,4-D by a negligible amount (i.e., 16%). Further increase of  $\text{NHCl}_2$  concentration up to 2 mM had a minor impact on the removal rate constant of 1,4-D compared to the impact of  $\text{NH}_2\text{Cl}$  (solid bars in [Figure 5A](#)). Furthermore, the experimentally measured rate constants were similar to the theoretical calculations when the  $\text{NHCl}_2$  concentration was  $<1 \text{ mM}$ , and a significant scavenging effect was most evident when the  $\text{NHCl}_2$  concentration reached 2 mM (striped bars in [Figure 5A](#)).

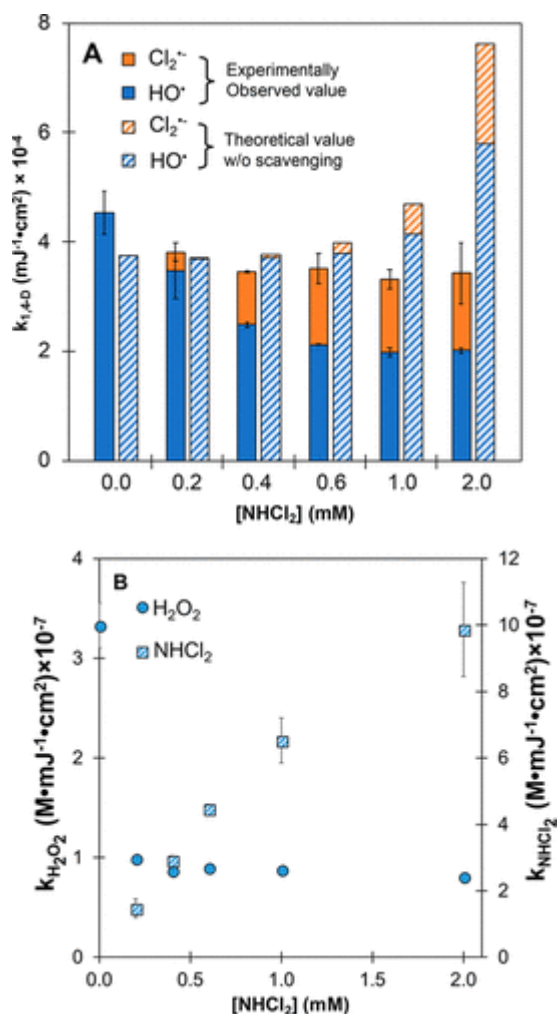


Figure 5. Impact of  $NH_4Cl_2$  coexistence with  $H_2O_2$  on the degradation of 1,4-dioxane and oxidant consumption. Error bars relate to radical contribution and not to 1,4-dioxane removal rate constant. (A) 1,4-D degradation rate constant; (B) oxidant photolysis rates. The concentration of  $H_2O_2$  was fixed at 2 mM in the mixture, [1,4-dioxane] = 25  $\mu$ M,  $[Cl^-]$  = 2 mM, pH = 5.8.

The difference between the impact of  $NH_2Cl$  vs  $NH_4Cl_2$  during  $H_2O_2$  photolysis was attributable to several factors. First,  $NH_4Cl_2$  reacts with  $HO\cdot$  and  $Cl_2^{\cdot-}$  at rates of  $2.6 \times 10^8$  and  $4.4 \times 10^6$   $M^{-1}\cdot s^{-1}$ , respectively, and produces nonoxidative  $NCl_2\cdot$  that did not contribute to 1,4-D removal (Scheme 1, R12–13). (37) Further, the scavenging of  $HO\cdot$  and  $Cl_2^{\cdot-}$  by  $NH_4Cl_2$  is 45% and 39% of  $NH_2Cl$ , respectively. As a result,  $NH_4Cl_2$  scavenged far fewer active radicals than  $NH_2Cl$  at the same concentrations. For example, 5% and less than 1% of  $HO\cdot$  and  $Cl_2^{\cdot-}$ , respectively, were scavenged by  $NH_4Cl_2$  at 0.2 mM. At 2 mM  $NH_4Cl_2$  this demand increases to 34% and 7% for  $HO\cdot$  and  $Cl_2^{\cdot-}$ . (Texts S8–S9, Figure S10).

Second,  $NH_4Cl_2$  has a lower molar absorbance coefficient than  $NH_2Cl$  (142 vs 388  $M^{-1}\cdot cm^{-1}$  at 254 nm). Therefore, the photon scavenging effects of  $NH_4Cl_2$  with respect to  $H_2O_2$  photolysis was much less than  $NH_2Cl$ . For example,  $NH_4Cl_2$  absorbs 43% of the UV light at 0.2 mM vs. 67% for  $NH_2Cl$  at the same concentration. At equimolar  $NH_4Cl_2$  and  $H_2O_2$ ,  $NH_4Cl_2$  accounts for 88% of UV light demand vs 95% for  $NH_2Cl$

([Figure S9](#) vs [Figure S11](#)). Thus, the  $\text{H}_2\text{O}_2$  photolysis rate in the presence of 0.2 mM chloramine decreases by 70% for  $\text{NHCl}_2$  and 79% for  $\text{NH}_2\text{Cl}$ .

[Figure 5B](#) illustrates the relationship between  $\text{NHCl}_2$  concentration and oxidant photolysis rate. With 2 mM  $\text{NHCl}_2$  and  $\text{H}_2\text{O}_2$  the photolysis rate of  $\text{H}_2\text{O}_2$  drops by slightly less than what is observed with 2 mM  $\text{NH}_2\text{Cl}$  (i.e., 76% vs 86%). The rate of chloramine photolysis increases with increasing chloramine concentration while the rate of  $\text{H}_2\text{O}_2$  photolysis drops precipitously at the first introduction of  $\text{NHCl}_2$ . As the concentration of  $\text{NHCl}_2$  increases, more UV light and reactive radicals are absorbed, increasing the direct photolysis rate ([Figure S11](#)). Further, the greater radical and photon absorption from increased  $\text{NHCl}_2$  concentrations decreases the photolysis rate of  $\text{H}_2\text{O}_2$ .

The relationship between oxidant photolysis and 1,4-D removal in both  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  with  $\text{H}_2\text{O}_2$  is shown in [Figure S12](#). The negative correlation between  $\text{NH}_2\text{Cl}$  and the 1,4-D degradation rate constant is significantly stronger than the correlation between  $\text{NHCl}_2$  and the 1,4-D removal rate constant (e.g.,  $R^2 = 0.94$  vs. 0.45). This is primarily due to  $\text{NH}_2\text{Cl}$  having a greater reactive radical scavenging than  $\text{NHCl}_2$ . Thus,  $\text{NHCl}_2$  has a lesser overall impact on the performance of UV/ $\text{H}_2\text{O}_2$  than  $\text{NH}_2\text{Cl}$ .

## Nitrogen Products from Chloramine Photolysis

The photolysis of chloramines produces inorganic nitrogen breakdown products, including nitrate, ammonia, gaseous nitrogen, and organic nitrogen products ([Figure 6](#)). Nitrite was not detected. Overall, ammonia accounted for 60–75% of the nitrogen products. The production of ammonia was likely via the breakdown of  $\text{NH}_2\cdot$  that was transformed into the intermediate  $\text{N}_2\text{H}_4$  and then  $\text{NH}_3$ . ([38](#)) The initial formation of nitrite was possible via decomposition of  $\text{NH}_2\cdot$ ; however, the subsequent oxidation of nitrite by chloramine generated nitrate. ([39](#)) The  $\text{NHCl}\cdot$  radical decayed to produce nitrogen gas and chloride. The nitrate production was higher in photolyzed  $\text{NHCl}_2$  than  $\text{NH}_2\text{Cl}$ . Furthermore, the presence of  $\text{H}_2\text{O}_2$  affected nitrogen product distribution in the  $\text{NH}_2\text{Cl}$  system more strongly than in the  $\text{NHCl}_2$  system ([Figure 6](#)). More nitrate was produced in conditions involving both  $\text{NH}_2\text{Cl}$  and  $\text{H}_2\text{O}_2$  photolysis due to increased production and subsequent oxidation of nitrite by  $\text{HO}\cdot$ . ([40](#)) The production of nitrate leads to depressed  $\text{HO}\cdot$  steady-state due to scavenging reactions between  $\text{NO}_3^{2-}$  and  $\text{HO}\cdot$ . Additionally, gaseous nitrogen production decreased in the presence of  $\text{H}_2\text{O}_2$  in UV/ $\text{NH}_2\text{Cl}$  but not in UV/ $\text{NHCl}_2$  due to  $\text{HO}\cdot$  being scavenged by  $\text{NH}_2\text{Cl}$ , preventing further oxidation of nitrogen products to gaseous nitrogen. Finally, less organic nitrogen was produced in the presence of  $\text{H}_2\text{O}_2$  also due to the increased reaction between  $\text{HO}\cdot$  and available organic nitrogen products which directly implies that fewer toxic transformation products are produced.

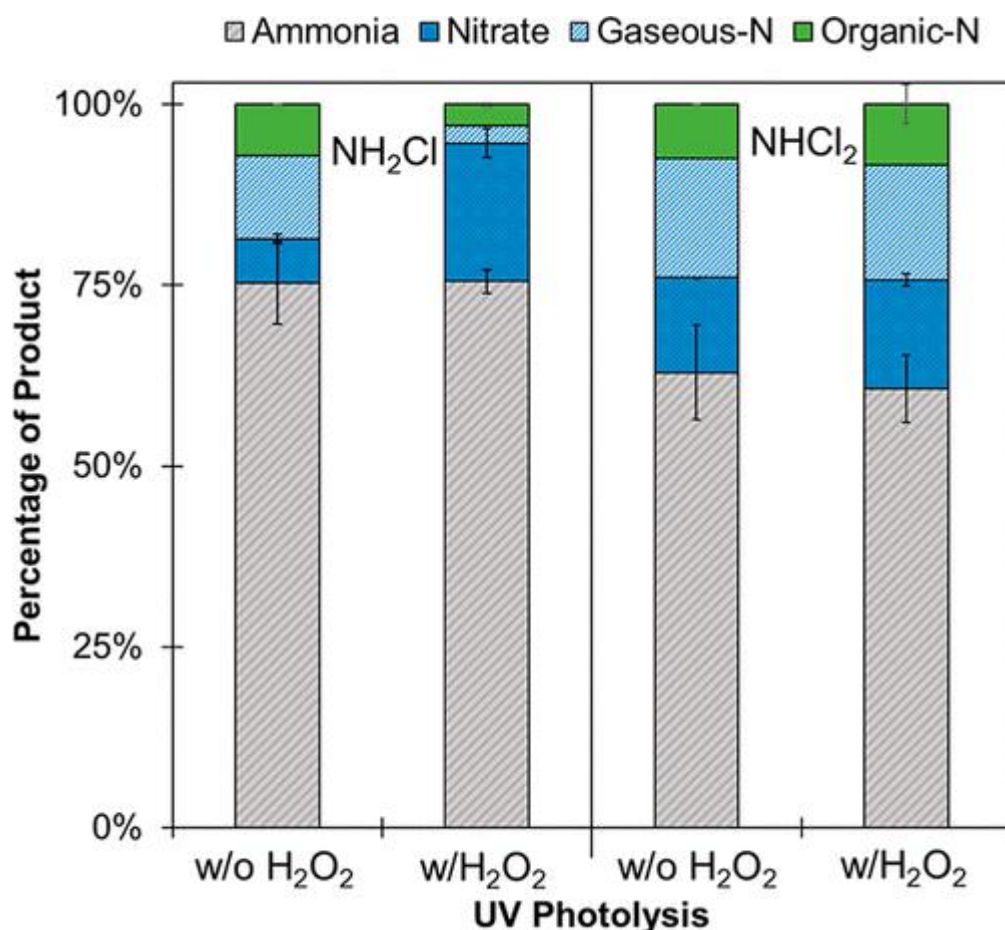


Figure 6. Nitrogenous products of chloramine photolysis with and without hydrogen peroxide. [Chloramine] = 2 mM, [1,4-D] = 250  $\mu$ M, pH = 5.8. In experiments with H<sub>2</sub>O<sub>2</sub>, its concentration was 2 mM. Product analysis was based on samples exposed to 3500 mJ/cm<sup>2</sup> of UV irradiation.

## Engineering Implications

Both NH<sub>2</sub>Cl and NHCl<sub>2</sub> were found to contribute to UV/AOP by producing a unique suite of reactive radicals (HO $\cdot$  and Cl<sub>2</sub><sup>-</sup>) which degraded 1,4-D. The reactive chlorine and amine species produced by chloramines could also remove other trace organics which react with them. The inclusion of chloramines into UV/H<sub>2</sub>O<sub>2</sub> during water reuse treatment trains can compromise the efficiency of 1,4-D removal by H<sub>2</sub>O<sub>2</sub> photolysis, mainly due to radical scavenging and light screening effects from chloramines, and NH<sub>2</sub>Cl exhibited a stronger effect than NHCl<sub>2</sub>. A chloramine effect during UV photolysis of H<sub>2</sub>O<sub>2</sub> was observed in real RO permeate ([Text S10, Figure S14](#)). The results suggest that the removal of chloramines prior to UV/H<sub>2</sub>O<sub>2</sub> can increase the treatment efficiency of trace organic contaminants, especially for those compounds with a strong reactivity toward HO $\cdot$ . In the likely event that chloramine removal is unfeasible, the chloramine speciation can be shifted toward NHCl<sub>2</sub> via acidification, however the potential formation of NDMA needs to be controlled. (41) Future work is needed to investigate the photolysis of chloramines and hydrogen peroxide in a mixed system with a diverse group of trace organic chemicals and the associated RO permeate chemistry effects on the UV/AOP.

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## Notes

The authors declare no competing financial interest.

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