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EPA

# Impact of UV Location and Sequence on By-Product Formation

Subject Area: Water Quality

# Impact of UV Location and Sequence on By-Product Formation

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# Impact of UV Location and Sequence on By-Product Formation

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# EXECUTIVE SUMMARY

## BACKGROUND

Regulation of drinking water quality regarding microbial pathogens and disinfection by-products set by the United States Environmental Production Agency (USEPA) has led many water utilities to consider disinfectants and/or disinfectant schemes alternative to traditional free chlorine. This trend toward alternative disinfectants has been particularly fueled by recent and more stringent regulation of disinfection by-products (DBPs) (trihalomethanes [THMs] and haloacetic acids [HAAs]) and chlorine resistant pathogens (*Giardia* and *Cryptosporidium parvum*). Among the available alternative disinfection schemes, ultraviolet (UV) light sequenced with chlorination or chloramination are considered particularly attractive because, unlike ozonation and chloramination, UV disinfection has not previously been associated with significant DBP formation.

## OBJECTIVES

The overall goal of this project was to investigate how the addition of UV disinfection may affect the formation of regulated, known but unregulated, and currently unknown DBPs when chlorination or chloramination is coupled with UV. UV disinfection using both low and medium pressure UV sources was examined in combination with a number of chlorination/chloramination strategies. These disinfectant combinations represent the current and expected practice of multiple barrier disinfection. Because different water qualities may affect the potential for DBP formation the research followed a tiered approach using waters with a range of total organic carbon (TOC) and specific ultraviolet absorbance (SUVA) values. In the first tier, DBP formation was examined under controlled conditions using model waters. In the second tier, natural waters from a number of different sources were used and were complemented through spiking in specific known or suspected precursors (such as nitrate and characterized NOM). Waters were collected from utilities just prior to the point of their existing disinfection practice and subjected to UV irradiation in the laboratory. A final tier of study examined samples directly from water utilities that have implemented full-scale UV disinfection with chlorine or chloramine post-disinfection. These waters were tested directly for DBPs.

The objectives of this research were as follows:

1. Develop a survey and database of UV disinfection practices in North America to understand how UV is combined with other oxidants/disinfectants such as chlorine, chloramines, and ozone.
2. Select at least three different waters from participating utilities. These waters vary in water quality parameters such as nitrate, sulfate, bromide, organic carbon and other qualities. Expose the selected waters to UV irradiation from either low or medium pressure UV sources and follow these exposures with free chlorine or chloramine addition. Examine these waters for regulated DBPs and develop a better understanding of the formation of other chlorinated or nitrogenated DBPs.



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3. Using knowledge from Objective two, re-evaluate waters from selected facilities including the influence of inorganic precursor materials (bromide and nitrate).
4. Using bench scale studies with model precursors in synthetic waters, develop a better understanding of fundamental formation mechanisms of DBPs that result from the use of UV disinfection in combination with chlorine and distinguish between effects from monochromatic (low pressure) and polychromatic (medium pressure) UV sources. In addition to light source and fluence, these studies investigate the effects of chlorine/chloramine dose and the sequence of disinfectant addition. Finally, these studies examine the effects of reaction conditions including concentrations of nitrate, bromide, and NOM.
5. Using pilot and full-scale UV installations evaluate the formation of DBPs in flow-through systems. Pilot-scale work allows manipulation of experimental conditions thus supporting the work performed in Objective 4. Full-scale study collects samples throughout the year to evaluate seasonal water quality changes and provides field results on actual effects of UV on formation of DBPs.

## APPROACH

Research has shown that UV light is highly effective at inactivating a broad range of pathogenic microorganisms. Because UV light does not provide a disinfectant residual, a disinfectant capable of maintaining a residual such as free chlorine or chloramines must be sequenced with UV disinfection to maintain a disinfectant residual in the drinking water distribution system. Compared to inactivation of pathogens, the effect of the UV chlorine/chloramines sequence on formation of DBPs has not been well studied, particularly with respect to emerging DBPs.

UV disinfection alone does not form regulated THMs or HAAs as without the addition of a halogen (i.e., chlorine or bromine) these DBPs do not form. When sequenced with free chlorine at UV disinfection doses (< 186 mJ/cm$^2$), a number of researchers reported no observed additional formation of THMs or HAAs. On the other hand, increased formation of nitrogenous DBP trichloronitromethane was observed after application of disinfection doses of medium pressure UV followed by application of free chlorine. While currently unregulated, nitrogenous DBPs have been shown to be more geno- and cyto- toxic than carbon only containing DBPs. Therefore, much remains unexplored with regard to the extent and mechanisms of UV chlorine/chloramines sequences on formation of emerging DBPs.

This research set out to study the full-scale process sequence of UV free chlorine/chloramines at a variety of scales (bench-, pilot-, and full-scale), under different UV lamp technologies (low pressure [LP] and medium pressure [MP]), a variety of secondary disinfectants (free chlorine and chloramines) and known precursor material (inorganic and organic), focusing on the formation of DBPs. In addition to physical laboratory/field research, a survey was conducted to determine the current state of application of the UV disinfection process combined with secondary disinfection in the United States.

## RESULTS/CONCLUSIONS

Overall, the process sequence of UV plus free chlorine/chloramines had little effect on formation of regulated DBPs at doses suitable for disinfection. In some cases, applying UV upstream of free chlorine or chloramines increased THM4 formation but these increased

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concentrations were on the order of a few µg/L only and were not statistically significant. With regard to emerging nitrogenous DBPs, halonitromethanes (primarily trichloronitromethane (chloropicrin) and tribromonitromethane (bromopicrin)) and chloral hydrate were increased when free chlorine or chloramines were applied downstream of the UV process, particularly with application of MP UV. On the other hand, nitrosamine formation appears to be decreased when MP UV was applied upstream of chloramination. Beyond these overall trends, pertinent conclusions associated with each objective is described:

1. Survey UV disinfection practices in drinking water in North America and how they are combined with other oxidants/disinfectants.

Based on the completed surveys from twenty-four drinking water treatment plants in the continental United States that currently have UV disinfection installed or have performed pilot testing and are currently installing UV, numerous key findings were identified. The majority of facilities employing a UV disinfection process treat surface water and utilized MP UV technology. More than half of the surveyed facilities do not maintain a chlorine residual through the UV disinfection system. Therefore, post-chlorination or post-chloramination is most commonly practiced. The facilities generally reported that no changes or decreases in secondary disinfection chemical usage and regulated DBP formation were observed. These survey results point to the fact that full-scale implementation of UV disinfection in drinking water, regardless, the sequence with a secondary disinfectant, has little to no effect on regulated DBP formation.

2. Evaluate at least three different waters of varied water quality from participating utilities for changes in regulated and emerging DBP formation from the UV free chlorine/chloramines sequence to develop baseline study conditions.

The impacts of UV on DBP formation observed in this section of the research were slight, but suggested that at high doses (400 mJ/cm$^2$), the addition of LP or MP UV prior to chlorination or chloramination can occasionally increase the formation of THMs and HAAs by ~10–20%. Treatment with MP UV upstream of chlorination or chloramination increased trichloronitromethane formation by ~20–50%, but LP UV pre-treatment did not show a similar effect. At one plant, LP or MP UV treatment followed by chlorination increased chloral hydrate formation by ~30%. Overall, UV treatment may increase the formation of certain DBPs, although generally by ≤25%, and this occurred at UV doses higher than used in disinfection applications. These results indicated that in our future studies (described below), atypical challenge conditions (i.e., higher than normal UV doses) would be needed to demonstrate the mechanistic aspects of any UV induced DBP changes.

3. Using knowledge from Objective Two, re-evaluate waters from selected facilities including the influence of inorganic precursor materials (bromide and nitrate).

Using two treated drinking waters originating from source waters of varied water quality and anthropogenic inputs as a baseline, various levels of inorganic DBP precursor (bromide and nitrate) were added. Furthermore, by studying at least four UV doses ranging from a disinfection range of less than 100 mJ/cm$^2$ to UV doses used for photolysis and oxidation of up to 1000 mJ/cm$^2$, trends could be used to evaluate overall changes in DBP formation more confidently. Both UV

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technologies increased THM formation with increased UV dose. These changes were minimal, where an observed increase of less than or equal to 10 µg/L was observed at the highest UV doses (1000 mJ/cm$^2$) studied. At disinfection doses of UV light, slight changes were observed but were within analytical and experimental variation. Therefore, while increases are expected during UV disinfection they are statistically irrelevant with respect to THMs, HAAs, and other selected emerging DBP species. However, increases in halonitromethanes, particularly tribromonitromethane were observed at disinfection doses (<186 mJ/cm$^2$) of UV. Similarly, chloral hydrate concentration was observed to increase slightly. While concentration increases were small, they were statistically significant. Recent study of relative toxicity of these species suggests that increases may be important, but further research on where the threshold of toxicity relevance lies is required. On the other hand, UV appears to deactivate or destroy nitrosamine precursors, as observed through NDMA formation, although the degree of destruction corresponded with the dose of UV applied prior to chloramination. Finally, it should be noted that with increasing UV dose the studied waters exhibited greater chlorine and chloramine demand. At 40 mJ/cm$^2$, change in chlorine demand was not identifiable; at doses greater that 186 mJ/cm$^2$ change in chlorine demand was minimal (~0.2 mg-$Cl_2$/L) unless a very high UV dose (1000 mJ/cm$^2$) was applied, and inorganic precursors were spiked, in which case increases in demand greater than 1 mg-$Cl_2$/L were observed.

4. Assess the fundamental formation mechanisms of DBPs associated with the UV plus free chlorine/chloramines process sequence using model precursors in synthetic waters, varied lamp technology type, and chlorination/chloramination processes.

Through the use of isolated NOM and varying concentrations of inorganic precursors, mechanisms and important pathways of DBP formation potential were evaluated. Similar to the trends observed in previous objectives, free chlorine demand increased when UV was applied prior to chlorine/chloramines, while monochloramine demand decreased or remained unchanged for concentrated NOM and NOM isolates. Under UV treatment, THM4 concentrations were observed to increase slightly when post-chlorinated. THM4 increases were greater in concentrated NOM than fractionated NOM isolates. Unlike other objectives, the higher concentration of NOM and elevated UV doses promoted slight decreases of HAA9 in NOM isolates and slight increases in samples with NOM concentrates after the treatment sequence. Increased formation of trichloronitromethane was observed when waters were irradiated with MP UV prior to chlorination or chloramination, which was thought to have been an indication that photonitration was involved in the reaction. Chloral hydrate increased notably when samples were spiked with either bromide or bromide and nitrate suggesting these inorganic precursors play an important role in the formation pathway of this emerging DBP species. Unlike the whole waters, dichloronitrate formation decreased and nitrosamine formation increased when pretreated with UV light.

5. Evaluate pilot- and full-scale UV reactors for formation of DBPs during the UV free chlorine/chloramines process sequence in flow-through systems.

The changes in chlorine demand and DBP formation observed during the study of flow-through reactors supported the bench-scale work performed in previous tasks. Using the pilot-scale reactors and manipulating influent water quality with respect to inorganic precursors (bromide and nitrate) and UV dose, trends observed were similar to bench-scale results. At high disinfection doses of UV (~200 mJ/cm$^2$), small increases (~0.1 mg-$Cl_2$/L) in chlorine demand were observed

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when UV disinfected samples were chlorinated. For the pilot LP UV system, the resulting changes in THM formation were nearly identical to that observed during bench-scale study of a similar water (same sample point just collected at an earlier date). Increased formation of THMs was observed at high UV doses (>500 mJ/cm$^2$), but overall changes were minimal (<20%). The pilot MP UV followed by application of free chlorine generally followed the patterns observed during bench-scale experiments but to a lesser extent. On the whole, the study results showed similar trends were observed between both lamp types indicating minimal increases in free chlorine demand and DBP formation. At the three full-scale water treatment plants studied, no changes in DBP formation or chlorine/chloramine demand were observed over a full year of testing.

## RECOMMENDATIONS

Numerous conclusions were drawn that can be used to provide insight into DBP formation, both regulated and unregulated, associated with the UV free chlorine/chloramines sequence. In the United States, the specific recommendations identified here should be considered when incorporating UV disinfection in an existing plant, or including UV treatment in the original design of a drinking water treatment plant in where a secondary disinfectant residual is maintained in the distribution system. These recommendations include:

1. At UV doses typical of disinfection (<186 mJ/cm$^2$):
   a. Free chlorine or chloramine demand will not be significantly altered regardless of the point of application of the secondary disinfectant, be it upstream or downstream of the UV reactor. It should be noted though that UV light does have the capability to photolyze these oxidants. Where possible, it is recommended that UV be installed upstream of a post-chlorination application.
   b. Regulated DBP (THM4 and HAA9) formation is not altered by the UV free chlorine or chloramines disinfection sequence when applying UV doses typical of disinfection practice. Addition of UV is recommended without reservation when source water quality requires a multiple barrier disinfection scheme.
   c. Halonitromethane formation, particularly trichloronitromethane and tribromonitromethane, and chloral hydrate, increases on the single µg/L level and is further exacerbated by elevated concentrations of bromide or nitrate. While concentration changes are low, they were statistically significant and the nature of this process should be noted, as research has suggested these species are more geno- and cytotoxic than regulated DBPs. Promotion of halonitromethane formation is elevated when polychromatic MP UV technology is applied. It is recommended that when formation of DBPs is a concern, the application of UV in combination with chlorine should be limited to disinfection doses and use of MP UV should be coupled with an assessment of possible formation of unregulated DBPs in a given water quality.
   d. Nitrosamine formation potential will likely be reduced to a small degree when UV is applied upstream of chloramination. However, this may vary depending on the nature of the NOM pool present in the water when being irradiated. It is recommended that utilities not be concerned with the effect of UV on formation of nitrosamines.

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2. At high UV doses (186–1000 mJ/cm$^2$):
   a. Chlorine/chloramines demand will increase on the order of up to 1 mg-$Cl_2$/L and correspondingly a number of DBPs may be formed at greater concentrations when chlorine or chloramines are applied downstream of the UV reactor.
   b. THM4 formation is likely to increase, possibly up to 10 µg/L, while halonitromethane and chloral hydrate formation could increase by a few µg/L in some waters.
   c. The formation of nitrosamines when chloramines are applied downstream of the UV reactor could be significantly reduced on the order of multiple ng/L when UV is used prior to chloramines.

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# CHAPTER 1
# INTRODUCTION

## BACKGROUND

Regulation of drinking water quality and more specifically microbial pathogens and disinfection by-products by the United States Environmental Production Agency (USEPA) has led many utilities to consider alternative disinfectants and/or disinfectant schemes. This trend toward alternate disinfectants has been particularly fueled by recent and more stringent regulation of disinfection by-products (DBPs) (trihalomethanes [THMs] and haloacetic acids [HAAs]) and chlorine resistant pathogens (*Giardia* and *Cryptosporidium*). Among the available alternative disinfection schemes, ultraviolet (UV) light sequenced with chlorination or chloramination has been considered particularly attractive because, unlike ozonation and chloramination, UV disinfection has not previously been associated with significant DBP formation.

## SIGNIFICANCE TO DRINKING WATER UTILITIES

Research has shown that UV light is highly effective at inactivating a broad range of pathogenic microorganisms (Hijnen et al., 2006). Because UV light does not provide a disinfectant residual, federal regulations require a disinfectant capable of maintaining a residual such as free chlorine or chloramines be sequenced with UV disinfection to maintain a disinfectant residual in the drinking water distribution system. Compared to inactivation of pathogens, the effect of the UV chlorine/chloramines sequence on formation of DBPs has been less studied, particularly with respect to emerging DBPs.

UV disinfection alone has not been shown to form regulated THMs or HAAs as without the addition of a halogen (i.e., chlorine or bromine) these DBPs do not form. When sequenced with free chlorine, a number of researchers have found the application of disinfection doses of UV (<186 mJ/cm$^2$) does not cause any additional formation of THMs or HAAs (Malley et al., 1995; Linden et al., 2004; Reckhow et al., 2010). On the other hand, small increases of the nitrogenous DBP trichloronitromethane were observed after application of disinfection doses of medium pressure UV, followed by application of free chlorine (Reckhow et al., 2010). While currently unregulated, nitrogenous DBPs have been shown to be more geno- and cyto-toxic than carbon-only containing DBPs (Plewa et al., 2004). Therefore, much remains unexplored with regard to the extent and mechanisms of UV chlorine/chloramines sequences on formation of emerging DBPs.

## PROJECT OBJECTIVES

The overall goal of this project was to investigate how the addition of UV disinfection may affect the formation of regulated, known but unregulated, and currently unknown DBPs when chlorination or chloramination is coupled with UV. UV disinfection using both low and medium pressure UV sources was examined in combination with a number of chlorination/chloramination strategies. These disinfectant combinations represent the current and expected practice of multiple barrier disinfection. Since different water qualities can affect the potential for DBP formation, the research followed a tiered approach using waters that have a range of total organic carbon (TOC)



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and specific ultraviolet absorbance (SUVA) values. In the first tier, DBP formation was examined under controlled conditions using model waters. In the second tier, natural waters from a number of different sources were utilized and complemented by spiking in specific known or suspected precursors (such as nitrate and NOM). Waters were collected from utilities just prior to the point of the existing disinfection practice and subjected to UV irradiation in the laboratory. A final tier of study examined samples directly from water utilities that have implemented UV disinfection combined with chlorine/chloramines. These waters were tested directly for DBPs.

The objectives of this research were as follows:

1. Develop a survey and database of UV disinfection practices in North America to understand how they are combined in practice with other oxidants/disinfectants such as chlorine, chloramines, and ozone.
2. Select at least three different waters from participating utilities. These waters vary in water quality parameters such as nitrate, sulfate, bromide, organic carbon and other qualities. Expose the selected waters to UV irradiation from either low or medium pressure UV sources and combine these exposures with various forms of oxidants such as free chlorine and chloramines. Examine these treated waters for regulated DBPs and develop a better understanding of the formation of other chlorinated or nitrogenated DBPs.
3. Using knowledge from Objective 2, re-evaluate waters from selected facilities of distinctly different water qualities collected prior to the existing disinfection location, and evaluate the influence of inorganic precursor materials (bromide and nitrate).
4. Using bench scale studies with model precursors in synthetic waters, develop a better understanding of fundamental formation mechanisms of DBPs that result from the use of UV disinfection in combination with other oxidants and distinguish between effects from monochromatic (low pressure) and polychromatic (medium pressure) UV sources. In addition to light source and UV dose, these studies investigate the effects of chlorine/chloramine dose and the sequence of disinfectant addition. Finally, these studies examine the effects of reaction conditions including the concentrations of nitrate, bromide, and NOM.
5. Using pilot- and full-scale UV reactors evaluate the formation of DBPs in flow-through systems. Pilot-scale work will allow for manipulation of experimental conditions thus mimicking the work performed in Objective 4. Full-scale study will collect samples throughout the year to evaluate seasonal water quality changes and will provide field results on actual UV systems regarding the formation of DBPs.

## LITERATURE REVIEW

This research studies the sequence of two water treatment processes from the perspective of change in chemistry of aqueous components and the resulting formation of potentially toxic by-products that may be either organic or inorganic. This literature review provides information pertinent to known and hypothesized reactions present during the sequence of UV chlorine/chloramines in drinking waters.

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## Role of Inorganic Nitrogen During UV Treatment

Compared with chlorination alone, recent research indicates the potential for the enhanced formation of nitrated and nitrosated DBPs when UV primary disinfection is coupled with chlorination or chloramination ($UV/Cl_2$ or $UV/NH_2Cl$). For example, a recent study indicated that treatment of a drinking water supply with realistic doses of UV light (0–140 mJ/cm$^2$) from a medium pressure mercury lamp followed by chlorination enhanced the formation of trichloronitromethane (~1–5 µg/L) compared with chlorination alone (Reckhow et al., 2010). This enhancement in trichloronitromethane formation likely was associated with the nitration of NOM constituents by reactive nitrogen species (RNS) formed by the photolysis of $NO_3^-$ (Reckhow et al., 2010). Chlorination of nitrated organics in UV-treated water can form trichloronitromethane. For example, chlorination of nitrophenols formed trichloronitromethane at yields up to ~50% (Merlet et al., 1985). Indeed, enhanced trichloronitromethane formation was observed when UV light was delivered using a medium pressure lamp, but not with a low pressure lamp (Reckhow et al., 2010). While low pressure lamps emit photons predominantly at 254 nm, medium pressure lamps emit photons over a broader range, including at lower wavelengths where absorption by $NO_3^-$ is more significant (e.g., a molar extinction coefficient of 1500 $M^{-1}$ $cm^{-1}$ at 225 nm [Reckhow et al., 2010]). In another study, nitrite and AOC concentrations increased when a Dutch water with 2 mg/L TOC and 11 mg/L nitrate was exposed to 70 mJ/cm$^2$ medium pressure UV in a bench-scale unit where the water depth was only 0.5 cm (Ijpelaar et al., 2005). The levels became barely discernible when the depth was increased to 10 cm, emphasizing the importance of reactor design for DBP formation.

When $UV/Cl_2$ or $UV/NH_2Cl$ disinfection is practiced in the presence of $NO_3^-$ or $NO_2^-$, NOM constituents could be nitrated by RNS formed either by UV treatment alone, or by chlorination of pre-existing nitrite or nitrite formed by UV treatment. In both cases, these RNS include species that can nitrosate or nitrate NOM constituents, potentially forming nitrosamines, such as N-nitrosodimethylamine (NDMA), or nitrated compounds such as trichloronitromethane.

### *UV Treatment Alone*

$NO_2^*$: Photolysis of $NO_3^-$ predominantly generates $NO_2^*$ (Reaction 1.1) with quantum yields near 0.1 at 228 nm (Sharpless and Linden, 2001). $NO_2^*$ can add to electron-rich aromatic rings (e.g., phenolate (Vione et al., 2004), generating nitro-organic radicals. Dissolved oxygen can react with nitro-organic radical intermediates to generate nitrated products by removing a proton to regenerate a stable aromatic ring.

$$NO_3^- + h\nu + H^+ \Rightarrow NO_2^* + OH^* \tag{1.1}$$

$N_2O_4$: Alternatively, aromatic structures in NOM can be nitrated by the strong nitrating agent, $N_2O_4$ formed via $2\ NO_2^* \Rightarrow N_2O_4$ (Challis and Kyrtopoulos, 1979; Vione et al., 2005). $N_2O_4$ isomerizes to form $ONONO_2$, a strong nitrosating agent (Challis and Kyrtopoulos, 1979) or can hydrolyze to form $NO_3^-$ and $NO_2^-$.

ONOOH: Reaction 1.1 results in rapid generation of $OH^*$ via $H^+ + O^{*-} \Rightarrow OH^*$. $OH^*$ reacts with $NO_2^*$ to form peroxynitrous acid via Equation 1.2:

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$$OH^* + NO_2^* \Rightarrow ONOOH \quad (1.2)$$

ONOOH nitrates NOM directly or via $NO_2^*$ formed by the reverse of Reaction 1.2. The reverse of Reaction 1.2 is less important (~15%) than isomerization to release nitric acid ($HNO_3$, ~85%) (Fischer and Warneck, 1996; Alvarez et al., 1996; Vione et al., 2005).

ONOO⁻: Peroxynitrite can contribute to nitration through its reaction with $CO_2$ (aq) (Reactions 1.2a–c) by forming nitrating agents, $NO_2OCO_2^-$ and $NO_2$*:

$$ONOO^- + CO_2(aq) \Rightarrow ONOOCO_2^- \quad (1.2a)$$
$$ONOOCO_2^- \Rightarrow NO_2OCO_2^- \text{ or} \quad (1.2b)$$
$$ONOOCO_2^- \Rightarrow NO_2^* + CO_3^- \quad (1.2c)$$

$N_2O_3$: $N_2O_3$ is a strong nitrosating agent that can form rapidly via $NO^* + NO_2^* \Rightarrow N_2O_3$ (Goldstein and Czapski, 1996). $NO^*$ arises from the decay of $ONOO^-$ (Reaction 1.3), the conjugate base of HOONO ($pK_a = 6.8$) (Suzuki et al., 2004; Ohshima and Bartsch, 1999; Masuda et al., 2000).

$$ONOO^- \Rightarrow NO^* + O_2^{*-} \quad (1.3)$$

Photolysis of $NO_3^-$ can generate $NO_2^-$ (Reaction 1.4), although this reaction is roughly an order of magnitude less important than $NO_2^*$ formation by Reaction 1.1 (Vione et al., 2003):

$$NO_3^- + h\nu \Rightarrow NO_2^- + O \quad (1.4)$$

Photolysis of $NO_2^-$ forms $NO^*$ (Reaction 1.5) with a quantum yield of 0.07 near 280 nm (Bilski et al., 1992; Caulfield et al., 1996; Fischer and Warneck, 1996).

$$NO_2^- + h\nu \Rightarrow NO^* + O^{*-} \quad (1.5)$$

Nitrosation of NOM constituents by $N_2O_3$ competes with $N_2O_3$ hydrolysis to $NO_2^-$ via $N_2O_3 + H_2O \Rightarrow 2\ H^+ + 2\ NO_2^-$ (Caulfield et al., 1996).

### *Chlorination of Nitrite*

Chlorination of $NO_2^-$ formed by photolysis of $NO_3^-$ (Reaction 1.4) generates the nitrating agent $ClNO_2$. Formation of the nitrating and nitrosating agent $N_2O_4$ also occurs via Reaction 1.6:

$$ClNO_2 + NO_2^- \Rightarrow N_2O_4 + Cl^- \quad (1.6)$$

Indeed, chlorination of $NO_2^-$ in the presence of dimethylamine was shown to form NDMA more rapidly than formation observed during chloramination (Choi and Valentine, 2003).

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The following reaction conditions should affect the formation of N-DBPs:

- *UV light source and dose*: N-DBP formation is likely to be important when medium pressure UV lamps are used, because they emit photons at wavelengths <250 nm where $NO_3^-$ absorbs strongly, in contrast to low pressure lamps. The applied UV dose may be critical. While UV photolysis of $NO_3^-$ initiates DBP formation, N-DBP products both photolyze in the UV (Wade et al., 2002; Sharpless et al., 2003). In the case of the nitrosamine, NDMA, a 100 mJ/cm$^2$ UV dose (a dose relevant to disinfection) would result in a ~20% removal of NDMA (Sharpless et al., 2003). Therefore, depending on the potential for nitrosamine formation initiated by UV photolysis of $NO_3^-$, it is possible that net nitrosamine formation may be detectable.
- *Chlorine/chloramine dose:* N-DBP formation depends strongly on the type and variety of secondary disinfectant. Chlorination of $NO_2^-$ formed by UV irradiation should form both nitrated and nitrosated DBPs via $ClNO_2$ and $N_2O_4$ intermediates. Trichloronitromethane formation from chlorination of $NO_2^-$ in the presence of phenols required a 6-fold molar excess of chlorine to phenols to fragment the aromatic rings (Merlet et al., 1985). In contrast, $ClNO_2$ and $N_2O_4$ formation were insignificant during chloramination (Merlet et al., 1985; Choi and Valentine, 2003). However, because UV treatment is unlikely to remove aliphatic amine precursors such as dimethylamine, chloramination may form nitrosamines via the hydrazine pathway identified during disinfection with chloramine alone (Schreiber and Mitch, 2006).
- *Order of disinfectant addition:* The influence of the order of disinfectant addition is unclear. Addition of high doses of chlorine before UV treatment is undesirable, due to formation of THMs and HAAs. However, addition of low doses of chlorine before UV treatment may reduce N-DBP formation by chlorinating precursors. The electron-withdrawing chlorine substituents should decrease the reactivity of the precursors with electrophilic RNS. However, the C-Cl or N-Cl bonds generated by pre-chlorination may be broken by UV light, potentially generating chlorine radicals. These radicals could enhance nitration or nitrosation of NOM by reacting with RNS or nitrite. Due to low reactivity, prior addition of chloramines should not significantly deactivate precursors, and may initiate nitrosamine formation by reaction with amine precursors.
- *$NO_3^-$ concentration:* Nitrated and nitrosated DBP formation is anticipated to increase proportionally with $NO_3^-$ concentration because $NO_3^-$ is not an effective RNS scavenger.
- *NOM concentration and source:* Different NOM fractions may exhibit different potentials to form nitrated and nitrosated DBPs. NOM fractions featuring high specific UV absorbance at 254 nm (SUVA) likely contain elevated concentrations of phenolic moieties that could serve as precursors for the formation of nitrated organics. While low NOM concentrations may enhance DBP formation by providing phenolic precursors, high concentrations may decrease DBP formation by competing with $NO_3^-$ for UV light. Additionally, $OH^*$ scavenging by NOM may hinder DBP formation by preventing $NO_2^*$ formation by the reaction $OH^* + NO_2^- \rightarrow NO_2^* + OH^-$.

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- *pH:* Although N-DBP formation likely depends strongly on pH, the nature of this dependence is unclear. Nitrated DBP formation may be promoted at low pH. Nitration of resorcinol during photolysis of $NO_3^-$ decreased with pH (Thibaud et al., 1987). The predominance of ONOOH at pH < 6.8 favors nitration (Suzuki et al., 2004; Alvarez et al., 1996). In addition, $N_2O_4$ hydrolysis is probably less important at low pH. However, nitration of phenols by photolysis of $NO_3^-$ and chlorination of $NO_2^-$ both increased with pH up to pH 10, presumably because phenolates are more reactive than phenols (Thibaud et al., 1987; Vione et al., 2004). The pH dependence of nitrosated DBP formation likely depends on the most important RNS. Nitrosation by $ONOO^-$ predominates above pH 6.8 (Suzuki et al., 2004; Alvarez et al., 1996), but hydrolysis of $N_2O_3$ and $N_2O_4$ increases with pH due to catalysis by $OH^-$ (Caulfield et al., 1996).
- *Alkalinity:* High alkalinities should decrease DBP formation. $HCO_3^-$ catalyzes $N_2O_3$ hydrolysis (Caulfield et al., 1996). At alkalinities above 1 mM (100 mg/L), alkalinity reduced nitration and nitrosation of tryptophan (Suzuki et al., 2004) and amines (Masuda et al., 2000) by converting $ONOO^-$ to a $ONOOCO_2^-$ complex that decayed predominantly to $NO_3^-$ (Sharpless and Linden, 2001; Uppu et al., 2000).
- *Iron concentration:* Iron may enhance DBP formation by two pathways. UV photon absorption by dissolved or colloidal Fe(III) generates $OH^*$ by the Fenton reaction (Vione et al., 2003):

$$\text{Fe(III)-OH} + h\nu \rightarrow \text{Fe(II)} + OH^* \tag{1.7}$$

  – Reaction of $OH^*$ with $NO_2^-$ forms $NO_2^*$. In addition, $NO^*$ and $NO_2^*$ may exhibit more reactive electrophilic characteristics similar to $NO^+$ and $NO_2^+$ upon complexation by transition metals such as Fe(III) (Challis and Kyrtopoulos, 1979).

**Role of Halogens During UV Treatment**

If pre-chlorination is followed by UV treatment, photolysis of hypochlorous acid (HOCl, $pK_a$=7.60) can form hydroxyl and chloride radicals (Jayson et al., 1973):

$$HOCl + h\nu \rightarrow \cdot OH + Cl\cdot$$

If bromide is present it can be oxidized by HOCl to hypobromous acid (HOBr, $pK_a$=8.63), an important halogenating agent (Amy et al. 1991), and a similar photolysis reaction may occur with UV irradiation:

$$HOBr + h\nu \rightarrow \cdot OH + Br\cdot$$

·OH can activate halogen ions (chloride, bromide, iodide) to form reactive halogen species such as $X_2\cdot^-$ and $XOH\cdot^-$, where X represents Cl, Br or I (Nowell and Hoigné, 1992; Grebel et al. 2009), though the extent to which these reactive halogen species may be involved in DBP formation is not well understood.

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## Transformation of Dissolved Organic Matter

At high doses (greater than 20 J/cm$^2$), UV photolysis has been shown to break down dissolved organic matter (DOM) into smaller, more hydrophilic molecules with lower molar absorptivities than the parent material (Buchanan et al., 2005). Using electrospray ionization mass spectrometry to investigate the effects of typical UV drinking water disinfection doses on organic matter extracted from Ohio River water, Magnuson et al. (2002) found that with increasing UV dose, there was a shift towards smaller NOM molecules. Malley et al. (1995) observed an increase in the ratio of hydrophilic to hydrophobic organic matter in filtered surface water after medium pressure UV irradiation (130 mJ/cm$^2$). However, UV treatment did not have an effect on the hydrophilic-hydrophobic ratio of the same water without pre-filtration or in other highly humic waters. The authors propose that this may be due to interference in UV absorbance by humic material or limitations of the resin extraction procedure used to separate the different polarity fractions (breakthrough of hydrophobic organic matter or retention of hydrophilic material due to high quantity of hydrophobic matter, preventing the method from being sensitive enough to observe small hydrophilic-hydrophobic ratio changes).

It has also been found that bromine and iodine (after being oxidized by HOCl to HOBr and HOI) are more reactive with hydrophilic and low molecular weight organic precursors than their hydrophobic and high molecular weight precursor counterparts, as measured by the formation and speciation of trihalomethanes (THMs) and haloacetic acids (HAAs) (Hua and Reckhow, 2007a; Liang and Singer, 2003). Therefore, if bromide or iodide are present, bromine- and iodine-incorporation into DBPs could be increased if UV photolysis forms more hydrophilic DOM moieties. Halogen speciation is of importance because iodine-containing DBPs have been shown to be more geno- and cytotoxic relative to their bromine-substituted counterparts, which are more toxic than the corresponding chlorine-containing by-products (Richardson et al., 2008). Chow et al. (2008) investigated solar irradiation of surface water DOM and observed a significant decrease in UV absorbance and increase in hydrophilic fraction, accompanied by increased bromine incorporation in THMs and HAAs for samples that were subjected to several days of sunlight photolysis and then chlorinated.

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# CHAPTER 2
# EXPERIMENTAL AND ANALYTICAL METHODS

## EXPERIMENTAL METHODS

The research performed herein was broad spanning from studying fundamental mechanisms to full-scale sampling. The methods described in this chapter are equally as broad beginning with sample collection and handling to detailed analytical methods for emerging disinfection by-products.

### Sample Collection and Handling

Water samples were collected from a variety of water treatment plants and source waters, generally prior to any chlorine addition or quenched of chlorine when necessary. Samples were collected in clean and sample rinsed polypropylene cubitainers or amber glass containers and shipped overnight to the appropriate laboratory. Upon receipt samples were refrigerated at 4°C until treatment or analysis. Twelve hours prior to treatment samples were removed from the refrigerator allowing temperature to come to equilibrium with the room.

### Reverse Osmosis Concentration

A custom portable reverse osmosis (RO) unit was used to concentrate NOM from a settled surface water at Orange County Water and Sewer Authority (OWASA, Carrboro, NC). The RO unit included a spiral wound membrane (celullosic acetate), four filter cartridge filters (10, 5, 1, and 0.45 µm) and cation exchange resin ($H^+$). A process flow diagram of the RO unit is shown in Figure 2.1. Note that the cation exchange resin was used to minimize the membrane fouling associated with high levels of silica. The system was operated in two-stages. First, source water was pumped through the filters and ion exchange resin and collected in a high density polypropylene 80 gallon reservoir (RO feed reservoir). Second, a high pressure pump pumped the collected water though the RO membrane. The retentate or RO concentrate was collected in the RO feed reservoir and the filtrate or RO permeate was discarded. The retentate was continuously recycled through the RO membrane to achieve a concentration factor of approximately 50.

#### *Dissolved Organic Matter Fractionation*

RO concentrate was fractionated by polarity and acid/base properties on XAD resins, following the approach of Leenheer (1981). The isolation herein was performed using XAD-8, which has not been commercially available for many years; readers should note that alternative resins of similar properties are available. Before use, the Amberlite XAD-8 and XAD-4 resins (Rohm & Haas, Philadelphia, PA) were rinsed in a large glass beaker of 0.1N NaOH for five days. Each day the fine particles were decanted off and the NaOH solution was replaced. After five days, the resins were washed with laboratory grade water (LGW) several times. Resins were then Soxhlet extracted sequentially with methanol, acetonitrile, and methanol for 24 hours each. After extraction, the resins were packed into glass columns (approximately 400 mL resin per column) and



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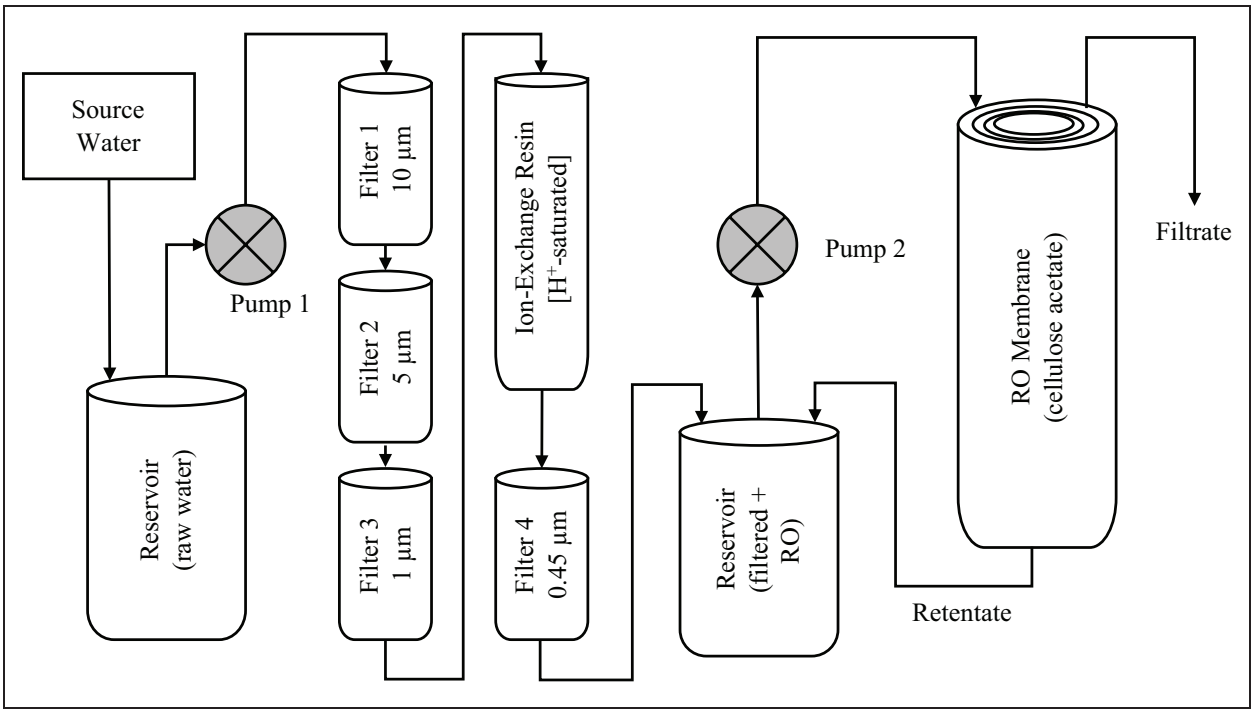


**Figure 2.1 RO concentration setup**

rinsed with LGW to remove residual methanol, until total organic carbon (TOC) in column effluent was less than 0.5 mg/L as C.

Dowex Marathon $H^+$ cation-exchange resin was packed into two glass columns (approximately 150 mL resin per column) and each was rinsed with 4 bedvolumes (BV) of 5% HCl, followed by 7 BV LGW, followed by 4 BV 4% NaOH, and finally with 7 BV LGW. The column was then filled with 10% HCl and left overnight. The next day, the columns were rinsed with several liters of LGW to remove residual acid. The amount of RO concentrate to pass through the column in one run was calculated according to Equation 2.1 (Leenheer, 1981):

$$V_{0.5r} = 2 \times V_0 \times (1 + k'_{0.5r}) \tag{2.1}$$

Where $V_{0.5r}$ is the volume of RO concentrate applied to the resin, $V_0$ is the void volume (approximately 65% of the total resin volume), and $k'_{0.5r}$ is the capacity factor of the resin (mass solute sorbed to resin)/(mass of solute in column void volume). A $k'_{0.5r}$ of 50 is commonly used for XAD-4 and XAD-8 resins. Because of the very high concentration of DOC of the RO concentrate, significantly higher than natural waters, to avoid exceeding the resin capacity 4 L of sample was applied between resin regenerations.

Approximately 16 L of RO concentrate was adjusted to pH 2 with HCl and fractionated through the two resin series. Fractionation was carried out in four runs (4 L per run) to ensure that the resin capacity was not exceeded. The fraction that passed through both resins is operationally defined as hydrophilic dissolved organic matter. The hydrophobic acid fraction was obtained by reverse eluting the XAD-8 column with 0.1N NaOH and then passing the eluent through the cation exchange resin. Hydrophobic neutrals were desorbed from the XAD-8 column with 2 BV of a 75% acetonitrile:25% water solution after rinsing the column with 1 BV LGW. The transphilic

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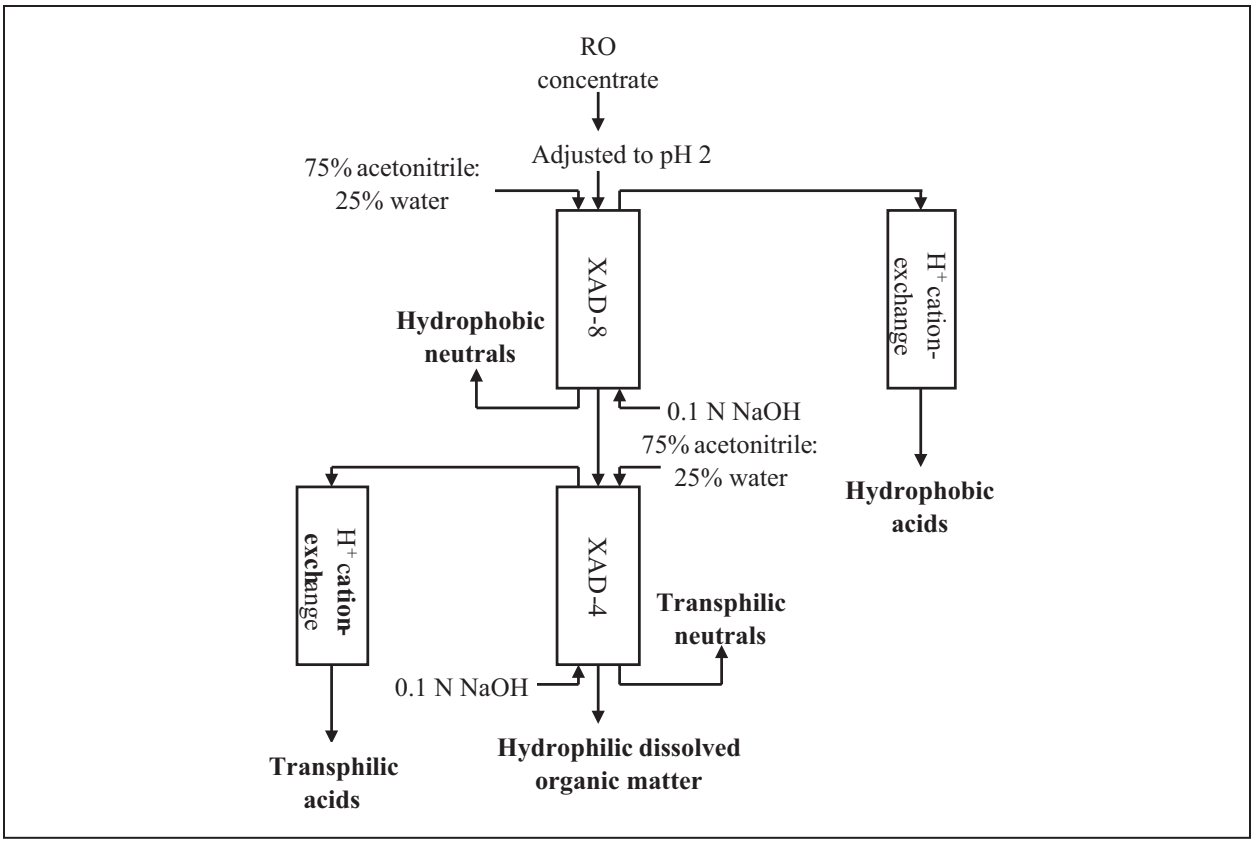


**Figure 2.2 Procedure used for DOM fractionation by polarity and acid/base properties**

acid fraction was desorbed from the XAD-4 column by reverse eluting with 0.1N NaOH and then passing the eluent through a separate cation exchange resin. Transphilic neutrals were desorbed from XAD-4 column with 2 BV of a 75% acetonitrile:25% water solution after rinsing the column with 1 BV LGW. Between runs, XAD resins were regenerated by rinsing with 6 BV 0.1 N NaOH, 2 BV LGW, 6 BV 0.1 N HCl, 2 BV LGW. Cation exchange resins were regenerated by rinsing with 15 BV 10% HCl and standing overnight in 10% HCl, then subsequently rinsed with LGW. The acetonitrile used to desorb the hydrophilic and transphilic neutral fractions was evaporated using a rotary evaporator prior to lyophilization. The remaining fractions were freeze-dried with a Virtis Genesis-12 SQXL lyophilizer. Organic carbon content was measured for each fraction using a Shimadzu TOC-V CPH/CPN total organic carbon analyzer. The fractionation procedure is illustrated in Figure 2.2.

### Bench-Scale UV Equipment

Bench-scale UV irradiations were performed at two of the three participating laboratories, the University of Colorado (CU) and Yale University (Yale). These bench-scale systems are described herein. Note that the University of Colorado studies were preceded by UV experiments at Duke University, where the PI was a faculty member when this study began.

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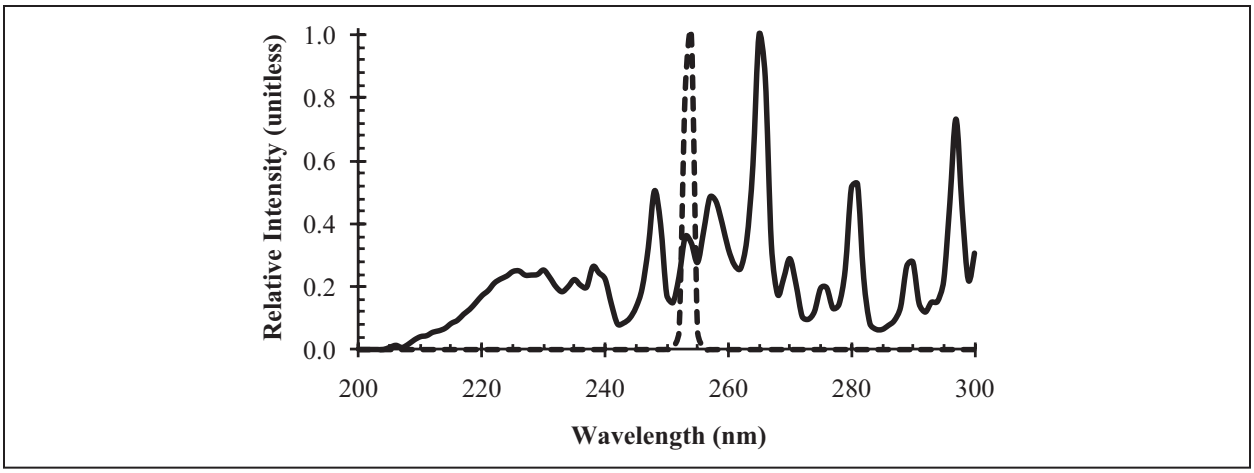


**Figure 2.3 Spectral output (unitless) of LP and MP UV lamps at University of Colorado**

### *Duke University and the University of Colorado*

The methods described below were performed at both Duke University and the University of Colorado-Boulder. It should be noted that the equipment and methods performed in these laboratories are identical as during the study the laboratory at Duke University was moved to the University of Colorado. Quasi-collimated beam UV systems were used to accurately determine the number of photons penetrating the water sample being irradiated. The LPUV and MPUV systems were constructed similarly and the method used to count the number of photons penetrating the sample was the same. The LPUV system was custom built while the MPUV was commercially built by Calgon Carbon Inc. (Pittsburgh, PA). Briefly, a lamp (1 kW MPUV or 4 × 15 W LPUV) was mounted above a circular aperture (4 inch diameter LPUV and 3 inch diameter MPUV). The water sample was retained in a quiescently stirred crystallization dish below the aperture. Sample temperature control was maintained by placing the dish in a heat sink connected to a chiller, which the temperature was electronically set. A manual (LPUV) or a pneumatic (MPUV) shutter was employed to rapidly start and end the irradiation.

UV irradiance at the water surface was measured using an International Light (Peabody, MA) a SED 240 detector with a W diffuser connected to an IL-1700 radiometer. The measured irradiance was converted to dose (or fluence) according to Bolton and Linden (2003). Briefly, UV irradiance between 200–300 nm was multiplied by radiometer sensor factor, reflection factor, petri factor, water factor, and germicidal factor (MPUV only) to yield an average irradiance (LPUV) or a germicidal irradiance (MPUV) in $mW/cm^2$. Irradiation time (seconds) was calculated by dividing the UV dose ($mJ/cm^2$ or $mW \cdot s/cm^2$) by average or germicidal irradiance. Relative output spectra of the LPUV and MPUV lamps are presented in Figure 2.3.

## Pilot-Scale UV Equipment

Pilot studies were performed at the UV pilot facility installed at the Greater Cincinnati Water Works Richard Miller WTP in Cincinnati, OH. Two UV reactors were previously installed

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as part of Water Research Foundation project #4040 (KWR, 2011). Conventional treated water was fed into the pilot area where the flow was split, one leg through each reactor. The reactors were supplied by Aquionics. The MP reactor was a model Photon II and consisted of one 2 kW MP lamp oriented parallel to the flow housed in a quartz sleeve. The LP reactor a model ALT320 consisted of eight 80 W LP lamps (of which only four were used) oriented parallel to the flow. The reactors included pre-calibrated UV monitors (Hanovia) connected to a control panel where intensity was displayed. The MP control panel also had the ability to calculate dose when water UV absorbance and flow rate was input. The flow range through the reactors could vary between 5 and 44 gpm. Samples were collected before and after the UV reactors and chlorinated on the bench-top according the adapted uniform formation conditions test.

For this study the lamp intensity set point was held constant and flow rate was varied to achieve different UV doses. For the MP reactor, UV dose was determined in-situ by the UV monitor and by correlating formation of nitrite due to UV treatment in the field to a bench-scale study of the same water. For the LP reactor, UV dose was determined correlating the decay of $UVA_{254}$ in the field to a bench-scale study of the same water.

## Chlorination/Chloramination Schemes

Two chlorination/chloramination schemes were used during the experimental work performed herein. Both methods were very similar except for the incubation time. Formation conditions used in Chapters 4 and 6 maintained a 72 hour incubation time with a target residual of 1 mg-$Cl_2$/L. Formation conditions used in Chapters 5 and 7 used an incubation time of 24 hours with a desired free chlorine residual of 1.0 mg-$Cl_2$/L or a desired total chlorine residual of 2.5 mg-$Cl_2$/L.

### *Formation Conditions*

The chlorination scheme used for this work blended aspects of the Uniform Formation Conditions (UFC) test (Summers et al., 1996) and the simulated distribution system (SDS) test. Briefly, the water samples were irradiated for the time required to achieve a calculated UV dose. Phosphate buffer (5 mM, 7.5 pH) was added to the irradiated sample and then free chlorine, sodium hypochlorite (reagent grade, J.T. Baker), or preformed monochloramine was added ten seconds after the shutter was closed. The sample was stirred for an additional fifteen seconds then transferred from the crystallization dish to headspace free amber glass incubation bottles (1 L amber glass bottles). The sample was held at room temperature (20–24°C) for 24 hours (±1 hour). The applied free chlorine (or a monochloramine in some cased) dose was such that after 24 hours or 72 hours a residual of 1.0±0.4 mg-$Cl_2$/L was present or in the case of monochloramine a dose such that after 24 hours a residual of 2.5 ±0.4 mg-$Cl_2$/L was present. After the incubation period chlorine residual was measured and the samples were transferred into DBP bottles containing chlorine quenching reagents. This method is illustrated in Figure 2.4.

To determine the dose of chlorine required to achieve 1.0±0.4 mg-$Cl_2$/L after 24 hours of incubation, a dose screening experiment was performed. The experiment was performed by applying varying doses of chlorine into five 20 mL samples of treated water. After 24 hours the chlorine residual was determined and plotted. From the plot the appropriate dose was selected and chlorine demand was calculated by subtracting the 24 hour chlorine residual from the initial chlorine dose.

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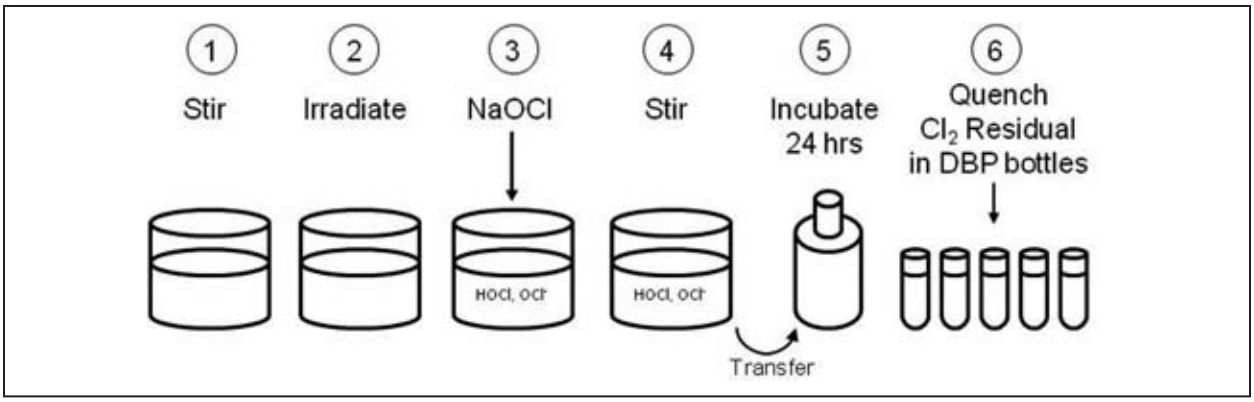


**Figure 2.4 Bench-scale UV chlorination treatment sequence**

## ANALYTICAL METHODS

### Basic Water Quality

Ammonia was measured using Hach method 10205 with a valid measurement range of 0.015 to 2.0 mg-N/L. Alkalinity was determined according to Hach Method 8203 with a digital titrator. Hardness was determined by titration according to standard methods (APHA et al. 1999, Standard Method 2340C). Turbidity in Nephelometric units was measured (Nitrate and nitrite were determined using a Dionex ion chromatography system according to standard methods (APHA et al. 1999, Standard Method 4500-NO3). A Shimadzu TOC-$V_{CSH}$ with attached TMN-1 unit was used to determine total organic carbon (TOC) and total nitrogen (TN) simultaneously. A Beckman F340 and VWR Model 2052 were used to measure pH and conductivity, respectively. Free chlorine was measured using Hach DPD method 8021with a valid measurement range of 0 to 2.0 mg-$Cl_2$/L. A Varian-Cary 100 spectrometer was used to measure ultraviolet absorbance at 254 nm ($UVA_{254}$). Determination of $UVA_{254}$ according to standard methods requires the filtration through a 0.45 µm filter. But the high degree of pretreatment of the water samples studied herein showed no difference in absorbance due to filtration. Without filtration the studied samples represent full-scale WTP water quality as they were previously filtered at full-scale. Furthermore this confirms the lack of particulate organic matter in the samples making TOC and TN synonymous with dissolved organic carbon (DOC) and total dissolved nitrogen (TDN). Dissolved organic nitrogen (DON) or total organic nitrogen (TON) was calculated mathematically by subtracting inorganic nitrogen species (ammonia, nitrate, and nitrite) from total nitrogen or total dissolved nitrogen.

### Disinfection By-Products

Disinfection by-products were measured by the University of Colorado, Yale University and University of North Carolina. These methods are described herein and a full list of DBPs is provided in Table 2.1.

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**Table 2.1**
**List of measured DBPs, acronyms, and detection limits**

| Compound | CAS # | Abbreviation | Compound class | Detection limit (µg/L) |
|---|---|---|---|---|
| Chloroform | 67-66-3 | $Cl_3CH$ | Trihalomethane | 0.1 |
| Dibromochloromethane | 124-48-1 | $Br_2ClCH$ | Trihalomethane | 0.1 |
| Dichloroiodomethane | 594-04-7 | $Cl_2ICH$ | Trihalomethane | 0.1 |
| Bromodichloromethane | 75-27-4 | $BrCl_2CH$ | Trihalomethane | 0.1 |
| Dibromoiodomethane | 593-94-2 | $Br_2ICH$ | Trihalomethane | 0.1 |
| Chlorodiiodomethane | 638-73-3 | $ClI_2CH$ | Trihalomethane | 0.1 |
| Bromodiiodomethane | 557-95-9 | $BrI_2CH$ | Trihalomethane | 0.1 |
| Iodoform | 75-47-8 | $I_3CH$ | Trihalomethane | 0.1 |
| Bromochloroiodomethane | 34970-00-8 | BrClICH | Trihalomethane | 0.1 |
| Bromoform | 75-25-2 | $Br_3CH$ | Trihalomethane | 0.1 |
| Chloroacetonitrile | 107-14-2 | CAN | Haloacetonitrile | 0.15 |
| Dichloroacetonitrile | 3018-12-0 | DCAN | Haloacetonitrile | 0.1 |
| Trichloroacetonitrile | 545-06-2 | TCAN | Haloacetonitrile | 0.1 |
| Bromochloroacetonitrile | 83463-62-1 | BCAN | Haloacetonitrile | 0.1 |
| Dibromoacetonitrile | 3252-43-5 | DBAN | Haloacetonitrile | 0.1 |
| Trichloronitromethane | 76-06-2 | TCNM | Halonitromethane | 0.1 |
| Tribromonitromethane | 464-10-8 | TBNM | Halonitromethane | 0.1 |
| Chloronitromethane | 1794-84-9 | CNM | Halonitromethane | 0.19 |
| Dichloronitromethane | 7119-89-3 | DCNM | Halonitromethane | 0.26 |
| 1,1-Dichloropropanone | 513-88-2 | 11DCP | Haloketone | 0.1 |
| 1,1,1-Trichloropropanone | 918-00-3 | 111TCP | Haloketone | 0.1 |
| Chloral hydrate | 75-87-6 | CH | Haloaldehyde | 0.1 |
| Bromoacetamide | 683-57-8 | BrAM | Haloacetamide | 0.1 |
| Dichloroacetamide | 683-72-7 | $Cl_2AM$ | Haloacetamide | 0.1 |
| Bromochloroacetamide | 62872-34-8 | BrClAM | Haloacetamide | 0.1 |
| Trichloroacetamide | 594-65-0 | $Cl_3AM$ | Haloacetamide | 0.1 |
| Dibromoacetamide | 598-70-9 | $Br_2AM$ | Haloacetamide | 0.1 |
| Chloroiodoacetamide | 62872-35-9 | ClIAM | Haloacetamide | 0.1 |
| Bromodichloroacetamide | 98137-00-9 | $BrCl_2AM$ | Haloacetamide | 0.1 |
| Bromoiodoacetamide | 62872-36-0 | BrIAM | Haloacetamide | 0.1 |
| Dibromochloroacetamide | 855878-13-6 | $Br_2ClAM$ | Haloacetamide | 0.1 |
| Tribromoacetamide | 594-47-8 | $Br_3AM$ | Haloacetamide | 0.1 |
| Diiodoacetamide | 5875-23-0 | $I_2AM$ | Haloacetamide | 0.1 |
| Chloroacetic acid | 79-11-8 | ClAA | Haloacetic acid | 1.2 |
| Bromoacetic acid | 79-08-3 | BrAA | Haloacetic acid | 0.8 |
| Dichloroacetic acid | 79-43-6 | $Cl_2AA$ | Haloacetic acid | 1.2 |
| Bromochloroacetic acid | 559-96-8 | BrClAA | Haloacetic acid | 0.8 |
| Trichloroacetic acid | 76-03-9 | $Cl_3AA$ | Haloacetic acid | 0.4 |
| Dibromoacetic acid | 631-64-1 | $Br_2AA$ | Haloacetic acid | 0.4 |
| Bromodichloroacetic acid | 71133-14-7 | $BrCl_2AA$ | Haloacetic acid | 0.8 |
| Dibromochloroacetic acid | 5278-95-5 | $Br_2ClAA$ | Haloacetic acid | 2.0 |
| Tribromoacetic acid | 75-96-7 | $Br_3AA$ | Haloacetic acid | 4.0 |
| Nitrosodimethylamine | 62-75-9 | NDMA | Nitrosamine | 0.002 |
| Nitrosmethylethylamine | 10595-95-6 | NMEA | Nitrosamine | 0.002 |
| Nitrosodiethylamine | 55-18-5 | NDEA | Nitrosamine | 0.002 |
| Nitrosodi-n-propylamine | 621-64-7 | NDPA | Nitrosamine | 0.002 |
| Nitrosodi-n-butylamine | 924-16-3 | NDBA | Nitrosamine | 0.002 |
| Nitrosopyrollidine | 930-55-2 | NPYR | Nitrosamine | 0.002 |
| Nitrosopiperidine | 100-75-4 | NPIP | Nitrosamine | 0.002 |

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### *Disinfection By-Products—University of North Carolina*

Chlorine/chloramine residuals were quenched with ammonium sulfate for haloacetic acid analysis and ascorbic acid for analysis of trihalomethanes, halonitromethanes, haloacetamides, haloacetonitriles, chloral hydrate and haloketones. Trihalomethanes (including 6 iodo-containing species), trichloronitromethane, tribromonitromethane, haloacetamides, haloacetonitriles, chloral hydrate, and two haloketones (1,1-dichloropropanone and 1,1,1-trichloropropanone) were liquid-liquid extracted with methyl tert-butyl ether (MtBE) and analyzed on a Hewlett-Packard 5890 gas chromatograph with $^{63}$Ni electron capture detector, using an adaption of USEPA Method 551.1 (USEPA, 1995) and Chinn et al. (2007). A Zebron (Phenomenex, Torrance, CA) ZB-1 capillary column (30 m length, 0.25 mm inner diameter, 1.0-µm film thickness) was used for separation of compounds, which were analyzed by the following temperature program: oven held at 35°C for 22 min, increased at 10°C/min to 145°C and held for 2 min, increased at 20°C/min to 225°C and held for 10 min, then increased at 20°C/min to 260°C and held for 5 min. Injection volume was 2 µL in splitless/split mode, injection temperature was 117°C and detector temperature was 290°C. Haloacetamides were co-extracted with the trihalomethanes and other halogenated by-products (not including haloacetic acids), but analyzed with a separate oven temperature program: held at 37°C for 1 min, increased at 5°C/min to 110°C and held for 10 min, then increased at 5°C/min to 280°C. Injection volume was 2 µL, injector temperature was 200°C and detector temperature was 300°C. Haloacetic acids were liquid-liquid extracted with MtBE and derivatized to their methyl ester form using diazomethane, as described by Brophy et al. (2000). Extracts were analyzed on a Hewlett-Packard 5890 gas chromatograph with $^{63}$Ni electron capture detector using the following oven temperature program: initial temperature was 37°C, held for 21 min, increased at 5°C/min to 136°C, held for 3 min, increased at 20°C/min to 250°C and held for 3 min. Injection volume was 1 µL, injector temperature was 180°C and detector temperature was 300°C. Samples were analyzed in duplicate and 1,2-dibromopropane was used as an internal standard. The minimum reporting limit (MRL) for each of the halogenated volatile species and haloacetamides was 0.1 µg/L, and for haloacetic acids, the MRL ranged from 0.4 to 4 µg/L for individual species. Figures A.1–A.3 and Tables A.1–A.3 presented in Appendix A show chromatograms and retention times for the halogenated DBPs suite, haloacetamides, and haloacetic acids (in their derivatized methyl ester forms). Figure A.4 in Appendix A shows the elution of haloacetamides using the halogenated volatiles temperature program and Figure A.5 in Appendix A shows the elution of halogenated volatile species by the haloacetamide temperature program.

Table 2.1 presents names and acronyms of each of the DBPs measured by the University of North Carolina.

### *Disinfection By-Products—Yale University*

The nitrosamine standards were purchased from Accustandard (New Haven, CT). The NDMA-$d_6$ internal standard was purchased from Cambridge Isotope Laboratories. All nitrosamines that were analyzed excluding the internal standard were provided in a combined USEPA 521 (USEPA, 2004) mix at 2000 µg/mL in methylene chloride. The nitrosamines in the USEPA 521 mix included nitrosodimethylamine (NDMA), nitrosomethylethylamine (NMEA), nitrosodiethylamine (NDEA), nitrosodibutylamine (NDBA), nitrosopyrrolidine (NPYR), nitrosopiperidine (NPIP), and nitrosodipropylamine (NDPA). The NDMA-$d_6$ was provided as a stock solution at 1000 µg/mL in

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**Table 2.2**
**Parent and daughter ions for quantitation of nitrosamines/nitramines using GC/MS/MS (chemical ionization with methanol)**

| Compound | Parent ion (m/z) | Daughter ions (m/z) |
|---|---|---|
| NDMA | 75 | 44+47+58 |
| NDMA-$d_6$ | 81 | 50+64 |
| DMNA | 91 | 44+45 |
| NMEA | 89 | 61 |
| NDEA | 103 | 75 |
| NDPA | 131 | 89 |
| NPIP | 115 | 69 |
| NPYR | 101 | 55 |
| NDBA | 159 | 57 |

methylene chloride. Dimethylnitramine, the nitrated analogue of NDMA, has recently been synthesized in Dr. Mitch's laboratory through a modified method described in Mezyk et al., 2006.

Analysis of the nitrosamines and dimethylnitramine (DMNA) were conducted according to USEPA 521 (USEPA, 2004) and summarized below. Experimental samples were first quenched and 500 mL samples were shipped on ice to Yale. After injection of $d_6$-NDMA as an internal standard, samples were extracted through solid-phase extraction cartridges containing activated carbon. Samples were left dry for ~30 min and then extracted with ~12 mL of methylene chloride. Anhydrous sodium sulfate was then added to these samples to remove residual water from the extract. The methylene chloride fraction was then removed from the salt and blown down to ~0.5 mL under nitrogen and analyzed by gas chromatography tandem mass spectrometry (GC/MS/MS; Agilent DB-1701, 30 m × 0.32 mm × 1 µm column) using chemical ionization (methanol) and large volume injection. The column temperature was held at 35°C for 3 min, ramped up to 130°C at 4°C/min and held for 3 min, ramped up to 210°C at 40°C/min and held for 5 min, and ramped up to 250°C at 40°C/min and held for 0.5 min. The injection port temperature was initially set at 37°C and ramped to 250°C over time. Standards were prepared fresh by spiking known concentrations of nitrosamines/nitramines and NDMA-$d_6$ into 1 mL of methylene chloride and analyzed on the GC/MS/MS. Parent and daughter ions of analyzed species are presented in Table 2.2.

### *Disinfection By-Products—Pilot-Scale Study*

Samples collected and chlorinated during pilot testing work were quenched with ammonium chloride to retard the chlorination reaction. Quenched samples were analyzed at the University of Colorado for total regulated trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform), trichloronitromethane, 1,1-Dichloro-2-propanone, 1,1,1-Trichloro-2-propanone and haloacetonitriles (trichloroacetonitrile, dichloroacetonitrile, bromochloroacetonitrile, and dibromoacetonitrile) (Method 551.1, USEPA 1995) using gas chromatography (Agilent 6890), with an electron capture detector and a high resolution gas chromatography column (RTX-1701).

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**Toxicity Assay**

Sample toxicity was monitored using the Ames II genotoxicity test. This test was chosen to parallel work done on Water Research Foundation project 4040 (KWR, 2011). Toxicity assay samples were concentrated by 10,000 similar to previous work performed by Heringa and colleagues (2011). Briefly, 1100 mL of sample taken from Cincinnati GAC influent water (before the GAC treatment to remove NOM and micropollutants) was subjected to a given treatment sequence including addition of hydrogen peroxide, UV irradiation, chlorination, and incubation. After the 24 hour incubation period and determination of residual free chlorine concentration the sample was quenched with two times the stoichiometric dose of sodium thiosulfate necessary to quench the measured free chlorine residual. The sample was then acidified to a pH of 2.3 using 15% hydrochloric acid. 1000 mL of sample was then passed through a glass 200 mg Waters Oasis HLB cartridge, which had been previously conditioned, at a flow rate of approximately 10 mL/min. Cartridge preparation was performed by applying and processing 2.5 mL of solvent (25% methanol, 75% acetonitrile) through the cartridge three times. The solvent was drawn from the cartridge and the cartridge was rinsed three times with 2.5 mL of pH 2.3 distilled water. Upon passing the entire sample through the cartridge, the water was drawn from the cartridge and the cartridge was extracted. The extraction procedure matched the solvent portion of the preparation procedure and the extract was captured in a test tube. The extract was then blown down under a stream of nitrogen to 100 µL. The concentrated extract was then transferred into a small conical bottom vial. The test tube was rinsed with a small amount of acetonitrile, which was added to the conical bottom vial. The extract in the conical vial was again blown down to approximately 100 µL and 100 µL of dimethylsulfoxide (DMSO) was added. The sample was blown down again to a volume less than 100 µL and additional DMSO was supplemented to bring the total volume back to 100 µL. The samples were then frozen at –20°C packed in a cooler with 4 kilograms of dry ice and shipped 2-day air to KWR in the Netherlands for further processing and analysis by the Ames II assay.

Detailed method discussion of the AMES II assay can be found elsewhere (Heringa et al., 2011) but is briefly described here. AMES II assay is a liquid culture version of the earlier AMES assay, which was performed on plates. AMES II assay was carried out in a multi-well plate and growth of the reverse-mutated bacteria (TA98) was measured by change in media color resulting from change in pH caused by bacterial growth. This assay was performed with and without the extract of metabolic enzymes from the liver (S9). When S9 was used the test measured the genotoxicity of S9 metabolites or indirect toxicity. The assay measures genotoxicity by quantifying the formation of (reverse) point mutations. It is important to note that this toxicity assay provides comparative numbers to look at changes due to treatment differences, however the assay results do not necessarily imply or relate to any specific human or ecological health outcome.

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# CHAPTER 3
# UNITED STATES SURVEY OF DISINFECTION PRACTICES

## OVERVIEW

In the past few years, numerous water treatment plants in North America have studied, begun planning for, or installed UV disinfection systems. These include unfiltered water utilities (e.g., in New York, Seattle, Boston etc.) and filtered systems (e.g., in Albany, Houston, Cincinnati, Contra Costa, Georgia, Utah etc.). Installation and potential installation have included both low pressure and medium pressure UV technologies. A number of drinking water treatment facilities that have installed or are planning installation of UV were contacted to establish a better understanding of where UV fits into their process treatment train. The contact list of utilities to survey was generated through discussions with key consultants and academics who have worked on UV projects and UV manufacturers who have sold UV systems. A specific focus of the survey was to establish the range of disinfection practices and sequencing of primary and secondary disinfectants.

## SURVEY RESULTS

The survey results are sorted into four relevant categories; basic facility information, sequence of UV disinfection with chlorine/chloramines, UV lamp type and applied dose, and chlorine/chloramines usage and DBP formation.

### Basic Facility Information

A link to the online survey (survey provided in Appendix B) was sent via email to 84 drinking water treatment facilities located in the US identified as potentially having installed a UV disinfection system. Of the 84 potential participating facilities, 22 surveys were returned complete and 2 surveys were returned partially complete. With the 24 surveys filed, a 28.6% return rate was observed and these results are likely to broadly represent the current implementation of UV disinfection in drinking water treatment. The participating facilities were located in 13 states, 17 of the 24 are located on the map shown in Figure 3.1 while 7 facilities requested their location remain anonymous.

The majority of facilities treated surface water (21) or a combination of surface water and groundwater (1). Facilities treating groundwater (2) made up the minority of the participating facilities. The majority of the facilities installed UV as part of a plant retrofit (17) while the minority installed as part of original construction (3). Of the remaining facilities, two facilities did not identify when their UV was installed and one of the participating facilities was currently performing pilot testing of UV disinfection and would soon be installing as part of a retrofit. The users of water treated by the facilities varied widely from 700 to 900,000 people. Facility design flows also varied from 0.4 to 180 MGD.



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**Figure 3.1 Locations of participating drinking water treatment plants**

### Sequence of Ultraviolet and Free Chlorine/Chloramines

Of the 24 facilities surveyed, 23 facilities applied free chlorine or chloramines as a secondary disinfectant while one groundwater facility did not apply any secondary disinfectant. The majority (68%) of facilities did not carry a secondary disinfectant residual through their UV reactor (Figure 3.2). Two facilities maintained applied chloramines upstream of the UV reactor and five facilities applied free chlorine upstream. Of these facilities applying secondary disinfectant upstream of the UV reactor, two of the facilities injected chlorine both upstream and downstream of their UV reactor (Figure 3.3) and maintained low residuals (0.1–0.3 mg-$Cl_2$/L) of free chlorine through the reactor. The other five facilities injected adequate concentrations of secondary disinfectant upstream of their UV reactors to maintain a distribution system residual, post-UV. Of these facilities, two applied chloramines with a dose of 2.5 mg-$Cl_2$/L and three utilized free chlorine with doses of 0.66–1.24 mg-$Cl_2$/L.

### UV Lamp Type and Dose

The majority of UV installations surveyed employed MP technology, followed by an equal number of installations of LP and LPHO (Figure 3.4). UV Dose was most often calculated using the "Calculated Dose Approach" followed by "UV Intensity Setpoint Approach" (Figure 3.5) as

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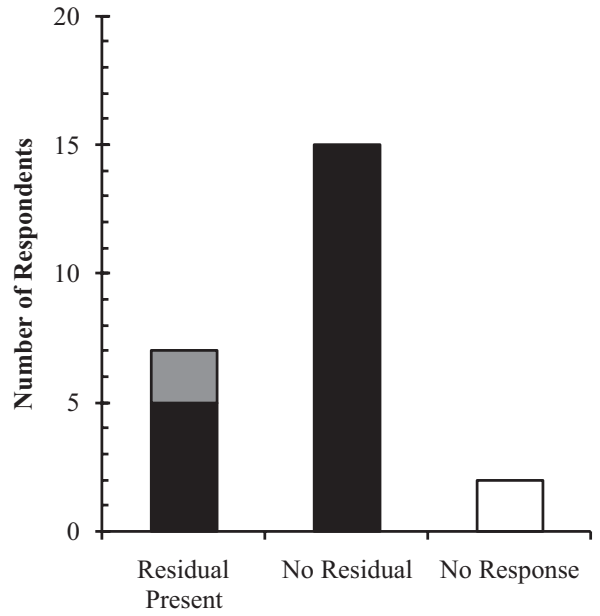


**Figure 3.2 Type of secondary disinfection and presence in UV reactor. Black—free chlorine, gray—chloramines, and white—no response.**

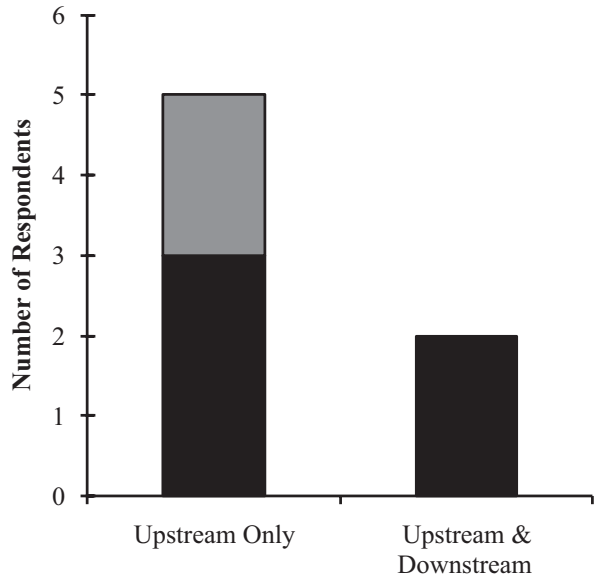


**Figure 3.3 Points of secondary disinfection application in relationship to UV reactor for facilities with a residual present in the UV reactor. Black—free chlorine, gray—chloramines.**

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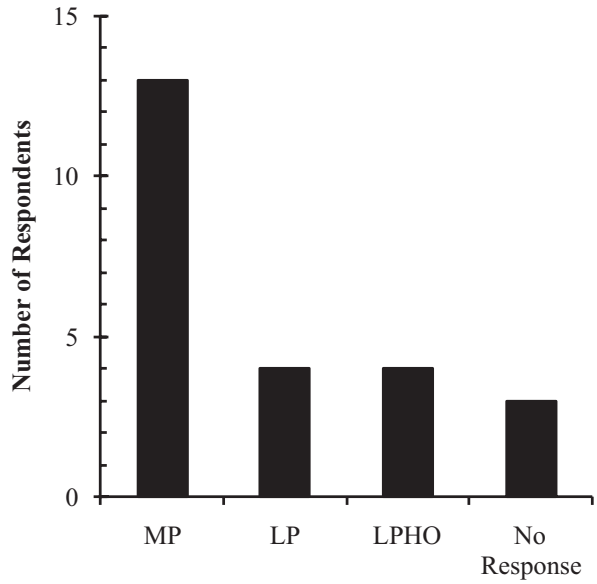


**Figure 3.4 Distribution of UV technologies installed**

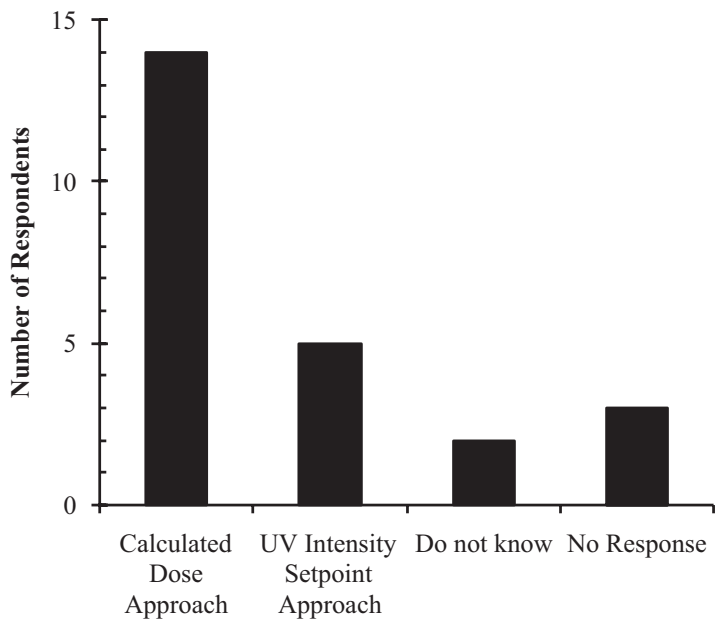


**Figure 3.5 UV dose calculation method**

described in the UV guidance manual (USEPA, 2006). Most facilities were designed to provide a 40 mJ/cm$^2$ UV dose (Figure 3.6). Installations of MP technology were identified to have design doses between 38 and 84 mJ/cm$^2$, all but one (25 mJ/cm$^2$) of the LP and LPHO installations were designed at 40 mJ/cm$^2$. Many of the facilities operated the UV treatment process at greater doses than the design dose. In the case of two of the Colorado facilities this is the result of other upstream process upgrades that have improved UV transmittance (UVT) through the reactor.

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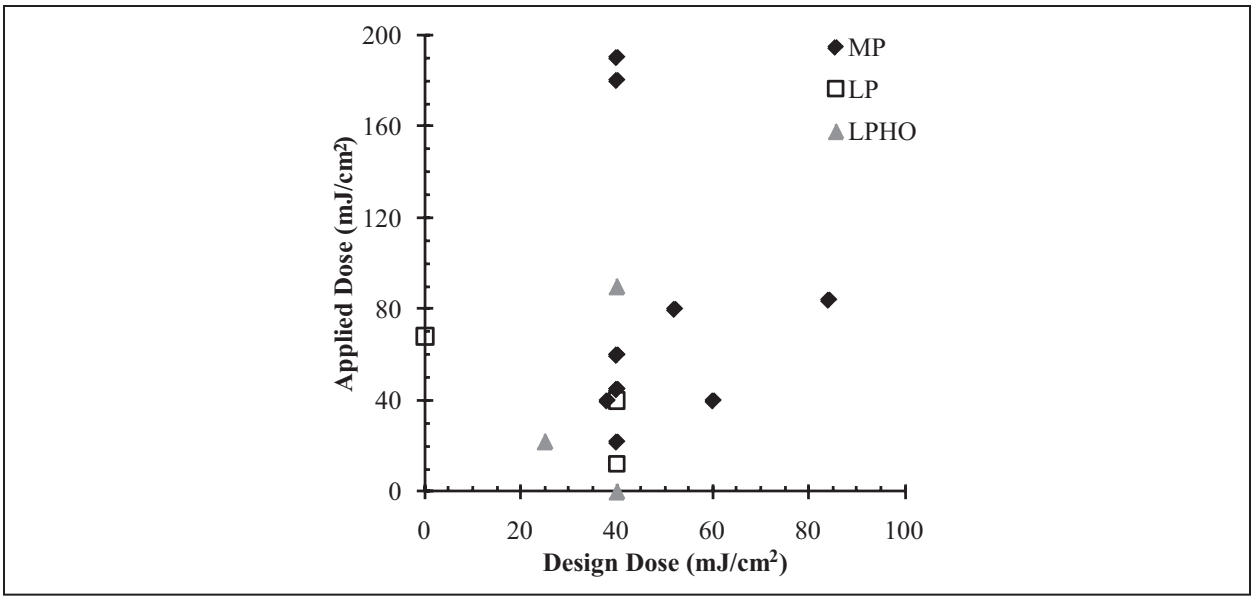


**Figure 3.6 Design versus applied dose reported by 17 facilities. Note: 0 indicates no response and 4 facilities did not report dose.**

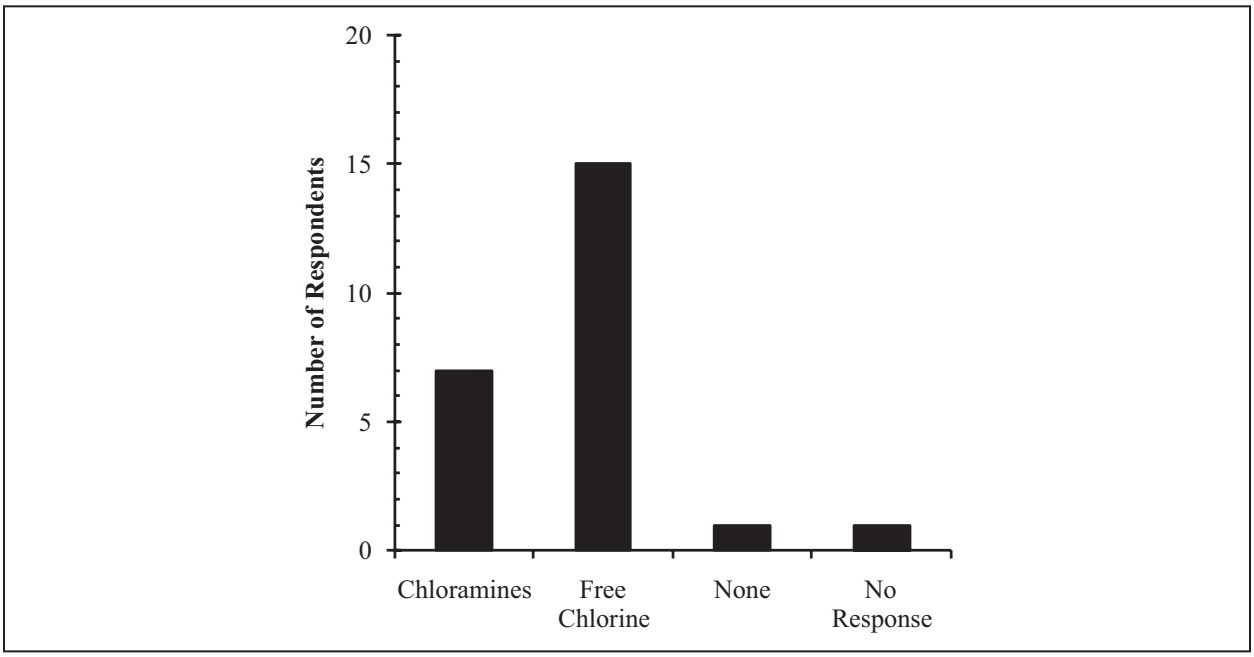


**Figure 3.7 Secondary disinfectant applied for distribution residual**

## Chlorine/Chloramine Usage and DBP Formation

The majority (63%) of facilities maintained a distribution system residual by applying free chlorine as a secondary disinfectant while the minority applied chloramines (29%) (Figure 3.7). As the majority (92%) of the UV disinfection installations were part of a plant retrofit, facilities were asked if they have observed a change in usage rate of chlorine/chloramines and formation of

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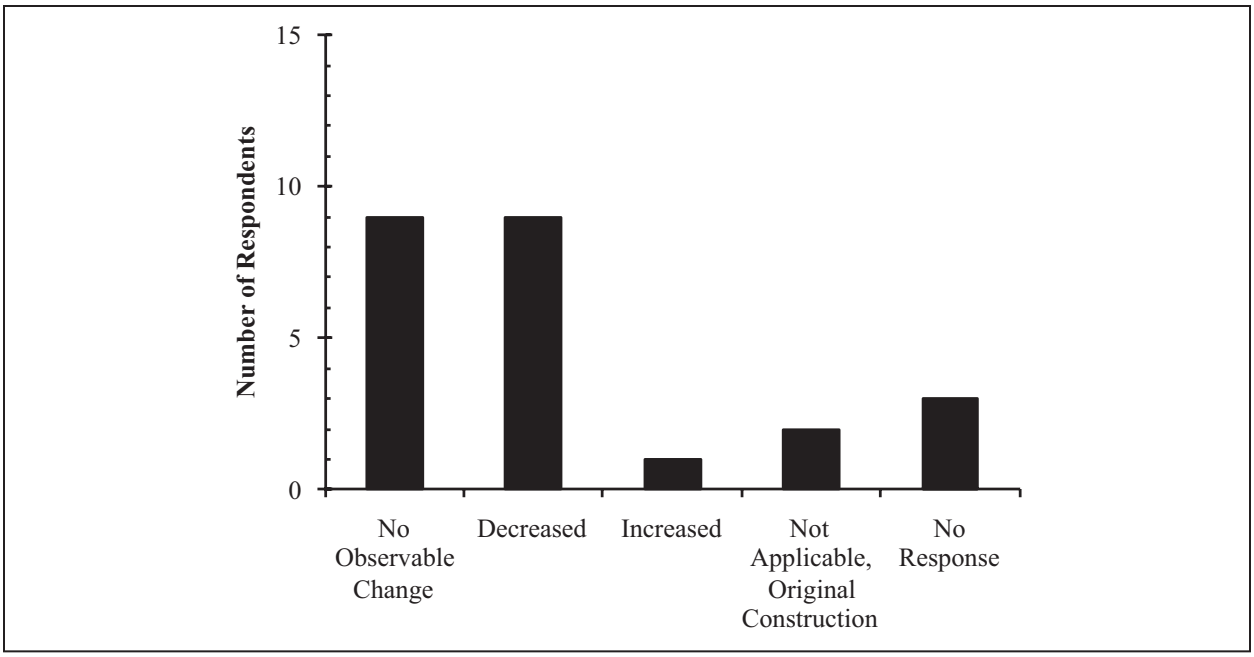


**Figure 3.8 Change in secondary disinfectant usage after installation of UV**

DBPs. Nine facilities did not observe a change in usage, nine observed a decrease in usage, and one observed an increase in usage of secondary disinfection chemicals (Figure 3.8). With respect to DBPs no facilities observed an increase in DBP formation and the majority of the facilities observed no change in DBP formation (Figure 3.9). A smaller group (29%) observed a decrease in DBP formation.

## SUMMARY

The pool of twenty-four drinking water treatment plants that filled out this survey appears to represent the current status of implementation of UV disinfection and secondary disinfection practices in the United States. Key findings of this survey include:

1. The majority of these facilities treat surface water (92%) and utilize MP UV technology (54%).
2. A secondary disinfectant residual is not carried through the UV reactor (67%) in the majority of facilities. Those facilities that do carry a secondary disinfectant residual through the reactor are more likely to apply the entire dose required for the distribution system upstream of the UV reactor (5/7) while the minority (2/7) apply a lower dose upstream of the reactor and then apply a second dose downstream of the reactor.
3. No observable change in secondary disinfectant usage and DBP formation was noted in 9/24 and 12/24 facilities, respectively.
4. Decreases in secondary disinfectant usage and DBP formation was noted in 9/24 and 7/24 facilities, respectively. One facility noted an increase in secondary disinfectant usage and no facilities noted an increase in DBP formation.

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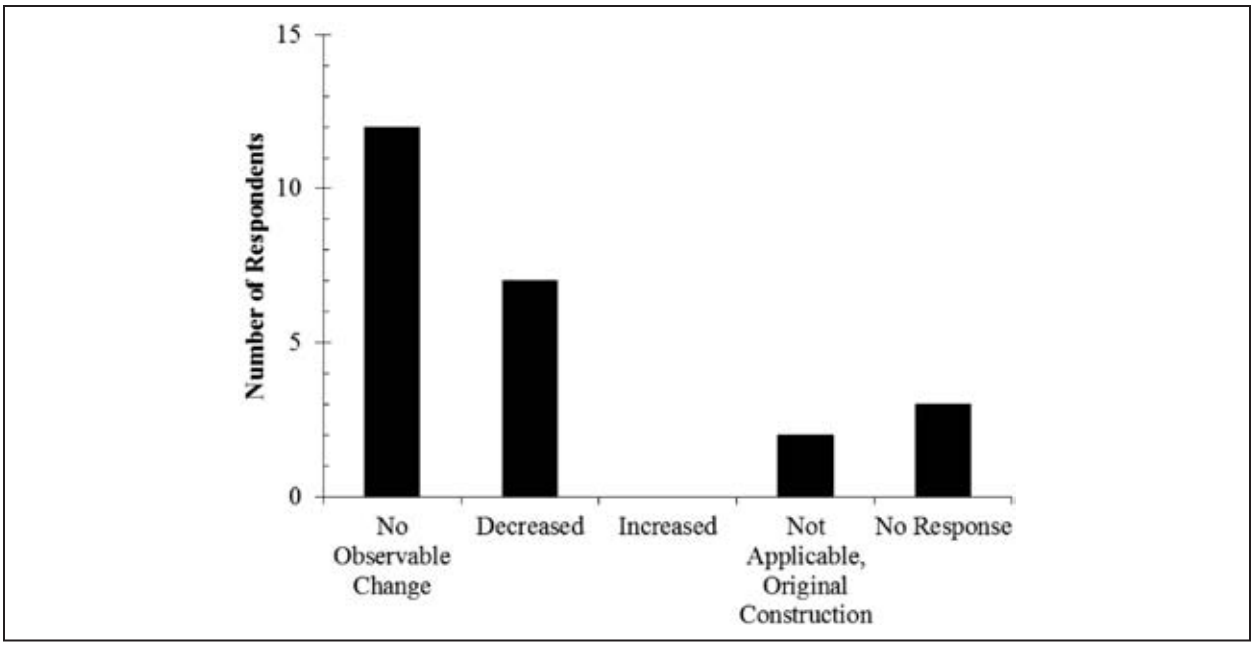


**Figure 3.9 Change in disinfection by-products formed after installation of UV**

This survey illustrates that increases, decreases, and no change in both secondary disinfectant usage and DBP formation was observed at full-scale when implementing UV disinfection. This finding pointed to the likelihood that the impacts of addition of UV disinfection to post-chlorination DBPs was negligible or within analytical error. Therefore a study on the fundamental mechanisms of how UV may impact DBP formation would need to be conducted using atypical conditions to elucidate potential effects of the treatment process sequence.

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# CHAPTER 4
# UV DISINFECTION AND CHLORINATION AT THREE WATER TREATMENT PLANTS

## OVERVIEW

The purpose of this set of experiments was to evaluate the importance of UV treatment on the formation of a range of disinfection by-products. Three drinking water treatment plants were selected for study. The first case study is from the Orange Water and Sewer Authority (OWASA; NC). The other two case studies include the Wilmington, NC Water Treatment Plant and a California water agency utilizing Delta water (CWA-D; CA). Grab samples were taken from various points in the treatment process (locations for each plant will be described below). These samples were exposed to UV treatment using bench-scale collimated beam systems in the laboratory containing either medium-pressure (MP) or low-pressure (LP) UV lamps and further treated with 0–5 mg/L $Cl_2$ of free chlorine or pre-formed $NH_2Cl$.

## RESULTS

Samples were obtained and treated in the lab with either MP or LP light under varying UV fluences from 0–400 mJ/cm$^2$ and exposed to post-chlorination/post-chloramination (0–5 mg/L $Cl_2$ free chlorine or $NH_2Cl$). The results are described in greater detail below, but a brief summary of the results will be provided here:

i. For the OWASA water, it was found that neither MP nor LP treatment up to 400 mJ/cm$^2$ altered THM4 or HAA5/HAA9 formation as the amount formed was similar to oxidant only controls.
ii. For the Wilmington water, it was found that THM4 or HAA5/HAA9 formation increased slightly from 10–50% for both lamps and both free chlorine and $NH_2Cl$ addition. However, TCNM formation was found to increase up to 2× the amount formed with oxidant alone when 400 mJ/cm$^2$ of MP or LP UV treatment was applied.
iii. For the Delta water, which was sampled at various treatment locations, no significant increase of nitrosamines, dimethylnitramine, halonitromethanes, and haloacetonitriles was observed for any waters tested. However, a significant increase was observed up to ~25% for HAA9 and THM4 formation when MP or LP UV treatment was applied.

### Case Study 1: Orange Water and Sewer Authority, NC

Figures 4.1 and 4.2 show THM4 and HAA5/HAA9 formation resulting from low and medium pressure UV treatment with subsequent chlorination or chloramination. Chlorinated samples showed higher THM and HAA formation compared to chloraminated samples, which was expected, but UV pre-treatment did not have a statistically significant effect on the formation of either THM4 or HAA9 nor the levels of their individual constituents. All samples contained analyte concentrations below the regulations of 60 µg/L and 80 µg/L for HAA5 and THM4, respectively. Due to instrumental problems, nitrosamines and dimethylnitramine were not analyzed.



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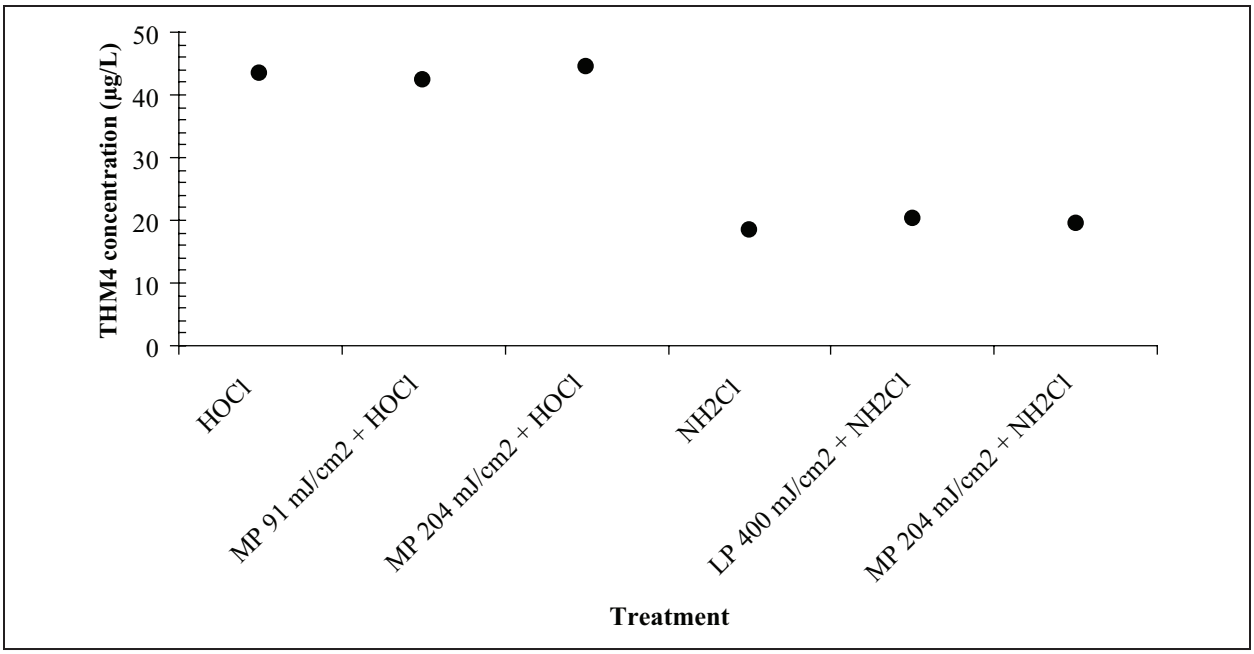


**Figure 4.1 THM4 formation in OWASA samples treated with UV and chlorine or chloramines. Bromoform was below the MRL (<1.0 µg/L) in all samples. Value shown represents average between duplicate samples (RPD = 0.7% to 6.3%).**

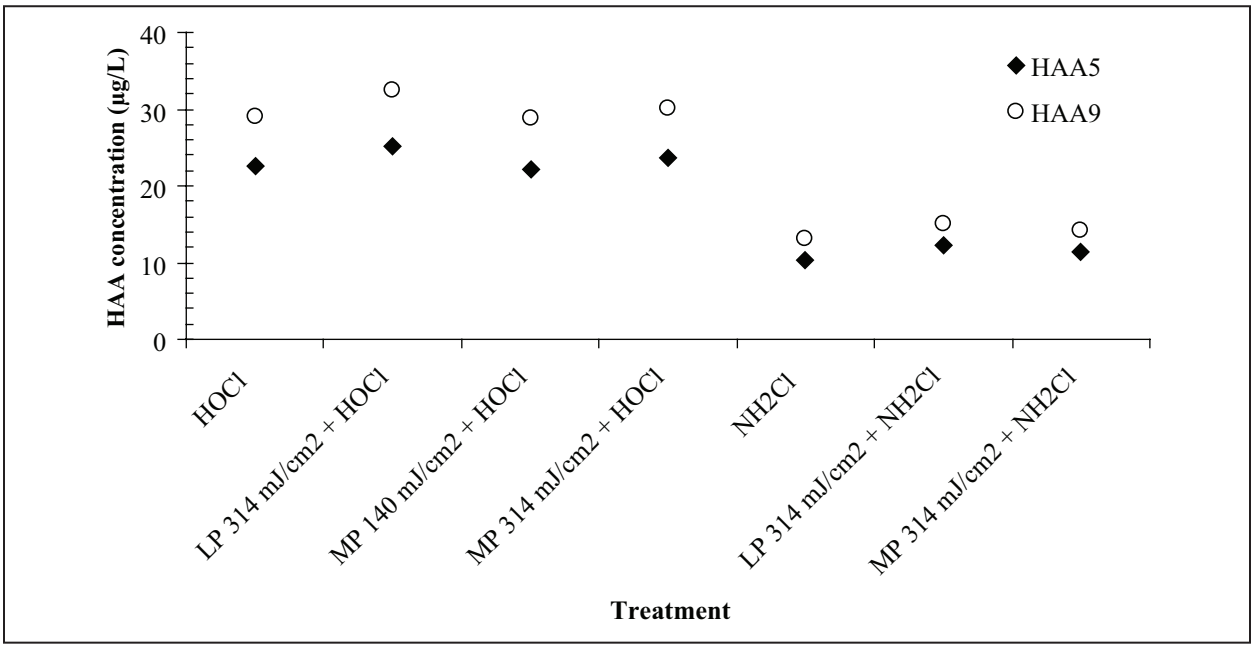


**Figure 4.2 HAA5 and HAA9 formation in OWASA samples treated with UV and chlorine or chloramines. Bromoacetic acid, dibromochloroacetic acid, and tribromoacetic acid were below the MRL (<0.4, <1.0, and <2.0 µg/L, respectively). Value shown represents average between duplicate samples (RPD = 0.7% to 22%).**

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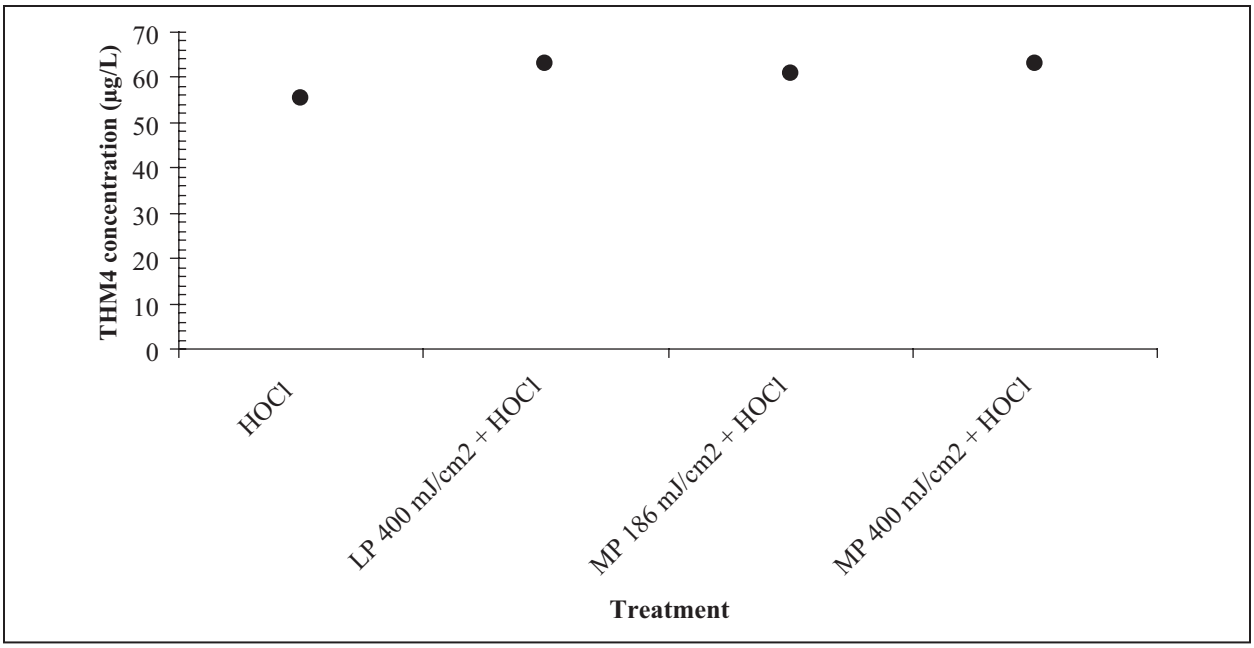


**Figure 4.3 THM4 formation in chlorine-treated Wilmington water treated with and without UV. Value shown represents average between duplicate samples (RPD <2%).**

## Case Study 2: Wilmington, NC, Water Treatment Plant

A suite of halogenated DBPs that were co-extracted with THMs, including haloacetonitriles, trichloronitromethane, two haloketones and chloral hydrate were measured in addition to THMs and HAAs for this case study. THM4 formation increased 10–14% when LP UV (400 mJ/cm$^2$) or MP UV (186 and 400 mJ/cm$^2$) irradiation preceded chlorination (Figure 4.3). The relative percent difference between duplicate THM samples was less than 2%, so this increase is statistically significant. 400 mJ/cm$^2$ is higher than a typical disinfection dose and perhaps similar changes were not observed in the first case study (OWASA) because lower doses were used. All samples contained analyte concentrations below the regulations of 80 µg/L and 60 µg/L for THM4 and HAA5, respectively (Figures 4.3 and 4.5).

As for OWASA, chloramination produced lower amounts of THM4 and HAA9 compared to chlorination with or without UV treatment (Figures 4.4 and 4.6). Irradiation with LP UV (400 mJ/cm$^2$) prior to chloramination increased the formation of THM4 from 3.4 to 4.9 µg/L. HAA formation was slightly increased when LP UV (400 mJ/cm$^2$) or MP UV (400 mJ/cm$^2$) were added prior to chlorination or chloramination. Trichloronitromethane formation after chlorination or chloramination, as measured by University of North Carolina (UNC), increased as a result of MP UV (Figure 4.7), most likely due to the formation of reactive nitrogen species from photolysis of nitrate by MP UV, and previously observed by Reckhow et al. (2010). Wilmington source water contained approximately 1 mg/L nitrate (as N).

Chloral hydrate formation was increased 30–35% with LP and MP UV treatment prior to chlorination, compared to chlorination alone. RPD between duplicate samples ranged from

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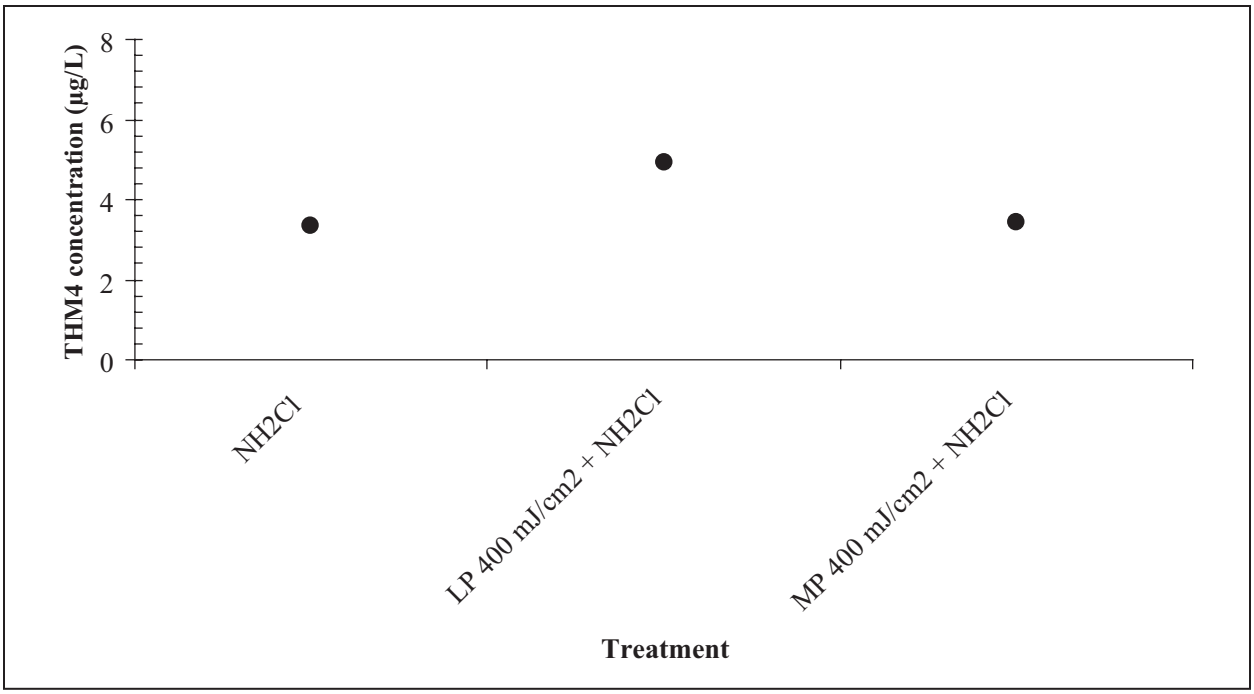


**Figure 4.4 THM4 formation in chloramine-treated Wilmington water with and without UV. Value shown represents average between duplicate samples (RPD = 0.5 to 10%). Bromoform was below the MRL (<0.1 µg/L).**

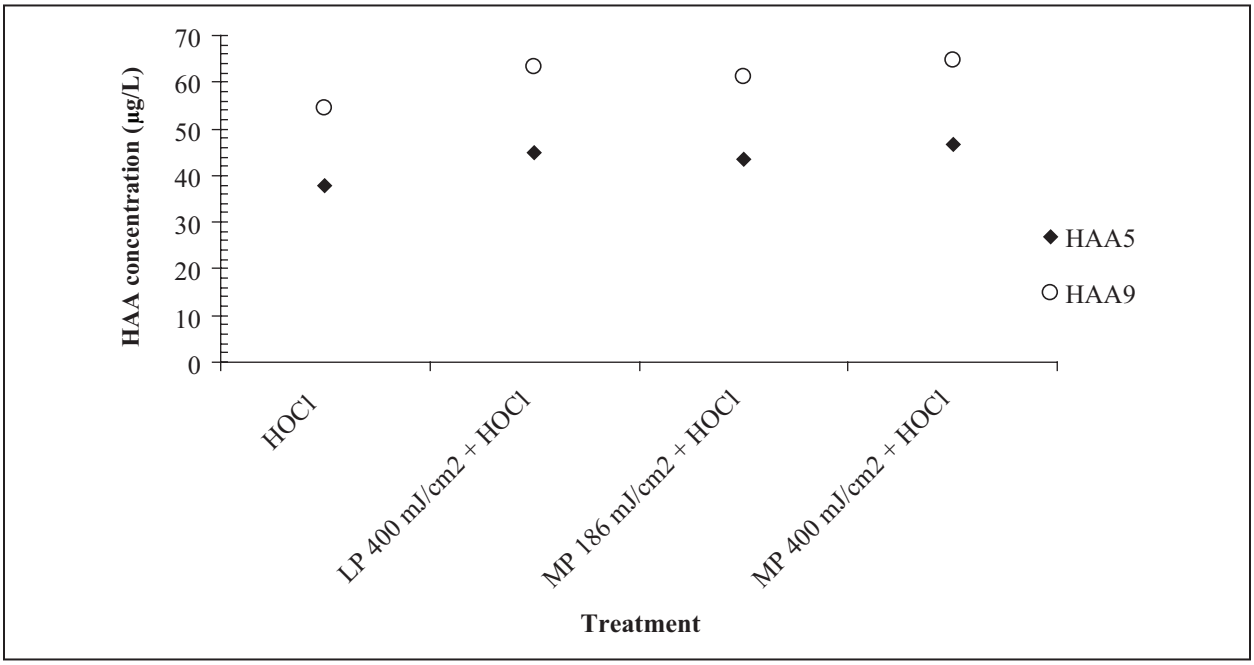


**Figure 4.5 HAA5 and HAA9 formation in Wilmington samples treated with UV and chlorine. Value shown represents average between duplicate samples (RPD = 2 to 7%). Dibromoacetic acid and tribromoacetic acid were below the MRL (<0.2 and <2.0 µg/L, respectively).**

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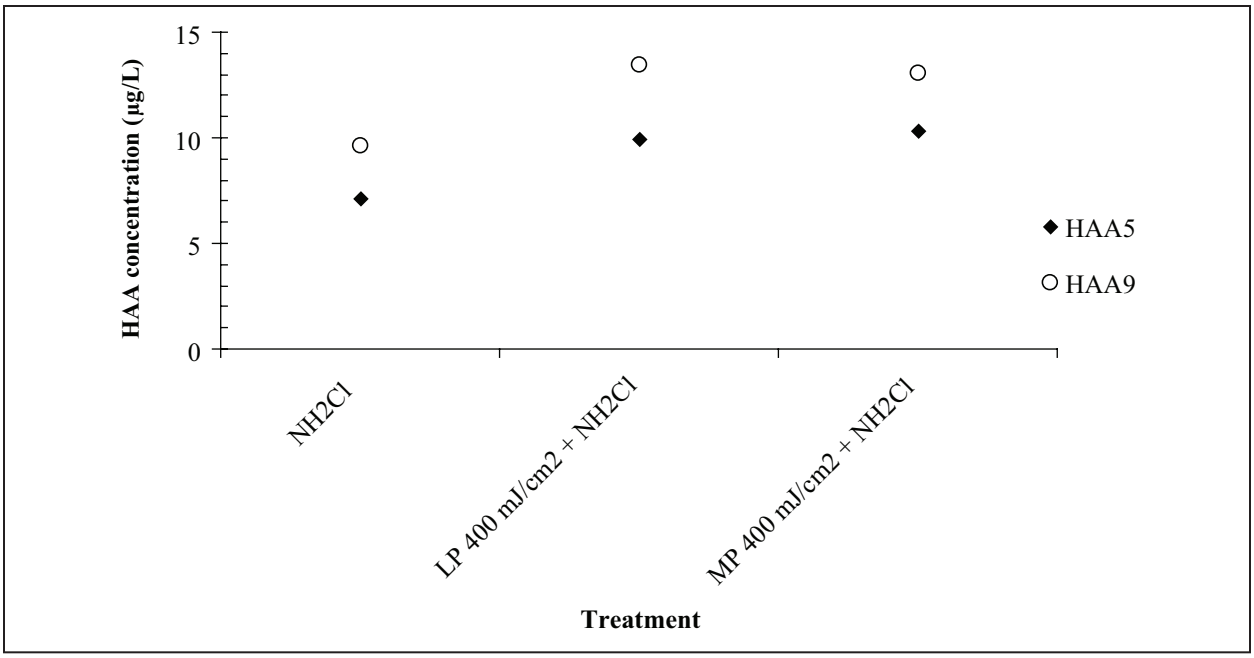


**Figure 4.6 HAA5 and HAA9 formation in Wilmington samples treated with UV and chloramine. Value shown represents average between duplicate samples (RPD = 5 to 7%). Bromoacetic acid, dibromoacetic acid, dibromochloroacetic acid, and tribromoacetic acid were below the MRL (<0.4, <0.2, <1.0, and <2.0 µg/L, respectively).**

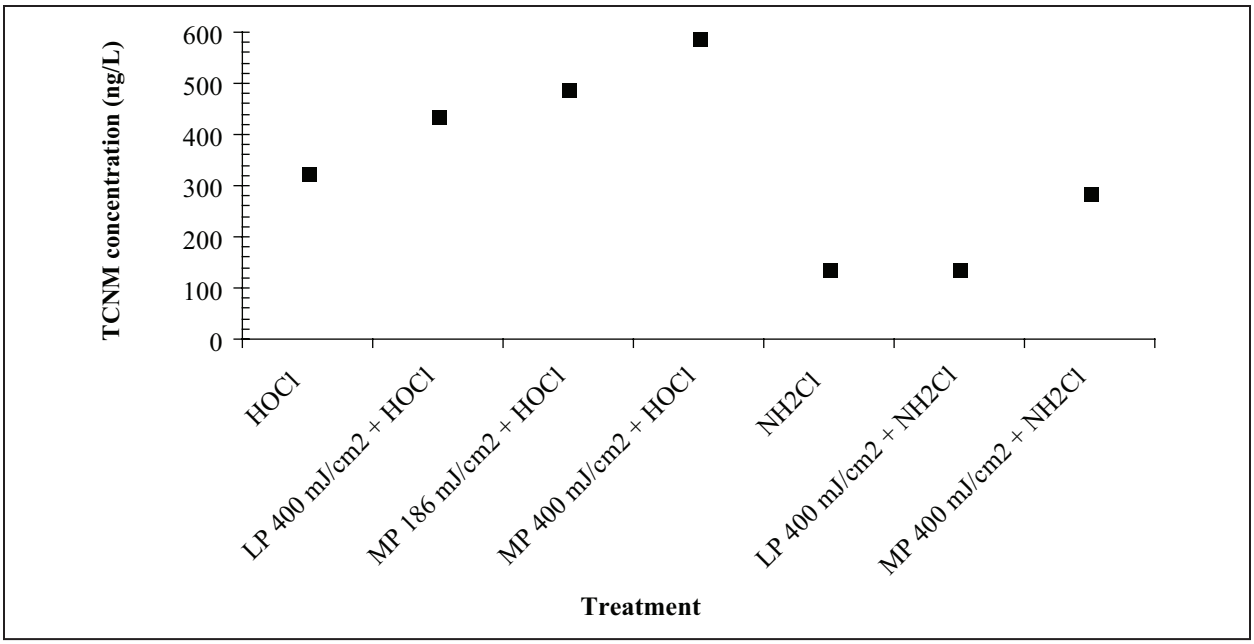


**Figure 4.7 Trichloronitromethane (TCNM) formation in Wilmington samples treated with UV and chlorine or chloramine. Value shown represents average between duplicate samples (RPD = 0.2 to 12%). (Note that concentration scale is in ng/L.)**

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**Table 4.1**
**Wilmington HAN and HNM results. One standard deviation of duplicate analyses is provided in the parentheses.**

| Lamp | Fluence (mJ/cm$^2$) | Post-oxidant | Oxidant dose (mg/L) | CAN (µg/L) | DCAN (µg/L) | TCAN (µg/L) | DCNM (µg/L) | CNM (µg/L) | TCNM (µg/L) |
|---|---|---|---|---|---|---|---|---|---|
| None | | $Cl_2$ | 5 | <0.2 | 0.81 (0.0001) | <0.46 | <0.26 | <0.36 | 0.67 (0.004) |
| MP | 260 | None | | <0.2 | <0.34 | <0.46 | <0.26 | <0.36 | <0.2 |
| MP | 121 | $Cl_2$ | 5 | <0.2 | 0.90 (0.002) | <0.46 | <0.26 | <0.36 | 0.75 (0.002) |
| MP | 260 | $Cl_2$ | 5 | <0.2 | 0.85 (0.004) | <0.46 | 0.29 (0.007) | <0.36 | 0.85 (0.006) |
| LP | 400 | $Cl_2$ | 5 | <0.2 | 0.85 (0.002) | <0.46 | <0.26 | <0.36 | 0.76 (0.007) |
| None | | $NH_2Cl$ | 3.5 | <0.2 | <0.34 | <0.46 | <0.26 | <0.36 | 0.46 (0.001) |
| LP | 400 | $NH_2Cl$ | 3.5 | <0.2 | <0.34 | <0.46 | <0.26 | <0.36 | 0.65 (0.002) |
| MP | 260 | $NH_2Cl$ | 3.5 | <0.2 | <0.34 | <0.46 | <0.26 | <0.36 | 0.68 (0.002) |

3–15%. Trichloroacetonitrile was not detected in Wilmington samples. Bromochloroacetonitrile and bromoform were below the MRL of 0.10 µg/L in chloraminated samples, but were formed in chlorinated samples, though UV did not affect their formation. Dichloro- and dibromo-acetonitrile were formed in both chlorinated and chloraminated samples but their formation was not impacted by UV pre-treatment. Formation of 1,1-dichloropropanone was higher in chloraminated samples compared to chlorinated samples (~1.5 µg/L compared to ~0.5 µg/L), unlike the other DBPs measured in Wilmington samples.

Yale University measured haloacetonitriles (HANs) and chlorinated halonitromethanes (HNMs) (Table 4.1). For HANs, only DCAN was detected, but only in the case of post-chlorination. Regardless of UV lamp type or fluence, the DCAN concentration detected did not differ remarkably from that detected during chlorination alone (at most 12%). We suggest that the mild difference is not likely to be significant.

As for the UNC analyses, trichloronitromethane was generally the most significant HNM. As for DCAN, no TCNM was detected in the absence of post-oxidation with chlorine or chloramines. For post-chlorination, we detected a 27% increase in TCNM with medium pressure exposures up through 260 mJ/cm$^2$. Even with low pressure UV exposures up to 400 mJ/cm$^2$ the increase in TCNM was much lower (12%). Chloramination alone formed roughly 30% less TCNM than did chlorination alone. Exposure to 260 mJ/cm$^2$ of medium pressure or 400 mJ/cm$^2$ of low pressure UV increased TCNM formation by ~50%. Note that levels are still below 1 µg/L in all cases.

No nitrosamines (NDMA, NMEA, NDEA, NDPA, NDBA, NPYR, or NPIP) were detected above 2 ng/L for any scenario.

### Case Study 3: California Water Agency Utilizing Delta Water (CWA-D)

To assess waters from different locations of the treatment process, grab samples were obtained from different locations at the California water agency utilizing Delta water pilot plant facility. Table 4.2 provides the codes by phase used to identify the source of the samples provided by CWA-D and the timeline for UV treatment and disinfection at Duke and subsequent extraction at UNC.

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**Table 4.2**
**Overview of CWA-D treatment and collection scheme**

| Phase | Date collected at CWA-D | CWA-D pilot plant location | Treated at Duke | Quenched | Extracted at UNC | |
|---|---|---|---|---|---|---|
| | | | | | HAA9 | Hal. vol. |
| 1A | 6/2/2008 | Ozone/GAC | 6/09/2008 | 6/10/2008 | 6/16/2008 | 6/12/2008 |
| 2A | 6/3/2008 | Ozone/peroxide/GAC | 6/11/2008 | 6/12/2008 | 6/17/2008 | 6/13/2008 |
| 1B | 6/9/2008 | Ozone/GAC | 6/22/2008 | 6/25/2008 | 7/02/2008 | 6/26/2008 |
| 2B | 6/10/2008 | Ozone/peroxide/GAC | 6/27/2008 | 6/30/2008 | 7/03/2008 | 7/01/2008 |
| 3A–FE | 6/30/2008 | Pre-nanofiltration (NF) | 7/11/2008 | 7/14/2008 | 7/17/2008 | 7/15/2008 |
| 3A–NF | 6/30/2008 | Post-NF | 7/21/2008 | 7/24/2008 | 8/01/2008 | 7/25/2008 |
| 3B–FE | 7/7/2008 | Pre-NF | 7/27/2008 | 7/30/2008 | 8/01/2008 | 7/31/2008 |
| 3B–NF | 7/7/2008 | Post-NF | 8/11/2008 | 8/14/2008 | NA | 8/15/2008 |

NA–not extracted; FE—filter effluent

**Table 4.3**
**Summary of water quality by organic parameters comparing measurements at CWA-D and UNC laboratories**

| | $UV_{254}$ (/cm) by UNC | $UV_{254}$ (/cm) by CWA-D | TOC (mg/L) by UNC | TOC (mg/L) by CWA-D | SUVA (L/mg-m) by UNC | SUVA (L/mg-m) by CWA-D |
|---|---|---|---|---|---|---|
| 1A | 0.0274 | 0.03 | 2.96 | 2.8 | 0.93 | 1.07 |
| 1B | 0.0298 | 0.04 | 2.86 | 2.8 | 1.04 | 1.43 |
| 2A | 0.0255 | 0.03 | 2.86 | 2.6 | 0.89 | 1.15 |
| 2B | 0.0224 | 0.04 | 2.96 | 2.8 | 0.76 | 1.43 |
| 3A-pre-NF | 0.0161 | 0.02 | 13.8 | 2.3 | 0.12 | 0.87 |
| 3A-post-NF | 0.0016 | 0.0 | 3.79 | 0.5 | 0.04 | 0.0 |
| 3B-pre-NF | 0.0159 | 0.02 | 13.4 | 2.3 | 0.12 | 0.87 |
| 3B-post-NF | 0.00179 | 0.0 | 4.10 | 0.5 | 0.04 | 0.0 |

Cells shaded appear to be anomalous readings

Tables 4.3 and 4.4 provide water quality data broken out by organic and inorganic parameters and comparing the analysis of samples performed upon receipt at the Duke and UNC laboratories with those provided by the CWA-D from their field analysis. TOC results at Duke/UNC were always higher than those provided by CWA-D and this results in a higher value for SUVA. The TOC results at Duke/UNC for all phase 3 samples are much higher than CWA-D values. These samples were reanalyzed but still generated the same higher values after dilution and use of a conversion factor so the reason for the differences are not known. The nitrate and bromide levels are sufficiently high to generate nitrogen and bromine-containing DBPs measurable by the analytical methods used in this study.

A reminder that the disinfection procedures carried out at the Duke laboratories were as follows: chlorination doses were selected from demand tests undertaken to calculate the does

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**Table 4.4**
**Summary of water quality by inorganic parameters comparing measurements at CWA-D and UNC laboratories**

| | Bromide (mg/L) by CWA-D | $NO_3^-$ (mg/L as N) by UNC | $NO_3^-$ (mg/L as N) by CWA-D | $NO_2^-$ (mg/L as N) by UNC |
|---|---|---|---|---|
| 1A | 0.4 | 0.71 | <2.0 | 0.51 |
| 1B | 0.5 | 0.76 | <2.0 | 0.37 |
| 2A | 0.4 | 0.65 | <2.0 | 0.40 |
| 2B | 0.6 | 0.50 | <2.0 | 0.26 |
| 3A-pre-NF | 0.4 | 2.28 | <2.0 | 3.07 |
| 3A-post-NF | 0.3 | 2.24 | <2.0 | 1.68 |
| 3B-pre-NF | 0.5 | 2.12 | <2.0 | 2.38 |
| 3B-post-NF | 0.3 | 2.07 | <2.0 | 1.58 |

required for a 1 mg/L free chlorine residual after 24 hours contact time (for phase 1A and 2A samples) and 72 hours contact time (for all other phases). Chloramination doses were generated without demand tests but by adjustment of the sample pH to 8.5, addition of free chlorine at 2 mg/L and held for 13 minutes before the addition of ammonium chloride to convert the free chlorine to monochloramine. Contact times were as described for chlorination. The residual disinfectants are presented in Table 4.5.

Results for DBP formation for these different test cases are presented in the following text.

### *THMs and HAAs*

For halogenated DBPs, the bromine-containing species were found at higher levels in comparison to those containing only chlorine, which indicates bromine incorporation during both chlorination and chloramination. In general, more pronounced differences between treatments were seen for the bromine-containing species, specifically bromodichloromethane, dibromochloromethane, bromoform, bromochloroacetonitrile, dibromoacetonitrile and dibromoacetic acid. Bromine-containing DBPs are of interest because they are more toxicologically potent than their chlorine-containing counterparts (Richardson et al., 2008).

For all phases, THM4 formation (Figures 4.8 and 4.9) increased three to four-fold in chlorinated compared to chloraminated samples, a trend that was expected based on previous research (Krasner et al., 1989). RPD between duplicate samples was less than 5%. In phases 1A and 1B THM4 was increased slightly (6–10%) with the addition of LP or MP UV prior to chlorination, which was likely not too significant with experimental precision taken into account. Compared to samples treated only with chlorine in phase 2B, THM4 formation was increased by 11% and 30% with the addition of 400 mJ/cm$^2$ LP or MP UV prior to chlorination, respectively. In phase 1A, THM4 formation increased 16% when 400 mJ/cm$^2$ MP UV treatment was added prior to chloramination, compared to chloramination alone. For chloramine-treated samples in phases 2A and 2B, THM4 formation did not change more than 10% with the addition of LP or MP UV.

All treated samples had significant bromine incorporation and HAA9 concentrations were two- to three-fold higher than HAA5. The biggest differences observed in HAA formation were

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**Table 4.5**
**Disinfectant residuals**

| | Phase 1A | | 1B | | 2A | | 2B | |
|---|---|---|---|---|---|---|---|---|
| Sample | free | combined | free | combined | free | combined | free | combined |
| No treatment | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $NH_2Cl$ | 0.0 | 1.05 | 0.0 | 1.67 | 0.0 | 2.18 | 0.0 | 2.13 |
| $Cl_2$ | 0.03 | 0.03 | 0.24 | 0.24 | 1.11 | 1.11 | 0.11 | 0.11 |
| LP400 $NH_2Cl$ | 0.0 | 1.54 | 0.0 | 1.74 | 0.0 | 1.89 | 0.0 | 2.44 |
| MP400 $NH_2Cl$ | 0.0 | 1.27 | 0.0 | 1.66 | 0.0 | 1.75 | 0.0 | 2.61 |
| MP400 $Cl_2$ | 0.02 | 0.02 | 0.06 | 0.06 | 1.3 | 1.3 | 0.22 | 0.22 |
| MP100 $NH_2Cl$ | 0.0 | 1.27 | 0.0 | 1.6 | 0.0 | 1.99 | 0.0 | 2.54 |
| LP400 $Cl_2$ | 0.17 | 0.17 | 0.21 | 0.21 | 1.2 | 1.2 | 0.23 | 0.23 |
| | Phase 3A-preNF | | 3A-post NF | | 3B-pre NF | | 3B-post NF | |
| Sample | free | combined | free | combined | free | combined | free | combined |
| No treatment | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $NH_2Cl$ | 0.0 | 2.74 | 0.0 | 0.83 | 0.0 | 2.17 | 0.0 | 0.57 |
| $Cl_2$ | 1.19 | 1.19 | 2.87 | 2.87 | 0.02 | 0.02 | 1.67 | 1.67 |
| LP400 $NH_2Cl$ | 0.0 | 2.55 | 0.0 | 0.67 | 0.0 | 1.53 | 0.0 | 0.32 |
| MP400 $NH_2Cl$ | 0.0 | 2.76 | 0.0 | 0.61 | 0.0 | 1.59 | 0.0 | 0.42 |
| MP400 $Cl_2$ | 1.08 | 1.08 | 3.03 | 3.03 | 1.53 | 1.53 | 1.72 | 1.72 |
| MP100 $NH_2Cl$ | 0.0 | 2.08 | 0.0 | 0.49 | 0.0 | 1.56 | 0.0 | 1.29 |
| LP400 $Cl_2$ | 0.95 | 0.95 | 3.0 | 3.0 | 1.4 | 1.4 | 1.7 | 1.7 |

between samples treated with chlorine compared to those treated with monochloramine, where HAA9 increased by 60–200%, regardless of UV treatment (Figures 4.10 and 4.11). In Phase 1A, no significant differences in DBP formation with either chlorine or chloramine were observed when preceded with UV irradiation, but in Phase 1B, addition of 400 mJ/cm$^2$ LP or MP UV prior to chlorination increased HAA9 formation by 25% and 20%, respectively. The addition of 400 mJ/cm$^2$ MP UV prior to chloramination increased HAA9 formation by 19% in phase 1B. RPD between duplicates was <15%. In Phases 2A and 2B, UV treatment did not significantly affect the formation of HAAs.

### *Nitrosamines, Dimethylnitramine, Haloacetonitriles, and Halonitromethanes*

The objective of this section was to assess the formation of various N-DBPs after UV treatment and post-chlorination or post-chloramination of CWA-D samples from various sampling points and time periods. The results are broken down into the different phases of treatment and are described in detail below.

### *Phases 1A and 1B*

For the Phase 1A and 1B post-ozonation sampling events (Tables 4.2 and 4.3), formation of CAN, TCAN and HNMs was never important. During Phase 1B, DCAN formation was detectable

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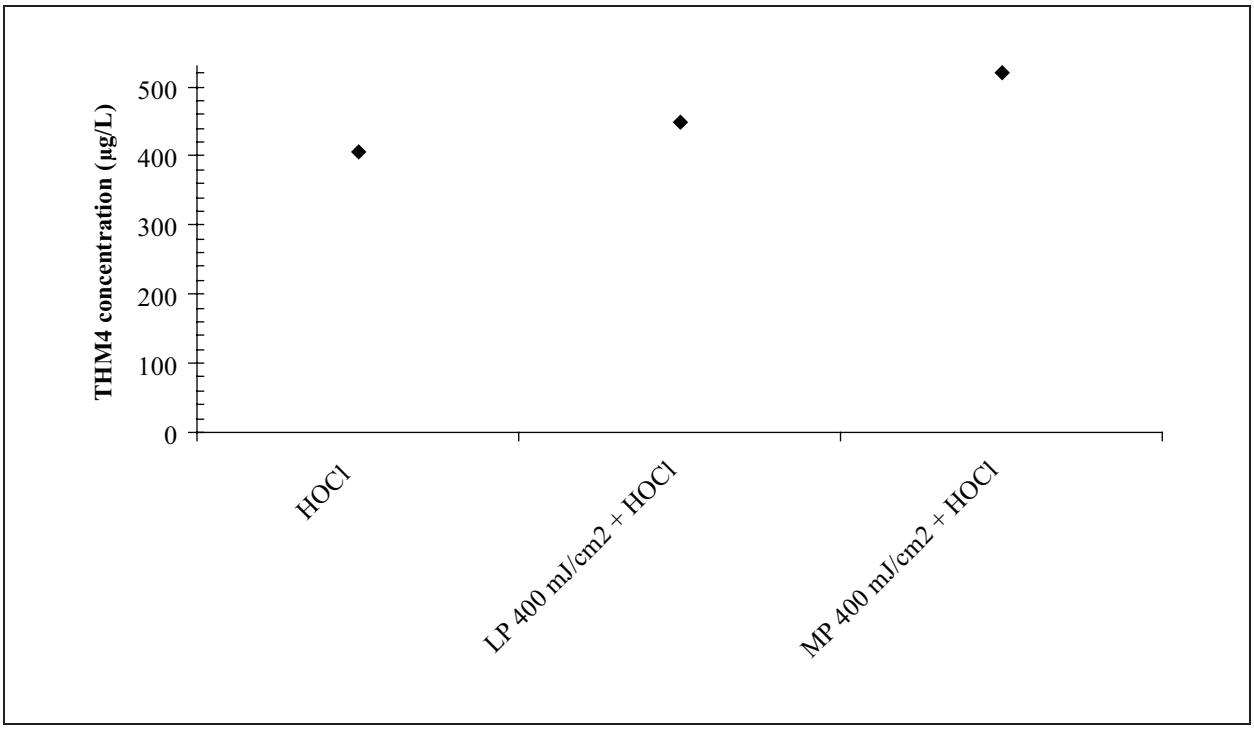


**Figure 4.8 THM4 formation in chlorinated CWA-D Phase 2B samples. Value shown represents average between duplicate samples (RPD <5%).**

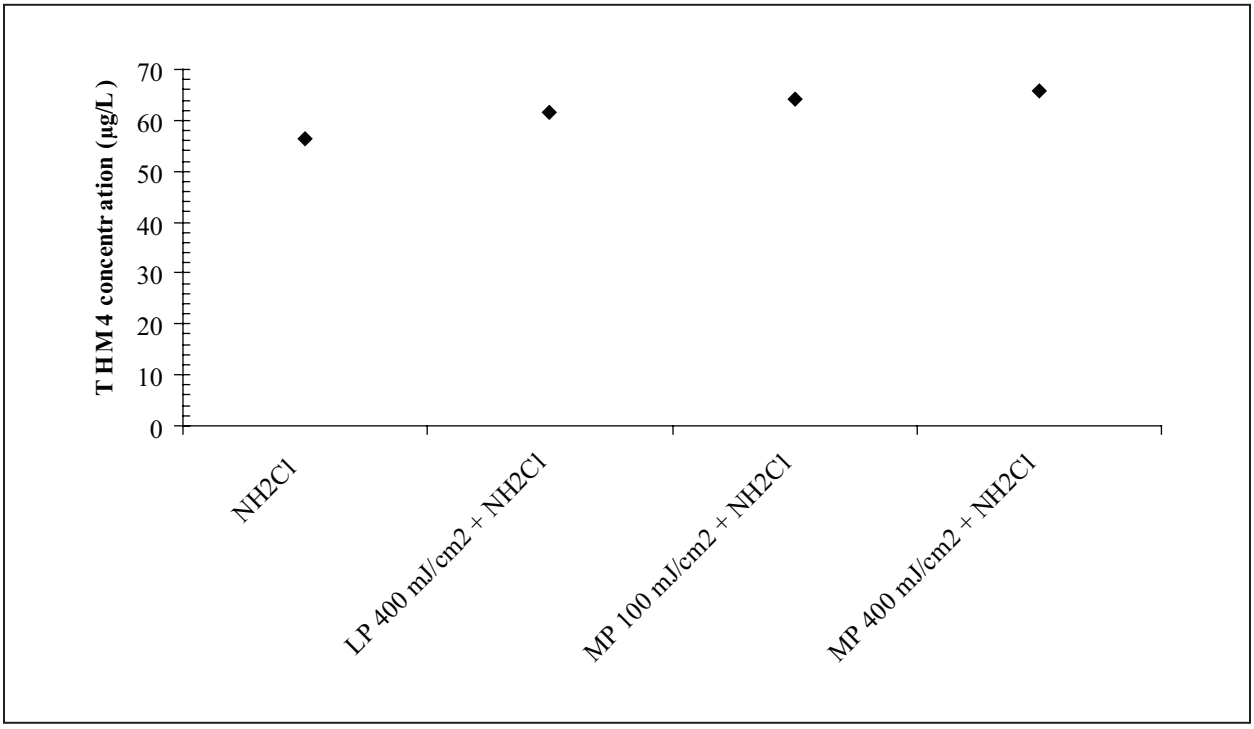


**Figure 4.9 THM4 formation in chloraminated CWA-D Phase 1A samples. Value shown represents average between duplicate samples (RPD <5%).**

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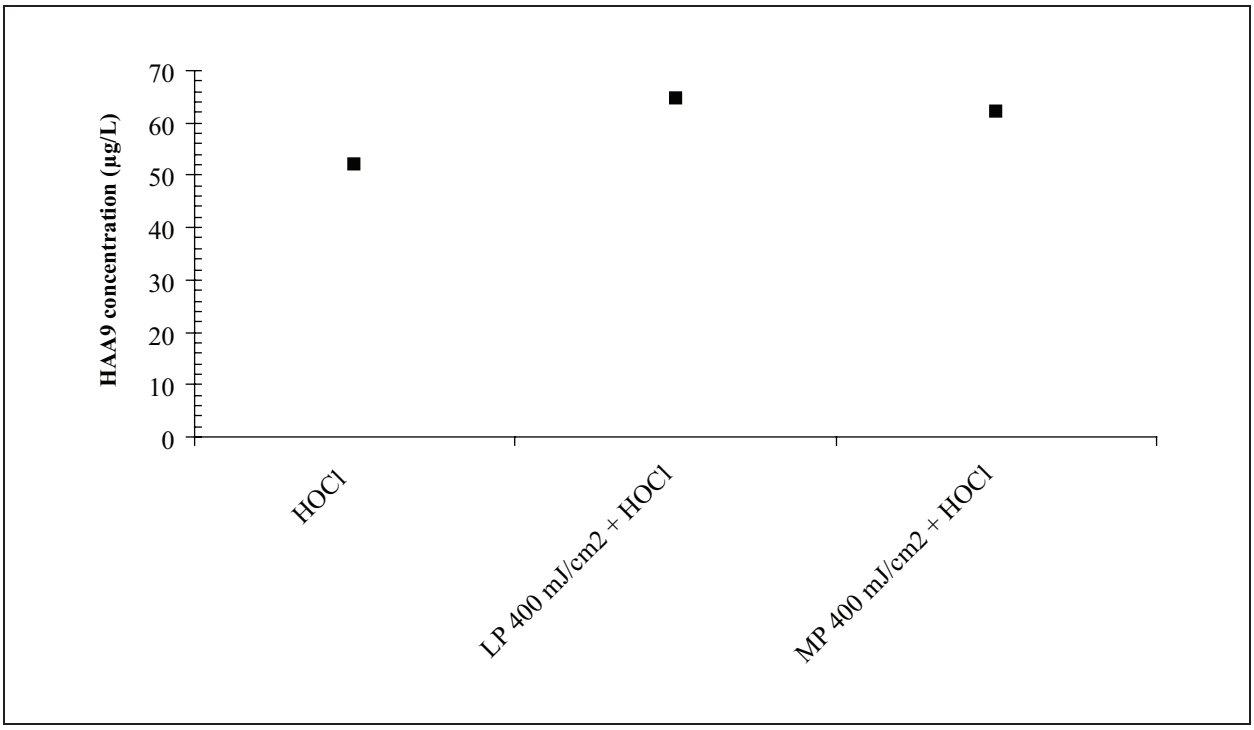


**Figure 4.10 HAA9 formation in chlorinated CWA-D Phase 1B samples. Value shown represents average between duplicate samples (RPD <15%).**

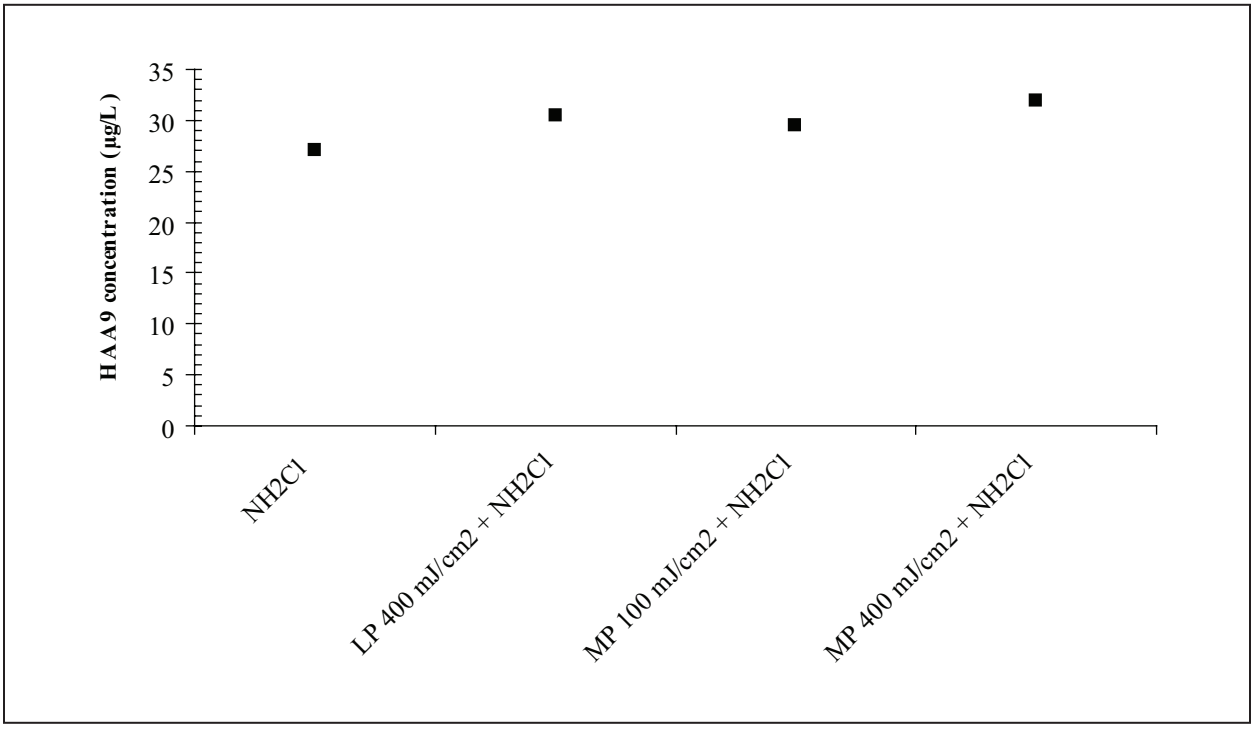


**Figure 4.11 HAA9 formation in chloraminated CWA-D Phase 1B samples. Value shown represents average between duplicate samples (RPD <15%).**

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and was higher for post-chlorination than post-chloramination. Regardless of lamp type or fluence during post-chloramination scenarios, UV pre-treatment promoted a modest enhancement in DCAN formation (~25%). For post-chlorination scenarios, the enhancement in DCAN formation associated with UV pre-treatment was much less important.

Regarding nitrosamines and dimethylnitramine, only NDMA and dimethylnitramine were detectable during these phases, usually during application of chloramines downstream. The results indicate that application of low pressure UV upstream may decrease NDMA formation associated with post-chloramination. On the other hand, application of medium pressure UV upstream either diminished this destruction or slightly enhanced NDMA formation. However, the highest NDMA concentration measured during these phases was for 400 mJ/cm$^2$ low pressure UV upstream coupled with chlorination downstream. This result conflicts with the trends described above. Dimethylnitramine was detected in a few cases. No other nitrosamines were detected.

### *Phases 2A and 2B*

As for Phases 1A and 1B, formation of CAN, TCAN and HNMs was never important for the Phases 2A and 2B post ozonation/hydrogen peroxide AOP treatment scenarios (Tables 4.4 and 4.5). In contrast to Phases 1A and 1B, DCAN formation was more pronounced for post-chloramination scenarios than for post-chlorination. During post-chloramination, low-pressure UV treatment may have enhanced DCAN formation by ~50%. As for Phases 1A and 1B, NDMA formation was primarily associated with post-chloramination scenarios, dimethylnitramine was detected in a few cases, and no other nitrosamines were detected. During post-chloramination, low pressure UV treatment upstream appeared to reduce nitrosamine formation. As for Phases 1A and 1B, medium pressure UV treatment upstream either enhanced NDMA formation, or moderated NDMA destruction when coupled with post-chloramination.

### *Phases 3A and 3B*

During Phases 3A and 3B, whether sampled upstream or downstream of nanofiltration, formation of HANs, HNMs and dimethylnitramine was never important for any combination of UV, chlorine or chloramines (Tables 4.6–4.13). NDMA formation was occasionally observed, but concentrations were always near the 2 ng/L detection limit and no significant trends were observed. No other nitrosamines were detected with the exception of a limited number of detections of NDEA during Phase 3B post-nanofiltration.

### *Other DBPs*

Trichloroacetonitrile and trichloronitromethane were not detected in any samples of the CWA-D case study. The two haloketones, 1,1-dichloropropanone (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP), were only detected in phases 1A and 2A, which suggests that they form within 24 hours and may not be stable over 72 hours. Yang et al. (2007) found a similar trend, with a maximum concentration of 1,1,1-trichloropropanone formed within 7 hours followed by a continuous decrease with increasing chlorine contact time. In Phase 1A, 1,1-DCP and 1,1,1-TCP formation (and in Phase 2A, 1,1-DCP formation) was higher in chloraminated samples compared to those treated with chlorine, a trend not observed for any other measured species. This result is

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**Table 4.6**
**CWA-D Phase 1A results: Ozone. One standard deviation of duplicate analyses is provided in the parentheses.**

| Lamp | Fluence mJ/cm$^2$ | Post-oxidant | Oxidant dose mg/L | CAN µg/L | DCAN µg/L | TCAN µg/L | DCNM µg/L | CNM µg/L | TCNM µg/L | NDMA µg/L | DMNA µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|
| None | | None | 5 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| None | | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 3.7 (0.1) | <2 |
| None | | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| LP | 400 | CWA-D | | <0.2 | 0.52 (0.003) | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| MP | 400 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 3.1 (0.3) | <2 |
| MP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| MP | 100 | CWA-D | | 0.8 (0.008) | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 2.7 (0.05) | <2 |
| LP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |

**Table 4.7**
**CWA-D Phase 1B results: Ozone. One standard deviation of duplicate analyses is provided in the parentheses.**

| Lamp | Fluence mJ/cm$^2$ | Post-oxidant | Oxidant dose mg/L | CAN µg/L | DCAN µg/L | TCAN µg/L | DCNM µg/L | CNM µg/L | TCNM µg/L | NDMA µg/L | DMNA µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|
| None | | None | 5 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| None | | CWA-D | | <0.2 | 0.42 (0.009) | <0.5 | <0.4 | <0.4 | <0.5 | 2.5 (0.3) | <2 |
| None | | $Cl_2$ | 1 | <0.2 | 0.79 (0.028) | <0.5 | <0.4 | <0.4 | <0.5 | BB | BB |
| LP | 400 | CWA-D | | <0.2 | 0.54 (0.005) | <0.5 | <0.4 | <0.4 | <0.5 | 2.78 (0.2) | 2.2 (0.4) |
| MP | 400 | CWA-D | | <0.2 | 0.54 (0.011) | <0.5 | <0.4 | <0.4 | <0.5 | 3.4 (0.03) | 3.2 (1.8) |
| MP | 400 | $Cl_2$ | 1 | <0.2 | 0.76 (0.031) | <0.5 | <0.4 | <0.4 | <0.5 | BB | BB |
| MP | 100 | CWA-D | | <0.2 | 0.56 (0.015) | <0.5 | <0.4 | <0.4 | <0.5 | 3.1 (0.1) | <2 |
| LP | 400 | $Cl_2$ | 1 | <0.2 | 0.87 (0.054) | <0.5 | <0.4 | <0.4 | <0.5 | 5.0 (0.3) | <2 |

BB = broken bottle

**Table 4.8**
**CWA-D Phase 2A results: Ozone/$H_2O_2$. One standard deviation of duplicate analyses is provided in the parentheses.**

| Lamp | Fluence mJ/cm$^2$ | Post-oxidant | Oxidant dose mg/L | CAN µg/L | DCAN µg/L | TCAN µg/L | DCNM µg/L | CNM µg/L | TCNM µg/L | NDMA µg/L | DMNA µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|
| None | | None | 5 | <0.2 | 0.26 (0.006) | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| None | | CWA-D | | <0.2 | 0.43 (0.002) | <0.5 | <0.4 | <0.4 | <0.5 | 4.3 (0.5) | <2 |
| None | | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| LP | 400 | CWA-D | | <0.2 | 0.62 (0.012) | <0.5 | <0.4 | <0.4 | <0.5 | 3.5 (0.3) | <2 |
| MP | 400 | CWA-D | | <0.2 | 0.45 (0.011) | <0.5 | <0.4 | <0.4 | <0.5 | 7.0 (1.2) | <2 |
| MP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| MP | 100 | CWA-D | | <0.2 | 0.43 (0.013) | <0.5 | <0.4 | <0.4 | <0.5 | 5.3 (0.4) | <2 |
| LP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |

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**Table 4.9**
**CWA-D Phase 2B results: Ozone/$H_2O_2$. One standard deviation of duplicate analyses is provided in the parentheses.**

| Lamp | Fluence mJ/cm$^2$ | Post-oxidant | Oxidant dose mg/L | CAN µg/L | DCAN µg/L | TCAN µg/L | DCNM µg/L | CNM µg/L | TCNM µg/L | NDMA µg/L | DMNA µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|
| None | | None | 5 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 2.0 (0.5) | <2 |
| None | | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 6.1 (0.3) | <2 |
| None | | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 2.0 (0.1) | 2.4 (1.0) |
| LP | 400 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 4.4 (0.6) | 2.5 (0.4) |
| MP | 400 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 6.3 (0.5) | 2.1 (0.4) |
| MP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| MP | 100 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 4.2 (0.8) | <2 |
| LP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 3 | <2 |

**Table 4.10**
**CWA-D Phase 3A results: Pre-nanofiltration. One standard deviation of duplicate analyses is provided in the parentheses.**

| Lamp | Fluence mJ/cm$^2$ | Post-oxidant | Oxidant dose mg/L | CAN µg/L | DCAN µg/L | TCAN µg/L | DCNM µg/L | CNM µg/L | TCNM µg/L | NDMA µg/L | DMNA µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|
| None | | None | 5 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | EE | EE |
| None | | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | EE | EE |
| None | | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 3.3 (0.2) | EE |
| LP | 400 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 2.5 (2.1) | EE |
| MP | 400 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | EE | EE |
| MP | 400 | $Cl_2$ | 1 | BB | BB | BB | BB | BB | BB | 2.5 (0.9) | <2 |
| MP | 100 | CWA-D | | NQ | NQ | NQ | NQ | NQ | NQ | BB | BB |
| LP | 400 | $Cl_2$ | 1 | BB | BB | BB | BB | BB | BB | BB | BB |

NQ = not quantifiable, too much interference in the chromatogram
EE = experimental error
BB = broken bottle

**Table 4.11**
**CWA-D Phase 3A results: Post-nanofiltration. One standard deviation of duplicate analyses is provided in the parentheses.**

| Lamp | Fluence mJ/cm$^2$ | Post-oxidant | Oxidant dose mg/L | CAN µg/L | DCAN µg/L | TCAN µg/L | DCNM µg/L | CNM µg/L | TCNM µg/L | NDMA µg/L | DMNA µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|
| None | | None | 5 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | EE | EE |
| None | | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | EE | EE |
| None | | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | NQ | NQ | <0.5 | EE | EE |
| LP | 400 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | EE | EE |
| MP | 400 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | EE | EE |
| MP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | NQ | NQ | <0.5 | EE | EE |
| MP | 100 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | EE | EE |
| LP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | NQ | NQ | <0.5 | EE | EE |

NQ = not quantifiable, too much interference in the chromatogram
EE = experimental error

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**Table 4.12**
**CWA-D Phase 3B results: Pre-nanofiltration. One standard deviation of duplicate analyses is provided in the parentheses.**

| Lamp | Fluence mJ/cm$^2$ | Post-oxidant | Oxidant dose mg/L | CAN µg/L | DCAN µg/L | TCAN µg/L | DCNM µg/L | CNM µg/L | TCNM µg/L | NDMA µg/L | DMNA µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|
| None | | None | 5 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| None | | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| None | | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | NQ | NQ | <0.5 | <2 | <2 |
| LP | 400 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 3.5 (0.3) | <2 |
| MP | 400 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 2.7 (0.6) | <2 |
| MP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | NQ | NQ | <0.5 | <2 | <2 |
| MP | 100 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| LP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | NQ | NQ | <0.5 | <2 | <2 |

NQ = not quantifiable, too much interference in the chromatogram

**Table 4.13**
**CWA-D Phase 3B results: Post-nanofiltration. One standard deviation of duplicate analyses is provided in the parentheses.**

| Lamp | Fluence mJ/cm$^2$ | Post-oxidant | Oxidant dose mg/L | CAN µg/L | DCAN µg/L | TCAN µg/L | DCNM µg/L | CNM µg/L | TCNM µg/L | NDMA µg/L | DMNA µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|
| None | | None | 5 | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | 3.5 |
| None | | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | 2.3 | 4.7 |
| None | | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | NQ | NQ | <0.5 | 2.8 | <2 |
| LP | 400 | CWA-D | | 0.21 (0.01) | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | 4.4 |
| MP | 400 | CWA-D | | 0.21 (0.01) | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | 2.7 |
| MP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | NQ | NQ | <0.5 | <2 | <2 |
| MP | 100 | CWA-D | | <0.2 | <0.4 | <0.5 | <0.4 | <0.4 | <0.5 | <2 | <2 |
| LP | 400 | $Cl_2$ | 1 | <0.2 | <0.4 | <0.5 | NQ | NQ | <0.5 | <2 | <2 |

NQ = not quantifiable, too much interference in the chromatogram

not surprising because haloketones have been shown to be stable in the presence of monochloramine, but when free chlorine is present, further oxidation to yield chloroform takes precedence (Reckhow and Singer, 1985; Yang et al., 2007). Dichloro- and bromochloroacetonitrile formation did not change significantly between chloraminated and chlorinated samples in Phase 1A, but did increase slightly in Phase 1B, perhaps due to the difference in contact times. In phases 2A and 2B, bromochloro- and dibromoacetonitrile formation was higher in chlorinated compared to chloraminated samples. UV treatment did not significantly affect the formation of detectable haloketones or haloacetonitriles. RPD between duplicate haloacetonitrile samples ranged from 0.1 to 16%.

## SUMMARY

The impacts of UV on DBP formation observed in this case study were slight, but suggest that at high doses (400 mJ/cm$^2$), the addition of LP or MP UV prior to chlorination or chloramination

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can occasionally increase the formation of THMs and HAAs by ~10–20%. Treatment with MP UV upstream of chlorination or chloramination increased trichloronitromethane formation by ~20–50%, but LP UV pre-treatment did not show a similar effect. At one plant (Wilmington, NC), LP or MP UV treatment followed by chlorination increased chloral hydrate formation by ~30%. Overall, these results indicated that UV treatment may increase the formation of certain DBPs, although generally by ≤25%. These trends and mechanisms were further investigated using NOM isolates that allowed for controlled batch reactions at elevated disinfectant dose to DOC ratios on carbon fractionated by polarity (see Chapter 6); these conditions represent challenge conditions to validate the trends observed at the treatment plants.

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# CHAPTER 5
# INFLUENCE OF BROMIDE AND NITRATE ON DISINFECTION BY-PRODUCTS FORMED DURING UV-CHLORINE/CHLORAMINE SEQUENCE IN TREATED DRINKING WATERS

## OVERVIEW

When UV light is absorbed by inorganic species they can become excited and/or cause oxidation/reduction reactions to occur. Selected inorganic species have been shown via direct precursors (e.g., bromide) or indirect precursors (e.g., nitrate) to impact regulated and unregulated DBP formation. Using treated but not disinfected drinking waters collected from notably different watersheds, the influence of elevated concentrations of bromide and nitrate were studied. Evaluation of the two treated water samples focused on determining changes in 24-hour chlorine/monochloramine demand and DBPs at varied UV doses, two in the disinfection range and two at higher UV doses.

## RESULTS

The results are sorted into two case studies; (1) Longmont WTP filter effluent and (2) Cincinnati conventionally treated (filtered, no GAC) WTP effluent. These two case studies subjected treated drinking water to numerous UV doses and evaluated the effect of elevated bromide and nitrate on the resulting formation of DBPs. Both conventionally treated (e.g., as collected from the WTP after filtration) waters (CONV) and inorganic precursor fortified waters (FCONV) (e.g., CONV samples spiked with 500 µg/L bromide and 8 mg-N/L nitrate]) were treated with UV irradiation.

### Case Study 1: Longmont WTP Filter Effluent

Treated (coagulation/flocculation, sedimentation, and filtration) but not disinfected water from the Nelson Flanders drinking water treatment plant in Longmont, CO, was collected and studied herein. The facility treats water from the St. Vrain watershed and at the time of sampling there was no industrial, agricultural, or wastewater inputs. Table 5.1 presents water quality of the collected sample. The sample contained very low concentrations of inorganics such as bromide and was very low in alkalinity.

#### *Free Chlorine and Chloramine Demand*

24 hour free chlorine and monochloramine demand increased as UV dose increased. The change in chlorine/chloramines demand was not notably different between lamp types in the CONV water samples for free chlorine preceded by UV doses less than 500 mJ/cm$^2$ and for all monochloramine dosed samples. When fortified with 500 µg/L bromide and 8 mg-N/L nitrate the initial demand increased and greater increases in demand were observed with increasing applied UV dose. In FCONV samples, MPUV treated samples were determined to have greater demands than LPUV. Some of this demand was likely attributed to the formation of nitrite which will react



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**Table 5.1**
**Water quality of Longmont filter effluent**

| Parameter | Units | Value |
|---|---|---|
| pH | — | 7.1 |
| Bromide | µg/L | 7.9 |
| Iodide | µg/L | 3.5 |
| Alkalinity | mg-$CaCO_3$/L | 8 |
| Total Organic Carbon | mg-C/L | 1.56 |
| Total Nitrogen | µg-N/L | 174 |
| $UV_{254}$ | $cm^{-1}$ | 0.038 |

**Table 5.2**
**Chlorine and monochloramine demand for Longmont filter effluent**

| UV Dose ($mJ/cm^2$) | LP | MP | LP | MP |
|---|---|---|---|---|
| | CONV | | FCONV | |
| Free Chlorine (mg-$Cl_2$/L) | | | | |
| 0 | 1.19 | | 1.61 | |
| 40 | 1.18 | 1.14 | 1.75 | 1.70 |
| 186 | 1.30 | 1.33 | 1.71 | 1.88 |
| 300 | 1.23 | 1.30 | 1.65 | 2.03 |
| 1000 | 1.34 | 1.50 | 1.93 | 2.54 |
| Monochloramine (mg-$Cl_2$/L) | | | | |
| 0 | 0.39 | | 0.58 | |
| 40 | 0.34 | 0.48 | 0.52 | 0.70 |
| 186 | 0.60 | 0.44 | 0.60 | 0.74 |
| 300 | 0.44 | 0.48 | 0.60 | 0.88 |
| 1000 | 0.59 | 0.54 | 0.86 | 1.20 |

Values shown are the average of duplicate tests.

with chlorine to reform nitrate. At disinfection doses (<186 $mJ/cm^2$) minor increases in chlorine demand were observed (0.1–0.2 mg-$Cl_2$/L). Free chlorine and monochloramine demands are presented in Table 5.2.

### *HAAs*

Aside from a few cases, no notable trends resulting from UV treatment were observed for haloacetic acids. As shown in Figures 5.1 and 5.2, the formation of trichloroacetic acid decreased with increasing MP UV dose in CONV samples that were subsequently treated with chlorine and formation of bromochloroacetic acid increased with increasing MP UV dose in FCONV samples. Relative percent difference between duplicate samples ranged from 5–15%. In chlorinated samples, HAA9 formation was less than 40 µg/L and HAA5 formation was less than 30 µg/L. During chloramination of the CONV sample, dichloroacetic acid was the only HAA9 species formed.

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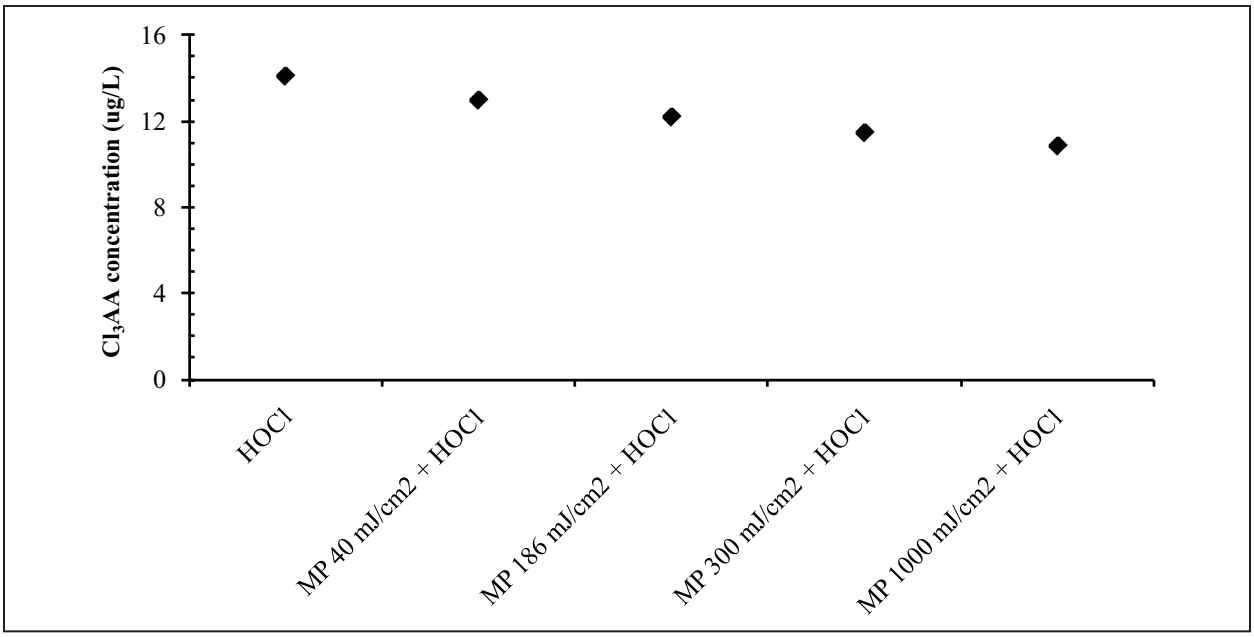


**Figure 5.1 Effect of MP UV followed by chlorination on the formation of trichloroacetic acid ($Cl_3AA$) in CONV Longmont samples**

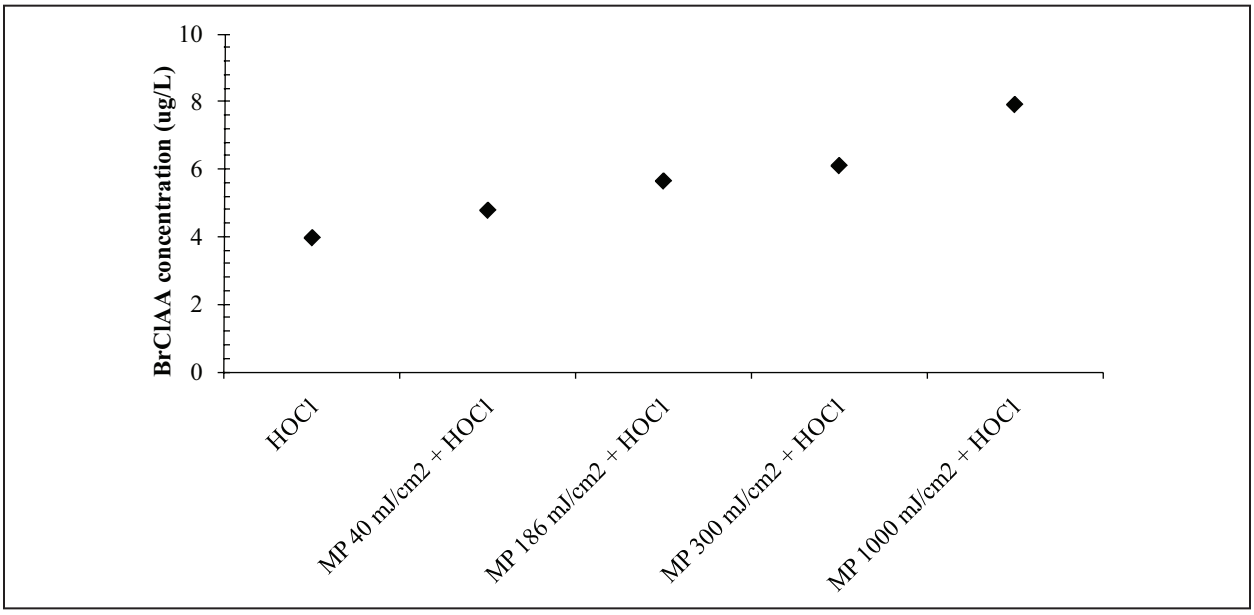


**Figure 5.2 Effect of MP UV followed by chlorination on the formation of bromochloroacetic acid (BrClAA) in FCONV Longmont samples**

Even in bromide-spiked samples, chloramination formed less than 4 µg/L HAA9. Compared to CONV samples, FCONV samples containing bromide and nitrate had lower formation of HAA5 but higher HAA9, due to the shift towards bromine-containing species. The formation of haloacetamides was not affected by UV treatment prior to chlorination. Haloacetamides were below the MRL in chloraminated samples.

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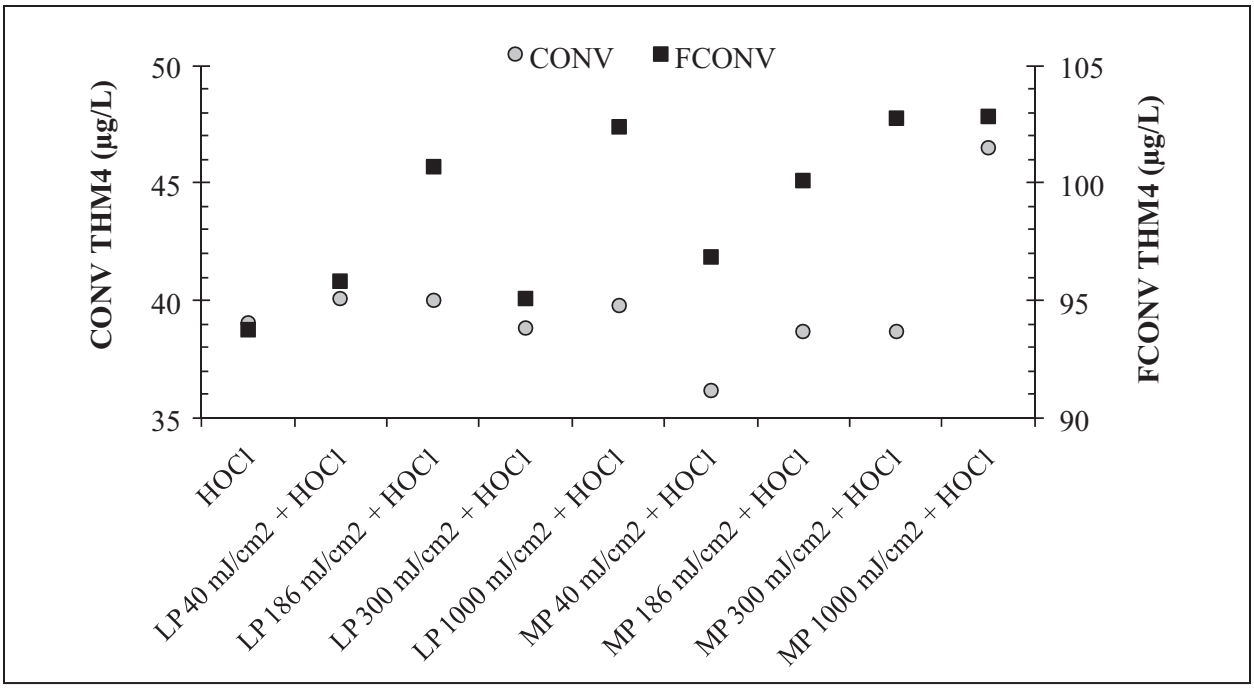


**Figure 5.3 Effect of LP and MP UV followed by chlorination on the formation of THM4 in the presence/absence of bromide and nitrate**

### *THMs and Emerging Halogen- and Nitrogen-Containing DBPs*

In CONV samples, chloroform formation increased by 20%, but the RPD between experimental duplicate samples ranged from less than 0.5% to 16%, so the changes observed in THM4 formation with 1000 mJ/cm$^2$ MP UV followed by chlorination were close to that of experimental error. It should be noted that the replicates for these samples were experimental duplicates (two solutions UV treated and chlorinated/chloraminated separately) rather than analytical duplicates (for which the error is usually smaller, less than 5%). Bromide- and nitrate-fortification more than doubled THM4 formation compared to the ambient samples and shifted speciation to the more bromine-containing THMs although UV treatment had negligible effect on the levels in the treated waters. These results are shown in Figure 5.3.

### *Iodo-THMs*

During chloramination, the formation of iodine-containing THMs (iodo-THMs) was observed, though the source of iodine is not clear and may have been contributed by something in the methods used. Despite this experimental uncertainty, the presence of iodine in the samples provided an opportunity to study iodo-THMs. Ambient iodide in CONV Longmont water was about 3.5 µg/L and ranged from 0.75 to 1.45 µg/L after UV irradiation (prior to chlorination/chloramination). This decrease in iodide is not enough to account for the levels of iodo-THMs formed (up to 32 µg/L as $I^-$). The phosphate buffer solution contributed less than 0.05 µg/L iodide and chlorine/monochloramine solutions contributed less than 0.4 µg/L iodide, and thus at the volumes added these are unlikely contributors. Formation of iodo-THMs has been typically observed when

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**Table 5.3**
**Formation of iodo-THMs (µg/L) in Longmont chloraminated samples. Samples for which RPD was less than 25% are shown here.**

| Sample | $Cl_3CH$ | $BrCl_2CH$ | $Br_2ClCH$ | $Cl_2ICH$ | $Br_3CH$ | $BrClICH$ | $Br_2ICH$ | $ClI_2CH$ | $BrI_2CH$ | $I_3CH$ | ∑THM4 | ∑THM10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $NH_2Cl$ alone | 1.2 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 1.2 | 1.2 |
| LP 186 mJ/cm$^2$ + $NH_2Cl$ | <0.1 | <0.1 | <0.1 | 4.9 | <0.1 | 1 | <0.1 | 5.9 | <0.1 | 23.6 | <0.10 | 35 |
| LP 300 mJ/cm$^2$ + $NH_2Cl$ | <0.1 | <0.1 | <0.1 | 0.9 | <0.1 | <0.1 | <0.1 | 2.5 | <0.1 | 6.3 | <0.10 | 9.7 |
| MP 40 mJ/cm$^2$ + $NH_2Cl$ | <0.1 | <0.1 | <0.1 | 2.5 | <0.1 | <0.1 | <0.1 | 4.1 | <0.1 | 16.5 | <0.10 | 23.2 |
| MP 1000 mJ/cm$^2$ + $NH_2Cl$ | 1.7 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 1.4 | <0.1 | 1.3 | 6.2 | 6.2 |
| Fortified $NH_2Cl$ alone | <0.1 | 2.7 | 2.3 | <0.1 | 1.3 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 6.2 | 6.2 |
| Fortified, LP 186 mJ/cm$^2$ + $NH_2Cl$ | <0.1 | 1.7 | 1.3 | 0.6 | 1 | 1.9 | 2.2 | 2 | 5.7 | 4.7 | 4 | 21.2 |
| Fortified, LP 300 mJ/cm$^2$ + $NH_2Cl$ | <0.1 | 0.9 | 0.6 | 1.6 | 0.5 | 2.8 | 2.6 | 3.9 | 7.6 | 15.5 | 2 | 36 |
| Fortified, MP 40 mJ/cm$^2$ + $NH_2Cl$ | <0.1 | 2.4 | 1.9 | 0.2 | 1.1 | 1.3 | 1 | 0.2 | 2 | <0.1 | 5.5 | 10.3 |
| Fortified, MP 1000 mJ/cm$^2$ + $NH_2Cl$ | <0.1 | 0.6 | 1 | <0.1 | 1.5 | 1.6 | 3 | 1.6 | 7.7 | 5.5 | 3.1 | 22.5 |

iodide was present and is favored during chloramination compared to chlorination (Bichsel and von Gunten, 2000). However, in a recent occurrence study, iodine-containing DBPs were formed in waters where iodide concentration was below detection or very low (Richardson et al., 2008). Duirk et al. (2009) found that the iodine-containing x-ray contrast media, which are not completely removed during wastewater treatment, were degraded in the presence of monochloramine and led to the formation of iodoform. In the same study, spiking of iodine-containing x-ray contrast media into source water also produced all six iodo-THM species upon subsequent chloramination. Longmont source water is not thought to be impacted by wastewater, so presumably x-ray contrast agents would not be present.

As shown in Table 5.3, iodo-THMs were formed in both CONV and FCONV samples, but only in samples treated with UV followed by chloramine (<0.10 µg/L in samples only treated with chloramine). Increasing LP or MP UV dose decreased the formation of iodo-THMs in CONV samples but their formation was increased with increasing UV dose in FCONV samples. When iodo-THMs were formed with UV and chloramine, THM4 formation was decreased, compared to the sample treated with chloramine only. It is possible that UV photolysis caused an iodine-containing organic compound to release iodide, which could further react to form HOI and be incorporated into THMs.

### *Chloral Hydrate*

Overall formation of chloral hydrate was lower in FCONV samples than in CONV samples. But when treated with 1000 mJ/cm$^2$ LP UV or with increasing MP UV in either sample the formation was increased over no UV treatment as illustrated in Figure 5.4. Taking into account precision (0.3–18% relative percent difference between duplicates), only the 1000 mJ/cm$^2$ MP UV dose significantly increased chloral hydrate formation. During chloramination, chloral hydrate was below the MRL (<0.1 µg/L) for all samples.

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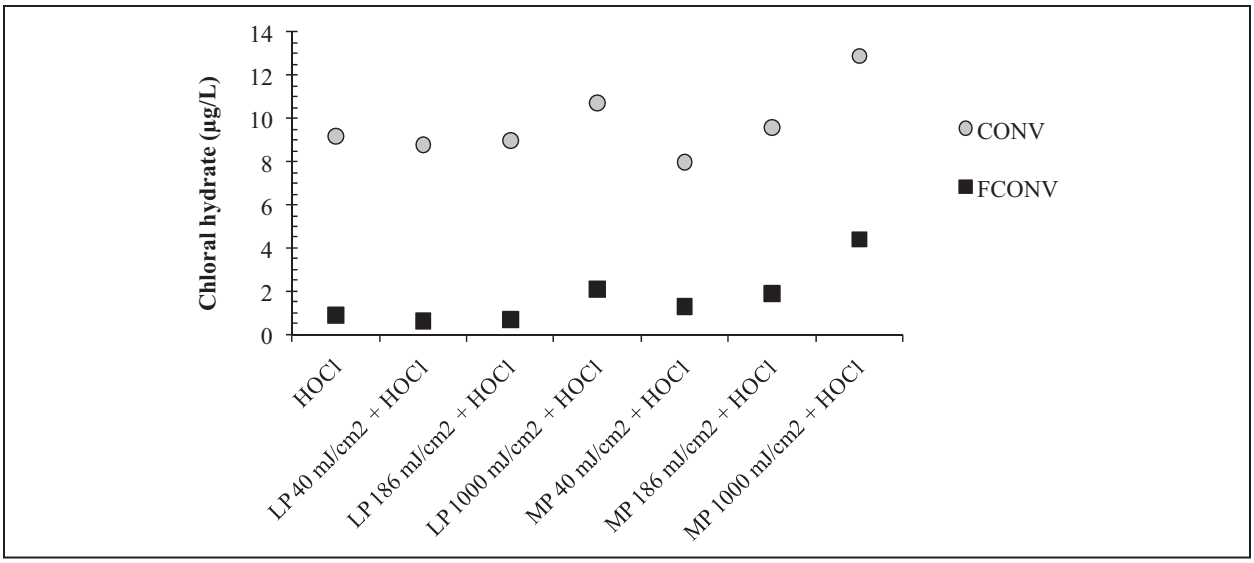


**Figure 5.4 Effect of LP and MP UV followed by chlorination on the formation of chloral hydrate in the presence/absence of bromide and nitrate**

### *Halonitromethanes*

Of all the compounds analyzed, the formation of tribromonitromethane was affected the most by UV treatment. Trichloronitromethane was below detection limit (<0.1 µg/L) in all samples except 1000 mJ/cm$^2$ MP UV followed by chlorination, where 0.6 µg/L was formed. Many of the trends among other halogenated volatiles were only observed at high UV doses, but tribromonitromethane formation was impacted even at disinfection doses (<186 mJ/cm$^2$). Tribromonitromethane was only formed in FCONV samples, and its formation was increased by pretreatment with LP or MP UV, shown in Figures 5.5 and 5.6. Tribromonitromethane formation increased more than ten-fold, from 0.7 µg/L with chlorine alone to 7.3 µg/L with 40 mJ/cm$^2$ MP UV followed by chlorination. 1000 mJ/cm$^2$ MP UV followed by chlorination formed 16.6 µg/L of tribromonitromethane. A similar trend of increasing tribromonitromethane formation with increasing LP or MP UV dose was observed in chloraminated samples, though the amounts formed were much lower compared to chlorinated samples (less than 3 µg/L).

Unlike trichloronitromethane, whose formation was not affected by LP UV in the previous experiments, tribromonitromethane formation doubled with 40 mJ/cm$^2$ LP UV, increased three-fold with 186 mJ/cm$^2$ LP UV and increased almost ten-fold from exposure to 1000 mJ/cm$^2$ LP UV, when each irradiation was followed by chlorination. It is hypothesized that NOM was nitrated by reactive nitrogen species formed during UV photolysis of nitrate. Subsequent chlorination/chloramination of nitrated NOM then forms trichloronitromethane (Reckhow et al., 2010). However, this mechanism does not completely explain the observed increase in tribromonitromethane formation from LP UV, since the majority of nitrate absorption occurs below 240 nm and LP UV outputs monochromatic at 254 nm. Employing a similar calculation to that used by Reckhow et al. (2010) and assuming that ortho-nitrophenol, a representative precursor that has been shown to produce trichloronitromethane upon chlorination (Merlet et al., 1985), produces comparable tribromonitromethane and trichloronitromethane yields (5.7%), only about 0.06% of the 8 mg/L nitrate would be required to account for the additional 5.6 µg/L tribromonitromethane

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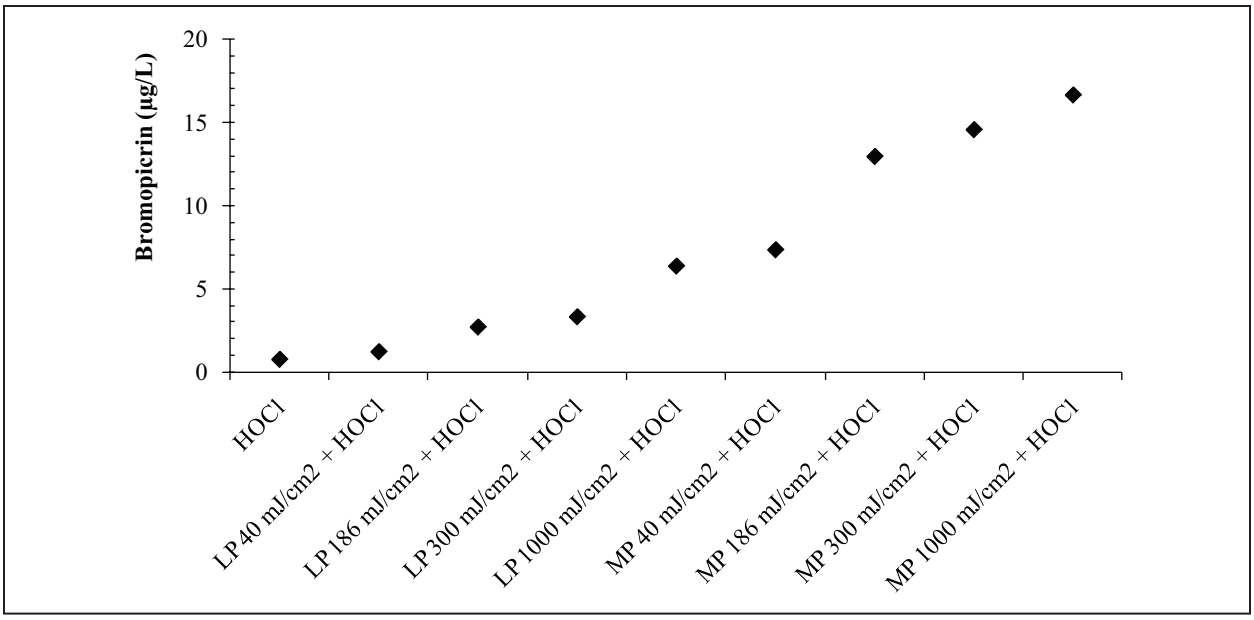


**Figure 5.5 Effect of LP and MP UV followed by chlorination on tribromonitromethane formation in bromide- and nitrate-fortified Longmont samples**

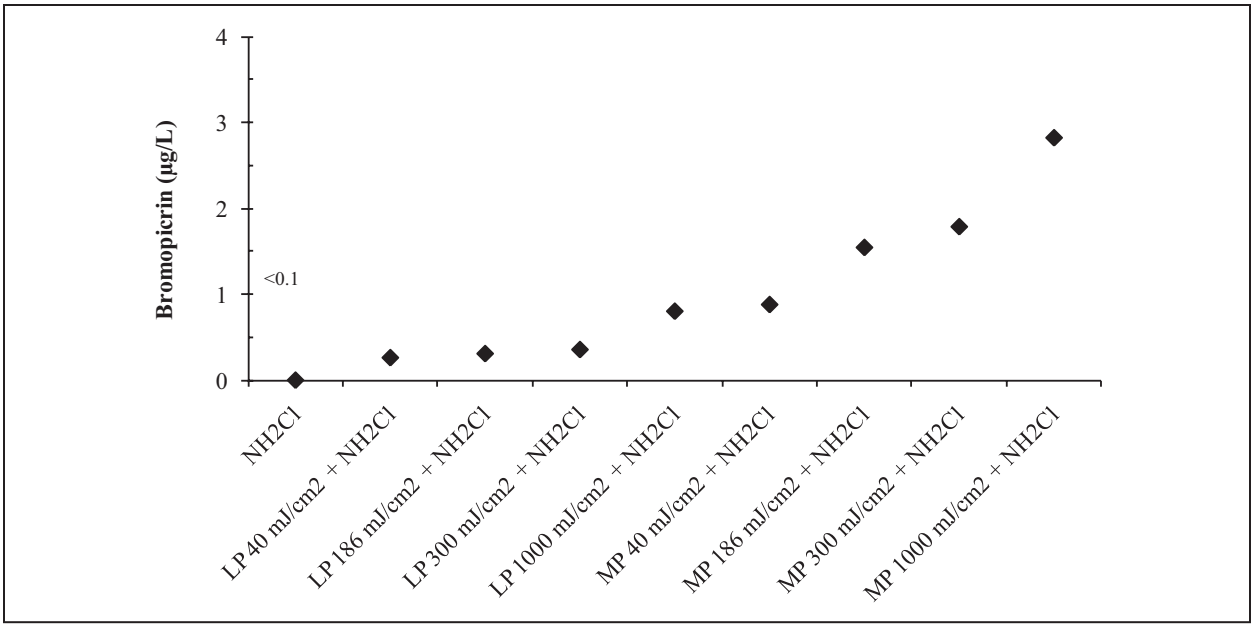


**Figure 5.6 Effect of LP and MP UV followed by chloramination on tribromonitromethane formation in bromide- and nitrate-fortified Longmont samples**

that was formed with 1000 mJ/cm$^2$ LP UV followed by chlorination. Thus, even if nitrate only absorbed a small amount of irradiation at 254 nm, it could be enough to form µg/L amounts of tribromonitromethane. This calculation also assumes that activated nitrate is converted to a nitration agent which reacts quantitatively with NOM. HOBr is a more effective halogenating agent than HOCl (Luong et al., 1982), which could explain why an increased trichloronitromethane formation

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**Table 5.4**
**NDMA formation for CONV or FCONV Longmont water not treated with UV and chlorinated**

| Sample | [NDMA] (ng/L) |
|---|---|
| FCONV A | 4.1 |
| FCONV B | 2.6 |
| CONV A | 4.9 |
| CONV B | 2.5 |

**Table 5.5**
**NDMA formation for CONV Longmont water not treated with UV and chloraminated (pre-formed)**

| Sample | [NDMA] (ng/L) |
|---|---|
| CONV A | 20.0 |
| CONV B | 24.3 |

resulting from LP UV irradiation has not been previously observed. Another explanation could be a mechanism in which LP UV photolysis activates organic nitrogen to create precursors, which are more reactive towards chlorine/chloramine.

### *N-Nitrosodimethylamine and Dimethylnitramine*

No significant dimethylnitramine (DMNA) formation (>2 ng/L) was observed in any of the Longmont samples with or without UV treatment. Results in Tables 5.4 and 5.5 present the formation of NDMA in unirradiated samples. The low levels of NDMA (<5.0 ng/L) formed during chlorination are expected as free chlorine has not been shown to produce notable concentrations of NDMA. Results for chloramination of the CONV samples are higher than free chlorine addition as chloramines are known to yield NDMA. Chloramination of the untreated spiked samples were found to be higher (>70 ng/L). However, these results were higher than expected and believed to have been contaminated and not trustworthy.

Results pertaining to samples irradiated with MP UV and chlorinated/chloraminated are shown in Tables 5.6 and 5.7. Overall NDMA was low (<6 ng/L) for both CONV and FCONV samples. For the chlorinated FCONV samples, a slight increase in NDMA formation was observed with increasing MP UV dose. This may potentially be due to the photolysis of $NO_3^-$, which can form a number of nitrosating species (e.g., $ONONO_2$ and $N_2O_3$). For the chloraminated samples (Tables 5.8 and 5.9), NDMA formation was low (<4.0 ng/L) and close to the detection limit (~2 ng/L). Results for the FCONV samples during chloramination show an opposite trend to those that were chlorinated. If the nitrosating agents formed during photolysis are the primary agents forming NDMA, it would be hypothesized that both oxidants would show similar trends.

Results pertaining to samples irradiated with LP UV and chlorinated/chloraminated are shown in Tables 5.10 through 5.13. In general, the results for NDMA formation using the LP lamp are low (<7.0 ng/L). The only influence of UV dose on NDMA formation was observed for CONV water samples that were chloraminated. For this set of data including UV doses from 0 to 1000 mJ/cm$^2$, NDMA concentration decreased from ~22 ng/L to ~2–3 ng/L, respectively. It is

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**Table 5.6**
**NDMA formation for CONV Longmont water treated with MP UV and chlorinated**

| MP UV dose (mJ/cm$^2$) | [NDMA] (ng/L) |
|---|---|
| 40 | 2.3 |
| 300 | 2.4 |
| 1000 A | 2.5 |
| 1000 B | 3.3 |

**Table 5.7**
**NDMA formation for FCONV Longmont water treated with MP UV and chlorinated**

| MP UV dose (mJ/cm$^2$) | [NDMA] (ng/L) |
|---|---|
| 40 | 1.7 |
| 300 | 3.3 |
| 1000 | 5.8 |

**Table 5.8**
**NDMA formation for CONV Longmont water treated with MP UV and chloraminated (pre-formed)**

| MP UV dose (mJ/cm$^2$) | [NDMA] (ng/L) |
|---|---|
| 40 | 2.1 |
| 1000 | 1.1 |

**Table 5.9**
**NDMA formation for FCONV Longmont water treated with MP UV and chloraminated (pre-formed)**

| MP UV dose (mJ/cm$^2$) | [NDMA] (ng/L) |
|---|---|
| 40 | 3.8 |
| 1000 | 1.8 |

**Table 5.10**
**NDMA formation for CONV Longmont water treated with LPUV and chlorinated**

| LP UV dose (mJ/cm$^2$) | [NDMA] (ng/L) |
|---|---|
| 40 | 5.1 |

**Table 5.11**
**NDMA formation for FCONV Longmont water treated with LPUV and chlorinated**

| LP UV dose (mJ/cm$^2$) | [NDMA] (ng/L) |
|---|---|
| 40 | 4.2 |
| 300 | 6.9 |
| 1000 | 3.0 |

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**Table 5.12**
**NDMA formation for CONV Longmont water treated with LPUV and chloraminated (pre-formed)**

| LP UV dose (mJ/cm$^2$) | [NDMA] (ng/L) |
|---|---|
| 40 | 5.8 |
| 186 | 3.2 |
| 300 | 2.3 |
| 1000 A | 1.3 |
| 1000 B | 5.6 |

**Table 5.13**
**NDMA formation for FCONV Longmont water treated with LPUV and chloraminated (pre-formed)**

| LP UV dose (mJ/cm$^2$) | [NDMA] (ng/L) |
|---|---|
| 40 | 3.8 |
| 186 | 4.1 |
| 300 | 3.1 |
| 1000 | 2.7 |
| 1000 | 2.0 |

hypothesized that exposure to LP lamp irradiation may remove or inactivate NDMA precursors either through direct or indirect photolysis.

These results are suggestive but not definitive of a negative UV impact on nitrosamine formation. Samples that were chlorinated but not exposed to UV treatment did not form significant levels of NDMA. This was expected as NDMA precursors are not likely to react with free chlorine to form NDMA. Samples that were chlorinated and exposed to UV treatment also did not form significant levels of NDMA, although some trends were observed (e.g., MP treatment with increased fluence for FCONV samples exposed to free chlorine). This suggests that while some nitrosating agents (e.g., $N_2O_3$) may be formed, they did not contribute strongly to NDMA formation or were rapidly photolyzed. The nitrosamine precursor content in the Longmont filter effluent water appears to be significant as samples that were chloraminated with no UV treatment formed ~22.0 ng/L NDMA. All chloraminated samples that were exposed to either MP or LP lamps at all fluences tested (40–1000 mJ/cm$^2$) exhibited low levels of NDMA (<7.0 ng/L) suggesting that any UV exposure may significantly reduce NDMA precursors either through direct or indirect photolysis.

### Case Study 2: Cincinnati WTP Filter Effluent

Treated (coagulation/flocculation, sedimentation, and filtration) but not GAC adsorbed or chlorine disinfected water (also referred to as CONV) from the Richard Miller drinking water treatment plant in Cincinnati, OH was collected and studied. Cincinnati employs a free chlorine mode of disinfection. The facility treats water from the Ohio River, which is known to be impacted

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**Table 5.14**
**Water quality for Cincinnati conventional WTP**

| Parameter | Units | Value |
|---|---|---|
| pH | — | 8 |
| Bromide | µg/L | 59.5 |
| Iodide | µg/L | 3.8 |
| Alkalinity | mg-$CaCO_3$/L | 61.7 |
| Total Organic Carbon | mg-C/L | 1.42 |
| Total Nitrogen | mg-N/L | 1.1 |
| $UV_{254}$ | $cm^{-1}$ | 0.028 |

**Table 5.15**
**Free chlorine and monochloramine demand for Cincinnati conventional WTP**

| UV Dose ($mJ/cm^2$) | LP | MP | LP | MP |
|---|---|---|---|---|
| | CONV | | FCONV | |
| Free Chlorine (mg-$Cl_2$/L) | | | | |
| 0 | 1.37 | | 2.01 | |
| 40 | 1.79 | 1.62 | 1.92 | 2.27 |
| 186 | 1.88 | 1.78 | 2.05 | 2.50 |
| 500 | 1.72 | 1.69 | 2.19 | 2.53 |
| 1000 | 1.74 | 2.17 | 2.06 | 2.55 |
| Monochloramine (mg-$Cl_2$/L) | | | | |
| 0 | 0.57 | | 0.68 | |
| 40 | 0.60 | 0.60 | 0.73 | 0.74 |
| 186 | 0.55 | 0.65 | 0.67 | 0.78 |
| 500 | 0.64 | 0.70 | 0.82 | 1.06 |
| 1000 | 0.68 | 0.79 | 0.75 | 1.24 |

Values shown are the average of duplicate tests

by industrial, agricultural, and wastewater inputs. Table 5.14 presents water quality of the collected sample. The sample had a moderate alkalinity and bromide concentration.

### *Free Chlorine and Chloramine Demand*

The sample collected from Cincinnati generally followed the same trend as observed for the Longmont sample. Where 24 hour free chlorine and monochloramine demand increased as UV dose applied increased. The change in demand was not notably different between lamp types in the CONV samples for free chlorine dosed at UV doses less than 500 $mJ/cm^2$ and for all monochloramine dosed samples. When spiked with 500 µg/L bromide and 8 mg-N/L nitrate, FCONV samples, the initial demand increased and greater increases in demand were observed with increasing applied UV dose. In these spiked samples, MPUV treated samples were determined to have greater demands than LPUV. Some of this demand was likely attributed to the UV-induced formation of

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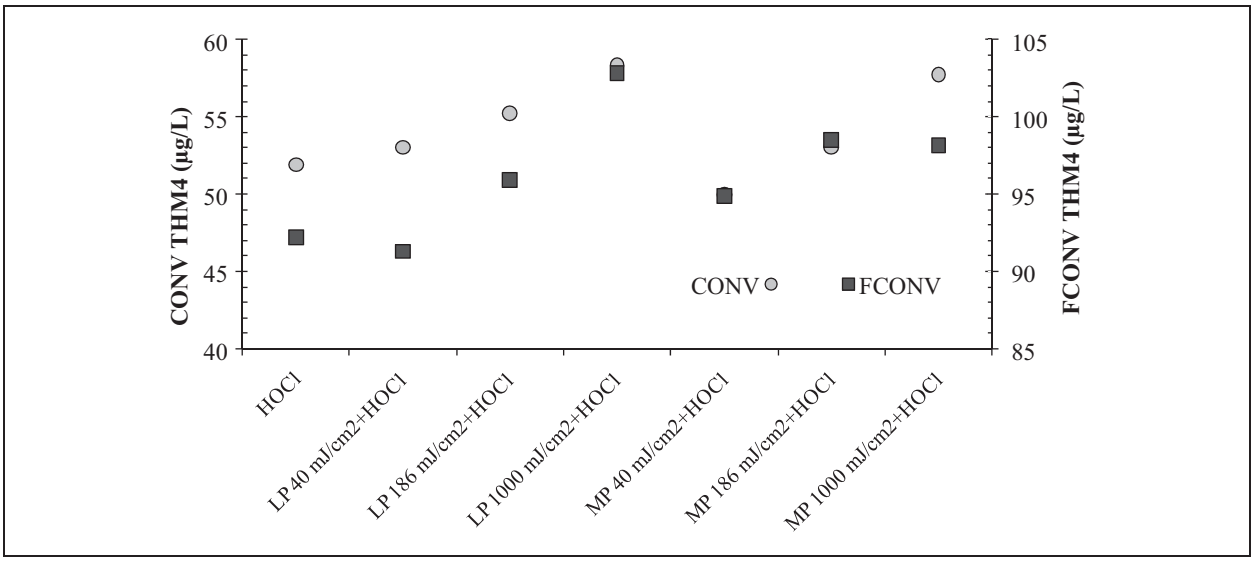


**Figure 5.7 Effect of LP and MP UV followed by chlorination on THM4 formation in the presence/absence of bromide and nitrate**

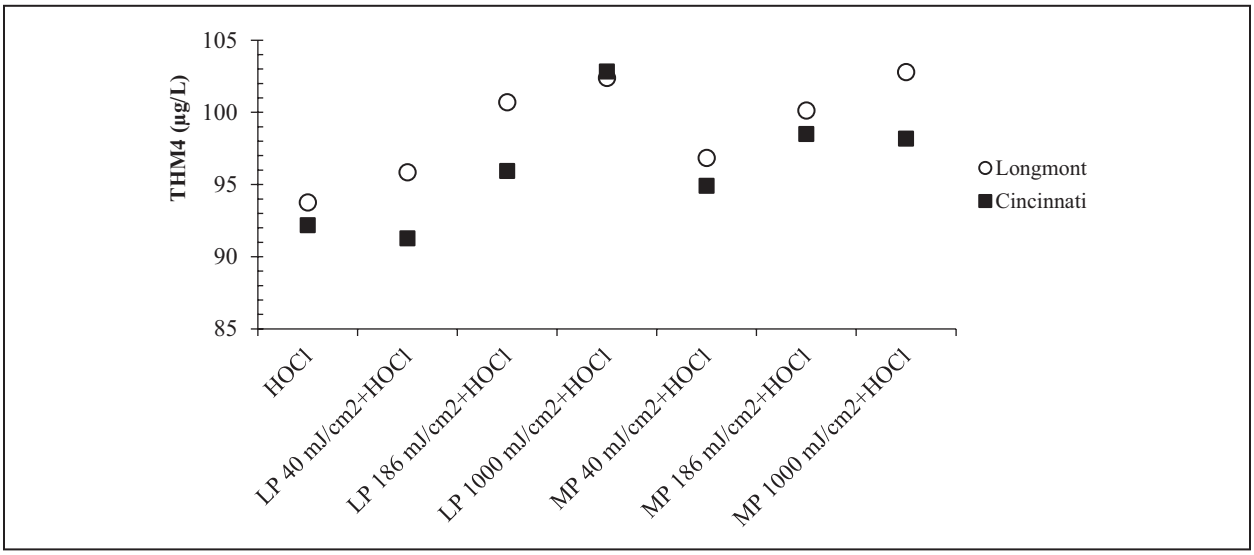


**Figure 5.8 Effect of LP and MP UV on THM4 formation in fortified chlorinated Longmont and Cincinnati samples**

nitrite which will react with chlorine to reform nitrate. At disinfection doses (<186 mJ/cm$^2$) minor increases in chlorine demand were observed (0.1–0.4 mg-$Cl_2$/L). Free chlorine and monochloramine demands are presented in Table 5.15.

### *THMs and Emerging Halogen- and Nitrogen-Containing DBPs*

For CONV samples, chloroform formation was increased 28% with 1000 mJ/cm$^2$ LP UV followed by chlorination and 30% with 1000 mJ/cm$^2$ MP UV followed by chlorination, compared to chlorination alone (Figure 5.7). Relative percentage differences between experimental duplicate

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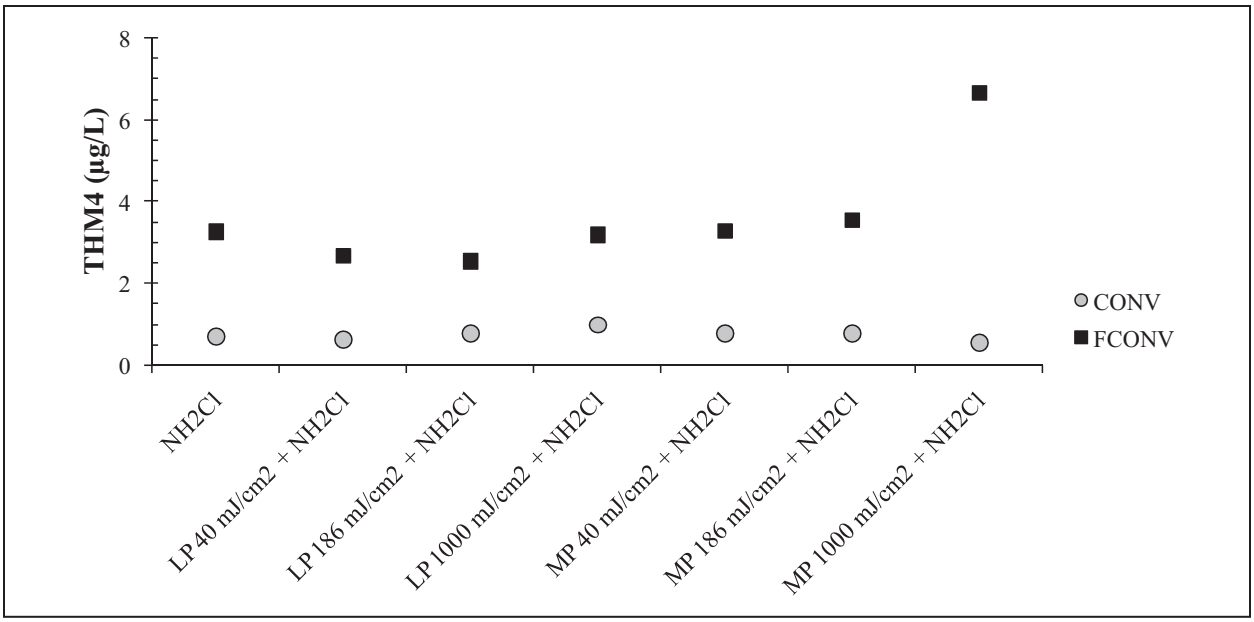


**Figure 5.9 Effect of LP and MP UV followed by chloramination on THM4 formation in the presence/absence of bromide and nitrate**

samples were 15% or less. During chlorination, THM4 formation in FCONV samples were quite similar between Longmont and Cincinnati, two very different source waters (see Table 5.1 and 5.14 for water quality data and Figure 5.8 for THM4 results). Spiking with bromide and nitrate caused a shift to the bromine-containing species and during chlorination, THM4 formation was greater than 80 µg/L THM4. For chloraminated samples, THM4 formation was below 4 µg/L (except for 1000 mJ/cm$^2$ MP UV followed by chloramination, in which 6.6 µg/L THM4 was formed) (Figure 5.9). Because UV had little impact on haloacetic acids and haloacetamides, these DBPs were not measured for the second treated water sample (Cincinnati).

### *Cyanogen Chloride*

Cyanogen chloride was not analyzed in Longmont samples, but was measured in chloraminated Cincinnati samples. Cyanogen chloride formation was increased with 1000 mJ/cm$^2$ MP UV prior to chloramination (1.3 µg/L compared to <0.4 µg/L for chloramination alone) (Figure 5.10). Relative percent difference between duplicate samples was less than 10%. An increase in cyanogen chloride formation following 60 mJ/cm$^2$ MP UV and chloramination (compared to chloramination alone) has been previously observed by Liu et al., 2006. An increase in formaldehyde formation resulting from UV treatment has been reported (Malley et al., 1995) and monochloramination of formaldehyde has also been shown to form cyanogen chloride (Pedersen et al., 1999).

### *Chloral Hydrate*

For both chlorination and chloramination of FCONV samples, chloral hydrate formation was increased with LP and MP UV, shown in Figure 5.11. During chloramination, ambient samples produced lower amounts of chloral hydrate compared to those spiked with bromide- and nitrate.

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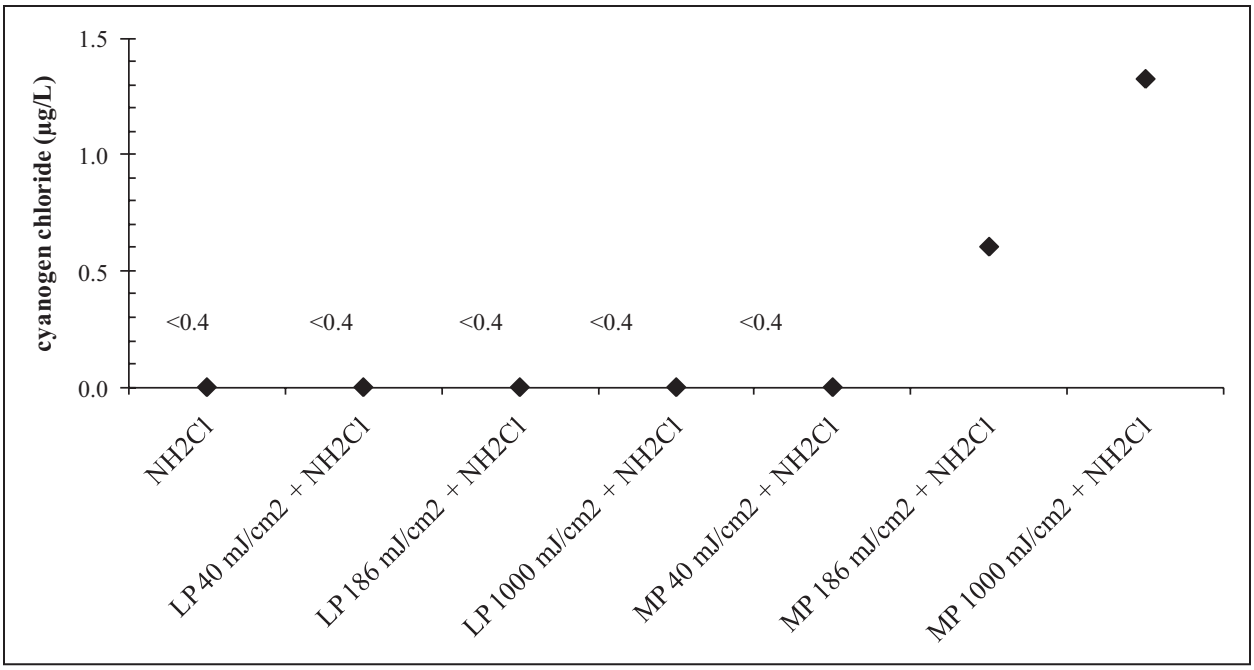


**Figure 5.10 Effect of MP UV followed by chloramination on the formation of cyanogen chloride in CONV Cincinnati samples**

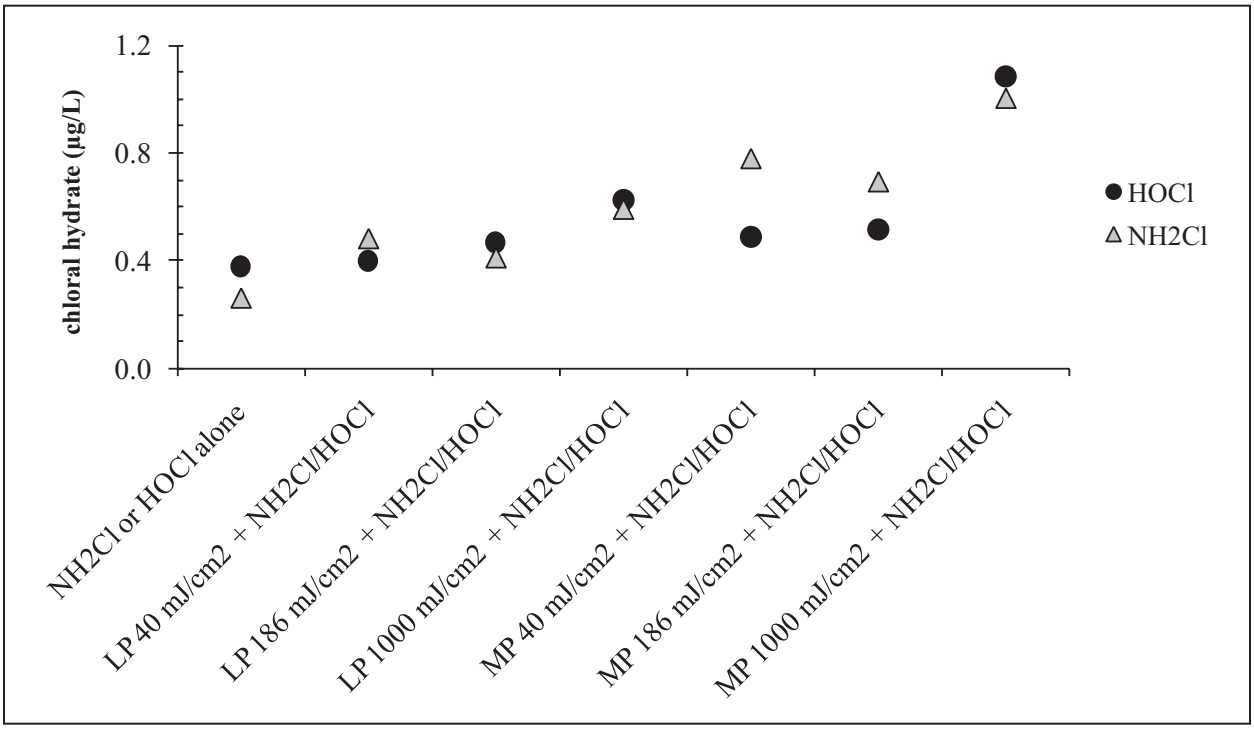


**Figure 5.11 Effect of LP and MP UV followed by chlorination or chloramination on the formation of chloral hydrate in FCONV Cincinnati samples**

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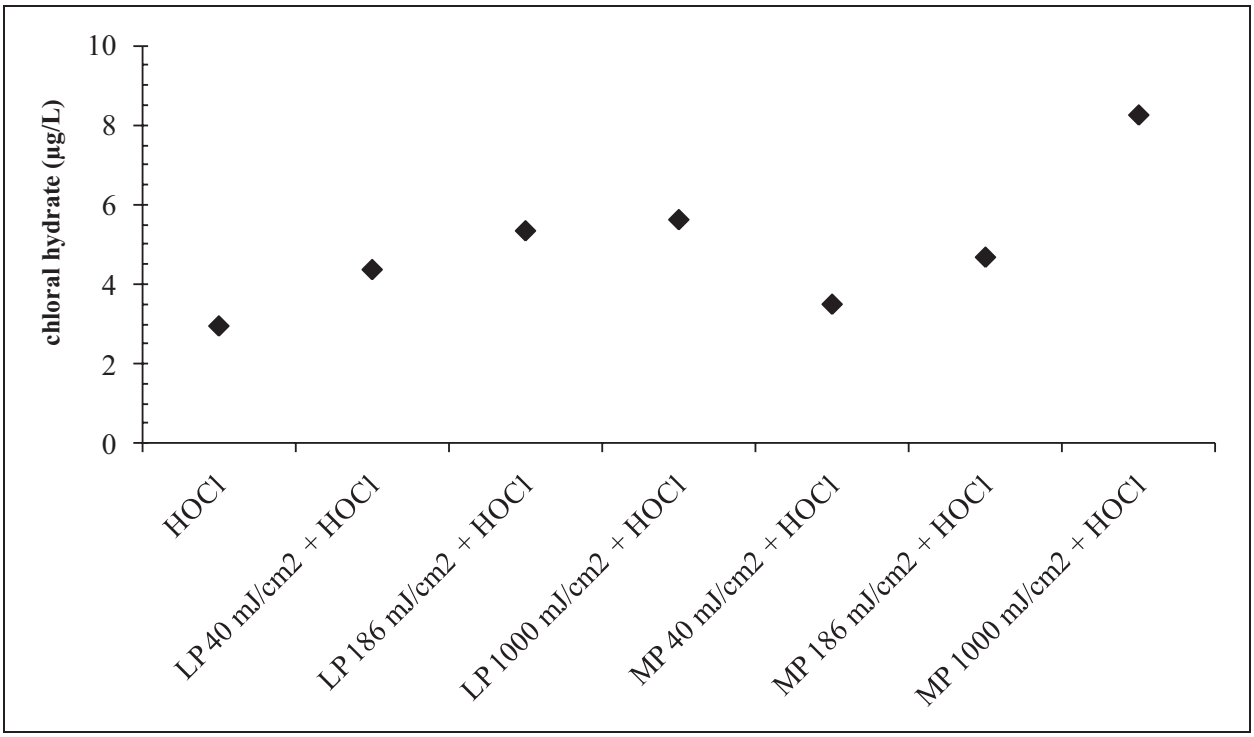


**Figure 5.12 Effect of LP and MP UV on the formation of chloral hydrate in CONV chlorinated Cincinnati samples**

In contrast, during chlorination, CONV samples produced higher levels of chloral hydrate than FCONV samples, which increased in concentration with increasing dose of LP UV or MP UV prior to chlorination, shown in Figure 5.12.

### *Halonitromethanes*

Trichloronitromethane was not detected in spiked FCONV samples, but in CONV water, MP UV (186 mJ/cm$^2$ and 1000 mJ/cm$^2$) followed by chlorination formed 0.25 and 0.60 µg/L trichloronitromethane, compared to <0.1 µg/L for chlorination alone (Figure 5.13). In contrast to Longmont, tribromonitromethane was formed in CONV Cincinnati samples, though formation was higher in FCONV samples. Ambient nitrate and bromide were 0.026 mg/L as N and 7.9 µg/L $Br^-$ for Longmont compared to 0.80 mg/L as N and 59.9 µg/L $Br^-$ for Cincinnati. LP UV did not increase tribromonitromethane formation in ambient samples. As Figure 5.14 shows, during chlorination, LP and MP UV impact on tribromonitromethane formation in FCONV samples was comparable between Longmont and Cincinnati. During chloramination, tribromonitromethane was not detected in CONV samples. In FCONV samples, MP UV followed by chloramination increased tribromonitromethane formation five-fold (dose of 186 mJ/cm$^2$) and sixteen-fold (dose of 1000 mJ/cm$^2$), shown in Figure 5.15.

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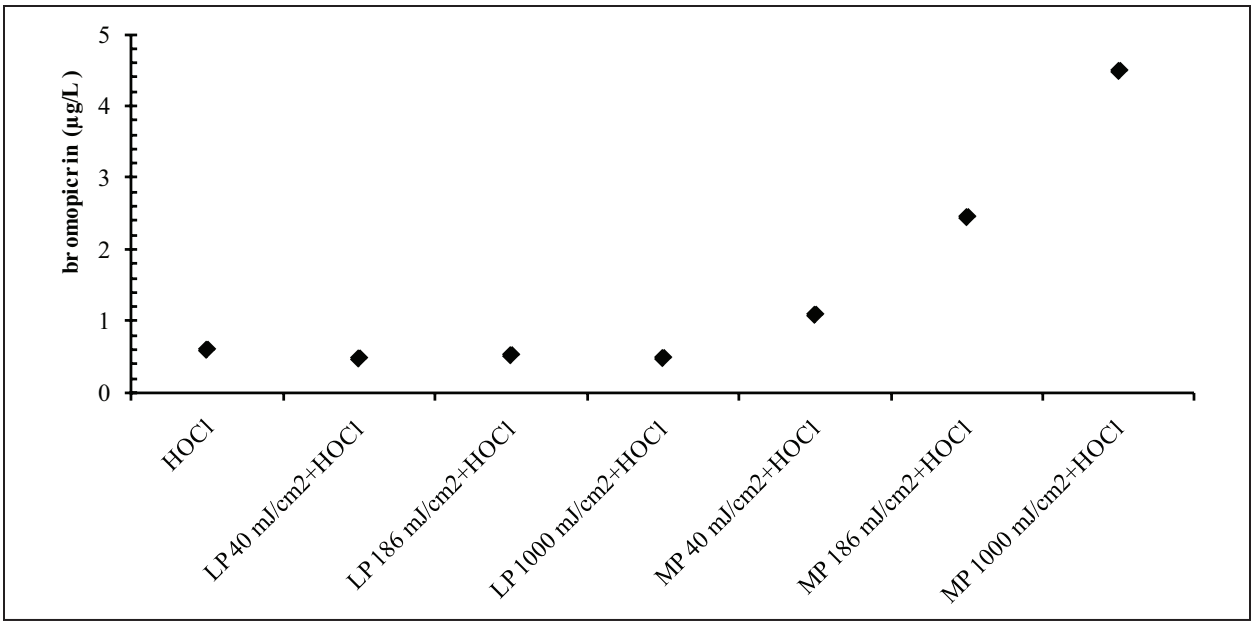


**Figure 5.13 Effect of MP UV followed by chlorination on the formation of tribromonitromethane in CONV Cincinnati samples**

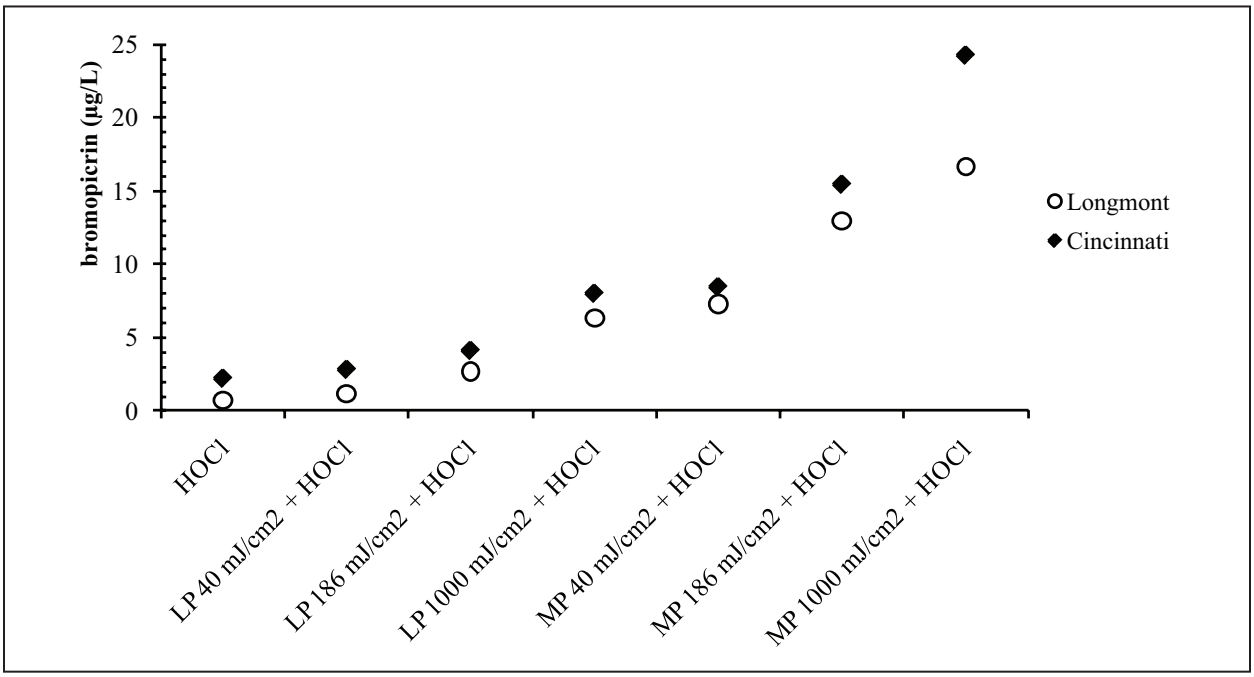


**Figure 5.14 Effect of LP and MP UV followed by chlorination on the formation of tribromonitromethane in FCONV Longmont and Cincinnati samples**

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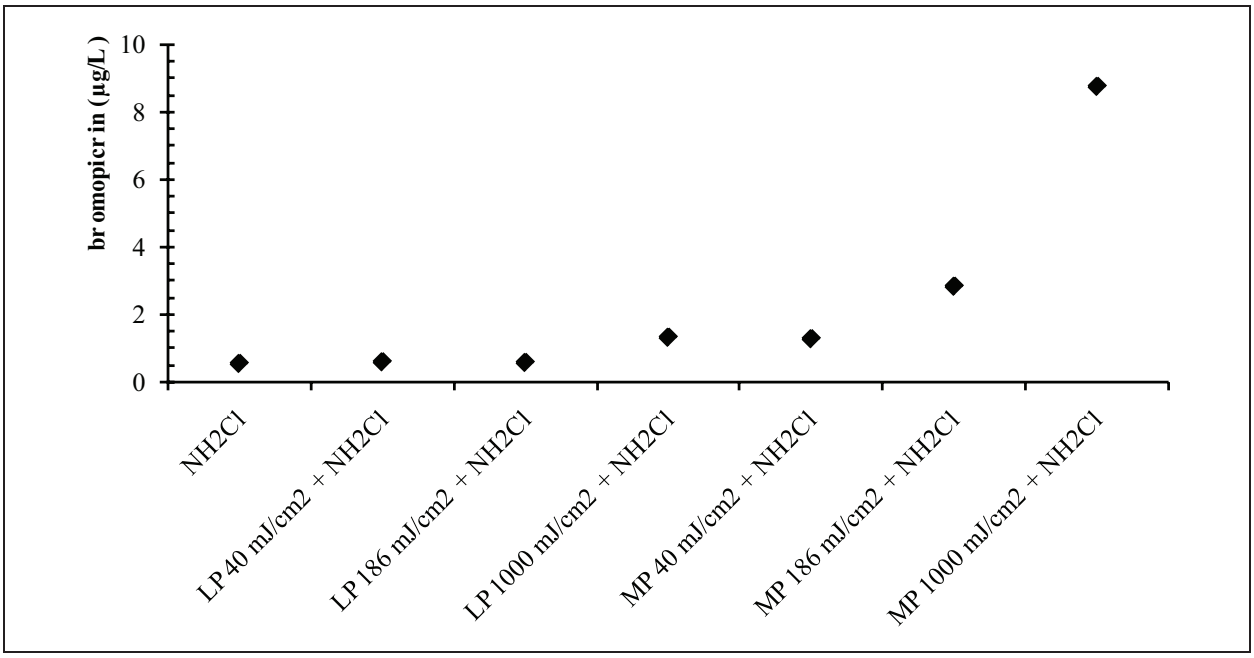


**Figure 5.15 Effect of LP and MP UV followed by chloramination on the formation of tribromonitromethane in FCONV Cincinnati samples**

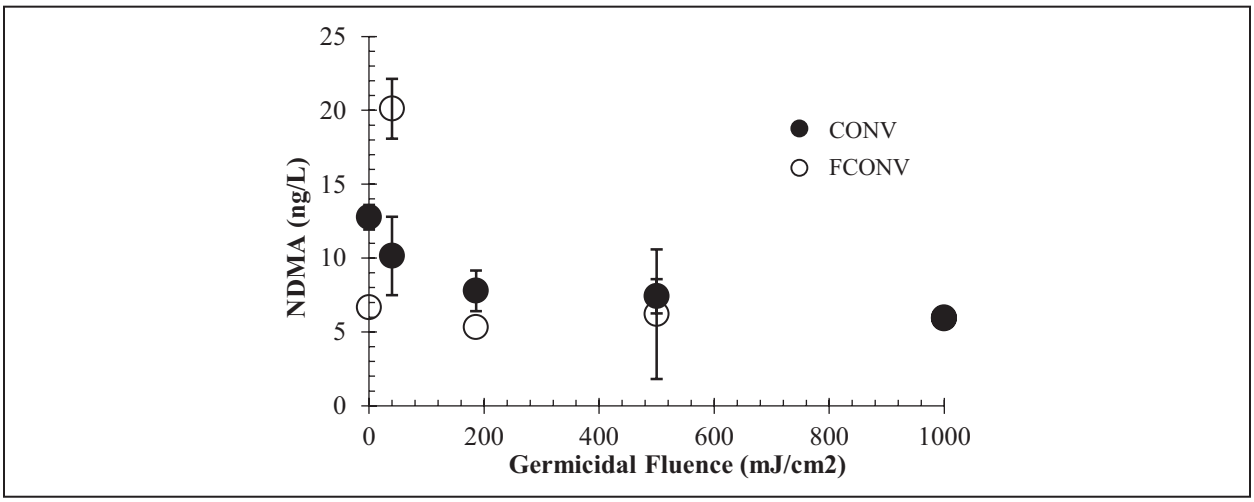


**Figure 5.16 Nitrosamine formation for samples treated with LP UV and post-chloraminated. Spiked FCONV samples contain 8.0 mg N/L $NO_3^-$ and 0.5 mg/L $Br^-$.**

### *N-Nitrosodimethylamine*

No significant formation of NDMA occurred when samples were treated with free chlorine, but considerable amounts of NDMA formed when samples were treated with chloramines following UV treatment.

NDMA formation is shown in Figure 5.16 when CONV or FCONV samples were treated with LP UV followed by chloramination. For the CONV samples, the trend shows that greater LP UV treatment leads to lower quantities of NDMA. A steady drop from ~12 ng/L to 5 ng/L was

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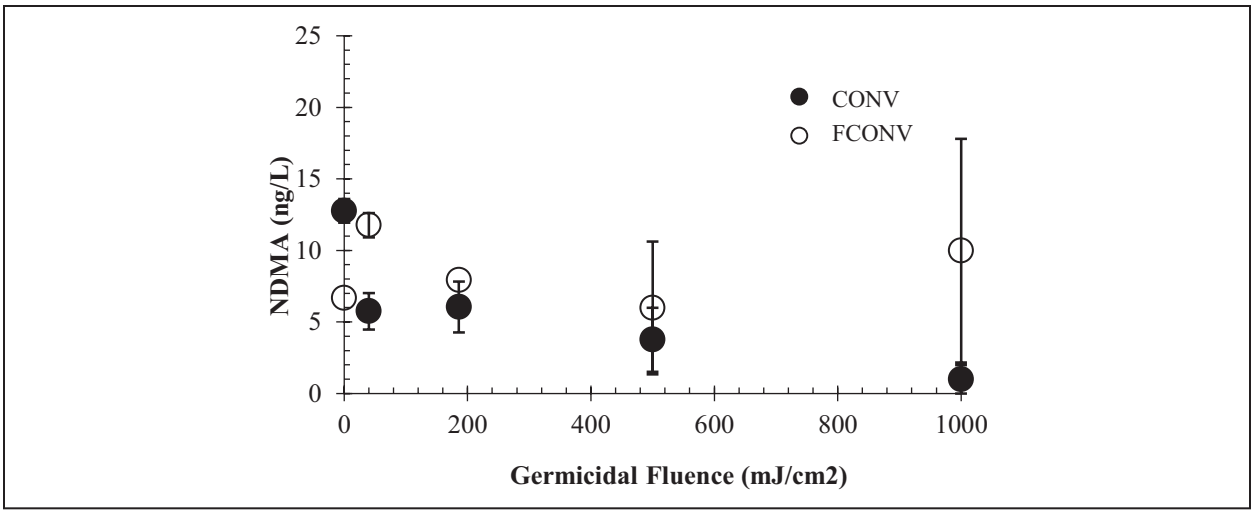


**Figure 5.17 Nitrosamine formation for samples treated with MP UV and post-chloraminated. Spiked FCONV samples contain 8.0 mg N/L $NO_3^-$ and 0.5 mg/L $Br^-$.**

observed when the UV dose was increased from 40 to 1000 mJ/cm$^2$. This trend clearly suggests that without nitrate or bromide addition, nitrosamine precursors are destroyed or inactivated during UV treatment. This effect is either though the direct or indirect photolysis of NDMA precursor material. The FCONV samples show a slightly different trend. No significant downward trend was observed and NDMA concentration remained around ~5 ng/L in all samples except for the one treated at 40 mJ/cm$^2$ where the NDMA formation increased significantly up to 20 ng/L. This indicates that nitrate and bromide addition plays some role in initially forming some NDMA. Most likely this was due to the photolysis of nitrate forming various nitrosating species (e.g., NO and $N_2O_3$) as discussed in Chapter 1. At higher doses, the formation of nitrosating species and subsequent forming of nitrosamines are competing with the direct photolysis of the nitrosamine compounds themselves which may be leading to the drop in formation at these higher UV doses. Overall, this indicates that without nitrate and bromide, LP UV treatment effectively reduces NDMA formation potential. However, with nitrate and bromide present, these is a slight potential for NDMA formation to increase, but the increase appears to be highly dependent on the UV dose applied.

NDMA formation is shown in Figure 5.17 when FCONV or CONV samples were treated with MP UV treatment followed by chloramination. For the FCONV MP UV treated samples, a similar trend was observed as was seen when the same type of samples were irradiated with LP UV. It is observed here, that as UV dose was increased, NDMA formation decreases. In this case, NDMA decreases from ~12 ng/L to close to the analytical detection limit of 2 ng/L. For the FCONV samples, a similar trend is also observed as was seen previously with the LP UV system although a few samples show more error with the replicates that were analyzed. Most of the samples, both the unirradiated and samples treated MP UV are close to each other in concentration (5–9 ng/L) while the 40 mJ/cm$^2$ treated sample has ~13 ng/L NDMA. The explanation for this trend is similar to that described for the LP UV. Overall, this indicates that without nitrate and bromide, MP UV treatment effectively reduces NDMA formation potential. However, with nitrate and bromide present, there was a slight potential for NDMA formation to increase, but the increase was highly dependent on the UV dose applied.

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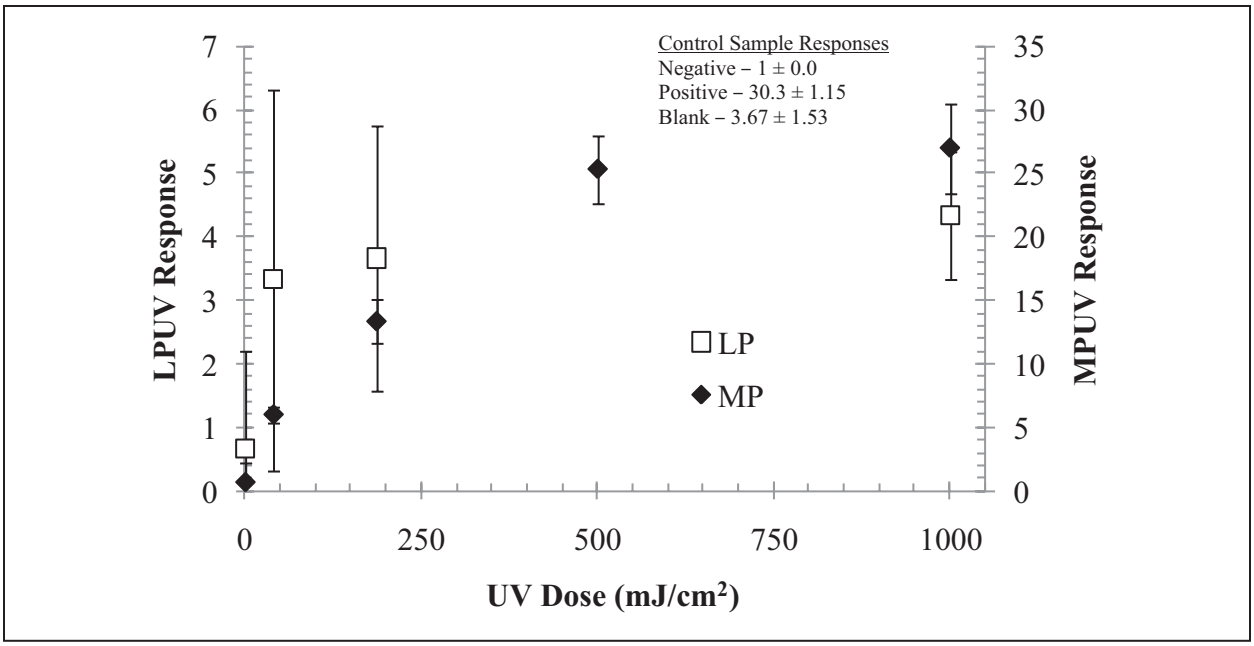


**Figure 5.18 AMES II response for UV sequenced with free chlorine for Cincinnati (TA98)**

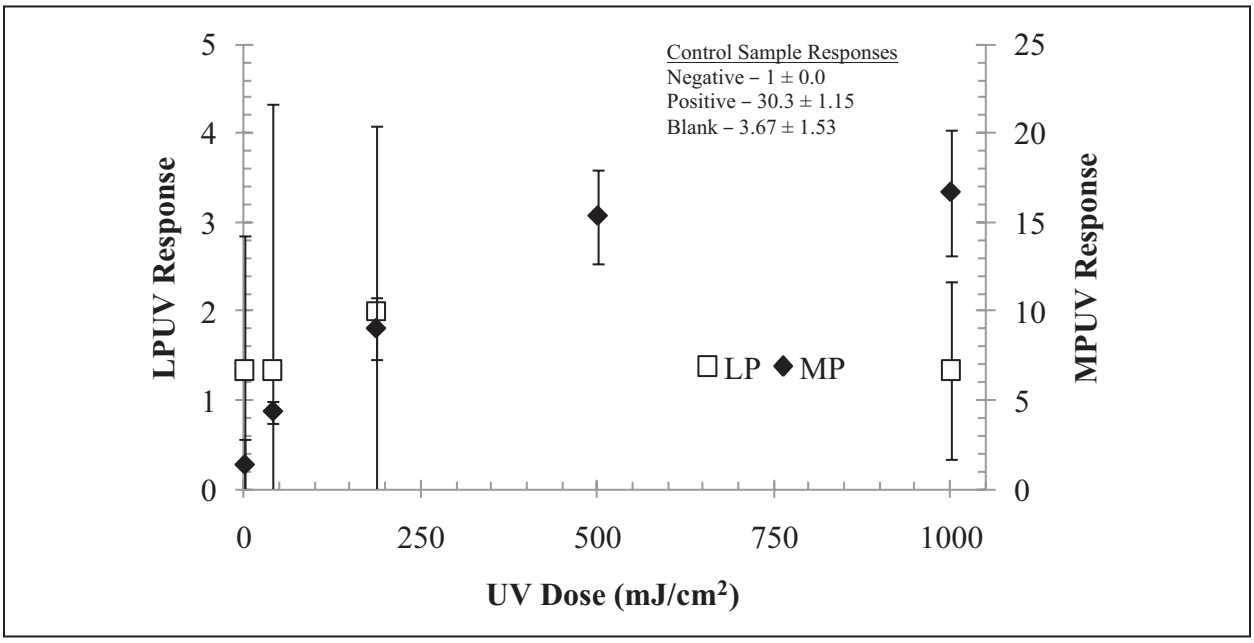


**Figure 5.19 AMES II response for UV sequenced with free chlorine for Cincinnati (TA98+S9)**

### *AMES II Toxicity*

In addition to measuring individual DBPs formed during the sequence of UV followed by free chlorine, sample toxicity was measured using the AMES II assay in select samples from Cincinnati. Figure 5.18 presents results of the assay without the S9 enzyme and Figure 5.19 presents results with the S9 enzyme. The enzyme allows for determination of indirect toxicity

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formed during chemical metabolism. Regardless of the UV lamp technology, with increased UV dose, the response observed during the toxicity assay increased with increasing UV dose, suggesting increased genotoxicity. At doses in the typical range of drinking water disinfection (<100 mJ/cm$^2$) used by the industry, the LP and MP responses are comparatively low and compare to the baseline toxicity of the blank sample (DI water passed through extraction cartridge). LP UV showed a significantly lower response with a maximum of 5 compared to the MPUV, which had maximum response of 27 (Figure 5.18). These responses were reduced in the presence of S9 enzyme, where LPUV had a maximum response of 2 and MPUV had a maximum response of 17 (Figure 5.19). The toxicity testing was conducted on GAC influent water from the Richard Miller water treatment plant, which has an additional GAC adsorption barrier for precursor reduction that could reduce toxicity levels to lower than those observed in this study. It is important to note that these toxicity data are simply comparative numbers to look at changes due to treatment differences, however the magnitudes of these numbers do not imply or relate to any specific human or ecological health outcome.

## SUMMARY

The waters from the two locations studied in this chapter originated from very different source waters but appeared very similar on the basis of DOC and $UVA_{254}$. In many ways the response of both waters with respect to DBP formation was also very similar. A number of broad conclusions can be drawn from the results presented in this chapter. These conclusions include:

1. At disinfection doses of UV (<186 mJ/cm$^2$) minimal or statistically irrelevant increases in THM4 and HAAs were observed regardless the water sample. At high doses (>500 mJ/cm$^2$) statistically relevant increases were observed but these were typically minimal also (≤10 µg-THM4/L).
2. Chlorine/chloramine demand was increased slightly (≤0.4 mg-$Cl_2$/L) when disinfection dosages of UV were applied upstream of chlorine/chloramine application. Chlorine/chloramine demand was significantly increased when samples were spiked with bromide and nitrate and treated with MP UV.
3. Formation of halonitromethanes, particularly tribromonitromethane, were observed and correlated with increasing UV dose. MP UV produced greater yields of tribromonitromethane than LP UV and can be likely attributed to nitrosation type reactions. For disinfection doses of UV, increased tribromonitromethane formation was always less than 10 µg/L.
4. Chloral hydrate was observed to increase (on the order of few µg/L) and correlate with increased UV dose. Similar to tribromonitromethane, MP UV produced greater yields than LP UV.
5. While these waters only produced small concentrations of NDMA when chloraminated, both UV technologies decrease NDMA formation with increased UV dose.
6. Increased AMES II toxicity response was observed to correspond with increased UV dose with and without the S9 enzyme. LPUV produced a significantly lower response in comparison to the MPUV, however at UV doses typical of disinfection practices, neither LP nor MP showed significant toxicity increases. In the presence of S9, response was decreased. Note that these toxicity data are simply comparative numbers and do not imply or relate to any specific human or ecological health outcome.

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# CHAPTER 6
# EFFECT OF UV-CHLORINE/CHLORAMINE SEQUENCE ON DISINFECTION BY-PRODUCT FORMATION IN SYNTHETIC WATER

## OVERVIEW

The objective of this portion of the research was to assess the precursor content of water collected at various points in the drinking water process and to determine the potential for these precursors to form various disinfection by-products during UV treatment followed by disinfection by free chlorine or chloramines. Water collected from OWASA was concentrated by reverse osmosis. UV application consisted of either 500 mJ/cm$^2$ LP UV or 1000 mJ/cm$^2$ of MP UV. 1 mg/L bromide and 10 mg/L nitrate (as N) were spiked into selected samples. Results and interpretation for DBP formation are provided below. Chlorination and chloramination were conducted to achieve residual concentrations of 1–1.5 mg/L as $Cl_2$ after 72 hours. These conditions represent extreme conditions and were designed to evaluate whether any significant effects of UV on DBP formation are possible.

## RESULTS

The results presented in this chapter span from NOM characterization to the disinfection by-products formed under a variety of chlorination schemes with free chlorine and chloramines.

### Whole and Fractionated NOM

Figure 6.1 shows the contribution of isolated NOM fractions accounting for 97% of organic carbon measured in the unfractionated RO concentrate. Differences in DBP formation were investigated through various combinations of UV, chlorination, and chloramination treatments in the presence/absence of nitrate and bromide on the hydrophobic acid and hydrophilic DOM fractions. These differences were compared to those produced with the same treatments on the original RO concentrate as well as commercially available Suwannee River natural organic matter (SRNOM) obtained from the International Humic Substance Society (St. Paul, MN). Concentrating the organic precursors and treating with correspondingly scaled-up doses of UV and chlorine/chloramines allowed for the observation of emerging DBPs that are often below detection in disinfected natural waters. This experiment was intended to elucidate a better understanding of the mechanisms of DBP formation and NOM reactivity as affected by UV treatment. Figure 6.2 is a comparison of the OWASA RO concentrate and a SRNOM sample isolated by Croué et al. (1999). Note that this SRNOM isolate is not the same standard sold by IHSS, but likely similar. The RO concentrate had a slightly higher hydrophilic/transphilic content and lower hydrophobic content compared to SRNOM.

Treatment conditions are shown in Table 6.1 and described in detail in Chapter 2. Spiking amounts, when applicable, were 1 mg/L bromide and 10 mg/L (as N) nitrate, administered in the sodium salt form. LP UV dose was 500 mJ/cm$^2$ and MP UV dose was 1000 mJ/cm$^2$. UV treated samples from each water type were subsequently chlorinated with a concentrated sodium hypochlorite stock solution or a concentrated pre-formed chloramines solution. A target residual of



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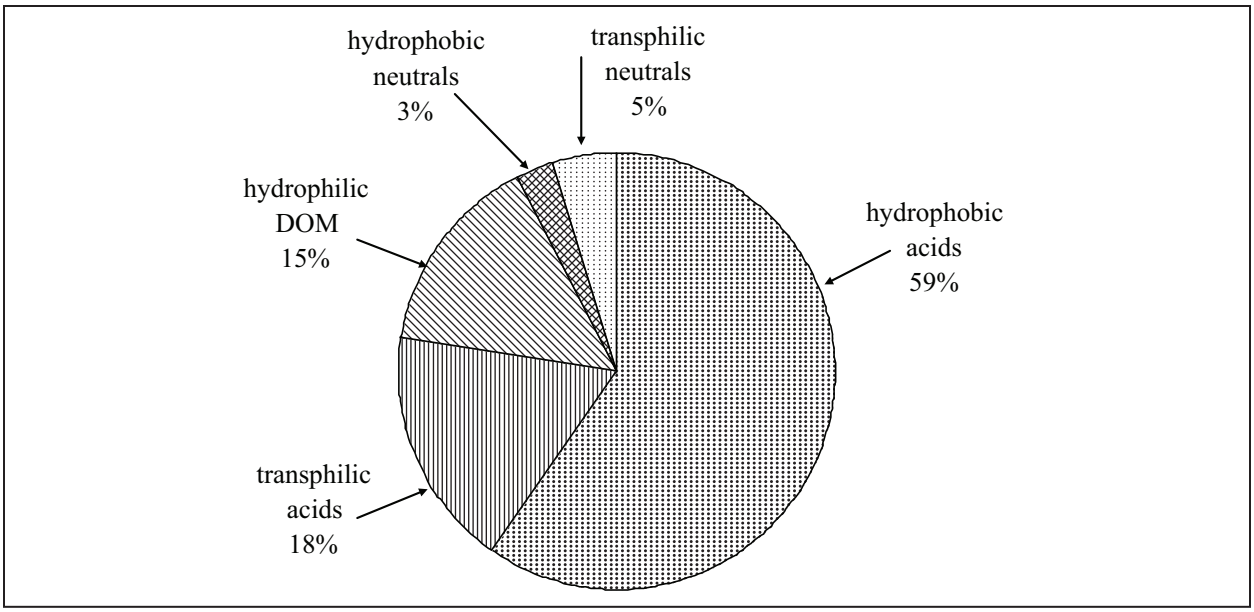


**Figure 6.1 Composition of reverse osmosis concentrate**

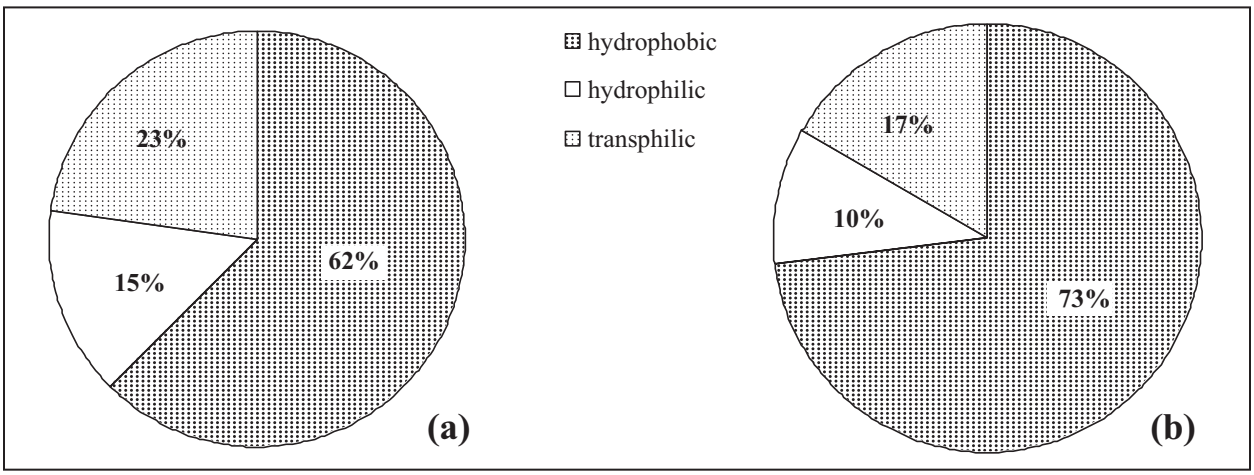


**Figure 6.2 Comparison of (a) OWASA RO concentrate and (b) SRNOM fractions**

**Table 6.1**
**Treatment conditions and disinfectant doses based on chlorine demand tests**

| Parameter | RO concentrate | Hydrophobic acids | Hydrophilic DOM | SRNOM |
|---|---|---|---|---|
| DOC (mg/L as C) | 9.5 | 9.9 | 10.7 | 10.4 |
| $SUVA_{254}$ (L/mg m) | 3.1 | 3.7 | 1.5 | 3.7 |
| Chlorine dose (mg/L as $Cl_2$) | 16 | 16 | 20 | 23 |
| Chloramine dose (mg/L as $Cl_2$) | 4.2 | 5.3 | 6 | 6.6 |

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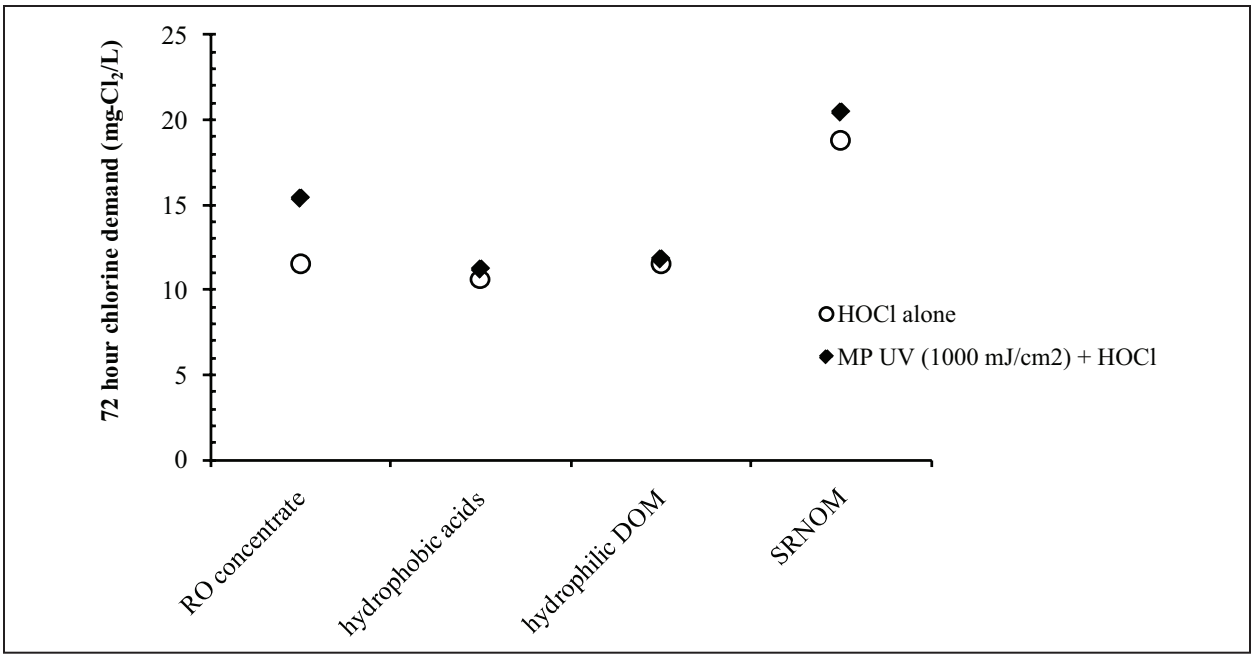


**Figure 6.3 Effect of MP UV on the 72-hour chlorine demand of CONV samples**

1 mg/L as $Cl_2$ was desired after a 72 hour contact time. The chlorine dose required for the sample with the highest chlorine/chloramine demand was used, so that each sample received an equivalent dose. Four sets of experiments were conducted on different days (one for each water type—RO concentrate, hydrophilic DOM, hydrophobic acids, and SRNOM).

**Disinfection By-Product Formation**

The 72 hour chlorine demand of the RO concentrate and SRNOM were increased by MP UV irradiation (1000 mJ/cm$^2$) (Figure 6.3). The increased chlorine demand resulting from MP UV was accompanied by an increased formation of THM4 in the RO concentrate, hydrophobic acid and SRNOM, suggesting that at these doses, UV irradiation increases the reactivity of THM precursors towards chlorine (Figure 6.4). UV treatment had a more significant effect on the formation of chloroform compared to brominated species. MP UV irradiation prior to chlorination increased HAA9 formation in the RO concentrate, decreased HAA9 formation in the hydrophilic fraction and did not impact HAA9 formation in hydrophobic or SRNOM samples (Figure 6.5). The chloramine demands of each fraction were lower than chlorine demands. LP UV (500 mJ/cm$^2$) and MP UV (1000 mJ/cm$^2$) decreased the 72 hour chloramine demand in hydrophobic acids, increased the chloramine demand in SRNOM and had no effect in the hydrophilic DOM (Figure 6.6). During chloramination, LP and MP UV irradiation had little impact on THM4 formation (Figure 6.7). There were no consistent trends associated with UV dose on HAA9 formation for the isolated DOM fractions or between chlorination and chloramination (Figure 6.8). Although during chloramination, the addition of LP or MP UV increased HAA9 formation in SRNOM. Precursors in the hydrophobic acid fraction contributed more to THM4 formation during chlorination, but during chloramination the hydrophilic fraction contributed more to THM4 formation. The hydrophobic acid fraction had higher HAA9 formation compared to the hydrophilic fraction, for both

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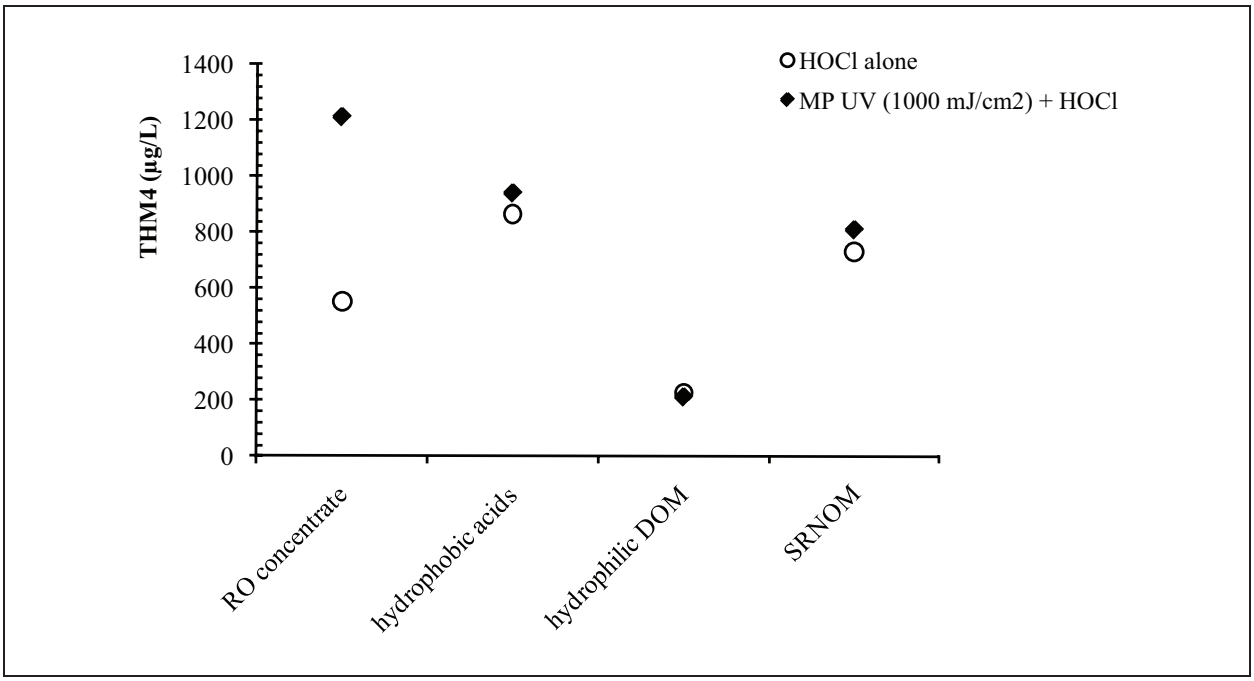


**Figure 6.4 Effect of MP UV followed by chlorination on THM4 formation in CONV samples**

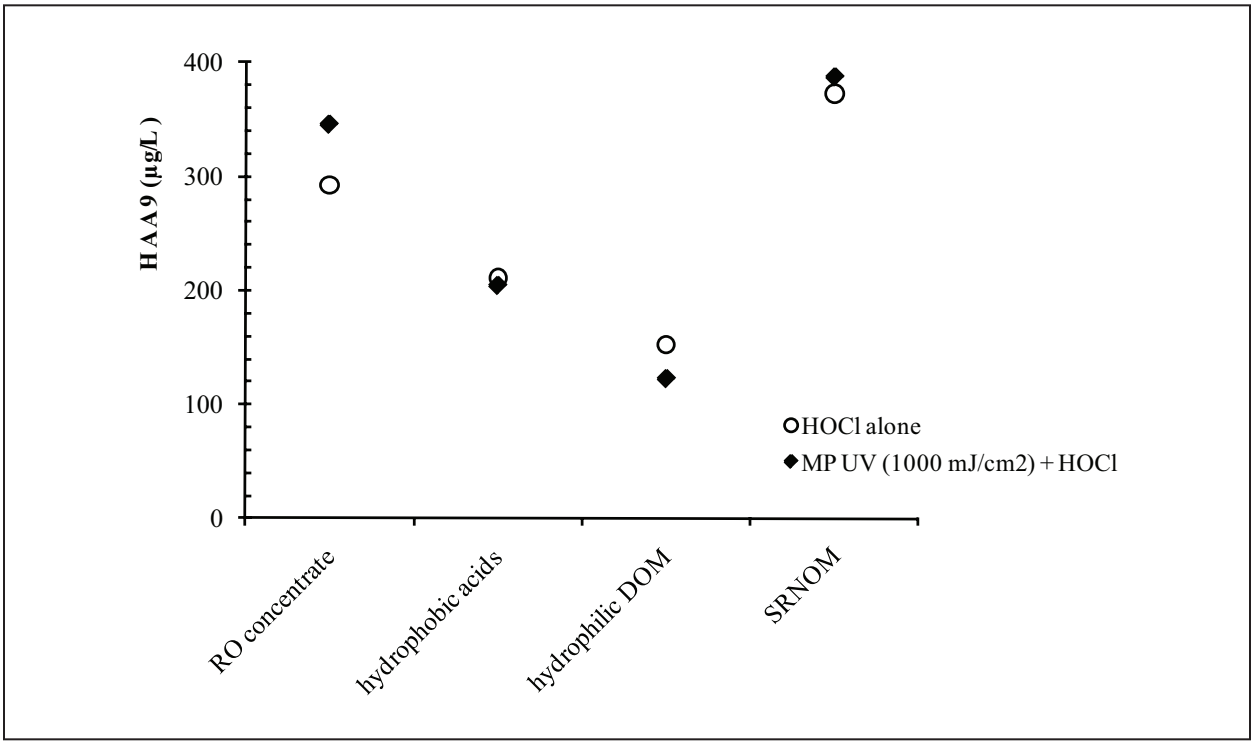


**Figure 6.5 Effect of MP UV followed by chlorination on HAA9 formation in CONV samples**

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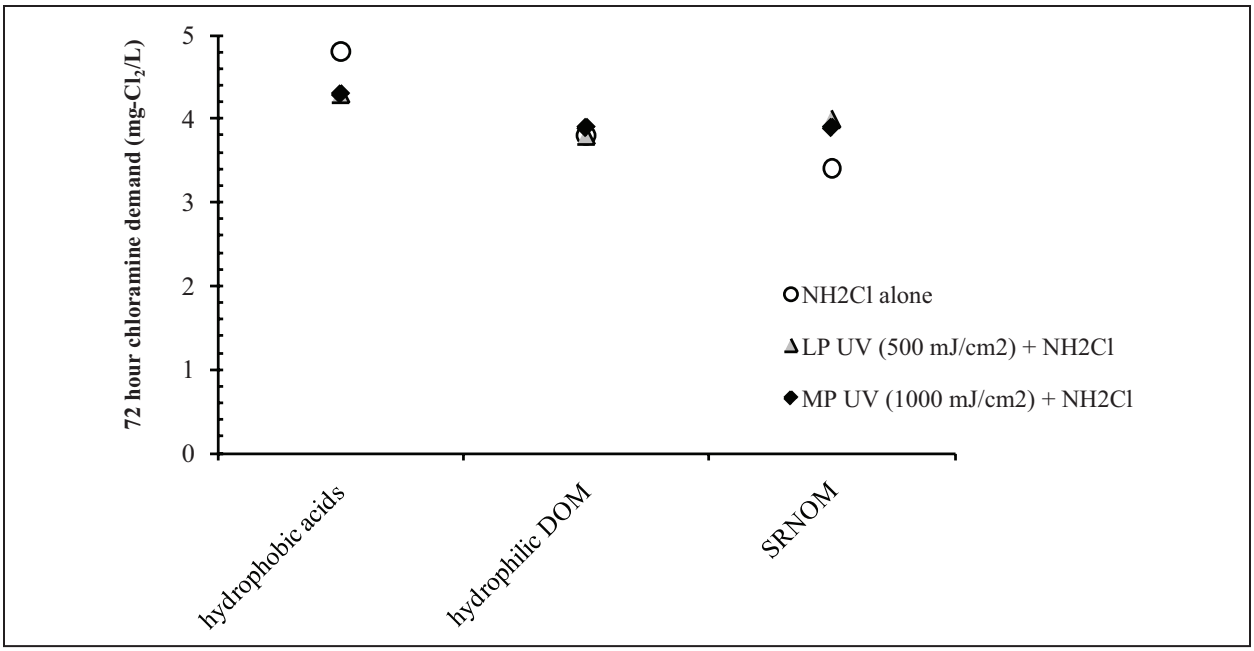


**Figure 6.6 Effect of LP and MP UV on the 72-hour chloramine demand of CONV samples**

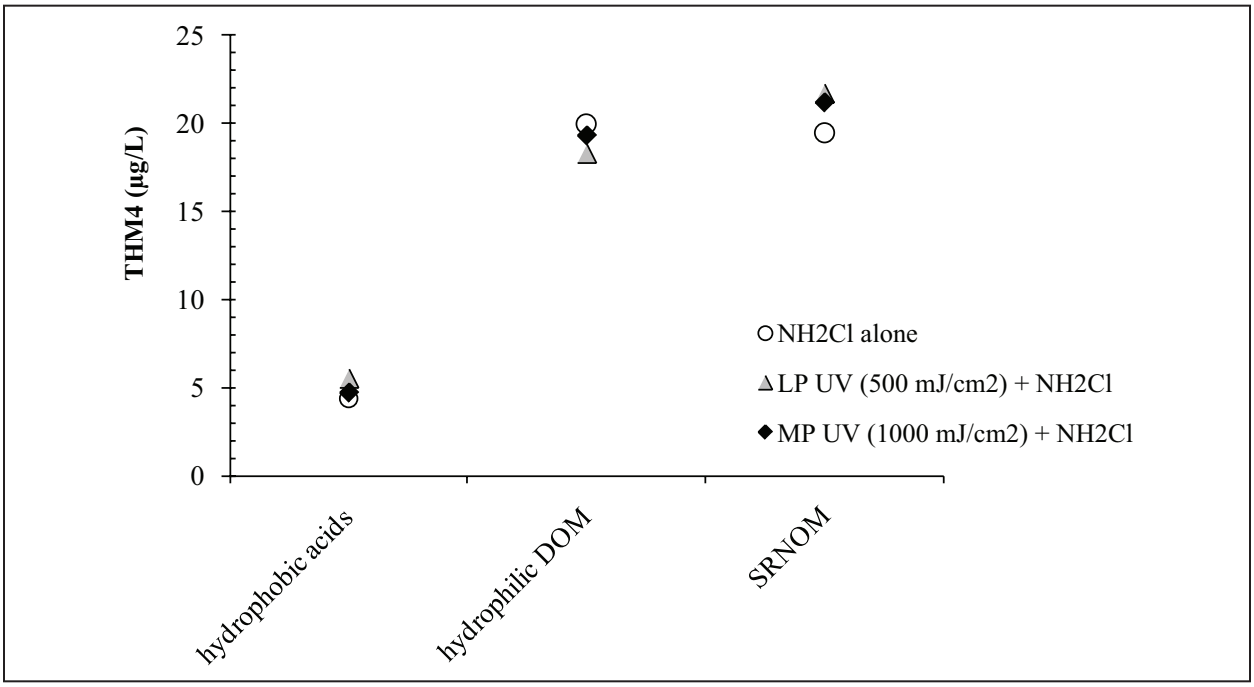


**Figure 6.7 Effect of LP and MP UV followed by chloramination on THM4 formation in CONV samples**

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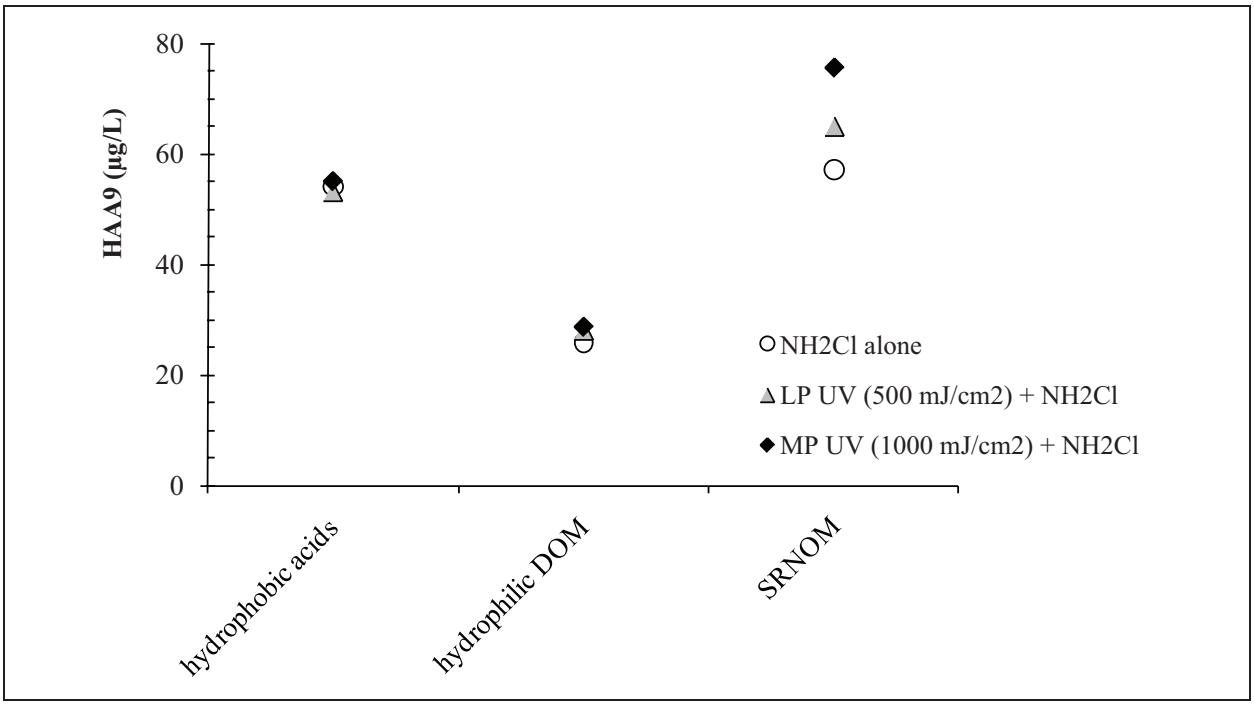


**Figure 6.8 Effect of LP and MP UV followed by chloramination on HAA9 formation in CONV samples**

chlorination and chloramination. Past research has shown that in general, the hydrophobic fraction contributes more to THM and HAA formation compared to hydrophilic precursors, which typically comprise only a small amount of the total DOM. However, the hydrophilic fraction can play an important role, especially in low humic-containing waters (Liang and Singer, 2003; Hua and Reckhow, 2007a).

Toxicological studies have shown that bromine-containing DBPs are more geno- and cytotoxic than their chlorine-containing counterparts (Richardson et al., 2008). For this reason, the speciation of halogenated DBPs is of interest. A bromine incorporation factor (BIF) can be calculated among a class of halogenated DBPs using the following equation (Gould et al., 1981; Obolensky and Singer, 2005):

$$\text{BIF} = \frac{\sum(\text{molar conc.} \times \#\text{Br})}{\sum(\text{molar conc.}) \times (\#\text{ halogens})}$$

An example calculation for the BIF in THM4:

| Species | Conc. (µM) |
|---|---|
| $CHCl_3$ | 2.12 |
| $BrCl_2CH$ | 2.43 |
| $Br_2ClCH$ | 1.57 |
| $CHBr_3$ | 0.31 |
| THM4 | 6.43 |

$$\text{BIF} = \frac{(2.12 \times 0) + (2.43 \times 1) + (1.57 \times 2) + (0.31 \times 3)}{(2.12 + 2.43 + 1.57 + 0.31) \times 3} = 0.34$$

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**Table 6.2**
**THM4 bromine incorporation during chlorination in bromide- and nitrate-spiked fractions and bulk samples**

| Sample | THM4 BIF |
|---|---|
| RO concentrate | 0.34 |
| Hydrophobic acid | 0.23 |
| Hydrophilic DOM | 0.63 |
| SRNOM | 0.19 |

**Table 6.3**
**THM4 BIF in SRNOM for treatments involving UV in the presence and absence of bromide and nitrate. Ambient bromide was below detection limit (<50 µg/L).**

| Treatment condition | Ambient | $Br^-$ and $NO_3^-$ spiked | $Br^-$ spiked |
|---|---|---|---|
| HOCl | 0.00 | 0.19 | 0.20 |
| LP UV + HOCl | 0.00 | 0.19 | 0.19 |
| MP UV + HOCl | 0.00 | 0.19 | 0.18 |
| $NH_2Cl$ | 0.00 | 0.07 | 0.07 |
| LP UV + $NH_2Cl$ | 0.00 | 0.05 | 0.06 |
| MP UV + $NH_2Cl$ | 0.00 | 0.15 | 0.04 |

The BIF was calculated for THM4, di- and tri- haloacetic acids ($X_2AA$, $X_3AA$) and di- and tri-haloacetamides for each of the waters used in the fractionation study. Table 6.2 shows the THM4 BIF for each fraction when spiked with bromide- and nitrate- and chlorinated. Tables 6.3, 6.4 and 6.5 show the THM4, $X_2AA$, and $X_3AA$ BIF, respectively, for treated SRNOM samples. During chloramination, dihaloacetic acids dominated the HAA pool, and $Cl_3AA$ was the only trihaloacetic acid species formed, even in bromide-spiked samples. This was expected, as past work has shown only trace $X_3AA$ formation after chloramination, which suggests that $X_2AA$ and $X_3AA$ have different precursors and formation occurs by distinct pathways (Hua and Reckhow, 2007b). In general, UV did not significantly affect bromine incorporation. In one case (SRNOM spiked with 1 mg/L bromide and 10 mg/L nitrate) the bromine incorporation doubled between chloramination alone and MP UV followed by chloramination. Other samples that were spiked with bromide and then chlorinated or chloraminated did show a shift to the bromine-containing by-products, but UV did not further change the BIF. Bromine incorporation into THMs and HAAs originates predominantly from hypobromous acid (e.g., bromide is oxidized by HOCl to HOBr, a very rapid halogenating agent) and that UV has little additional effect. Bromine incorporation was higher in the hydrophilic fraction compared to hydrophobic acid fraction, which was expected based on previous research showing bromine to be more reactive with lower molecular weight, hydrophilic precursors (Liang and Singer, 2003). This was further confirmed by a higher BIF in the slightly more hydrophilic OWASA RO concentrate compared to the SRNOM.

Of the emerging halogen- and nitrogen-containing by-products analyzed in the fractionation study, UV had the most pronounced effects on trichloronitromethane and chloral hydrate. In nitrate-spiked SRNOM samples, MP UV followed by chlorination or chloramination formed 17 and 23 µg/L of trichloronitromethane, respectively. The corresponding LP UV and chlorine/chloramine

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**Table 6.4**
**Dihaloacetic acid ($X_2AA$) BIF in SRNOM for treatments involving UV in the presence and absence of bromide and nitrate**

| Treatment condition | Ambient | $Br^-$ and $NO_3^-$ spiked | $Br^-$ spiked |
|---|---|---|---|
| HOCl | 0.00 | 0.20 | 0.20 |
| LP UV + HOCl | 0.00 | 0.19 | 0.19 |
| MP UV + HOCl | 0.00 | 0.19 | 0.19 |
| NH2Cl | 0.00 | 0.13 | 0.13 |
| LP UV + $NH_2Cl$ | 0.00 | 0.11 | 0.12 |
| MP UV + $NH_2Cl$ | 0.00 | 0.16 | 0.10 |

**Table 6.5**
**Trihaloacetic acid ($X_3AA$) BIF in SRNOM for treatments involving UV in the presence and absence of bromide and nitrate**

| Treatment condition | Ambient | $Br^-$ and $NO_3^-$ spiked | $Br^-$ spiked |
|---|---|---|---|
| HOCl | 0.00 | 0.26 | 0.25 |
| LP UV + HOCl | 0.00 | 0.22 | 0.25 |
| MP UV + HOCl | 0.00 | 0.26 | 0.24 |
| $NH_2Cl$ | 0.00 | 0.00 | 0.00 |
| LP UV + $NH_2Cl$ | 0.00 | 0.00 | 0.00 |
| MP UV + $NH_2Cl$ | 0.00 | 0.00 | 0.00 |

alone samples formed less than 0.10 µg/L trichloronitromethane (Figures 6.9 and 6.10). The RPD between duplicate samples was less than 10% for trichloronitromethane analysis. Though the doses used in this study were high relative to typical disinfection doses, trichloronitromethane formation after MP UV and chlorination has been previously observed at lower doses (40–140 mJ/cm$^2$) (Reckhow et al., 2010). The authors hypothesized that photonitration of NOM and subsequent chlorination leads to formation of nitroorganics, which form halonitromethanes when nitrate is present during UV treatment. The majority of nitrate absorbance occurs below 240 nm, which can explain why LP UV did not increase the formation of trichloronitromethane. LP UV emits monochromatic light at 254 nm, while MP UV emits light over a range from about 190 nm to 500 nm. Trichloronitromethane was below detection limit (<0.10 µg/L) in the hydrophobic acid fraction. Past work has shown higher trichloronitromethane yields after chlorination of hydrophilic DOM isolates compared to the hydrophobic and transphilic fractions (Dotson et al., 2009). Hu et al. (2010) also found that hydrophilic NOM had higher halonitromethane formation potentials than hydrophobic and transphilic fractions upon chlorination and ozonation-chlorination. Pre-ozonation followed by chlorination has been shown to increase trichloronitromethane formation (Hoigné and Bader, 1988; Krasner et al., 2006) though the actual mechanism involving ozone and halonitromethane formation has not been experimentally proven.

Formation of chloral hydrate increased as a result of LP and MP UV when followed by chlorination or chloramination. Chloral hydrate was formed at higher levels in chlorinated compared to chloraminated samples, but UV effects were smaller. During chloramination, chloral hydrate formation increased five-fold from MP UV treatment in bromide- and nitrate-spiked SRNOM

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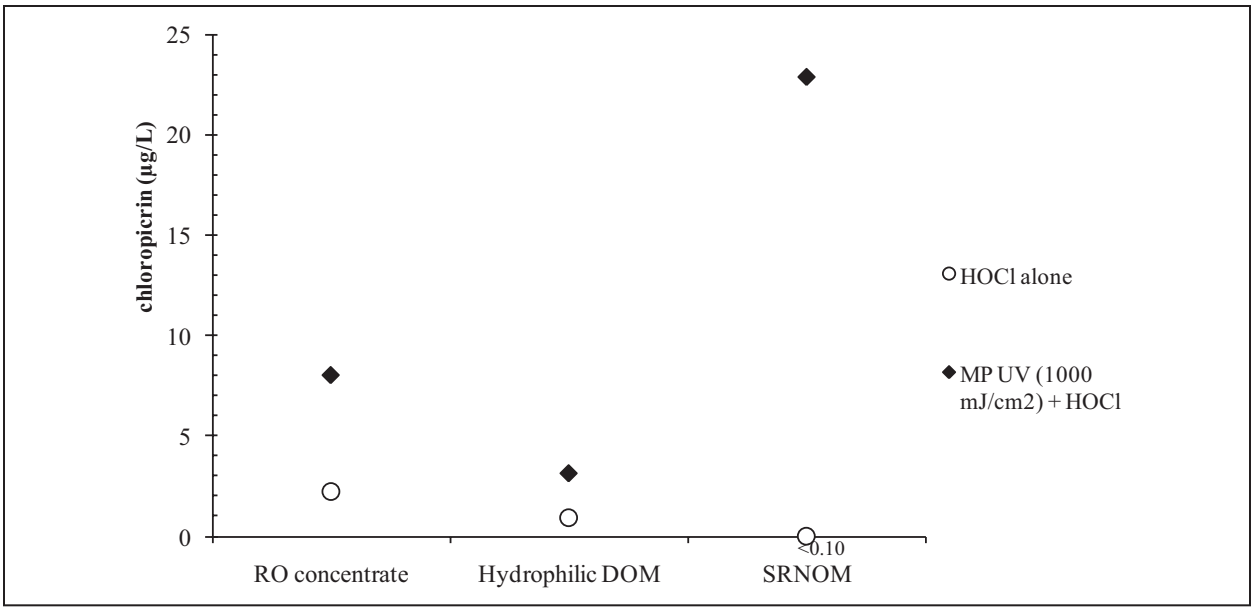


**Figure 6.9 Effect of MP UV followed by chlorination on trichloronitromethane formation in nitrate-spiked fractions**

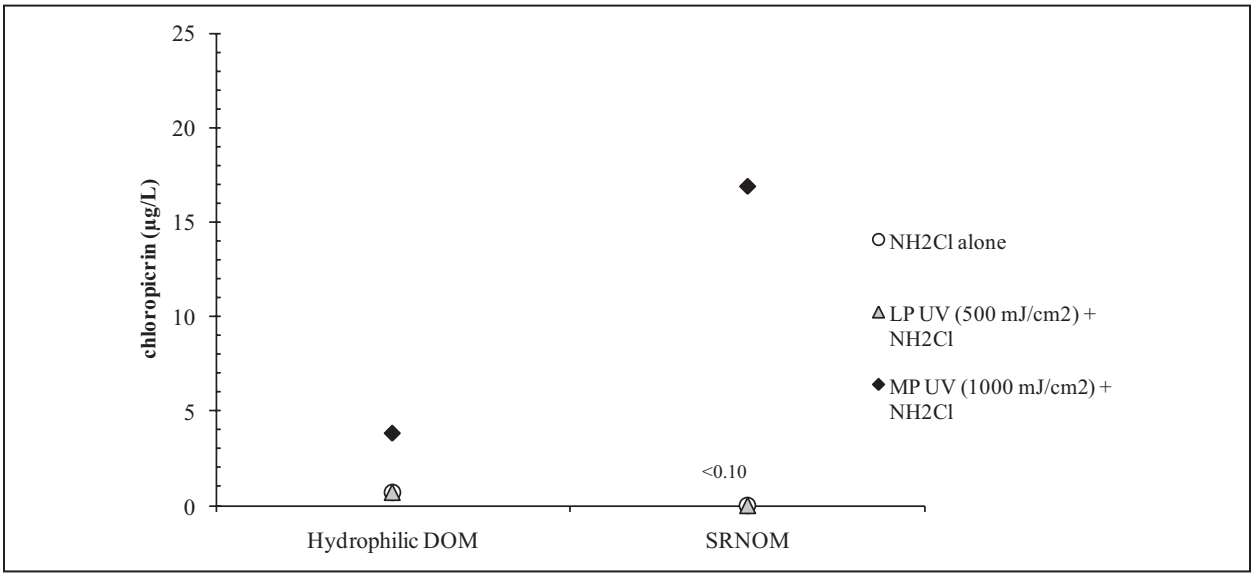


**Figure 6.10 Effect of LP and MP UV followed by chloramination on trichloronitromethane formation in nitrate-spiked fractions**

samples and doubled in bromide-only spiked SRNOM samples (Figure 6.11). Chloral hydrate was below detection (<0.10 µg/L) in ambient samples. The greater increase in chloral hydrate formation resulting from UV in the presence of nitrate suggests that nitrate plays an important role in the formation mechanism, which may be ·OH-induced. Unlike trichloronitromethane, formation of chloral hydrate was impacted by LP UV. Acetaldehyde, a DBP associated with ozonation, can react with chlorine to form chloroacetaldehyde and further react with excess free chlorine to form di- and tri-chloroacetaldehyde (McKnight and Reckhow, 1992).

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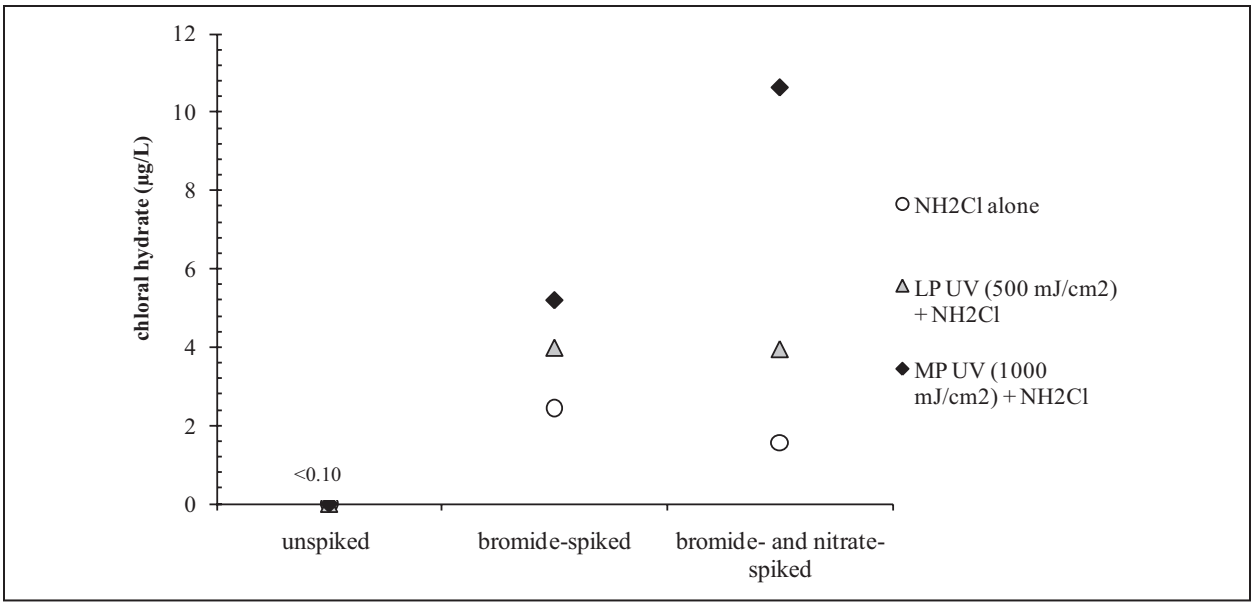


**Figure 6.11 Effect of LP and MP UV treatment on formation of chloral hydrate in SRNOM during chloramination in the presence/absence of bromide and nitrate**

### *Chloroacetonitriles*

Samples associated with free chlorine addition could not be assessed due to matrix interference, and therefore, only the chloramine results for dichloroacetonitrile (DCAN) are shown in Figure 6.12. No chloroacetonitrile (CAN) or trichloroacetonitrile (TCAN) were detected. Our method does not detect brominated analogues. The error bars represent the standard deviation of 2 replicates.

The results indicate that chloramination alone formed significant DCAN (~12.5 nM or 1.4 µg/L). As expected, treatment with 500 mJ/cm$^2$ low pressure UV or 1000 mJ/cm$^2$ medium pressure UV did not significantly increase formation of DCAN, as chlorination or chloramination would be needed for chlorine addition. Similarly, DCAN formation was observed for chloramination upstream of these UV treatments as was it also observed for chloramination alone, indicating that UV had minimal impact on the formation process. For example, UV photolysis of DCAN, inorganic chloramines, or any potential organic chloramine intermediates seems to be negligible, even for elevated UV fluences. However, DCAN formation declined ~70% to ~4 nM when these UV treatments were followed by chloramination. These results may indicate that UV treatment deactivates DCAN precursors.

### *Chloronitromethanes*

Samples were also evaluated for chloronitromethanes. Data sets for chloronitromethane (CNM), dichloronitromethane (DCNM), trichloronitromethane (TCNM), and their totals are shown in Figure 6.13. As for haloacetonitriles, we could not evaluate halonitromethane formation for samples exposed to chlorine, due to massive matrix interference.

Low and medium pressure exposures alone produced no significant HNMs, as chlorination or chloramination would be needed for halogen addition. Chloramination alone produced ~10 nM

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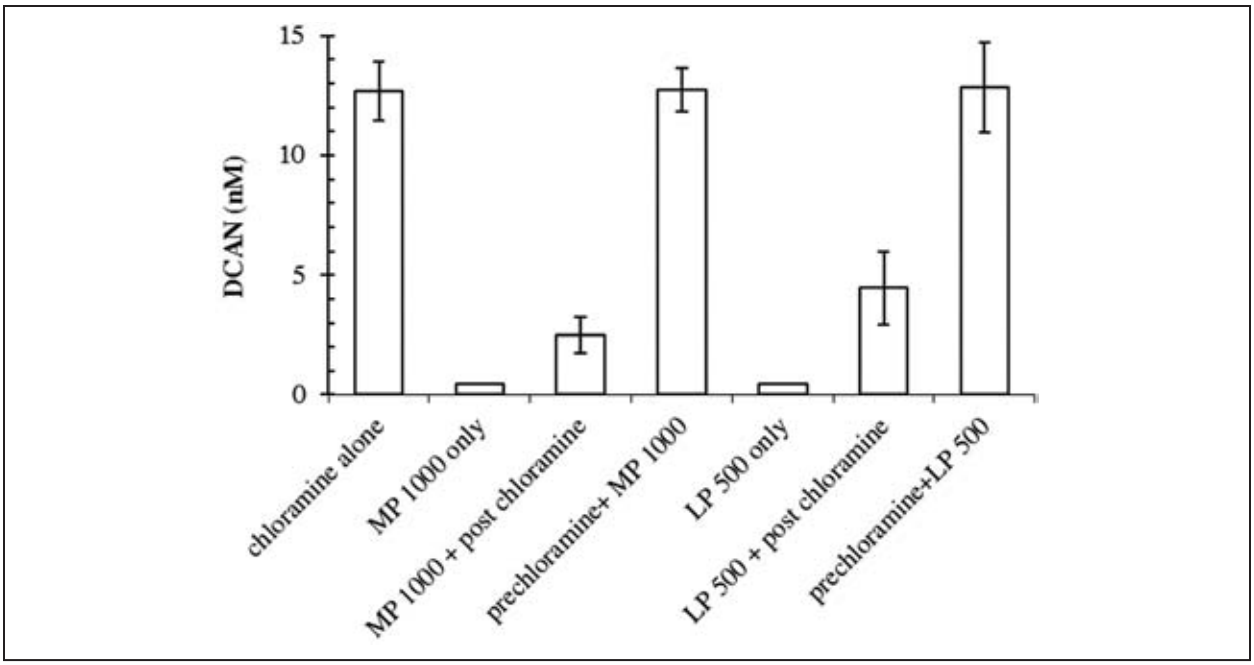


**Figure 6.12 Chloroacetonitrile formation from OWASA RO concentrate**

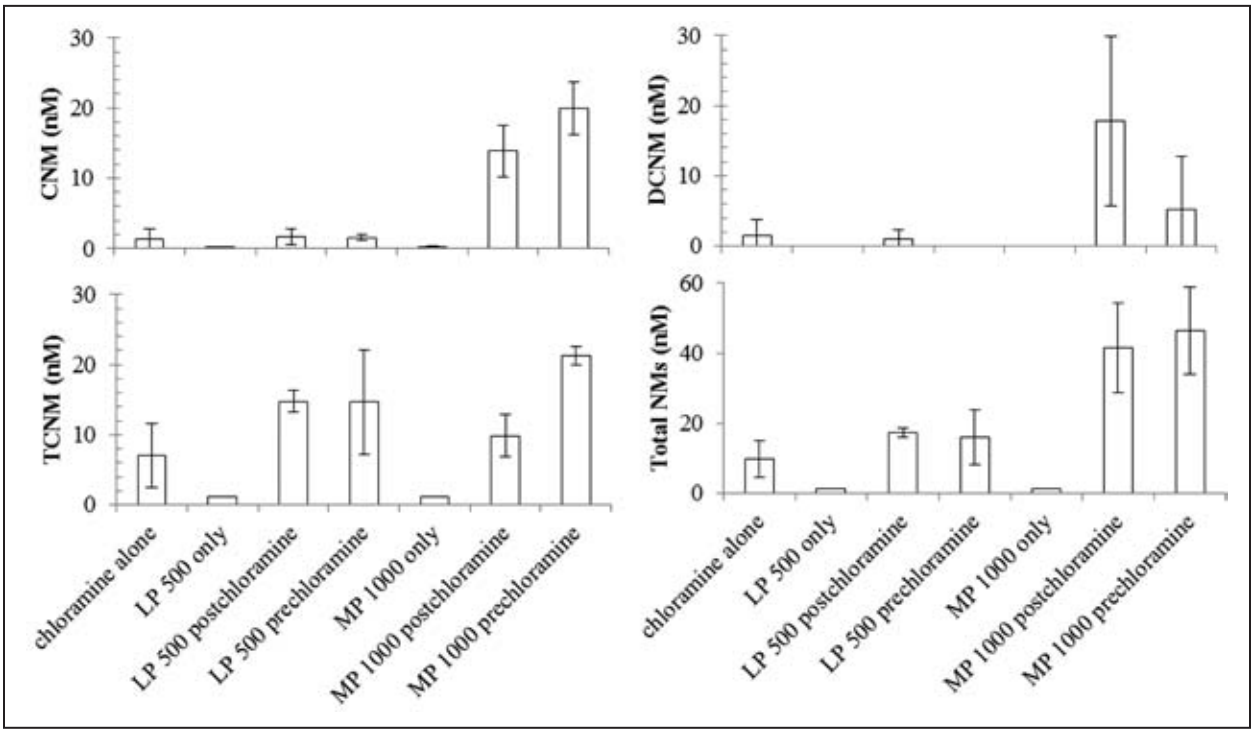


**Figure 6.13 Chloronitromethane formation from OWASA RO concentrate**

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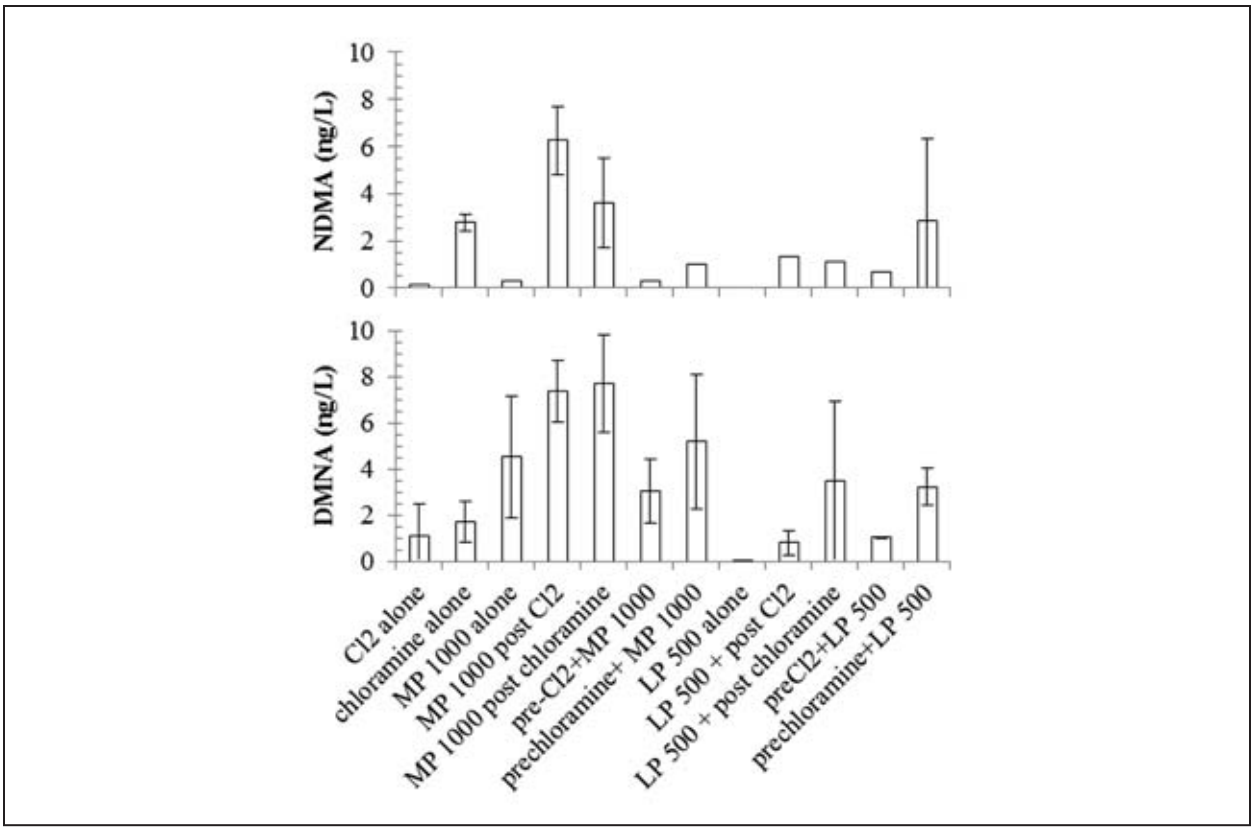


**Figure 6.14 NDMA and DMNA formation**

chloronitromethanes, predominantly trichloronitromethane. With a few exceptions, trichloronitromethane dominated the chloronitromethanes, in line with previous studies (e.g., Joo and Mitch, 2007; Mitch and Schreiber, 2008). When 500 mJ/cm$^2$ low pressure UV was combined with chloramination either upstream or downstream, no significant difference in chloronitromethane formation was observed compared with chloramination alone. However, when 1000 mJ/cm$^2$ medium pressure UV was combined with chloramination either upstream or downstream, a 300% increase in total chloronitromethanes was observed. Some DCNM was observed when chloramines were applied downstream of medium pressure UV. These results are in accordance with the lack of photolysis of nitrate by low pressure UV exposures and nitrate photolysis by medium pressure UV due to a significant action spectrum for nitrate via the medium pressure emission band below 240 nm and near 313 nm.

### *Nitrosamine and Dimethylnitramine Formation*

With the exception of NDMA and dimethylnitramine (DMNA), no significant formation of nitrosamines was observed. For NDMA, significant formation (above the 2 ng/L method detection limit) was observed for chloramination (Figure 6.14), but not for chlorination, in line with previous studies (Schreiber and Mitch, 2006). No significant formation was observed for low or medium pressure UV treatment alone. The only significant increase in NDMA formation was observed when the water was treated with 1000 mJ/cm$^2$ medium pressure UV upstream of chlorination, where ~6 ng/L NDMA was observed, approximately a 300% increase compared with chlorination

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alone. This formation may be associated with $N_2O_4$ formation via the chlorination of nitrite formed by medium pressure UV photolysis of nitrate; however, further research would be needed to clarify this result. For chloramination/UV combinations, no significant increase in NDMA formation was observed associated with UV treatment.

In the case of DMNA, neither chlorination nor chloramination alone formed significant DMNA. Medium pressure UV treatment alone, but not low pressure treatment alone, formed ~4.5 ng/L DMNA. This formation may be associated with $N_2O_4$ formation via medium pressure UV photolysis of nitrate. In the case of medium pressure UV combinations with chlorine or chloramines, chloramination upstream produced no significant differences from medium pressure treatment alone. However, chlorination upstream reduced DMNA formation, likely due to deactivation of organic nitrogen precursors, similar to the effects observed for chlorination of NDMA precursors (Schreiber and Mitch, 2005); indeed, the precursors are likely similar (Schreiber and Mitch, 2007). DMNA formation increased to ~8 ng/L with post-chlorination or post-chloramination. This formation may be associated with $N_2O_4$ formation via chlorine or chloramine reactions with nitrite formed by UV photolysis of nitrate. For low pressure UV treatments, such effects were not observed, probably because low pressure UV does not significantly photolyze nitrate.

## SUMMARY

Using extreme conditions (e.g., concentrated NOM, spiking of high concentrations of bromide and nitrate, and high doses of UV irradiation) the formation of a number of classes of DBPs were increased. Furthermore, the study of fractionated NOM revealed differences in reactivity from both a UV and chlorine/chloramines prospective. A number of important findings were identified:

1. Treatment with 1000 mJ/cm$^2$ of MP UV promoted greater free chlorine demand suggesting changes in NOM character.
2. Greater THM4 formation was observed when samples were pretreated with MP UV. Concentrated NOM samples (e.g., RO concentrate and SRNOM) were observed to have greater increases in THM4 formation than the NOM isolates.
3. HAA9 formation increased in the concentrated NOM samples and decreased in the NOM isolates when compared to the unirradiated sample when pretreated with either LP or MP UV.
4. When chloraminated after treatment with UV, demand increased for SRNOM, decreased for hydrophobics, and was unchanged for hydrophilics. This trend loosely corresponded with change in formation of THM4 and HAA9.
5. Trichloronitromethane formation was increased when chlorinated or chloraminated after MP UV treatment but no change in formation was observed when pretreated with LPUV. This was likely due to nitrosation reactions caused by photolysis of nitrate by the MP UV.
6. Chloral hydrate increased notably when samples were pretreated by either UV technology and spiked with either bromide or bromide and nitrate. This increase was greater when pretreated with MP UV.
7. Dichloroacetonitrile formation during chloramination was decreased by pretreatment with UV suggesting precursor inactivation by the UV process.
8. MP UV promoted increased formation of NDMA and DNMA during post-chlorination and chloramination. Similar to trichloronitromethane nitrosation reactions caused by photolysis of nitrate by MP UV are suspected.

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# CHAPTER 7
# FLOW-THROUGH EVALUATION OF DISINFECTION BY-PRODUCT FORMATION AFTER UV CHLORINATION/ CHLORAMINATION SEQUENCE

## OVERVIEW

For many drinking water treatment processes there are slight differences between laboratory and full-scale. Previously the study of UV disinfection processes has primarily focused on the microbiological aspects of the disinfection process. This chapter discusses the field scale results (pilot- and full-scale study) of the effect of UV disinfection processes on disinfection by-product formation. This chapter is segregated in two sections: (1) pilot-scale UV treatment and (2) full-scale UV treatment. First, a UV pilot plant located at the Richard Miller water treatment plant in Cincinnati, OH was used in a manner such that experiments using a flow-through UV pilot could be compared to the bench-scale results presented in Chapter 5. Second, three full-scale facilities were sampled with and without their UV disinfection systems operated to clearly isolate the influence of the UV disinfection process on downstream disinfection by-product formation due to chlorination/chloramination.

## RESULTS

Results are separated into pilot- and full-scale studies. The pilot scale study was performed as a single experiment using two lamp technologies, LP and MP, varying flow rate through the reactor to achieve different UV doses and spiking in inorganic DBP precursors (bromide and nitrate). The full-scale study evaluated three drinking water treatment plants at three different occasions. At full-scale facilities samples were collected from a single point in the process train with the UV disinfection system operating and again with the system turned off.

### Pilot-Scale Testing at the Cincinnati UV Pilot Plant

The UV pilot plant was operated for a full day isolating a single train, either LP or MP, for study. Influent water, which was conventionally treated (coagulation, flocculation, sedimentation, sand filtration) but not GAC adsorbed or chlorine disinfected, was continuously piped to a break-tank upstream of the pilot plant. It should be noted that the water studied in Chapter 5 was collected from the same location in the Richard Miller WTP as the water that fed the UV pilot plant. Variation in water quality throughout the day of testing was minimal (Table 7.1). Pilot plant TOC was approximately 2.2 mg-C/L and $UVA_{254}$ was approximately 0.047 $cm^{-1}$.

The LPUV system, while equipped with an intensity sensor, was not able to process this reading into a dose. Therefore, samples were collected under each flow condition and analyzed in the field for $UVA_{254}$ absorbance in a 5-cm pathlength cell and compared to the $UVA_{254}$ of the pilot influent. In the laboratory, loss in $UVA_{254}$ associated with increasing UV dose was determined and used to calculate the UV dose applied at pilot scale. LP UV doses were estimated to be 122, 390, and 676 $mJ/cm^2$. The doses calculated corresponded with flow rates through the pilot of 40,10, and 5 gpm, respectively.



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**Table 7.1**
**Water quality of Cincinnati pilot feed water**

| Parameter | Units | Value |
|---|---|---|
| Total Organic Carbon | mg-C/L | 2.15–2.31 |
| Total Nitrogen | mg-N/L | 1.11–1.17 |
| $UV_{254}$ | $cm^{-1}$ | 0.046–0.048 |

**Table 7.2**
**Chlorinated pilot-scale LP UV treated Cincinnati water**

| UV dose ($mJ/cm^2$) $UVA_{254}$ | $Cl_2$ demand mg-$Cl_2$/L | THM4 (µg/L) | TCNM (µg/L) | DCAN (µg/L) | BCAN (µg/L) | DBAN (µg/L) | 11DCP (µg/L) | 111TCP (µg/L) |
|---|---|---|---|---|---|---|---|---|
| 0 | 1.6 | 64.1 | BDL | 1.1 | 1.8 | 0.9 | BDL | 0.8 |
| 122 | 1.7 | 67.4 | BDL | 1.2 | 1.8 | 0.9 | BDL | 0.8 |
| 390 | 1.9 | 72.5 | BDL | 1.4 | 1.8 | 0.9 | BDL | 1.3 |
| 676 | 1.9 | 75.6 | BDL | 1.3 | 1.8 | 0.9 | BDL | 1.4 |

**Table 7.3**
**Chlorinated pilot-scale LP UV spiked treated Cincinnati water**

| UV dose ($mJ/cm^2$) $UVA_{254}$ | $Cl_2$ demand mg-$Cl_2$/L | THM4 (µg/L) | TCNM (µg/L) | DCAN (µg/L) | BCAN (µg/L) | DBAN (µg/L) | 11DCP (µg/L) | 111TCP (µg/L) |
|---|---|---|---|---|---|---|---|---|
| 0 | 2.1 | 135.6 | BDL | BDL | 2.7 | 8.7 | BDL | 0.1 |
| 122 | 2.2 | 148.6 | BDL | BDL | 2.8 | 8.5 | BDL | 0.1 |
| 390 | 2.3 | 168.0 | BDL | BDL | 2.6 | 10.5 | BDL | BDL |
| 676 | 2.5 | 174.7 | BDL | BDL | 2.5 | 11.0 | BDL | BDL |

Samples were collected in duplicate at each flow condition and chlorinated with a dose of sodium hypochlorite such that a residual of 1.0±0.4 mg-$Cl_2$/L was present after 24 hours of incubation at room temperature (22–25°C). The chlorine demand and DBP results shown in Table 7.2 are the average of duplicates (typical of Tables 7.2–7.5). With increased dose of LP UV followed by chlorine, chlorine demand increased by as much at 0.2 mg-$Cl_2$/L and THM4 followed suit increasing by up to 11.4 µg/L (predominantly chloroform). No trichloronitromethane or 11DCP was measured and BCAN and BCAN formation appeared unaffected by LP UV irradiation. DCAN slightly increased with increased LP UV dose but this change was very slight (<0.2 µg/L) and is not statistically significant. 111TCP also increased in concentration at LP UV doses higher than disinfection doses by as much as 0.6 µg/L.

Bromide and nitrate were spiked into the conventionally treated pilot influent to achieve similar conditions to that reported in Chapter 5. Similar trends to the unspiked testing conditions were observed but the formed DBPs halogen incorporation shifted to brominated species. Chlorine demand increased (0.4 mg-$Cl_2$/L) with increasing LPUV dose and so did THM4 formation (39.1 µg/L) (predominantly bromoform). Similarly, no trichloronitromethane or DCAN was

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**Table 7.4**
**Chlorinated pilot-scale MP UV treated Cincinnati water**

| UV dose ($mJ/cm^2$) | | | $Cl_2$ demand | THM4 | TCNM | DCAN | BCAN | DBAN | 11DCP | 111TCP |
|---|---|---|---|---|---|---|---|---|---|---|
| Sensor | $NO_2$ | $UVA_{254}$ | mg-$Cl_2$/L | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) |
| 0 | 0 | 0 | 1.7 | 70.7 | BDL | 1.6 | 1.9 | 0.9 | BDL | 0.6 |
| 95 | 74 | 204 | 1.9 | 70.1 | BDL | 1.3 | 1.8 | 0.9 | 0.8 | 0.7 |
| 399 | 302 | 517 | 2.1 | 71.2 | BDL | 1.2 | 1.8 | 0.9 | 1.9 | 1.0 |
| 878 | 597 | 795 | 2.3 | 72.1 | BDL | 1.5 | 1.8 | 0.9 | 2.9 | 1.2 |

**Table 7.5**
**Chlorinated pilot-scale MP UV spiked treated Cincinnati water**

| UV dose ($mJ/cm^2$) | | | $Cl_2$ demand | THM4 | TCNM | DCAN | BCAN | DBAN | 11DCP | 111TCP |
|---|---|---|---|---|---|---|---|---|---|---|
| Sensor | $NO_2$ | $UVA_{254}$ | mg-$Cl_2$/L | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) |
| 0 | 0 | 0 | 2.1 | 163.2 | BDL | BDL | 2.5 | 11.0 | BDL | BDL |
| 95 | 74 | 204 | 2.3 | 164.9 | BDL | BDL | 2.5 | 11.5 | BDL | BDL |
| 399 | 302 | 517 | 2.8 | 161.6 | BDL | BDL | 2.7 | 10.9 | BDL | 0.5 |
| 878 | 597 | 795 | 3.6 | 222.9 | BDL | BDL | 2.1 | 27.6 | BDL | BDL |

formed but it should be noted that with the spiked bromide it would be unlikely that these compounds would form as the brominated analogues would form more rapidly. BCAN, 11DCP, and 111TCP formation did not change with increasing LP UV dose. DBAN increased with increasing LPUV dose and at more statistically relevant concentrations (up to 2.3 µg/L) at high doses.

The configuration of the MPUV pilot and the nature of MPUV light allowed for three techniques of dose measurement to be used: (1) the on-board sensors, (2) formation of nitrite ($NO_2^-$) and (3) the decay of $UVA_{254}$. The method for calculating dose from formation of $NO_2^-$ mirror that of $UVA_{254}$ and was described previously in the discussion of LPUV irradiation. The doses applied were disinfection range (95–204 $mJ/cm^2$), medium dose (302–517 $mJ/cm^2$), and a high dose (597–878 $mJ/cm^2$).

With increasing dose of MPUV, chlorine demand increased by as much as 0.6 mg-$Cl_2$/L which was greater than with LPUV. THM4 increased slightly by 1.4 µg/L at the highest dose and no discernable difference was observed with medium MPUV dose. TCNM, DCAN, BCAN, and DBAN formation was unaffected by MP UV dose. 111DCP and 111TCP increased with increasing MP UV dose. 11DCP formation was statistically relevant at the high disinfection dose of MPUV. Numeric results are presented in Table 7.4.

Bromide and nitrate were spiked in similar to as discussed previously with the LP UV pilot. Chlorine demand increased significantly at the highest MPUV dose (1.5 mg-$Cl_2$/L) some of which was likely attributed to the oxidation of formed $NO_2^-$ back to nitrate ($NO_3^-$). As reported in Table 7.5, THM4 formation did not appear to be affected by MP UV dose until the highest dose where a notable increase was observed (~60 µg/L, predominantly as bromoform). DBAN followed a similar trend to THM4 formation, increasing only at the highest dose by 16.7 µg/L. TCNM,

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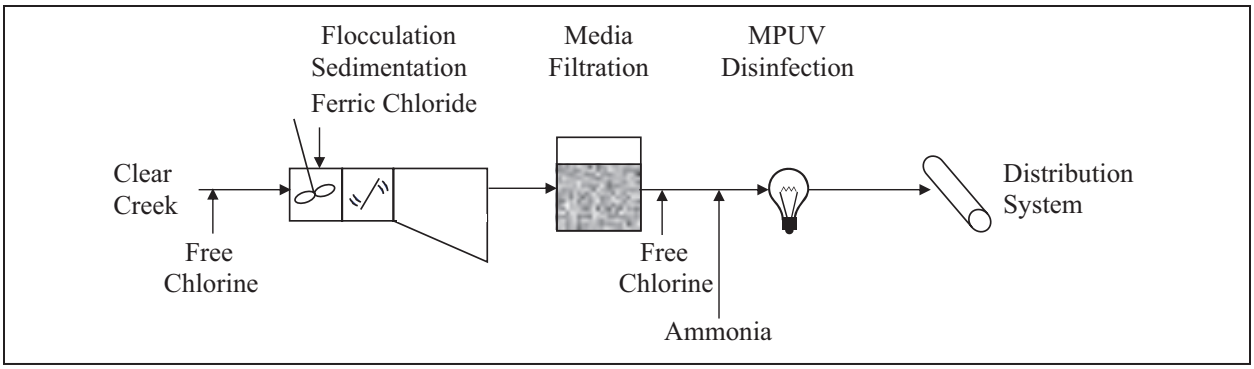


**Figure 7.1 Thornton water treatment plant process flow diagram**

**Table 7.6**
**NDMA concentration for samples treated with or without UV on-site and post-chloraminated off-site at the Thornton WTP**

| Samples | UV | July 2010 [NDMA] (ng/L) |
|---|---|---|
| Thornton | Off | 2.4 |
| Thornton | On | 5.8 |

DCAN, 11DCP, and 111TCP did not form in this experiment. BCAN formed but appeared unaffected by increasing MP UV dose.

**Full Scale**

Three drinking water treatment plants employing a variety of UV technologies in a variety of sequences were studied. Two of these facilities were located in Colorado and one in Illinois. Detailed process train and chlorination sequences are described in the sections below.

***Thornton WTP***

Thornton WTP provides drinking water to Thornton, CO using Clear Creek as a source water. The facility is a conventional treatment plant that practices pre-chlorination and maintains a distribution system with chloramines. Chloramines are applied upstream of the UV reactor. The UV reactor was installed as a retrofit and is a Hanovia Crossflow system equipped with MP UV lamps. The design dose is 40 mJ/cm$^2$ but due to upstream process changes/optimization the system is often operated at higher doses (upward of 190 mJ/cm$^2$) and cannot be turned down. The UV dose is calculated online using in-situ sensors that measure lamp intensity, UV transmittance and flowrate. A process flow diagram is shown in Figure 7.1.

No samples collected during round 1 (April) as the plant had not been turned on after the winter shutdown yet as well as during the October sampling as the plant had been preemptively shutdown for the winter season.

Thornton samples were only analyzed for the July sampling period. During the sampling the DOC was determined to be 1.85 mg/L with the UV lamps on and 2.09 mg/L with the UV lamps

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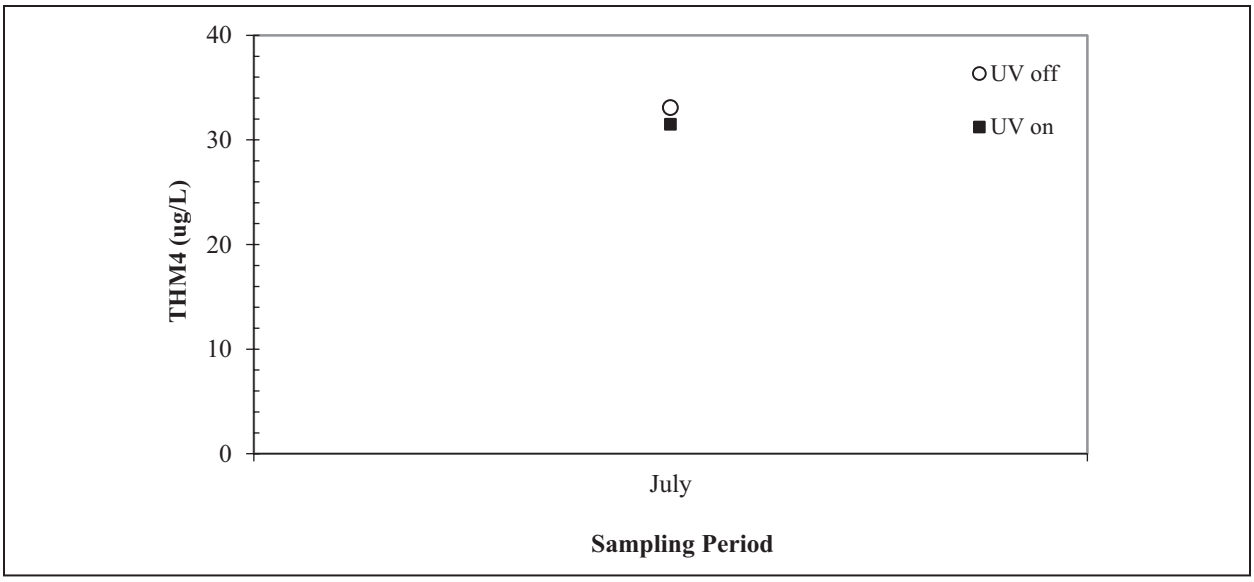


**Figure 7.2 Total trihalomethane formation with and without UV treatment at Thornton WTP. RPD between replicates <7%.**

off. At the time of sampling the reactor was applying 140 mJ/cm$^2$ of irradiation. Changes in THM4 formation from UV were not statistically significant. TCAN and TBNM were below detection (<0.1 µg/L). The only iodo-THM detected was $Cl_2ICH$ (0.2–0.3 µg/L). THM4 results are shown in Figure 7.2. Low amounts of NDMA were found (<6 ng/L) with either the UV on or off (Table 7.6). This is likely due to the low levels of precursor present in the water, and therefore any effect of UV treatment are difficult to discern.

### *Wes Brown WTP*

Wes Brown WTP provides water to Thornton, CO using the South Platte River as the primary source water. The South Platte River is highly wastewater impacted and often has very low water quality. This facility has undergone a variety of retrofits in the recent years. The plant process is illustrated in Figure 7.3. Briefly, the source water is prechlorinated then is coagulated and settled. The settled water is process by Zenon Ultrafilter membranes followed by Hanovia Crossflow UV disinfection system equipped with MP UV lamps. A small free chlorine concentration is carried through the entire plant for microbial control. Similar to the Thornton WTP, the design dose of the UV system was 40 mJ/cm$^2$ but due to upstream retrofits the UV system often operates at doses significantly higher (upward of 180 mJ/cm$^2$).

Water quality remained the same in samples collected from the Wes Brown WTP with and without the MP UV lamps online (Table 7.7). During the first sampling, samples were collected prior to plant chloramination and monochloramines were applied in the CU laboratory. Upon collection the samples contained 0.32 mg-$Cl_2$/L of free chlorine but at the time of chloramination no residual was present. Monochloramine was added at the same dose as the current dose the full-scale WTP was applying, 2.5 mg-$Cl_2$/L. After 24 hours of incubation a residual of 1.1 mg-$Cl_2$/L was measured.

Furthermore, these were analyzed for trihalomethanes, trichloronitromethane, tribromonitromethane, haloacetonitriles, chloral hydrate, and two haloketones (1,1-dichloropropanone and

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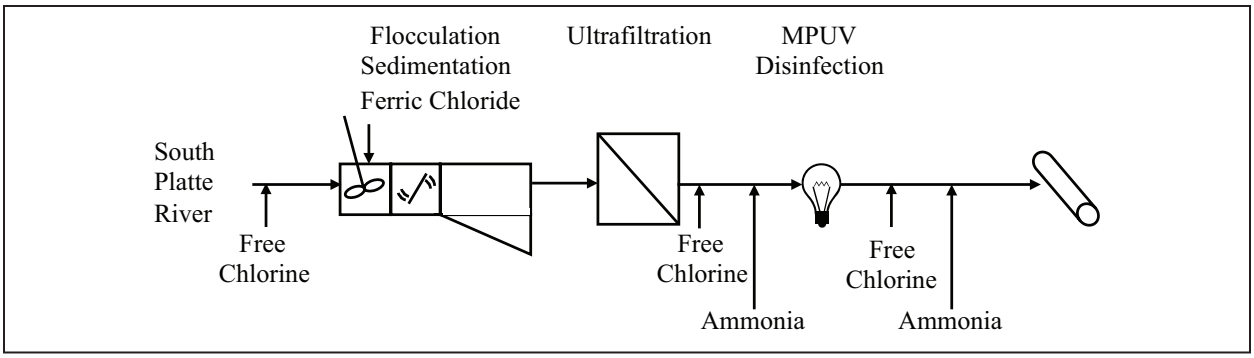


**Figure 7.3 Wes Brown water treatment plant process flow diagram**

**Table 7.7**
**Wes Brown water quality**

| | | April 2010 | | July 2010 | | October 2010 | |
|---|---|---|---|---|---|---|---|
| Parameter | Units | On | Off | On | Off | On | Off |
| UV Dose | mJ/cm$^2$ | 79 | 0 | 71 | 0 | 42 | 0 |
| DOC | mg/L | 4.04 | 4.10 | 4.03 | 4.13 | 4.39 | 4.30 |
| TDN | mg/L | 0.60 | 0.60 | n/a | n/a | 0.92 | 0.94 |

1,1,1-trichloropropanone). Changes in THM4 formation resulting from UV were not statistically significant. THM4 formation was highest in the July sampling period (60–63.2 µg/L) and lowest in October (30.8–32.1 µg/L). TCAN, TBNM, $ClI_2CH$, $BrI_2CH$, and $I_3CH$ were not detected (<0.1 µg/L) during any sampling periods. Two iodo-THMs ($Cl_2ICH$ and $Br_2ICH$) were formed at levels ranging from 0.2–1 µg/L, but UV did not affect their formation (Figure 7.4).

Negligible amounts of NDMA (<4 ng/L) were found in the April sampling event with either the UV on or off (Table 7.8). Here, #1 and #2 represent replicates. Therefore, this water contained a limited amount of precursor material and any effects of UV treatment are hard to discern in this case. For the July and September sampling events, the level of NDMA formation appeared to increase from 4–6 ng/L in July to 12.5–14 ng/L in September; however, there was no difference between samples that were UV treated and ones that are not treated. This indicates that there might be a seasonal difference in the precursor material in the water that leads to greater NDMA formation after the water is chloraminated, but UV treatment plays no role in affecting this observed trend.

### *Central Lake County Joint Action Water Agency (CLCJAWA)*

CLCJAWA provides treated Lake Michigan water to about 200,000 people in Lake County, Illinois. Their Paul M. Neal WTP is located north of Chicago in Lake Bluff, Illinois. The plant process is illustrated in Figure 7.5. Briefly, the source water is preozonated then is coagulated and settled. The settled water is processed through biologically active filters followed by a Trojan UVSwift system equipped with MP UV lamps. The UV target dose is 12 mJ/cm$^2$ but typically operates closer to 30 mJ/cm$^2$ due to turn-down limitations.

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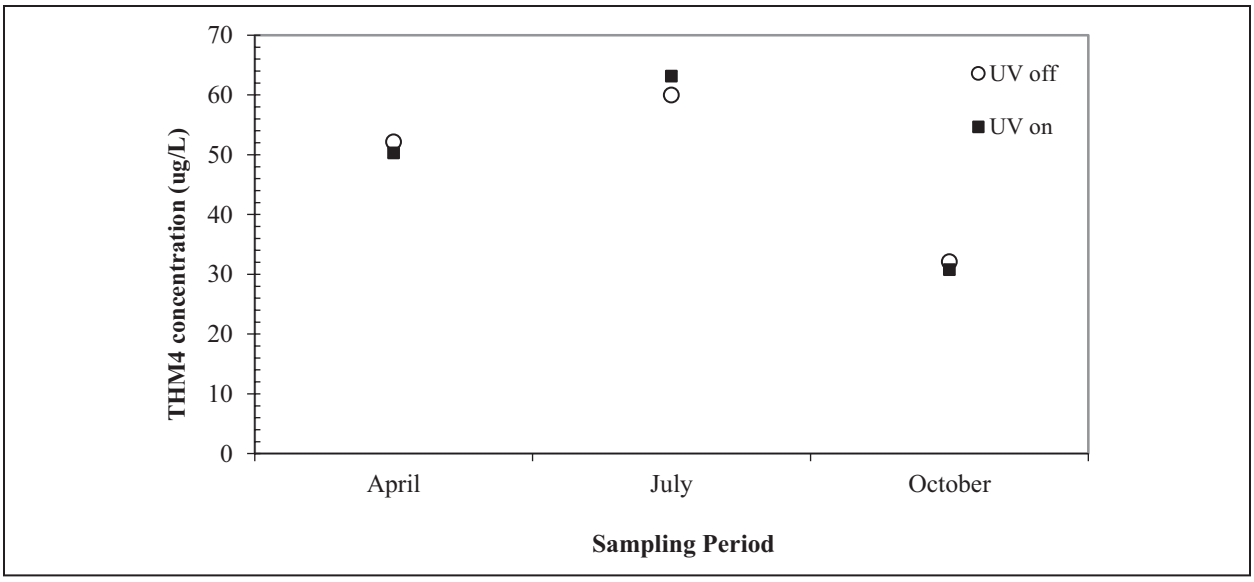


**Figure 7.4 Total trihalomethane formation with and without UV treatment at Wes Brown WTP. RPD between replicates <7%.**

**Table 7.8**
**NDMA concentration for samples treated with or without UV on-site and post-chloraminated off-site at the Wes Brown WTP**

| Samples | UV | April 2010 [NDMA] (ng/L) | July 2010 [NDMA] (ng/L) | September 2010 [NDMA] (ng/L) |
|---|---|---|---|---|
| Wes Brown | Off #1 | 0.4 | 4.7 | 14 |
| Wes Brown | Off #2 | 3.5 | | |
| Wes Brown | On #1 | 2.4 | 5.6 | 12.5 |
| Wes Brown | On #2 | 1.4 | | |

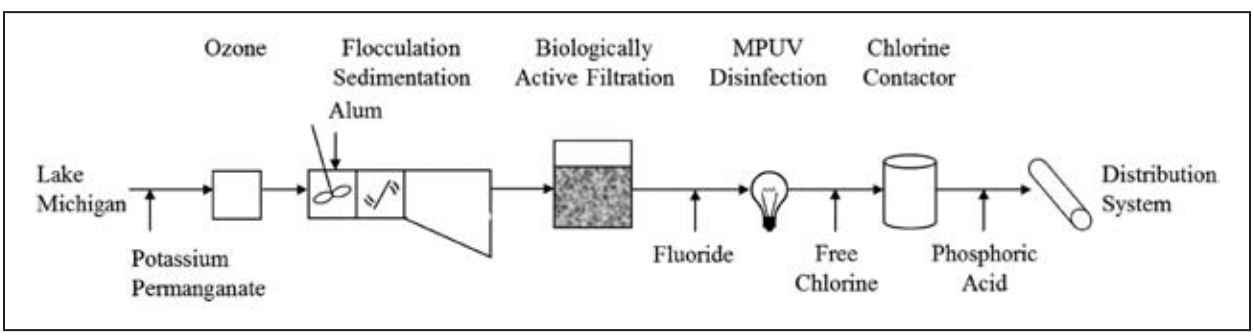


**Figure 7.5 CLCJAWA water treatment plant process flow diagram**

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**Table 7.9**
**CLCJAWA water quality**

| | | April 2010 | | July 2010 | | October 2010 | |
|---|---|---|---|---|---|---|---|
| Parameter | Units | On | Off | On | Off | On | Off |
| UV Dose | $mJ/cm^2$ | 28 | 0 | 41 | 0 | 33 | 0 |
| DOC | mg/L | 1.73 | 1.67 | 1.69 | 1.70 | 1.58 | 1.61 |
| TDN | mg/L | 0.52 | 0.53 | 0.38 | 0.37 | 0.46 | 0.48 |

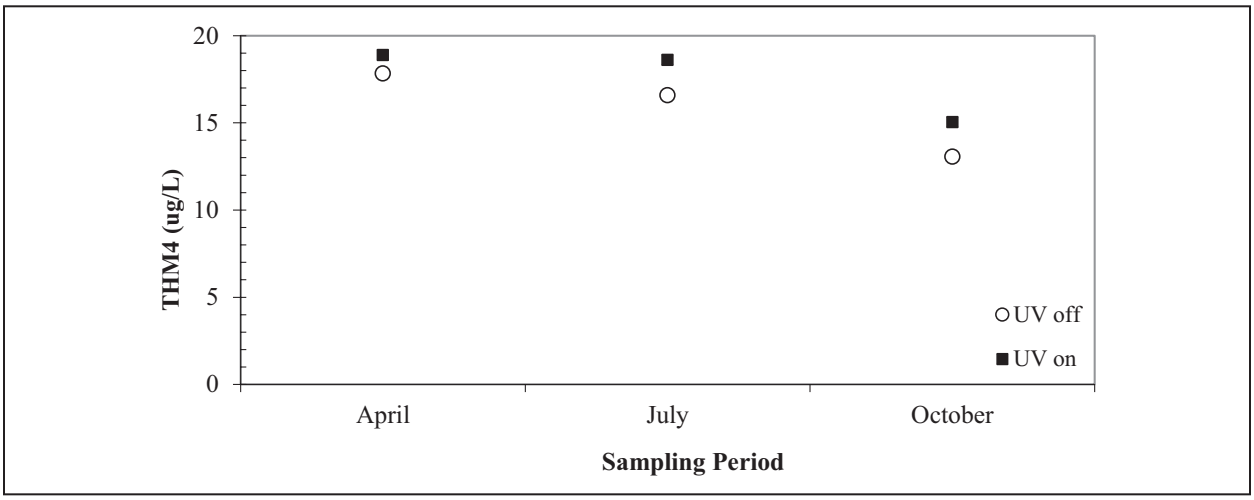


**Figure 7.6 Total trihalomethane formation with and without UV treatment at CLCJAWA. RPD between replicates <4%.**

Water quality remained the same in samples collected from the CLCJAWA WTP with and without the LP UV lamps online (Table 7.9). During the April sampling, samples were collected after chlorination at the entrance to the clearwell. The chlorine residual at the time of sampling was between 0.92–1.0 mg-$Cl_2$/L. Chlorine demand was not determined as a final residual was not measured after the incubation time.

These samples were analyzed for trihalomethanes, trichloronitromethane, tribromonitromethane, haloacetonitriles, chloral hydrate, and two haloketones (1,1-dichloropropanone and 1,1,1-trichloropropanone) pre- and post-UV treatment. Increases in THM4 resulting from UV treatment were in the 1–2 µg/L range and not statistically significant (Figure 7.6). THM4 formation was higher in the April and July sampling periods (16.6–18.9 µg/L) compared to the October sampling period (13.1–15 µg/L). Iodo-THMs were not detected during any of the sampling periods, which was expected because iodo-THM formation is favored during chloramination, rather than chlorination (Bichsel and von Gunten, 2000). During all sampling periods, chloral hydrate formation was increased 17–19% with the addition of UV prior to chlorination. RPD between replicate chloral hydrate analyses ranged from 0.3–4%. TCAN, 11DCP, and TCNM were not detected during any of the sampling periods, and BCAN was detected in July and October (0.7–0.8 µg/L), but not in April (<0.1 µg/L). Unlike the other full-scale plants, CLCJAWA samples favored the formation of tribromonitromethane over trichloronitromethane.

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**Table 7.10**
**NDMA concentration for samples treated with or without UV at the CLCJAWA**

| Samples | UV | [NDMA] (ng/L) |
|---|---|---|
| CLCJAWA | Off #1 | 6.1 |
| CLCJAWA | On #2 | 3.0 |
| CLCJAWA | On #2 | 6.0 |

Small amounts of NDMA were found (<6 ng/L) for the April and July sampling both with the UV on or off. Therefore, this water contains a limited amount of precursor material and any effects of UV treatment are hard to discern in this case. For the September 2010 sampling event, the NDMA concentration was found to be 15 ng/L when UV treatment was off and 25 ng/L when UV treatment was on. In this case, UV treatment seems to increase NDMA. However, duplicates need to be run to verify that these concentrations are reproducible and accurate. Replicates were analyzed for only the April 2010 sampling event, indicated in Table 7.10 by using the labels #1 and #2.

## SUMMARY

Flow-through study of the UV chlorine/chloramination sequence followed trends similar to that observed in the bench studies (Chapter 5). Pilot-scale study allowed for direct reconstruction of conditions studied on the bench. Full-scale study provided the means to support bench- and pilot-scale findings at operating facilities already utilizing UV technologies and operating a sequence of disinfection steps. Important conclusions/findings of the flow-through UV chlorine/chloramines sequence evaluation are:

1. LP UV sequenced with free chlorine at pilot-scale mimic the observed findings of the bench-scale LP UV free chlorine sequence. Application of disinfection doses of LP UV followed by free chlorine does not change the formation of regulated or measurable unregulated DBPs. LP UV doses greater than that applied for disinfection when sequenced with free chlorine will slightly increase chlorine demand (<0.4 mg-$Cl_2$/L), THM formation (<10 µg/L), and selected emerging DBPs (selected halopropanones and haloacetonitriles).
2. Similar but slightly lower DBP results were observed for the pilot-scale MP UV free chlorine sequence. No significant change in downstream DBPs was observed at disinfection doses and a significant, but small, change in DBP formation was observed at the highest dose tested.
3. Evaluation of three full-scale UV reactors show slight changes in DBP formation when UV disinfection was applied but in most cases these are on the order of analytical and experimental error. Therefore, at these facilities the UV chlorine/chloramination had no effect of DBP formation over chlorine/chloramines alone.

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# CHAPTER 8
# PROJECT CONCLUSIONS AND RECOMMENDATIONS

## CONCLUSIONS

This investigation's evaluation of the UV disinfection and secondary disinfectant (free chlorine and chloramines) sequence in drinking water treatment has developed a number of industry relevant conclusions. This research has studied in detail the sequence of processes using the most commonly applied UV lamp technologies (low and medium pressure UV), UV doses, and secondary disinfectants (free chlorine and monochloramine). To evaluate the fundamentals of DBP formation mechanisms, UV doses greater than that required for disinfection (186–1000 mJ/cm$^2$), concentrated organic precursor material (NOM isolates and concentrates), and elevated concentrations of inorganic precursor materials (bromide and nitrate) were employed. Returning to the objectives presented in Chapter 1, conclusions associated with each objective are presented herein:

1. Survey UV disinfection practices in drinking water in North America and how UV is combined with other oxidants/disinfectants.

Based on the completed surveys from twenty-four drinking water treatment plants in the continental United States that currently have UV disinfection installed or have performed pilot testing and are currently installing UV, numerous key findings were identified. The majority of facilities that employ a UV disinfection process treat surface water, and utilize MP UV technology. More than half of the surveyed facilities do not run a residual chemical disinfectant through the UV disinfection system. Therefore, post-chlorination or post-chloramination is most commonly practiced. The facilities generally reported that no change in either secondary disinfection chemical usage or regulated DBP formation was observed. These survey results indicate that full-scale implementation of UV disinfection in drinking water, regardless of the sequence with a secondary disinfectant, has little or no effect on regulated DBP formation.

2. Evaluate at least three different waters of broadly varied water quality from participating utilities for changes in regulated and emerging DBP formation from the UV free chlorine/chloramines sequence to develop baseline study conditions.

The impacts of UV on DBP formation observed in this section of the research were slight, but suggested that at high UV doses (400 mJ/cm$^2$), the addition of LP or MP UV prior to chlorination or chloramination can occasionally increase the formation of THMs and HAAs by ~10–20%. Treatment with MP UV upstream of chlorination or chloramination increased trichloronitromethane formation by ~20–50%, but LP UV pre-treatment did not show a similar effect. At one plant, LP or MP UV treatment followed by chlorination increased chloral hydrate formation by ~30%. Overall, UV treatment may increase the formation of certain DBPs, although generally by ≤25%, and this occurred at UV doses higher than used in disinfection applications. These results indicated that in our subsequent studies (described below), atypical challenge conditions would be needed to demonstrate the mechanistic aspects of any UV induced DBP changes.



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3. Using knowledge gained from previous objectives; evaluate waters from selected facilities of distinctly different water qualities collected prior to the existing disinfection location with respect to important precursor aspects, particularly inorganic precursor materials (bromide and nitrate).

Studies of two treated drinking waters originating from source waters of varied water quality and anthropogenic inputs were performed with varying inorganic DBP precursor (bromide and nitrate) concentrations. Furthermore, through then studying at least four UV doses ranging from disinfection range to about 1000 mJ/cm$^2$, trends could be used to evaluate overall changes in DBP formation more confidently. Both UV technologies slightly increased THM formation with increased UV dose. These changes were minimal, where an increase of less than or equal to 10 µg/L was observed at the highest UV doses (1000 mJ/cm$^2$) studied. At disinfection doses of UV light, slight changes were observed but were within analytical and experimental variation. Therefore, while increases are expected during UV disinfection, they are statistically irrelevant with respect to THMs, HAAs, and selected other emerging DBP species. Minor increases in halonitromethanes, particularly tribromonitromethane were observed even at disinfection doses of UV. Similarly, chloral hydrate concentration was observed to increase. While concentration increases were small, on the single µg/L level, it should be noted that a recent study indicated the relative toxicity of these species is higher than regulated DBPs, so more research would be required to determine if the slight changes due to UV were at all relevant. On the other hand, UV appears to have the power to deactivate or destroy nitrosamine precursors, as observed through NDMA analysis, with the degree of destruction corresponding to the dose of UV applied prior to chloramination. Finally, it should be noted that with increasing UV dose the studied waters exhibited greater chlorine and chloramine demand. At 40 mJ/cm$^2$ change in chlorine demand was not clearly identified, whereas with doses greater that 186 mJ/cm$^2$ they were quite clear although minimal (~0.2 mg-$Cl_2$/L) unless a very high UV dose (1000 mJ/cm$^2$) and inorganic precursors were spiked in, where increases greater than 1 mg-$Cl_2$/L were observed.

4. Assess the fundamental formation mechanisms of DBPs associated with the UV free chlorine/chloramines process sequence using model precursors in synthetic waters, varied lamp technology type, and chlorination/chloramination processes.

Through the use of isolated NOM and varying concentrations of inorganic precursors, mechanisms and important pathways of changed DBP formation potential were evaluated. Free chlorine demand increased when UV was applied prior to chlorine/chloramines while monochloramine demand decreased or remained unchanged for concentrated NOM and NOM isolates. With UV treatment, THM4 concentrations were observed to increase slightly when post-chlorinated. THM4 increases were greater in concentrated NOM than fractionated NOM isolates. Unlike the findings from other research objectives, the higher concentration of NOM and elevated UV doses promoted slight decreases of HAA9 in NOM isolates and slight increases in NOM concentrates after the treatment sequence. Increased formation of trichloronitromethane was observed when irradiated with MP UV prior to chlorination or chloriittttamination as photonitration was likely to have been involved. Chloral hydrate increased notably when samples were spiked with either bromide alone or bromide and nitrate suggesting these inorganic precursors play an important role in the formation pathway of this emerging DBP species. Unlike the whole waters, dichloronitrate formation decreased when pretreated with UV light, and nitrosamine formation increased.

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5. Using pilot- and full-scale UV reactors, evaluate the formation of DBPs during the UV free chlorine/chloramines process sequence in flow-through systems.

The changes in chlorine demand and DBP formation observed during the study of flow-through reactors supported the bench-scale work performed in previous tasks. Using the pilot-scale reactors and manipulating influent water quality with respect to inorganic precursors (bromide and nitrate), UV dose trends observed mimicked bench-scale results. At high disinfection doses of UV (~200 mJ/cm$^2$), small increases (~0.1 mg-$Cl_2$/L) in chlorine demand were observed when UV disinfected samples were chlorinated. For the pilot LP UV system, the resulting changes in THM formation was nearly identical to that observed during bench-scale study of the similar water. Increased formation of THMs was observed at high UV doses (>500 mJ/cm$^2$), but overall were minimal (<20%). The pilot MP UV followed by application of free chlorine generally followed that observed during bench-scale experiments but to a lesser extent. Therefore generally speaking it was observed that similar trends were observed between both lamp types with respect to minimal free chlorine demand increases and minor DBP formation. At the full-scale UV disinfection facilities, no changes in DBPs or chlorine/chloramine demand was observed.

## RECOMMENDATIONS

Throughout this report numerous conclusions have been drawn that can be used to provide insight into the DBP formation, both regulated and unregulated, associated with the use of UV disinfection as a primary disinfectant, followed by a free chlorine/chloramines secondary disinfectant application. This section provides specific recommendations identified from this study that should be considering when implementing UV into an existing, or including UV into the original design of a, drinking water treatment plant in the United States that maintains a secondary disinfectant residual in the distribution system. These recommendations include:

1. At UV doses capable of disinfection (<186 mJ/cm$^2$):
   a. Free chlorine or chloramine demand will not be significantly altered regardless the point of application of the secondary disinfectant, be it upstream or downstream of the UV reactor. It should be noted though that UV light does have the capability to photo-degrade these oxidants, although the level of chlorine decay may be imperceptible at disinfection doses. Where possible, it is recommended that UV be installed upstream of a post-chlorination application.
   b. Regulated DBP (THM4 and HAA9) formation is not altered by the UV free chlorine or chloramines disinfection sequence when applying UV doses typical of disinfection practice. Addition of UV is recommended without reservation when source water quality requires a multiple barrier disinfection scheme.
   c. Halonitromethane formation, particularly trichloronitromethane and tribromonitromethane, and chloral hydrate, increases on the single µg/L level and is further exacerbated by elevated concentrations of bromide or nitrate. While concentration changes are low, they were statistically significant and the nature of this process should be noted, as research has suggested these species are more geno- and cyto-toxic than regulated DBPs. Promotion of halonitromethane formation is elevated when polychromatic MP UV technology is applied. It is recommended that when formation of DBPs is a concern, the application of UV in combination

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with chlorine should be limited to disinfection doses and use of MP UV should be coupled with an assessment of possible formation of unregulated DBPs in a given water quality.

d. Nitrosamine formation potential will likely be reduced to a small degree when UV is applied upstream of chloramination. However, this may vary depending on the nature of the NOM pool present in the water when being irradiated. It is recommended that utilities not be concerned with the effect of UV on formation of nitrosamines.

2. At high UV doses (186–1000 mJ/cm$^2$):
   a. Chlorine/chloramines demand will increase on the order of up to 1 mg-$Cl_2$/L and correspondingly a number of DBPs may be formed at greater concentrations when chlorine or chloramines are applied downstream of the UV reactor.
   b. THM4 formation is likely to increase, possibly up to 10 µg/L, while halonitromethane and chloral hydrate formation could increase by a few µg/L in some waters.
   c. The formation of nitrosamines when chloramines are applied downstream of the UV reactor could be significantly reduced on the order of multiple ng/L when UV is used prior to chloramines.

## PRACTICAL CONSIDERATIONS

As many drinking water utilities turn to alternative disinfectants and disinfection schemes consideration of the changes to disinfection by-product formation is required. However, there is only a small amount of literature currently available and it has been focused on regulated disinfection by-products. The tradeoffs of using LP or MP UV in a disinfection application are primarily decided based upon site-specific engineering considerations. This report provides information that can now be incorporated into these engineering decisions on the relative trade-offs of LP and MP systems regarding DBP formation. From a chemical standpoint, the possible photonitration of nitrate by MP UV, which is likely to promote the formation of nitrogenous DBPs, must be considered. While currently not regulated, formation of these emerging nitrogenous DBPs could occur from known precursor material originating from treated wastewater and agricultural discharge into surface water.

As the drinking water industry moves forward, the approach of using multiple barriers of treatment may increase the use of combined UV chlorine/chloramines processes. In some cases, a holistic evaluation of the complete treatment train relating to management of NOM or inorganic precursors upstream of a combined disinfection approach should be made. Consideration of the entire drinking water process train must clearly be considered when implementing new innovative processes to limit unintended consequences. Based on the research findings presented herein and current regulations, the UV disinfection plus chlorine/chloramines sequence does not affect currently regulated water quality parameters.

## SUGGESTED FUTURE RESEARCH

As an emerging process being applied in drinking water treatment, there are numerous aspects of UV technology that require further research. These are related to both UV processes

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alone and to the application of UV as a component of a process sequence. A few of these future directions for research, based on the findings of this study, are described below:

1. The polychromatic nature of MP UV is absorbed by a greater fraction of NOM. How does this type of light change or lead to indirect changes in NOM character, that promote or hinder the operation of downstream processes, particularly DBPs formation?
2. Nitrosamine formation appears to be reduced even when low MP UV doses are applied upstream of chloramination. What nitroso-precursors is the MP UV system affecting?
3. This study found that UV treatment prior to chloramination appeared to have an effect on the formation of iodinated haloforms even when iodine was not able to be measured in the bulk water. What is the role of UV in the formation of iodinated species and/or how can this technology help us identify some of the questions regarding why iodinated species form in waters without measured iodine?
4. To what extent can toxicity screening assays be used to better understand the impacts of adding UV or other technologies into a drinking water treatment train? What are the benefits and limitations of employing a toxicity screening assay? What do toxicity assay results mean, in the context of multibarrier treatment with emerging technologies, for public health?

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# APPENDIX A
# DISINFECTION BY-PRODUCT CHROMATOGRAMS—
# UNIVERSITY OF NORTH CAROLINA

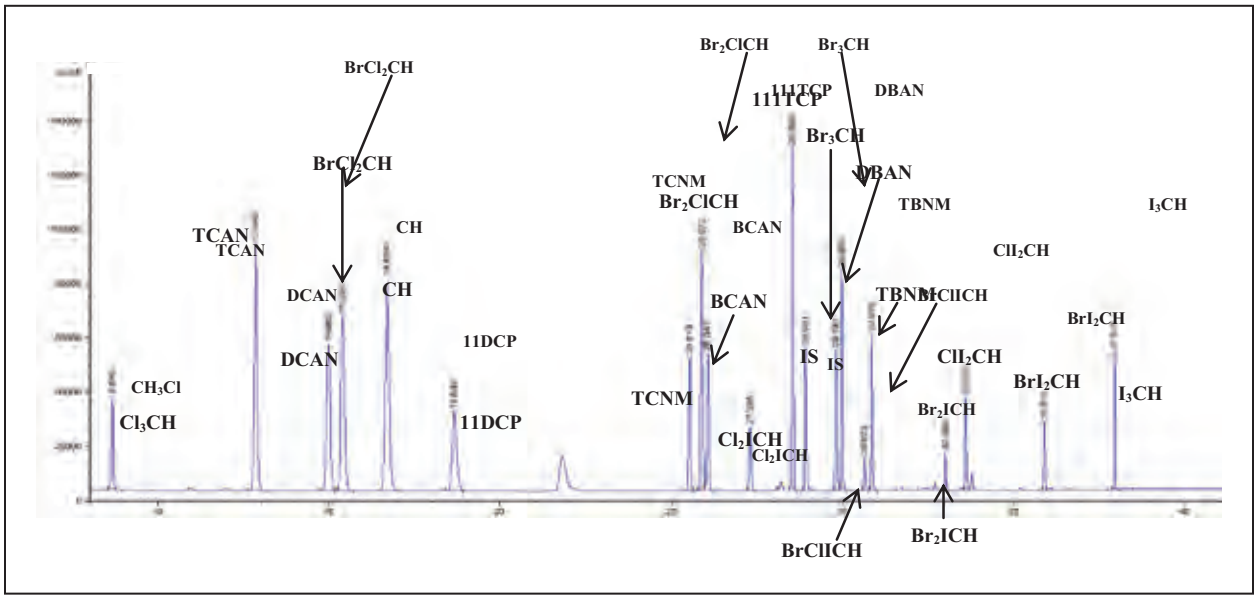


**Figure A.1 Chromatogram of trihalomethanes and additional halogenated DBPs**



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**Table A.1**
**Abbreviations for suite of halogenated DBPs**

| Retention time (min) | Abbreviation | Compound |
|---|---|---|
| 8.65 | $Cl_3CH$ | Chloroform |
| 12.84 | TCAN | Trichloroacetonitrile |
| 14.96 | DCAN | Dichloroacetonitrile |
| 15.34 | $BrCl_2CH$ | Bromodichloromethane |
| 16.68 | CH | Chloral hydrate (trichloroacetaldehyde) |
| 18.64 | 11DCP | 1,1-Dichloropropanone |
| 25.51 | TCNM | Trichloronitromethane (chloropicrin) |
| 25.87 | $Br_2ClCH$ | Dibromochloromethane |
| 26.04 | BCAN | Bromochloroacetonitrile |
| 27.29 | $Cl_2ICH$ | Dichloroiodomethane |
| 28.51 | 111TCP | 1,1,1-Trichloropropanone |
| 28.90 | IS | Internal standard (1,2-dibromopropane) |
| 29.79 | $Br_3CH$ | Bromoform |
| 29.96 | DBAN | Dibromoacetonitrile |
| 30.62 | BrClICH | Bromochloroiodomethane |
| 30.84 | TBNM | Tribromonitromethane (bromopicrin) |
| 32.99 | $Br_2ICH$ | Dibromoiodomethane |
| 33.58 | $ClI_2CH$ | Chlorodiiodomethane |
| 35.87 | $BrI_2CH$ | Bromodiiodomethane |
| 37.92 | $I_3CH$ | Iodoform |

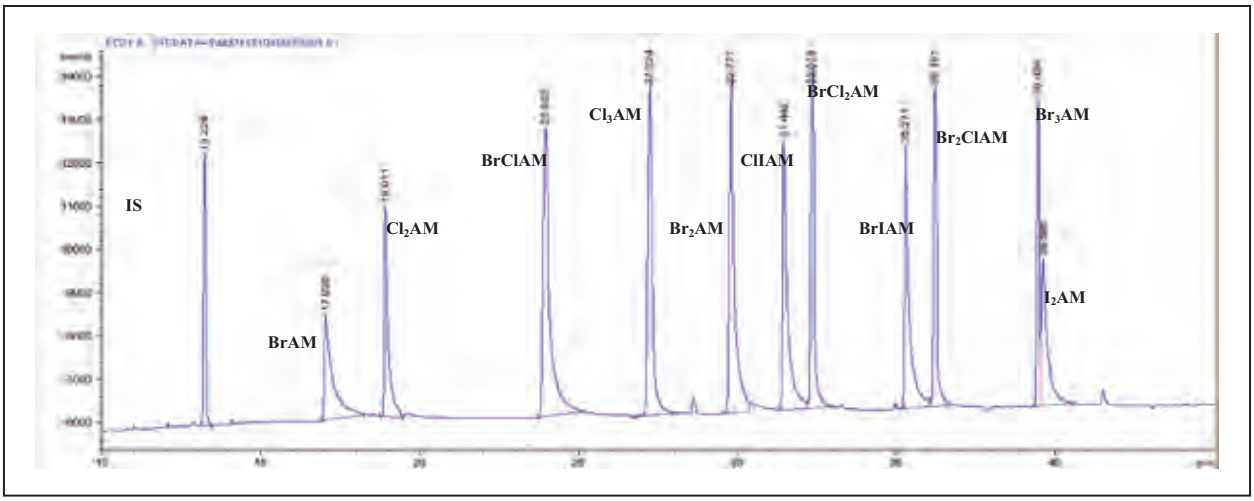


**Figure A.2 Haloacetamide chromatogram**

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**Table A.2**
**Haloacetamide abbreviations**

| Retention time (min) | Abbreviation | Compound |
|---|---|---|
| 13.23 | IS | Internal standard (1,2-dibromopropane) |
| 17.04 | BrAM | Bromoacetamide |
| 18.91 | $Cl_2AM$ | Dichloroacetamide |
| 23.93 | BrClAM | Bromochloroacetamide |
| 27.22 | $Cl_3AM$ | Trichloroacetamide |
| 29.78 | $Br_2AM$ | Dibromoacetamide |
| 31.44 | ClIAM | Chloroiodoacetamide |
| 32.33 | $BrCl_2AM$ | Bromodichloroacetamide |
| 35.27 | BrIAM | Bromoiodoacetamide |
| 36.18 | $Br_2ClAM$ | Dibromochloroacetamide |
| 39.24 | $Br_3AM$ | Tribromoacetamide |
| 39.59 | $I_2AM$ | Diiodoacetamide |

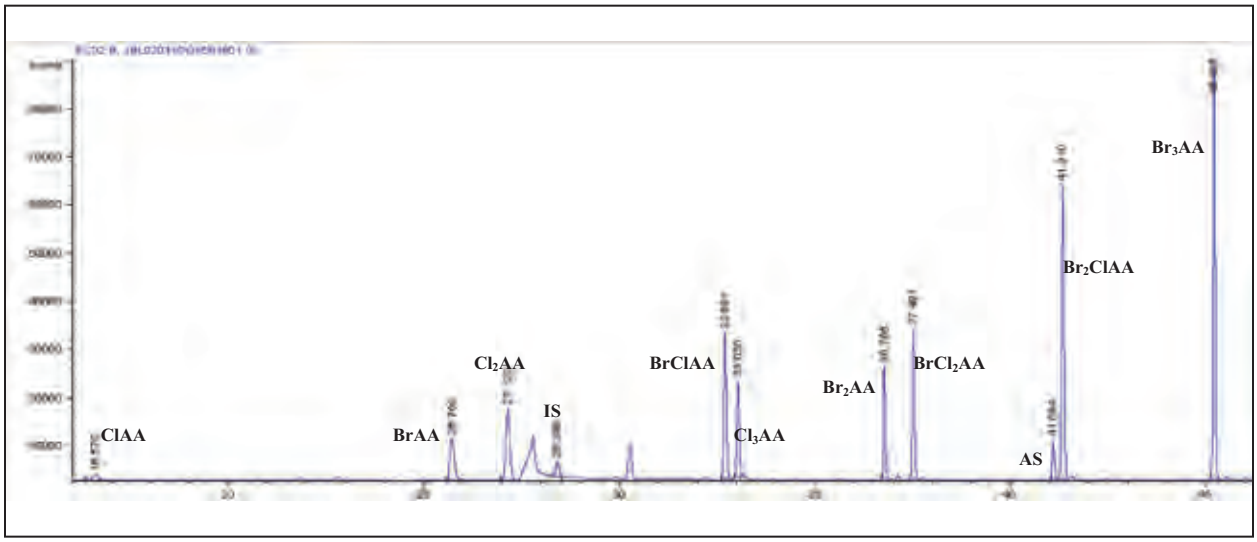


**Figure A.3 Chromatogram of haloacetic acids (methyl ester form)**

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**Table A.3**
**Haloacetic acid abbreviations**

| Retention time (min) | Abbreviation | Compound |
|---|---|---|
| 16.57 | ClAA | Chloroacetic acid |
| 25.7 | BrAA | Bromoacetic acid |
| 27.1 | $Cl_2AA$ | Dichloroacetic acid |
| 28.37 | IS | Internal standard (1,2-dibromopropane) |
| 32.67 | BrClAA | Bromochloroacetic acid |
| 33.02 | $Cl_3AA$ | Trichloroacetic acid |
| 36.76 | $Br_2AA$ | Dibromoacetic acid |
| 37.48 | $BrCl_2AA$ | Bromodichloroacetic acid |
| 41.07 | AS | Acid surrogate (2,3-dibromopropionic acid) |
| 41.3 | $Br_2ClAA$ | Dibromochloroacetic acid |
| 45.18 | $Br_3AA$ | Tribromoacetic acid |

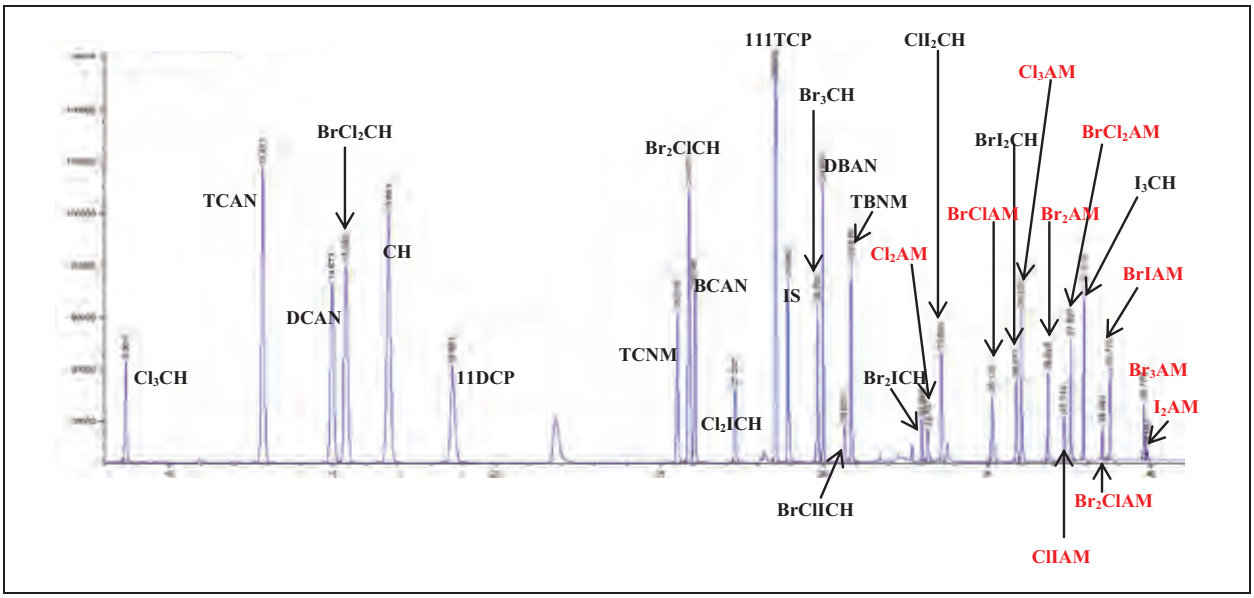


**Figure A.4 Chromatogram of haloacetamides and halogenated DBPs run using the halogenated DBPs temperature program**

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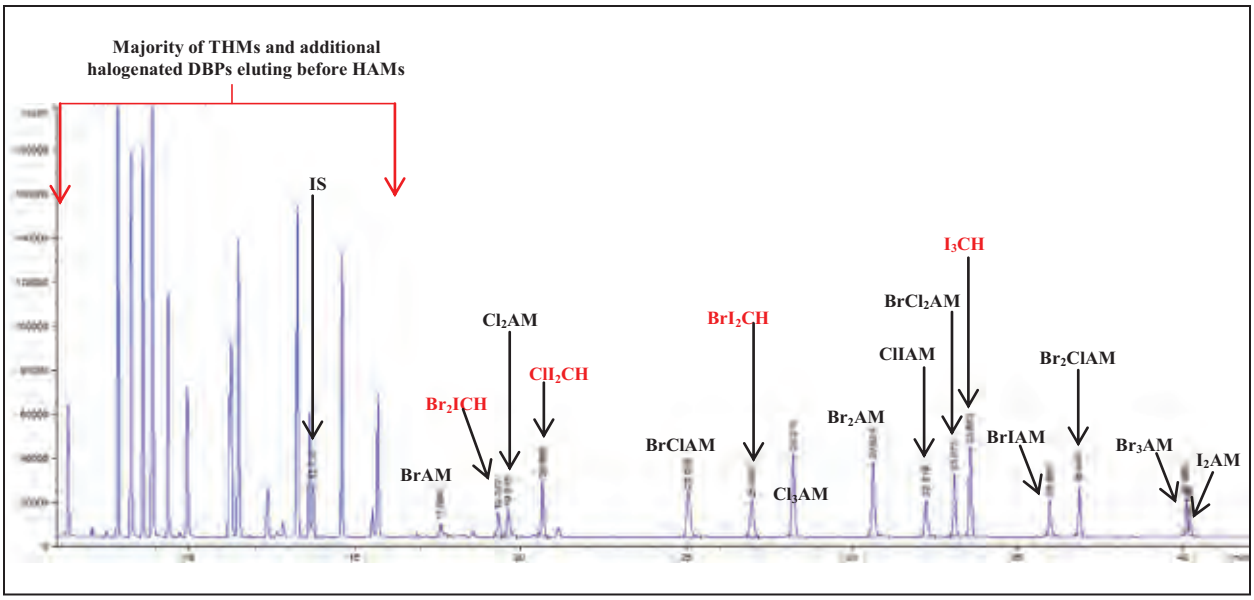


**Figure A.5 Chromatogram of halogenated DBPs and haloacetamides run using the haloacetamides temperature program**

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# APPENDIX B
# UV SURVEY EXAMPLE SENT TO WATER UTILITIES

## 1. Basic Information

**IF YOUR UTILITY/COMPANY HAS MULTIPLE DRINKING WATER TREATMENT PLANTS THAT USE UV DISINFECTION PLEASE FILL OUT SEPARATE SURVEYS FOR EACH WATER TREATMENT PLANT.**

Select questions will provide a link to additional information or examples that will spawn another browser window or tab upon being clicked.

### 1. Personal Information:

Your Name

Company/Agency/Utility

Address

City

State

Zip Code

Phone Number

E-mail Address

### 2. Water Treatment Plant Information

(For acronym definitions click here)

Name:

Location (City, State):

Average Flow (MGD):

Design Flow (MGD):

How many people does your facility serve:

### 3. Would you like your water treatment plant name and/or location to be kept anonymous?

- No
- Yes, Water Treatment Plant Name ONLY
- Yes, Water Treatment Plant Name and Location



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## 2. Influent Water Quality

Select questions will provide a link to additional information or examples that will spawn another browser window or tab upon being clicked.

**1. What type of water does your facility treat?**

- ◯ Groundwater
- ◯ Surface Water
- ◯ Groundwater under the influence of surface water
- ◯ Combined Source (ground and surface water)

**2. What is the name of your primary source water or aquifer (e.g. Colorado River)?**

**3. Is your source influenced by (check all that apply):**

- ☐ algae
- ☐ industry
- ☐ mining
- ☐ wastewater
- ☐ agriculture
- ☐ none of the above
- ☐ other

If you answered "other", please provide an answer here

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**4. What are your three most challenging water quality issues (check three of the following)?**

- [ ] Disinfection Byproduct Precursors
- [ ] High Turbidity
- [ ] Inorganic Pollutants
- [ ] Organic Pollutants
- [ ] Taste and Odor
- [ ] Challenge to Coagulate
- [ ] Biological Stability
- [ ] Seasonable Variability
- [ ] Other

If you answered "other", please provide an answer here

**5. Average Water Treatment Plant Source Water Quality (best guesses are OK here and if you do not know what to respond please leave the field blank)**

**(For acronym definitions click here)**

| | |
|---|---|
| TOC (mg-C/L) | |
| DOC (mg-C/L) | |
| %UVT at 254nm | |
| UVA@254 nm (1/cm) | |
| Alkalinity (mg-CaCO3/L) | |
| Hardness (mg-CaCO3/L) | |
| Total Dissolved Solids (mg/L) | |
| Turbidity (NTU) | |
| pH | |
| Dissolved Iron (mg/L) | |
| Nitrate (mg-N/L) | |
| Nitrite (mg-N/L) | |
| Ammonia (mg-N/L) | |

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## 3. Treatment Process

Select questions will provide a link to additional information or examples that will spawn another browser window or tab upon being clicked.

**1. Please build your water treatment process and chemical addition points. (For an example of how to fill out this question click here)**

| | Process Description |
|---|---|
| Process 1: | |
| Process 2: | |
| Process 3: | |
| Process 4: | |
| Process 5: | |
| Process 6: | |
| Process 7: | |
| Process 8: | |
| Process 9: | |
| Process 10: | |
| Process 11: | |
| Process 12: | |
| Process 13: | |
| Process 14: | |
| Process 15: | |
| Process 16: | |
| Process 17: | |
| Process 18: | |
| Process 19: | |
| Process 20: | |

**2. If any of the processes in the previous question were "other", please provide the process number (from previous question) and description below:**

| | |
|---|---|
| Other 1: | |
| Other 2: | |
| Other 3: | |
| Other 4: | |
| Other 5: | |

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**3. Which oxidant does your facility use to maintain a distribution system residual?**

- ◯ Free Chlorine
- ◯ Chloramines
- ◯ Other

If you answered "other", please provide an answer here

**4. What is your facilities target disinfectant residual (in mg-Cl2/L) leaving the plant?**

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## 4. Ultraviolet Disinfection/Irradiation

Select questions will provide a link to additional information or examples that will spawn another browser window or tab upon being clicked.

**1. What year was UV installed?**

**2. Was the UV installed as part of:**

- ◯ Original Construction
- ◯ Retrofit

**3. Why was UV disinfection installed (check all that apply)?**

- ☐ disinfection by-product control
- ☐ additional barrier of protection
- ☐ chemical oxidant reduction
- ☐ public preference
- ☐ cryptosporidium inactivation
- ☐ to meet current or future regulations
- ☐ other

If you answered "other", please provide an answer here

**4. Who is the manufacturer of the installed UV system?**

- ◯ Aquaray
- ◯ Aquionics
- ◯ Calgon
- ◯ Hanovia
- ◯ Trojan
- ◯ Wedeco
- ◯ Other

If you answered "other", please provide an answer here

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**5. What type of lamp is installed in your reactor?**

- ◯ low pressure high output
- ◯ conventional low pressure
- ◯ medium pressure

**6. What is the bulb orientation compared to the water flow?**

- ◯ perpendicular flow
- ◯ parallel flow
- ◯ hybrid

**7. UV Reactor Properties**

Reactor model [ ]

Individual bulb wattage [ ]

Number of bulbs in each reactor [ ]

**8. UV Process Configuration (please respond with numerical answers)**

Number of reactors installed [ ]

Number in series [ ]

Number in parallel [ ]

Redundant reactors [ ]

**9. How is your UV dose calculated?**

- ◯ UV Intensity Setpoint Approach
- ◯ Calculated Dose Approach
- ◯ Do not know
- ◯ Other

If you answered "other", please provide an answer here

[ ]

**10. What is your UV design dose and what dose do you typically operate at in mJ/square cm or mW seconds/square cm?**
**(For acronym definitions click here)**

Design Dose [ ]

Operation Dose [ ]

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**11. Have you had lamp breakage issues within the reactor during active treatment? Select how many times this has occurred below.**

- ◯ No
- ◯ 1
- ◯ 2
- ◯ 3
- ◯ other

Please provide details of the lamp breakage incident(s) below if you answered 1, 2, 3, or other to the question above

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## 5. Pre-UV Water Quality

Select questions will provide a link to additional information or examples that will spawn another browser window or tab upon being clicked.

**1. Does your facility carry a chlorine or chloramine residual through the UV reactor?**

- ◯ Yes, Free Chlorine
- ◯ Yes, Chloramines
- ◯ No

If you answered "yes", please provide the average disinfectant residual concentration in mg-Cl2/L

**2. What is the average ultraviolet transmittance (UVT) of the water entering the reactor(s)?**

- ◯ > 95%
- ◯ 90 - 95%
- ◯ 85 - 90%
- ◯ 80 - 85%
- ◯ < 80%

**3. Does your UVT vary seasonally?**

- ◯ Yes
- ◯ No

**4. If yes, what is the lowest UVT?**

- ◯ 80-90%
- ◯ 70-80%
- ◯ 60-70%
- ◯ <60%

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## 6. Finished Water Quality

Select questions will provide a link to additional information or examples that will spawn another browser window or tab upon being clicked.

### 1. Average Finished Water Quality (that which enters the distribution system)

**(For acronym definitions click here)**

| | |
|---|---|
| TOC (mg-C/L) | |
| DOC (mg-C/L) | |
| %UVT at 254nm | |
| UVA@254 nm (1/cm) | |
| Alkalinity (mg-CaCO3/L) | |
| Hardness (mg-CaCO3/L) | |
| Total Dissolved Solids (mg/L) | |
| Turbidity (NTU) | |
| pH | |
| Dissolved Iron (mg/L) | |
| Nitrate (mg-N/L) | |
| Nitrite (mg-N/L) | |
| Ammonia (mg-N/L) | |
| Free Chlorine(mg-Cl2/L): | |
| Total Chlorine(mg-Cl2/L): | |

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## 7. General Observations

Select questions will provide a link to additional information or examples that will spawn another browser window or tab upon being clicked.

**1. Have measured disinfection by-products in your distribution changed since installing your UV process?**

- ◯ not applicable, UV part of original design
- ◯ increased
- ◯ decreased
- ◯ no observable change

**2. Has your use of chemical disinfectants changed since installing your UV process?**

- ◯ not applicable, UV part of original design
- ◯ increased
- ◯ decreased
- ◯ no observable change

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## 8. Additional Information

Select questions will provide a link to additional information or examples that will spawn another browser window or tab upon being clicked.

**1. Would your utility/company be interested to provide additional information if the project team would like to use your facility as a case study?**

- ◯ Yes
- ◯ No

**2. Do you have any other pertinent information that you would like to provide the project team that this survey did not cover regarding your UV process?**

- ◯ Yes
- ◯ No

**3. If yes, please write your additional information below. If you would like to provide files or any other information please attach or include them in an email.**

**For example - detailed process flow diagram of a more complex treatment train, presentations or papers describing your experience with UV disinfection.**

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# REFERENCES


Alvarez, B., H. Rubbo, M. Kirk, S. Barnes, B. Freeman, and R. Radi. 1996. Peroxynitrite-Dependent Tryptophan Nitration. *Chem. Res. Toxicol.*, 390–396.

Amy, G.L., T. Lo, and M.K. Davis. 1991. The Effects of Ozonation and Activated Carbon Adsorption on Trihalomethane Speciation. *Water Res*., 25(2):191–202.

APHA, AWWA, and WEF (American Public Health Association, American Water Works Association, and Water Environment Federation). 1999. *Standard Methods for the Examination of Water and Wastewater.* 20th ed. Washington, D.C.: APHA.

Bichsel, Y., and U. von Gunten. 2000. Formation of Iodo-Trihalomethanes During Disinfection and Oxidation of Iodide-Containing Waters. *Environ. Sci. Technol.*, 34(13):2784–2791.

Bilski, P., C.F. Chignell, J. Szychlinski, A. Borkowski, E. Oleksy, and K. Reszka. 1992. Photooxidation of Organic and Inorganic Substrates During UV Photolysis of Nitrite Anion in Aqueous Solution. *Jour. Am. Chem. Soc.*, 114(2):549–556.

Bolton, J.R., and K.G. Linden. 2003. Standardization of Methods for Fluence (UV Dose) Determination in Bench-Scale UV Experiments. *Jour. Environ. Eng.-ASCE*, 129(3):209–215.

Brophy, K.S., H.S. Weinberg, and P.C. Singer. 2000. Quantification of Nine Haloacetic Acids Using Gas Chromatography With Electron Capture Detection. In *Natural Organic Matter and Disinfection By-Products, ACS Symposium Series,* 761:343–355.

Buchanan, W., F. Roddick, N. Porter, and M. Drikas. 2005. Fractionation of UV and VUV Pretreated Natural Organic Matter From Drinking Water. *Environ. Sci. Technol*., 39(12):4647–4654.

Caulfield, J.L., S.P. Singh, J.S. Wishnock, W.M. Deen, and S.R. Tannenbaum. 1996. Bicarbonate Inhibits *N*-Nitrosation in Oxygenated Nitric Oxide Solutions. *Jour. Biol. Chem.*, 271(42):25859–25863.

Challis, B., and S. Kyrtopoulos. 1979. Chemistry of Nitroso-Compounds. 11. Nitrosation of Amines by the 2-Phase Interaction of Amines in Solution With Gaseous Oxides of Nitrogen. *Jour. Chem. Soc.-Perkin Trans.*, *1*, 299–304.

Chinn, R., T. Lee, S.W. Krasner, M. Dale, S.D. Richardson, J. Pressman, T. Speth, R. Miltner, and J.E. Simmons. 2007. Solid-Phase Extraction of 35 DBPs With Analysis by GC/ECD and GC/MS. In *Proc. AWWA WQTC.* Denver, Colo.: AWWA.

Choi, J., and R. Valentine. 2003. N-Nitrosodimethylamine Formation by Free-Chlorine-Enhanced Nitrosation of Dimethylamine. *Environ. Sci. Technol.*, 4871–4876.

Chow, A.T., D.M. Leech, T.H. Boyer, and P.C. Singer. 2008. Impact of Simulated Solar Irradiation on Disinfection Byproduct Precursors. *Environ. Sci. Technol.*, 42(15):5586–5593.

Croué, J.P., G.V. Korshin, and M. Benjamin. 1999. *Characterization of Natural Organic Matter in Drinking Water.* Denver, Colo.: AWWA and Water Research Foundation.

Dotson, A.D., P. Westerhoff, and S.W. Krasner. 2009. Nitrogen Enriched Dissolved Organic Matter (DOM) Isolates and Their Affinity to Form Emerging Disinfection By-Products. *Water Sci. Technol.*, 60(1):135–143.

Duirk, S.E., C. Lindell, C.C. Cornelison, T.A. Ternes, and S.D. Richardson. 2009. Iodo-DBP Formation From the Reaction of Chlorinated Oxidants With X-Ray Contrast Media in the Presence of Natural Organic Matter. In *Proc. of Micropol and Ecohazard: Assessment and Control of Micropollutants/Hazardous Substances in Water.* San Francisco, Calif.

Fischer, M., and P. Warneck. 1996. Photodecomposition of Nitrite and Undissociated Nitrous Acid in Aqueous Solution. *Jour. Phys. Chem*., 100(48):18749–18756.




©2012 Water Research Foundation. ALL RIGHTS RESERVED.

Goldstein, S., and G. Czapski. 1996. Mechanism of the Nitrosation of Thiols and Amines by Oxygenated Center Dot NO Solutions: The Nature of the Nitrosating Intermediates. *Jour. Am. Chem. Soc.*, 3419–3425.

Goldstein, S., and J. Rabani. 2008. The Ferrioxalate and Iodide-Iodate Actinometers in the UV Region. *Jour. Photochem. Photobiol. A-Chem.*, 50–55.

Gould, J.P., L.E. Fitchhorn, and E. Urheim. 1981. Formation of Brominated Trihalomethanes—Extent and Kinetics. *Proc. of 4th Conference on Water Chlorination*. Ann Arbor, Mich.

Grebel, J.E., J.J. Pignatello, W. Song, W.J. Cooper, and W.A. Mitch. 2009. Impact of Halides on the Photobleaching of Dissolved Organic Matter. *Marine Chem.*, 115:134–144.

Heringa, M.B., D.J.H. Harmsen, E.F. Beeredonk, A.A. Reus, C.A.M. Krul, D.H. Metz, and G.F. Ijpelaar. 2011. Formation and Removal of Genotoxic Activity During UV/$H_2O_2$–GAC Treatment of Drinking Water. *Water Res.*, 45(1):366–374.

Hijnen, W.A., E.F. Beerendonk, and G.J. Medema. 2006. Inactivation Credit of UV Radiation for Viruses, Bacteria and Protozoan (Oo)Cysts in Water: A Review. *Water Res.*, 40(1):3–22.

Hoigné, J., and H. Bader. 1988. The Formation of Trichloronitromethane (Chloropicrin) and Chloroform in a Combined Ozonation/Chlorination Treatment of Drinking Water. *Water Res.*, 22(3):313–319.

Hu, J., H. Song, J.W. Addison, and T. Karanfil. 2010. Halonitromethane Formation Potentials in Drinking Waters. *Water Res.*, 44(1):105–114.

Hua, G., and D.A. Reckhow. 2007a. Characterization of Disinfection Byproduct Precursors Based on Hydrophobicity and Molecular Size. *Environ. Sci. Technol.*, 41(9):3309–3315.

Hua, G., and D.A. Reckhow. 2007b. Comparison of Disinfection Byproduct Formation From Chlorine and Alternative Disinfectants. *Water Res.*, 41(8):1667–1678.

Ijpelaar, G.F., A.J. van der Veer, G.J. Medema, and J.C. Kruithof. 2005. By-Product Formation During Ultraviolet Disinfection of a Pretreated Surface Water. *Jour. Environ. Eng. Sci.*, 4(Suppl. 1):S51–S56.

Jayson, G.G., B.J. Parsons, and A.J. Swallow. 1973. Some Simple, Highly Reactive, Inorganic Chlorine Derivatives in Aqueous Solution. *Jour. Chem. Soc., Faraday Trans. 1*, 69(9):1597–1607.

Joo, S.-H., and W.A. Mitch. 2007. Nitrile, Aldehyde, and Halonitroalkane Formation During Chlorination/Chloramination of Primary Amines. *Environ. Sci. Technol.*, 41, 1288–1296.

Kitis, M., T. Karanfil, A. Wigton, and J.E. Kilduff. 2002. Probing Reactivity of Dissolved Organic Matter for Disinfection By-Product Formation Using XAD-8 Resin Adsorption and Ultrafiltration Fractionation. *Water Res.*, 36(15):3834–3848.

Krasner, S.W., M.J. McGuire, J.G. Jacangelo, N.L. Patania, K.M. Reagan, and E.M. Aieta. 1989. The Occurrence of Disinfection By-Products in U.S. Drinking Water. *Jour. AWWA*, 81(8): 41–53.

Krasner, S.W., H.S. Weinberg, S.D. Richardson, S.J. Pastor, R. Chinn, M.J. Sclimenti, G.D. Onstad, and A.D. Thruston Jr. 2006. Occurrence of a New Generation of Disinfection Byproducts. *Environ. Sci. Technol.*, 40(23):7175–7185.

KWR 2011. *New Concepts of UV/$H_2O_2$ Oxidation*. Edited by C.H.M. Hofman-Caris and E.F. Beerendonk. KWR and Water Research Foundation.

Leenheer, J.A. 1981. Comprehensive Approach to Preparative Isolation and Fractionation of Dissolved Organic Carbon From Natural Waters and Wastewaters. *Environ. Sci. Technol.*, 15(5):578–587.

©2012 Water Research Foundation. ALL RIGHTS RESERVED.

Liang, L., and P.C. Singer. 2003. Factors Influencing the Formation and Relative Distribution of Haloacetic Acids and Trihalomethanes in Drinking Water. *Environ. Sci. Technol*., 37(13):2920–2928.

Linden, K.G., C.M. Sharpless, S.A. Andrews, K.Z. Atasi, V. Korategere, M. Stefan, and I.H. Suffet. 2004. *Innovative UV Technologies to Oxidize Organic and Organoleptic Chemicals.* Denver, Colo.: Awwa Research Foundation.

Liu, W., L-M. Cheung, X. Yang, and C. Shang. 2006. THM, HAA and CNCl Formation From UV Irradiation and Chlor(am)ination of Selected Organic Waters. *Water Res.*, 40:2033–2043.

Luong, T.V., C.J. Peters, and R. Perry. 1982. Influence of Bromide and Ammonia Ion Upon the Formation of Trihalomethanes Under Water-Treatment Conditions. *Environ. Sci. Technol.*, 16(8):473–479.

Magnuson, M.L., C.A. Kelty, C.M. Sharpless, K.G. Linden, W. Fromme, D.H. Metz, and R. Kashinkunti. 2002. Effect of UV Irradiation on Organic Matter Extracted From Treated Ohio River Water Studied Through the Use of Electrospray Mass Spectrometry. *Environ. Sci. Technol.*, 36(23):5252–5260.

Malley, J.P., J.P. Shaw, and J.R. Ropp. 1995. *Evaluation of By-Products Produced by Treatment of Groundwater With Ultraviolet Irradiation.* Denver, Colo.: Awwa Research Foundation.

Masuda, M., H. Mower, B. Pignatelli, I. Celan, M. Friesen, H. Nishino, and H. Ohshima. 2000. Formation of N-Nitrosamines and N-Nitramines by the Reaction of Secondary Amines With Peroxynitrite and Other Reactive Nitrogen Species: Comparison With Nitrotyrosine Formation. *Chem. Res. Toxicol.*, 301–308.

McKnight, A., and D.A. Reckhow. 1992. Reactions of Ozonation By-Products With Chlorine and Chloramines. In *Proc. of the AWWA Annual Conference*. Denver, Colo.: AWWA.

Merlet, N., H. Thibaud, and M. Dore. 1985. Chloropicrin Formation During Oxidative Treatments in the Preparation of Drinking Water. *Sci. Total Environ.*, 47: 223–228.

Mezyk, S., D. Ewing, J. Kiddle, and K. Madden. 2006. Kinetics and Mechanisms of the Reactions of Hydroxyl Radicals and Hydrated Electrons With Nitrosamines and Nitramines in Water. *Jour. Phys. Chem. A*, 4732–4737.

Mitch, W.A., and I.M. Schreiber. 2008. Degradation of Tertiary Alkylamines During Chlorination/Chloramination: Implications for Formation of Aldehydes, Nitriles, Halonitroalkanes, and Nitrosamines. *Environ. Sci. Technol.*, 42(13):4811–4817.

Nowell, L.H., and J. Hoigné. 1992. Photolysis of Aqueous Chlorine at Sunlight and Ultraviolet Wavelengths: Hydroxyl Radical Production. *Water Res.*, 26(5):599–605.

Obolensky, A., and P.C. Singer. 2005. Halogen Substitution Patterns Among Disinfection Byproducts in the Information Collection Rule Database. *Environ. Sci. Technol.*, 39(8):2719–2730.

Ohshima, H., and H. Bartsch. 1999. Quantitative Estimation of Endogenous N-Nitrosation in Humans by Monitoring N-Nitrosoproline in Urine. *Nitric Oxide, Pt. C*, 40–49.

Pedersen, E.J., E.T. Urbansky, B.J. Mariñas, and D.W. Margerum. 1999. Formation of Cyanogen Chloride From the Reaction of Monochloramine With Formaldehyde. *Environ. Sci. Technol.*, 33(23):4239–4249.

Plewa, M.J., E.D. Wagner, P. Jazwierska, S.D. Richardson, P.H. Chen, and A.B. McKague. 2004. Halonitromethane Drinking Water Disinfection Byproducts: Chemical Characterization and Mammalian Cell Cytotoxicity and Genotoxicity. *Environ. Sci. Technol.*, 38(1):62–68.

**©2012 Water Research Foundation. ALL RIGHTS RESERVED.**

Reckhow, D.A., and P.C. Singer. 1985. Mechanisms of Organic Halide Formation During Fulvic Acid Chlorination and Implications With Respect to Preozonation. In *Water Chlorination: Chemistry, Environmental Impact and Health Effects*, Vol. 5. Edited by R.L. Jolley, et al. Lewis Publishers, pp. 1229–1257.

Reckhow, D.A., K.G. Linden, J. Kim, H. Shemer, and G. Makdissy. 2010. Effect of UV Treatment on DBP Formation. *Jour. AWWA*, 102(6):100–113.

Richardson, S.D., F. Fasano, J.J. Ellington, F.G. Crumley, K.M. Buettner, J.J. Evans, B.C. Blount, L.K. Silva, T.J. Waite, G.W. Luther, A.B. McKague, R.J. Miltner, E.D. Wagner, and M.J. Plewa. 2008. Occurrence and Mammalian Cell Toxicity of Iodinated Disinfection Byproducts in Drinking Water. *Environ. Sci. Technol.*, 42(22):8330–8338.

Schreiber, I., and W. Mitch. 2005. Influence of the Order of Reagent Addition on NDMA Formation During Chloramination. *Environ. Sci. Technol.*, 3811–3818.

Schreiber, I., and W. Mitch. 2006. Nitrosamine Formation Pathway Revisited: The Importance of Chloramine Speciation and Dissolved Oxygen. *Environ. Sci. Technol.*, 40, 6007–6014.

Schreiber, I., and W. Mitch. 2007. Enhanced Nitrogenous Disinfection Byproduct Formation Near the Breakpoint: Implications for Nitrification Control. *Environ. Sci. Technol.*, 41, 7093–7046.

Sharpless, C., and K. Linden. 2003. Experimental and Model Comparisons of Low- and Medium-Pressure Hg Lamps for the Direct and $H_2O_2$ Assisted UV Photodegradation of N-Nitrosodiemthylamine in Simulated Drinking Water. *Environ. Sci. Technol.*, 37:1933–1940.

Sharpless, C.M., and K.G. Linden. 2001. UV Photolysis of Nitrate: Effects of Natural Organic Matter and Dissolved Inorganic Carbon and Implications for UV Water Disinfection. *Environ. Sci. Technol.*, 35(14):2949–2955.

Sharpless, C.M., M.A. Page, and K.G. Linden. 2003. Impact of Hydrogen Peroxide on Nitrite Formation During UV Disinfection. *Water Res*., 37(19):4730–4736.

Summers, R.S., S.M. Hooper, H.M. Shukairy, G. Solarik, and D. Owen. 1996. Assessing the DBP Yield: Uniform Formation Conditions. *Jour. AWWA*, 88(6):80–93.

Suzuki, T., H. Mower, M. Friesen, I. Gilibert, T. Sawa, and H. Ohshima. 2004. Nitration and Nitrosation of N-Acetyl-L-Tryptophan and Tryptophan Residues in Proteins by Various Reactive Nitrogen Species. *Free Radical Biol. Med.*, 671–681.

Thibaud, H., J. De Laat, N. Merlet, and M. Doré. 1987. Chloropicrin Formation in Aqueous Solution: Effect of Nitrites on Precursors Formation During the Oxidation of Organic Compounds. *Water Res.*, 21(7):813–821.

Uppu, R.M., G.L. Squadrito, R.M. Bolzan, and W.A. Pryor. 2000. Nitration and Nitrosation by Peroxynitrite: Role of $CO_2$ and Evidence for Common Intermediates. *Jour. Am. Chem. Soc.*, 122:6911–6916.

USEPA (U.S. Environmental Protection Agency). 1995. *Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography With Electron-Capture Detection*. Cincinnati, Ohio: USEPA National Exposure Research Laboratory, Office of Research and Development. <www.caslab.com/EPA-Methods/PDF/EPA-Method-551-1.pdf>.

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USEPA (U.S. Environmental Protection Agency). 2004. *Determination of Nitrosamines in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography With Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry (MS/MS)*. EPA/600/R-05/054. Cincinnati, Ohio: USEPA, National Exposure Research Laboratory, Office of Research and Development. <www.epa.gov/microbes/m_521.pdf>.

USEPA (U.S. Environmental Protection Agency). 2006. *Ultraviolet Disinfection Guidance Manual for the Final Long Term 2 Enhanced Surface Water Treatment Rule.* EPA 815-R-06-007. Washington, D.C.: USEPA.

Vione, D., V. Maurino, C. Minero, and E. Pelizzetti. 2005. Aqueous Atmospheric Chemistry: Formation of 2,4-Dinitrophenol Upon Nitration of 2-Nitrophenol and 4-Nitrophenol in Solution. *Environ. Sci. Technol.*, 7921–7931.

Vione, D., V. Maurino, C. Minero, D. Borghesi, M. Lucchiari, and E. Pelizzetti. 2003. New Processes in the Environmental Chemistry of Nitrite. 2. The Role of Hydrogen Peroxide. *Environ. Sci. Technol.*, 4635–4641.

Vione, D., V. Maurino, E. Pelizzetti, and C. Minero. 2004. Phenol Photonitration and Photonitrosation Upon Nitrite Photolysis in Basic Solution. *Int. Jour. Environ. Anal. Chem.*, 493–504.

Wade, E.A., K.E. Reak, B.F. Parsons, T.P. Clemes, and K.A. Singmaster. 2002. Photochemistry of Chloropicrin in Cryogenic Matrices. *Chem. Phys. Lett.*, 365(5-6):473–479.

Yang, X., C. Shang, and P. Westerhoff. 2007. Factors Affecting Formation of Haloacetonitriles, Haloketones, Chloropicrin and Cyanogen Halides During Chloramination. *Water Res.*, 41(6):1193–1200.

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# ABBREVIATIONS

| | |
|---|---|
| AOC | assimilable organic carbon |
| Br | bromide |
| BV | bed volume |
| C | carbon |
| Cl | chloride |
| $Cl_2$ | chlorine |
| CONV | conventionally treated water, post filtration |
| CU | University of Colorado |
| CWA-D | California water agency utilizing Delta water |
| DBP | disinfection by-product |
| DMSO | dimethyl sulfoxide |
| DOC | dissolved organic carbon |
| DOM | dissolved organic matter |
| DON | dissolved organic nitrogen |
| FCONV | conventionally treated water, post-filtration, fortified with inorganics |
| Fe | iron |
| GC/MS/MS | gas chromatography tandem mass spectrometry |
| H | hydrogen |
| HAAs | haloacetic acids |
| I | iodide |
| LGW | laboratory grade water |
| LPHO | low pressure high output ultraviolet |
| LPUV | low pressure ultraviolet |
| MPUV | medium pressure ultraviolet |
| MRL | minimum reporting limit |
| N | nitrogen |
| N-DBP | nitrogenous disinfection by-product |
| $NH_2CL$ | monochloramine |
| NOM | natural organic matter |
| O | oxygen |
| OWASA | Orange County Water and Sewer Authority |



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| | |
|---|---|
| RNS | reactive nitrogen species |
| RO | reverse osmosis |
| RPD | relative percentage difference |
| | |
| SDS | simulated distribution system |
| SRNOM | Suwannee River natural organic matter |
| SUVA | specific ultraviolet absorbance |
| | |
| TDN | total dissolved nitrogen |
| THM | trihalomethane |
| TN | total nitrogen |
| TOC | total organic carbon |
| TON | total organic nitrogen |
| | |
| UFC | uniform formation conditions |
| UNC | University of North Carolina |
| USEPA | United States Environmental Protection Agency |
| UV | ultraviolet |
| UVA | ultraviolet absorbance |
| UVT | ultraviolet transmittance |
| | |
| WTP | water treatment plant |

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