# Understanding DBP Formation during Chloramination

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Trihalomethanes (THM) and haloacetic acids (HAA) are the two major disinfection byproducts (DBPs) commonly found in waters disinfected with free chlorine. Because of the potential risk of such DBPs to public health, the United States Environmental Protection Agency (EPA) has imposed stringent regulations under its Disinfectants/Disinfection Byproducts Rule (D/DBPR).

Stage 1 of the D/DBPR set the maximum contaminant levels (MCLs) of THM and HAA₅ at 80 and 60 µg/L, respectively, for the running annual average of a water system. Stage 2 of the D/DBPR requires utilities to comply with the DBP regulations at individual locations in distribution system (i.e., locational running annual averages).

To comply with current and future DBP regulations, drinking water utilities have been considering various treatment and disinfection strategies. Chloramination has received increased attention in recent years because it almost suppresses THM formation while reducing HAA concentrations to 3-30 percent of the levels observed with chlorination.

It appears that during chloramination, formation and speciation of HAA, rather than THM, will dictate the compliance of water utilities with more stringent DBP regulations. To date, it is believed that HAA formation during chloramination was attributed primarily to the formation of chlorine (HOCl) during monochloramine (NH₂Cl) decomposition (reaction 1 in Figure 1); however, the significance of direct reaction between NH₂Cl and dissolved organic matter (DOM) on HAA formation has not been investigated.

Since there are three possible reactants—NH₂Cl, HOCl, and dichloramine (NHCl₂) can interact with DOM to form HAA during chloramination (Figure 1)—*the first objective of this study was to examine the relative significance of these reactions resulting in HAA formation during chloramination.*

Today, there is significant discrepancy among the limited chloramination literature that has been reported by various researchers (Figure 2). Singer et al. (1999) reported that 50 percent of the 72-hour dihaloacetic acid (DXAA) (the major species of HAA during chloramination) formed within the first hour at pH 8. Speitel et al. (2004) and Hua and Reckhow (2005) reported even faster HAA formation kinetics, showing about 70-75 percent of the 72-hour DXAA formed after only 0.5 hour at pH 8.

By contrast, in some of the preliminary experiments of the authors' study, only 10 percent of 72-hour DXAA formation occurred in the first hour at pH 7, and its formation gradually increased with time.

All these chloramination experiments were performed at similar pHs, and monochloramine were dosed to maintain approximately 2 mg/L residual after 24-hour incubation time as required by the uniform formation condition (UFC) protocol (Summers et al., 1996); therefore, research was needed to elucidate the factors responsible for the observed differences. *The second objective of this study was to investigate the potential causes of significantly different patterns observed for DXAA (HAA) formation kinetics in the literature.*

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## Materials & Methods

### DOM Solutions

Two surface waters with significantly different DOM characteristics were obtained from the influents of two water treatment plants in South Carolina. Myrtle Beach water has a high specific ultraviolet absorbance at 254 nm (SUVA₂₅₄) (5 L/mg-m), whereas Greenville water has relatively low SUVA₂₅₄ value (2.5 L/mg-m). The DOMs in these waters were concentrated using a pilot-scale reverse osmosis (RO) system.

Before each experiment, RO isolate was diluted by distilled and deionized water (DDW) to the target dissolved organic carbon (DOC) concentration of 7.5 mg/L. Solution pH was adjusted by addition of 4 mM carbonate buffer and acid/base solutions at different strengths.

(1) $NH_2Cl + H_2O \rightarrow HOCl + NH_3$
(2) $HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$
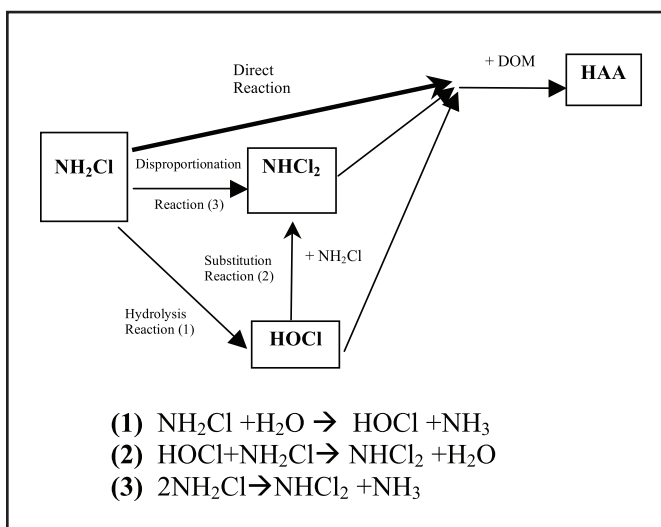(3) $2NH_2Cl \rightarrow NHCl_2 + NH_3$

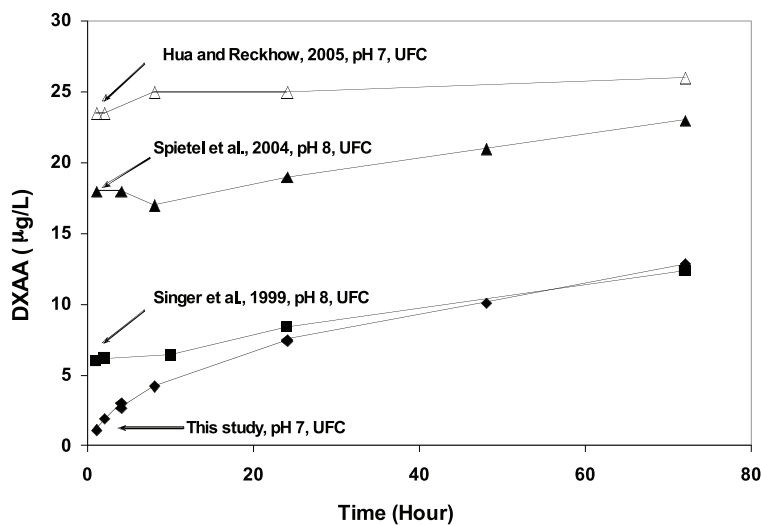Figure 1: Conceptual illustration of HAA formation pathways during chloramination.



Figure 2: DXAA formation kinetics reported by different researchers.

### Chloramination Experiments

Before each experiment, a fresh chloramine stock solution was prepared by mixing sodium hypochlorite (5 to 6 percent available free chlorine) and ammonium sulfate solutions in water at a $Cl_2/N$ mass ratio of 3.5:1 at pH 9.0. Preliminary experiments were conducted for each water sample to determine the ratio of $NH_2Cl/DOC$ that would provide a total combined residual of about 2 mg/L chloramine as $Cl_2$ after 24 hours of contact time following the UFC protocol.

Kinetic experiments were performed for 0.5, 1, 2, 4, 8, 24, 48, and 72 hours. At the end of each target contact time, samples were collected for pH, free and combined chlorine measurements. Then samples were quenched immediately with a stoichiometric amount of sodium sulfite ($Na_2SO_3$) and stored in a refrigerator (4-6°C). All the samples of a kinetic experiment were analyzed together for DBPs after the last sample (i.e., 72-hour) of the kinetic experiment.

## Results & Discussions

### HAA Formation Pathway Study

It is evident from the reactions in Figure 1 that by increasing background ammonia concentration, autodecomposition of $NH_2Cl$, thus HOCl production (reaction 1) and formation of $NHCl_2$ (reactions 2 and 3), can be significantly suppressed. When HOCl and $NHCl_2$ formations are minimized, the occurrence of reactions involving these species will also be reduced, so by performing experiments in the absence and presence of high background ammonia, it is possible to assess the relative significance of

Table 1: Background ammonia effect on monochloramine decay and DBP formation at pH 6.

| NH₃-N* | TCM | DCAA | NH₂Cl | NHCl₂ |
|---|---|---|---|---|
| (mg/L) | (µg/L) | (µg/L) | (mg/L) | (mg/L) |
| 0 | 3 | 21 | 1.7 | 0.4 |
| 10 | 3 | 18 | 2.1 | <MRL |
| 20 | 2 | 18 | 2.2 | <MRL |
| 30 | 2 | 18 | 2.2 | <MRL |
| 40 | 2 | 16 | 2.2 | <MRL |
| 50 | 2 | 16 | 2.3 | <MRL |
| 100 | 2 | 17 | 2.3 | <MRL |

*: Additional amount of $NH_3$-N added in each bottle at the beginning of the experiment. MRL: Minimum Reporting Level. Initial $NH_2Cl$ =3.5 mg/L. Greenville water DOC=7.5 mg/L. Free chlorine after 24-hour reaction period was always below the MRL.

direct reaction of $NH_2Cl$ with DOM in the HAA formation during chloramination.

Initial experiments were conducted using Greenville water RO isolate and preformed chloramine at pH 6 at several background ammonia concentrations. Dichloroacetic acid (DCAA) was the only HAA species observed in these experiments.

Table 1 shows the concentrations of chloroform (TCM), DCAA, $NH_2Cl$, and $NHCl_2$ measured after 24-hour contact time during these experiments. Constant concentrations of $NH_2Cl$, TCM, and DCAA measured and the absence of $NHCl_2$ formation above 10 mg/L background $NH_3$-N indicated that decomposition of $NH_2Cl$ leading to HAA

formation (through production of HOCl and/or formation of $NHCl_2$) was significantly suppressed. Finally, 20 mg/L ammonia was used for later kinetic study.

Parallel kinetics experiments were performed using the same DOM solution under two different ammonia conditions, i.e., in the absence and presence of 20 mg/L background ammonia. The results of experiments in the presence of ammonia (where $NH_2Cl$ hydrolysis and $NHCl_2$ formation were significantly suppressed) were compared with those in the absence of ammonia (where $NH_2Cl$ decomposition can occur) to assess the relative importance of the direct reaction of $NH_2Cl$ with DOM in the HAA formation.

HAA formation under two different ammonia conditions is shown in Figure 3. DCAA was the only HAA species formed during these experiments. Considering the slow nature of HOCl and $NHCl_2$ production from $NH_2Cl$ decay, they were probably not significant enough to impact $NH_2Cl$ decay and HAA formation during the early reaction period.

After the first four-hour period, HAA formation trends start to separate for the two test conditions. A higher degree of HAA formation was observed with increasing reaction time in the absence than in the presence of background ammonia. At the end of 24 hours, the HAA concentrations were 26 and 20 ppb in the absence and presence of background ammonia samples, respectively (Figure 3), indicating that direct reaction of $NH_2Cl$ with DOM is the major pathway, accounting for about 80 percent of HAA formation during chloramination. An experiment performed with only preformed $NHCl_2$ and DOM at pH 6 showed no HAA formation; therefore, the HOCl pathway accounts for the other 20 percent.
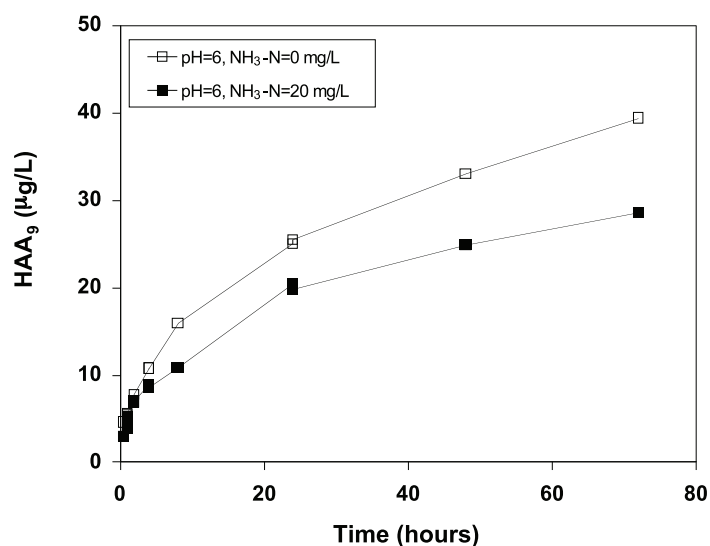


Figure 3: Formation of HAA in the absence (NH3=0 mg/L) and presence (NH3=20 mg/L) of additional background ammonia at pH 6.
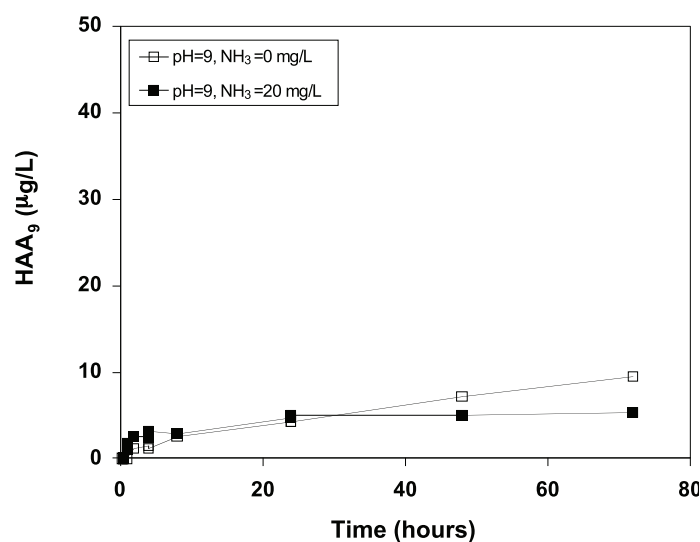


Figure 4: Formation of HAA in the absence (NH3=0 mg/L) and presence (NH3=20 mg/L) of background ammonia addition at pH 9.

A similar experiment was also performed at pH 9. Because monochlormaine decomposition and HOCl formation was suppressed at high pH, the difference in HAA formation was very small (within 2 ppb) for the two ammonia level experiments (Figure 4). The 24-hour DCAA concentration at pH 9 in the presence of background ammonia (where direct reaction of $NH_2Cl$ with DOM is dominant) was 28 percent of DCAA formed at pH 6, indicating that DCAA formation from direct reaction strongly depends on pH.

## The Impact of Quenching Agent on HAA Kinetic Experiments

It is evident from the kinetic experiment results presented in Figures 3 and 4 that no fast formation kinetics were observed in this study. Furthermore, the results obtained with the high background ammonia experiments showed that direct reaction of monochloramine with DOM plays the major role in the HAA formation.

Currently, EPA Method 552.3, approved for compliance monitoring under the D/DBPR, requires the use of ammonium chloride ($NH_4Cl$) as a chlorine quenching agent for HAA samples. $NH_4Cl$ is not a quenching agent for $NH_2Cl$; however, $NH_4Cl$ significantly minimizes $NH_2Cl$ decomposition, as discussed above, without eliminating it from sample vials.

Since the direct reaction of $NH_2Cl$ with DOM appears to be dominant in HAA formation, the residual $NH_2Cl$ can continue to react with the DOM until the sample is extracted. As a result, the use of $NH_4Cl$ may create an artifact on the HAA determination in chloraminated samples.

To assess the significance of quenching agent selection on chloramination kinetics, a comparison experiment was performed at pH 6 and pH 9 using Myrtle Beach DOM.

Chloraminated samples were quenched using either a stoichiometric amount of $Na_2SO_3$ or 100 mg/L of $NH_4Cl$ at the end of each contact time. They were stored immediately in a refrigerator (4-6°C) until extraction, which was performed for all samples together right after the last sample of the kinetic experiment (48-hour). The results are presented in Figure 5.

The samples quenched with $NH_4Cl$ showed a significantly higher and faster HAA formation than the samples quenched with $Na_2SO_3$ at both pH values. The difference between the two kinetic patterns (i.e., $NH_4Cl$ vs. $Na_2SO_3$) increased with decreasing reaction times. These observations indicated that the fast kinetic patterns reported in Figure 2 were caused by unsuccessful quenching and long sample storage time.

These findings clearly show that selection of a quenching method has an impact on the determination of HAA formation.
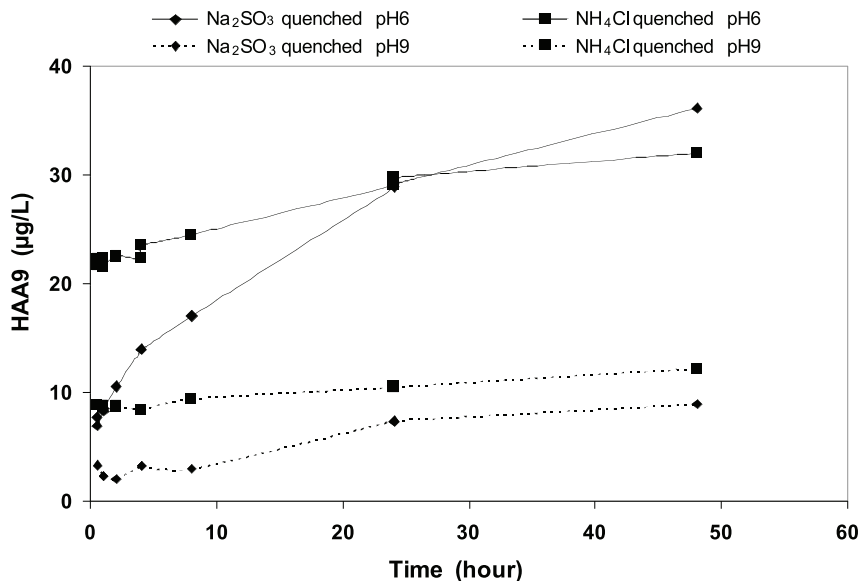


Figure 5: HAA formation kinetics determined at pH 6 and 9 using Na₂SO₃ or NH₄Cl as quenching agents.

Chloramination experiments also were performed to check the reliability of stoichiometric amount of $Na_2SO_3$ on preserving HAA samples. Results (data not shown) indicated that no HAA concentrations in the samples were changed after three days' storage time, since residuals of $NH_2Cl$ in the sample were destroyed by $Na_2SO_3$; however, HAA concentrations in samples quenched with $NH_4Cl$ increased with sample storage time because of the continued reaction of $NH_2Cl$ and DOM.

## Conclusions

◆ Experiments performed in the presence (where HOCl and $NHCl_2$ formation is significantly suppressed) and absence (where $NH_2Cl$ decomposition can occur) of background ammonia indicated that a major amount (~80 percent) of HAA is formed from the direct reaction of $NH_2Cl$ with DOM. DXAA is the major HAA species formed during chloramination, and its formation decreased significantly with increasing pH.

◆ Selection of a quenching agent is important to obtain reliable results from chloramination experiments. The use of $NH_4Cl$, the quenching agent recommended by EPA Method 552.3 for DBP samples, can create an artifact on the HAA results. Since $NH_4Cl$ does not quench the residual chloramines, the reactions of chloramines with DOM forming HAA can occur until the samples are analyzed. As a result, false high HAA concentrations are measured at *early reaction periods.* The type of quenching agent used appears to be the cause of different kinetic patterns reported for chloramination kinetics in the literature.

## References

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