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Effect of Natural Organic Matter on Monochloramine Decomposition: Pathway Elucidation through the Use of Mass and Redox Balances

PETER J. VIKESLAND,
KENAN OZEKIN, AND
RICHARD L. VALENTINE*

*Department of Civil and Environmental Engineering,
The University of Iowa, Iowa City, Iowa 52242*

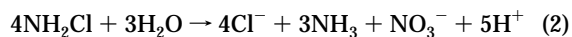
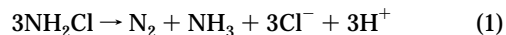
Monochloramine is often employed as a drinking water disinfectant for systems where free chlorine residuals are difficult to maintain or where disinfection byproduct formation is significant. Monochloramine is, however, unstable and decomposes, leading to nitrogen oxidation and chlorine reduction (auto-decomposition). The role of natural organic matter (NOM) in monochloramine loss is unclear. NOM could catalyze monochloramine auto-decomposition, or it could act as an external reductant. This study elucidates the decay pathways of monochloramine in the presence and absence of NOM. When monochloramine decomposes in the absence of NOM, ammonia and nitrogen gas are the primary nitrogen decay products. When NOM is present, the product speciation changes such that little nitrogen gas production occurs, yet production of ammonia and nitrate increases. This product speciation shift indicates that under these conditions, NOM acts primarily as a reductant and not as a catalyst. This conclusion was verified using a redox balance which compares oxidized product, N_2 and NO_3^- , production to monochloramine loss. The number of electrons accounted for by oxidized product production correlates well with monochloramine loss in the absence of NOM (60–100% recovery). However, there is a deficit in the presence of NOM (25–60% recovery). Clearly, much of the oxidizing capacity of monochloramine goes toward NOM oxidation.

Introduction

Chloramine disinfectants are produced by a reaction between free chlorine and ammonia in a process called chloramination. Strictly speaking, chloramines include monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3). However, monochloramine is the predominant chloramine species under the conditions typically found in water treatment facilities and distribution networks. Monochloramine has the same oxidizing capacity as free chlorine on a chlorine atom basis, but it is a weaker disinfectant (1). It is often used when chlorine residuals are difficult to maintain or when they lead to excessive trihalomethane (THM) formation. Chloramines are nonetheless inherently unstable at neutral pH values, even without the presence of reactive inorganic or organic substances, and decompose by a complex set of reactions which ultimately result in the

oxidation of ammonia and reduction of active chlorine (auto-decomposition) (2). The rate of these reactions depends on the ratio of chlorine to ammonia nitrogen (Cl:N ratio) as well as on pH. In general, the greater the ratio of chlorine to nitrogen, the faster this process occurs.

During the course of the decomposition reactions, it is generally believed that the nitrogen in monochloramine [present as $N(-III)$] is preferentially oxidized to N_2 with smaller quantities of NO_3^- , and possibly one or more minor unidentified products (3). The net decay reaction is expected to increase the free ammonia concentration by an amount which depends on the specific products formed, as shown for the formation of nitrogen gas and nitrate:



The belief that N_2 is the predominant oxidized product is implied by the measured stoichiometry between the change in the ammonia concentration and the change in the monochloramine concentration. This belief is further supported by the fact that while some nitrate is produced, the levels are typically quite small (4, 5). Nitrogen gas formation has always been presumed but until recently was never directly experimentally measured (6).

Previous researchers have followed the course of the auto-decomposition reaction in the absence of other reactive species through the use of chlorine mass balances (4, 5). These mass balances measure the disappearance of chlorine in the +1 oxidation state (Cl^+) and compare it to the production of chloride (Cl^-). To date, work incorporating simultaneous nitrogen mass balances which include the measurement of nitrate, nitrogen gas, and ammonia, has not been done in either the presence or absence of added natural organic matter (NOM).

Several studies have demonstrated that the presence of natural organic matter (NOM) in water accelerates the decay of monochloramine (7–11). This has been attributed to oxidation and substitution reactions involving NOM. However, only a small fraction of the monochloramine which disappears in the presence of NOM can be directly accounted for by measuring known halogenated disinfection byproducts (DBPs) and total organic halogen (TOX) (10, 12). The bulk of the monochloramine lost does not lead to easily identifiable organic products. Thus, the fate of the monochloramine and the nature of the reactions involving NOM cannot be inferred by organic product measurements.

NOM could also increase monochloramine decay through interactions that do not lead to its oxidation or to the formation of halogenated products. Humic substances have been shown to act as general acid catalysts (13). Studies have also shown that the auto-decomposition of monochloramine is general acid catalyzed (8, 14). This is hypothesized to involve the catalysis of the second-order reaction involving two monochloramine molecules to form dichloramine which quickly decomposes. Taken together, these findings suggest that NOM, especially humic and fulvic acids, may catalyze the auto-decomposition of NH_2Cl .

Maintaining a stable disinfectant residual and minimizing DBP formation in the presence of NOM and other possible reactants are important goals in water treatment. Typically, this is attempted by removing NOM or by treatment that renders it less reactive. However, this largely empirical approach is not necessarily satisfactory. An improved understanding of the extent and significance of reactions of

* Corresponding author phone: (319)335-5653; fax: (319)335-5660; e-mail: richard-valentine@uiowa.edu.

monochloramine, especially those involving NOM, could help achieve these treatment objectives.

This paper demonstrates a new approach to the study of reactions that govern the loss of monochloramine in drinking water. Specifically, this paper reports on experiments which examine the role of NOM in the enhancement of monochloramine decay. This was done using mass balances to monitor the flow of electrons. These balances are of use in evaluating the NH_2Cl loss pathways since product speciation depends on the loss mechanism. The methodology presented allows differentiation between redox and substitution reactions which may produce DBPs, and the more benign auto-decomposition pathway.

Materials and Methods

The laboratory grade water used for all experiments and for the cleaning of glassware was produced using a Barnstead ULTROpure water system. This system is composed of a reverse osmosis (RO) unit connected in series to a Barnstead NANOpure system. To reduce the organic concentration of the finished water, the effluent from the Nanopure system is treated via a Barnstead ORGANOpure UV reactor. This system produces a water with a chemical resistivity greater than $18 \text{ M}\Omega\cdot\text{cm}$ and a total organic carbon concentration less than 0.25 mg C/L . All chemicals used in these experiments were analytical laboratory grade. Aldrich humic acid (AHA, Lot 01816HH) was utilized as model NOM. The Aldrich humic acid was purified prior to use in order to remove residual ash and heavy metal contaminants (15). The pH of all solutions was measured with a Fisher model 420 meter after appropriate calibration. All glassware was cleaned by soaking it in a concentrated chlorine bath ($\sim 5000 \text{ mg/L Cl}_2$) for a period of at least 24 h. After the glassware was cleaned, it was thoroughly rinsed with laboratory grade water and allowed to dry.

A low chloride sodium hypochlorite solution was produced using the method of Reinhard and Stumm (16). The solution produced using this procedure had a HOCl/Cl^- molar ratio of 7.89:1 and was used to prepare all monochloramine solutions. The DPD–FAS method was employed for the measurement of free chlorine and chloramine residuals (17). This method is based on the principle that different chlorine species have distinct reactivities toward the DPD reagent and potassium iodide (KI). The method detection limit (MDL) for this technique was determined to be $0.001 \text{ mM NH}_2\text{Cl}$, based on seven replicate measurements of a $0.01 \text{ mM NH}_2\text{Cl}$ solution.

A Dionex 2000I IC, equipped with an AS4A anion separatory column and an AS4G guard column was used for the chloride, nitrite, and nitrate measurements. A set of control experiments indicated that monochloramine is not reduced by the AS4A/AS4G columns and that its presence does not interfere with the measurement of these anions. Chloride was measured in both unreduced and reduced monochloramine samples. The unreduced samples measure chloride production, while the reduced samples account for the total amount of chlorine present in solution. The samples were reduced using sodium sulfite since previous work indicated that sulfite readily reduces the unknown chloramine byproduct(s), which form during monochloramine decay, to chloride (18). The nitrate concentrations measured in both the unreduced and reduced injections were the same. The MDLs determined for Cl^- , NO_2^- , and NO_3^- are 0.001, 0.002, and 0.001 mM, respectively (19).

Ammonia concentrations were measured using a Dionex 4000I IC equipped with a cation AS10 separatory column and an AG10 guard column. To eliminate reactions which occur between the cation resin and monochloramine, all of the samples were reduced with sodium sulfite prior to injection. This reduction made it necessary to subtract the

monochloramine concentration from the measured $\text{N}(-\text{III})$ concentration in order to calculate the free ammonia concentration:

$$\text{NH}_{3,\text{free}} = \text{measured N}(-\text{III}) - \text{NH}_2\text{Cl} \quad (3)$$

where $\text{N}(-\text{III})$ represents all of the nitrogen present in solution in the -3 valence state. The MDL for ammonium was determined to be 0.01 mM .

Gas chromatography/mass spectrometry (GC/MS) was utilized for the measurement of $^{15}\text{N}_2$, as described previously (6). The GC/MS system was calibrated using $^{15}\text{N}_2$ standards prepared by serial dilutions of 98% $^{15}\text{N}_2$ (Cambridge Isotope Labs, Lot ED-314). By monitoring the ion count at 30 m/z for a concentration range which spanned the measured nitrogen gas production in the experimental samples, a calibration curve was obtained. The calibration curve was then utilized to convert the ion counts obtained for the experimental samples into N_2 concentrations, correcting for N_2 solubility using the Henry's constant for $^{15}\text{N}_2$ at the temperature of interest and the ideal gas law (6). In general, 93% of the nitrogen gas produced partitions in the headspace.

The monochloramine solutions used in the mass balance experiments were prepared using a preformed monochloramine stock which was made using isotopically labeled ammonium sulfate [$(^{15}\text{NH}_4)_2\text{SO}_4$, 98% ^{15}N , Aldrich Chemical Co.] (20). Solution aliquots of 100 mL were placed into 120 mL septum-capped vials, leaving a 20 mL headspace. These vials were capped using PTFE-coated silicone septa and then placed upside down in a 25°C incubator. The reliability of these vials for nitrogen gas measurements was previously established (6).

The monochloramine kinetic experiments used monochloramine solutions that were prepared in a manner identical to those utilized in the mass balance experiments, except that unlabeled ammonium sulfate was used to produce the monochloramine stock. Sodium perchlorate (NaClO_4) was used to set the ionic strength ($I = 0.1 \text{ M}$) in the kinetic experiments. It was not possible to control the ionic strength in the mass balance experiments because perchlorate was found to interfere with anion measurements on the ion chromatograph.

Results and Discussion

Kinetic Studies. The addition of NOM causes an increase in the loss of monochloramine relative to the controls in laboratory grade water (Figure 1). When NOM was added at concentrations of 1.7, 3.3, and 5.0 mg/L , the observed acceleration is greater than can be accounted for by experimental variation in the controls without added NOM. This type of accelerated disinfectant decomposition has also been observed for the reaction between free chlorine and fulvic acid (21).

Several experiments were conducted at two relatively high ammonia concentrations that repressed the normally occurring non-NOM mediated auto-decomposition pathway (Figure 2). These experiments were conducted by making up a monochloramine solution at a given Cl/N molar ratio and then adding ammonia to the solution to achieve the desired final ammonia concentration. This process facilitates elucidation of the loss mechanism by adjusting reaction conditions so that all observed decay is attributable solely to the effect of NOM. The added NOM greatly increased the rate of monochloramine decay, which was essentially the same at both 1 and 10 mM ammonia over the first 20 h period in which approximately 50% of the monochloramine decayed. However over a longer time frame, a somewhat slower monochloramine decay is evident at the higher ammonia concentration. From this we conclude that the effect of NOM during the first 20 h is not manifested through

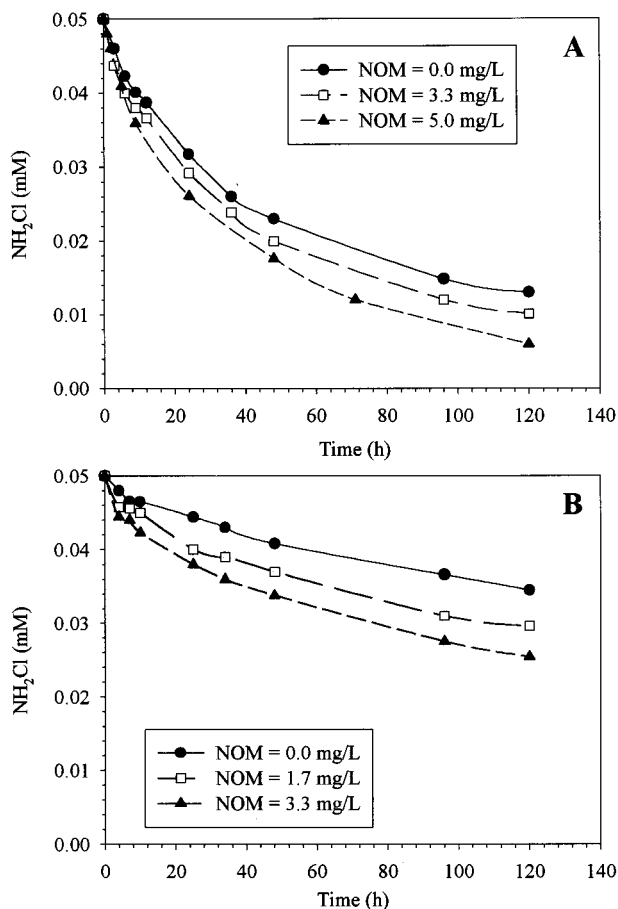


FIGURE 1. Effect of NOM on monochloramine decay at (A) pH 6.5 and (B) pH 7.5. In all cases, $[\text{NH}_2\text{Cl}]_0 = 0.05 \text{ mM}$, $\text{Cl}/\text{N} = 0.7 \text{ (mol/mol)}$, $C_{\text{T},\text{CO}_3} = 4 \text{ mM}$, $\mu = 0.1 \text{ M}$, $T = 25^\circ\text{C}$.

rate-limiting reactions which involve HOCl. This is because the HOCl concentrations differ by approximately a factor of 10 since they are governed by equilibrium with monochloramine and ammonia. Therefore if the effect of NOM depended directly on the concentration of HOCl, differences in decay should be observed which are proportional to this difference.

The effect of ammonia over the longer time frame suggests possible HOCl involvement in the decay of monochloramine when NOM is present. This may indicate that, as suggested by others (21), NOM contains two types of reactive sites, one which readily reacts with NH_2Cl and one which reacts only with the HOCl produced by NH_2Cl hydrolysis. A direct reaction of monochloramine might also create HOCl reactive sites. These observations are consistent with either NOM catalysis of monochloramine auto-decomposition or the direct involvement of monochloramine with NOM in redox and substitution reactions. They are, however, not enough to allow the determination of reaction pathways.

Mass Balances. To provide direct evidence of the mechanism by which monochloramine and NOM interact, experiments were conducted in which the inorganic monochloramine decay products chloride, nitrate, nitrite, nitrogen gas, and ammonia were measured. By comparing the product distribution in the presence of added NOM with that obtained in its absence it is possible to gain insight into monochloramine loss pathways.

Development of Mass Balances. Nitrogen and chlorine mass balances were developed by measuring chloride, nitrogen gas, nitrite, nitrate, and ammonia in decayed monochloramine samples. The comparison of chloride production to monochloramine loss makes it possible to get

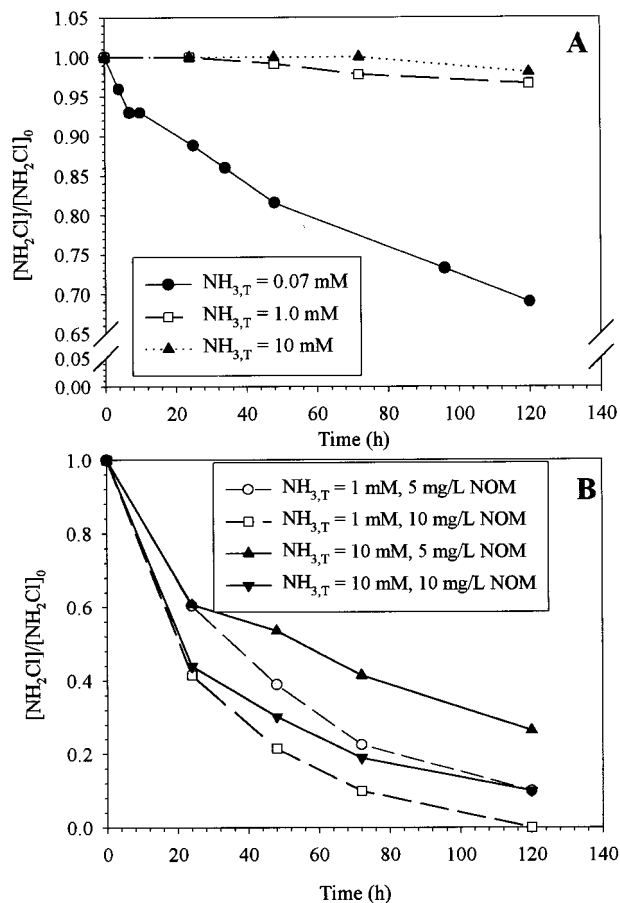


FIGURE 2. Normalized NH_2Cl decay as a function of (A) total ammonia concentration and (B) total ammonia and NOM concentration. In all cases, $[\text{NH}_2\text{Cl}]_0 = 0.055 \pm 0.005 \text{ mM}$, $\text{pH} = 7.6$, initial $\text{Cl}/\text{N} = 0.7 \text{ (mol/mol)}$, $C_{\text{T},\text{CO}_3} = 4 \text{ mM}$, $\mu = 0.1 \text{ M}$, $T = 25^\circ\text{C}$.

a chlorine atom balance, and a comparison of the yield of nitrogen gas, ammonia, nitrite, and nitrate (on a nitrogen atom basis) to monochloramine decay allows a nitrogen balance to be derived. A representative set of plots of the chlorine and nitrogen mass balances obtained in the presence and absence of NOM is depicted in Figure 3. The product recovery percentages obtained for each experiment are tabulated in Table 1. These recovery percentages are defined as the amount of recovered products divided by the amount of monochloramine decayed at any point in time.

Chlorine Mass Balances. Chloride was found to be the major halogen decay product both in the presence and absence of NOM. This finding corroborates previous studies which examined monochloramine decay (22, 23). When NOM is not present in solution, the chloride recovery in the unreduced samples was greater than 57% under all of the conditions studied, and it was greater than 80% in most cases. The apparently low chloride recovery has been attributed to the formation of an unidentified monochloramine decay product (18, 24–26). Closure in the chlorine mass balance, however, was attainable when the samples were reduced (data not shown), and therefore the low recovery percentages are not believed to be analytical errors. The identity of the unidentified product(s) currently remains elusive but is the subject of ongoing research.

When NOM was added to the solutions, the chloride recovery was similar to that obtained in its absence (Table 1). To substantiate this conclusion, chloride production was compared to monochloramine decay for experiments with and without NOM present (Figure 4). Linear regressions were fit to data from both the non-NOM and the NOM

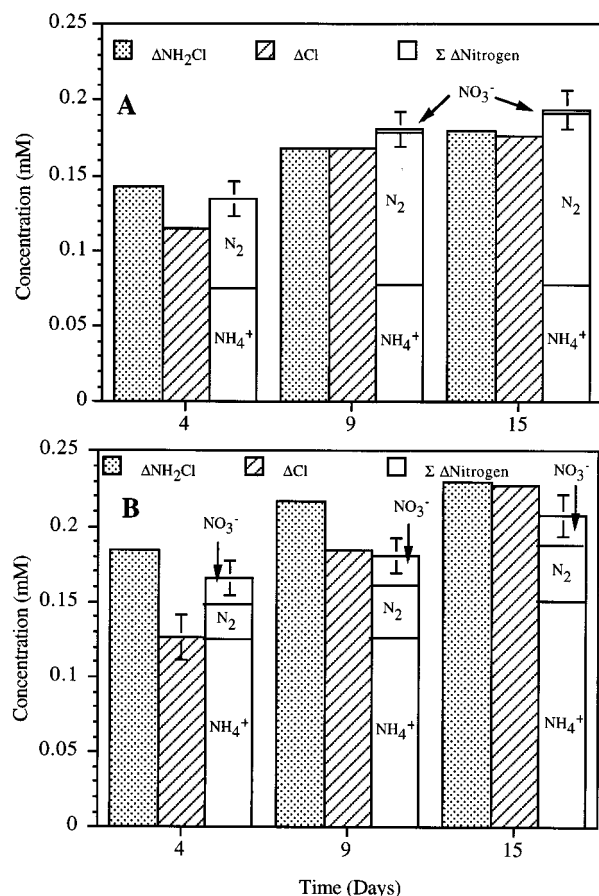


FIGURE 3. Chlorine and nitrogen mass balances for (A) samples without NOM and (B) samples with 5 mg/L NOM. In all cases, $[\text{NH}_2\text{Cl}]_0 = 0.23 \text{ mM}$, $\text{pH} = 6.5$, $\text{Cl}/\text{N} = 0.7 \text{ (mol/mol)}$, $C_{\text{T,CO}_3} = 4 \text{ mM}$, $T = 25^\circ\text{C}$. The error bars for ΔCl^- are the standard deviations obtained for each sample day, and the error bars for $\Sigma\Delta\text{nitrogen}$ are a summation of the errors of the individual measurements.

experiments and were found to be statistically indistinguishable at the 95% confidence level. This indicates that under these reaction conditions humic material does not substantially affect the amount of chloride produced for a given level of monochloramine decay. By reducing the samples with sulfite it was possible to recover the chlorine missing from the mass balances obtained with NOM present. This possibly indicates that the missing chlorine may be part of the unidentified product discussed previously.

In these experiments, no detectable chlorine incorporation into NOM was found. It should however be noted that some chlorine incorporation must occur since DBPs and TOX are known to form in monochloramine solutions which contain NOM (7, 10). It would appear that the amount of chlorine incorporated is too small to be discernible relative to the accuracy of the chloride and monochloramine measurements. Although neither DBP nor TOX formation were measured in these experiments, it is possible to gain some insight into the amount of TOX which could form under our reaction conditions by using literature values (Table 2). Using the representative TOX values tabulated in Table 2, we calculate that for our reaction conditions, the amount of chlorine which may be incorporated in TOX amounts to less than 5% of the total chlorine. This amount is below the detection limit of our measurements of the chlorine mass balance. Clearly from a mass balance perspective, a very small fraction of chlorine is incorporated into either TOX or DBPs.

Nitrogen Balances. The average total nitrogen recovery was $90 \pm 7.0\%$ for the samples which do not contain NOM.

TABLE 1. Molar Percent Recoveries for Chlorine and Nitrogen Species^a

$[\text{NH}_2\text{Cl}]_0$ (mM)	pH	time (day)	% Cl recovered	% $\text{NH}_3\text{-N}$	% $\text{NO}_3\text{-N}$	% $\text{N}_2\text{-N}$	total % N recovered
No NOM Added							
0.049	6.5	4	85	46	0.0	20	66
		9	88	41	0.0	42	83
		15	81	42	0.0	40	82
0.048	7.5	4	— ^b	43	0.0	11	54
		9	100	63	0.0	28	91
		15	95	55	5.0	26	86
0.230	6.5	4	81	47	0.0	47	94
		9	100	42	0.3	66	110
		15	98	41	0.7	66	110
0.240	7.5	4	69	58	0.0	26	84
		9	98	50	1.7	41	93
		15	83	42	2.7	38	82
0.860	6.5	4	80	47	0.9	59	110
		9	84	42	1.2	69	110
		15	87	39	1.8	60	100
0.950	7.5	4	57	56	1.9	35	93
		9	77	48	1.9	48	97
		15	98	41	2.9	43	87
NOM Concentration, 5 mg C/L							
0.048	6.5	4	60	61	0.0	0.0	61
		9	90	40	4.4	1.7	46
		15	89	40	5.2	2.9	48
0.048	7.5	4	69	9	0.0	0.0	29
		9	95	44	6.9	0.4	51
		15	98	42	9.0	2.1	53
0.230	6.5	4	68	70	6.5	13	90
		9	85	60	7.4	18	86
		15	99	65	8.7	16	90
0.240	7.5	4	85	68	13	0.0	80
		9	91	67	15	4.5	87
		15	94	72	14	4.7	90
0.950	7.5	4	81	51	6.5	22	80
		9	81	50	5.5	25	80
		15	83	51	6.3	23	80

^a $\text{Cl}/\text{N} = 0.7 \text{ (mol/mol)}$, $C_{\text{T,CO}_3} = 4 \text{ mM}$, $T = 25^\circ\text{C}$. ^b The amount of chloride produced was below the MDL for the ion chromatograph.

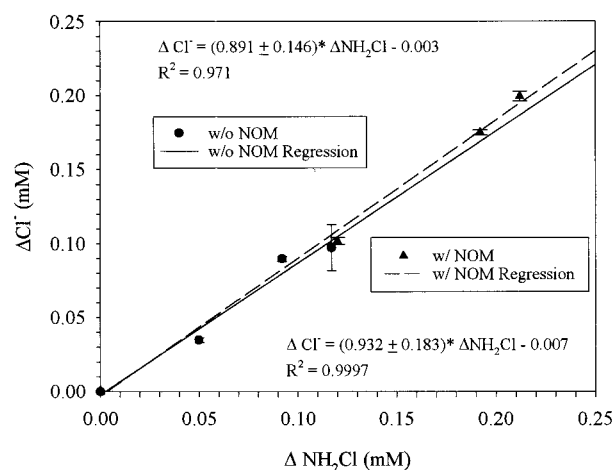


FIGURE 4. ΔCl^- versus $\Delta\text{NH}_2\text{Cl}$ for $[\text{NH}_2\text{Cl}]_0 = 0.23 \text{ mM}$, $\text{pH} = 7.5$, $\text{Cl}/\text{N} = 0.7 \text{ (mol/mol)}$, $C_{\text{T,CO}_3} = 4 \text{ mM}$, $T = 25^\circ\text{C}$, $\text{NOM} = 5 \text{ mg of C/L}$. Linear regressions for the samples with and without NOM were found to be statistically indistinguishable at the 95% confidence level.

It was found that ammonia and nitrogen gas are the primary nitrogen atom containing decay products of monochloramine (Figure 3). Ammonia production typically corresponds to $47 \pm 3.4\%$ of monochloramine nitrogen, while nitrogen gas corresponds to $43 \pm 7.9\%$. These levels are quite close to the 1:1 stoichiometry expected if monochloramine decomposes

TABLE 2. Literature Values for TOX Formation by the Reaction between Monochloramine and NOM

NOM source	conditions	chloramine-produced TOX (μg of Cl^-/mg of TOC)	ref
peat fulvic acid	pH 7, TOC = 1–5 mg/L, reaction time = 100 h, NH_2Cl dose = 20 mg/L (as Cl_2)	27–31	7
humic acid	pH 7, TOC = 3 mg/L, reaction time = 100 h, NH_2Cl dose = 20 mg/L (as Cl_2)	12–52	7
Black Lake fulvic acid	pH 9, TOC = 21 mg/L, reaction time = 24 h, NH_2Cl dose = 12.4 mg/L (as Cl_2)	17	10

according to eq 1. Small but significant levels of nitrate were also formed; however, no nitrite was ever detected. The amount of monochloramine nitrogen which formed nitrate never exceeded 5% with an average level of $1.2 \pm 0.66\%$. Although the nitrogen recovery is less than 100%, the missing amount is roughly half that missing from the chlorine mass balance. Whether this missing nitrogen is associated with the missing chlorine is unknown.

When NOM is added to the monochloramine solutions, the product speciation changes. For high $\text{NH}_2\text{Cl}/\text{NOM}$ ratios, ammonia comprised $53 \pm 5.7\%$ of total N, while nitrate comprised $7.0 \pm 1.8\%$ of total N. These levels were much higher than those measured without NOM present. Conversely, nitrogen gas production, $11 \pm 4.5\%$ of total N, decreased substantially. The increases in ammonia and nitrate production were not enough to offset the decrease in nitrogen gas production, therefore the nitrogen balances in the presence of NOM can account for only $71 \pm 8.6\%$ of the initial nitrogen in NH_2Cl versus $90 \pm 7.0\%$ in the absence of NOM. This decrease in the nitrogen recovery may be attributable to the incorporation of N(III) into the NOM matrix. Ginwalla and Mikita (27) observed the reaction between chloramines and Suwannee River fulvic acid (SRFA) using ^{15}N NMR and concluded that some of the ammonia released by monochloramine decay may be incorporated into NOM in the form of amines. Jensen (28) suggested that the incorporated nitrogen came from monochloramine and not ammonia, citing the increased nucleophilicity of the nitrogen in monochloramine relative to the nitrogen in free ammonia. As discussed in the following sections, our results appear to support Jensen's conclusion.

If NOM acts as a simple reductant of the chlorine (as Cl^+) in NH_2Cl to yield chloride ion, then an increase in ammonia would be expected. As shown in Figure 5, this was observed in the 0.25 and 1 mM monochloramine samples. The increase in ammonia production occurs because the oxidation state of the nitrogen in ammonia is the same as that of the nitrogen in monochloramine. This makes ammonia the preferred decay product under these conditions. At low $\text{NH}_2\text{Cl}/\text{NOM}$ ratios, there was no significant measurable increase in the ammonia concentration for $[\text{NH}_2\text{Cl}]_0 = 0.05$ mM in the presence of NOM. This is due to the difficulty associated with differentiating between changes in ammonia of only ± 0.01 mM, which is at the detection limit for our method.

Surprisingly, the presence of NOM significantly enhanced the amount of nitrate produced for a given level of monochloramine decay. This trend was detected under all of the experimental conditions examined. A representative increase is depicted in Figure 6. While the nitrate production was increased in the presence of NOM, the amount of nitrogen gas produced decreased by 50–80% (Figure 7). A possible explanation for the observed decrease in nitrogen gas formation with a commensurate increase in nitrate formation is that in the presence of NOM, the pathway by which nitrate forms predominates over that which leads to nitrogen gas formation. This interaction leads to a decrease in the nitrogen gas production and an increase in the amount of nitrate produced. It is also possible, however, that

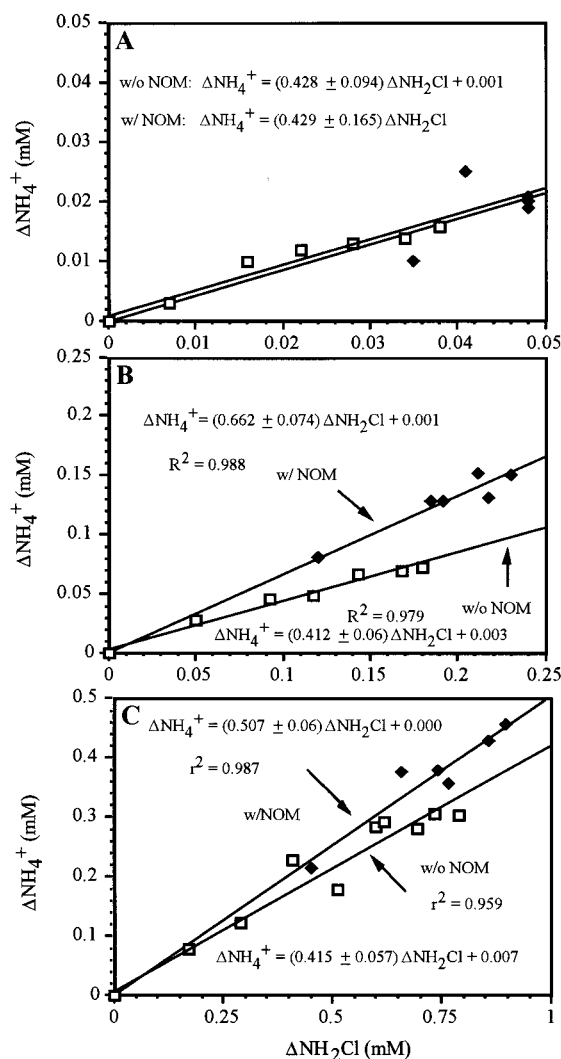


FIGURE 5. Ammonia production due to monochloramine decay for (A) 0.05 mM, (B) 0.23 mM, and (C) 1.00 mM NH_2Cl . $\text{Cl}^-/\text{N} = 0.7$ (mol/mol), initial pH = 6.5 and 7.5, $C_{\text{T,CO}_3} = 4$ mM, $T = 25^\circ\text{C}$, NOM = 5 mg of C/L. The error in the slope is based on the 95% confidence interval for the data.

monochloramine reacts with nitrogen-containing moieties in the humic structure leading to the formation of nitrate. A series of control experiments, however, showed that no nitrate is formed when NOM was treated with hypochlorous acid. If monochloramine truly oxidizes organic nitrogen species present in NOM to produce nitrate, then one would expect hypochlorous acid to act in a similar manner. Since this was not found to occur, it appears that when monochloramine reacts with NOM a product speciation shift toward the formation of nitrate relative to nitrogen gas occurs.

Redox Balances. Redox balances which attempt to account for all known oxidation and reduction reactions for solutions which do not contain NOM were derived (20). These

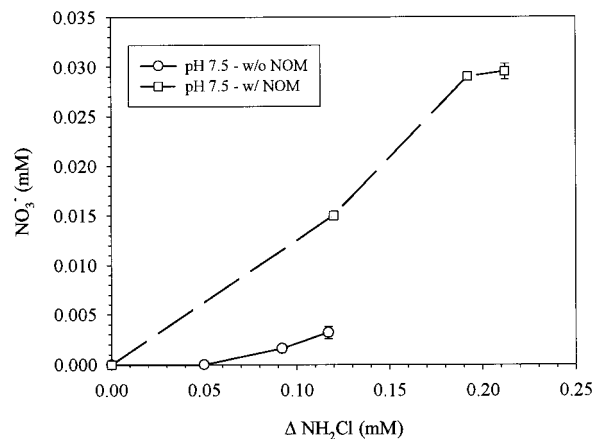


FIGURE 6. NO_3^- vs NH_2Cl for $[\text{NH}_2\text{Cl}]_0 = 0.23 \text{ mM}$ and pH 7.5. $\text{Cl}/\text{N} = 0.7 \text{ (mol/mol)}$, $C_{\text{T,CO}_3} = 4 \text{ mM}$, $T = 25^\circ\text{C}$, $\text{NOM} = 5 \text{ mg of C/L}$. The error bars represent the standard deviation of at least three measurements.

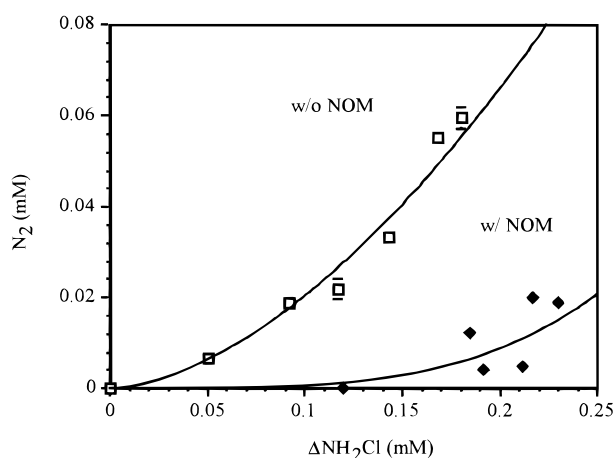


FIGURE 7. ΔN_2 vs $\Delta\text{NH}_2\text{Cl}$ for $[\text{NH}_2\text{Cl}]_0 = 0.023 \text{ mM}$ with initial pH 6.5 and 7.5. $\text{Cl}/\text{N} = 0.7 \text{ (mol/mol)}$, $C_{\text{T,CO}_3} = 4 \text{ mM}$, $T = 25^\circ\text{C}$, $\text{NOM} = 5 \text{ mg of C/L}$.

balances equate the number of electrons involved in the formation of oxidized monochloramine decay products (NO_3^- and N_2) to the loss of monochloramine; they also equate the number of electrons involved in the formation of the reduced decay product, chloride, to monochloramine loss.

By equating the observed production of oxidized products (normalized to equivalences) to the decay of monochloramine, it is possible to gain insight into the recovery of the electrons transferred by the oxidation reaction. Therefore, the oxidized product balance obtained in the presence of NOM can be used as a tool to determine how much of the oxidizing capacity of monochloramine goes to NOM oxidation and how much to oxidation of N(III). The reduced product balance similarly can be used to show the recovery of the reduced products.

In the absence of NOM, the measured amounts of oxidation and reduction products correspond to 60–100% of the amount of NH_2Cl lost after 15 days (Table 3). In the presence of NOM, only 25–60% of the monochloramine loss can be accounted for by nitrate and nitrogen gas production, while ~90% of the reduction products may be recovered (Figure 8). The lack of closure in the oxidized product balance indicates that unaccounted for oxidation products have been produced by the reaction between monochloramine and NOM.

It was previously discussed that active chlorine is not likely to be significantly incorporated into the NOM matrix, as

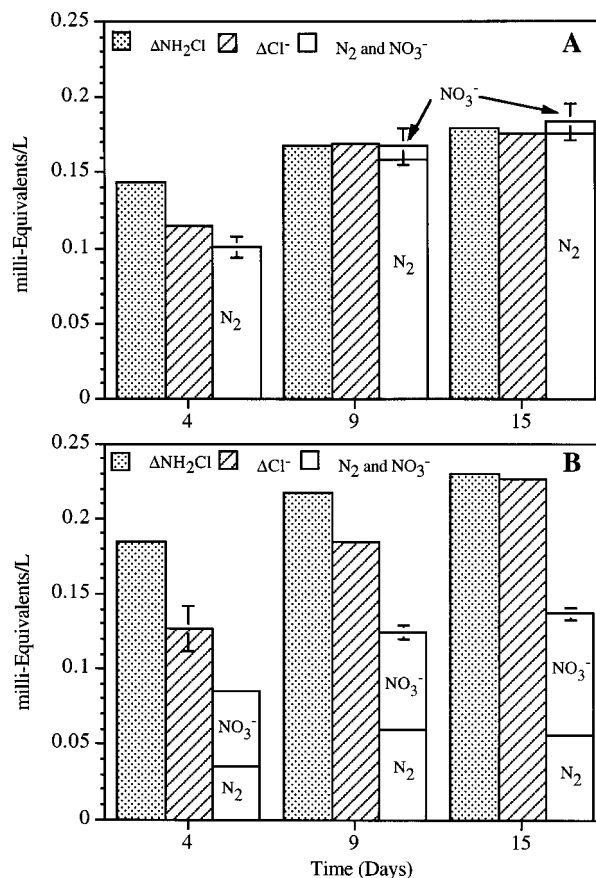


FIGURE 8. Redox balance for (A) samples without NOM and (B) samples with 5 mg/L. In all cases, $[\text{NH}_2\text{Cl}]_0 = 0.23 \text{ mM}$, pH = 6.5, $\text{Cl}/\text{N} = 0.7 \text{ (mol/mol)}$, $C_{\text{T,CO}_3} = 4 \text{ mM}$, $T = 25^\circ\text{C}$. The error bars for ΔCl^- are the standard deviations obtained for each sample day, and the error bars for N_2 and NO_3^- are a summation of the errors of the individual measurements.

would occur via a substitution reaction. This suggests that NOM primarily reacts, at these $\text{NH}_2\text{Cl}/\text{NOM}$ ratios, via oxidation reactions which lead to the production of chloride and ammonia. This conclusion is further corroborated by the fact that, while the nitrogen mass balances obtained in the presence of NOM can account for approximately 71% of the initial nitrogen in monochloramine, the oxidized product balance can account for only 60% of the oxidized nitrogen decay products. This indicates that part of the oxidizing capacity of NH_2Cl goes to NOM oxidation and that unknown oxidized organic species are produced.

Ideally, it would be useful to take the oxidized product deficit measured in the presence of NOM and determine quantitatively how much NOM is oxidized (in terms of equivalences) by NH_2Cl under a given set of conditions. While this can be done for our results, the lack of closure in the mass and redox balances obtained in the absence of NOM makes it difficult to interpret. However, these calculations do set an upper limit on how much monochloramine reacts with NOM under these conditions. A comparison of the oxidized product deficits measured in the presence and absence of NOM reveals that roughly half of the available oxidizing potential of NH_2Cl went toward monochloramine auto-decomposition and not the oxidation of NOM.

These experiments indicate that NOM reacts directly with monochloramine via redox and substitution reactions and that the role of NOM as a catalyst is negligible. The reactions between NOM and monochloramine result in decreased nitrogen gas formation but increased ammonia and, surprisingly, increased nitrate. The increased formation of ammonia is a concern because it has been associated with incidences

TABLE 3. Summary of Reduced and Oxidized Product Redox Balances for Experiments Conducted with an Initial Monochloramine Concentration of 0.25 and 0.05 mm^a

[NH ₂ Cl] ₀ (mM)	pH	time (day)	ΔNH ₂ Cl (mequiv/L)	reduced species (mequiv/L)	% reduced species recovered	oxidized species (mequiv/L)	% oxidized species recovered
No NOM Added							
0.049	6.5	4	0.028	0.0238 ± 0.0022	85	0.0084 ± 0.0006	30
		9	0.034	0.0300 ± 0.0017	88	0.0213 ± 0.0015	63
		15	0.038	0.0309 ± 0.0034	81	0.0228 ± 0.0016	60
0.048	7.5	4	0.007	<i>b</i>	<i>b</i>	0.0012 ± 0.0001	17
		9	0.016	0.0236 ± 0.0001	101	0.0066 ± 0.0005	41
		15	0.022	0.0283 ± 0.0004	95	0.0131 ± 0.0006	60
0.230	6.5	4	0.143	0.1151 ± 0.0026	81	0.1005 ± 0.0071	70
		9	0.168	0.1686 ± 0.0024	100	0.1673 ± 0.0117	100
		15	0.180	0.1759 ± 0.0021	98	0.1836 ± 0.0126	100
0.240	7.5	4	0.050	0.0347 ± 0.0016	69	0.0198 ± 0.0014	40
		9	0.092	0.0897 ± 0.0016	98	0.0631 ± 0.0040	69
		15	0.117	0.0974 ± 0.0155	83	0.0788 ± 0.0047	67
0.860	6.5	4	0.620	0.4961 ± 0.0232	80	0.5700 ± 0.0387	92
		9	0.735	0.6181 ± 0.0272	84	0.7963 ± 0.0539	110
		15	0.790	0.6869 ± 0.0080	87	0.7641 ± 0.0501	97
0.950	7.5	4	0.410	0.2355 ± 0.0199	57	0.2478 ± 0.0153	60
		9	0.600	0.4596 ± 0.0202	77	0.4758 ± 0.0304	79
		15	0.694	0.6776 ± 0.0245	98	0.5303 ± 0.0318	76
NOM Concentration, 5 mg C/L							
0.048	6.5	4	0.041	0.0247 ± 0.0015	60	0.0000 ± 0.0000	0.0
		9	0.048	0.0434 ± 0.0005	90	0.0096 ± 0.0001	20
		15	0.048	0.0429 ± 0.0001	89	0.0121 ± 0.0001	25
0.048	7.5	4	0.035	0.0241 ± 0.0002	69	0.0000 ± 0.0000	0.0
		9	0.048	0.0458 ± 0.0008	95	0.0135 ± 0.0000	28
		15	0.048	0.0470 ± 0.0001	98	0.0187 ± 0.0001	39
0.230	6.5	4	0.185	0.1266 ± 0.0149	68	0.0849 ± 0.0026	46
		9	0.217	0.1845 ± 0.0032	85	0.1244 ± 0.0042	57
		15	0.230	0.2269 ± 0.0024	99	0.1367 ± 0.0040	59
0.240	7.5	4	0.120	0.1018 ± 0.0022	85	0.0600 ± 0.0000	50
		9	0.192	0.1749 ± 0.0017	91	0.1289 ± 0.0009	67
		15	0.212	0.1993 ± 0.0034	94	0.1330 ± 0.0011	63
0.950	7.5	4	0.740	0.6005 ± 0.0181	81	0.4399 ± 0.0175	59
		9	0.857	0.6942 ± 0.0061	81	0.5049 ± 0.0223	59
		15	0.895	0.7411 ± 0.0136	83	0.5354 ± 0.0219	60

^a Cl/N = 0.7 (mol/mol), C_{T,CO₂} = 4 mm, T = 25 °C; reduced species = ΔCl⁻, oxidized species = 4ΔNO₃⁻ + 3ΔN₂. ^b The amount of chloride produced was below the MDL for the ion chromatograph.

of nitrification in water distribution systems (30, 31). While a biological origin of increased nitrate concentrations in distribution systems has been previously assumed, this work suggests the existence of an additional abiotic pathway involving a reaction of NOM with monochloramine. The direct reaction of monochloramine with NOM may also account for the incorporation of N(III) into the humic matrix in mixtures of NH₂Cl and NOM, as reported by Ginwalla and Mikita (27).

The direct reaction between monochloramine and NOM may mechanistically explain the observed differences in the disinfection byproducts formed by free chlorine and monochloramine. Some DBPs, such as the trihalomethanes (THMs) and the haloacetic acids (HAAs), are observed in both chlorinated and chloraminated systems. However, there are a number of DBPs such as chloropicrin and cyanogen chloride which have been observed in chloraminated systems but are not formed at significant levels in chlorinated systems. The results discussed in this paper suggest that the DBPs formed in chloraminated systems which are the same as those formed in chlorinated systems may be a result of the interaction between HOCl derived by monochloramine hydrolysis and NOM. Conversely, the DBPs found primarily in chloraminated systems may be a result of the direct interaction between NH₂Cl and the NOM matrix.

In summary, this work demonstrates a new approach to the study of reactions that govern the loss of monochloramine in drinking water. Although DBP formation remains an important issue in water treatment, the maintenance of

disinfecting residuals in distribution systems is the primary concern. With further refinements, this approach may ultimately be a valuable tool in attaining a better understanding of the complex chemistry involved in these systems and may lead to improved strategies to maintain the both the biological and chemical integrity of drinking water.

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