Environ. Sci. Technol. **1999**, *33*, 932−937

Formation of Cyanogen Bromide and Other Volatile DBPs in the Disinfection of Bromide-Rich Lake Water

LILLY HELLER-GROSSMAN,*,† ANNA IDIN,† BRACHA LIMONI-RELIS,‡ AND MENAHEM REBHUN†

Environmental and Water Resources Engineering, Technion—Israel Institute of Technology, Haifa 32000, Israel, and Mekorot Water Supply Company, P.O. Box 610, Nazareth, Israel

Production of cyanogen bromide (CNBr) and other volatile DBPs was studied in bromide-rich lake water during disinfection with chlorine, chloramine, and chlorine dioxide. The different disinfectants were dosed to the lake water in laboratory experiments, and the resulting concentrations of CNBr, trihalomethanes (THMs), and haloacetonitriles (HACNs) were measured. CNBr concentration is a resultant of formation and decomposition by hydrolysis. Maximum concentration (36 μg/L) was obtained at low chlorine dose (1.5 mg/L) at pH 7.5 and 10 h contact time. Under these conditions, the molar distribution of the volatile DBPs was 50% CNBr, 40% THMs, and 10% HACNs. It is suggested that CNBr is formed by the reaction of hypobromous acid with organic N precursors present in lake water. Fulvic acid was found to be a good precursor for THMs but a poor precursor for CNBr. With chloramination, yields of CNBr, THMs, and HACNs were much lower, only 6, 11, and 2 μg/L, respectively. CNBr concentration was stable for 10 days. Chlorine dioxide produced insignificant quantities of CNBr, THMs, and HACNs, less than 1 μg/L. A combination of chlorine dioxide and chloramine enhanced production of CNBr and THMs to maximum yields of 7.8 and 19 μg/L, respectively.

Introduction

To minimize DBPs formation, many water utilities turned to chloramine (*1*), chlorine dioxide (*1*), or ozone (*2*) as a total or partial replacement to chlorine. Cyanogen halides (CNX) are part of the volatile DBPs.

Cyanogen chloride (CNCl) is rapidly metabolized to cyanide in the body. The WHO (*3*) proposed a guideline value of 70 μg/L as the sum of all cyanide species, which includes cyanogens. CNCl is included in the U.S. EPA Information Collection Rule (ICR) (*4*).

A median concentration of 1 μg/L of CNCl (maximum 4.5 μg/L) in chlorinated water and about 2 μg/L (maximum 12 μg/L) in chloraminated waters was reported in a study of 35 utilities (*5*). Preozonation enhanced CNCl production upon post-chloramination (*6*). Chlorination of different surface waters or of their hydrophobic organic extracts formed low to nondetectable levels of CNCl (*6*).

CNCl was formed by the reaction of chloramine with humic acid (*7*), peptides (*8*), and purines (*9*). Several mechanisms were suggested for CNCl formation: reaction of formaldehyde, a known chlorine and ozone byproduct, with monochloramine (*10*, *11*). In chloramination of aliphatic amino acids (*8*), the nitrogen source in CNCl came from the amino group in the acid. For peptide precursors, chloramine cleaved the aromatic ring and the CNCl nitrogen originated from the chloramine. Chloramination of purine bases using ^{14}C and ^{15}N demonstrated that the origin of the nitrogen in CNCl was the imidazole ring (*9*). Chlorination of purines and pirimidines in the absence of ammonia also yielded CNCl (*12*). Thus, the organic N in aliphatic amino acids and in heterocyclic compounds is the source for the nitrogen in CNCl.

In bromide-rich water, chlorine oxidizes the bromide to HBrO, and cyanogen bromide is formed. In chloramination of fulvic acid at different bromide concentrations, CNBr became the dominant form at bromide concentration above 0.3 mg/L (*13*) while the molar sum of the two CNX species was little affected. However, THM formation during bromination was enhanced as compared with chlorination (*14*). Formation of CNBr in natural waters during disinfection with chloramine (*15*) and ozone (*16*) was studied.

Lake Kinneret (Sea of Glilee) is the major surface water source in Israel. The water has very high bromide content—1.9 mg/L. The disinfection scheme includes chlorination followed later by a combination of chlorine dioxide with chloramine. The information available on the formation of CNBr during chlorination is scarce and nonexistent for the application of chlorine dioxide or its combination with chloramine. The objective of the present work was to study the formation and decomposition of CNBr and to correlate it with the formation of other volatile DBPs, THMs and haloacetonitriles (HACNs, DBPs containing nitrogen), in the application of chlorine, chlorine dioxide, chloramine, and their combination.

Study Program

The program included three major laboratory studies simulating the full-scale plant.

(i) Formation of CNX and other DBPs during disinfection of Lake Kinneret water. Four disinfectants were applied in doses used in practical disinfection: chlorine (1.5 and 2.5 mg/L), chloramine (1.5 mg/L), ClO_2 (1 mg/L), and a combination of chloramine and ClO_2 (1.5 and 1 mg/L, respectively).

(ii) Formation of CNX and other DBPs from fulvic acid, a reference natural organic matter, in solutions containing the same bromide ion content as the lake water.

(iii) Stability of CNBr.

Experimental Procedures

Chemicals. CNBr (Sigma Chemical Co.) primary stock solution (4−8 mg/L) was prepared gravimetrically in acetone. Standard solution of CNCl (2 mg/L) in acetone was obtained from Protocol Analytical Inc. Standard stock solution containing bromochloroacetonitrile, dibromoacetonitrile, dichloroacetonitrile, and trichloroacetonitrile (2 mg/L) was obtained from Supelco Inc. Primary stock solutions (1−5 mg/L) of bromoacetonitrile (Aldrich) in acetone and the four trihalomethanes (bromodichloromethane, bromoform, chlo-

* Corresponding author fax: 972-4-8228898; phone: 972-4-8293328; e-mail: cvrlili@tx.technion.ac.il.

† Technion—Israel Institute of Technology.

‡ Mekorot Water Supply Company.

10.1021/es980147e CCC: $18.00 © 1999 American Chemical Society
Published on Web 02/11/1999

rodibromomethane, and chloroform) in methanol were prepared gravimetrically. The primary stocks were kept at −10 °C. Aqueous standards were obtained by volumetrically diluting the stocks.

Fulvic Acid Solution. Humic acid (Aldrich) was dissolved in 1 N NaOH, then the pH was lowered to 2 by addition of 1 N HCl, and the solution was left for a period of 18 h to precipitate the humic acid fraction. After filtration through a 0.45-μm filter, the pH was adjusted to 7 with 1 N NaOH. Organic carbon concentration of the fulvic acid solution was determined with a TOC analyzer (Shimadzu 5000A) and found to be 120 mg/L.

Sampling. Water from Lake Kinneret was stored at 4 °C. TOC, pH, ammonia, total N-(Kjeldahl), and UV absorbance (254 nm) were determined for each water sample.

Disinfection. Chlorination was performed by the addition of the desired amount of sodium hypochlorite solution. Two chlorine doses were applied: 1.5 and 2.5 mg/L. Chloramination was performed by the addition of a solution of ammonium chloride followed by 1.5 mg/L hypochlorite. ClO_2 was prepared by the addition of sulfuric acid to a solution of sodium chlorite. Concentration of the ClO_2 solution was determined prior to every application by iodometric titration (*17*). Experiments were performed at pH 7.5 or at pH 8.3. The pH of the water was adjusted to the desired level by 1 M H_2SO_4 or by 3% $NaHCO_3$. All experiments were performed in headspace-free bottles at 26 °C in the absence of light. Total residual oxidant was measured at the specified time period by the DPD colorimetric method (*17*) and expressed as milligrams per liter of Cl_2. The reaction was terminated by the addition of 5% ascorbic acid (final concentration 100 ppm) and the addition of 1 M H_2SO_4 in quantity needed to reduce the pH to pH <3. Analyses of volatile DBPs were performed right after termination of the reaction.

Chlorination of Fulvic Acid. KBr was added to a solution containing fulvic acid (TOC 2 mg/L) to obtain a final concentration of 1.9 mg/L bromide. pH was adjusted to 7.5 and then chlorinated in a similar way as Lake Kinneret water.

Analyses of Volatile DBPs. Analyses of cyanogen bromide, five haloacetonitriles, and the four trihalomethanes were performed by gas chromatography according to Sclimenti et al. (*15*). The only difference was the application of manual shaking for 2 min. To analyze CNCl, the shaking period was extended to 7 min. Method detection limit (MDL) for CNBr and CNCl was 1 μg/L.

Gas Chromatography. CNBr, CNCl, haloacetonitriles, and trihalomethanes analyses were carried out on Varian 3300 GC with a split/splitless injector and an electron capture detector (ECD). The column used was a 30m × 0.32 mm, DB 1701.

Stability of Cyanogen Bromide. CNBr was added to distilled water having the pH adjusted to 7.5. Bromide (final concentration 1.9 mg/L), fulvic acid, or chlorine was added according to the experimental conditions. The solutions were kept in headspace-free bottles at 26 °C in the dark. After a specified time period, CNBr concentration was determined.

Results and Discussion

Lake Kinneret water characteristics are shown in Table 1, Section A. Significant levels of TOC and organic nitrogen were present. Bromide ion concentration (1.9 mg/L) is extremely high as compared to the bromide levels commonly found in surface water around the world, which are between 0.04 and 1 mg/L (*18*).

CNBr and Other DBPs Formation during Chlorination of Lake Kinneret Water. As expected for high bromide contents, CNBr was the only CNX detected. Brominated species were dominant among THMs and HACNs. Distribution of the individual THMs in Lake Kinneret water was reported previously (*14, 19*). Figure 1 shows the formation of high concentrations of CNBr reaching a maximum of 36 μg/L. Since monochloramine could not be formed (NH_4^+ concentration 0.08 mg/L), the suggested mechanism (*10, 11*) of reaction between formaldehyde and halamine is unlikely. Organic nitrogen concentration and also the N/C ratio (Table 1, Section A) in the lake water are high. Therefore, a direct reaction of HOBr with the organic nitrogenous precursors that provide the nitrogen for CNBr is suggested.

CNBr concentration increased over time, reached a maximum, and then decreased to zero (Figure 1). CNBr

TABLE 1. Lake Kinneret Water and Fulvic Acid Solution

	Lake Kinneret water	fulvic acid solution
Section A: Relevant Characteristics		
Br^- (mg/L)	1.9	1.9
pH	8.3	7.5
TOC (mg/L)	4.4	2
specific absorbance A_{254}/DOC (cm^{-1})	0.0087	0.032
Kjeldahl-N (mg/L)	0.73	0.1
organic-N/TOC	0.17	0.05
Section B: CNBr Production during Chlorinations (Performed at pH 7.5)		
chlorination: chlorine dose 1.5 mg/L, 3 h		
CNBr formation (μg/L)	23	2.4
CNBr/TOC (μg/mg of C)	5.2	1.2
CNBr/organic-N (μgr/mg of N)	32	24
THMs/TOC (μg/mg of C)	12	33.5
maximum CNBr formation (μg/L)		
Cl_2 dose 2.5 mg/L, 6 h		4.5
Cl_2 dose 1.5 mg/L, 8−20 h	36	
maximum CNBr formation		
CNBr/organic-N (μg/mg of N)	50	45
CNBr/TOC (μg/mg of C)	8.2	2.3

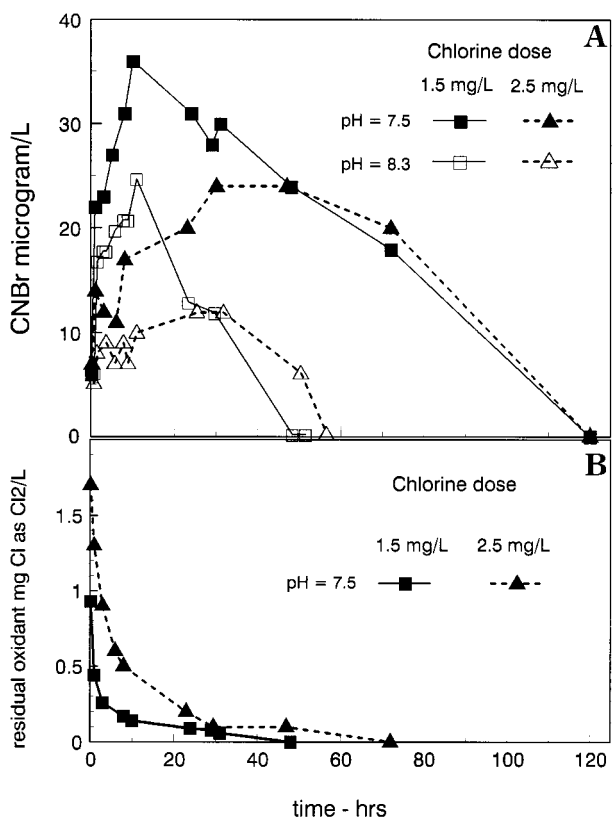

FIGURE 1. Formation of CNBr in chlorination of Lake Kinneret water, effect of chlorine dose and pH. (A) Formation of CNBr. (B) Residual oxidant as chlorine at pH 7.5.

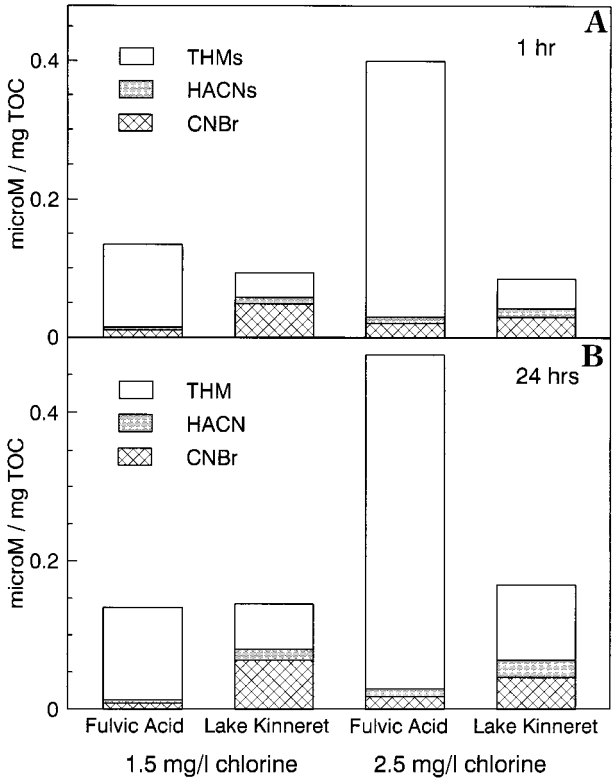

FIGURE 2. Specific formation (per mg of C) of volatile DBPs in chlorination of fulvic acid and Lake Kinneret water; pH 7.5.

concentration is determined by the formation and decomposition reactions:

$$\mathrm{HOCl} + \mathrm{Br}^- \xrightarrow{k_1} \mathrm{HOBr} + \mathrm{Cl}^- \quad (1)$$

$$\text{organic N precursors} + \mathrm{HOBr} \xrightarrow{k_2} \mathrm{CNBr} + \mathrm{H_2O} \quad (2)$$

$$\mathrm{CNBr} + \mathrm{OH}^- \xrightarrow{k_3,\ \text{chlorine catalysis}} \mathrm{CNO}^- + \mathrm{Br}^- + \mathrm{H}^+ \quad (3)$$

Oxidation of bromide by chlorine (reaction 1) is fast, the rate constant k_1 is 2.95×10^3 L mol^{-1} s^{-1} (*20*). As $k_1 > k_2$, brominated DBPs are produced (*14*). CNCl is decomposed by basic hydrolysis (*21*). By analogy and based on the present results, it is assumed that CNBr is decomposed according to reaction 3. During the initial period, the reactants concentrations in reaction 2 are high, and rate 2 > rate 3. With time, the residual halogen and the N precursors are exhausted resulting in rate 2 < rate 3.

Increasing the chlorine dose produced higher concentrations of THMs and HACNs (Figure 2) but lower concentrations of CNBr (Figsures 1 and 2). The peak of maximum CNBr concentration shifted from contact time of 10 h to contact time of 30 h. CNBr is an intermediate in consecutive reactions 2 and 3. In such reactions, when the intermediate's ratio of rate of formation to decomposition decreases the results are as follows: (a) reduction in the maximum concentration of the intermediate; (b) shift of the peak to longer times (*22*). Increasing the chlorine dose enhances both formation (reaction 2) and decomposition (reaction 3). If decomposition is enhanced more than formation, then the rate ratio rate 2/rate 3 is reduced, resulting in the above findings. CNCl and CNBr hydrolysis were reported to be catalyzed by chlorine (*13, 21*). Bromine did not catalyze CNCl hydrolysis (*21*). Figure 3 shows that CNBr's initial hydrolysis rate (prior to the oxidant's exhaustion) in solution containing chlorine and bromide (HOBr the only oxidant) was identical to the rate with chlorine alone, indicating that bromine can catalyze

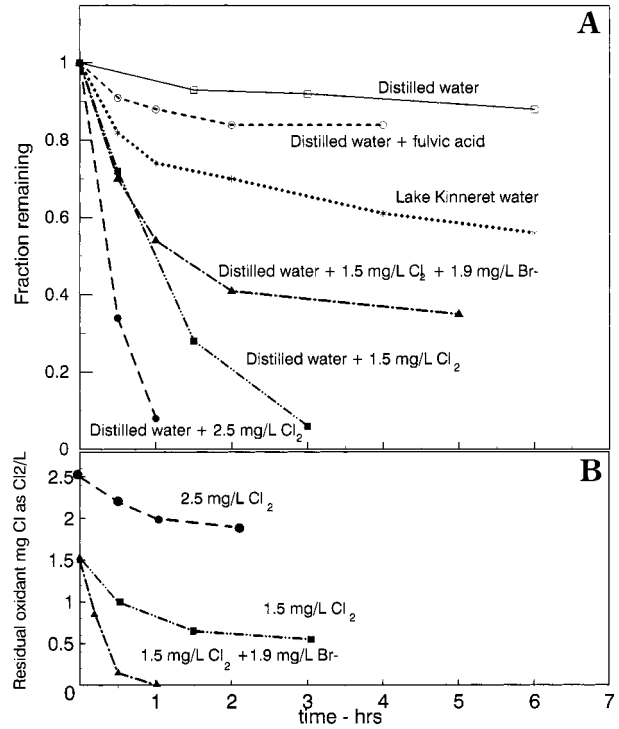

FIGURE 3. Stability of CNBr at pH 7.5. Fulvic acid: TOC, 2 mg/L; lake water, TOC 2.8 mg/L. (A) Fraction of CNBr remaining. (B) Concentration of residual oxidant as chlorine.

TABLE 2. Maximum Formation of CNBr, THMs, and HACNs by Chlorine, Chloramine, Chlorine Dioxide, and Their Combination in Lake Kinneret Water[a]

	contact time (h)	CNBr (μg/L)	THMs (μg/L)	HACNs (μg/L)
Cl_2	10	36	63	12
NH_2Cl	250	6	11	1.6
$NH_2Cl + ClO_2$	200	7.5	18	1.5
ClO_2	24	<1	0	0

[a] pH 7.5; chlorine, 1.5 mg/L; chloramine, 1.5 mg/L; ClO_2, 1 mg/L.

CNBr hydrolysis to the same extent as chlorine. Thus, the higher the oxidant concentration, the faster the decomposition of CNBr (reaction 3) is, resulting in lower net concentrations of CNBr.

On a weight basis, concentrations of THMs were higher than CNBr (Table 2), but on a molar basis, CNBr was the major volatile product formed at 1.5 mg/L chlorine (Figure 2). At 2.5 mg/L chlorine, THMs mole fraction increased; however, the contribution of CNBr remained significant.

Effect of pH. CNBr concentrations were significantly reduced by increasing the pH (Figure 1). The pH affects DBPs production through deprotonation of the hypochlorous and hypobromous acids. The dissociation constant (K_a) for deprotonation of HOCl is 3.2×10^{-8} M^{-1} and for HOBr is 2×10^{-9} M^{-1}. At pH 7.5, [HOCl] ≅ [OCl$^-$] (50% protonated), but the hypobromous acid is 94% protonated. At pH 8.3, only 13% of the hypochlorous acid and 60% of the hypobromous acid are in protonated form. The protonated form is the more effective brominating agent, resulting in higher productions of CNBr. The pH affects also CNBr decomposition; the hydrolysis is base catalyzed and enhanced with the increase in pH. The first-order rate constant of CNCl hydrolysis was found to increase 2.5 times when the pH was raised from 7.95 to 8.45 (*21*).

CNBr in Other Water Supply Systems. Concentrations of CNBr formed in Lake Kinneret water were high when

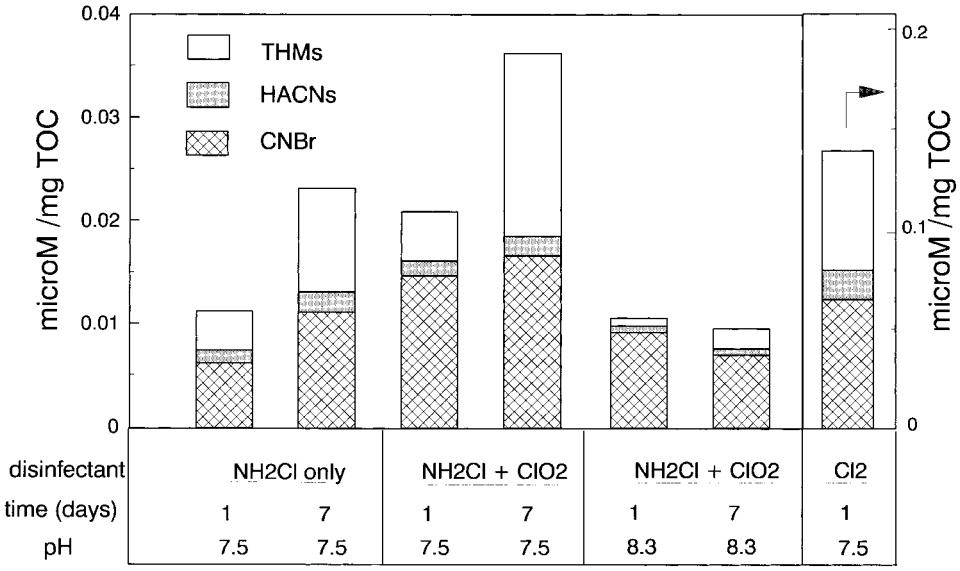

FIGURE 4. Specific molar formation (per mg of TOC) of volatile DBPs in chloramination alone, in combination with ClO_2, and in chlorination of Lake Kinneret water. Chloramine dose 1.5 mg/L (as chlorine), Cl_2/NH_3-N (g) 3.2, ClO_2 1 mg/L, Cl_2 1.5 mg/L.

compared with the average low concentration of CNCl (<1 μg/L) reported in water supply systems using chlorine alone for disinfection (*5*). The present high concentrations of CNBr may be explained by the high content of bromide and CNBr precursors in Lake Kinneret water. The low concentrations of CNCl in other water utility systems may be a result of high concentrations (>1 mg/L) of residual free chlorine that catalyzes the hydrolysis of CNCl to a larger extent than that of CNBr. In the presence of 1 mg/L free chlorine, the half-life of CNCl is 30 min while it is 60 min for CNBr (*13*).

CNBr Formation during Chlorination of Fulvic Acid. Fulvic acid from terrestrial origin may differ from aquatic fulvic acid; therefore, it was used only as a reference organic matter as was done in other studies of DBPs formation (*23*). Since half of the natural organic matter (NOM) (TOC, 4.4 mg/L) in the lake water are fulvic compounds (*24*), a concentration of 2 mg/L (as TOC) fulvic acid was selected. Characterization of the fulvic acid solution and typical formation of CNBr are summarized in Table 1. The NOM of the lake water has a higher organic nitrogen content and a lower UV specific absorbance than the fulvic acid solution. Formation of CNBr during chlorination of fulvic acid was by far lower than in the lake water (Table 1, Section B and Figure 2). Specific CNBr yield (2.5 μg/mg DOC) similar to the maximum specific yield in the fulvic acid solution (2.3 μg/mg DOC) was reported during chlorination followed by chloramination of fulvic acid (Br^- = 2 mg/L) (*13*). In Lake Kinneret water, CNBr constituted the major volatile DBP with the highest molar fraction (46 mol % at 1.5 mg/L Cl_2 and 1 h), while in fulvic acid solution THMs were the major volatile product and accounted for over 90% of the total volatile DBPs.

The differences in DBPs formation between fulvic acid and Lake Kinneret water (Figure 2) correspond with the differences in the character of the organic matter in the two waters. The content of organic nitrogen, a CNBr precursor, is much higher in the lake water (Table 1), resulting in increased CNBr formation. CNBr formation per mass of organic nitrogen in both waters is quite similar (30% and lower at maximum formation), while the formation per mass of organic carbon varied widely showing that CNBr formation correlates better with the organic nitrogen content than with the carbon content. CNCl production during chloramination of hydrophobic organic extracts did not show correlation with the organic nitrogen content (*6*). Fulvic acid was a better precursor to THMs than the NOM in Lake Kinneret water

TABLE 3. Chloramination: Volatile DBPs Formation and Ratios of Rates of Formation of Chloramine (rate 4) to Hypobromous Acid (rate 1)[a]

expt	NH_3-N (mg/L)	pH	CNBr (μg/L)	THMs (μg/L)	HACNs (μg/L)	rate 4/ rate 1	HOBr formed (calcd) (μg/L)
1	0.58	7.5	2	1.6	0.5	63	30
2	0.47	7.5	2.8	3.5	0.9	50	41
3	0.58	8.3	<1	0.6	0.1	368	5
4	0.47	8.3	<1	0.6	0.2	294	7

[a] Cl_2 = 1.5 mg/L, Br^- = 1.9 mg/L, contact time 1 day.

(Table 1, Section B). THMs precursors have substituted aromatic rings and conjugated double bonds with high UV absorbance. Indeed, fulvic acid has a higher UV specific absorbance than lake water (Table 1, Section A), which corresponds to the higher THMs production. It can be concluded that CNBr formation does not correlate with THMs formation.

CNBr Formation during Chloramination of Lake Kinneret Water. Experiments with chloramine were carried out at chloramine dose equivalent to 1.5 mg/L chlorine, at two pH values (7.5 and 8.3) and two chlorine-to-ammonia ratios (3.2 and 2.6) (Cl_2:NH_3-N) corresponding to a molar ratio of 0.63 and 0.51, respectively. Considerably lower yields of DBPs were observed in chloramination than in chlorination (Tables 2 and 3 and Figure 4, note the different scales). The highest yields of DBPs in these experiments were obtained at pH 7.5 and at Cl_2:NH_3-N 3.2 and are presented in Table 2. Residual combined chlorine was present for a long period, resulting in continuing THMs formation up to 11 μg/L in 10 days. Concentrations of CNBr and HACNs reached a final maximum concentration after 68 h. It is possible that, in the presence of chloramine under these conditions, a steady state was reached between the slow formation of HACNs and CNBr and their decomposition. In most chloramination experiments, CNBr was the major product on a molar basis (Figure 4). At very long reaction times—1 week and over—molar concentrations of THMs sometimes exceeded those of CNBr. CNX concentrations similar to those in Table 3 were reported in a study of CNX formation during chloramination (*15*). At a Cl_2/NH_3 ratio of 3 and pH 8, CNX formation was 4 μg/L.

In the present study, chloramination was carried out at two chlorine/ammonia ratios that present a molar excess of ammonia resulting in the formation of monochloramine only.

Monochloramine itself probably does not form CNBr. Two pathways are suggested here for the formation of CNBr using monochloramine. The first mechanism is a reaction with HOBr that is formed in small concentrations when the monochloramine is produced in situ. When chlorine is introduced into water containing ammonia and bromide, it can react both with ammonia (reactions 4) and bromide (reaction 1):

$$HOCl + NH_3 \xrightarrow{k_4} NH_2Cl + H_2O \quad (4)$$

The rate constant for this reaction is $k_4 = 6.2 \times 10^6$ L mol^{-1} s^{-1} (*25*). The relative rates of reactions 1 and 4 depend on the pH and reactant concentrations. The relative rates were calculated according to Galal-Gorchev and Morris (*26*) and are shown in Table 3. It can be seen that formation of monochloramine was by far faster than oxidation of Br^- to HOBr. Still some HOBr was formed, exceeding the quantity needed to produce the amount of the volatile brominated DBPs that were obtained in these experiments. The maximum quantity of HOBr produced was calculated to be 41 μg/L (experiment 2), while only 3 μg/L of bromide was incorporated into CNBr, HACNs, and THMs. When production of HOBr was faster, higher quantities of HOBr were produced and higher quantities of DBPs were obtained. pH significantly affects the ratio of the reaction rates. At pH 8.3, HOBr formation was very low (5−7 μg/L), and consequently, insignificat amounts of CNBr, THMs, and HACNs were produced (experimets 3 and 4). This pathway can explain the formation of brominated species at short contact time and is probably responsible for the formation of a small part of DBPs. During the first hour, about 15% of the maximum amount of DBPs were formed. The second pathway suggested here for CNBr formation is the oxidation of bromide by monochloramine to form bromochloramine, which can react with organic matter to form brominated DBPs. The bromide ion oxidation by NH_2Cl is a complex reaction that proceeds in stages, and the overall reaction is described as (*27*):

$$2NH_2Cl + H^+ + Br^- \xrightarrow{k'_5} NHBrCl + NH_4^+ + Cl^- \quad (5)$$

The reaction is first-order with respect to monochloramine, bromide ion, and hydrogen ion concentrations. The overall empirical rate constant k'_5 was evaluated as 3.5×10^6 L^2 mol^{-2} s^{-1} (*28*). The rate of bromide oxidation by NH_2Cl was calculated for Lake Kinneret water. At 1.5 mg/L NH_2Cl (as Cl_2) and pH 7.5, the rate of NH_2Cl decomposition is 0.3 mg/L in 24 h. At pH 8.3, the rate is much slower—0.05 mg/L in 24 h. This mechanism may explain the long-term slow formation of DBPs at pH 7.5 and the insignificant DBPs formation at pH 8.3.

CNBr Formation during Disinfection with Chlorine Dioxide and with a Combination of Chlorine Dioxide and Chloramine. Application of 1 mg/L ClO_2 alone at pH 7.5 and at pH 8.3 produced minimal quantities of DBPs, <1 μg/L. Experiments conducted with a combination of ClO_2 and chloramine (Table 2 and Figure 4) produced higher concentrations of CNBr and THMs than the arithmetic sum of THMs and CNBr produced by each disinfectant alone. HACNs production during chloramination was only slightly affected by the addition of ClO_2. ClO_2 was exhausted within 12 h, and concentration of the residual chloramine was lower when ClO_2 was added.

The higher concentrations of CNBr and THMs produced are the result of the combined action of the two disinfectants on the organic matter. ClO_2 most probably oxidizes some organic molecules to form new precursors to CNBr and THMs. A similar phenomenon was reported in a study on ClO_2 reactions with hydroxybenzoic acids—compounds representing active sites in humic acids (*29*). When a combination of ClO_2 together with chlorine was applied, $CHCl_3$ formation was enhanced (compared to chlorine alone) by the ClO_2 promoting oxidative decarboxylation. Enhancement of CNCl production was reported when ozone was applied prior to chloramination (*5*). The degree of CNX enhancement tended to increase with the ozone dose and the formaldehyde concentration. Formaldehyde is an ozonation byproduct and a CNX precursor. ClO_2 is a strong oxidizing agent and was reported to form aldehydes when applied on natural water (*30*). It is plausible that the formaldehyde produced by ClO_2 reacts with the mixed halamine to form CNBr.

Stability of CNBr. Figure 3 presents the decomposition of CNBr under different conditions. In distilled water CNBr was fairly stable. The addition of bromide alone without oxidant (not shown in the figure) did not affect CNBr stability. Addition of organic matter (fulvic acid) increased somewhat the decomposition rate. In Lake Kinneret water, the decomposition was significantly faster, and after 24 h all CNBr disappeared. Bailey and Bishop (*21*) suggested that hydrolysis of CNCl undergoes general base catalysis. pH of the different solutions was identical—7.5. The alkalinity of the lake water (120 mg/L as $CaCO_3$) was considerably higher than of distilled water and probably catalyzed CNBr hydrolysis. Addition of chlorine into distilled water enhanced CNBr hydrolysis; the half-life was reduced to 1 h or less. The higher the chlorine dose, the faster the hydrolysis rate. As mentioned in a previous section on CNBr formation, when chlorine was added in the presence of bromide, the initial hydrolysis rate of CNBr was the same as the rate without bromide. After a period of 1 h, all the oxidant was consumed and the hydrolysis rate was reduced. Bailey and Bishop (*21*) reported that bromine addition at pH 9.2 did not affect CNCl hydrolysis. The present study revealed that the effect of chlorine and bromine on CNBr hydrolysis rate was essentially identical.

Acknowledgments

This work was supported by Mekorot Water Supply Company.

Literature Cited

(1) Water Quality Division Disinfection Committee. *J. Am. Water Works Assoc.* **1992**, *84* (*9*), 121.
(2) Tate, C. H. *J. Am. Water Works Assoc.* **1991**, *83* (5), 40.
(3) World Health Organization. *Guidelines for drinking water quality*, 2nd ed.; Volume I, Recommendations; World Health Organization: Geneva, 1993.
(4) U.S. EPA. *M*onitoring requirements for public drinking water supplies; *Cryptosporidium, Giardia,* disinfection byproducts, water treatment plant data and other information requirements. Final Rule. *Fed. Regist.* **1996**, *61* (94), 24354.
(5) Krasner, S. W.; McGuire, M. J.; Jacangelo, J. G.; Patania, N. L.; Reagan, K. M.; Aieta, M. E. *J. Am. Water Works Assoc.* **1989**, *81* (8), 41−53.
(6) Smith, M. E.; Singer, P. C. *Proceedings of the American Water Works Association Water Quality Technology Conference*, San Francisco CA; AWWA: 1994; pp 925−945.
(7) Ohya, T.; Kanno, S. *Chemosphere* **1985**, *14*, 1717.
(8) Hirose, Y.; Maeda, N.; Ohya, T.; Njima, K.; Kanno, S. *Chemosphere* **1989**, *18*, 2101.
(9) Ohya, T.; Kanno, S. *Chemosphere* **1989**, *19*,1835.
(10) Scully, F. E., Jr. Presented at the American Chemical Society National Meeting, Washington, DC, 1990.
(11) Pedersen, E. J.; Marinas, B. J. *Proceedings of the American Water Works Association Annual Conference, Water Quality,* Anaheim, CA; AWWA: 1995; pp 359−369.
(12) Young, M. S.; Uden, P. C. *Environ. Sci. Technol.* **1994**, *28*, 1755−1758.
(13) Xie, J.; Reckhow, D. A. *Water Res.* **1993**, *27*, 507−511.
(14) Rebhun, M.; Heller-Grossman, L.; Manka, J.; Kimmel, D.; Limoni, B. In *Water Chlorination: Chemistry Environmental Impact and Health Effects;* Jolley R. L., et al., Eds; Lewis: Chelsea, MI, 1990; Vol. 6, pp 665−680.

(15) Sclimenti, J. M.; Hwang, C. J.; Speitel, G. E.; Diehl, A. C. *Proceedings of the American Water Works Association Water Quality Technology Conference*, San Francisco, CA; 1994, p 489.
(16) Najm, N.; Krasner, S. W. *J. Am. Water Works Assoc.* **1995**, *87* (1), 106−115.
(17) *Standard Methods for the Examination of Water and wastewater;* Eaton, A. D., Clesceri, L. S., Greenberg, A. E., Eds.; APHA, AWWA, and WPCF: Washington, DC, 1995.
(18) Flury, M.; Papriz, A. *J. Environ. Qual.* **1993**, *22* (4), 747.
(19) Rebhun, M.; Manka, J.; Zilberman, A. *J. Am. Water Works Assoc.* **1988**, *80* (6), 84.
(20) Farkas, L.; Lewin, M.; Bloch, R. *J. Am. Chem. Soc.* **1949**, *70*, 1988.
(21) Bailey, P. L.; Bishop, E. *J. Chem. Soc., Dalton Trans.* **1973**, *9*, 912.
(22) Stone, A. T.; Morgan, J. J. In *Aquatic chemical kinetics*; Stumm, W., Ed.; Wiley-Interscience: New York, 1990; p 10.
(23) Stevens, A. A.; Moore, L. A.; Slocum, C. J.; Smith, B. L.; Seeger, D. R.; Ireland, J. C. In *Aquatic Humic Substances, Influence on Fate and Treatment of Pollutants*; Suffet, I. H., MacCarthy, P., Eds.; American Chemical Society: Washington, DC, 1989; p 681.
(24) Huber, S. A.; Frimmel, F. H. University of Karlsruhe, Germany, unpublished results.
(25) Weil, I.; Morris, C. J. *J. Am. Chem. Soc.* **1949**, *71*, 1664.
(26) Galal-Gorchev, H.; Morris, C. J. *J. Inorg. Chem.* **1965**, *4* (6), 899−905.
(27) Trofe, T. W.; Inman, G. W.; Johnson, D. J. *Environ. Sci. Technol*, **1980**, *14*, 544.
(28) Bousher, A.; Brimblecombe, P.; Midgley, D. *Water Res.* **1989**, *23* (8), 1049−1058.
(29) Lin, S.; Livkkonen, R. J.; Thom, R. E.; Bastian, J. G.; Lukasewycz, M. T.; Carlson, R. M. *Environ. Sci. Technol.* **1984**, *18*, 932.
(30) Stevens, A. A. *Environ. Health Perspect.* **1982**, *46*, 101.

Received for review February 12, 1998. Revised manuscript received December 14, 1998. Accepted December 23, 1998.

ES980147E