Environmental Science & Technology

Article

pubs.acs.org/est

Formation of Brominated Disinfection Byproducts during Chloramination of Drinking Water: New Polar Species and Overall Kinetics

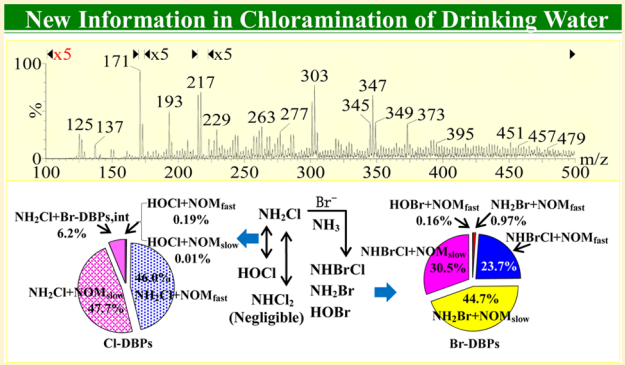
Hongyan Zhai,[†,‡] Xiangru Zhang,[*,‡] Xiaohu Zhu,[‡] Jiaqi Liu,[‡] and Min Ji[†]

[†]School of Environmental Science and Engineering, Tianjin University, No. 92 Weijin Road, Nankai District, Tianjin, China

[‡]Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

Supporting Information

ABSTRACT: The formation of brominated disinfection byproducts (Br-DBPs), which are generally significantly more cytotoxic and genotoxic than their chlorinated analogues, in chloramination has not been fully examined. In this work, the formation of new polar Br-DBPs in simulated drinking waters was examined using state-of-the-art ultraperformance liquid chromatography/electrospray ionization-triple quadrupole mass spectrometry. As many as 29 aliphatic, aromatic, or nitrogenous polar Br-DBPs were detected in chloramination, and five of them (including 2,4,6-tribromoresorcinol, 2,6-dibromo-4-nitrophenol, 2,2,4-tribromo-5-hydroxy-4-cyclopentene-1,3-dione, 2,2,4-dibromochloro-5-hydroxy-4-cyclopentene-1,3-dione, and 2,2,4-bromodichloro-5-hydroxy-4-cyclopentene-1,3-dione) were tentatively identified. Unlike chlorination, chloramination favored the formation of aromatic and nitrogenous polar Br-DBPs and was mild enough to allow polar intermediate Br-DBPs to accumulate. To further explore the formation mechanism of Br-DBPs in chloramination, a quantitative empirical model involving 33 major reactions was developed to describe the overall kinetics. According to the modeling results, bromochloramine and monobromamine were the major species responsible for 54.2−58.1% and 41.7−45.7%, respectively, of the formed Br-DBPs, while hypobromous acid accounted for only 0.2% of the formed Br-DBPs; direct reactions between monochloramine and natural organic matter accounted for the majority of the formed chlorinated DBPs (93.7−95.1%); hypochlorous acid and hypobromous acid in the chloramination were at ng/L or subng/L levels, which were not enough to cause polar intermediate Br-DBPs to decompose.



INTRODUCTION

Disinfection inactivates disease-causing organisms in a drinking water supply to ensure safe consumption. Chloramination is a popular disinfection process for maintaining a residual disinfectant throughout the distribution system and depressing the formation of common disinfection byproducts (DBPs) such as trihalomethanes and haloacetic acids.[1,2] However, in chloramination, monochloramine (NH_2Cl) and its derived reactive products such as hypochlorous acid (HOCl) can oxidize bromide, which is ubiquitous in many source waters worldwide, to form brominated DBPs (Br-DBPs).[3] Recently, Br-DBPs have become a great concern following reports that they are dozens to hundreds of times more cytotoxic and genotoxic than their chlorinated analogues.[4,5] Study on the speciation and formation mechanisms of Br-DBPs in chloramination is very limited.

The level of total organic bromine (TOBr) produced in chloramination was reported to be just 31% of that produced in chlorination,[3] yet a higher percentage of the TOBr produced in chloramination (86%) was unknown than in chlorination (40%).[3] Epidemiological studies have suggested that unknown total organic halogen (TOX) may contain substantial amounts of toxic compounds,[6] so it is imperative to further explore unknown Br-DBPs in chloramination. Commonly known Br-DBPs were mainly identified using gas chromatography/mass spectrometry,[7−9] which is not amenable to the detection of polar or highly polar Br-DBPs. Recently, a novel precursor ion scan (PIS) approach employing negative electrospray ionization-triple quadrupole mass spectrometry (ESI-tqMS) has been developed for the fast selective detection of polar Br-DBPs in chlorinated waters.[10,11] Briefly, bromine-containing compounds may generate bromide ions ($^{79}Br^-$ and $^{81}Br^-$) in the collision chamber of the mass spectrometer; by setting ESI-tqMS PISs of Br^- (m/z 79 and 81), almost all polar bromine-containing compounds in a sample could be selectively detected as

Received: August 5, 2013
Revised: February 6, 2014
Accepted: February 10, 2014
Published: February 10, 2014

   dx.doi.org/10.1021/es4034765 | Environ. Sci. Technol. 2014, 48, 2579−2588

molecular ions or ion clusters with specific isotopic abundance ratios. Then, product ion scans of the molecular ions corresponding to a new polar Br-DBP are performed to obtain structural information. Besides, coupling ultraperformance liquid chromatography (UPLC) with ESI-tqMS for preseparation was found to be even more effective in proposing or identifying structures of unknown polar Br-DBPs.[12] The UPLC retention time (RT) is a good indicator for the structure of a bromine-containing compound. For instance, the bromine-containing aliphatic acids, benzoic acids, and phenols generally fell within the UPLC RT ranges of 0−2.5, 2.5−6.0, and 6.0−8.0 min, respectively.[12] According to m/z values, isotopic abundance ratios, fragment ions, and the UPLC RT, a tentative structure of a newly detected Br-DBP can be proposed and then the corresponding standard compound can be purchased or synthesized to confirm the proposed structure. This novel UPLC/ESI-tqMS approach can thus be used to selectively detect and identify new/unknown polar Br-DBPs and reveal their formation characteristics in chloramination.

The formation mechanisms of polar/overall Br-DBPs in chloramination have not been fully understood due to the complex series of reactions involved, e.g., reactions of chloramines (e.g., NH_2Cl to $HOCl/OCl^-$, NH_2Cl to $NHCl_2$, NH_2Cl autodecomposition),[13,14] oxidation of bromide,[1,15] formation of bromamines (e.g., NH_2Br, NHBrCl, and $NHBr_2$),[15−17] and reactions of these chloramines, bromamines, and other active halogen species with natural organic matter (NOM).[3,18] Models can overcome limitations of kinetic experimental studies to provide deep insights into the formation mechanisms of DBPs. One popular conceptual model suggested that the formation of halogenated DBPs in chloramination could be considered as a special case of chlorination with a low level of HOCl, a decomposition product of NH_2Cl.[1,3] According to the conceptual model, Zhang et al.[3] developed a simple analytical solution and predicted that the reaction of NOM and HOCl (from hydrolysis of NH_2Cl) accounted for approximately 26% of the total organic chlorine (TOCl) in chloramination without the presence of bromide. Few quantitative models for chloramination exist and they can only describe the formation kinetics of certain individual DBPs or the loss kinetics of NH_2Cl.[18−20] Duirk et al.[19] reported that the direct reaction between NH_2Cl and NOM was rapid but accounted for only a small fraction of the NH_2Cl loss; the slow hydrolysis of NH_2Cl to HOCl, which then reacts with NOM, accounted for the majority of the NH_2Cl loss. Hong et al.[21] assumed that hydrolysis of NH_2Cl to HOCl was greatly inhibited by the excess ammonia in their samples, and estimated that the direct reaction of NH_2Cl and NOM accounted for about 80% of the haloacetic acids formed. The presence of bromide makes the reactions more complex, so models investigating the formation of Br-DBPs in chloramination are rare. Duirk and Valentine incorporated a bromine−NOM submodel[20] into the NH_2Cl−NOM model[19] and predicted the NH_2Cl loss and the dihaloacetic acid formation in chloramination with the presence of bromide. They treated various active bromine species in the +1 valence state as Br(I) and assumed that these active bromine species reacted with NOM with the same reaction rate constant. They reported that the oxidation of bromide to Br(I) played an important role in the NH_2Cl loss, and the reaction rate constant of Br(I) with the NOM was 4 orders of magnitude greater than that of HOCl with the same NOM. Alsulaili[22,23] investigated 35 possible reactions in chloramination in the presence of bromide, and reported the reaction rate constants for reactions of HOCl, HOBr, NH_2Cl, and bromamines (NH_2Br, $NHBr_2$, and NHBrCl) with NOM. Similar to Duirk and Valentine,[20] Alsulaili also assumed that major reactive bromamines (NH_2Br, $NHBr_2$, and NHBrCl) react with NOM with the same reaction rate constant through a slow reaction phase. There is currently no model that can quantitatively illustrate or separately evaluate the contributions of various reactions in the formation of polar/overall Br-DBPs in chloramination.

The objectives of this study were to detect and identify new/unknown polar Br-DBPs in chloramination using UPLC/ESI-tqMS and to investigate key reactions responsible for polar/overall Br-DBP formation in chloramination using a quantitative empirical model. By adopting the UPLC/ESI-tqMS PIS approach, the formation of new polar Br-DBPs in chloramination under different contact times was examined. TOBr and TOCl levels were also examined.

EXPERIMENTAL METHODS

Materials. Suwannee River humic acid (SRHA) was purchased from the International Humic Substances Society. Standard compounds of resorcinol, 1,2,4-benzenetriol, 1,2,3-benzenetriol, 1,3,5-benzenetriol, 2,6-dibromo-4-nitrophenol, 2,5-dibromo-1,4-hydroquinone, 2,6-dibromo-1,4-hydroquinone, 2,4,6-tribromoresorcinol, and HPLC-grade methanol, acetonitrile, and methyl *tert*-butyl ether (MtBE) were purchased from Aldrich. Ultrapure water (18.2 MΩ·cm) was obtained from a NANOpure Diamond purifier system (Barnstead). A free chlorine stock solution (NaOCl, ∼2500 mg/L as Cl_2) was prepared by diluting a commercial sodium hypochlorite solution (Allied Signal) and measured using the *N*,*N*-diethyl-*p*-phenylene diamine (DPD) ferrous titrimetric method.[24] A NH_2Cl stock solution (∼1600 mg/L as Cl_2) was prepared just before use by adding the free chlorine stock solution to an ammonium chloride solution at a chlorine to ammonium mole ratio of 0.8:1.0. A bromine stock solution (8000 mg/L as Br_2), which was used to synthesize some bromine-containing compounds, was prepared through the reaction of sodium bromate, sodium bromide, and sulfuric acid in the laboratory and measured using the DPD ferrous titrimetric method.[24]

Simulated Drinking Water Sample Preparation. Simulated raw water was prepared by dissolving 3 mg/L SRHA as C, 90 mg/L $NaHCO_3$ as $CaCO_3$, and 2 mg/L NaBr as Br^- (a relatively high level of bromide reported in several drinking water supplies in different parts of the world,[9,25,26] which was used to amplify the formation of Br-DBPs) in ultrapure water. Chloramination or chlorination with different contact times (1, 24, and 120 h) was performed with the simulated raw water by dosing 5 mg/L of NH_2Cl or NaOCl as Cl_2. After the dosage of NH_2Cl or NaOCl, all samples were adjusted to pH 7.5 with 1.8 M HCl or 1.0 M NaOH and kept in darkness at ambient temperature (22 °C). After a given contact time, the total chlorine residual in a sample was quenched immediately with 105% of the requisite stoichiometric dose of $NaAsO_2$.[27] Then, 900 mL of a quenched sample was pretreated for (UPLC/)ESI-tqMS analyses and 100 mL of a quenched sample was used for TOCl and TOBr analyses.

To determine whether there were any impurities in the reagents or any artifacts in the disinfection and subsequent pretreatment, one control sample was prepared by repeating

the aforementioned procedure but without dosing NH_2Cl or NaOCl.

To develop and validate the quantitative models for chloramination and chlorination, additional simulated drinking water samples were prepared and tested. The initial concentrations of SRHA (3 mg/L as C) and $NaHCO_3$ (90 mg/L as $CaCO_3$) were kept the same. For chloramination, three series of samples were prepared by varying NH_2Cl dose and initial Br^- concentration: 5 mg/L as Cl_2, 2 mg/L Br^-; 5 mg/L as Cl_2, 1 mg/L Br^-; and 4 mg/L as Cl_2, 2 mg/L Br^-. Each series of samples were chloraminated with contact times of 1, 10, 24, 48, and 120 h at pH 7.5. For chlorination, three series of samples were prepared by varying NaOCl dose and initial Br^- concentration: 5 mg/L as Cl_2, 2 mg/L Br^-; 6 mg/L as Cl_2, 2 mg/L Br^-; and 5 mg/L as Cl_2, 1 mg/L Br^-. Each series of samples were chlorinated with contact times of 0.17, 1, 3, 9, 24, and 48 h at pH 7.5. After a given contact time, the total chlorine residual in each sample was measured[24] and quenched immediately with 105% of the requisite stoichiometric dose of $NaAsO_2$.[27] Then, TOCl and TOBr in the sample were measured.

Simulated Drinking Water Sample Pretreatment. Water sample pretreatment followed the procedure in a previous study.[12] Briefly, a 900 mL water sample was adjusted to pH 0.5 with 70% (v/v) aqueous sulfuric acid, and Na_2SO_4 was added at a water/Na_2SO_4 mass ratio of 10/1. Then, the sample was extracted with MtBE at a water/MtBE volume ratio of 10/1. After extraction, the MtBE layer was transferred to a rotary evaporator and concentrated to 0.5 mL. The 0.5 mL solution in MtBE was mixed with 20 mL of acetonitrile, and the mixture was rotoevaporated back to 0.5 mL. The 0.5 mL solution in acetonitrile was stored at 4 °C. Prior to (UPLC/)ESI-tqMS analyses, the 0.5 mL solution was diluted with ultrapure water to 1.0 mL.

Bromine-Containing Compound Synthesis. To identify new Br-DBPs, model compounds of resorcinol, 1,2,4-benzenetriol, 1,2,3-benzenetriol, and 1,3,5-benzenetriol were allowed to react with bromine to synthesize bromine-containing compounds. Water solutions of 100 mL each, which contained 20 mg/L of one model compound and 180 mg/L of $NaHCO_3$ as $CaCO_3$ (used to maintain pH ~7.5 after the addition of the bromine stock solution), were dosed with bromine at a model compound to Br_2 mole ratio of 1:4. After a reaction time of 2 h for resorcinol or 8 h for benzenetriols, the 100 mL solutions were pretreated in the same way as the simulated drinking water samples. The reaction time of 2 or 8 h was selected so that high levels of target compounds could be generated. The synthesis of 2,4,6-tribromoresorcinol is detailed in the Supporting Information (SI).

(UPLC/)ESI-tqMS Analyses. The pretreated samples were analyzed using a Waters Acquity ESI-tqMS coupled with a Waters UPLC system. The UPLC separation was carried out with an HSS T3 column (100 × 2.1 mm, 1.8 μm particle size, Waters). The (UPLC/)ESI-tqMS parameters used in a previous study[12] were adopted.

Ultra-Fast Liquid Chromatography/Ion Trap-Time of Flight-MS (UFLC/IT-TOF-MS) Analyses. To determine the accurate m/z values of some newly detected Br-DBPs, a UFLC (20A UFLC-XR LC system, Shimadzu) coupled with IT-TOF-MS (Shimadzu) was applied. The IT-TOF-MS was set as follows: ESI negative mode, interface voltage −3.5 kV, detector voltage 1.7 kV, heat block temperature 200 °C, curved desolvation line temperature 200 °C, nebulizing gas 1.5 L/min, dry gas 10 L/min, ion accumulation 50 ms, collision energy 50%, and collision gas 50%. Five microliters of a pretreated sample was injected into the UFLC. UFLC separation was carried out with a Shimadzu Shim-pack XR-ODS column (100 × 2.0 mm, 2.2 μm particle size). The gradient eluent was water/acetonitrile. The composition of water/acetonitrile (v/v) changed linearly in the first 5 min from 95/5 to 5/95, remained steady at 5/95 for 2 min, and then reverted back to 95/5 in 0.1 min. The composition was finally held at 95/5 for 2.9 min for re-equilibration. The flow rate was kept at 0.30 mL/min.

TOCl and TOBr Analyses. TOCl and TOBr were determined in duplicate using a precombustion station (AQF-100, Mitsubishi) with an online ion chromatography system (ICS-90, Dionex).[24,28−30]

RESULTS AND DISCUSSION

Identification of New Polar Br-DBPs in Chloramination. As shown in Table 1, 29 polar Br-DBPs were detected in the 120 h chloraminated SRHA sample by performing the (UPLC/)ESI-tqMS full scans and PISs of bromide ions. These Br-DBPs included bromoacetic acid, bromopropenoic acid,

Table 1. Ion Clusters of Polar Br-DBPs in the 120 h Chloraminated SRHA Sample

m/z (RT[a])	formula or structure
137/139 (0.75)	bromoacetic acid[c]
149/151 ([b])	bromopropenoic acid[c]
151/153 ([b])	bromopropionic acid[c]
171/173/175 (0.78)	bromochloroacetic acid[c]
193/195 (0.77)	2-bromobutenedioic acid[c]
215/217/219 (0.80)	dibromoacetic acid[c]
232/234/236 (0.76)	dibromo-nitromethanol[d]
252/254/256 (4.61)	containing 2Br+1N[d]
257/259/261/263 (2.03)	bromodichloroHCD[e]
264/265/266/267/268/269 (5.32)	2,6-dibromo-1,4-benzoquinone[d]
265/267/269 (5.04)	2,6-dibromo-1,4-hydroquinone[c]
267/269/271 (1.07)	dibromo-2,4-hexadienoic acid[d]
274/276/278 (3.81)	containing 2Br+1N[d]
278/280/282 (6.57)	containing 2Br+1N[d]
293/295/297 (3.02)	3,5-dibromo-4-hydroxybenzoic acid[c]
294/296/298 (3.71)	2,6-dibromo-4-nitrophenol[f]
301/303/305/307 (2.10)	dibromochloroHCD[e]
305/307/309 (5.40)	containing 2Br[d]
307/309/311 (5.23)	2,6-dibromo-4-(hydroxypropyl)-phenol[d]
307/309/311/313 (5.56)	tribromobutanol[d]
325/327/329/331 (5.47)	containing 3Br[d]
327/329/331/333 (7.75)	2,4,6-tribromophenol[c]
328/330/332/334 (4.06)	containing 3Br+1N[d]
343/345/347/349 (6.50)	2,4,6-tribromoresorcinol[f]
345/347/349/351 (2.16)	tribromoHCD[e]
355/357/359/361 (5.56)	containing 3Br[d]
369/371/373/375/377 (5.56)	1,2,3,3-tetrabromopropenol[d]
369/371/373/375 (6.21)	containing 3Br[d]
385/387/389/391 (5.00)	containing 3Br[d]

[a]RT (min). [b]Observed in direct infusion ESI-tqMS PIS of m/z 79 and 81 only. [c]Confirmed with an authentic standard compound. [d]Proposed according to the UPLC/ESI-tqMS spectra. [e]Identified according to the UFLC/IT-TOF-MS spectra, the ESI-tqMS spectra, and with a synthesized standard compound. [f]Identified according to the ESI-tqMS spectra and with an authentic standard compound.

bromopropionic acid, bromochloroacetic acid, 2-bromobutenedioic acid, and dibromoacetic acid,[10] and three that were newly identified in previous studies, namely, 2,6-dibromo-1,4-hydroquinone (m/z 265/267/269), 3,5-dibromo-4-hydroxybenzoic acid (m/z 293/295/297), and 2,4,6-tribromophenol (m/z 327/329/331/333).[12,31]

In the 120 h chloraminated SRHA sample, there were three prominent ion clusters m/z 257/259/261/263, 301/303/305/307, and 345/347/349/351, which have been reported to be a group of analogues with different numbers of bromine and chlorine atoms in a 1 h chlorinated SRHA sample.[12] Ion cluster m/z 345/347/349/351 has been confirmed to be a polar Br-DBP containing three bromine atoms and at least one oxygen atom.[12] After deduction, the remaining mass is 92. A reasonable composition of 92 would be C_7H_8, C_6H_4O, or C_5O_2, so ion cluster m/z 345/347/349/351 could correspond to $C_7H_8OBr_3$, $C_6H_4O_2Br_3$, or $C_5O_3Br_3$. In this study, by performing a high resolution mass spectrometry analysis with UFLC/IT-TOF-MS, the accurate m/z values of ion cluster m/z 345/347/349/351 were measured to be 344.7393/346.7372/348.7351/350.7328. The average mass errors between the measured accurate m/z values and the theoretical accurate m/z values of $C_7H_8OBr_3$, $C_6H_4O_2Br_3$, and $C_5O_3Br_3$ were 210.9, 106.3, and 1.7 ppm, respectively. Accordingly, ion cluster m/z 345/347/349/351 should correspond to the molecular ion, $[M-H]^-$, of a new polar Br-DBP with the formula of $C_5HO_3Br_3$. A previous study has shown that $C_5HO_3Br_3$ is not 3,4,5-tribromo-2-furoic acid.[12] In the literature, halogenated cyclopentadienes such as hexachlorocyclopentadiene and bromopentachlorocyclopentadiene have been identified in drinking water.[32] In reactions of the model compounds with bromine, only 1,2,4-benzenetriol and 1,2,3-benzenetriol were found to be precursors of ion cluster m/z 345/347/349/351. As shown in Figure 1a, the reaction product of 1,2,4-benzenetriol (or 1,2,3-benzenetriol) and bromine with the formula of $C_5HO_3Br_3$ can be 2,2,4-tribromo-5-hydroxy-4-cyclopentene-1,3-dione (tribromoHCD). Accordingly, ion cluster m/z 345/347/349/351 in the sample should be tribromoHCD. Likewise, ion cluster m/z 301/303/305/307 and 257/259/261/263 should be dibromochloroHCD and bromodichloroHCD, respectively. Theoretically, trichloroHCD would form in the chloramination if the bromide level in the simulated raw water is low enough. Weil and Linder[33] have reported that trichloroHCD is a monobasic acid, so it is reasonable to believe that trihaloHCDs can produce negative ions and thus be detected in the negative ESI-tqMS. Furthermore, the existence of 2,2,4-trichloro-5-methoxy-4-cyclopentene-1,3-dione (trichloroMCD), a new mutagenic chlorinated DBP (Cl-DBP),[34] further verifies these trihaloHCDs: trichloroMCD contains three chlorine atoms and a methoxyl group, while correspondingly tribromoHCD contains three bromine atoms and a hydroxyl group; also, trichloroMCD and tribromoHCD share similar fragmentation pathways in their product ion scan spectra (i.e., sequentially losing two halogen atoms); additionally, the most optimal precursor of trichloroMCD is syringaldehyde (Figure 1b), which has a similar structure to 1,2,4-benzenetriol and 1,2,3-benzenetriol, the precursors of tribromoHCD. Although the molecular ion clusters corresponding to tribromoHCD and other trihaloHCDs have been detected in real and simulated chlorinated drinking waters,[10,12] this is the first time that the chemical structures of this group of new DBPs are confirmed.

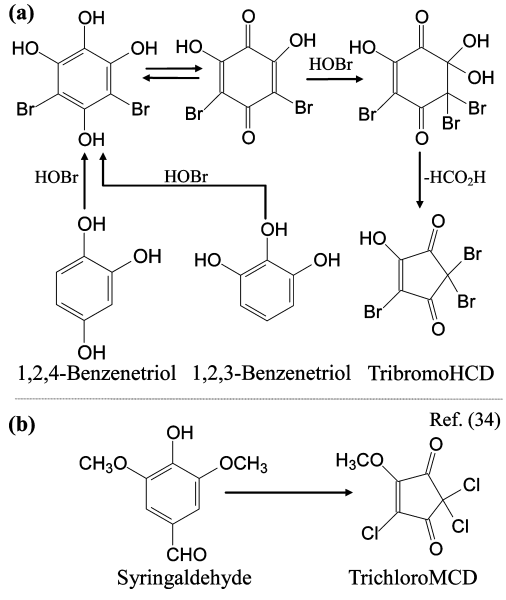


Figure 1. (a) Proposed formation pathways of tribromoHCD from 1,2,4-benzenetriol and 1,2,3-benzenetriol. (b) TrichloroMCD and its precursor syringaldehyde.

Ion cluster m/z 343/345/347/349 with an isotopic ratio of 1:3:3:1 and an RT of 6.50 min was detected in the UPLC/ESI-tqMS full scan. The isotopic ratio and the relatively long UPLC RT indicate that this Br-DBP contains three bromine atoms and has an aromatic structure. After deduction of 3Br and 6C, the remaining mass is 34. A reasonable composition of 34 would be 2OH, so this Br-DBP should be a tribromo-dihydroxy-benzene with the molecular formula of $C_6H_3O_2Br_3$. According to the orientation effect,[35] the proposed tribromo-dihydroxy-benzene could be 2,4,6-tribromoresorcinol. 2,4,6-Tribromoresorcinol can be synthesized by the reaction of "resorcinol + bromine" as described in the SI. Figures S1 and S2 show the UPLC/ESI-tqMS multiple reaction monitoring (MRM) scan chromatograms of the 120 h chloraminated SRHA sample and the synthesized 2,4,6-tribromoresorcinol standard solution, as well as the product ion scan spectra of ion cluster m/z 343/345/347/349 at RT 6.50 min. The same RTs and identical product scan spectra confirm that ion cluster m/z 343/345/347/349 was 2,4,6-tribromoresorcinol. Later, we purchased a commercially available standard compound of 2,4,6-tribromoresorcinol, which further confirmed the structure of this DBP (SI Figure S3). This is the first time that 2,4,6-tribromoresorcinol is reported as a DBP.

Ion cluster m/z 264/265/266/267/268/269 had an RT of 5.32 min in the UPLC/ESI-tqMS full scan spectra. The isotopic ratios for ions m/z 265, 267, and 269 and ions m/z 264, 266, and 268 were both 1:2:1, which is the same as the isotopic ratio of a compound containing two bromine atoms. Of ion cluster m/z 264/265/266/267/268/269, ions m/z 265, 267, and 269 have the same m/z values as the ion clusters of 2,5-dibromo-1,4-hydroquinone[12] (RT 4.88 min) and 2,6-dibromo-1,4-hydroquinone[12] (RT 5.04 min). Moreover, ions m/z 265, 267, and 269 and the ion clusters of the two dibromo-hydroquinones share similar fragmentation pathways in their product ion scan spectra (SI Figure S4a–c).[12] This indicates that the new Br-DBP could have a similar structure to dibromo-hydroquinone. However, neither of the two dibromo-hydroquinones generated ions at m/z 264, 266, and 268. It has been reported that 2,6-dichloro-1,4-benzoquinone can undergo an

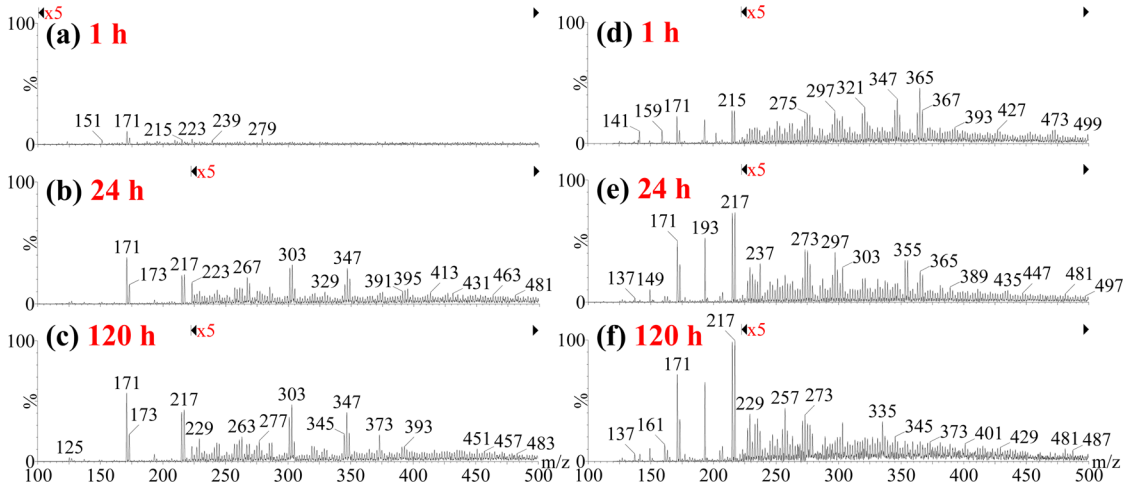


Figure 2. ESI-tqMS PIS spectra of m/z 79 of (a–c) the chloraminated SRHA samples with contact times of 1, 24, and 120 h, respectively; (d–f) the chlorinated SRHA samples with contact times of 1, 24, and 120 h, respectively. The y-axes are on the same scale of 2.57×10^7.

electrochemical reduction at the spraying tip to form $[M+H]^-$ (m/z 177/179/181) and simultaneously forms molecular ions of $[M]^-$ (m/z 176/178/180) in negative ESI spectra when its concentration is high (e.g., 2 mg/L).[36−38] Likewise, 2,6-dibromo-1,4-benzoquinone should form $[M+H]^-$ ions (i.e., m/z 265/267/269) and $[M]^-$ ions (i.e., m/z 264/266/268) simultaneously. Accordingly, ion cluster m/z 264/265/266/267/268/269 should be 2,6-dibromo-1,4-benzoquinone. Additionally, ion clusters m/z 267/269/271, 307/309/311, 307/309/311/313, and 369/371/373/375/377 are tentatively proposed as dibromo-2,4-hexadienoic acid, 2,6-dibromo-4-(hydroxypropyl)-phenol, tribromobutanol, and 1,2,3,3-tetrabromopropenol (or their isomers), respectively (see Table 1 and SI Figure S4g–l). Details for proposing these structures are presented in the SI.

Some ion clusters in the negative ESI-tqMS spectra had even-numbered m/z values, mainly including ion clusters m/z 232/234/236, 252/254/256, 274/276/278, 278/280/282, 294/296/298, and 328/330/332/334, which should correspond to nitrogenous Br-DBPs. Ion cluster m/z 294/296/298 was confirmed to be 2,6-dibromo-4-nitrophenol by comparing its RT and fragment ions with those of the standard compound (SI Figure S5).[39] This is the first time that this DBP is identified in chloraminated drinking water, although it has been identified in a chlorinated saline sewage effluent.[39] Ion cluster m/z 232/234/236 is tentatively proposed to be dibromonitromethanol (SI Figure S6). As for other ion clusters with even-numbered m/z values (SI Figure S7), their intensities were too low to give informative product ion scan spectra. Nevertheless, their relatively long RTs, e.g., RT 4.61 min for m/z 252/254/256, RT 3.81 min for m/z 274/276/278, RT 6.57 min for m/z 278/280/282, and RT 4.06 min for m/z 328/330/332/334, indicate that they might be aromatic Br-DBPs according to Zhai and Zhang.[12] Since the nitrogen content in SRHA is low (1.17%, w/w), the nitrogen in these nitrogenous Br-DBPs might also come from NH_2Cl. These nitrogenous Br-DBPs may be new for their m/z values do not match any known nitrogenous DBPs in the literature.[9,40,41]

Effect of Contact Time on the Formation of New Polar Br-DBPs. Figure 2a–c shows the ESI-tqMS PIS spectra of m/z 79 of the chloraminated SRHA samples with contact times of 1, 24, and 120 h. The overall levels of polar Br-DBPs increased with contact time. The ions or ion clusters with m/z 137, 149, 151, 171/173, 193, 215/217, 301/303/305, and 345/347/349 corresponded to bromoacetic acid, bromopropenoic acid, bromopropionic acid, bromochloroacetic acid, 2-bromobutenedioic acid, dibromoacetic acid, dibromochloroHCD, and tribromoHCD, respectively. The intensities of these confirmed polar Br-DBPs and ion groups m/z 100–199, 200–299, 300–399, and 400–500 and the total ion intensity (TII) were separately examined. The intensity of a confirmed Br-DBP was equal to the sum of the intensities of all its isotopic ions. The intensity of an ion group was equal to the sum of the intensities of ions (except for the ions that were detected to be the confirmed Br-DBPs) in the m/z range of the ion group. TII was the total intensity of all ions in the m/z range of 100–500. SI Figure S8a–c shows the ion intensities of polar Br-DBPs and the concentration of TOX in chloramination. The intensities of ion groups with m/z 100–199, 200–299, 300–399, and 400–500 and TII rose dramatically by 2.3, 4.3, 4.2, 4.7, and 5.7 times, respectively, as the contact time increased from 1 to 24 h, and further went up by 29%, 18%, 23%, 14%, and 30%, respectively, as the contact time further increased from 24 to 120 h. The intensities of bromoacetic acid, bromopropenoic acid, bromopropionic acid, bromochloroacetic acid, 2-bromobutenedioic acid, dibromoacetic acid, dibromochloroHCD, and tribromoHCD rose by 10.3, 7.5, 1.0, 15.0, 16.9, 40.7, 15.1, and 22.5 times, respectively, as the contact time increased from 1 to 24 h, and further went up by 47%, 74%, −17%, 47%, 92%, 75%, 29%, and 42%, respectively, as the contact time further increased from 24 to 120 h. Meanwhile, the concentration of TOBr, which had a strong correlation with TII, shot up by 5.5 times as the contact time increased from 1 to 24 h, and by another 87% as the contact time increased from 24 to 120 h. Thus, the prolonged chloramination resulted in the accumulation of both high and low molecular weight (MW) polar Br-DBPs. This could be ascribed partly to the slow reactions among NH_2Cl, bromide, and NOM and partly to the stability of the intermediate polar Br-DBPs in the chloramination. The ratio of TOBr to TOX increased with contact time, so a prolonged chloramination favored the formation of Br-DBPs.

Characteristics of New Polar Br-DBPs in Chloramination in Comparison with Chlorination. As shown in Figure 2 and SI Figure S8, with the increase of contact time, the levels of polar Br-DBPs increased in chloramination, whereas the levels of some relatively high MW polar Br-DBPs (m/z > 300)

dx.doi.org/10.1021/es4034765 | Environ. Sci. Technol. 2014, 48, 2579–2588

Table 2. Reactions and Rate Constants in Chloramination and Chlorination of SRHA Samples with the Presence of Br^- [a]

Chloramination Including Reactions 1–33:			
reaction	k	reaction	k
(1) $NH_2Cl + H_2O \rightarrow HOCl + NH_3$	3.0×10^{-5} s^{-1} [43]	(18) $NH_2Cl + NHBrCl \rightarrow N_2 + Br^- + 3H^+ + 2Cl^-$	5.0×10^{-3} $M^{-1}s^{-1}$ [i]
(2) $HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	2.55×10^{6} $M^{-1}s^{-1}$ [43b]	(19) $NH_2Cl + NOM_{dec} \rightarrow pro + NH_3$	5.0×10^{-2} $M^{-1}s^{-1}$ [i]
(3) $NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$	1.4×10^{2} $M^{-1}s^{-1}$ [44c]	(20) $HOCl + NOM_{fast} \rightarrow Cl\text{-}DBPs$	3.0×10^{3} $M^{-1}s^{-1}$ [i]
(4) $NHCl_2 + H_2O \rightarrow NH_2Cl + HOCl$	6.4×10^{-7} s^{-1} [44]	(21) $HOCl + NOM_{slow} \rightarrow Cl\text{-}DBPs$	1.0 $M^{-1}s^{-1}$ [i]
(5) $NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$	3.76×10^{-4} $M^{-1}s^{-1}$ [14d]	(22) $HOBr + NOM_{fast} \rightarrow Br\text{-}DBPs,int$	1.36×10^{6} $M^{-1}s^{-1}$ [51]
(6) $NHCl_2 + NH_3 \rightarrow NH_2Cl + NH_2Cl$	1.2×10^{3} $M^{-1}s^{-1}$ [14e]	(23) $HOBr + NOM_{slow} \rightarrow Br\text{-}DBPs$	6.5 $M^{-1}s^{-1}$ [i]
(7) $NH_2Cl + NHCl_2 \rightarrow N_2 + 3H^+ + 3Cl^-$	1.5×10^{-2} $M^{-1}s^{-1}$ [45]	(24) $NH_2Cl + NOM_{fast} \rightarrow Cl\text{-}DBPs + NH_3$	0.4 $M^{-1}s^{-1}$ [i]
(8) $NHCl_2 + H_2O \rightarrow int + 2HCl$	1.1×10^{2} s^{-1} [46]	(25) $NH_2Cl + NOM_{slow} \rightarrow Cl\text{-}DBPs + NH_3$	3.0×10^{-3} $M^{-1}s^{-1}$ [i]
(9) $int + NHCl_2 \rightarrow HOCl + N_2 + HCl$	2.8×10^{4} $M^{-1}s^{-1}$ [45]	(26) $NH_2Br + NOM_{fast} \rightarrow Br\text{-}DBPs,int + NH_3$	1.0×10^{2} $M^{-1}s^{-1}$ [i]
(10) $int + NH_2Cl \rightarrow H_2O + N_2 + HCl$	8.3×10^{3} $M^{-1}s^{-1}$ [45]	(27) $NH_2Br + NOM_{slow} \rightarrow Br\text{-}DBPs + NH_3$	40 $M^{-1}s^{-1}$ [i]
(11) $HOCl + Br^- \rightarrow HOBr + Cl^-$	7.75×10^{2} $M^{-1}s^{-1}$ [47f]	(28) $NHBrCl + NOM_{fast} \rightarrow Br\text{-}DBPs,int + NH_2Cl$	28 $M^{-1}s^{-1}$ [i]
(12) $HOBr + NH_3 \rightarrow NH_2Br + H_2O$	5.1×10^{6} $M^{-1}s^{-1}$ [48g]	(29) $NHBrCl + NOM_{slow} \rightarrow Br\text{-}DBPs + NH_2Cl$	1.6×10^{-2} $M^{-1}s^{-1}$ [i]
(13) $NH_2Br + H_2O \rightarrow HOBr + NH_3$	1.5×10^{-3} s^{-1} [49]	(30) $Cl\text{-}DBPs \rightarrow pro + Cl^-$	1.0×10^{-6} s^{-1} [i]
(14) $HOBr + NH_2Cl \rightarrow NHBrCl + H_2O$	2.7×10^{5} $M^{-1}s^{-1}$ [16h]	(31) $Br\text{-}DBPs \rightarrow pro + Br^-$	1.0×10^{-6} s^{-1} [i]
(15) $NH_2Cl + Br^- \rightarrow NH_2Br + Cl^-$	1.4×10^{-2} $M^{-1}s^{-1}$ [50]	(32) $Br\text{-}DBPs,int \rightarrow pro + Br^-$	1.0×10^{-6} s^{-1} [i]
(16) $NH_2Cl + Br^- \rightarrow NH_2Br,int + Cl^-$	8.85×10^{-2} $M^{-1}s^{-1}$ [15]	(33) $NH_2Cl + Br\text{-}DBPs,int \rightarrow Cl\text{-}DBPs + Br^-$	1.0×10^{-2} $M^{-1}s^{-1}$ [i]
(17) $NH_2Cl + NH_2Br,int \rightarrow NHBrCl + NH_3$	1.0×10^{12} $M^{-1}s^{-1}$ [i]		
Chlorination Including Reactions 11, 20–23, 30–32, and 34–41:			
reaction	k	reaction	k
(34) $HOCl + NOM_{dec} \rightarrow pro + Cl^-$	5.0 $M^{-1}s^{-1}$ [i]	(38) $HOBr + Cl\text{-}DBPs \rightarrow pro + Br^- + Cl^-$	0.1 $M^{-1}s^{-1}$ [i]
(35) $HOBr + NOM_{dec} \rightarrow pro + Br^-$	7.0 $M^{-1}s^{-1}$ [i]	(39) $HOBr + Br\text{-}DBPs \rightarrow pro + 2Br^-$	0.3 $M^{-1}s^{-1}$ [i]
(36) $HOCl + Cl\text{-}DBPs \rightarrow pro + 2Cl^-$	0.1 $M^{-1}s^{-1}$ [i]	(40) $HOCl + Br\text{-}DBPs,int \rightarrow Cl\text{-}DBPs + Br^-$	6.0 $M^{-1}s^{-1}$ [i]
(37) $HOCl + Br\text{-}DBPs \rightarrow pro + Br^- + Cl^-$	0.3 $M^{-1}s^{-1}$ [i]	(41) $HOBr + Br\text{-}DBPs,int \rightarrow pro + 2Br^-$	6.0 $M^{-1}s^{-1}$ [i]

[a] $[NOM_{fast}]_{initial}$ = 2.20×10^{-6} M; $[NOM_{slow}]_{initial}$ = 2.70×10^{-5} M; $[NOM_{dec}]_{initial}$ = 4.83×10^{-5} M; $[NOM_{fast}]_{initial}$ + $[NOM_{slow}]_{initial}$ + $[NOM_{dec}]_{initial}$ = 7.75×10^{-5} M (aromatic carbon in SRHA); int: intermediate; NH_2Br,int: reactive intermediate of bromamine; Br-DBPs,int: intermediate Br-DBPs. NOM_{dec}: reactive sites in NOM responsible for the decay of NH_2Cl, HOCl, and HOBr without the formation of halogenated DBPs. [b] $k_2 = (\alpha_{OCl^-} \times \alpha_{NH_4^+} + \alpha_{HOCl} \times \alpha_{NH_3}) \times 5.1 \times 10^6 = 2.55 \times 10^6$ $M^{-1}s^{-1}$. [c] $k_3 = \alpha_{HOCl} \times 2.8 \times 10^2 = 1.4 \times 10^2$ $M^{-1}s^{-1}$. [d] $k_5 = 6940 \times [H^+] + 1.11 \times [H_2CO_3] + 0.22 \times [HCO_3^-] = 3.76 \times 10^{-4}$ $M^{-1}s^{-1}$. [e] $k_6 = \alpha_{NH_3} \times 6.0 \times 10^4 = 1.2 \times 10^3$ $M^{-1}s^{-1}$. [f] $k_{11} = \alpha_{OCl^-} \times 9 \times 10^{-4} + \alpha_{HOCl} \times 1550 = 775$ $M^{-1}s^{-1}$. [g] $k_{12} = (\alpha_{OBr^-} \times \alpha_{NH_4^+} + \alpha_{HOBr} \times \alpha_{NH_3}) \times 7.5 \times 10^7 = 5.1 \times 10^6$ $M^{-1}s^{-1}$. [h] $k_{14} = \alpha_{OBr^-} \times 2.2 \times 10^4 + \alpha_{HOBr} \times 2.86 \times 10^5 = 2.7 \times 10^5$ $M^{-1}s^{-1}$. [i] Data was obtained from this study; α is the fraction of $HOCl/OCl^-$, $HOBr/OBr^-$, or NH_4^+/NH_3 in the total species concentrations.

decreased and the levels of low MW polar Br-DBPs (m/z < 300) increased in chlorination. This obviously shows that polar Br-DBPs formed slowly and accumulated in chloramination, so most polar Br-DBP species were observed in the 120 h chloraminated sample. In chlorination, many high MW polar Br-DBPs formed quickly and decayed rapidly, leading to an increase in the concentrations of low MW Br-DBPs. For instance, tribromoHCD, whose intensity increased with contact time in chloramination, was generated to a significant level within a short contact time and later decayed rapidly in chlorination (Figure 2).[12] Therefore, chloramination was mild enough to allow new intermediate polar Br-DBPs to accumulate. Using UPLC/ESI-tqMS, 36 polar Br-DBPs were detected in the chlorination,[12] whereas 27 were detected in the chloramination (Table 1). Chloramination and chlorination both generated bromoacetic acid, bromochloroacetic acid, 2-bromobutenedioic acid, dibromoacetic acid, 2,6-dibromo-1,4-hydroquinone, 3,5-dibromo-4-hydroxybenzoic acid, tribromoHCD, dibromochloroHCD, bromodichloroHCD, 2,4,6-tribromophenol, and 2,4,6-tribromoresorcinol, as well as the ion clusters with m/z 325/327/329/331 and 369/371/373/375/377. However, polar Br-DBPs with m/z 264/265/266/267/268/269 (2,6-dibromo-1,4-benzoquinone), 267/269/271, 305/307/309, 307/309/311, 307/309/311/313, 355/357/359/361, 369/371/373/375, and 385/387/389/391 and the six nitrogenous polar Br-DBPs were only detected in chloramination. This indicates that chloramination and chlorination generate some Br-DBP species through common reaction mechanisms, but chloramination generates certain polar Br-DBPs through its own set of reaction mechanisms. Moreover, 67% and 48% of the 27 polar Br-DBPs in chloramination had RTs longer than 2.5 min (a dividing line for bromine-containing aliphatic and carboxylic-aromatic compounds[12]) and 5.0 min, respectively, whereas 47% and 19% of the 36 polar Br-DBPs in chlorination had RTs longer than 2.5 and 5.0 min, respectively. This demonstrates that chloramination favored the formation of polar aromatic Br-DBPs, whereas chlorination favored the formation of polar aliphatic Br-DBPs. Additionally, as contact time increased from 24 to 120 h, the slight decrease of TOBr and the increase of TII in chlorination (SI Figure S8d and f) indicate that the portion of polar Br-DBPs in TOBr likely increased.

Key Reactions Governing the Formation of Polar Br-DBPs in Chloramination. To further explore the formation mechanism of polar Br-DBPs in chloramination, a quantitative empirical model for polar/overall Br-DBP formation was developed using the software Dynafit.[42] Since the TII level of polar Br-DBPs was strongly correlated with the TOBr concentration (SI Figure S9), the level of polar Br-DBPs was represented by TOBr in the model. Likewise, the level of Cl-DBPs was represented by TOCl. Among the massive reactions in chloramination, 33 key reactions were found to be responsible for the formation of polar/overall Br-DBPs (Table 2). In accordance with the literature,[18,20,22,23] fast and

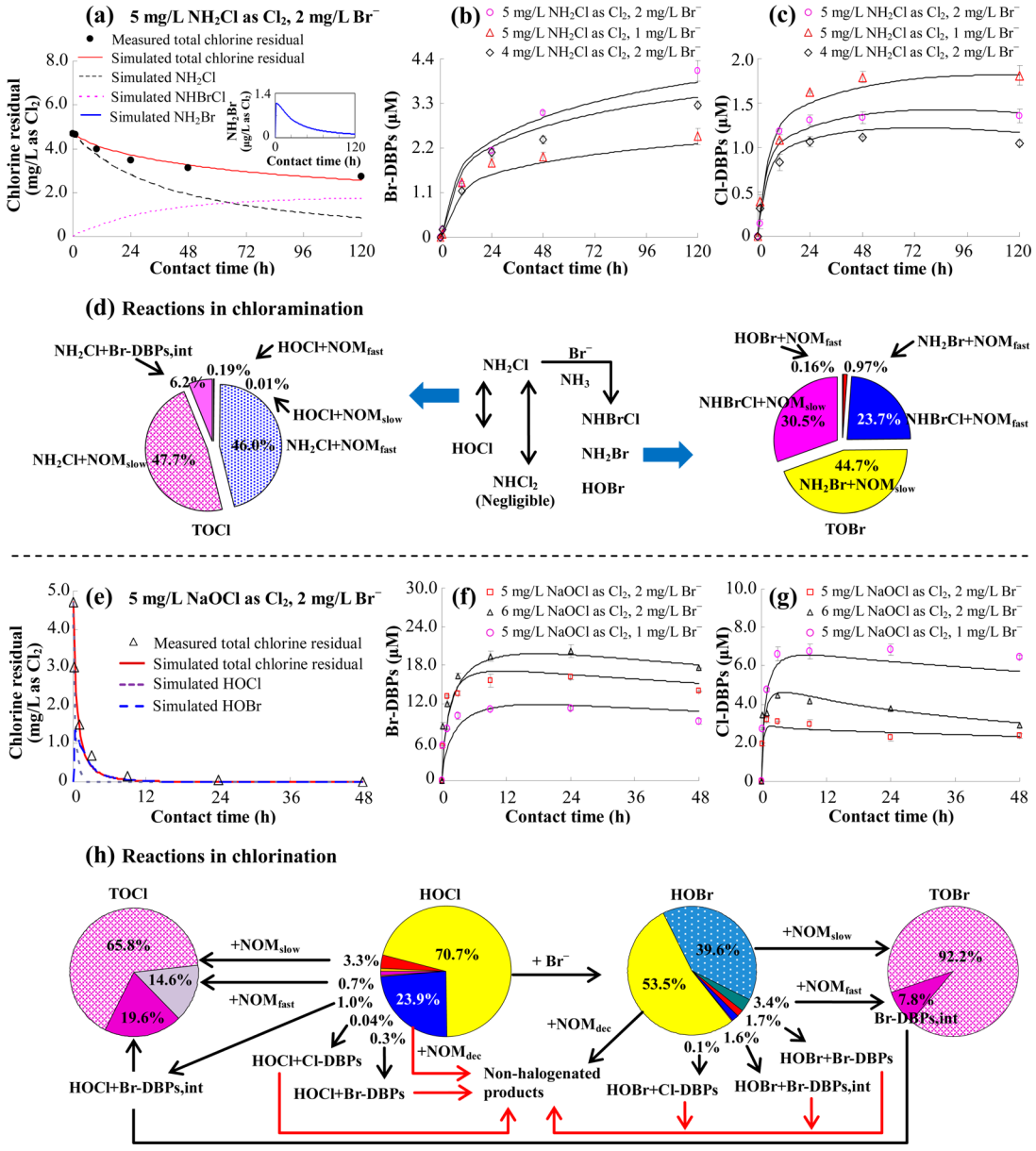


Figure 3. Modeling results for (a–d) chloramination and (e–h) chlorination: (a) and (e) are measured/simulated chlorine residuals in chloramination and chlorination, respectively; (b) and (f) are measured/simulated TOBr levels in chloramination and chlorination, respectively, under different scenarios; (c) and (g) are measured/simulated TOCl levels in chloramination and chlorination, respectively, under different scenarios; (d) and (h) are key reactions and their contribution factors in chloramination and chlorination, respectively. The simulated chlorine residual, simulated TOCl, and simulated TOBr were obtained from the Dynafit model, the simulated chlorine residual = $[NH_2Cl] + [NH_2Br] + 2[NHCl_2] + 2[NHBrCl] + [HOCl] + [HOBr]$, the simulated TOCl level = [Cl-DBPs], and the simulated TOBr level = [Br-DBPs] + [Br-DBPs,int]. The data of measured TOBr and TOCl present the means and the standard deviations of duplicate analyses.

slow reaction sites in NOM are defined as NOM_{fast} and NOM_{slow}. In this study, NOM_{dec} was defined as reactive sites in NOM which were responsible for the decay of NH_2Cl but did not cause the formation of halogenated DBPs. The reaction rate constants of NH_2Br and NHBrCl with NOM_{fast} and NOM_{slow} were achieved through best-fitting of the experimental data. The Br-DBPs formed from the fast reactions was defined as intermediate Br-DBPs (Br-DBPs,int), which would further react with HOCl[12] or other active chlorine species to form Cl-DBPs. It was found that the autodecompositions of Cl-DBPs, Br-DBPs, and Br-DBPs,int (reactions 30–32) were necessarily incorporated into the model to improve the fitting. Other major assumptions for the model are described in the SI. The reaction rate constants and initial levels of reactants followed those in the literature[14−16,43−51] or were obtained through best fitting.

The developed quantitative model predicted the formation of TOBr and TOCl and the loss of total chlorine residual under the three chloramination scenarios well (Figure 3a–c and SI Figure S10). The contribution factor of a reaction was calculated as illustrated in the SI. NHBrCl and NH_2Br were found to be major species for the formation of Br-DBPs. In chloramination with 5 mg/L NH_2Cl as Cl_2 and 2 mg/L Br^-, the modeling results indicated that reactions of NHBrCl+NOM_{fast}, NHBrCl+NOM_{slow}, NH_2Br+NOM_{fast}, and NH_2Br+NOM_{slow} accounted for 23.7%, 30.5%, 0.97%, and 44.7%, respectively, of the formed Br-DBPs, while HOBr accounted for only 0.2%

dx.doi.org/10.1021/es4034765 | Environ. Sci. Technol. 2014, 48, 2579–2588

of the formed Br-DBPs (Figure 3d). Of the formed Cl-DBPs, reactions of NH_2Cl+NOM_{slow} and NH_2Cl+NOM_{fast} totally accounted for 93.7%, reactions of HOCl+NOM_{slow} and HOCl +NOM_{fast} totally accounted for 0.2%, and the transformation of Br-DBPs,int to Cl-DBPs accounted for 6.2%. $NHCl_2$ could be neglected for its concentration was 10^9−10^{10} times lower than NH_2Cl. The monochloramine dose and bromide concentration had slight effects on the contribution factors of the reactions in the chlorine consumption and DBP formation (SI Table S1): when the NH_2Cl dose was lowered to 4 mg/L as Cl_2 (with 2 mg/L Br^-), reactions of NHBrCl+NOM_{fast}, NHBrCl +NOM_{slow}, NH_2Br+NOM_{fast}, and NH_2Br+NOM_{slow} accounted for 27.6%, 28.7%, 1.0%, and 42.5%, respectively, of the formed Br-DBPs; when the bromide concentration was lowered to 1 mg/L Br^- (with 5 mg/L NH_2Cl as Cl_2), reactions of NHBrCl +NOM_{fast}, NHBrCl+NOM_{slow}, NH_2Br+NOM_{fast}, and NH_2Br +NOM_{slow} accounted for 31.0%, 27.1%, 1.0%, and 40.7%, respectively, of the formed Br-DBPs.

For comparison, a quantitative empirical model for the formation of polar/overall Br-DBPs in chlorination was also developed. This model incorporated 16 reactions (Table 2). It predicted the formation of TOBr and TOCl and the loss of total chlorine residual well under the three chlorination scenarios (Figure 3e−g and SI Figure S11). In chlorination with 5 mg/L NaOCl as Cl_2 and 2 mg/L Br^-, the modeling results indicated that, of the consumed chlorine, 70.7% oxidized bromide to HOBr, 23.9% reacted with NOM_{dec} to form nonhalogenated products, 0.7% reacted with NOM_{fast} to form Cl-DBPs (14.6%), and 3.3% reacted with NOM_{slow} to form Cl-DBPs (65.8%) (Figure 3h). Of the generated HOBr, 3.4% reacted with NOM_{fast} to form Br-DBPs,int, and 39.6% reacted with NOM_{slow} to form Br-DBPs (92.2%). The chlorine dose and bromide concentration had significant effects on the contribution factors of the reactions in the chlorine consumption and DBP formation (SI Table S1). Of the consumed chlorine in chlorination with 6 mg/L NaOCl as Cl_2 and 2 mg/L Br^-, 63.4% oxidized bromide to HOBr, 29.0% reacted with NOM_{dec} to form nonhalogenated products, 0.6% reacted with NOM_{fast} to form Cl-DBPs (9.8%), and 4.8% reacted with NOM_{slow} to form Cl-DBPs (72.7%). Of the consumed chlorine in chlorination with 5 mg/L NaOCl as Cl_2 and 1 mg/L Br^-, 41.7% oxidized bromide to HOBr, 45.8% reacted with NOM_{dec} to form nonhalogenated products, 1.1% reacted with NOM_{fast} to form Cl-DBPs (9.4%), and 8.7% reacted with NOM_{slow} to form Cl-DBPs (77.1%) (SI Table S1).

The decomposition reactions of Cl-DBPs and Br-DBPs by HOCl or HOBr in chlorination could not be neglected for they played important roles in consumption of chlorine and regeneration of bromide. On the contrary, the decomposition reactions of Cl-DBPs and Br-DBPs by HOCl, HOBr, chloramines, or bromamines in chloramination could be neglected. This is because hypochlorous acid and hypobromous acid in chloramination were at ng/L or subng/L levels (SI Figure S10), which were not enough to cause polar intermediate Br-DBPs to decompose, and chloramines and bromamines are much weaker oxidants. Moreover, the transformation of Br-DBPs,int into Cl-DBPs was greater in chlorination than in chloramination. That is likely why many high MW polar intermediate Br-DBPs formed quickly and decayed rapidly in chlorination, while the levels of nearly all polar Br-DBPs increased with contact time in chloramination (Figure 2).

Our findings indicate that chloramination is not equivalent to slow chlorination, as others have proposed, nor is it a safe substitute for chlorination (although chloramination generates less TOBr than chlorination), as judged by the reactions of NH_2Cl and NaOCl with the isolated humic acid. Chloramination favors the formation of aromatic and nitrogenous Br-DBPs, which are relatively stable and accumulated in the presence of monochloramine, bromochloramine, bromamines, and trace levels of free chlorine in chloramination. In a drinking water distribution system, the contact time may range from hours to days mainly depending on the distribution distance. The generation and accumulation of aromatic (nitrogenous) Br-DBPs in chloramination should be of concern, and their comparative toxicities need to be examined. Additionally, higher levels of Br-DBPs than Cl-DBPs could form after a certain contact time in chloramination (e.g., after 3.6 h contact time with 5 mg/L NH_2Cl as Cl_2 and 2 mg/L Br^-, or after 18 h contact time with 5 mg/L NH_2Cl as Cl_2 and 1 mg/L Br^-). Owing to the significantly higher toxicity of Br-DBPs, the application of chloramination to disinfection of bromide-rich raw waters should be cautious and an unnecessarily prolonged contact time in chloramination should be avoided to minimize their formation.

■ ASSOCIATED CONTENT

Supporting Information

Additional details, Table S1, Figures S1−S11. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +852-2358-8479; fax: +852-2358-1534; e-mail: xiangru@ust.hk.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by grants from the Research Grants Council of the Hong Kong Special Administrative Region, China (Projects 622607 and 622913).

■ REFERENCES

(1) Cowman, G. A.; Singer, P. C. Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances. *Environ. Sci. Technol.* **1996**, *30* (1), 16−24.

(2) Diehl, A. C.; Speitel, G. E.; Symons, J. M.; Krasner, S. W.; Hwang, C. J.; Barrett, S. E. DBP formation during chloramination. *J. Am. Water Works Assoc.* **2000**, *92* (6), 76−90.

(3) Zhang, X.; Echigo, S.; Minear, R. A.; Plewa, M. J. Characterization and comparison of disinfection by-products of four major disinfectants. In *Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water*; Barrett, S. E., Krasner, S. W., Amy, G. L., Eds.; American Chemical Society: Washington, DC, 2000; pp 299−314.

(4) Richardson, S. D.; Plewa, M. J.; Wagner, E. D.; Schoeny, R.; DeMarini, D. M. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutat. Res.* **2007**, *636* (1−3), 178−242.

(5) Komaki, Y.; Pals, J.; Wagner, E. D.; Mariñas, B. J.; Plewa, M. J. Mammalian cell DNA damage and repair kinetics of monohaloacetic acid drinking water disinfection by-products. *Environ. Sci. Technol.* **2009**, *43* (21), 8437−8442.

(6) Bull, R. J.; Krasner, S. W.; Daniel, P. A.; Bull, R. D. *Health Effects and Occurrence of Disinfection By-Products*; AWWA Research Foundation: Denver, CO, 2001.
(7) Richardson, S. D. Drinking water disinfection by-products. In *Encyclopedia of Environmental Analysis and Remediation*; Meyers, R. A., Ed.; John Wiley & Sons: New York, 1998; pp 1398−1421.
(8) Pressman, J. G.; Richardson, S. D.; Speth, T. F.; Miltner, R. J.; Narotsky, M. G.; Hunter, E. S.; Rice, G. E.; Teuschler, L. K.; McDonald, A.; Parvez, S.; Krasner, S. W.; Weinberg, H. S.; McKague, A. B.; Parrett, C. J.; Bodin, N.; Chinn, R.; Lee, C. F. T.; Simmons, J. E. Concentration, chlorination, and chemical analysis of drinking water for disinfection byproduct mixtures health effects research: U.S. EPA's four lab study. *Environ. Sci. Technol.* **2010**, *44* (19), 7184−7192.
(9) Krasner, S. W.; Weinberg, H. S.; Richardson, S. D.; Pastor, S. J.; Chinn, R.; Sclimenti, M. J.; Onstad, G. D.; Thruston, A. D., Jr. Occurrence of a new generation of disinfection byproducts. *Environ. Sci. Technol.* **2006**, *40* (23), 7175−7185.
(10) Zhang, X.; Talley, J. W.; Boggess, B.; Ding, G.; Birdsell, D. Fast selective detection of polar brominated disinfection byproducts in drinking water using precursor ion scans. *Environ. Sci. Technol.* **2008**, *42* (17), 6598−6603.
(11) Zhai, H.; Zhang, X. A new method for differentiating adducts of common drinking water DBPs from higher molecular weight DBPs in electrospray ionization-mass spectrometry analysis. *Water Res.* **2009**, *43* (8), 2093−2100.
(12) Zhai, H.; Zhang, X. Formation and decomposition of new and unknown polar brominated disinfection byproducts during chlorination. *Environ. Sci. Technol.* **2011**, *45* (6), 2194−2201.
(13) Morris, J. C.; Isaac, R. A. A critical review of kinetic and thermodynamic constants for aqueous chlorine-ammonia system. In *Water Chlorination: Environmental Impact and Health Effects*; Jolley, R. L., Brungs, W. A., Cotruvo, J. A., Cumming, R. B., Mattice, J. S., Jacobs, V. A., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1983; Vol. 4, pp 49−62.
(14) Vikesland, P. J.; Ozekin, K.; Valentine, R. L. Monochloramine decay in model and distribution system waters. *Water Res.* **2001**, *35* (7), 1766−1776.
(15) Trofe, T. W.; Inman, G. W.; Johnson, J. D. Kinetics of monochloramine decomposition in the presence of bromide. *Environ. Sci. Technol.* **1980**, *14* (5), 544−549.
(16) Gazda, M.; Margerum, D. W. Reactions of monochloramine with Br_2, Br_3^-, HOBr, and OBr^-: Formation of bromochloramines. *Inorg. Chem.* **1994**, *33* (1), 118−123.
(17) Lei, H.; Mariñas, B. J.; Minear, R. A. Bromamine decomposition kinetics in aqueous solutions. *Environ. Sci. Technol.* **2004**, *38* (7), 2111−2119.
(18) Duirk, S. E.; Valentine, R. L. Modeling dichloroacetic acid formation from the reaction of monochloramine with natural organic matter. *Water Res.* **2006**, *40* (14), 2667−2674.
(19) Duirk, S. E.; Gombert, B.; Croue, J. P.; Valentine, R. L. Modeling monochloramine loss in the presence of natural organic matter. *Water Res.* **2005**, *39* (14), 3418−3431.
(20) Duirk, S. E.; Valentine, R. L. Bromide oxidation and formation of dihaloacetic acids in chloraminated water. *Environ. Sci. Technol.* **2007**, *41* (20), 7047−7053.
(21) Hong, Y.; Liu, S.; Song, H.; Karanfil, T. HAA formation during chloramination-significance of monochloramine's direct reaction with DOM. *J. Am. Water Works Assoc.* **2007**, *99* (8), 57−69.
(22) Alsulaili, A. D. Impact of bromide, NOM, and prechlorination on haloamine formation, speciation, and decay during chloramination; Ph.D. dissertation; University of Texas, Austin, TX, 2009.
(23) Alsulaili, A. D.; Speitel, G. E.; Katz, L. E. Monochloramine and total haloamine decay after a short prechlorination time in the presence of bromide. *Water Sci. Technol.: Water Supply* **2010**, *10* (4), 512−516.
(24) APHA, AWWA, and WEF. *Standard Methods for the Examination of Water and Wastewater*, 21th ed.; Washington, DC, 2005.
(25) Heller-Grossman, L.; Idin, A.; Limoni-Relis, B.; Rebhun, M. Formation of cyanogen bromide and other volatile DBPs in the disinfection of bromide-rich lake water. *Environ. Sci. Technol.* **1999**, *33* (6), 932−937.
(26) Richardson, S. D.; Fasano, F.; Ellington, J. J.; Crumley, F. G.; Buettner, K. M.; Evans, J. J.; Blount, B. C.; Silva, L. K.; Waite, T. J.; Luther, G. W.; McKague, A. B.; Miltner, R. J.; Wagner, E. D.; Plewa, M. J. Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water. *Environ. Sci. Technol.* **2008**, *42* (22), 8330−8338.
(27) Liu, J.; Zhang, X. Effect of quenching time and quenching agent dose on total organic halogen. *Int. J. Environ. Anal. Chem.* **2013**, *93* (11), 1146−1158.
(28) Hua, G.; Reckhow, D. A. Determination of TOCl, TOBr and TOI in drinking water by pyrolysis and off-line ion chromatography. *Anal. Bioanal. Chem.* **2006**, *384* (2), 495−504.
(29) Li, Y.; Zhang, X.; Shang, C. Effect of reductive property of activated carbon on total organic halogen analysis. *Environ. Sci. Technol.* **2010**, *44* (6), 2105−2111.
(30) Li, Y.; Zhang, X.; Shang, C.; Krasner, S. W. Evaluation and improvement of total organic bromine analysis with respect to reductive property of activated carbon. *Water Res.* **2011**, *45* (3), 1229−1237.
(31) Pan, Y.; Zhang, X. Four groups of new aromatic halogenated disinfection byproducts: Effect of bromide concentration on their formation and speciation in chlorinated drinking water. *Environ. Sci. Technol.* **2013**, *47* (3), 1265−1273.
(32) Richardson, S. D. Disinfection by-products: Formation and occurrence in drinking water. In *The Encyclopedia of Environmental Health*; Nriagu, J. O., Ed.; Elsevier: Burlington, 2011; pp 110−136.
(33) Weil, E. D.; Linder, J. The reactions of alcohols with highly chlorinated cyclopentenones. *J. Org. Chem.* **1962**, *28* (9), 2218−2225.
(34) Gong, H.; You, Z.; Xian, Q.; Shen, X.; Zou, H.; Huan, F.; Xu, X. Study on the structure and mutagenicity of a new disinfection byproduct in chlorinated drinking water. *Environ. Sci. Technol.* **2005**, *39* (19), 7499−7508.
(35) Larson, R. A.; Weber, E. J. *Reaction Mechanisms in Environmental Organic Chemistry*; Lewis Publishers: Boca Raton, FL, 1994.
(36) Qin, F.; Zhao, Y. Y.; Zhao, Y.; Boyd, J. M.; Zhou, W.; Li, X. F. A toxic disinfection by-product, 2,6-dichloro-1,4-benzoquinone, identified in drinking water. *Angew. Chem., Int. Ed.* **2010**, *49* (4), 790−792.
(37) Zhao, Y.; Qin, F.; Boyd, J. M.; Anichina, J.; Li, X. F. Characterization and determination of chloro- and bromobenzoquinones as new chlorination disinfection byproducts in drinking water. *Anal. Chem.* **2010**, *82* (11), 4599−4605.
(38) Zhao, Y.; Anichina, J.; Lu, X.; Bull, R. J.; Krasner, S. W.; Hrudey, S. E.; Li, X. F. Occurrence and formation of chloro- and bromobenzoquinones during drinking water disinfection. *Water Res.* **2012**, *46* (14), 4351−4360.
(39) Ding, G.; Zhang, X.; Yang, M.; Pan, Y. Formation of new brominated disinfection byproducts during chlorination of saline sewage effluents. *Water Res.* **2013**, *47* (8), 2710−2718.
(40) Hrudey, S. E. Chlorination disinfection by-products, public health risk tradeoffs and me. *Water Res.* **2009**, *43* (8), 2057−2092.
(41) Richardson, S. D.; Postigo, C. Drinking water disinfection by-products. In *Emerging Organic Contaminants and Human Health*; Barceló, D., Ed.; Springer-Verlag: Berlin, 2011; pp 93−137.
(42) Kuzmic, P. Program DYNAFIT for the analysis of enzyme kinetic data: Application to HIV proteinase. *Anal. Biochem.* **1996**, *237* (2), 260−273.
(43) Morris, J. C. Kinetics of reactions between aqueous chlorine and nitrogenous compounds. In *Principles and Applications of Water Chemistry*; Faust, S. D., Hunter, J. V., Eds.; John Wiley: New York, 1967.
(44) Margerum, D. W.; Gray, E. T.; Huffman, R. P. Chlorination and the formation of N-chloro compounds in water treatment. In *Organometals and Organometalloids: Occurance and Fate in the Environment*; Brinkman, F. E., Bellama, J. M., Eds.; American Chemical Society: Washington, DC, 1978; pp 278−291.

(45) Leao, S. F. Kinetics of combined chlorine: Reactions of substitution and redox; Ph.D. dissertation; University of California, Berkeley, CA, 1981.
(46) Jafvert, C. T.; Valentine, R. L. Dichloramine decomposition in the presence of excess ammonia. *Water Res.* **1987**, *21* (8), 967−973.
(47) Kumar, K.; Margerum, D. W. Kinetics and mechanism of general-acid-assisted oxidation of bromide by hypochlorite and hypochlorous acid. *Inorg. Chem.* **1987**, *26* (16), 2706−2711.
(48) Wajon, J. E.; Morris, J. C. Bromination chemistry: Rates of formation of NH_2Br and some N-bromamino acids. In *Water Chlorination: Environmental Impact and Health Effects*; Jolley, R. L., Brungs, W. A., Crumming, R. B., Jacobs, V. A., Eds; Ann Arbor Science: Ann Arbor, MI, 1980; Vol. 3, pp 171−181.
(49) Haag, W. R.; Lietzke, M. H. A kinetic model for predicting the concentrations of active halogen species in chlorinated saline cooling waters. In *Water Chlorination: Environmental Impact and Health Effects*; Jolley, R. L., Brungs, W. A., Crumming, R. B., Jacobs, V. A., Eds; Ann Arbor Science: Ann Arbor, MI, 1980; Vol. 3, pp 415−426.
(50) Buffle, M.; Galli, S.; von Gunten, U. Enhanced bromate control during ozonation: The chlorine-ammonia process. *Environ. Sci. Technol.* **2004**, *38* (19), 5187−5195.
(51) Echigo, S. Kinetics and speciation of brominated disinfection by-products during ozonation; Ph.D. dissertation; University of Illinois, Urbana-Champaign, IL, 2002.