School of Molecular and Life Sciences

## The Influence of Cu(II) on the Chloramination of Bromide-Containing Waters: Mechanistic Investigation of the Decay of Oxidants and the Formation of Disinfection By-products

Wei Hu

This thesis is presented for the Degree of Doctor of Philosophy of Curtin University

December 2019

#### Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature:

Wei Hu

Date: 18 December 2019

### Acknowledgments

I would like to express my sincere gratitude to Dr. Sébastien Allard, my supervisor, for his patience, guidance and support throughout these years. He provided a lot of professional feedbacks toward my research work and gave me patient guidance in technical writing. Also, I would like to thank Professor Jean-Philippe Croué for his encouragement and support throughout my studies.

I would like to offer my special thanks to Prof. Frants R. Lauritsen (University of Southern Denmark, Denmark) for the fruitful discussion about the usage of membrane introduction mass spectrometry. I am thankful to Prof. Yunho Lee (Gwangju Institute of Science and Technology, South Korea) for his valuable comments. I also want to thank Dr. Chao Liu and Prof. Tanju Karanfil (Clemson University, United States) for offering me the opportunities to visit their labs and conduct experimental work.

My sincere appreciation goes to Peter Chapman and Peter Hopper for their help on the instrumentation. I would like to express my thanks to all group members at Curtin Water Quality Research Group for their support and assistance. I also want to thank my friends in Australia and China for their help and encouragement during my hard times.

I want to acknowledge China Scholarship Council (CSC) and Curtin International Postgraduate Research Scholarship (CIPRS) for providing the scholarship.

Finally, I would like to express my deep appreciation to my parents for their support, understanding and love throughout the years.

### Abstract

Monochloramine (NH<sub>2</sub>Cl) is increasingly being used by water utilities as an alternative disinfectant to chlorine in drinking water distribution systems. This is due to the fact that NH<sub>2</sub>Cl is more stable than chlorine, thereby providing a longer lasting residual disinfectant to inactivate pathogenic microorganisms during long distance delivery of water. In addition, it is known that NH<sub>2</sub>Cl has less potential than chlorine to produce common regulated disinfection byproducts (DBPs), e.g., trihalomethanes (THMs) and haloacetic acids (HAAs). However, NH<sub>2</sub>Cl favors the formation of other classes of DBPs, such as nitrogenous DBPs (N-DBPs), e.g., haloacetonitriles (HANs) and haloacetamides (HAcAms). Bromide is ubiquitous in source waters with concentrations ranging from 10 to 2000  $\mu$ g/L. The presence of bromide decreases the stability of NH<sub>2</sub>Cl by forming bromamines (NH<sub>2</sub>Br, NHBr<sub>2</sub>) and bromochloramine (NHBrCl), The most abundant of these brominated halamine species in drinking waters is NHBrCl. Thus, chloramines (NH<sub>2</sub>Cl, NHCl<sub>2</sub>), bromamines and NHBrCl may form in bromide containing waters during chloramination. Bromamines and NHBrCl are more reactive than chloramines, and these brominated halamines can react with natural organic matter (NOM) in water to promote the formation of brominated DBPs (Br-DBPs), which are more toxic than their chlorinated analogues. Therefore, it is important to understand the speciation and determine the concentrations of these halamines in drinking water distribution systems. However, the discrimination and quantification of these halamines are difficult to achieve with traditional methods.

Copper is frequently detected in water systems because of the leaching from copper pipes or added as a biocide to control the growth of biofilm. Copper oxide (CuO) is known to catalyze the decay of different oxidants (ClO<sub>2</sub>, HOCl, HOBr and HOCl+Br<sup>-</sup>/ $\Gamma$ ). While, Cu(II) (refers to soluble copper(II)) has been found to slightly enhance the decay of NH<sub>2</sub>Cl but has no effect on the decay of chorine. Studies have also shown that the addition of Cu(II)/CuO promoted the formation of THMs, HAAs, bromate, Br-DBPs, HANs and HAcAms during chloramination. It has also been reported that Cu(II) increased the formation of THMs from model compounds and humic acid (HA) during chloramination. The effect of Cu(II) on the formation and speciation of HANs and HAcAms during chloramination has not been investigated.

This thesis focuses on the mechanistic investigation of the decay of oxidants and the formation of disinfection by-products during chloramination of bromide containing waters in the presence of Cu(II). There are several knowledge gaps that have been investigated. First, due to the presence of different chlorinated and brominated-amines (NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br, NHBr<sub>2</sub> and NHBrCl) in drinking water during chloramination, it is important to be able to differentiate and quantify these different halogenatedamines to understand their fate during the disinfection process. Second, CuO is known to catalyze the decomposition of several halogenated oxidants, but the effect of CuO on NH<sub>2</sub>Cl decomposition in the presence of bromide is largely unknown. Third, where Cu(II) is present in distribution systems it slightly enhances the decay of NH<sub>2</sub>Cl, however the effect of Cu(II) on bromamines decomposition has not been studied. Fourth, the impact of Cu(II) on the stability of NH<sub>2</sub>Cl under realistic conditions during chloramination of bromide containing waters needs to be investigated. Fifth, understanding the fate of DBPs formation is vital to ensure safe delivery of drinking water, therefore the effect of Cu(II) on DBPs formation and speciation during chloramination of bromide containing waters needs to be assessed.

This thesis contributes to the advancement of these five knowledge gaps. Following a short overview of the thesis outline in Chapter 1, Chapter 2 focuses on the development of a new analytical method allowing the quantification of bromochloramine using Membrane Introduction Mass Spectrometry (MIMS). Chapter 3 further investigated the identification and quantification of all halamines potentially present in drinking water (chloramines, bromamines and bromochloramine) by MIMS. Chapter 4 focuses on the effect of copper oxide (CuO) on monochloramine decomposition in bromide-containing waters. Chapter 5 explores the effect of Cu(II) on the kinetics of bromamines decomposition and the formation of byproducts. Chapter 6 focuses on the effect of Cu(II) on the kinetics of monochloramine decomposition and the formation of byproducts. Chapter 7 explores the effect of Cu(II) on disinfection byproducts (DBPs) formation and speciation during chloramination of bromide containing waters.

In Chapter 2, we report a method to accurately quantify NHBrCl with Membrane Introduction Mass Spectrometry (MIMS). Initially, the molar absorption coefficient of NHBrCl was determined by quantifying NHBrCl as 2,4,6-tribromophenol by HPLC-UV and comparing the results with the direct UV response at 320 nm. A molar absorption coefficient of  $304 \text{ M}^{-1}\text{cm}^{-1}$  was obtained. The results obtained by direct UV measurements were then compared to the MIMS signal recorded at m/z 131 corresponding to the mass of the molecular ion and used to establish a calibration curve. A limit of detection of  $2.9 \,\mu\text{M}$  (378  $\mu\text{g/L}$ ) was determined. MIMS is the only method enabling the unambiguous quantification of NHBrCl, as it is based on m/z 131, while with other analytical techniques, other halamines can interfere, i.e., overlapping peaks with direct UV measurements and reaction of several halamines with colorimetric reagents or phenols. While the detection limit is not quite low enough to measure NHBrCl in most drinking waters, this analytical method will benefit the scientific community by allowing further mechanistic studies on the contribution of NHBrCl to the formation of toxic disinfection by-products.

In Chapter 3, a Membrane Introduction Mass Spectrometry (MIMS) method was developed to differentiate and quantify the different chlorinated and brominatedamines, present in drinking water during chloramination. Specific mass spectra were obtained for these halamines. The representative mass to charge ratio (m/z) of 53, 85, 97, 175 and 131 corresponding to the mass of the parent compound were selected to monitor monochloramine (NH<sub>2</sub>Cl), dichloramine (NHCl<sub>2</sub>), monobromamine (NH<sub>2</sub>Br), dibromamine (NHBr<sub>2</sub>) and bromochloramine (NHBrCl), respectively. Detection limit for NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br, NHBr<sub>2</sub> and NHBrCl were found to be 0.48, 0.23, 1.44, 0.84 and 2.51 µM, corresponding to 0.034, 0.033, 0.10, 0.12 and 0.36 mg/L as Cl<sub>2</sub>, respectively. NH<sub>2</sub>Br and NHBr<sub>2</sub> were quantified by MIMS for the first time. However, NHCl<sub>2</sub>, NHBr<sub>2</sub> and NHBrCl created ions interfering with the analysis of NH<sub>2</sub>Cl and NH<sub>2</sub>Br via decomposition reactions at hot metal surfaces inside the mass spectrometer. Therefore, a method was developed to accurately measure NH<sub>2</sub>Cl or NH<sub>2</sub>Br concentration in mixtures of NH2Cl/NHCl2 or NH2Br/NHBr2 solutions. If NHBrCl and NH<sub>2</sub>Br are simultaneously present in solution, NH<sub>2</sub>Br cannot be accurately quantified since the interference from the NHBrCl fragment cannot be quantified. The interference from NHBrCl on NH<sub>2</sub>Cl was found to be negligible under drinking water conditions. The different halamines were monitored and quantified for the first time in two surface waters and one seawater that were chloraminated to mimic a realistic disinfection scenario. The MIMS method developed in this study will also allow real time monitoring of the halamines formation and decomposition. This may ultimately assist water utilities to better manage chloraminated systems.

The effect of CuO on NH<sub>2</sub>Cl decay in the presence of bromide was investigated in Chapter 4. Results showed that in presence of CuO, NH<sub>2</sub>Cl slightly decays under acidic conditions. When bromide was present in NH<sub>2</sub>Cl solutions, the total oxidant (sum of the different bromo-chloro-amines) was significantly decreased by the presence of CuO. This was primarily due to the degradation of bromochloramine (NHBrCl) by CuO which was evidenced by MIMS. The decomposition rate of the total oxidant did not change with different CuO dosage (0.02-0.2 g/L), but increased with increasing bromide concentration (0-80  $\mu$ M) and decreasing pH (8-6.5). An apparent second-order rate constant of 0.73 M<sup>1</sup>s<sup>-1</sup> was determined with respect to NH<sub>2</sub>Cl and bromide concentrations for a CuO concentration of 0.05 g/L. Our findings suggest that, during water transportation in copper pipes or in distribution systems where copper oxide is present, a special attention should be drawn on the stability of disinfectant when bromide containing waters are chloraminated.

Chapter 5 demonstrated that Cu(II) can significantly enhance the decomposition rate of bromamines. Apparent second order rate constants of 2.31 M<sup>-1</sup>s<sup>-1</sup> and 0.36 M<sup>-1</sup>s<sup>-1</sup> at pH 7.5 were determined for the reaction of Cu(II) with bromamines and the selfdecomposition of bromamines, respectively. Increasing the pH from 6.0 to 8.5, decreased the rate of bromamines self-decomposition while the rate of Cu(II)catalyzed decomposition of bromamines increased. Experiments were carried out with <sup>15</sup>N-labeled bromamine to analyze the nitrogenous degradation products of bromamines in the presence and absence of Cu(II). The main bromamines selfdecomposition product was found to be N<sub>2</sub> with low concentration of N<sub>2</sub>O, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> detected. When Cu(II) was present, the product speciation changed and the concentrations of NO<sub>2</sub><sup>-</sup> and N<sub>2</sub>O became significant, while N<sub>2</sub> and NO<sub>3</sub><sup>-</sup> were produced at low levels. Increasing the Cu(II) concentration from 1.0 to 5.0 mg/L led to an increase of N<sub>2</sub>O production and a decrease of NO<sub>2</sub><sup>-</sup> formation. Based on these results a mechanism for Cu(II)-catalyzed bromamines decomposition was proposed. These novel findings may have important implications to control the stability of disinfectant in drinking water distribution systems.

Chapter 6 demonstrated that Cu(II) can catalyze the decay of oxidants during the chloramination process. In the absence of Cu(II), 16% of the total oxidant (chloramines, bromamines and NHBrCl) was consumed during chloramination in bromide-

containing waters at pH 6.5 after 6 h, while the presence of Cu(II) significantly accelerated the total oxidant decay with 65% % of the total oxidant consumed under the same conditions. Higher bromide concentrations and lower pH led to an increase in total oxidant decomposition. This was mainly attributed to the higher formation of NHBrCl and its further catalytic degradation in presence of Cu(II) (evidenced by Membrane Introduction Mass Spectrometry). The nitrogen degradation products in presence of bromide and Cu(II) were identified and found to be similar to the degradation of NH<sub>2</sub>Cl alone. Nitrogen gas and ammonia were found to be the main products and a mechanism involving NHBrCl decomposition was proposed. These findings may provide useful information for water utilities to better manage and maintain the stability of disinfectant residual allowing safe distribution of drinking water over a wide geographical area.

Chapter 7 investigated the effect of Cu(II) on disinfection byproducts formation during chloramination of different model compounds and a natural organic matter extract. It was observed that Cu(II) did not catalyze the formation of trihalomethanes (THMs) during chloramination of amino acids and phenolic compounds. In presence of Cu(II), haloacetonitriles (HANs) and dichloroacetamide (DCAcAm) formation was enhanced for histidine, aspartic acid, hydroquinone and p-hydroxybenzoic acid, but decreased for cysteine and resorcinol. Interestingly, the formation of brominated DBPs (Br-DBPs) was inhibited in presence of Cu(II), probably because the brominated-amines are catalytically degraded by Cu(II). The impact of pH was found to be an important factor affecting the impact of Cu(II) on DBPs formation during chloramination of the model compounds. During chloramination of NOM, DBPs formation increased with increasing Cu(II) concentration from 0 to 2.0 mg/L, and then decreased with 5.0 mg/L of Cu(II). It was observed that Cu(II) was more likely to promote the formation of chlorinated DBPs (Cl-DBPs) but reduce the formation of Br-DBPs.

## **Table of Contents**

Acknowledgmentsi
Abstractii
List of Figures
List of Tablesxvii
List of Abbreviationsxviii
List of Publications and Presentations Arising from this Thesisxx
Chapter 1. Thesis Overview
Chapter 2. Method Development for Quantification of Bromochloramine Using
Membrane Introduction Mass Spectrometry
2.1 Introduction
2.2 Materials and Methods
2.2.1 Reagents
2.2.2 Analytical Methods9
2.2.3 Kinetic Modeling10
2.3 Results and Discussion
2.3.1 Optimization of Experimental Conditions for Minimizing/Controlling the
Presence of Other Halogenated Oxidants by Kinetic Modeling10
2.3.2 Comparison of Direct UV Measurements, MIMS Signal, and Modeling
Results for NH <sub>2</sub> Cl and NHBrCl12
2.3.3 Comparison of Direct UV Measurements, DPD, and HPLC-UV Method
for Quantification of NHBrCl14
2.3.4 Calibration of the MIMS for NHBrCl Measurements Using Direct UV
Measurements17
2.4 Implication for Future Research
2.5 References
Chapter 3. Identification and Quantification of Chloramines, Bromamines and
Bromochloramine by Membrane Introduction Mass Spectrometry (MIMS)23
3.1 Introduction
3.2 Materials and Methods
3.2.1 Reagents and Preparation of Chlorine and Bromine Solutions
3.2.2 Synthesis of Halamines
3.2.3 System Optimization

3.2.4 Experimental Procedures	28
3.3 Results and Discussion	29
3.3.1 Representative Mass Spectra	29
3.3.2 Calibration and Determination of Detection and Quantification Limits	
(LOD and LOQ) for the Different Halamines by MIMS	33
3.3.3 Quantification of NH <sub>2</sub> X (X=Br or Cl)) in a NH <sub>2</sub> X/NHX <sub>2</sub> Mixture	35
3.3.4 Application of MIMS to Real Waters and Its Limitations	37
3.4 Conclusions	39
3.5 References	39
Chapter 4. Effect of Copper Oxide on Monochloramine Decomposition in Bromio	le-
Containing Waters	43
4.1 Introduction	44
4.2 Materials and Methods	45
4.2.1 Reagents	45
4.2.2 Analytical Methods	45
4.2.3 Experimental Procedures	46
4.3 Results and Discussion	46
4.3.1. Effect of CuO on NH <sub>2</sub> Cl Decomposition at Different pHs	46
4.3.2 Synergistic Effect of CuO and Bromide on NH <sub>2</sub> Cl Decomposition	48
4.4 Conclusions	51
4.5 References	52
Chapter 5. Mechanistic Investigation of Bromamines Decomposition in the Preser	nce
of Cu(II)	55
5.1 Introduction	56
5.2 Materials and Methods	58
5.2.1 Standards and Reagents	58
5.2.2 Analytical Methods	58
5.2.3 Kinetic Study	60
5.2.4 Mechanistic study	60
5.3 Results and Discussion	61
5.3.1 Impact of Different Copper Species on Bromamines Decomposition	61
5.3.2 Effect of Cu(II) Concentration on Bromamines Decomposition Kinetic	62
5.3.3 Effect of pH on Bromamines Decomposition	64
5.3.4 Mechanistic Investigation	67

5.3.5 Proposed Reaction Mechanism
5.4 Practical Implications
5.5 References
Chapter 6. Effect of Cu(II) on Monochloramine Stability in Bromide-Containing
Waters
6.1 Introduction
6.2 Materials and Methods77
6.2.1 Reagents77
6.2.2 Analytical Methods78
6.2.3 Experimental Procedures
6.3 Results and Discussion
6.3.1 Synergistic Effect of Cu(II) and Bromide on the Decomposition of the
Total Oxidant and Halamines Speciation80
6.3.2 Effect of Cu(II) Concentration on the Decomposition of the Total Oxidant
and Halamines Speciation81
6.3.3 Effect of Bromide Concentration on the Total Oxidant Decay Kinetic 82
6.3.4 Effect of pH on the Decomposition of the Total Oxidant
6.3.5 Product Analysis
6.4 Practical Implications
6.5 References
Chapter 7. Effect of Cu(II) on Disinfection Byproducts Formation during
Chloramination
7.1 Introduction
7.2 Materials and Methods94
7.2.1 Chemicals
7.2.2 Analytical Methods95
7.2.3 Experimental Procedures
7.3 Results and Discussion
7.3.1 DBPs Formation from Different Model Compounds
7.3.2 DBPs Formation from HQ and PHBA101
7.3.3 DBPs Formation from NOM 105
7.4 Conclusions
7.5 References

Appendix 2	
Appendix 3	
Appendix 4	
Appendix 5	
Appendix 6	
Appendix 7	

### **List of Figures**

Chapter 2-7

Figure 2-1. Variation of NHBrCl, NH<sub>2</sub>Cl, NH<sub>2</sub>Br, NHBr<sub>2</sub>, and HOBr concentrations. Figure 2-2. Comparison of monochloramine (top) and bromochloramine (bottom) Figure 2-3. Comparison of direct UV measurements and DPD methods for Figure 2-4. Comparison between 2,4,6-tribromophenol formation and NHBrCl concentration determined by direct UV measurements (using  $\epsilon$ NHBrCl,320 = 195 and  $320 \text{ M}^{-1}\text{cm}^{-1}$ ) for various conditions at pH 6 (C<sub>T,PO4</sub> = phosphate buffer concentration). Figure 2-5. Determination of the molar absorptivity of NHBrCl at 320 nm Figure 2-6. Comparison between MIMS signals (m/z = 131), bromochloramine concentration determined by direct UV measurements, and modeling for 6 different Figure 2-7. MIMS calibration curves for NHBrCl determined by direct UV 

Figure 4-1. Effect of CuO on NH<sub>2</sub>Cl decomposition at (a) pH 8.0 and (b) pH 6.5..47

 Figure 4-2. Effect of CuO on the total oxidant decomposition and different halamines

 species in chloraminated bromide-containing water. (a) Impact of CuO concentration

 and comparison with modelling data. (b) Comparison between DPD, MIMS and

 modelling data.
 48

 Figure 4-3. Effect of varying bromide concentrations on the total oxidant

 decomposition in the presence of NH<sub>2</sub>Cl and CuO. (a) Total oxidant decay; (b) pseudo

 first order rate constant (k<sub>obs</sub>) of the total oxidant decomposition as a function of

 bromide concentration.
 49

 Figure 4-4. Effect of pH on the total oxidant decay in the presence of CuO and bromide.
 51

 Figure 5-1. Impact of CuO and Cu(II) on total bromamine decomposition.
 61

 Figure 5-2. Impact of Cu(II) on (a) NH<sub>2</sub>Br (m/z 97) and (b) NHBr<sub>2</sub> (m/z 175)
 62

 decomposition monitored by MIMS.
 62

 Figure 5-3. Effect of Cu(II) concentration on total bromamine decomposition rate. (a)
 62

 Total bromamine decomposition as a function of time. (b) Pseudo first order rate
 63

 Figure 5-4. Total bromamine decomposition at different pHs in the presence and absence of Cu(II).
 65

 Figure 5-5. Cu(II)-induced total bromamine decomposition pseudo first order rate
 66

 Figure 5-6. Nitrogen mass balance for total bromamine decomposition in presence
 66

Figure 6-4. Effect of pH (6.5, 7.5, 8.5) on the total oxidant decay in the presence of	)f
NH <sub>2</sub> Cl, bromide and Cu(II)	4
Figure 6-5. Nitrogen mass balance and formation of degradation products in presence	e
or absence of bromide and/or Cu(II)	5

Figure 7-1. Formation of (a) THMs, (b) HANs and (c) DCAcAm during
chloramination of nine different model compounds under different experimental
conditions
Figure 7-2. Effect of Cu(II) concentration on the formation of (a) TCM, (b) HANs and
(c) DCAM from HQ, and (d) TCM, (e) HANs and (f) DCAM from PHBA during
chloramination101
Figure 7-3. Effect of reaction time on the formation of (a) TCM, (b) HANs and (c)
DCAM from HQ, and (d) TCM, (e) HANs and (f) DCAM from PHBA during
chloramination103
Figure 7-4. Effect of pH on the formation of (a) TCM and (b) HANs from HQ, and (c)
TCM and (d) HANs from PHBA during chloramination
Figure 7-5. Effect of Cu(II) concentration on the formation of (a) TCM, (b) HANs and
(c) DCAM from NOM during chloramination105
Figure 7-6. Effect of bromide concentration on the formation of (a) THMs, (b) HANs
and (c) DCAM during chloramination of NOM in the absence and presence of Cu(II).

### Appendix 1–6

Figure A-1-1. Representative mass spectra of a solution of monochloramine in
presence of bromide: Evidence of NHBrCl formation
Figure A-1-2. Modeling of the formation of NHBrCl from reaction between HOBr
and NH <sub>2</sub> Cl for 10 min
Figure A-1-3. Modeling of the formation of NHBrCl from reaction between HOBr
and NH <sub>2</sub> Cl for 10 min
Figure A-1-4. Variation of $[NHBrCl]_{max}/[NH_2Cl]_0$ depending on the pH and $[NH_2Cl]_0$
from 0.125 to 1.25 mM with [Br <sup>-</sup> ] =5 mM (ratio 0.025 to 0.25)
Figure A-1-5. Modelling of oxidants for all experimental conditions used in this study.

Figure A-1-6. Percentage of NHBrCl remaining in solution for different pH	I after 30
min	116
Figure A-1-7. Bromochloramine decomposition at different pHs.	117

Figure A-2-1. Representative MIMS response for chloramines and bromamines
standards. (a) NH <sub>2</sub> Cl, (b) NHCl <sub>2</sub> , (c) NH <sub>2</sub> Br, (d) NHBr <sub>2</sub> 121
Figure A-2-2. Comparison of direct UV measurements ( $\epsilon_{NHBrCl,320nm}$ = 304 M <sup>-1</sup> cm <sup>-1</sup> )
and MIMS response (m/z 131) for determination of NHBrCl at different experimental
conditions and days
Figure A-2-3. Speciation of halamines during in-line chloramination
Figure A-2-4. Speciation of halamines during pre-formed chloramination

Figure A-3-1. NH<sub>2</sub>Cl decomposition and NHCl<sub>2</sub> formation at (a) pH 8 and (b) pH 6.5 Figure A-3-2. Released soluble copper determined by AAS under different CuO Figure A-3-3. Effect of CuO on NHCl<sub>2</sub> decomposition during the reaction of NH<sub>2</sub>Cl Figure A-3-4. Model prediction of total oxidant and NHBrCl for NH<sub>2</sub>Cl decomposition in the presence of different bromide concentrations. (a) Total oxidant decay in the presence of 0.05 g/L CuO determined by the experiments (solid symbols) and total oxidant decay in the absence of CuO determined by the modelling (dashed Figure A-3-5. Pseudo first order kinetic model for the total oxidant decomposition Figure A-3-6. Model predictions for the kinetic of the total oxidant and the different halamines in the presence of NH<sub>2</sub>Cl and bromide at different pHs. (a) The total oxidant decay determined by experiment and modelling; (b) NHBrCl formation (modelling); 

Figure A-4-4. Effect of pH on bromamines speciation during its self-decomposition
determined by UV scan. (a) monobromamine decomposition as a function of time, (b)
dibromamine decomposition as a function of time130
Figure A-4-5. Pseudo-first-order linearisation for total bromamine decomposition at
different Cu(II) concentration
Figure A-4-6. Effect of pH on total bromamine decomposition (a) without Cu(II), and
(b) with Cu(II)
Figure A-4-7. Pseudo-first order linearisation for total bromamine decomposition at
different pHs in the presence and absence of Cu(II)133
Figure A-4-8. MIMS response for total bromamine decomposition products in the
presence of different Cu(II) concentration. (a) ${}^{15}N_2O$ (m/z 46); (b) ${}^{15}NO_2$ (m/z 47).
Figure A-4-9. Cu 2p XPS spectra of CuCl <sub>2</sub> standard and copper particles from the
bromamine reaction

Figure A-5-1. Calibration curve for ${}^{15}N_2$ (m/z 30) analysis by GC/MS 135
Figure A-5-2. Calibration curve for ${}^{14}N_2O$ (m/z 44) analysis by MIMS 136
Figure A-5-3. Effect of Cu(II) concentration on NHCl <sub>2</sub> formation and decomposition
determined by MIMS136
Figure A-5-4. Model prediction for the effect of bromide concentration on the
different halamines formation in the presence of NH <sub>2</sub> Cl. (a) NH <sub>2</sub> Cl; (b) NHCl <sub>2</sub> ; (c)
NHBrCl
Figure A-5-5. Pseudo first order kinetic model for total oxidant decomposition with
different bromide concentration138
Figure A-5-6. Model prediction for the effect of pH on the different halamines
formation in the presence of bromide. (a) NH <sub>2</sub> Cl; (b) NHCl <sub>2</sub> ; (c) NHBrCl139
Figure A-5-7. Cu 2p XPS spectra of CuCl <sub>2</sub> standard and copper particles obtained
from the reaction

Figure A-6-1. Residual oxidant after 72 h chloramination of nine differen	t model
compounds under different experimental conditions	142
Figure A-6-2. Effect of Cu(II) concentration on the residual oxidant decay	<sup>,</sup> during
chloramination of HQ and PHBA.	142

Figure	A-6-3.	Effect	of	reaction	time	on	the	residual	oxidant	decay	during
chloram	ination	of HQ a	nd F	РНВА	•••••	•••••		•••••			143
Figure	<b>A-6-4.</b> ]	Effect o	of C	u(II) cond	centrat	ion	on tł	ne residua	al oxidan	t decay	during
chloram	ination	of NOM	I	•••••	•••••	•••••		•••••			144
Figure	<b>A-6-5.</b> I	Effect of	f bro	omide cor	ncentra	ation	on t	he residu	al oxidan	t decay	during
chloram	ination	of NOM	I		•••••	•••••					144
Figure	<b>A-6-6.</b> E	affect of	Cu(	II) on the	BSF v	varia	tion	of (a) THI	Ms and (b	) HANs	during
chloram	ination	of NOM	I								145

## **List of Tables**

<b>Table 3-1.</b> LOD and LOQ for chloramines, bromamines and bromochloramine 34
Table A-2-1. Main water quality parameters    118
Table A-2-2. Fragmentation of the different halamines in the mass spectrometer . 118
<b>Table A-2-3.</b> Reproducibility of chloramines and bromamines       120
<b>Table A-4-1.</b> Molar percent recoveries of the different nitrogen species
<b>Table A-5-1.</b> Molar percent recoveries of the different nitrogen species
Table A-6-1. Physicochemical properties of model compounds

# List of Abbreviations

Asp	Aspartic acid
BCAN	Bromochloroacetonitrile
Br-DBPs	Brominated disinfection by-products
Br-HANs	Brominated-HANs
Br-THMs	Brominated-THMs
BSF	Bromine substitution factor
CA	Citric acid
C-DBPs	Carbonaceous disinfection by-products
Cl-DBPs	Chlorinated disinfection by-products
Cl-THMs	Chlorinated-THMs
$CuCl_2 \cdot 2H_2O$	Cupric chloride dihydrate
CuO	Copper oxide
Cys	Cysteine
DBAN	Dibromoacetonitrile
DBCM	Dibromochloromethane
DBPs	Disinfection by-products
DCAcAm	Dichloroacetamide
DCAN	Dichloroacetonitrile
DCBM	Dichlorobromomethane
DOC	Dissolved organic carbon
DPD	N,N-diethyl-p-phenylenediamine
ECD	Electron capture detector
GC/MS	Gas Chromatography/Mass Spectrometry
Gly	Glycine
HA	Humic acid
HAAs	Haloacetic acid
HAcAms	Haloacetamides
HANs	Haloacetonitriles
His	Histidine
HOBr	Hypobromous acid
HQ	Hydroquinone

IC	Ion Chromatography
KBr	Potassium bromide
LOD	Limit of detection
LOQ	Limit of quantification
m/z	Mass to charge ratio
MBAN	Monobromoacetonitrile
MCAN	monochloroacetonitrile
MIMS	Membrane introduction mass spectrometry
N-DBPs	Nitrogenous disinfection by-products
NH <sub>2</sub> Br	Monobromamine
NH <sub>2</sub> Cl	Monochloramine
NHBr <sub>2</sub>	Dibromamine
NHBr <sub>3</sub>	Tribromamine
NHBrCl	Bromochloramine
NHCl <sub>2</sub>	Dichloramine
NHCl <sub>3</sub>	Trichloramine
NiO	Nickel oxide
NOM	Natural organic matter
PHBA	P-hydroxybenzoic acid
PhOH	Phenol
RC	Resorcinol
TBM	Bromoform
TCAN	Trichloroacetonitrile
TCM	Chloroform
THMs	Trihalomethanes
TN	Total nitrogen
TOBr	Total organic bromine
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
XPS	X-Ray Photoelectron Spectroscopy

# List of Publications and Presentations Arising from this Thesis

#### Peer-reviewed journal articles

Allard, S., **Hu, W.**, Le Menn, J. B., Cadee, K., Gallard, H., & Croué, J. P. (2018). Method Development for Quantification of Bromochloramine Using Membrane Introduction Mass Spectrometry. *Environmental Science & Technology*, 52(14), 7805-7812.

**Hu, W.**, Lauritsen, F. R., & Allard, S. Identification and Quantification of Chloramines, Bromamines and Bromochloramine by Membrane Introduction Mass Spectrometry (MIMS). (submitted to *Science of the Total Environment*)

Hu, W., Croué, J. P., & Allard, S. Effect of Copper Oxide on Monochloramine Decomposition in Bromide-containing Waters. (submitted to *Science of the Total Environment*)

**Hu, W.**, Lee, Y., & Allard, S. Mechanistic Investigation of Bromamines Decomposition in the Presence of Cu(II). (to be submitted to *Environmental Science* & *Technology*)

**Hu, W.**, & Allard, S. Effect of Cu(II) on Monochloramine Stability in Bromide-Containing Waters. (to be submitted to *Environmental Science & Technology*)

**Hu, W.**, Liu, C., Allard, S., Croué, J. P., & Karanfil, T. Effect of Cu(II) on Disinfection Byproducts Formation during Chloramination. (to be submitted to *Chemosphere*)

#### **Oral presentations**

**Hu, W.**, Allard, S., & Croue, J. P. Mechanistic Investigation of Bromamines Decomposition in the Presence of Cu (II). 257th ACS National Meeting and Exposition, March 2019, Orlando, Florida, USA.

Lauritsen, F. R., **Hu, W.**, & Allard, S. On-site Applications of MIMS and the Importance of Interface Design as Exemplified by Highly Unusual "Fragments" in MIMS Mass Spectra of Chloramines and Bromamines. Workshop on Harsh-Environment Mass Spectrometry (HEMS), September 2019, Myrtle Beach, South Carolina, USA.

#### **Poster presentations**

**Hu, W.**, Allard, S., & Croue, J. P. Effect of Cu(II) on Monochloramine Stability in Bromide-Containing Waters. Gordon Research Conference on Drinking Water Disinfection Byproducts, July 2017, Mount Holyoke College, South Hadley, MA, USA.

**Hu, W.**, Allard, S., & Croue, J. P. Mechanistic Investigation of Bromamines Decomposition in the Presence of Cu(II). What's in Our Water Symposium (WIOW), October 2018, Canberra, Australia.

# **Chapter 1. Thesis Overview**

This thesis consists of 7 chapters. Chapter 1 gives the overview of this thesis. Chapters 2 to 7 present the results of different research topics (one published peer-reviewed articles and five manuscripts to be submitted to peer-reviewed journals). Supporting information for all of the journal articles are presented sequentially in Appendix 1 to 6. Publisher permission for the including published article in this thesis is attached as Appendix 7.

Chapter 2 presents the method to quantify bromochloramine (NHBrCl) using Membrane Introduction Mass Spectrometry (MIMS). This method allows the accurate quantification of NHBrCl without interference by monitoring the MIMS signal at m/z 131, corresponding to the mass of NHBrCl molecular ion. This work was published in Environmental Science & Technology: "Allard, S., Hu, W., Le Menn, J. B., Cadee, K., Gallard, H., & Croué, J. P. (2018). Method development for quantification of bromochloramine using membrane introduction mass spectrometry. Environmental Science & Technology, 52(14), 7805-7812".

Chapter 3 further develops the MIMS method to differentiate and quantify all the halamines (NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br, NHBr<sub>2</sub> and NHBrCl) present in drinking water during chloramination. This method will help understand the kinetics of the different halamines in real scenarios. This chapter was recently submitted to Science of the Total Environment for peer-review.

Chapter 4 investigates the effect of CuO on monochloramine decomposition in bromide-containing waters. This study follows the kinetics of the total oxidant and the different halamines in presence/absence of CuO. This chapter was recently submitted to Science of the Total Environment for peer-review.

Chapter 5 is a kinetic and mechanistic study on bromamines decomposition in the presence of Cu(II). This work experimentally identified bromamines decomposition products in presence/absence of Cu(II) for the first time. This chapter will be submitted to Environmental Science & Technology soon for peer-review.

Chapter 6 investigates the kinetic of monochloramine decay in bromide containing waters in presence/absence of Cu(II) and proposes a mechanism involving NHBrCl decomposition. This chapter will be submitted to Environmental Science & Technology soon for peer-review.

Chapter 7 presents the formation of disinfection byproducts from chloramination of model compounds and natural organic matter in the presence of Cu(II). The mechanism for Cu(II) induced DBPs formation during chloramination were described. This chapter will be submitted to Chemosphere soon.

# Chapter 2. Method Development for Quantification of Bromochloramine Using Membrane Introduction Mass Spectrometry

Sébastien Allard, Wei Hu, Jean-Baptiste Le Menn, Keith Cadee, Hervé Gallard and Jean-Philippe Croué

Environmental Science & Technology, 2018, 52(14): 7805-7812. DOI: https://doi.org/10.1021/acs.est.8b00889

#### Statement of Contribution to Co-authored Published Paper

This Chapter includes the co-authored paper 'Method development for quantification of bromochloramine using membrane introduction mass spectrometry', published in Environmental science & technology. The bibliographic details of the co-authored paper, including all authors are:

Allard, S., Hu, W., Le Menn, J. B., Cadee, K., Gallard, H., & Croué, J. P. (2018). Method development for quantification of bromochloramine using membrane introduction mass spectrometry. Environmental science & technology, 52(14), 7805-7812.

I, Wei Hu, contributed to the paper by conducting part of the laboratory work and data analysis, including creating figures and tables, and writing and editing the manuscript.

I, as a Co-Author, endorsed that this level of contribution by the candidate indicated above is appropriate.

<u>Sébastien Allard</u> Jean-Baptiste Le Menn <u>Keith Cadee</u> <u>Hervé Gallard</u> Jean-Philippe Croué

#### **2.1 Introduction**

Monochloramine (NH<sub>2</sub>Cl) is an alternative to the use of chlorine for the disinfection of drinking water (Sedlak and von Gunten 2011). Monochloramine is a more stable compound than chlorine in the presence of natural organic matter (NOM) which enables the residual disinfectant to persist over longer distances. Monochloramine is produced by the reaction between ammonia and chlorine (Jafvert and Valentine 1992, Weil and Morris 1949). In the presence of bromide, many halamines can form from reactions between chlorine, bromide, and ammonia, i.e., chloramines (NHCl<sub>2</sub>, NH<sub>2</sub>Cl), bromamines (NH<sub>2</sub>Br, NHBr<sub>2</sub>), and bromochloramine (NHBrCl) (Galal-Gorchev and Morris 1965, Gazda et al. 1993, Gazda and Margerum 1994, Inman and Johnson 1984, Wajon and Morris 1982).

In the literature, different models have been developed to predict the formation and stability of inorganic chloramines depending on the main water quality parameters (pH, temperature, ionic strength, concentration of inorganic compounds) (Jafvert and Valentine 1992, Vikesland et al. 2001). Kinetic models have also been developed to simulate the kinetics of formation and decomposition of inorganic bromamines and bromochloramine (Lei et al. 2004, Luh and Mariñas 2014, Vikesland et al. 2001). A recent study modeled the behavior of the different halamines species for preformed (injection of NH<sub>2</sub>Cl) and in-line (prechlorination followed by ammonia) chloramination of iodide/bromide containing waters in the absence of organic matter (Allard et al. 2018). During in-line chloramination, chlorine reacts with bromide to form hypobromous acid (HOBr) which in turn may react with natural organic matter by electrophilic substitution or redox reactions (Criquet et al. 2015). Once ammonia is added, bromine either is already trapped as total organic bromine (TOBr) (Langsa et al. 2017, Tan et al. 2016) or reacts with ammonia and NH<sub>2</sub>Cl to form brominated amines (Galal-Gorchev and Morris 1965, Gazda and Margerum 1994, Wajon and Morris 1982). It was demonstrated that, at pH 7-8 commonly found in drinking water and in the absence of NOM, NHBrCl accumulated during the first day and was the main brominated amine present (Allard et al. 2018).

It has been shown that bromamines are more reactive than chloramines with acetic acid, phenolic compounds, and NOM (Duirk and Valentine 2007, Heeb et al. 2017, Pope and Speitel Jr 2008). As an undesired side effect, the reaction of HOBr and

brominated amines with NOM may lead to the formation of disinfection by-products (DBPs) (Langsa et al. 2017, Le Roux et al. 2012, Lei et al. 2006, Tan et al. 2016). Moreover, the relative abundance of chloramines, bromamines, and bromochloramine can strongly affect the stability of the oxidant residual required to deliver safe and healthy drinking water (Allard et al. 2018). Despite its potential role in DBPs formation, the quantification of NHBrCl is challenging and this impedes mechanistic studies.

The presence of bromochloramine was discovered by Trofe et al. from the absorbance spectrum of an ether extract of a bromide-containing monochloramine solution (Trofe et al. 1980). NHBrCl exhibits a strong absorption peak at 220 nm and a weak peak at 320 nm. In this work, the molar absorptivity of NHBrCl was estimated to be 2100 M<sup>-</sup> <sup>1</sup>cm<sup>-1</sup> at 220 nm on the basis of the comparison with the aqueous spectrum of NHCl<sub>2</sub> and NHBr<sub>2</sub>, which exhibits a peak at 206 nm with a molar absorptivity of 2100 M<sup>-1</sup>cm<sup>-</sup> <sup>1</sup> and a peak near 232 nm with a molar absorptivity of approximately 1900 M<sup>-1</sup>cm<sup>-1</sup>, respectively. As NH<sub>2</sub>Cl also absorbs at 220 nm, the weak peak (320 nm) of NHBrCl is commonly used for quantification. On the basis of the molar absorptivity ( $\varepsilon_{\text{NHBrCl}} =$ 2100 M<sup>-1</sup>cm<sup>-1</sup> at 220 nm) and an aqueous HPLC/diode array spectrum of NHBrCl, Gazda determined  $\varepsilon_{\text{NHBrCl}} = 170 \text{ M}^{-1} \text{cm}^{-1}$  at 300 and 340 nm for the weak peak of NHBrCl (Gazda 1996). A value of 195 M<sup>-1</sup>cm<sup>-1</sup> at 320 nm was derived from this study and used by Luh and Mariñas (Luh and Mariñas 2014) to develop their kinetic model. Valentine estimated a different value of  $\varepsilon_{NHBrCl} = 300 \text{ M}^{-1}\text{cm}^{-1}$  at 320 nm also on the basis of the comparison with the aqueous spectrum of NHCl<sub>2</sub> and NHBr<sub>2</sub> but using another weak peak at 294 nm with a molar absorptivity of 276 M<sup>-1</sup>cm<sup>-1</sup> for NHCl<sub>2</sub> and a weak peak near 350 nm with a molar absorptivity of approximately 325 M<sup>-1</sup>cm<sup>-1</sup> for NHBr<sub>2</sub> (Valentine 1986). This difference may lead to discrepancies in terms of kinetic modeling and the further study of the impact of NHBrCl on DBP formation.

The main issue for its quantification is that it is not possible to synthesize a pure NHBrCl solution. NHBrCl is always present in a mixture with some other halamine species, and it is not stable. Therefore, most research on NHBrCl has been performed by subtracting the NH<sub>2</sub>Cl concentration from the total oxidant concentration (Pope 2006) or by solving the simultaneous equation of Beer's law since other halamines are absorbing in the same range of wavelengths (Luh and Mariñas 2014). Moreover, UV

spectrometry is not suitable for low concentration as the molar extinction coefficient is low and cannot be used for real samples due to interferences with the water matrix and other oxidants. Membrane introduction mass spectrometry (MIMS) has previously been used to confirm the presence of NHBrCl (Gazda et al. 1993, Pope and Speitel Jr 2008). MIMS is composed of a semipermeable membrane that acts as an interface between a liquid or gas sample and a mass spectrometer. This analytical device enables unstable analytes to be identified by their mass-to-charge ratio. In this study, different analytical methods were used and compared to quantify NHBrCl and a novel method allowing the quantification of NHBrCl by MIMS to be developed. The three main research objectives were to (1) find the optimal conditions for preparation of NHBrCl such that interferences from HOBr and other halamines formed are minimized; (2) determine the molar absorptivity of NHBrCl by comparing direct UV measurements with an HPLC-UV method based on the derivatization of NHBrCl into 2,4,6tribromophenol; (3) compare the direct UV measurements to the MIMS signal at m/z 131 to establish a calibration curve for MIMS.

#### 2.2 Materials and Methods

#### 2.2.1 Reagents

All solutions were prepared in ultrapure water (18.2 M $\Omega$ .cm) supplied by an Elga water purification system, and all chemicals were of the highest purity grade (AR grade  $\geq$ 99%).

NH<sub>2</sub>Cl was prepared by dropwise addition of an equal volume of a sodium hypochlorite solution to an ammonium sulfate solution at pH 8 (Cl<sub>2</sub>/N weight ratio = 4:1; molar ratio = 0.79:1) (Allard et al. 2018). The solutions were buffered with 10 mM phosphate and chilled in an ice bath under continuous stirring to avoid the formation of dichloramine. NHBrCl solutions were prepared under various experimental conditions as described in the Results and Discussion section. The variables studied included initial monochloramine concentration (0.2-2 mM), bromide ion concentration (0.5-5 mM), pH (5.0-6.2), and the total concentration of phosphate (10-50 mM).

#### 2.2.2 Analytical Methods

Four analytical methods were evaluated in parallel (direct UV measurements, DPD (N,N-diethyl-p-phenylenediamine), HPLC-UV, MIMS) for the determination of NHBrCl and NH<sub>2</sub>Cl.

#### 2.2.2.1 Direct UV Measurements

NH<sub>2</sub>Cl and NHBrCl concentrations were measured by UV spectrophotometry using a Shimadzu UV Pharmaspec 1700 spectrophotometer with a 1 cm path length cuvette. The concentrations of monochloramine and bromochloramine were determined by solving the simultaneous equations of Beer's law using four molar extinction coefficients at 243 and 320 nm ( $\epsilon_{NH_2Cl,243} = 461 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\epsilon_{NHBrCl,243} = 500 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\epsilon_{NH_2Cl,320} = 7 \text{ M}^{-1}\text{cm}^{-1}$ , and  $\epsilon_{NHBrCl,320} = 195 \text{ M}^{-1}\text{cm}^{-1}$  or 300 M<sup>-1</sup>cm<sup>-1</sup>) (Kumar et al. 1986, Luh and Mariñas 2014, Valentine 1986).

#### 2.2.2.2 DPD Method

The concentrations of NH<sub>2</sub>Cl and NHBrCl were measured with the DPD colorimetric method with or without addition of KI, respectively (APHA 1998, Valentine 1986).

#### 2.2.2.3 HPLC-UV

For NHBrCl measurements, solutions were quenched with 2,4-dibromophenol and analyzed as 2,4,6-tribromophenol by HPLC-UV (Wefer-Roehl et al. 2001). 2,4-Dibromophenol (100 mM) was added in a large excess (at least 100 times the initial concentration of  $NH_2Cl$ ) to the sample to form 2,4,6-tribromophenol by reaction with NHBrCl. The samples were

vigorously shaken for 10 s before the oxidant residual was quenched by a slight excess of sodium thiosulfate  $(1.5[NH_2Cl]_0)$ . NHBrCl was then analyzed as 2,4,6tribromophenol by HPLC-UV assuming a 100% conversion yield, as has been demonstrated for the reactions of HOBr and HOI with phenolic compounds (Gallard et al. 2009, Shah et al. 2015). The HPLC separation was undertaken on an Agilent 1100 series with an Alltima C18 5 µm column and an eluent consisting of 55% acetonitrile, 44.9% water, and 0.1% acetic acid. The UV detection at 280 nm yielded a detection limit of 0.2 µg Br/L with a precision of 2%.

#### 2.2.2.4 Membrane Introduction Mass Spectrometry

MIMS measurements were performed with a MIMS 2000 (Microlab, Aarhus, Denmark). For NHBrCl and NH<sub>2</sub>Cl analysis with MIMS, the membrane inlet temperature was set to 65°C, and the sample flow rate, to 2.8 mL min<sup>-1</sup>. The cathode voltage was set to -70 V, and the emission current to 1.5 mA. The mass to charge ratios m/z of the molecular ion m/z 131 and m/z 53 were used to quantify NHBrCl and NH<sub>2</sub>Cl, respectively. m/z 131 corresponds to the molecular ion of two isotopes (NH<sup>79</sup>Br<sup>37</sup>Cl and NH<sup>81</sup>Br<sup>35</sup>Cl) which gave the highest MS signal compared to m/z 129 (NH<sup>79</sup>Br<sup>35</sup>Cl) and m/z 133 (NH<sup>81</sup>Br<sup>37</sup>Cl) (Figure A-1-1). The signals corresponding to the fragmentation of NHBrCl were not used to avoid interferences from other halamines present in solution. The membrane of the MIMS was first conditioned using a NH<sub>2</sub>Cl solution at the desired concentration for 10 min; thereafter, a concentrated bromide solution was spiked into the 250 mL beaker containing the NH<sub>2</sub>Cl solution.

#### 2.2.3 Kinetic Modeling

Modeling was performed using the Kintecus software (Ianni 2008). The model developed by Luh and Mariñas (Luh and Mariñas 2014) and modified by Allard et al. (Allard et al. 2018) was used in this study. The model was used to simulate different experimental conditions including bromine concentration (50-300  $\mu$ M), bromide ion concentration (0.5-5 mM), initial monochloramine concentration (0.05-5 mM), and pH (5-8).

#### 2.3 Results and Discussion

# 2.3.1 Optimization of Experimental Conditions for Minimizing/Controlling the Presence of Other Halogenated Oxidants by Kinetic Modeling

The kinetic model developed by Luh and Mariñas (Luh and Mariñas 2014) was first used to determine the optimal experimental conditions to prepare a solution containing NHBrCl with low concentrations of other oxidants, i.e., the different halamines and HOBr. The presence of any halogenated oxidants might interfere with DPD and/or direct UV measurements, while the presence of brominated oxidants might interfere with HPLC-UV measurements. Different parameters were tested, i.e., pH, concentration of reactants and buffer, ionic strength, and temperature to determine the

optimum conditions. A preliminary study was conducted where the formation of NHBrCl from the reaction of an equimolar concentration of HOBr and NH<sub>2</sub>Cl was modelled (Figures A-1-2 and A-1-3). This reaction leads to an immediate formation of NHBrCl with 100% conversion. However, the degradation of NHBrCl leads to a recycling of a considerable amount of HOBr back into solution (10% of the initial NHBrCl concentration for pH 7 (Figure A-1-2)). This approach is therefore not suitable for the measurement of NHBrCl by the HPLC-UV method which involved quenching with 2,4-dibromophenol and formation of 2,4,6-tribromophenol since it is not possible to differentiate between 2,4,6-tribromophenol formed from reaction with HOBr or NHBrCl or other brominated amines. HOBr is very reactive toward phenolic groups compared to HOCl, chloramines, bromamines, and bromochloramine (Heeb et al. 2014, Heeb et al. 2017). Therefore, the synthesis of NHBrCl was carried out with NH<sub>2</sub>Cl and Br<sup>-</sup>. Small differences in the oxidant species were observed for different ionic strengths and temperatures. However, the pH and the initial concentration of NH<sub>2</sub>Cl ([NH<sub>2</sub>Cl]<sub>0</sub>) and bromide ion ([Br<sup>-</sup>]<sub>0</sub>) have significant effects on the formation and decomposition of bromochloramine (Figure A-1-4). For all the data presented in this paper, i.e., experiments carried out with 0.2-5 mM [NH<sub>2</sub>Cl]<sub>0</sub>, 0.5-5 mM [Br<sup>-</sup>]<sub>0</sub>, and pH 5.0-6.2, the kinetic model was used to ensure that the concentrations of HOBr, NH<sub>2</sub>Br, and NHBr<sub>2</sub> were negligible and would not lead to interferences during HPLC-UV measurements (an example is given in Figure 2-1 and Figure A-1-5 shows output from the model for all the experimental conditions). Since the HOBr, NH<sub>2</sub>Br, and NHBr<sub>2</sub> concentrations are several orders of magnitude lower than the NHBrCl concentration (Figure 2-1 and Figure A-1-5), the contribution of these oxidants to the formation of 2,4,6-tribromophenol during HPLC-UV measurement and to the DPD measurement will be negligible. NH<sub>2</sub>Cl will not affect HPLC-UV measurements but might affect direct UV measurements if NH<sub>2</sub>Cl is present at high concentration compared to NHBrCl by overlapping the signal of NHBrCl at 320 nm. Considering that NH<sub>2</sub>Cl slightly absorbed at 320 nm ( $\epsilon_{NH_2Cl,320} = 7 \text{ M}^{-1}\text{cm}^{-1}$ ), a small interference is expected only at the very beginning of the experiment when virtually no NHBrCl is formed and a high amount of NH<sub>2</sub>Cl is present. Actually, the first minutes of the reaction could not be used for MIMS calibration of NHBrCl because it corresponds to the time response of our MIMS setup, i.e., the time for the solution to reach the membrane and therefore the mass spectrometer from the beaker where the reaction between NH<sub>2</sub>Cl and Br<sup>-</sup> was initiated.



**Figure 2-1.** Variation of NHBrCl, NH<sub>2</sub>Cl, NH<sub>2</sub>Br, NHBr<sub>2</sub>, and HOBr concentrations. Model of Luh and Mariñas (Luh and Mariñas 2014) was used with  $[Br^-]_0 = [NH_2Cl]_0 = 5 \text{ mM}$  at pH 6 and 10 mM phosphate buffer.

The model was then used to investigate if it was possible to stabilize NHBrCl by changing the pH once NHBrCl reached its maximum concentration at pH 6. Figure A-1-6 shows the comparison of the NHBrCl remaining at different pH values after 30 min compared to the maximum bromochloramine concentration. The optimal pH to stabilize the solution of NHBrCl is 7-8 (Figure A-1-6). However, only 8% of the initial concentration of NHBrCl remains after 30 min at pH 7 (Figure A-1-7). Moreover, the bromochloramine decomposition is significant during the first few minutes even at the optimal pH (Figure A-1-7). After 5 min, only 25% of the initial concentration was still present in the solution, which highlights the high instability of this oxidant. Therefore, we concluded that stabilizing the NHBrCl solution through pH of the solution was not effective.

#### 2.3.2 Comparison of Direct UV Measurements, MIMS Signal, and Modeling Results for NH<sub>2</sub>Cl and NHBrCl

Figure 2-2 shows a comparison of direct UV measurements and MIMS experimental results with output from the model for monochloramine and bromochloramine kinetics. This experiment was conducted at pH 6 using experimental conditions similar to Luh and Mariñas (Luh and Mariñas 2014) to enable comparison with their results.



**Figure 2-2.** Comparison of monochloramine (top) and bromochloramine (bottom) kinetics based on modeling with direct UV measurements and MIMS signal. Two experimental conditions were tested:  $[NH_2Cl]_0 = 0.2 \text{ mM}$ , phosphate buffer = 10 mM,  $T = 23.7^{\circ}C$ , pH 6, and  $[Br^-]_0 = 2$  and 4 mM. Symbols represent direct UV experimental data; lines represent MIMS data, and dotted lines represent the model predicted concentration profiles.  $\varepsilon_{NHBrCl,320} = 195 \text{ M}^{-1}\text{cm}^{-1}$ , similar to Luh and Mariñas (Luh and Mariñas 2014), was used for quantification of NHBrCl. MIMS signal is presented in amperes which represent the intensity of ion current for m/z = 131. For information about NH<sub>2</sub>Cl and NHBrCl quantification by direct UV, please refer to the Materials and Methods section.

As predicted by the model, results from direct UV measurements for 2 and 4 mM bromide showed that NH<sub>2</sub>Cl concentration rapidly decreased while bromochloramine is formed in the first 10 to 20 min and then decreased. The discrepancies observed for the concentration of bromochloramine between the model and the direct UV measurements are similar to results published by Luh and Mariñas (Luh and Mariñas 2014). The trends of NHBrCl formation and decomposition obtained with the MIMS were comparable to the direct UV measurements even though these results are not quantitative. However, the monochloramine profile obtained with the MIMS was different from the UV signal and the predicted concentration by the model. The "bump" observed for the MIMS response at m/z = 53 (Figure 2-2 (top)) was identified as an
NHBrCl interference. We hypothesized that NHBrCl was fragmented to NHCl, protonated in the mass spectrometer, and generated a signal at m/z ratio corresponding to NH<sub>2</sub>Cl. This result highlights the need to use the mass of the molecular ion and not a fragment for detection of NHBrCl to avoid interferences coming from other halamines with similar molecular structures or a surface catalyzed reaction in the vacuum system (Hansen et al. 1996).

# 2.3.3 Comparison of Direct UV Measurements, DPD, and HPLC-UV Method for Quantification of NHBrCl

According to Valentine (Valentine 1986), the reaction of NHBrCl with the DPD is instantaneous. Therefore, it is possible to discriminate NHBrCl from NH<sub>2</sub>Cl since the latter only slowly reacts with DPD in the absence of iodide. Figure 2-3 shows a good agreement between the direct UV measurements and the DPD measurements for NH<sub>2</sub>Cl. However, even though a similar pattern is observed, a large difference is observed for NHBrCl with a much higher concentration measured by using direct UV measurements compared to the DPD method.



**Figure 2-3.** Comparison of direct UV measurements and DPD methods for monochloramine and bromochloramine measurements. Crossed hexagons are DPD measurements, and black circles are UV measurements.  $[NH_2Cl]_0 = 0.2 \text{ mM}$ ,  $[Br^-]_0 = 2 \text{ mM}$ , 10 mM phosphate buffer, pH 6.  $\varepsilon_{NHBrCl,320} = 195 \text{ M}^{-1}\text{cm}^{-1}$ , similar to Luh and Mariñas (Luh and Mariñas 2014), was used for quantification of NHBrCl.

Therefore, another analytical method was tested to compare the direct UV measurement method to the DPD method. Valentine (Valentine 1986) and Gazda et al. (Gazda et al. 1993) showed that the bromine atom of NHBrCl is very labile and reactive. Considering this, another method was developed to indirectly quantify bromochloramine by reacting NHBrCl with 2,4-dibromophenol which leads to the formation of 2,4,6-tribromophenol. It was verified that the chlorine atom was not reacting by electrophilic substitution as no peaks corresponding to the 2,4-dibromo-6-chlorophenol was detected by HPLC-UV. The experimental procedure for quantification of NHBrCl by HPLC-UV was used for various experimental conditions (Br<sup>-</sup> and NH<sub>2</sub>Cl concentrations).

Figure 2-4 shows the comparison of results obtained with direct UV measurements and HPLC-UV to quantify NHBrCl.



**Figure 2-4.** Comparison between 2,4,6-tribromophenol formation and NHBrCl concentration determined by direct UV measurements (using  $\varepsilon_{\text{NHBrCl},320} = 195$  and 320 M<sup>-1</sup>cm<sup>-1</sup>) for various conditions at pH 6 (C<sub>T,PO4</sub> = phosphate buffer concentration).

The shape of 2,4,6-tribromophenol formation kinetics is similar to the direct UV response, but a significant difference in concentration is observed for  $\varepsilon_{\text{NHBrCl},320} = 195$  M<sup>-1</sup>cm<sup>-1</sup>. As previously stated, two different molar absorptivity coefficients at 320 nm are reported for NHBrCl in the literature, i.e., 300 and 195 M<sup>-1</sup>cm<sup>-1</sup>. If the concentration of NHBrCl is calculated using  $\varepsilon_{\text{NHBrCl},320} = 300 \text{ M}^{-1}\text{cm}^{-1}$ , both direct UV measurements and HPLC-UV concentrations are almost identical. The concentrations are much higher when calculated with  $\varepsilon_{\text{NHBrCl},320} = 195 \text{ M}^{-1}\text{cm}^{-1}$ . The HPLC-UV method seems to be accurate for measurements of NHBrCl assuming a 100% conversion of NHBrCl to 2,4,6-tribromophenol and negligible concentrations of bromamines and HOBr as predicted by the kinetic model. For contact times >20 min, the differences observed between the 2,4,6-tribromophenol and the direct UV results are due to the reactivity of the other brominated oxidants (e.g., NH<sub>2</sub>Br, NHBr<sub>2</sub>, HOBr)

formed from degradation of NHBrCl leading to formation of additional 2,4,6tribromophenol. In order to estimate the molar extinction coefficient based on our data, the direct UV absorbance at 320 nm was plotted against the concentration of NHBrCl determined by HPLC-UV for reaction time <20 min (Figure 2-5).



**Figure 2-5.** Determination of the molar absorptivity of NHBrCl at 320 nm ( $\varepsilon_{\text{NHBrCl},320}$ ). 66 data points were used.

It was verified that the contribution of NH<sub>2</sub>Cl to the absorbance at 320 nm was negligible in our experimental conditions by using the kinetic model and  $\varepsilon_{\rm NH_2Cl,320} =$  7 M<sup>-1</sup>cm<sup>-1</sup>. Using the Beer-Lambert law and the slope of the linear trend curve (R<sup>2</sup> = 0.95),  $\varepsilon_{\rm NHBrCl,320}$  was found to be 304 M<sup>-1</sup>cm<sup>-1</sup>. This is in agreement with the value from Trofe et al. (Trofe et al. 1980) but significantly differs from 195 M<sup>-1</sup>cm<sup>-1</sup> determined from the work of Gazda and Margerum (Gazda and Margerum 1994) and used by Luh and Mariñas (Luh and Mariñas 2014). Consequently, lower concentrations of NHBrCl are expected compared to the kinetic model developed by Luh and Mariñas (Luh and Mariñas 2014).

# 2.3.4 Calibration of the MIMS for NHBrCl Measurements Using Direct UV Measurements

Figure 2-6 shows a comparison between MIMS signals for bromochloramine (m/z = 131), its concentration calculated by direct UV measurements (using  $\varepsilon_{\text{NHBrCl},320} = 300$  M<sup>-1</sup>cm<sup>-1</sup>), and the prediction based on the kinetic model.



**Figure 2-6.** Comparison between MIMS signals (m/z = 131), bromochloramine concentration determined by direct UV measurements, and modeling for 6 different experimental conditions ( $C_{T,PO4}$  = phosphate buffer concentration). Symbols represent experimental data calculated by direct UV measurements; smooth lines represent the model predicted concentration profiles, and dark lines are signals obtained by MIMS at m/z = 131. The delay observed for the MIMS signal compared to the direct UV measurements corresponds to the response time, i.e., the time that the sample needs to go from the beaker through the membrane and reach the mass spectrometer.

Results from the MIMS analysis and the direct UV measurements showed signals with an identical shape. However, outputs from the model are quite different because  $\varepsilon_{\text{NHBrCl},320} = 195 \text{ M}^{-1}\text{cm}^{-1}$  was used instead of  $\varepsilon_{\text{NHBrCl},320} = 300 \text{ M}^{-1}\text{cm}^{-1}$ . This implies that the 6 rate constants related to the formation of NHBrCl and the 6 rate constants related to its decomposition need to be revisited. Further experimentation is necessary to determine these rate constants and provide an improved kinetic model. The implication of this finding to the overall behavior of the different halamines described in the model might also warrant further investigation.

Figure 2-7 shows 3 different calibrations carried out in 3 different days for different ranges of NHBrCl concentrations (different concentrations of NH<sub>2</sub>Cl and Br<sup>-</sup> and pH). The LOD was calculated as 3 times the standard deviation of the blank ( $s_b$ ), using the standard error of regression of the standard calibration curve ( $s_{y/x}$ ) as an estimate of  $s_b$  (Miller and Miller 2018). The LOD (average of the 3 calibrations) for NHBrCl was found to be 2.9 (±0.3)  $\mu$ M (378  $\mu$ g/L). This is in a similar range to the LOD determined for the NH<sub>2</sub>Cl by MIMS (1.4  $\mu$ M) but higher than the LOD determined for NHCl<sub>2</sub> (0.28  $\mu$ M) (Shang and Blatchley 1999).



**Figure 2-7.** MIMS calibration curves for NHBrCl determined by direct UV measurements at 3 different experimental conditions. MIMS parameters:  $T_{inlet} = 65^{\circ}C$ ; flow rate = 2.8 mL/min; cathode voltage = -70 V; emission current = 1.5 mA.

# **2.4 Implication for Future Research**

A membrane introduction mass spectrometry (MIMS) method for quantification of bromochloramine in aqueous solution was developed on the basis of a calibration using direct UV measurements. The molar absorption coefficient for NHBrCl was determined to be 304 M<sup>-1</sup>cm<sup>-1</sup> by comparing results obtained by quantifying NHBrCl (after quenching with 2,4-dibromophenol) as 2,4,6-tribromophenol to the direct UV response at 320 nm. This value of 304 M<sup>-1</sup>cm<sup>-1</sup> instead of 195 M<sup>-1</sup>cm<sup>-1</sup> used by Luh and Mariñas (Luh and Mariñas 2014) implies that the kinetic model describing the

formation and decomposition of NHBrCl must be partially revised. NHBrCl was directly quantified by direct UV measurements and by the MIMS signal at m/z 131 corresponding to the mass of the molecular ion. On the basis of these calibration curves, a limit of detection of 2.9 µM was determined for NHBrCl with the MIMS. These experiments demonstrated the advantage of MIMS relative to titration in that MIMS was able to unambiguously quantify NHBrCl based on m/z 131 compared to other quantification methods where other halamines can interfere, i.e., overlapping peaks with UV, reaction of several halamines with colorimetric reagents, or phenols used as quenching agents. However, the main limitations of the MIMS method are, in contrast to the titration methods, the cost of the instrument and the expertise needed in mass spectrometry to run the instrument. Under well-defined experimental conditions where HOBr and other brominated oxidants are negligible, the HPLC-UV method might be an attractive alternative to the use of the MIMS since it is much easier to implement and has lower LOD. Overall, MIMS is a powerful device which will enable the determination of rate constants for reaction of NHBrCl with inorganic or organic compounds potentially leading to the formation of toxic DBPs. It will also encourage further mechanistic studies of DBP formations from NHBrCl to be undertaken as the kinetic constants may be derived directly from the online monitoring of the molecular ion, without performing numerous experiments. Once calibrated, the MIMS analytical method is simple and time-saving for NHBrCl quantification. However, the LOD obtained in this study with the MIMS will not allow online monitoring of NHBrCl in real drinking water treatment conditions as the concentrations expected in real systems (<1  $\mu$ M), based on kinetic modeling, are lower than the LOD (Allard et al. 2018).

# 2.5 References

- Allard, S., Cadee, K., Tung, R. and Croué, J.-P. (2018) Impact of brominated amines on monochloramine stability during in-line and pre-formed chloramination assessed by kinetic modelling. Science of the Total Environment 618, 1431-1439.
- APHA (1998) Standard methods for the examination of water and wastewater, 20th ed. American Public Health Association, Washington, DC.
- Criquet, J., Rodriguez, E.M., Allard, S., Wellauer, S., Salhi, E., Joll, C.A. and Von Gunten, U. (2015) Reaction of bromine and chlorine with phenolic compounds and natural organic matter extracts–Electrophilic aromatic substitution and oxidation. Water Research 85, 476-486.
- Duirk, S.E. and Valentine, R.L. (2007) Bromide oxidation and formation of dihaloacetic acids in chloraminated water. Environmental Science & Technology 41(20), 7047-7053.

- Galal-Gorchev, H. and Morris, J.C. (1965) Formation and stability of bromamide, bromimide, and nitrogen tribromide in aqueous solution. Inorganic Chemistry 4(6), 899-905.
- Gallard, H., Allard, S., Nicolau, R., Von Gunten, U. and Croué, J.P. (2009) Formation of iodinated organic compounds by oxidation of iodide-containing waters with manganese dioxide. Environmental Science & Technology 43(18), 7003-7009.
- Gazda, M. (1996) Non-metal redox reactions of chloramines with bromide ion and with bromine and the development and testing of a mixing cell for a new pulsed-accelerated-flow spectrophotometer with position-resolved observation.
- Gazda, M., Dejarme, L.E., Choudhury, T.K., Cooks, R.G. and Margerum, D.W. (1993) Mass-spectrometric evidence for the formation of bromochloramine and Nbromo-N-chloromethylamine in aqueous solution. Environmental Science & Technology 27(3), 557-561.
- Gazda, M. and Margerum, D.W. (1994) Reactions of monochloramine with bromine, tribromide, hypobromous acid and hypobromite: formation of bromochloramines. Inorganic Chemistry 33(1), 118-123.
- Hansen, K., Gylling, S. and Lauritsen, F.R. (1996) Time-and concentration-dependent relative peak intensities observed in electron impact membrane inlet mass spectra. International Journal of Mass Spectrometry and Ion Processes 152(2-3), 143-155.
- Heeb, M.B., Criquet, J., Zimmermann-Steffens, S.G. and Von Gunten, U. (2014) Oxidative treatment of bromide-containing waters: formation of bromine and its reactions with inorganic and organic compounds—a critical review. Water Research 48, 15-42.
- Heeb, M.B., Kristiana, I., Trogolo, D., Arey, J.S. and Von Gunten, U. (2017) Formation and reactivity of inorganic and organic chloramines and bromamines during oxidative water treatment. Water Research 110, 91-101.
- Ianni, J. (2008) Kintecus Version 3.95.
- Inman, G.W. and Johnson, J.D. (1984) Kinetics of monobromamine disproportionation-dibromamine formation in aqueous ammonia solutions. Environmental Science & Technology 18(4), 219-224.
- Jafvert, C.T. and Valentine, R.L. (1992) Reaction scheme for the chlorination of ammoniacal water. Environmental Science & Technology 26(3), 577-586.
- Kumar, K., Day, R.A. and Margerum, D.W. (1986) Atom-transfer redox kinetics: general-acid-assisted oxidation of iodide by chloramines and hypochlorite. Inorganic Chemistry 25(24), 4344-4350.
- Langsa, M., Heitz, A., Joll, C.A., Von Gunten, U. and Allard, S. (2017) Mechanistic aspects of the formation of adsorbable organic bromine during chlorination of bromide-containing synthetic waters. Environmental Science & Technology 51(9), 5146-5155.
- Le Roux, J., Gallard, H. and Croué, J.-P. (2012) Formation of NDMA and halogenated DBPs by chloramination of tertiary amines: the influence of bromide ion. Environmental Science & Technology 46(3), 1581-1589.
- Lei, H., Mariñas, B.J. and Minear, R.A. (2004) Bromamine decomposition kinetics in aqueous solutions. Environmental Science & Technology 38(7), 2111-2119.
- Lei, H., Minear, R.A. and Mariñas, B.J. (2006) Cyanogen bromide formation from the reactions of monobromamine and dibromamine with cyanide ion. Environmental Science & Technology 40(8), 2559-2564.
- Luh, J. and Mariñas, B.J. (2014) Kinetics of bromochloramine formation and decomposition. Environmental Science & Technology 48(5), 2843-2852.

- Miller, J. and Miller, J.C. (2018) Statistics and chemometrics for analytical chemistry, Pearson education.
- Pope, P.G. (2006) Haloacetic acid formation during chloramination: role of environmental conditions, kinetics, and haloamine chemistry.
- Pope, P.G. and Speitel Jr, G.E. (2008), ACS Publications.
- Sedlak, D.L. and von Gunten, U. (2011) The chlorine dilemma. Science 331(6013), 42-43.
- Shah, A.D., Liu, Z.-Q., Salhi, E., Höfer, T. and von Gunten, U. (2015) Peracetic acid oxidation of saline waters in the absence and presence of H2O2: secondary oxidant and disinfection byproduct formation. Environmental Science & Technology 49(3), 1698-1705.
- Shang, C. and Blatchley, E.R. (1999) Differentiation and quantification of free chlorine and inorganic chloramines in aqueous solution by MIMS. Environmental Science & Technology 33(13), 2218-2223.
- Tan, J., Allard, S., Gruchlik, Y., McDonald, S., Joll, C. and Heitz, A. (2016) Impact of bromide on halogen incorporation into organic moieties in chlorinated drinking water treatment and distribution systems. Science of the Total Environment 541, 1572-1580.
- Trofe, T.W., Inman, G.W. and Johnson, J.D. (1980) Kinetics of monochloramine decomposition in the presence of bromide. Environmental Science & Technology 14(5), 544-549.
- Valentine, R.L. (1986) Bromochloramine oxidation of N, N-diethyl-pphenylenediamine in the presence of monochloramine. Environmental Science & Technology 20(2), 166-170.
- Vikesland, P.J., Ozekin, K. and Valentine, R.L. (2001) Monochloramine decay in model and distribution system waters. Water Research 35(7), 1766-1776.
- Wajon, J.E. and Morris, J.C. (1982) Rates of formation of N-bromo amines in aqueous solution. Inorganic Chemistry 21(12), 4258-4263.
- Wefer-Roehl, A., Graber, E., Borisover, M., Adar, E., Nativ, R. and Ronen, Z. (2001) Sorption of organic contaminants in a fractured chalk formation. Chemosphere 44(5), 1121-1130.
- Weil, I. and Morris, J.C. (1949) Kinetic studies on the chloramines. I. The rates of formation of monochloramine, N-chlormethylamine and Nchlordimethylamine. Journal of the American Chemical Society 71(5), 1664-1671.

Every reasonable effort has been made to acknowledge the owners of copyright material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged.

# Chapter 3. Identification and Quantification of Chloramines, Bromamines and Bromochloramine by Membrane Introduction Mass Spectrometry (MIMS)

The contents of Chapter 3 & Appendix 2 are unable to be reproduced here as they are under embargo due to current consideration for publication in the journal *Science of the Total Environment*.

# **3.1 Introduction**

Chloramines (NH<sub>2</sub>Cl, NHCl<sub>2</sub> and NCl<sub>3</sub>), bromamines (NH<sub>2</sub>Br, NHBr<sub>2</sub> and NBr<sub>3</sub>) and bromochloramine (NHBrCl) are widely present in swimming pool, cooling water and drinking water systems (Capuzzo, 1979; Heeb et al., 2017; Johannesson, 1960; Trogolo and Arey, 2016; Weaver et al., 2009). Their concentrations differ depending on the water characteristics, such as pH, chlorine, ammonia and bromide concentration (Allard et al., 2018a; Luh and Mariñas, 2014; Wajon and Morris, 1982; Wolfe et al., 1984). The presence of chlorine and ammonia lead to the formation of  $NH_2Cl$ .  $NH_2Cl$ is usually applied as a secondary disinfectant to maintain a disinfectant residual in long drinking water distribution systems, due to its higher stability than chlorine (Bougeard et al., 2010; Hua and Reckhow, 2007; Vikesland et al., 2001). NHCl<sub>2</sub> can be produced from the disproportionation of NH<sub>2</sub>Cl (Vikesland et al., 2001), and NCl<sub>3</sub> from the reaction between chlorine and NHCl<sub>2</sub> (Jafvert and Valentine, 1992). However, NCl<sub>3</sub> does not form under drinking water conditions, but is formed in pool water from the reaction of urea with chlorine (Blatchley and Cheng, 2010). Bromide is widely present in natural waters with concentrations varying from several  $\mu g/L$  to mg/L (Agus et al., 2009; Soltermann et al., 2016). During chlorination, bromine (HOBr) is formed in the presence of bromide and further reacts with ammonia to produce NH<sub>2</sub>Br (Inman and Johnson, 1984). Also, NH<sub>2</sub>Br can be formed from the reaction between NH<sub>2</sub>Cl and bromide at a much lower rate (Trofe et al., 1980). Similar to the formation of NHCl<sub>2</sub> and NHCl<sub>3</sub>, NH<sub>2</sub>Br disproportionation leads to the formation of NHBr<sub>2</sub>, and NBr<sub>3</sub> can be produced from bromine reacting with NHBr<sub>2</sub> (Inman and Johnson, 1984; Lei et al., 2004). NBr<sub>3</sub> concentration is considered to be negligible in disinfected waters due to the high ammonia to bromine ratio (Hofmann and Andrews, 2001). When bromide is present, NHBrCl can be formed during chloramination and is the main halamine detected in drinking waters (Bousher et al., 1989; Gazda and Margerum, 1994; Luh and Mariñas, 2014; Trofe et al., 1980). Overall, in typical drinking waters, NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br, NHBr<sub>2</sub> and NHBrCl are formed at different rates and extents (Allard et al., 2018a).

These halamines can react with natural organic matter (NOM) to produce disinfection by-products (DBPs) (Heeb et al., 2017). Bromamines are less stable and more reactive than chloramines (Heeb et al., 2017). The presence of bromamines decrease the oxidant residual needed to deliver safe drinking water and lead to the formation of brominated disinfection by-products (Br-DBPs) that are more toxic than Cl-analogues (Allard et al., 2018a; Pope and Speitel, 2008; Simon et al., 2015; Uyak and Toroz, 2007). Therefore, it is important to understand the speciation of halamines during drinking water treatment and determine their concentrations. However, the discrimination and quantification of these halamines are difficult to achieve with traditional methods. Direct UV measurement can separately measure the halamines concentrations in a solution which contains one or two halamines (NH<sub>2</sub>Cl, NHCl<sub>2</sub> or NH<sub>2</sub>Br, NHBr<sub>2</sub>) based on their representative molar absorptivities (Lei et al., 2004; Schreiber and Mitch, 2005). However, it is unable to measure the concentrations of more than two halamines in a mixture due to their neighbouring overlapping spectra. Furthermore, except NH<sub>2</sub>Cl, theses halamines are found in a mixture at a few  $\mu$ g/L or lower concentrations in drinking water. Due to their low molar absorptivity, it is not possible to accurately discriminate/quantify the different halamines by direct UV measurement (Valentine et al., 1986). Overall, direct UV measurement is not suitable to analyse halamines in real water samples. The N,N-diethyl-p-phenylenediamine (DPD) method, the most commonly used method to differentiate combined chlorine and free chlorine, is based on the fact that NH<sub>2</sub>Cl is not able to react by itself with the DPD reagent. Therefore, iodide is added and oxidised to I<sub>2</sub> by NH<sub>2</sub>Cl which is reacting with the DPD reagent (Lee et al., 2007). However, it is not clear which other halamines are able to react directly with the DPD indicator and thus the DPD method cannot be used to differentiate the different halamines (Allard et al., 2018b; Federation and Association, 2005; Scully et al., 1996). The indophenol method is also used to specifically quantify NH<sub>2</sub>Cl (Lee et al., 2007; Ngo et al., 1982). This method is specific to the quantification of NH<sub>2</sub>Cl and the concentration is determined by its absorbance at 655 nm.

Membrane Introduction Mass Spectrometry (MIMS) has been extensively used to monitor chemicals in water, such as in drinking water and swimming pool waters (Bauer and Solyom, 1994; Bocchini et al., 1999; Kristensen et al., 2010; Soltermann et al., 2014; Weaver et al., 2009). MIMS has previously been used to quantify NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NCl<sub>3</sub> and NHBrCl. Shang and Blatchley (1999) used a mass spectrometer combined with a flow through membrane cell and obtained detection limits for NH<sub>2</sub>Cl, NHCl<sub>2</sub> and NCl<sub>3</sub> of 1.41, 0.14 and 0.28  $\mu$ M, respectively (0.1, 0.02, and 0.06 mg/L as

Cl<sub>2</sub>, respectively). The formation of NHBrCl from the reactions of NH<sub>2</sub>Cl with HOBr or bromide was evidenced by using the MIMS (Gazda et al., 1993). Thereafter, NHBrCl was quantified by comparing the MIMS response with the direct UV response and indirectly by measuring 2,4,6-tribromophenol formed by reaction of NHBrCl with 2,4-dibromophenol (Allard et al., 2018b). The detection limit was found to be 2.9  $\mu$ M (412  $\mu$ g/L as Cl<sub>2</sub>) (Allard et al., 2018b). Even though chloramines and NHBrCl have been quantified by MIMS previously, bromamines have not been identified and quantified by MIMS. Bromamines are difficult to quantify because they are not stable in solutions, especially dibromamine (Lei et al., 2004).

The objective of this study was to develop a method allowing for the first time to quantify all halamines (NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br, NHBr<sub>2</sub> and NHBrCl), which are currently present in drinking water systems by using the MIMS. In a first step, different mass spectra information were collected and the best m/z were selected to represent these halamines. In a second step, calibration curves were acquired to determine the halamines concentrations and the limits of detection. Finally, the formation and decomposition of the different halamines were followed in two chloraminated raw waters and one chloraminated seawater.

# **3.2 Materials and Methods**

#### 3.2.1 Reagents and Preparation of Chlorine and Bromine Solutions

Analytical grade chemicals and deionized water (18.2 M $\Omega$ ·cm, Milli-Q, Millipore) were used to prepare all solutions in this study. A sodium hypochlorite solution (10-15% active chlorine) was purchased from Sigma Aldrich and used as the source of chlorine. The concentration of chlorine was determined by a UV-Vis spectrometer (Cary 60, Agilent) at  $\lambda_{max}$  of 292 nm with a molar absorptivity of 362 M<sup>-1</sup>cm<sup>-1</sup> (Nicoson and Margerum, 2002). The hypobromite stock solution was prepared by reacting NaOCl with Br<sup>-</sup> at a molar Br/Cl ratio of 1.05 at pH 11 adjusted by sodium hydroxide (Lei et al., 2004). This solution was stored at 4°C and the concentration was determined by monitoring the absorbance at  $\lambda_{max}$  329 nm ( $\epsilon$ =332 M<sup>-1</sup>cm<sup>-1</sup>) (Liu et al., 2012).

#### 3.2.2 Synthesis of Halamines

NH<sub>2</sub>Cl stock solution was prepared by diluting an ammonium chloride stock solution (chlorine to ammonia molar ratio of 1:1.2) in deionized water adjusted to pH 9 with sodium hydroxide. Thereafter, sodium hypochlorite was added dropwise to a vigorously stirred ammonium chloride solution of equal volume (Le Roux et al., 2016). NHCl<sub>2</sub> stock solution was prepared by adjusting the pH of a NH<sub>2</sub>Cl solution to pH 4.5-5.0 with a 50 mM acetate buffer, the solution was kept in the fridge for more than 4 hours to allow a high conversion of NH<sub>2</sub>Cl to NHCl<sub>2</sub> (Aoki, 1989). NH<sub>2</sub>Br was synthesized by mixing equal volumes of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and HOBr (both prepared in 20 mM pH 10 borate buffer) at a N/Br molar ratio of 1000:1 (Lei et al., 2004). Since NHBr<sub>2</sub> is not stable, it was prepared by introducing equal volumes of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and HOBr (both prepared in 10 mM pH 5 phosphate buffer) at a N/Br molar ratio of 2:1 using a multichannel peristaltic pump. The two solutions were pumped at the same flow rate (1.1 mL/min) and reached a T connection (diameter 3.2 mm) connected to a mixing coil to ensure the solutions were appropriately mixed. The mixing coil was directly connected to the MIMS and the solution reached the MIMS after 20 s of mixing time. According to kinetic modelling (Allard et al., 2018a), the decomposition of NHBr<sub>2</sub> should be negligible (< 2%) during this short time.

NH<sub>2</sub>Cl and NHCl<sub>2</sub> stock concentrations were determined spectrophotometrically from their absorbance at their respective  $\lambda$  by solving simultaneous equations using  $\varepsilon_{\text{NH}_2\text{Cl},245} = 445 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\varepsilon_{\text{NH}_2\text{Cl},295} = 14 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\varepsilon_{\text{NHCl}_2,245} = 208 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\varepsilon_{\text{NHCl}_2,295} = 267 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\varepsilon_{\text{NH}_2\text{Cl},295} = 14 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\varepsilon_{\text{NHCl}_2,245} = 208 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\varepsilon_{\text{NHCl}_2,295} = 267 \text{ M}^{-1}\text{cm}^{-1}$  (Schreiber and Mitch, 2005). NH<sub>2</sub>Br and NHBr<sub>2</sub> stock concentrations were determined similarly by using  $\varepsilon_{\text{NH}_2\text{Br},232} = 82 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\varepsilon_{\text{NH}_2\text{Br},278} = 425 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\varepsilon_{\text{NHBr}_2,232} = 2000 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\varepsilon_{\text{NHBr}_2,278} = 715 \text{ M}^{-1}\text{cm}^{-1}$  (Lei et al., 2004). All the chloramines and bromamines stock solutions were of high purity (> 97%). NHBrCl was produced by reacting NH<sub>2</sub>Cl (200 or 400  $\mu$ M) and bromide (2 or 4 mM) at pH 6 (buffered with 10 mM phosphate). NHBrCl concentration was determined by UV spectrophotometry ( $\varepsilon$ =304 M<sup>-1</sup>cm<sup>-1</sup> at 320 nm) and compared with the MIMS results according to Allard et al. (2018b).

#### 3.2.3 System Optimization

The MIMS was purchased from Mikrolab Aarhus A/S in Denmark. It consists of a flat sheet 0.127 mm thick silicon membrane (Sil-Tec sheeting, Technical Products, Decatur, GA, USA) and a Prisma quadrupole mass spectrometer (Pfeiffer Vacuum, Asslar, Germany). An open electron ionization ion source was utilized for this application. Details of the MIMS overall configuration are available in Lauritsen's publication (Kristensen et al., 2010). The inlet membrane temperature was controlled at 40 °C and the liquid flow rate was set to 2.2 mL/min. Before analysis of the different halamines, the peak position and shape was tuned in order to reduce peak shifts, interferences between neighbouring mass to charge ratios (m/z) and to increase the sensitivity of the instrument. For this purpose, different ion source settings including cathode, focus, field axis, extraction and resolution were tested. After a series of adjustment, the optimized settings were achieved for cathode -80, focus -5, field axis -7, extraction -35 and resolution 40. The spectra of the different halamines were obtained in a full scan mode (48-200 amu) and the quantification of the different halamines were monitored in a selected ion mode.

### **3.2.4 Experimental Procedures**

#### 3.2.4.1 Calibration

NH<sub>2</sub>Cl and NHCl<sub>2</sub> standard solutions were obtained by serial dilution of the stock solution in deionized water and introduced to the MIMS in a sequence from low concentration to high concentration. Each standard of NH<sub>2</sub>Br and NHBr<sub>2</sub> solutions were freshly synthesized before being introduced into the MIMS due to their higher decay rate compared to the chloramines. Each standard was run for 8-12 mins through the MIMS to obtain a stable signal. NHBrCl was calibrated by monitoring both UV-Vis spectrometer and MIMS for 1 hour during the reaction of NH<sub>2</sub>Cl and bromide according to Allard et al. (2018b).

#### **3.2.4.2 Experiments with Raw Waters**

The water quality characteristics of the three natural water samples (two surface waters and one seawater) are presented in Table A-2-1. 50  $\mu$ M (3.5 mg Cl<sub>2</sub>/L) of NH<sub>2</sub>Cl was applied to these waters. No buffer was used and the solution pH variation was less than 0.3.

# **3.3 Results and Discussion**

#### 3.3.1 Representative Mass Spectra

The identification and quantification of halamines by MIMS are based on the steadystate response obtained for selected ions. The introduced analyte is fragmented in the mass spectrometer and produced a variety of different fragment ions.

Figure 3-1a-d represent the mass spectra of NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br and NHBr<sub>2</sub> corresponding to a continuous injection of 100  $\mu$ M of each halamine under the optimum MIMS conditions described previously. Figure 3-1e represents the NHBrCl spectra after 8.5 min reaction of 400  $\mu$ M NH<sub>2</sub>Cl and 4 mM bromide. The different fragments formed during the analysis of the halamines are listed in Table A-2-2.





**Figure 3-1.** Representative MIMS spectra (m/z 48-200) of the different halamines. (a) NH<sub>2</sub>Cl 100  $\mu$ M, (b) NHCl<sub>2</sub> 100  $\mu$ M, (c) NH<sub>2</sub>Br 100  $\mu$ M, (d) NHBr<sub>2</sub> 100  $\mu$ M, (e) NHBrCl, 400  $\mu$ M NH<sub>2</sub>Cl + 4 mM Br<sup>-</sup>, pH 6 with 10 mM phosphate buffer, the spectra (a mixture of NH<sub>2</sub>Cl and NHBrCl) was obtained at 8.5 min.

#### 3.3.1.1 Selection of m/z for Quantification of Halamines

Since the different halamines have similar molecular composition a lot of these fragment ions have similar m/z (Table A-2-2). To avoid any interferences, the parent ions of the different halamines were selected for quantification since they have a unique m/z. In addition, since the different atoms constituting the halamines have different isotopes (<sup>35</sup>Cl, <sup>37</sup>Cl, <sup>79</sup>Br, <sup>81</sup>Br), several parent ions could be used. Therefore, the peak intensity of these different parent ions are also taken into consideration to select the most sensitive m/z ratio.

The molecular ions  $NH_2^{35}Cl^+$  (m/z 51) and  $NH_2^{37}Cl^+$  (m/z 53) from monochloramine can be observed in Figure 3-1a. m/z 51 exhibited the highest peak. However, m/z 53 was selected to quantify  $NH_2Cl$  since m/z 51 is not solely representative of the m/z of the parent compound but also corresponds to the fragment  $N^{37}Cl^+$  which can be produced during fragmentation of other halamines (NHCl<sub>2</sub> and NHBrCl). Figure 3-1b shows the spectrum obtained from dichloramine. Ions in the molecular ion region are observed at m/z 85 ( $NH^{35}Cl_2^+$ ), 87 ( $NH^{35}Cl^{37}Cl^+$ ) and 89 ( $NH^{37}Cl_2^+$ ). m/z 85 was selected to monitor  $NHCl_2$  since it exhibited the highest intensity peak among the three parent ions because  $^{35}Cl$  is the most abundant isotope (Coplen et al., 2002). The NH<sub>2</sub>Br spectra (Figure 3-1c) shows that the parent ions m/z 95 (NH<sub>2</sub><sup>79</sup>Br<sup>+</sup>) and m/z 97 (NH<sub>2</sub><sup>81</sup>Br<sup>+</sup>) have the highest signals. This spectrum confirmed that the synthesized NH<sub>2</sub>Br standard solution was of high purity since no peak corresponding to NHBr<sub>2</sub> was observed at m/z 173, 175, 177. Similar to NH<sub>2</sub>Cl, since m/z 95 also corresponds to the fragment N<sup>81</sup>Br<sup>+</sup> which can be formed from fragmentation of NHBr<sub>2</sub> and NHBrCl (Figure 3-1d and 3-1e), m/z 97 was selected to quantify NH<sub>2</sub>Br. Figure 3-1d showed the NHBr<sub>2</sub> spectrum with the expected cluster of ions around the molecular ions (m/z 173, 175 and 177). Even though the fragments obtained by the loss of hydrogen (m/z 172, 174 and 176) were more abundant than the molecular ions, and have a unique m/z, the most abundant parent ion NH<sup>79</sup>Br<sup>81</sup>Br<sup>+</sup> (m/z 175) was used for quantitation for consistency with the other halamines.

The spectra obtained for the determination of NHBrCl (Figure 3-1e) is more complex because it consists of a solution containing both NH<sub>2</sub>Cl and NHBrCl. The expected cluster of NHBrCl molecular ions is found at m/z 129, 131, and 133 which represent NH<sup>79</sup>Br<sup>35</sup>Cl<sup>+</sup>, NH<sup>81</sup>Br<sup>35</sup>Cl<sup>+</sup>/NH<sup>79</sup>Br<sup>37</sup>Cl<sup>+</sup> and NH<sup>81</sup>Br<sup>37</sup>Cl<sup>+</sup>, respectively (Table A-2-2). These peaks confirm that NHBrCl was formed during the reaction of NH<sub>2</sub>Cl with bromide. m/z 131, which includes two parent compounds (NH<sup>81</sup>Br<sup>35</sup>Cl<sup>+</sup> and NH<sup>79</sup>Br<sup>37</sup>Cl<sup>+</sup>), has the highest signal compared to the other NHBrCl parent ions at m/z 129 and 133 (NH<sup>79</sup>Br<sup>35</sup>Cl<sup>+</sup> and NH<sup>81</sup>Br<sup>37</sup>Cl<sup>+</sup>) and was selected to quantify NHBrCl. Similar results were obtained in a previous study (Gazda et al., 1993).

# 3.3.1.2 Fragment Ions and the Influence of Surface Catalysed Reactions Inside the MIMS upon Halamine Mass Spectra

The small peaks found in the NH<sub>2</sub>Cl spectra in Figure 3-1a, at around m/z 55, 70 and 85 can be attributed to the ubiquitous organic carbon present in the mass spectrometer. These undesired small peaks are also present in the other halamines mass spectra. As shown in Figure 3-1b, in addition to the cluster of ions in the molecular ion region of NHCl<sub>2</sub>, fragment ions caused by loss of one Cl is observed at 49 (N<sup>35</sup>Cl<sup>+</sup>), 50 (NH<sup>35</sup>Cl<sup>+</sup>), 51 (NH<sub>2</sub><sup>35</sup>Cl<sup>+</sup>, N<sup>37</sup>Cl<sup>+</sup>) and 52 (NH<sup>37</sup>Cl). The peak at m/z 60 is due to the acetate buffer used to maintain the pH when preparing the NHCl<sub>2</sub> solution. A very abundant cluster of ions from m/z 79 to m/z 81 is observed in the NH<sub>2</sub>Br and NHBr<sub>2</sub> spectra (Figure 3-1c and 3-1d) which correspond to <sup>79</sup>Br<sup>+</sup>, H<sup>79</sup>Br<sup>+</sup>,<sup>81</sup>Br<sup>+</sup> and H<sup>81</sup>Br<sup>+</sup>. The expected clusters of ions around the fragments (m/z 94 and 96) caused by loss of

one Br are shown in the NHBr<sub>2</sub> Spectra (Figure 3-1d). Figure 3-1e shows the expected clusters of ions around m/z 51 (NH<sub>x</sub>Cl<sup>+</sup> ions) and m/z 95 (NH<sub>x</sub>Br<sup>+</sup> ions) of NHBrCl.

The mass spectra recorded from the halamines showed a number of odd ions that cannot be directly assigned as fragment ions from the analyte molecules. Most dominant were ion clusters around m/z 72 (Cl<sub>2</sub>), m/z 80 (HBr), m/z 116 (BrCl) and m/z 160 (Br<sub>2</sub>). The same molecules were observed and explained by Hansen et al. (1996) in connection with MIMS analysis of haloethylenes. Here the same gases (Cl<sub>2</sub>, BrCl, Br<sub>2</sub>) and acids (HCl and HBr) were observed and shown to originate via surface catalysed decomposition at the hot surfaces inside a closed ion source. It was also explained that these ions have different transients during MIMS monitoring than the normal molecular ions and molecular fragments thereof and how the process of surface catalysed decomposition could lead to non-linearities at concentrations close to the detection limit. The above discussed ion clusters do not directly interfere with any of the ions used to quantify the halamines.

In addition to the ions described above we also observed "odd" fragment ions that potentially interferes with quantitation of halamines in mixtures. The chloramine spectra obtained in our study are similar to Shang and Blatchley (1999). However, in both these studies there is a small peak at m/z 53 corresponding to  $NH_2^{37}Cl$  in the NHCl<sub>2</sub> spectra. The direct UV measurement confirmed that NH<sub>2</sub>Cl accounted for less than 3% in the NHCl<sub>2</sub> standard. According to the calibration curve presented in Figure 3-2a, the signal at m/z 53 from a 100  $\mu$ M concentration of NHCl<sub>2</sub> corresponds to 46  $\mu$ M NH<sub>2</sub>Cl. This indicates that m/z 53 signal in the NHCl<sub>2</sub> spectra is not originating from a NH<sub>2</sub>Cl contamination in the standard. It is hypothesised that the peak at m/z 53  $(NH_2^{37}Cl^+)$  is formed via surface-catalysed decomposition reactions inside the vacuum system of the mass spectrometer as previously described by Hansen et al. (1996). This interference should be taken into consideration when quantifying NH<sub>2</sub>Cl since for similar concentrations of NH<sub>2</sub>Cl and NHCl<sub>2</sub>, the peak intensity of the interfering ion coming from NHCl<sub>2</sub> accounts for ~50% of the peak intensity of the parent ions NH<sub>2</sub>Cl. Similar to dichloramine, which gave rise to an interfering NH<sub>2</sub>Cl<sup>+</sup> ion for monochloramine quantification, dibromamine also gave rise to an interfering NH<sub>2</sub>Br<sup>+</sup> ion for monobromamine quantification. The NH<sub>2</sub>Br<sup>+</sup> ion can affect the quantification of NH<sub>2</sub>Br if NH<sub>2</sub>Br and NHBr<sub>2</sub> are present in the same solution.

Overall, all dihalamines (NHCl<sub>2</sub>, NHBr<sub>2</sub> and NHBrCl) gave rise to  $NH_2X^+$  ions potentially interfering with monohalamine analysis. Just like the ions from the gases and acids above these "odd" fragments also had different MIMS transients than normal molecular ions and fragments thereof (Hansen et al., 1996).

# **3.3.2** Calibration and Determination of Detection and Quantification Limits (LOD and LOQ) for the Different Halamines by MIMS

In order to obtain calibration curves for the different halamines, standards at known concentrations were introduced to the MIMS in a stepwise manner. Figure A-2-1 shows the MIMS response for different standards of chloramines and bromamines in the range 2  $\mu$ M to 200  $\mu$ M. Figure 3-2a,b,d shows that the MIMS response and halamines concentrations for NH<sub>2</sub>Cl, NHCl<sub>2</sub> and NHBr<sub>2</sub> are in good linear relationship with R<sup>2</sup> > 0.99 (0-200  $\mu$ M), indicating that MIMS is capable of quantifying NH<sub>2</sub>Cl, NHCl<sub>2</sub> and NHBr<sub>2</sub>. Unlike the halamines described above, the NH<sub>2</sub>Br calibration curve does not show a linear relationship but a good polynomial relationship which can also be used for quantification (Figure 3-2c). The non-linearity of NH<sub>2</sub>Br might be the result of surface catalysed decomposition reactions as described in section 3.3.1.2.





**Figure 3-2.** MIMS calibration curves for different chloramines and bromamines (0-200  $\mu$ M). (a) NH<sub>2</sub>Cl, (b) NHCl<sub>2</sub>, (c) NH<sub>2</sub>Br, (d) NHBr<sub>2</sub>. MIMS response were recorded after background subtraction. Error bars represent the range of results of duplicated injection obtained in two different days.

Figure A-2-2a,b show the MIMS response for NHBrCl (m/z 131) and its concentration determined by direct UV measurements during the reaction of NH<sub>2</sub>Cl and bromide based on Allard et al. (2018b). Two linear calibration curves with  $R^2 > 0.99$  were obtained (Figure A-2-2c). According to the above results, MIMS is a stable instrument allowing to identify and quantify the different halamines present in drinking waters.

LOD and LOQ for chloramines and bromamines were determined based on 3 and 10 times the standard deviation of a low concentration standard (Shrivastava and Gupta, 2011), respectively. Reproducibility experiments at low concentrations of chloramines (10 samples of 5  $\mu$ M NH<sub>2</sub>Cl and 2  $\mu$ M NHCl<sub>2</sub>, respectively) and bromamines (7 samples of 10  $\mu$ M NH<sub>2</sub>Br and 4  $\mu$ M NHBr<sub>2</sub>, respectively) were performed to calculate the standard deviation and the LOD/LOQ (results are shown in Table 3-1 and Table A-2-3).

Halamines	NH <sub>2</sub> Cl	NHCl <sub>2</sub>	NH <sub>2</sub> Br	NHBr <sub>2</sub>	NHBrCl
LOD	0.48 (0.034)	0.23 (0.033)	1.44 (0.10)	0.84 (0.12)	2.51(0.36)
LOQ	1.61 (0.11)	0.77 (0.11)	4.78 (0.34)	2.79 (0.40)	NA

Table 3-1. LOD and LOQ for chloramines, bromamines and bromochloramine

Unit:  $\mu$ M (mg/L as Cl<sub>2</sub>)

The relative standard deviation for NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br and NHBr<sub>2</sub> equal to 3.2%, 3.8%, 4.8% and 7.0%, respectively (Table A-2-3). The LODs for NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br and NHBr<sub>2</sub> were found to be 0.48, 0.23, 1.44 and 0.84  $\mu$ M, respectively. The LOQ of NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br and NHBr<sub>2</sub> were 1.61, 0.77, 4.78 and 2.79  $\mu$ M,

respectively. According to the method used in the literature (Allard et al., 2018b), the LOD of NHBrCl was calculated to be 2.51  $\mu$ M. Shang determined similar LODs of 0.1 and 0.02 mg/L as Cl<sub>2</sub> for NH<sub>2</sub>Cl and NHCl<sub>2</sub> by MIMS, respectively (Shang and Blatchley, 1999). Results from this study allowed for the first time to quantify NH<sub>2</sub>Br and NHBr<sub>2</sub> by MIMS with LODs ~ 0.1 mg/L as Cl<sub>2</sub>.

### 3.3.3 Quantification of NH<sub>2</sub>X (X=Br or Cl)) in a NH<sub>2</sub>X/NHX<sub>2</sub> Mixture

As described in the representative mass spectra sections all dihalamines (NHCl<sub>2</sub>, NHBr<sub>2</sub> and NHBrCl) had a low abundance ion corresponding to  $NH_2X^+$ , which interferes with the quantification of monochloramine (NH<sub>2</sub>Cl) at m/z 53 and monobromamine (NH<sub>2</sub>Br) at m/z 97. This is important to consider when a mixture of halamines are present in solution and the signal interference derived from NHCl<sub>2</sub> or NHBr2 needs to be subtracted to calculate the accurate concentration of NH2Cl or NH<sub>2</sub>Br. Figure 3-3a shows the signal of m/z 53 produced from different concentrations of NHCl<sub>2</sub>. In contrast to the linear calibration curve (Figure 3-2b) obtained using m/z 85 the signal shows a saturation effect. Regular fragment ions in EI mass spectra should have a linear relationship, whereas ions generated via surface catalyzed decomposition often display this non-linear saturation effect (Allard et al., 2018b). The non-linearity is due to saturation in the mass spectrometer detector. The ionization process produces too many analyte ions which saturate the detector therefore the relative response per concentration unit decreases as the analyte concentration increases. A similar plot (Figure 3-3b) for dibromamine, plotting m/z 97 against concentration, shows the same behavior as dichloramine. In both cases the plots could be described by simple polynomials regression making subtraction of the interference from the dihalamine upon monohalamine quantification at m/z 53 (monochloramine) and m/z 85 (monobromamine) straight forward.



**Figure 3-3.** Interference on monohalamines quantification from dihalamines. (a) The signal of ions at m/z 53 derived from NHCl<sub>2</sub> standards monitored by MIMS. (b) The signal of ions at m/z 97 derived from NHBr<sub>2</sub> standards monitored by MIMS. Error bars represent the range of results of duplicate experiments.

According to Schreiber and Mitch (2006), under typical chloramination conditions, NHCl<sub>2</sub> represents a maximum of 5% of the chloramines speciation. From our data, it can be calculated that the interference on the NH<sub>2</sub>Cl signal coming from NHCl<sub>2</sub> fragmentation represents only 2% of the original signal coming from NH<sub>2</sub>Cl. Therefore, MIMS can be used to accurately quantify NH<sub>2</sub>Cl and NHCl<sub>2</sub> under drinking water treatment conditions in a NH<sub>2</sub>Cl/NHCl<sub>2</sub> mixture without subtracting the interfering signal coming from NHCl<sub>2</sub> fragmentation. As previously mentioned, no data are available for bromamines concentrations under drinking water treatment conditions since it is difficult to accurately quantify them in a mixture of halamines. However, based on modelling using typical in-line chloramination conditions, i.e., in the presence of 3 mgCl<sub>2</sub>/L (42  $\mu$ M) HOCl, 0.9 mg/L (51  $\mu$ M NH<sub>3</sub> and 0.4 mg/L (5  $\mu$ M) Br<sup>-</sup> at pH 8 (NH<sub>3</sub>/HOCl molar ratio of 1.2:1 was used to produce NH<sub>2</sub>Cl), NHBr<sub>2</sub> accounted for ~ 50% of the total bromamines (NH<sub>2</sub>Br and NHBr<sub>2</sub>) after 10 min of reaction (Figure A-2-3) (Allard et al., 2018a). Based on our data, the interference from NHBr<sub>2</sub> fragmentation represents 69% of the total NH<sub>2</sub>Br signal. Therefore, the presence of NHBr<sub>2</sub> will interfere on the analysis of NH<sub>2</sub>Br significantly when these two bromamines are present in a mixture. In order to accurately quantify  $NH_2Br$  in a mixture of NH<sub>2</sub>Br/NHBr<sub>2</sub> using the MIMS, the interference from NHBr<sub>2</sub> fragmentation should be subtracted as described in the previous paragraph. Overall, MIMS can accurately quantify NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br and NHBr<sub>2</sub> when these four halamines are present simultaneously in drinking waters.

NHBrCl is also fragmented in the mass spectrometer. The protonated fragments formed might interfere with both the analysis of NH<sub>2</sub>Cl (m/z 53) and NH<sub>2</sub>Br (m/z 97) (Figure 3-1e). It is not possible to quantify the interference coming from NHBrCl since a pure NHBrCl standard is not available (Allard et al., 2018b). According to model simulation (Figure A-2-3 and A-2-4) (Allard et al., 2018a) and MIMS experimental results presented in section 3.3.4 (Figure 3-4b), the concentration of NHBrCl represented less than 5% of the NH<sub>2</sub>Cl concentration under typical drinking water conditions. Therefore, similar to the interference coming from NHCl<sub>2</sub> fragmentation, the interference from NHBrCl is expected to be negligible and NH<sub>2</sub>Cl can be quantified accurately by MIMS. However, for the same experimental conditions (Figure A-2-3) after 12 h of reaction, similar concentrations of NH<sub>2</sub>Br and NHBrCl (~0.11  $\mu$ M) are present in solution according to the model. In this case, NHBrCl fragmentation will significantly impact NH<sub>2</sub>Br quantification by MIMS.

#### 3.3.4 Application of MIMS to Real Waters and Its Limitations

To evaluate the possibility of using MIMS for monitoring the different halamines in real water samples, two surface waters (SW1 and SW2) with relatively low bromide (80  $\mu$ g/L) and high bromide (986  $\mu$ g/L) concentrations and one seawater (SW3) with extremely high bromide (73.5 mg/L) concentration were selected.

Figure 3-4a-c shows the evolution of NH<sub>2</sub>Cl (m/z 53), NHCl<sub>2</sub> (m/z 85), NH<sub>2</sub>Br (m/z 97), NHBr<sub>2</sub> (m/z 175) and NHBrCl (m/z 131) concentrations in the real waters after disinfection with 50  $\mu$ M (3.5 mg Cl<sub>2</sub>/L) NH<sub>2</sub>Cl over a 20 h period.





**Figure 3-4.** Evolution of the different halamines (NH<sub>2</sub>Cl m/z 53, NHCl<sub>2</sub> m/z 85, NH<sub>2</sub>Br m/z 97, NHBr<sub>2</sub> m/z 175 and NHBrCl m/z 131) in real water samples disinfected by NH<sub>2</sub>Cl monitored by MIMS. (a) SW1, (b) SW2, (c) Seawater. [NH<sub>2</sub>Cl]<sub>0</sub> = 50  $\mu$ M, the main water characteristics are presented in Table A-2-1.

As shown in Figure 3-4a, NH<sub>2</sub>Cl concentration in SW1 decreased constantly from 50  $\mu$ M to 21  $\mu$ M in 20 h. A similar trend was observed for NH<sub>2</sub>Cl in SW2 (Figure 3-4b). Due to the low bromide concentration and high pH in SW1, no detectable NHBr<sub>2</sub>, NHCl<sub>2</sub> and NHBrCl were observed (the signals were below the LOD). The concentrations of NH<sub>2</sub>Br and NHBr<sub>2</sub> were also negligible in SW2. NHBrCl and NHCl<sub>2</sub> concentrations increased to a maximum at around 5 h with ~  $1.8 \mu$ M and ~  $1.1 \mu$ M in SW2, respectively (Figure 3-4b). Subsequently, their concentrations decreased to below 0.4 µM after 20 h. A seawater was also chloraminated to illustrate the limitation of the MIMS when high concentration of brominated amines are encountered. Figure 3-4c shows the evolution of NHBrCl and NHBr<sub>2</sub> in seawater during chloramination. It can be observed that NHBrCl concentration increased to a maximum of 7.5 µM at 3 h and decreased to 0.2 µM after 20 h. NHBr<sub>2</sub> was also detected and its concentration reached a plateau of 1.6  $\mu$ M at 4 h and slowly decreased to 0.8  $\mu$ M after 20 h. The observation of NHBrCl and NHBr<sub>2</sub> can be attributed to the high bromide concentration (73.5 mg/L, 0.92 mM) present in the seawater. NHCl<sub>2</sub> was not detected. Based on MIMS data, the high concentration of NHBrCl accounted for 30% of the total halamines (Figure 3-4c). In this case NH<sub>2</sub>Cl and NH<sub>2</sub>Br data could not be accurately determined because of the unknown intensity of the interference coming from the fragmentation of NHBrCl in the mass spectrometer.

# **3.4 Conclusions**

A new MIMS method was developed to differentiate and quantify all halamines present in drinking water, namely, NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br, NHBr<sub>2</sub> and NHBrCl. The identification and quantification of NH<sub>2</sub>Br and NHBr<sub>2</sub> was achieved by MIMS for the first time. After optimization of the MIMS system, specific MIMS mass spectra for the different halamines were obtained and the m/z corresponding to the mass of the parent compounds were selected. m/z 53, 85, 97, 175 and 131 were chosen to represent NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br, NHBr<sub>2</sub> and NHBrCl, respectively. The LOD obtained for NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br, NHBr<sub>2</sub> and NHBrCl were 0.48, 0.23, 1.44, 0.84 and 2.51  $\mu$ M, respectively. A method was setup to quantify NH<sub>2</sub>Cl or NH<sub>2</sub>Br accurately in mixtures of chloramines and/or bromamines to avoid interferences from the dihalamines (NHCl<sub>2</sub>, NHBr<sub>2</sub> and NHBrCl). However, the presence of NHBrCl interferes with the accurate quantification of NH<sub>2</sub>Br under drinking water conditions.

The different halamines were successfully monitored for the first time in real chloraminated waters. Compared to the DPD method or direct UV measurements, MIMS can distinguish and quantify these halamines. The application of MIMS in drinking water is a powerful online monitoring tool that allows to follow the formation and decomposition kinetics of the different halamines. The use of MIMS will assist in the design and operation of chloraminated systems, in particular to better understand the stability of the oxidant residual in long distribution systems. MIMS can also be used to explore the mechanisms and kinetics of bromamines-related reactions. For example, further in-depth studies can be accomplished with the MIMS looking at the kinetics of bromamine interaction with NOM or metal ions, and the formation of toxic DBPs.

# 3.5 References

- Agus, E., Voutchkov, N. and Sedlak, D.L., 2009. Disinfection by-products and their potential impact on the quality of water produced by desalination systems: a literature review. Desalination 237(1-3), 214-237.
- Allard, S., Cadee, K., Tung, R. and Croué, J.-P., 2018a. Impact of brominated amines on monochloramine stability during in-line and pre-formed chloramination assessed by kinetic modelling. Science of the Total Environment 618, 1431-1439.
- Allard, S., Hu, W., Le Menn, J.-B., Cadee, K., Gallard, H. and Croue, J.-P., 2018b. Method development for quantification of bromochloramine using membrane introduction mass spectrometry. Environmental Science & Technology.

- Aoki, T., 1989. Continuous flow method for simultaneous determination of monochloramine, dichloramine, and free chlorine: application to a water purification plant. Environmental Science & Technology 23(1), 46-50.
- Bauer, S. and Solyom, D., 1994. Determination of volatile organic compounds at the parts per trillion level in complex aqueous matrixes using membrane introduction mass spectrometry. Analytical Chemistry 66(24), 4422-4431.
- Blatchley, E.R. and Cheng, M., 2010. Reaction mechanism for chlorination of urea. Environmental Science & Technology 44(22), 8529-8534.
- Bocchini, P., Pozzi, R., Andalo, C. and Galletti, G., 1999. Membrane inlet mass spectrometry of volatile organohalogen compounds in drinking water. Rapid Communications in Mass Spectrometry 13(20), 2049-2053.
- Bougeard, C.M., Goslan, E.H., Jefferson, B. and Parsons, S.A., 2010. Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine. Water Research 44(3), 729-740.
- Bousher, A., Brimblecombe, P. and Midgley, D., 1989. Kinetics of reactions in solutions containing monochloramine and bromide. Water Research 23(8), 1049-1058.
- Capuzzo, J.M., 1979. The effect of temperature on the toxicity of chlorinated cooling waters to marine animals—A preliminary review. Marine Pollution Bulletin 10(2), 45-47.
- Coplen, T.B., Böhlke, J.K., De Bievre, P., Ding, T., Holden, N., Hopple, J., Krouse, H., Lamberty, A., Peiser, H. and Revesz, K., 2002. Isotope-abundance variations of selected elements (IUPAC Technical Report). Pure and Applied Chemistry 74(10), 1987-2017.
- Federation, W.E. and Association, A.P.H., 2005. Standard methods for the examination of water and wastewater. American Public Health Association (APHA): Washington, DC, USA.
- Gazda, M., Dejarme, L.E., Choudhury, T.K., Cooks, R.G. and Margerum, D.W., 1993. Mass-spectrometric evidence for the formation of bromochloramine and Nbromo-N-chloromethylamine in aqueous solution. Environmental Science & Technology 27(3), 557-561.
- Gazda, M. and Margerum, D.W., 1994. Reactions of monochloramine with bromine, tribromide, hypobromous acid and hypobromite: formation of bromochloramines. Inorganic Chemistry 33(1), 118-123.
- Hansen, K., Gylling, S. and Lauritsen, F.R., 1996. Time-and concentration-dependent relative peak intensities observed in electron impact membrane inlet mass spectra. International journal of mass spectrometry and ion processes 152(2-3), 143-155.
- Heeb, M.B., Kristiana, I., Trogolo, D., Arey, J.S. and Von Gunten, U., 2017. Formation and reactivity of inorganic and organic chloramines and bromamines during oxidative water treatment. Water Research 110, 91-101.
- Hofmann, R. and Andrews, R.C., 2001. Ammoniacal bromamines: a review of their influence on bromate formation during ozonation. Water Research 35(3), 599-604.
- Hua, G. and Reckhow, D.A., 2007. Comparison of disinfection byproduct formation from chlorine and alternative disinfectants. Water Research 41(8), 1667-1678.
- Inman, G.W. and Johnson, J.D., 1984. Kinetics of monobromamine disproportionation-dibromamine formation in aqueous ammonia solutions. Environmental Science & Technology 18(4), 219-224.

- Jafvert, C.T. and Valentine, R.L., 1992. Reaction scheme for the chlorination of ammoniacal water. Environmental Science & Technology 26(3), 577-586.
- Johannesson, J., 1960. The bromination of swimming pools. American Journal of Public Health and the Nations Health 50(11), 1731-1736.
- Kristensen, G.H., Klausen, M.M., Hansen, V.A. and Lauritsen, F.R., 2010. On-line monitoring of the dynamics of trihalomethane concentrations in a warm public swimming pool using an unsupervised membrane inlet mass spectrometry system with off-site real-time surveillance. Rapid Communications in Mass Spectrometry 24(1), 30-34.
- Le Roux, J., Nihemaiti, M. and Croué, J.-P., 2016. The role of aromatic precursors in the formation of haloacetamides by chloramination of dissolved organic matter. Water Research 88, 371-379.
- Lee, W., Westerhoff, P., Yang, X. and Shang, C., 2007. Comparison of colorimetric and membrane introduction mass spectrometry techniques for chloramine analysis. Water Research 41(14), 3097-3102.
- Lei, H., Mariñas, B.J. and Minear, R.A., 2004. Bromamine decomposition kinetics in aqueous solutions. Environmental Science & Technology 38(7), 2111-2119.
- Liu, C., Von Gunten, U. and Croué, J.-P., 2012. Enhanced bromate formation during chlorination of bromide-containing waters in the presence of CuO: catalytic disproportionation of hypobromous acid. Environmental Science & Technology 46(20), 11054-11061.
- Luh, J. and Mariñas, B.J., 2014. Kinetics of bromochloramine formation and decomposition. Environmental Science & Technology 48(5), 2843-2852.
- Ngo, T., Phan, A., Yam, C. and Lenhoff, H., 1982. Interference in determination of ammonia with the hypochlorite-alkaline phenol method of Berthelot. Analytical Chemistry 54(1), 46-49.
- Nicoson, J.S. and Margerum, D.W., 2002. Kinetics and mechanisms of aqueous chlorine reactions with chlorite ion in the presence of chloride ion and acetic acid/acetate buffer. Inorganic Chemistry 41(2), 342-347.
- Pope, P.G. and Speitel, G.E. (2008) Reactivity of bromine-substituted haloamines in forming haloacetic acids, pp. 182-197, Oxford University Press.
- Schreiber, I.M. and Mitch, W.A., 2005. Influence of the order of reagent addition on NDMA formation during chloramination. Environmental Science & Technology 39(10), 3811-3818.
- Schreiber, I.M. and Mitch, W.A., 2006. Nitrosamine formation pathway revisited: the importance of chloramine speciation and dissolved oxygen. Environmental Science & Technology 40(19), 6007-6014.
- Scully, F.E., Hartman, A.C., Rule, A. and LeBlanc, N., 1996. Disinfection interference in wastewaters by natural organic nitrogen compounds. Environmental Science & Technology 30(5), 1465-1471.
- Shang, C. and Blatchley, E.R., 1999. Differentiation and quantification of free chlorine and inorganic chloramines in aqueous solution by MIMS. Environmental Science & Technology 33(13), 2218-2223.
- Shrivastava, A. and Gupta, V.B., 2011. Methods for the determination of limit of detection and limit of quantitation of the analytical methods. Chronicles of Young Scientists 2(1), 21.
- Simon, V., Berne, F. and Gallard, H., 2015. Chloramination and bromamination of amino acids. Disinfection By-products in Drinking Water 352, 70.
- Soltermann, F., Abegglen, C., Gotz, C. and Von Gunten, U., 2016. Bromide sources and loads in Swiss surface waters and their relevance for bromate formation

during wastewater ozonation. Environmental Science & Technology 50(18), 9825-9834.

- Soltermann, F., Widler, T., Canonica, S. and von Gunten, U., 2014. Comparison of a novel extraction-based colorimetric (ABTS) method with membrane introduction mass spectrometry (MIMS): Trichloramine dynamics in pool water. Water Research 58, 258-268.
- Trofe, T.W., Inman, G.W. and Johnson, J.D., 1980. Kinetics of monochloramine decomposition in the presence of bromide. Environmental Science & Technology 14(5), 544-549.
- Trogolo, D. and Arey, J.S., 2016. Equilibria and Speciation of Chloramines, Bromamines, and Bromochloramines in Water. Environmental Science & Technology 51(1), 128-140.
- Uyak, V. and Toroz, I., 2007. Investigation of bromide ion effects on disinfection byproducts formation and speciation in an Istanbul water supply. Journal of Hazardous Materials 149(2), 445-451.
- Valentine, R.L., Brandt, K.I. and Jafvert, C.T., 1986. A spectrophotometric study of the formation of an unidentified monochloramine decomposition product. Water Research 20(8), 1067-1074.
- Vikesland, P.J., Ozekin, K. and Valentine, R.L., 2001. Monochloramine decay in model and distribution system waters. Water Research 35(7), 1766-1776.
- Wajon, J.E. and Morris, J.C., 1982. Rates of formation of N-bromo amines in aqueous solution. Inorganic Chemistry 21(12), 4258-4263.
- Weaver, W.A., Li, J., Wen, Y., Johnston, J., Blatchley, M.R. and Blatchley III, E.R., 2009. Volatile disinfection by-product analysis from chlorinated indoor swimming pools. Water Research 43(13), 3308-3318.
- Wolfe, R.L., Ward, N.R. and Olson, B.H., 1984. Inorganic chloramines as drinking water disinfectants: a review. Journal-American Water Works Association 76(5), 74-88.

Every reasonable effort has been made to acknowledge the owners of copyright material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged.

# Chapter 4. Effect of Copper Oxide on Monochloramine Decomposition in Bromide-Containing Waters

The contents of Chapter 4 & Appendix 3 are unable to be reproduced here as they are under embargo due to current consideration for publication in the journal *Science of the Total Environment*.

# 4.1 Introduction

Monochloramine (NH<sub>2</sub>Cl) is a popular disinfectant in drinking water distribution systems, since it provides longer lasting disinfectant residual than chlorine and leads to a lower formation of regulated disinfection byproducts (DBPs) (Duirk et al. 2005, Fu et al. 2009b, Heeb et al. 2017, Vikesland et al. 2001). Bromide is ubiquitous and found at concentrations up to several mg/L in source water (Pan and Zhang 2013, Richardson et al. 1999). It can react with chloramines to form bromamines and bromochloramine (NHBrCl) (Heeb et al. 2014). NHBrCl was found to be the main product under typical water conditions, produced from the reaction of NH<sub>2</sub>Cl with bromide (Trofe et al. 1980). The presence of brominated amines decreases the stability of chloramines and affects the maintenance of the residual disinfectant (Allard et al. 2018a, Allard et al. 2018b, Bousher et al. 1989, Gazda et al. 1993, Luh and Mariñas 2014, Trofe et al. 1980).

It has recently been demonstrated that the presence of metal oxides can catalyse the decay of different chlorine-based disinfectants used in drinking water treatment as well as other halogenated oxidants found in distribution systems (Hassan et al. 2006, Liu et al. 2013a, Sharma et al. 2017). For example, iron oxide (goethite) slightly enhanced the decay of chlorine in the presence of bromide, while nickel oxide (NiO) showed a much more significant enhancement (Li et al. 2007, Liu et al. 2013a). Copper Oxide (CuO) has been identified as one major corrosion product when copper pipes are applied in municipal distribution systems and household plumbing (Li et al. 2008, Li et al. 2007, Zhang and Andrews 2012). The addition of  $Cu^{2+}$  as a biocide in the distribution systems may also leads to the formation of CuO. CuO catalysed the decomposition of chlorine and induced the formation of chlorate by disproportionation. Toxic bromate was also detected in chlorinated distribution systems where bromide and CuO were present (Liu et al. 2012). This was unexpected since chlorine is not able to oxidise bromine to bromate and the formation of bromate is usually associated to the use of ozone (Von Gunten 2003). Similar to chlorine, it was found that CuO complexed with HOBr/OBr<sup>-</sup> and induced a catalytic disproportionation of HOBr that leads to the production of bromate (Liu et al. 2012). Chlorination of iodide-containing waters in presence of CuO also exhibited a catalytic formation of iodate and the

formation of periodate (Liu et al. 2014). In addition, in the presence of 0.1 g/L CuO, chlorine dioxide catalytically decays 4-5 orders of magnitude faster (Liu et al. 2013b).

Overall, the presence of CuO in drinking water systems has been shown to greatly decrease the stability of the oxidants during chlorination and chlorine dioxide disinfection. The risk of running out of disinfectant during drinking water transportation especially in long distribution systems where copper has been dosed as a biocide might pose a health hazard to the consumer. Therefore, the effect of CuO on NH<sub>2</sub>Cl decomposition in absence or presence of bromide remains unclear, and needs to be further investigated.

# 4.2 Materials and Methods

#### 4.2.1 Reagents

Reagent grade chemicals were used in this study and the reaction solutions were prepared with deionized water (18.2 M $\Omega$ ·cm, Milli-Q, Millipore). Sodium hypochlorite solutions with 10-15% active chlorine was purchased from Sigma Aldrich and used as the source of chlorine. NH<sub>2</sub>Cl stock solutions were synthesized by dropwise addition of chlorine into a rapidly stirred solution containing ammonium chloride at pH 9 (NH<sub>4</sub><sup>+</sup>/ClO<sup>-</sup> molar ratio of 1.2:1) (Allard et al. 2018b). Bromide was added in the form of potassium bromide. CuO powder was prepared according to a method described previously (Liu et al. 2012). HOBr stock solutions were prepared by reacting NaClO and KBr with a Br<sup>-</sup>/ClO<sup>-</sup> molar ratio of 1.05:1 at pH 11 (Criquet et al. 2012).

## 4.2.2 Analytical Methods

Chlorine concentration was determined by UV-Vis spectrometry (Cary 60, Agilent) at  $\lambda_{max}$  of 292 nm with a molar absorptivity of 362 M<sup>-1</sup>cm<sup>-1</sup> (Furman and Margerum 1998). The total oxidant (chloramines, bromamines and NHBrCl) concentration was measured spectrophotometrically at 515 nm by the N,N-diethyl-p-phenylenediamine (DPD) method (APHA 1998). The BET surface area of CuO was measured with a Micromeritics Tristar II and was 18.1 m<sup>2</sup> g<sup>-1</sup>. Dissolved copper concentration was determined by Atomic Absorption Spectrometry (AAS) at 324.8 nm with a detection limit of 0.05 mg/L. The pH of all solutions was measured by an Orion Star Series pH

Meter (Thermo Fisher Scientific). The software Kintecus was used to simulate the halamines formation and decomposition under different conditions (Ianni 2008). Membrane Introduction Mass Spectrometry (MIMS, Microlab Aarhus, Denmark) was used to quantify NH<sub>2</sub>Cl (m/z 53), NHCl<sub>2</sub> (m/z 85) and NHBrCl (m/z 131) according to methods described in the literature (Allard et al. 2018a, Hu et al. unpublished results).

#### 4.2.3 Experimental Procedures

All experiments in this study were performed in the dark (flasks were wrapped in aluminium foil) to prevent lights from influencing the reaction mechanisms and kinetics, and under continuous agitation with a magnetic stirrer. Each experiment was performed in duplicate. All reaction solutions were buffered with 20 mM borate at room temperature ( $24 \pm 1^{\circ}$ C) unless otherwise specified. Solution pHs were adjusted by the addition of NaOH or HCl. Samples were taken periodically and filtered with a 0.2 µm syringe filter to separate the solid copper from the solution (Liu et al. 2012). All filters were pretreated with 3.5 mg/L chlorine solution to remove any reducing substance and then rinsed with deionized water. The NH<sub>2</sub>Cl stock solution was spiked to the solution under moderate stirring. The impact of CuO dosage ranging from 0.05 to 1.0 g/L, pH ranging from 6.5 to 8.0, and bromide concentration ranging from 10 to 80 µM on NH<sub>2</sub>Cl stability were investigated.

# 4.3 Results and Discussion

### 4.3.1. Effect of CuO on NH<sub>2</sub>Cl Decomposition at Different pHs

 $NH_2Cl$  decomposition in the presence of CuO ranging from 0.2 to 1.0 g/L at pH 8.0 is shown in Figure 4-1a.



**Figure 4-1.** Effect of CuO on NH<sub>2</sub>Cl decomposition at (a) pH 8.0 and (b) pH 6.5. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M \ (3.55 \ mg/L \ as \ Cl_2), \ [CuO]_0 = 0-1.0 \ g/L$ , borate buffer = 20 mM.

Based on kinetic modelling (Figure A-3-1a) and the literature (Valentine and Jafvert 1988), there is no NHCl<sub>2</sub> produced during NH<sub>2</sub>Cl decomposition at pH 8, the total oxidant determined by the DPD method solely consisted of NH<sub>2</sub>Cl. The addition of CuO did not promote NH<sub>2</sub>Cl decomposition at pH 8.0 (Figure 4-1a). After 54 h reaction time, 0.2, 0.5 and 1.0 g/L CuO led to a decrease of NH<sub>2</sub>Cl of 12.5%, 14.7% and 14.0%, respectively, which were similar to  $NH_2Cl$  self-decay (13.6%). This is different from the CuO-catalysed decay observed for HOCl, HOBr, HOI and ClO<sub>2</sub> decomposition (Liu et al. 2014, Liu et al. 2013a, b, Liu et al. 2012). At pH 6.5, NHCl<sub>2</sub> is formed at low concentration (Figure A-3-1b), indicating that the total oxidant consisted of NH<sub>2</sub>Cl and NHCl<sub>2</sub>. In this case, the presence of 0.2 g/L CuO slightly enhanced the total oxidant decomposition with 13.5% degradation after 6 h, while the total oxidant only decreased by 6.8% in absence of CuO (Figure 4-1b). A rapid drop of the total oxidant concentration was observed upon the addition of CuO, but there was no further effect with increasing time. It is hypothesised that NHCl<sub>2</sub> is reacting with CuO instead of NH<sub>2</sub>Cl (Figure A-3-1b). Previous study have shown that NH<sub>2</sub>Cl decomposition rate was enhanced by the catalytic effect of soluble copper (Fu et al. 2009a, Fu et al. 2009b). In our study, no soluble copper was detected in the pH 8.0 experiment (below the detection limit 0.05 mg/L), while at pH 6.5, 0.2 g/L CuO released  $0.54 \pm 0.04$  mg/L of soluble copper after 3 h of reaction (Figure A-3-2). Therefore, the small impact of CuO on NH<sub>2</sub>Cl decomposition observed under acidic conditions might also come from the released soluble copper.

#### 4.3.2 Synergistic Effect of CuO and Bromide on NH<sub>2</sub>Cl Decomposition

#### 4.3.2.1 Impact of CuO Dosage

The kinetic profiles of the total oxidant and the different halamines in presence of NH<sub>2</sub>Cl (50  $\mu$ M), bromide (20 or 40  $\mu$ M) and CuO (0-0.2 g/L) at pH 6.5 are shown in Figure 4-2.



**Figure 4-2.** Effect of CuO on the total oxidant decomposition and different halamines species in chloraminated bromide-containing water. (a) Impact of CuO concentration and comparison with modelling data. (b) Comparison between DPD, MIMS and modelling data. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$  (3.55 mg/L as Cl<sub>2</sub>),  $[Br]_0 = 20 \text{ or } 40 \ \mu M$  (1.6 or 3.2 mg/L),  $[CuO]_0 = 0$ -0.2 g/L, pH 6.5, borate buffer = 20 mM. Solid symbols represent experimental data and dashed lines represent modelling data for the different halamines (NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br, NHBr<sub>2</sub> and NHBrCl) in absence of CuO.

The total oxidant concentration determined by the DPD method was significantly reduced in the presence of CuO. Interestingly, the variation of the CuO dosage did not change the total oxidant decomposition rate. In comparison to the experiment without CuO,  $48 \pm 1\%$  of the total oxidant was consumed in the presence of CuO. Modelling of the different halamines formation and decomposition in absence of CuO showed that NH<sub>2</sub>Cl decayed fast in the presence of bromide and that NHBrCl was the main halamine formed at pH 6.5 (Figure 4-2a). After 6 h of reaction, the model prediction indicated that NH<sub>2</sub>Cl accounted for 53.0% of the initial NH<sub>2</sub>Cl concentration, NHBrCl and NHCl<sub>2</sub> accounted for 37.9% and 3.72% at pH 6.5, respectively. NH<sub>2</sub>Br and NHBr<sub>2</sub>cl concentration. It can be seen that the total oxidant decomposition in presence of CuO (modelling) and not to the sum of the different halamines (mainly NH<sub>2</sub>Cl and NHBrCl) especially in the first 3 hours of reaction. This suggests that NHBrCl is preferentially

decomposed in presence of CuO and that the total oxidant measured in the CuOcatalysed experiment is primarily NH<sub>2</sub>Cl. In addition to the total oxidant concentration, MIMS was used to assess the behaviour of the different halamines species under similar experimental conditions (20 µM of bromide and 0.05 g/L CuO). Figure 4-2b shows the total oxidant determined by DPD measurement, NH<sub>2</sub>Cl and NHBrCl concentrations determined by MIMS and the output of the halamines kinetic model without copper. It was demonstrated by MIMS that in presence of CuO, NHBrCl is quickly degraded. Compared to NHBrCl, NHCl<sub>2</sub> is formed at lower levels but it was also decomposed by CuO (Figure A-3-3). The similar NH<sub>2</sub>Cl concentration determined by MIMS, total oxidant concentration (DPD) and the model prediction (in absence of CuO) further strengthen our assumption that NHCl<sub>2</sub> and NHBrCl were decomposed by CuO. The MIMS results gave strong evidence that the total oxidant decomposition in presence of CuO was mainly due to the degradation of NHBrCl and that the main oxidant was NH<sub>2</sub>Cl. This explains the fact that increasing the CuO concentration did not increase the kinetic of the total oxidant degradation (Figure 4-2a) since the rate limiting step was the formation of NHBrCl (and NHCl<sub>2</sub>) and not its reactivity with CuO.

### 4.3.2.2 Impact of Bromide concentration

The effect of bromide concentration ranging from 0 to 80  $\mu$ M on the total oxidant decomposition in the presence of NH<sub>2</sub>Cl and CuO at pH 6.5 is shown in Figure 4-3a.



**Figure 4-3.** Effect of varying bromide concentrations on the total oxidant decomposition in the presence of NH<sub>2</sub>Cl and CuO. (a) Total oxidant decay; (b) pseudo first order rate constant ( $k_{obs}$ ) of the total oxidant decomposition as a function of bromide concentration. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$  (3.55 mg/L as Cl<sub>2</sub>),  $[Br^-]_0 = 0.80 \ \mu M$  (0-6.4 mg/L),  $[CuO]_0 = 0.05 \ g/L$ , pH 6.5, borate buffer = 20 mM. Solid symbols represent experimental data and dashed lines represent the modelling result of CuO-induced total oxidant decay.
The total oxidant decomposition rate increased with increasing bromide concentration, with 21.0% and 86.7% decrease of the total oxidant for 0 and 80  $\mu$ M bromide after 8 h, respectively. The total oxidant decay was estimated in absence of CuO by kinetic modelling (Figure A-3-4) and was found to decreased by 2.1% and 23.3% for 0 and 80  $\mu$ M of bromide, respectively. This confirms that the presence of CuO significantly promoted the total oxidant decay under different bromide concentrations. As shown in Figure A-3-4b, in absence of CuO the formation of NHBrCl increased with increasing bromide concentration and as previously observed the formation of NHBrCl obtained by kinetic modelling is anticorrelated to the total oxidant decay.

The total oxidant decomposition in the presence of CuO fitted pseudo first order rate kinetics with  $R^2 > 0.99$  (Figure A-3-5). The  $k_{obs}$  for total oxidant decomposition were determined to be  $8.6 \times 10^{-6}$ ,  $1.98 \times 10^{-5}$ ,  $2.88 \times 10^{-5}$ ,  $4.27 \times 10^{-5}$  and  $6.87 \times 10^{-5}$  s<sup>-1</sup> for 0, 10, 20, 40 and 80 µM bromide, respectively.  $k_{obs}$  showed a good linear relationship with bromide concentrations (Figure 4-3b), indicating that the overall total oxidant (NH<sub>2</sub>Cl, NHCl<sub>2</sub> and NHBrCl) decay follows second order kinetics.

The rate law for the total oxidant decay in the presence of NH<sub>2</sub>Cl, bromide and CuO at pH 6.5 was expressed as the following:

$$-d[total oxidant]/dt = k_0[total oxidant] + k_{app}[total oxidant][Br]$$
(1)

 $k_0$  refers to the total oxidant decay rate without bromide,  $k_0$  was determined to be 1.18  $\times 10^{-5}$  s<sup>-1</sup> from the intercept of Figure 4-3b.  $k_{app}$  represents the second order rate constant for the total oxidant decay in the presence of bromide and was determined to be 0.73 M<sup>-1</sup>s<sup>-1</sup> from the slope of Figure 4-3b.

The determined  $k_0$  and  $k_{app}$  were used as input in Kintecus to simulate the CuO-induced total oxidant decay in the presence and absence of bromide. This simulation result fitted well with the experimental result (Figure 4-3a), suggesting that this model can be used to predict the CuO-induced total oxidant decay in the presence of NH<sub>2</sub>Cl and bromide.

### 4.3.2.3 Impact of pH

The effect of pH ranging from 6.5 to 8.0 on the total oxidant decomposition in the presence of 0.05 g/L CuO and 5  $\mu$ M bromide was investigated.



**Figure 4-4.** Effect of pH on the total oxidant decay in the presence of CuO and bromide. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$  (3.55 mg/L as Cl<sub>2</sub>),  $[Br]_0 = 5 \ \mu M$  (400  $\mu$ g/L),  $[CuO]_0 = 0.05 \ g/L$ , pH 6.5-8.0, borate buffer = 20 mM. Solid symbols represent experimental data of the total oxidant and dashed lines represent the model predictions of NH<sub>2</sub>Cl.

Figure 4-4 shows that in presence of CuO the total oxidant decay increase with decreasing pH with 9.3% and 60.3% decrease of the total oxidant for pH 8.0 after 29 h and pH 6.5 after 26 h, respectively. As shown in Figure 4-4 and A-3-6, a lower pH led to a faster degradation of NH<sub>2</sub>Cl, and higher formation of NHCl<sub>2</sub> and NHBrCl, according to the modelling results. NH<sub>2</sub>Br and NHBr<sub>2</sub> were negligible since their concentrations were below 0.2% of the initial NH<sub>2</sub>Cl concentration. As previously demonstrated by MIMS, NHCl<sub>2</sub> and NHBrCl were decomposed by CuO (Figure 4-2 and A-3-3), resulting in a higher total oxidant decay rate at lower pH. The modelled NH<sub>2</sub>Cl decay was added to Figure 4-4 since it was previously demonstrated that the main halamine present in solution was NH<sub>2</sub>Cl in Figure 4-2b. Under this experimental condition, the total oxidant decay was higher than the modelled NH<sub>2</sub>Cl for all pHs. Since it was observed that NH<sub>2</sub>Cl was only slightly affected by CuO (Figure 4-1a,b) it does not account for the difference observed between the modelled NH<sub>2</sub>Cl and the total oxidant concentration. It is likely that once NHBrCl is degraded, bromide is released in solution and recycled inducing additional formation of NHBrCl which led to an enhanced NH<sub>2</sub>Cl decay.

## **4.4 Conclusions**

This study investigated the effect of CuO on NH<sub>2</sub>Cl stability in bromide-containing waters. During chloramination in the presence of bromide, NHBrCl is the main halamine produced together with low levels of NHCl<sub>2</sub>. It was verified that the presence

of copper oxide catalysed the decomposition of NHBrCl and NHCl<sub>2</sub>, leading to an enhanced oxidant decay mainly consisting of NH<sub>2</sub>Cl. The total oxidant decay was increasing with increasing bromide concentrations since higher concentrations of NHBrCl were produced. The pH also played an important role in the decomposition of the total oxidant. As pH decreased, the total oxidant decay rate was enhanced since there was more NHBrCl and NHCl<sub>2</sub> generated. It is also hypothesised that when NHBrCl is degraded, bromide is released and recycled leading to additional NHBrCl formation and therefore additional loss of disinfectant.

This study have important implications to the management of drinking water transportation in household copper pipes. In the presence of copper, the disinfectant stability decreased by copper catalysed reactions and might induce a health risk to the consumers.

## 4.5 References

- Allard, S., Cadee, K., Tung, R. and Croué, J.-P. (2018a) Impact of brominated amines on monochloramine stability during in-line and pre-formed chloramination assessed by kinetic modelling. Science of the Total Environment 618, 1431-1439.
- Allard, S., Hu, W., Le Menn, J.-B., Cadee, K., Gallard, H. and Croue, J.-P. (2018b) Method development for quantification of bromochloramine using membrane introduction mass spectrometry. Environmental Science & Technology.
- APHA (1998) Standard methods for the examination of water and wastewater. USA: APHA.
- Bousher, A., Brimblecombe, P. and Midgley, D. (1989) Kinetics of reactions in solutions containing monochloramine and bromide. Water Research 23(8), 1049-1058.
- Criquet, J., Allard, S., Salhi, E., Joll, C.A., Heitz, A. and Von Gunten, U. (2012) Iodate and iodo-trihalomethane formation during chlorination of iodide-containing waters: Role of bromide. Environmental Science & Technology 46(13), 7350-7357.
- Duirk, S.E., Gombert, B., Croué, J.-P. and Valentine, R.L. (2005) Modeling monochloramine loss in the presence of natural organic matter. Water Research 39(14), 3418-3431.
- Fu, J., Qu, J., Liu, R., Qiang, Z., Zhao, X. and Liu, H. (2009a) Mechanism of Cu (II)catalyzed monochloramine decomposition in aqueous solution. Science of the Total Environment 407(13), 4105-4109.
- Fu, J., Qu, J., Liu, R., Zhao, X. and Qiang, Z. (2009b) The influence of Cu (II) on the decay of monochloramine. Chemosphere 74(2), 181-186.
- Furman, C.S. and Margerum, D.W. (1998) Mechanism of chlorine dioxide and chlorate ion formation from the reaction of hypobromous acid and chlorite ion. Inorganic Chemistry 37(17), 4321-4327.
- Gazda, M., Dejarme, L.E., Choudhury, T.K., Cooks, R.G. and Margerum, D.W. (1993) Mass-spectrometric evidence for the formation of bromochloramine and N-

bromo-N-chloromethylamine in aqueous solution. Environmental Science & Technology 27(3), 557-561.

- Hassan, K.Z., Bower, K.C. and Miller, C.M. (2006) Iron oxide enhanced chlorine decay and disinfection by-product formation. Journal of Environmental Engineering 132(12), 1609-1616.
- Heeb, M.B., Criquet, J., Zimmermann-Steffens, S.G. and Von Gunten, U. (2014) Oxidative treatment of bromide-containing waters: formation of bromine and its reactions with inorganic and organic compounds—a critical review. Water Research 48, 15-42.
- Heeb, M.B., Kristiana, I., Trogolo, D., Arey, J.S. and Von Gunten, U. (2017) Formation and reactivity of inorganic and organic chloramines and bromamines during oxidative water treatment. Water Research 110, 91-101.
- Hu, W., Lauritsen, F.R., Croué, J.-P. and Allard, S. (unpublished results) Identification and quantification of chloramines, bromamines and bromochloramine by Membrane Introduction Mass Spectrometry (MIMS).
- Ianni, J. (2008) Kintecus Version 3.95.
- Li, B., Liu, R., Liu, H., Gu, J. and Qu, J. (2008) The formation and distribution of haloacetic acids in copper pipe during chlorination. Journal of Hazardous Materials 152(1), 250-258.
- Li, B., Qu, J., Liu, H. and Hu, C. (2007) Effects of copper (II) and copper oxides on THMs formation in copper pipe. Chemosphere 68(11), 2153-2160.
- Liu, C., Salhi, E., Croué, J.-P. and Von Gunten, U. (2014) Chlorination of iodidecontaining waters in the presence of CuO: formation of periodate. Environmental Science & Technology 48(22), 13173-13180.
- Liu, C., Von Gunten, U. and Croue, J.-P. (2013a) Chlorination of bromide-containing waters: Enhanced bromate formation in the presence of synthetic metal oxides and deposits formed in drinking water distribution systems. Water Research 47(14), 5307-5315.
- Liu, C., Von Gunten, U. and Croue, J.-P. (2013b) Enhanced chlorine dioxide decay in the presence of metal oxides: Relevance to drinking water distribution systems. Environmental Science & Technology 47(15), 8365-8372.
- Liu, C., Von Gunten, U. and Croué, J.-P. (2012) Enhanced bromate formation during chlorination of bromide-containing waters in the presence of CuO: catalytic disproportionation of hypobromous acid. Environmental Science & Technology 46(20), 11054-11061.
- Luh, J. and Mariñas, B.J. (2014) Kinetics of bromochloramine formation and decomposition. Environmental Science & Technology 48(5), 2843-2852.
- Pan, Y. and Zhang, X. (2013) Four groups of new aromatic halogenated disinfection byproducts: effect of bromide concentration on their formation and speciation in chlorinated drinking water. Environmental Science & Technology 47(3), 1265-1273.
- Richardson, S.D., Thruston, A.D., Caughran, T.V., Chen, P.H., Collette, T.W., Floyd, T.L., Schenck, K.M., Lykins, B.W., Sun, G.-r. and Majetich, G. (1999) Identification of new drinking water disinfection byproducts formed in the presence of bromide. Environmental Science & Technology 33(19), 3378-3383.
- Sharma, V.K., Yang, X., Cizmas, L., McDonald, T.J., Luque, R., Sayes, C.M., Yuan, B. and Dionysiou, D.D. (2017) Impact of metal ions, metal oxides, and nanoparticles on the formation of disinfection byproducts during chlorination. Chemical Engineering Journal 317, 777-792.

- Trofe, T.W., Inman, G.W. and Johnson, J.D. (1980) Kinetics of monochloramine decomposition in the presence of bromide. Environmental Science & Technology 14(5), 544-549.
- Valentine, R.L. and Jafvert, C.T. (1988) General acid catalysis of monochloramine disproportionation. Environmental Science & Technology 22(6), 691-696.
- Vikesland, P.J., Ozekin, K. and Valentine, R.L. (2001) Monochloramine decay in model and distribution system waters. Water Research 35(7), 1766-1776.
- Von Gunten, U. (2003) Ozonation of drinking water: Part II. Disinfection and byproduct formation in presence of bromide, iodide or chlorine. Water Research 37(7), 1469-1487.
- Zhang, H. and Andrews, S.A. (2012) Catalysis of copper corrosion products on chlorine decay and HAA formation in simulated distribution systems. Water Research 46(8), 2665-2673.

Every reasonable effort has been made to acknowledge the owners of copyright material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged.

## Chapter 5. Mechanistic Investigation of Bromamines Decomposition in the Presence of Cu(II)

The contents of Chapter 5 & Appendix 4 are unable to be reproduced here as they are under embargo due to current consideration for publication in the journal *Environmental Science & Technology*.

## **5.1 Introduction**

Bromamines are formed from reactions between the ubiquitous bromide and chlorine/ozone/peracetic acid in the presence of ammonia or chloramines (Heeb et al. 2017, Inman and Johnson 1984, Inman et al. 1976, Luh and Mariñas 2014, Pope and Speitel 2008, Soulard et al. 1981, Trogolo and Arey 2016). During these oxidative treatments, bromide is oxidized to bromine (HOBr) which further reacts with ammonia to produce monobromamine (NH<sub>2</sub>Br) in equilibrium with dibromamine (NHBr<sub>2</sub>) (Alsulaili et al. 2010, Buffle et al. 2004). Another pathway to form NH<sub>2</sub>Br is the reaction between monochloramine (NH<sub>2</sub>Cl) and bromide (Trofe et al. 1980). Even though, NH<sub>2</sub>Br is formed at a much lower rate in chloraminated systems, it was shown by kinetic modelling that NH<sub>2</sub>Br accumulated at alkaline pH used in long distribution system to stabilise NH<sub>2</sub>Cl (Allard et al. 2018). Bromamines include three species: monobromamine (NH<sub>2</sub>Br), dibromamine (NHBr<sub>2</sub>) and tribromamine (NBr<sub>3</sub>). The distribution of these bromamines is highly dependent on the pH and N/Br ratio (Johnson and Overby 1971, Kirmeyer 2004, Wajon and Morris 1982). In typical drinking water conditions (pH 6-8.5, bromide ~ 10-2000 µg/L (Allard et al. 2018), ammonia ~ 0-15 mg/L (Turan and Celik 2003, Vartiainen et al. 1988)), NH<sub>2</sub>Br and NHBr<sub>2</sub> are the major bromamine species present in solutions (Allard et al. 2018, Hofmann and Andrews 2001, Lei et al. 2004). In the following of the manuscript bromamines refer to the sum of NH<sub>2</sub>Br and NHBr<sub>2</sub>.

NH<sub>2</sub>Br and NHBr<sub>2</sub> are highly reactive towards different inorganic and organic substances compared to their chloramines analogues (Heeb et al. 2017). For example, NH<sub>2</sub>Br is more reactive than NH<sub>2</sub>Cl with CN<sup>-</sup> with second order rate constants of  $2.63 \times 10^4 \,\mathrm{M}^{-1}\mathrm{s}^{-1}$  and  $1.96 \times 10^{-2} \,\mathrm{M}^{-1}\mathrm{s}^{-1}$ , respectively (Lei et al. 2006, Schurter et al. 1995). The same behaviour is observed with organic compounds, e.g. NH<sub>2</sub>Br reacts 4 orders of magnitude faster with phenol compared to NH<sub>2</sub>Cl (Heeb et al. 2017); NH<sub>2</sub>Br reaction rates with amino acids are hundred times higher than NH<sub>2</sub>Cl (Simon et al. 2015). It has also been demonstrated that NH<sub>2</sub>Br and NHBr<sub>2</sub> have higher potential to produce disinfection byproducts (DBPs) in comparison to NH<sub>2</sub>Cl (Allard et al. 2018, Pope and Speitel 2008). For example, trihalomethanes (THMs) and haloacetic acids (HAAs) formation are significantly enhanced when amino acids reacting with NH<sub>2</sub>Br compared to NH<sub>2</sub>Cl (Simon et al. 2015). The presence of bromamines also lead to a

shift from chlorinated DBPs (Cl-DBPs) to brominated DBPs (Br-DBPs) and it is well accepted that Br-DBPs have a higher toxicity than their chlorinated analogues (Sharma et al. 2014). Therefore, the presence of bromamines and its potential of producing DBPs are of concern. Chloramines decomposition byproducts have been experimentally identified previously. Vikesland and Valentine showed that nitrogen gas and ammonia were the major nitrogen decay products of NH<sub>2</sub>Cl self-decomposition (Vikesland et al. 1998). In the presence of NOM, the products speciation changed, nitrogen gas formation was reduced and ammonia and nitrate formation were promoted (Vikesland et al. 1998). However, bromamines decay products have not yet been experimentally determined.

Dissolved copper is present in drinking water either as an added biocide to prevent nitrification or as a corrosion product from copper pipes (Borkow and Gabbay 2005, Liu et al. 2013c, Lytle and Nadagouda 2010, Xiao et al. 2007, Zhang and Andrews 2012). The guideline value for copper in drinking water is set at 2.0 mg/L and 1.3 mg/L by the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA), respectively (PAEPA 2002, WHO 2017). Metals (Cu(II) and Fe(II)) enhanced the decomposition rate of monochloramine (Fu et al. 2009a, Fu et al. 2009b, Vikesland and Valentine 2000). Copper oxide (CuO) has been extensively investigated since it catalysed oxidant (ClO<sub>2</sub>, HOCl, HOBr and HOCl+Br<sup>-</sup>/I<sup>-</sup>) decay in the drinking water distribution pipeline (Liu et al. 2014, Liu et al. 2013a, b, Liu et al. 2012, Zhang et al. 2008). It was also observed that the presence of Cu(II) could promote THMs formation during chloramination (Fu et al. 2009a), hence the effect of Cu(II) on promoting DBPs formation in presence of bromide is also a concern.

In areas where distribution systems are large and extend up to several hundred kilometers, the stability of the residual disinfectant is crucial to guarantee the delivery of safe drinking water to consumers (Li et al. 2019). This study aims to explore the catalytic properties of copper with bromamines formed in distribution system containing ammonia and bromide. Several parameters (the type of copper, pH and Cu(II) concentration), based on typical water treatment conditions, were investigated on bromamines decomposition. Species-specific rate constants were determined and the degradation products of bromamines decomposition were characterised. Based on these findings a mechanism for monobromamine degradation was proposed.

## 5.2 Materials and Methods

### 5.2.1 Standards and Reagents

All chemicals used in this study were of analytical grade purity and stock solutions were prepared with deionized water (18.2 M $\Omega$ ·cm, Milli-Q, Millipore). Ammonium chloride, ammonium sulfate, potassium bromide and copper(II) sulfate pentahydrate were obtained from Chem-Supply Pty Ltd. CuO powder was prepared according to the method described previously and it was insoluble at pH 8.6 (Liu et al. 2012). Stock copper solutions (2 g/L) were prepared by dissolving copper(II) sulfate in deionized water. Chlorine stock solutions were prepared by diluting a commercial sodium hypochlorite solution (10-15% active chlorine, Sigma Aldrich) and standardized spectrophotometrically at  $\lambda_{max}$  of 292 nm using a molar absorptivity of 362 M<sup>-1</sup>cm<sup>-1</sup> for OCl<sup>-</sup> (Furman and Margerum 1998). 2 mM bromine stock solutions were prepared by the aqueous reaction of NaOCl with KBr (molar ratio Br<sup>-</sup>/OCl<sup>-</sup> of 1.05) at pH 11 (adjusted by NaOH) for 24 h for full conversion of OCl<sup>-</sup> to OBr<sup>-</sup> (Lei et al. 2004, Liu et al. 2012). The prepared bromine stock solution was kept at 4 °C and used for a maximum of 2 weeks after its preparation. The bromine concentration was standardized spectrophotometrically at  $\lambda_{max}$  of 329 nm using a molar absorptivity of 332 M<sup>-1</sup>cm<sup>-1</sup> for OBr<sup>-</sup> (Liu et al. 2012). NH<sub>2</sub>Br stock solutions were prepared by mixing equal volumes of NH<sub>4</sub>Cl or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and HOBr (both prepared in 20 mM pH 9 borate buffer) solutions at a N/Br molar ratio of 1000:1 (Galal-Gorchev and Morris 1965, Lei et al. 2004). The influence of the anions chloride and sulfate on total bromamine decomposition with and without Cu(II) is presented in Figure A-4-1 and Text A-4-1. According to the results, NH<sub>4</sub>Cl was used for the kinetic investigation while (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was used for the mechanistic investigation. The resulting NH<sub>2</sub>Br and NHBr<sub>2</sub> concentrations were quantified by UV-Vis spectrometry using their representative molar absorptivities ( $\varepsilon_{NH_2Br,232} = 82 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\varepsilon_{NH_2Br,278} = 425 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\epsilon_{\text{NHBr}_{2},232} = 2000 \text{ M}^{-1} \text{cm}^{-1}, \epsilon_{\text{NHBr}_{2},278} = 715 \text{ M}^{-1} \text{cm}^{-1}$ ) as described previously (Lei et al. 2004).

### **5.2.2 Analytical Methods**

The presence of Cu(II) in bromamine solutions could interfere with direct UV measurement, thus total bromamine (NH<sub>2</sub>Br and NHBr<sub>2</sub>) concentration during the

reaction of bromamines with copper was analysed spectrophotometrically with the N,N-diethyl-p-phenylenediamine (DPD) method at 515 nm (Liu et al. 2012). Nitrite and nitrate analysis were performed by a Dionex ICS-3000 Ion Chromatography (IC) with a suppressed conductivity detection and an IonPac AS9-HC column (Salhi and Von Gunten 1999). Total copper concentration was determined by Atomic Absorption Spectroscopy at 324.8 nm with a detection limit of 0.05 mg/L. X-Ray Photoelectron Spectroscopy (XPS) was used to differentiate different copper species, i.e., Cu(I) and Cu(II) (Biesinger 2017). In order to get an adequate amount of solid copper to perform the XPS analysis, a 1 L solution containing 500  $\mu$ M NH<sub>2</sub>Br and 1 mM Cu(II) was reacting for 2 h. Thereafter, the solution was placed in an oven at 70 °C until the aqueous phase was evaporated and the solid completely dried.

<sup>15</sup>N<sub>2</sub> analysis was performed by a Gas Chromatography/Mass Spectrometry (GC/MS), based on the method developed by Vikesland and Valentine (Vikesland et al. 1996). A cylinder containing <sup>15</sup>N<sub>2</sub> gas (98% purity) (Sigma-Aldrich) was used as a <sup>15</sup>N<sub>2</sub> standard to calibrate the GC/MS. <sup>15</sup>N-labelled ammonium sulfate was used to avoid the interference of the ubiquitous <sup>14</sup>N<sub>2</sub> present in the air. 20 mL sealed amber vials with 10 mL reaction solution and 10 mL headspace was used, while an equilibrium of nitrogen gas between the aqueous phase and gas phase could be achieved. 10 μL gas in the headspace was introduced to the GC/MS for the analysis of nitrogen gas. Ion count at mass-to-charge (m/z) value of 30 was monitored to quantify the nitrogen gas production from bromamines decomposition. An example of calibration curve obtained for <sup>15</sup>N<sub>2</sub> quantification is shown in Figure A-4-2.

Membrane Introduction Mass Spectrometry (MIMS, Microlab Aarhus, Denmark) was used to separately analyse the different bromamines, <sup>15</sup>N<sub>2</sub>O and <sup>15</sup>NO<sub>2</sub>. MIMS enabled the quantification of both NH<sub>2</sub>Br and NHBr<sub>2</sub> free of interference, as it is based on m/z, while with UV, overlapping peaks might leads to uncertainties and colorimetric reagents measure the sum of the bromamines. <sup>15</sup>N-labelled ammonium sulfate was used to avoid interference from CO<sub>2</sub>, which has the same m/z as <sup>14</sup>N<sub>2</sub>O. The inlet membrane temperature was set to 40 °C and the liquid sample flow rate was controlled at 2.2 mL/min. m/z 97 and 175 were selected for NH<sub>2</sub>Br and NHBr<sub>2</sub>, respectively. <sup>14</sup>N<sub>2</sub>O gas was prepared according to the boiling water bath method (Li and Blatchley 2008). A saturated <sup>14</sup>N<sub>2</sub>O solution at 25°C was obtained by dissolution of the <sup>14</sup>N<sub>2</sub>O

gas. <sup>14</sup>N<sub>2</sub>O standard solutions were obtained by serial dilutions of the saturated solution in 20 mL amber vials with no headspace. m/z 44 was used to calibrate the MIMS for <sup>14</sup>N<sub>2</sub>O and m/z 46 was used to calculate the concentration of <sup>15</sup>N<sub>2</sub>O for real samples with <sup>15</sup>N-labeled precursors. It was considered that <sup>14</sup>N<sub>2</sub>O and <sup>15</sup>N<sub>2</sub>O produced similar mass spectra in the MIMS except for the mass shift of 2 amu (Li and Blatchley 2008). The <sup>14</sup>N<sub>2</sub>O concentrations and MIMS response presented a good linear relationship with correlation coefficient of 0.9994 (Figure A-4-3). <sup>15</sup>NO<sub>2</sub> formation was also monitored by MIMS using m/z 47 but not quantified due to the lack of analytical standard.

All samples in this study were analysed in duplicate. It was not possible to quantify ammonia because of the high N/Br molar ratio of 1000:1 used to synthesize monobromamine that the produced ammonia accounted for a maximum of 0.1% of the total ammonia in the solution

#### 5.2.3 Kinetic Study

The experiments were conducted in a batch reactor (100 mL volume) under gentle magnetic stirring at room temperature ( $24 \pm 1$  °C). The bromamines solutions (50 µM) were prepared by diluting the freshly prepared monobromamine stock (200 µM) solutions with deionized water. The pH of the solutions was established by addition of HCl/H<sub>2</sub>SO<sub>4</sub> or NaOH using an automatic pH titrator (Metrohm 857 Titrando) before addition of Cu(II) (0-5 mg/L). The concentration of the acid and base in the pH titrator varied according to the targeted pH to ensure a minimal variation of the initial volume. The pH titrator was used because borate buffer is not effective when high concentration of ammonia is present, and in presence of phosphate buffer, copper-phosphate complexes are formed (Liu et al. 2013a). The pH variations during the experiments were less than 0.1 pH unit from the targeted pH conditions. Samples were collected periodically for total bromamine concentration analysis. The kinetic simulations of bromamines decomposition in the presence and absence of Cu(II) were carried out by the Program Kintecus (Allard et al. 2018).

### 5.2.4 Mechanistic study

Due to the interference of chloride on nitrite analysis by IC,  $(NH_4)_2SO_4$  (Sigma-Aldrich) was used instead of NH<sub>4</sub>Cl to synthesize NH<sub>2</sub>Br at a N/Br molar ratio of 100:1.

Different Cu(II) dosages (0-5 mg/L) were added to the bromamine solution (200  $\mu$ M). The solutions were left in the dark for 52 h until all the oxidant was consumed, except for the experiment without copper where the sample was quenched with sodium sulphite for nitrite and nitrate analysis since a residual oxidant was present. <sup>15</sup>N-labeled chemicals were used to determine <sup>15</sup>N<sub>2</sub>, <sup>15</sup>N<sub>2</sub>O and <sup>15</sup>NO<sub>2</sub>. These experiments were carried out at pH 9.2 with 20 mM borate buffer.

## 5.3 Results and Discussion

### 5.3.1 Impact of Different Copper Species on Bromamines Decomposition

Figure 5-1 shows total bromamine decomposition in absence and presence of CuO and Cu(II) at pH 7.5. It was verified by direct UV measurement that  $NH_2Br$  accounted for ~90% of the total bromamine at pH 7.5 with a N/Br molar ratio of 1000:1 (Figure A-4-4).



**Figure 5-1.** Impact of CuO and Cu(II) on total bromamine decomposition. Experimental conditions: [total bromamine] $_0 = 50 \,\mu$ M, pH = 7.5, NH<sub>4</sub>Cl/Br molar ratio = 1000:1, the total bromamine concentration was determined with the DPD method and the pH was regulated by automatic titration.

In absence of copper, the total bromamine decay at pH 7.5 accounted for 28% of the initial concentration after 3 h. The addition of Cu(II) (0.5 mg/L, 7.8  $\mu$ M) increased total bromamine decomposition with 40% degradation after 3 h. Increasing the Cu(II) concentration to 2.0 mg/L (31.2  $\mu$ M) increased the total bromamine decomposition to 65%. In contrast to Cu(II), the presence of CuO showed a moderate effect on total bromamine decomposition with only 38% of bromamines decomposed in 3 h for 50

mg/L (625  $\mu$ M) CuO. The dissolved Cu(II) concentration from the solution containing 50 mg/L CuO was less than 0.05 mg/L (below the detection limit). This indicated that for an equivalent molar copper concentration, Cu(II) is more efficient in degrading total bromamine than CuO. This behaviour differs from other oxidants where Cu(II) had a little effect on HOCl and NH<sub>2</sub>Cl decay (Fu et al. 2009c, Nguyen et al. 2011), and CuO catalytically degraded HOCl, HOBr and ClO<sub>2</sub> (Liu et al. 2013b, Liu et al. 2012). This result is also different from our previous findings where CuO has no effect on NH<sub>2</sub>Cl decay at pH 8.

#### 5.3.2 Effect of Cu(II) Concentration on Bromamines Decomposition Kinetic

To identify if both NH<sub>2</sub>Br and NHBr<sub>2</sub> were impacted by the presence of Cu(II), the MIMS response was recorded for NH<sub>2</sub>Br (m/z 97) and NHBr<sub>2</sub> (m/z 175) in the presence and absence of Cu(II) (Figure 5-2). It is known that NHBr<sub>2</sub> fragments in the MIMS will interfere with the analysis of NH<sub>2</sub>Br (Hu et al. under review), thus a high pH of 9.2 was applied here for the low proportion of NHBr<sub>2</sub>. Figure 5-2a,b shows that the presence of Cu(II) significantly enhanced the decomposition of NH<sub>2</sub>Br and NHBr<sub>2</sub>.



**Figure 5-2.** Impact of Cu(II) on (a) NH<sub>2</sub>Br (m/z 97) and (b) NHBr<sub>2</sub> (m/z 175) decomposition monitored by MIMS. Experimental conditions: [total bromamine]<sub>0</sub> =  $200 \mu$ M, NH<sub>4</sub>Cl/Br molar ratio = 100:1, pH 9.2, 20 mM borate buffer.

In our experimental conditions, the half-lives of  $NH_2Br$  decay decreased from > 6 h to 55 min, 27 min and 13 min with 0, 1.0, 2.0 and 5.0 mg/L Cu(II), respectively. The same trend was observed for  $NHBr_2$  with half-lives decreasing from 1.7 h to 13.8 min, 7.8 min and 3.9 min for similar Cu(II) concentrations, respectively.

Thereafter, the total bromamine decomposition in the presence of varying Cu(II) concentrations ranging from 0 to 5.0 mg/L at pH 7.5 was followed. As shown in Figure

5-3a, the total bromamine decomposition rate increased with increasing Cu(II) concentration from 0.2 to 5.0 mg/L.



**Figure 5-3.** Effect of Cu(II) concentration on total bromamine decomposition rate. (a) Total bromamine decomposition as a function of time. (b) Pseudo first order rate constant ( $k_{obs}$ ) of total bromamine decomposition as a function of Cu(II) concentration. Experimental conditions: [total bromamine]<sub>0</sub> = 50 µM, NH<sub>4</sub>Cl/Br molar ratio = 1000:1, pH = 7.5, the total bromamine concentration was determined with the DPD method and the pH was regulated by automatic titration. Solid symbols represent experimental data and dashed lines represent the model predictions.

Pseudo first order rate constant ( $k_{obs}$ ) for total bromamine decomposition was determined by linearization for all Cu(II) concentrations (Figure A-4-5). Even though Cu(II) was not present in large excess, good linearization was obtained using pseudo first order rate equation with R<sup>2</sup> ranging from 0.9859 to 0.9998, indicating that Cu(II) acted as a catalyst. Figure 5-3b shows the  $k_{obs}$  as a function of Cu(II) concentration.  $k_{obs}$  value increased linearly with increasing Cu(II) concentrations with R<sup>2</sup> = 0.9988. This indicated that the reaction between bromamines and Cu(II) was first order with respect to bromamines and Cu(II), respectively, suggesting that the overall reaction follows second order rate law.

Since  $NH_2Br$  accounted for ~90% of the total bromamine,  $NH_2Br$  was used to model the system. The rate law for total bromamine (mainly  $NH_2Br$ ) decomposition in the presence of Cu(II) at pH 7.5 was expressed as the following:

$$-d[NH_2Br]/dt = k_0[NH_2Br]^2 + k_{app}[NH_2Br][Cu(II)]$$
(1)

Where  $k_0$  represents the second order rate constant for NH<sub>2</sub>Br self-decomposition,  $k_{app}$  represents the second order rate constant for Cu(II)-induced NH<sub>2</sub>Br decomposition.  $k_0$  was determined to be 0.36 M<sup>-1</sup>s<sup>-1</sup> from the experiment without Cu(II).  $k_{app}$  was

obtained from the slope of  $k_{obs}$  versus Cu(II) concentration and found to be 2.31  $M^{-1}s^{-1}$  (Figure 5-3b).

The calculated rate constants were used to simulate total bromamine decomposition with and without Cu(II). The modelling results are in good agreement with experimental data for total bromamine decomposition in the presence of Cu(II) at pH 7.5 (Figure 5-3a).

#### 5.3.3 Effect of pH on Bromamines Decomposition

The total bromamine decomposition in the absence and presence of 2.0 mg/L Cu(II) for varying pHs from 6.0 to 8.5 is shown in Figure 5-4. The total bromamine decay in absence of Cu(II) decreased with pH with 45.9% and 12.4% decomposition for pH 6.0 and 8.5 after 3 h, respectively (Figure A-4-6a). In presence of Cu(II), the total bromamine decay is relatively similar for all pHs with 54.4%, 52.7%, 57.7% and 53.5% for pH 6.0, 7.0, 8.0 and 8.5 after 3 h, respectively (Figure A-4-6b). However, Cu(II)-induced total bromamine decomposition, i.e., the difference between the total bromamine self-decomposition and the experiment with Cu(II) is increasing with increasing pHs (Figure 5-4).



**Figure 5-4.** Total bromamine decomposition at different pHs in the presence and absence of Cu(II). Experimental conditions: [total bromamine]<sub>0</sub> = 50  $\mu$ M, NH<sub>4</sub>Cl/Br molar ratio = 1000:1, pH ranging from 6.0 to 8.5. The total bromamine concentration was determined with the DPD method and the pH was regulated by automatic titration.

In order to calculate "Cu(II)-induced" total bromamine decomposition first order rate constant ( $k_{Cu(II)}$ ), the total bromamine "self-decomposition" first order rate constant ( $k_0$ ) was subtracted to the first order rate constant of total bromamine decomposition in the presence of 2 mg/L Cu(II) ( $k_{obs}$ ). Pseudo first order linearization were used for both experiments with and without Cu(II) (Figure A-4-7). Total bromamine self-decomposition pseudo first order rate increased from  $1.17 \times 10^{-5} \text{ s}^{-1}$  to  $6.00 \times 10^{-5} \text{ s}^{-1}$  with decreasing pH from 8.5 to 6.0. This pH related trend is consistent with the previous study conducted by Lei (Lei et al. 2004). The calculated Cu(II)-induced first order rate constants for total bromamine decomposition are presented in Figure 5-5.



**Figure 5-5.** Cu(II)-induced total bromamine decomposition pseudo first order rate constant  $k_{Cu(II)}$  as a function of pH. Red symbols represent experimental data, black line represents modelling data. Experimental conditions: [total bromamine]<sub>0</sub> = 50 µM, [Cu(II)] = 2.0 mg/L, NH<sub>4</sub>Cl/Br molar ratio = 1000:1, the total bromamine concentration was determined with the DPD method and the pH was regulated by automatic titration.

Similar to the oxidation of manganese by bromine (Allard et al. 2013), the pH dependency of  $k_{Cu(II)}$  can be explained by the speciation of Cu(II) and the speciation of the bromamines. Monobromamine (~97%) was the dominant bromamine species at pH 8.5, whereas dibromamine (~62%) was dominant at pH 6.0 (Figure A-4-4). The distribution of Cu(II) species is also dependent on pH (Essington 2015). The species-specific rate constant were determined according to equation 2.

$$k_{Cu(II)} = \alpha_{Cu^{2+}} * (k_{Cu^{2+}/NH_2Br} * \alpha_{NH_2Br} + k_{Cu^{2+}/NHBr_2} * \alpha_{NHBr_2}) + \alpha_{Cu(OH)^+} * (k_{Cu(OH)^+/NH_2Br} * \alpha_{NH_2Br} + k_{Cu(OH)^+/NHBr_2} * \alpha_{NHBr_2}) + \alpha_{Cu(OH)_2} * (k_{Cu(OH)_2/NH_2Br} * \alpha_{NH_2Br} + k_{Cu(OH)_2/NHBr_2} * \alpha_{NHBr_2})$$
(2)

Where  $\alpha_{Cu^{2+}}$ ,  $\alpha_{Cu(OH)^+}$  and  $\alpha_{Cu(OH)_2}$  represent the fraction of  $Cu^{2+}$ ,  $Cu(OH)^+$  and  $Cu(OH)_2$ . For example,  $\alpha_{Cu^{2+}} = [Cu^{2+}]/[Cu^{2+}]_{tot}$  with  $[Cu^{2+}]_{tot} = [Cu^{2+}] + [Cu(OH)^+] + [Cu(OH)_2]$ . Similarly,  $\alpha_{NH_2Br}$  and  $\alpha_{NHBr_2}$  represent the fraction of NH<sub>2</sub>Br and NHBr<sub>2</sub>, respectively.  $k_{Cu^{2+}/NH_2Br}$ ,  $k_{Cu^{2+}/NHBr_2}$ ,  $k_{Cu(OH)^+/NH_2Br}$ ,  $k_{Cu(OH)^+/NH_2Br_2}$ ,  $k_{Cu(OH)_2/NH_2Br}$  and  $k_{Cu(OH)_2/NH_2Br_2}$  represent the species-specific second order rate constant. Bromamines speciation and the initial ratio of NH<sub>2</sub>Br and NHBr<sub>2</sub> at different pHs were determined by kinetic modelling while the speciation of copper was determined by calculation. The species-specific rate constants were determined via nonlinear regression analyses

using Sigma Plot.  $k_{Cu^{2+}/NHBr_2}$ ,  $k_{Cu(OH)^+/NHBr_2}$ ,  $k_{Cu(OH)_2/NH_2Br}$  and  $k_{Cu(OH)_2/NHBr_2}$  were determined to be  $1.33 \times 10^{-5} \text{ M}^{-1} \text{s}^{-1}$ ,  $2.78 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1}$ ,  $6.25 \times 10^{-5} \text{ M}^{-1} \text{s}^{-1}$  and  $1.29 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$ , respectively, while  $k_{Cu^{2+}/NH_2Br}$  and  $k_{Cu(OH)^+/NH_2Br}$  were found negligible. Modeling the rate data for Cu(II)-induced decomposition of total bromamine provides a good agreement with the experimental data (Figure 5-5). The most reactive copper species is Cu(OH)\_2 which is more nucleophilic.

#### **5.3.4 Mechanistic Investigation**

It was verified that bromate was not formed during total bromamine decomposition in the presence of Cu(II). Therefore, bromine in total bromamine is fully reduced to bromide. The loss of total bromamine and the production of N<sub>2</sub>, N<sub>2</sub>O, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> for total bromamine decomposition in the presence and absence of Cu(II) after 52 h reaction time at pH 9.2 are shown in Figure 5-6. The nitrogen decay products provide direct evidence of the mechanism of the reaction between monobromamine and Cu(II). Comparing the products speciation in presence or absence of Cu(II) will help to gain insight into bromamines loss pathways. The percentage recoveries (in mole) of the different nitrogen species are presented in Table A-4-1. In absence of Cu(II), the total nitrogen recovery for NH<sub>2</sub>Br self-decomposition was 109.2%. Similar to NH<sub>2</sub>Cl decomposition in pure water system (Vikesland et al. 1998), N<sub>2</sub> was the primary nitrogen decay product accounting for 76.5%, while N<sub>2</sub>O, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> were measured at low concentrations with 11.6, 15.2 and 6.0% of total nitrogen, respectively (Figure 5-6 and Table A-4-1).



**Figure 5-6.** Nitrogen mass balance for total bromamine decomposition in presence and absence of Cu(II). Experimental conditions: [total bromamine]<sub>0</sub> = 200  $\mu$ M, borate buffer = 20 mM, pH = 9.2, (<sup>15</sup>NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/Br molar ratio = 50:1, reaction time = 52 h.

In presence of Cu(II), the nitrogen-containing degradation products speciation changed. The addition of Cu(II) led to a significant reduction of N<sub>2</sub>. N<sub>2</sub> formation only accounted for 11.6%, 6.6% and 6.0% of the total nitrogen in presence of 1.0 mg/L, 2.0 mg/L and 5.0 mg/L of Cu(II), respectively. N<sub>2</sub>O and NO<sub>2</sub><sup>-</sup> were found to be the major products during the Cu(II)-induced total bromamine decomposition with a much higher proportion of the total nitrogen than total bromamine self-decomposition. Interestingly, N<sub>2</sub>O formation increased while NO<sub>2</sub><sup>-</sup> formation decreased with increasing Cu(II) concentrations. In the presence of 1.0 mg/L Cu(II), N<sub>2</sub>O represented 29.5% and NO<sub>2</sub><sup>-</sup> 51.8% of total nitrogen. Conversely, N<sub>2</sub>O accounted for 48.1% and NO<sub>2</sub><sup>-</sup> for 24.0% of total nitrogen in the presence of 5.0 mg/L Cu(II). Figure A-4-8a shows the initial stage (1 hour) of N<sub>2</sub>O production monitored by MIMS, it confirms that N<sub>2</sub>O formation was increasing with Cu(II) concentrations. NO<sub>3</sub><sup>-</sup> was formed at low concentrations in all tested conditions.

Overall, the total nitrogen recoveries in presence of Cu(II) were ranging from 98% to 80% for 1.0 and 5.0 mg/L Cu(II), respectively. It was hypothesized that other nitrogen decay products may have formed in the presence of Cu(II), such as  $NH_4^+$  and NO<sub>2</sub>. Figure A-4-8b shows the MIMS response for m/z 47 which corresponds to the mass of <sup>15</sup>NO<sub>2</sub>. NO<sub>2</sub> is increasing with increasing Cu(II) concentration, therefore it might be one of the missing nitrogen decay products but it was not quantified in this study due to the lack of an analytical standard.

#### 5.3.5 Proposed Reaction Mechanism

In order to elucidate the different reaction pathways involved in bromamines decomposition by Cu(II), XPS was used to investigate the change in oxidation state during copper reaction with bromamines. Figure A-4-9 compares the XPS spectra of a CuCl<sub>2</sub>(s) standard and the copper particles collected after reaction with bromamines. Cu 2p of CuCl<sub>2</sub> standard showed that it had two peaks at binding energy of 934.8 eV and 954.5 eV, similar to 934.6 eV and 954.4 eV of CuCl<sub>2</sub> reported in the literature (Van der Laan et al. 1981). It was found that the copper particle sample presented two peaks at binding energy of 931.7 eV and 951.5 eV. The literature reported that CuCl (932.2 eV and 952.1 eV) had peaks at similar binding energy (Robert and Offergeld 1972), indicating that the copper particle could be Cu(I). Hence, it was assumed that Cu(I) was produced in the reaction.

Based on the copper species produced, the formation of degradation products observed in the previous section and according to the literature, the following reaction mechanism for monobromamine decomposition in the presence of Cu(II) is proposed in Scheme 1. At pH 9.2 monobromamine is the dominant bromamine species, therefore only monobromamine is described in the reaction mechanism.

**Scheme 5-1.** Proposed reaction mechanism for monobromamine decomposition in the presence of Cu(II)

(3)  $\operatorname{NH}_{2}\operatorname{Br} + \operatorname{Cu}(\operatorname{II}) \longrightarrow \operatorname{\circ}\operatorname{NH}_{2}\operatorname{Br} + \operatorname{Cu}(\operatorname{II}) + \operatorname{H}^{+}$ (4)  $\operatorname{NH}_{2}\operatorname{Br} + \operatorname{Cu}(\operatorname{II}) \longrightarrow \operatorname{\circ}\operatorname{NH}_{2} + \operatorname{Cu}(\operatorname{II}) + \operatorname{Br}^{-}$ (5)  $\operatorname{\circ}\operatorname{NH}_{2} + \operatorname{O}_{2} \longrightarrow \operatorname{H}_{+}^{+}\operatorname{N} \cdot \operatorname{O} \cdot \operatorname{O} \cdot \underbrace{\operatorname{opathway 1}}_{\operatorname{pathway 2}} \operatorname{HNO} - \operatorname{O} \cdot \underbrace{\operatorname{opathway 2}}_{\operatorname{pathway 2}} \operatorname{HNO} + \operatorname{H}_{2}\operatorname{O}_{2}$ (6)  $4\operatorname{NO} + 2\operatorname{H}_{2}\operatorname{O} + \operatorname{O}_{2} \longrightarrow 4\operatorname{HNO}_{2}$ (7)  $2\operatorname{NO} + \operatorname{O}_{2} \longrightarrow 2\operatorname{NO}_{2}$ (8)  $\operatorname{NH}_{2}\operatorname{Br} + \operatorname{NO}_{2}^{-} + \operatorname{H}_{2}\operatorname{O} \longrightarrow \operatorname{NO}_{3}^{-} + \operatorname{NH}_{4}^{+} + \operatorname{Br}^{-}$ (9)  $3\operatorname{NO}_{2} + \operatorname{H}_{2}\operatorname{O} \longrightarrow 2\operatorname{HNO}_{3} + \operatorname{NO}$ (10)  $2\operatorname{HNO} \longrightarrow \operatorname{N}_{2}\operatorname{O} + \operatorname{H}_{2}\operatorname{O}$ 

Similar to the mechanism of  $H_2O_2$  decay in the presence of Cu(II) (Lee et al. 2014), it is hypothesised that Cu(II) is reduced to Cu(I) via a one-electron transfer reaction and produces a •NHBr radical (3). Cu(I) is oxidised to Cu(II) by NH<sub>2</sub>Br forming an amine radical (•NH<sub>2</sub>) and bromide (4). This confirms the catalytic behaviour of Cu(II) allowing to use pseudo first order conditions to determine rate constants. Once •NH<sub>2</sub> is formed, it quickly reacts with O<sub>2</sub> and forms an intermediate peroxyl radical (NH<sub>2</sub>O<sub>2</sub>•) (5) (Clarke et al. 2008, Laszlo et al. 1998). Thereafter, NH<sub>2</sub>O<sub>2</sub>• decomposed in two parallel reaction pathways. Pathway 1 leads to the formation of NO and H<sub>2</sub>O (Laszlo et al. 1998). NO is not a stable product and is oxidized to nitrite in the presence of O<sub>2</sub> (Ignarro et al. 1993) or leads to the formation of NO<sub>2</sub> as evidenced by MIMS (6 and 7). Pathways 2 leads to the formation of HNO which decays rapidly to N<sub>2</sub>O and H<sub>2</sub>O (10) (Bazylinski and Hollocher 1985, Schreiber and Mitch 2007). This is consistent with our findings (Figure 5-6), i.e., the 2 main byproducts, NO<sub>2</sub> and N<sub>2</sub>O, are in competition since one is coming from pathway 1 and the other one from pathway 2. NO<sub>3</sub> formation is coming from NO<sub>2</sub> oxidation by monobromamine or NO<sub>2</sub> dissolution in water (8 and 9). Similar to •NH<sub>2</sub>, it is hypothesised that •NHBr radical reacts with O<sub>2</sub> to produce a peroxyl radical NHBrO<sub>2</sub>• that further degrades and forms N<sub>2</sub>O and NO<sub>3</sub> as the major end products.

## **5.4 Practical Implications**

Cu(II) is present in distribution systems, due to its used as biocide to prevent nitrification, or in household water distribution systems due to copper pipes leaching. To further improve monochloramine stability, the drinking water is maintained at high pH (8-9). However, in presence of bromide monobromamine will form and accumulate (Allard et al. 2018). Even though bromamines are normally present in much lower concentrations than chloramines, their fate in drinking water is important since they have high potential to produce DBPs and they decrease the disinfectant residual. The result presented in this work illustrates that Cu(II) can significantly enhance the decay of bromamines. For example, 2.0 mg/L Cu(II) can lead to a decrease of more than 50% of 50  $\mu$ M bromamines in 2 hours at pH 7.5. The obtained monobromamine-Cu(II) model can be applied to predict monobromamine loss kinetics in waters containing Cu(II) and its impact on the stability of the oxidants. Furthermore, the bromide regenerated from bromamines decomposition and the presence of Cu(II) can lead to a faster decomposition of chloramines.

In addition, this is the first study to experimentally identify the bromamines selfdecomposition products, as well as the Cu(II) induced decomposition products. The formation of nitrite demonstrates that nitrification might not only have occurred from ammonia oxidising bacteria but also during bromamination in the presence of Cu(II). It helps us to understand the nitrogen balance of halamine reactions in the water system. On one hand copper is used as a biocide to avoid nitrification but on the other hand in presence of bromide it induces a chemical nitrification. Therefore, the use of copper as a biocide should be restricted when source water contains high concentration of bromide. At high pH, copper pipes will not release soluble copper. However, at neutral pH or lower, soluble copper can be released from copper pipes. Therefore, copper pipes in household should be replaced under neutral (or lower) pH conditions.

## **5.5 References**

- Allard, S., Cadee, K., Tung, R. and Croué, J.P. (2018) Impact of brominated amines on monochloramine stability during in-line and pre-formed chloramination assessed by kinetic modelling. Science of the Total Environment 618, 1431-1439.
- Allard, S., Fouche, L., Dick, J., Heitz, A. and Von Gunten, U. (2013) Oxidation of manganese (II) during chlorination: role of bromide. Environmental Science & Technology 47(15), 8716-8723.
- Alsulaili, A., Speitel, G. and Katz, L. (2010) Monochloramine and total haloamine decay after a short prechlorination time in the presence of bromide. Water Science and Technology: Water Supply 10(4), 512-516.
- Bazylinski, D.A. and Hollocher, T.C. (1985) Evidence from the reaction between trioxodinitrate (II) and nitrogen-15-labeled nitric oxide that trioxodinitrate (II) decomposes into nitrosyl hydride and nitrite in neutral aqueous solution. Inorganic Chemistry 24(25), 4285-4288.
- Biesinger, M.C. (2017) Advanced analysis of copper X-ray photoelectron spectra. Surface and Interface Analysis 49(13), 1325-1334.
- Borkow, G. and Gabbay, J. (2005) Copper as a biocidal tool. Current Medicinal Chemistry 12(18), 2163-2175.
- Buffle, M.-O., Galli, S. and Von Gunten, U. (2004) Enhanced bromate control during ozonation: the chlorine-ammonia process. Environmental Science & Technology 38(19), 5187-5195.
- Clarke, K., Edge, R., Johnson, V., Land, E., Navaratnam, S. and Truscott, T. (2008) Direct observation of NH2• reactions with oxygen, amino acids, and melanins. The Journal of Physical Chemistry A 112(6), 1234-1237.

Essington, M.E. (2015) Soil and water chemistry: an integrative approach, CRC press.

- Fu, J., Qu, J., Liu, R., Qiang, Z., Liu, H. and Zhao, X. (2009a) Cu (II)-catalyzed THM formation during water chlorination and monochloramination: A comparison study. Journal of Hazardous Materials 170(1), 58-65.
- Fu, J., Qu, J., Liu, R., Qiang, Z., Zhao, X. and Liu, H. (2009b) Mechanism of Cu (II)catalyzed monochloramine decomposition in aqueous solution. Science of the Total Environment 407(13), 4105-4109.
- Fu, J., Qu, J., Liu, R., Zhao, X. and Qiang, Z. (2009c) The influence of Cu (II) on the decay of monochloramine. Chemosphere 74(2), 181-186.

- Furman, C.S. and Margerum, D.W. (1998) Mechanism of chlorine dioxide and chlorate ion formation from the reaction of hypobromous acid and chlorite ion. Inorganic Chemistry 37(17), 4321-4327.
- Galal-Gorchev, H. and Morris, J.C. (1965) Formation and stability of bromamide, bromimide, and nitrogen tribromide in aqueous solution. Inorganic Chemistry 4(6), 899-905.
- Heeb, M.B., Kristiana, I., Trogolo, D., Arey, J.S. and Von Gunten, U. (2017) Formation and reactivity of inorganic and organic chloramines and bromamines during oxidative water treatment. Water Research 110, 91-101.
- Hofmann, R. and Andrews, R.C. (2001) Ammoniacal bromamines: a review of their influence on bromate formation during ozonation. Water Research 35(3), 599-604.
- Hu, W., Lauritsen, F.R., Croué, J.-P. and Allard, S. (under review) Identification and quantification of chloramines, bromamines and bromochloramine by Membrane Introduction Mass Spectrometry (MIMS).
- Ignarro, L.J., Fukuto, J.M., Griscavage, J.M., Rogers, N.E. and Byrns, R.E. (1993) Oxidation of nitric oxide in aqueous solution to nitrite but not nitrate: comparison with enzymatically formed nitric oxide from L-arginine. Proceedings of the National Academy of Sciences 90(17), 8103-8107.
- Inman, G.W. and Johnson, J.D. (1984) Kinetics of monobromamine disproportionation-dibromamine formation in aqueous ammonia solutions. Environmental Science & Technology 18(4), 219-224.
- Inman, G.W., LaPointe, T.F. and Johnson, J.D. (1976) Kinetics of nitrogen tribromide decomposition in aqueous solution. Inorganic Chemistry 15(12), 3037-3042.
- Johnson, J.D. and Overby, R. (1971) Bromine and bromamine disinfection chemistry. Journal of the Sanitary Engineering Division 97(5), 617-628.
- Kirmeyer, G.J. (2004) Optimizing chloramine treatment, American Water Works Association.
- Laszlo, B., Alfassi, Z., Neta, P. and Huie, R.E. (1998) Kinetics and Mechanism of the Reaction of NH2 with O2 in Aqueous Solutions. The Journal of Physical Chemistry A 102(44), 8498-8504.
- Lee, H.-J., Lee, H. and Lee, C. (2014) Degradation of diclofenac and carbamazepine by the copper (II)-catalyzed dark and photo-assisted Fenton-like systems. Chemical Engineering Journal 245, 258-264.
- Lei, H., Mariñas, B.J. and Minear, R.A. (2004) Bromamine decomposition kinetics in aqueous solutions. Environmental Science & Technology 38(7), 2111-2119.
- Lei, H., Minear, R.A. and Mariñas, B.J. (2006) Cyanogen bromide formation from the reactions of monobromamine and dibromamine with cyanide ion. Environmental Science & Technology 40(8), 2559-2564.
- Li, J. and Blatchley, E.R. (2008) UV photodegradation of inorganic chloramines. Environmental Science & Technology 43(1), 60-65.
- Li, R.A., McDonald, J.A., Sathasivan, A. and Khan, S.J. (2019) Disinfectant residual stability leading to disinfectant decay and by-product formation in drinking water distribution systems: A systematic review. Water Research.
- Liu, C., Salhi, E., Croué, J.-P. and Von Gunten, U. (2014) Chlorination of iodidecontaining waters in the presence of CuO: formation of periodate. Environmental Science & Technology 48(22), 13173-13180.
- Liu, C., Von Gunten, U. and Croue, J.-P. (2013a) Chlorination of bromide-containing waters: Enhanced bromate formation in the presence of synthetic metal oxides

and deposits formed in drinking water distribution systems. Water Research 47(14), 5307-5315.

- Liu, C., Von Gunten, U. and Croue, J.-P. (2013b) Enhanced chlorine dioxide decay in the presence of metal oxides: Relevance to drinking water distribution systems. Environmental Science & Technology 47(15), 8365-8372.
- Liu, C., Von Gunten, U. and Croué, J.-P. (2012) Enhanced bromate formation during chlorination of bromide-containing waters in the presence of CuO: catalytic disproportionation of hypobromous acid. Environmental Science & Technology 46(20), 11054-11061.
- Liu, S.-g., Zhu, Z.-l., Tan, X.-c., Feng, X.-h., Huang, Z.-y., Qiu, Y.-l. and Zhao, J.-f. (2013c) The influence of cu (II) on the formation and distribution of disinfection by-products during the chlorination of drinking water. Water, Air, & Soil Pollution 224(4), 1493.
- Luh, J. and Mariñas, B.J. (2014) Kinetics of bromochloramine formation and decomposition. Environmental Science & Technology 48(5), 2843-2852.
- Lytle, D.A. and Nadagouda, M.N. (2010) A comprehensive investigation of copper pitting corrosion in a drinking water distribution system. Corrosion Science 52(6), 1927-1938.
- Nguyen, C.K., Powers, K.A., Raetz, M.A., Parks, J.L. and Edwards, M.A. (2011) Rapid free chlorine decay in the presence of Cu (OH) 2: Chemistry and practical implications. Water Research 45(16), 5302-5312.
- PAEPA (2002) National primary drinking water regulations: Long Term 1 Enhanced Surface Water Treatment Rule. Final rule. Federal Register 67(9), 1811.
- Pope, P.G. and Speitel, G.E. (2008) Reactivity of bromine-substituted haloamines in forming haloacetic acids, pp. 182-197, Oxford University Press.
- Robert, T. and Offergeld, G. (1972) Spectres de photoélectrons X de composés solides de cuivre Relation entre la présence de raies satellites et l'état d'oxydation du cuivre. Physica Status Solidi (a) 14(1), 277-282.
- Salhi, E. and Von Gunten, U. (1999) Simultaneous determination of bromide, bromate and nitrite in low μg l- 1 levels by ion chromatography without sample pretreatment. Water Research 33(15), 3239-3244.
- Schreiber, I.M. and Mitch, W.A. (2007) Enhanced nitrogenous disinfection byproduct formation near the breakpoint: implications for nitrification control. Environmental Science & Technology 41(20), 7039-7046.
- Schurter, L.M., Bachelor, P.P. and Margerum, D.W. (1995) Nonmetal redox kinetics: mono-, di-, and trichloramine reactions with cyanide ion. Environmental Science & Technology 29(4), 1127-1134.
- Sharma, V.K., Zboril, R. and McDonald, T.J. (2014) Formation and toxicity of brominated disinfection byproducts during chlorination and chloramination of water: A review. Journal of Environmental Science and Health, Part B 49(3), 212-228.
- Simon, V., Berne, F. and Gallard, H. (2015) Chloramination and bromamination of amino acids. Disinfection By-products in Drinking Water 352, 70.
- Soulard, M., Bloc, F. and Hatterer, A. (1981) Diagrams of existence of chloramines and bromamines in aqueous solution. Journal of the Chemical Society, Dalton Transactions (12), 2300-2310.
- Trofe, T.W., Inman, G.W. and Johnson, J.D. (1980) Kinetics of monochloramine decomposition in the presence of bromide. Environmental Science & Technology 14(5), 544-549.

- Trogolo, D. and Arey, J.S. (2016) Equilibria and Speciation of Chloramines, Bromamines, and Bromochloramines in Water. Environmental Science & Technology 51(1), 128-140.
- Turan, M. and Celik, M. (2003) Regenerability of Turkish clinoptilolite for use in ammonia removal from drinking water. Journal of Water Supply: Research and Technology-Aqua 52(1), 59-66.
- Van der Laan, G., Westra, C., Haas, C. and Sawatzky, G. (1981) Satellite structure in photoelectron and Auger spectra of copper dihalides. Physical Review B 23(9), 4369.
- Vartiainen, T., Liimatainen, A., Kauranen, P. and Hiisvirta, L. (1988) Relations between drinking water mutagenicity and water quality parameters. Chemosphere 17(1), 189-202.
- Vikesland, P.J., Ozekin, K. and Valentine, R.L. (1998) Effect of natural organic matter on monochloramine decomposition: pathway elucidation through the use of mass and redox balances. Environmental Science & Technology 32(10), 1409-1416.
- Vikesland, P.J. and Valentine, R.L. (2000) Reaction pathways involved in the reduction of monochloramine by ferrous iron. Environmental Science & Technology 34(1), 83-90.
- Vikesland, P.J., Valentine, R.L. and Ozekin, K. (1996) Application of product studies in the elucidation of chloramine reaction pathways. Water Disinfection and Natural Organic Matter 649, 105-114.
- Wajon, J.E. and Morris, J.C. (1982) Rates of formation of N-bromo amines in aqueous solution. Inorganic Chemistry 21(12), 4258-4263.
- WHO (2017) Guidelines for drinking-water quality: first addendum to the fourth edition.
- Xiao, W., Hong, S., Tang, Z., Seal, S. and Taylor, J.S. (2007) Effects of blending on surface characteristics of copper corrosion products in drinking water distribution systems. Corrosion Science 49(2), 449-468.
- Zhang, H. and Andrews, S.A. (2012) Catalysis of copper corrosion products on chlorine decay and HAA formation in simulated distribution systems. Water Research 46(8), 2665-2673.
- Zhang, Z., Stout, J.E., Victor, L.Y. and Vidic, R. (2008) Effect of pipe corrosion scales on chlorine dioxide consumption in drinking water distribution systems. Water Research 42(1-2), 129-136.

Every reasonable effort has been made to acknowledge the owners of copyright

material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged.

## **Chapter 6. Effect of Cu(II) on Monochloramine Stability in Bromide-Containing Waters**

The contents of Chapter 6 & Appendix 5 are unable to be reproduced here as they are under embargo due to current consideration for publication in the journal *Environmental Science & Technology*.

## **6.1 Introduction**

Monochloramine (NH<sub>2</sub>Cl) is extensively used in drinking water distribution systems as a secondary disinfectant to maintain a disinfectant residual over long distances (McCurry et al. 2015, Vikesland et al. 1998, 2001). NH<sub>2</sub>Cl has the advantage to be a weaker and more stable disinfectant producing less disinfection by-products (DBPs) than chlorine (Hua and Reckhow 2007, Sadiq and Rodriguez 2004). When bromidecontaining surface waters (bromide ~ 10-2000  $\mu$ g/L (Allard et al. 2018a, Bond et al. 2014, Pan and Zhang 2013)) are disinfected with monochloramine, a range of brominated-amines (e.g., NH<sub>2</sub>Br, NHBr<sub>2</sub>, NHBrCl) can be produced, NHBrCl being the most prominent in most cases (Allard et al. 2018a, Bousher et al. 1989, Le Roux et al. 2012, Luh and Mariñas 2014, Trofe et al. 1980, Trogolo and Arey 2016). These brominated amines are less stable than NH<sub>2</sub>Cl (Heeb et al. 2017, Luh and Mariñas 2014). Hence, the relative abundance of chloramines (NH<sub>2</sub>Cl and NHCl<sub>2</sub>) and bromamines (NH<sub>2</sub>Br and NHBr<sub>2</sub>) can strongly affect the stability of the oxidant residual required to deliver safe drinking water. In addition, bromamines and NHBrCl are able to react with organic precursors to produce toxic DBPs, such as brominated DBPs (Allard et al. 2018a, Heeb et al. 2017, Hua and Reckhow 2012, Liu et al. 2018) and N-Nitrosodimethylamine (Le Roux et al. 2012, Luh and Mariñas 2012). Therefore, it is of great significance to understand the fate of the different halamines during chloramination in the presence of bromide.

Dissolved copper might also be present in drinking water distribution systems as a corrosion product from copper pipes or applied as a biocide to control the growth of biofilm and ultimately nitrification events (Feng et al. 1996, Hu et al. 2016, Zhang and Andrews 2012). Copper(oxide) was reported to catalyse the decomposition of several halogenated disinfectants and to affect DBPs formation yields in drinking water (Fu et al. 2009b, Hu et al. 2016, Huang et al. 2019, Liu et al. 2012, 2013, Liu et al. 2019). The presence of Cu(II) catalysed the decay of NH<sub>2</sub>Cl via the formation of radicals (•OH and •NH<sub>2</sub>), thereby reducing NH<sub>2</sub>Cl concentration (Fu et al. 2009b). THM formation was also promoted in presence of Cu(II) during chloramination of humic acid (Fu et al. 2009a). Nevertheless, the impact of the simultaneous presence of bromide and Cu(II) on NH<sub>2</sub>Cl stability has not been investigated to date.

Since NH<sub>2</sub>Cl is highly stable it mainly degrades through autodecomposition. The main degradation products of NH<sub>2</sub>Cl self-decay were experimentally determined to be ammonia and nitrogen gas (Vikesland et al. 1998). In the presence of natural organic matter (NOM), the major decay products shifted to ammonia and nitrate (Vikesland et al. 1998). As previously mentioned, in presence of bromide the main halamine produced during chloramination is NHBrCl. Pope assumed that nitrogen gas was the main product of NHBrCl self-decay without experimental evidence (Pope 2006). In a recent study, the main degradation products of NH<sub>2</sub>Br were identified, in presence of Cu(II), to be nitrite and nitrous oxide (Hu et al. under review-a). Therefore, the formation of chloramine degradation products might be affected by the presence of both bromide and Cu(II).

This study aims to understand how Cu(II) affects the disinfectant stability and the degradation products of chloramine in bromide-containing waters. This will give valuable insights to the water utilities allowing a better management of disinfectant stability in drinking water systems and delivery of safe waters. The investigated parameters include reaction time, Cu(II) concentrations, bromide concentrations and solution pH.

## 6.2 Materials and Methods

## 6.2.1 Reagents

All chemicals used in this study were of analytical grade purity and all solutions were prepared with deionized water (18.2 M $\Omega$ ·cm, Milli-Q, Millipore). A sodium hypochlorite solution (10-15% active chlorine) purchased from Sigma Aldrich was used as the source of chlorine. Copper(II) sulfate pentahydrate ( $\geq$ 99.5%, Chem-Supply Pty Ltd) was used to prepare Cu(II) solutions. NH<sub>2</sub>Cl stock solutions were prepared with an ammonium chloride solution adjusted to pH 10 with sodium hydroxide. Afterwards, an equal volume of a sodium hypochlorite was added dropwise to a well stirred ammonia solution with a chlorine to ammonia molar ratio of 1:1.2 (Le Roux et al. 2016). In some experiments, <sup>15</sup>N-labelled ammonium sulfate (98% <sup>15</sup>N, Sigma Aldrich Corporation) was used to prepare NH<sub>2</sub>Cl solutions (for <sup>15</sup>N<sub>2</sub> and <sup>15</sup>N<sub>2</sub>O analysis). The <sup>15</sup>N<sub>2</sub> standard was obtained from Sigma Aldrich Corporation with 98% purity.

#### **6.2.2 Analytical Methods**

The concentration of the NH<sub>2</sub>Cl stock solution was determined by UV-Vis spectrometry at its representative wavelength  $\lambda$  ( $\epsilon_{\rm NH_2Cl, 245} = 445 \, {\rm M}^{-1} {\rm cm}^{-1}$ ,  $\epsilon_{\rm NH_2Cl, 295} = 14 \, {\rm M}^{-1} {\rm cm}^{-1}$ ) (Schreiber and Mitch 2005). The total oxidant (NH<sub>2</sub>Cl, NHCl<sub>2</sub>, NH<sub>2</sub>Br, NHBr<sub>2</sub> and NHBrCl) concentration was determined by N,N-diethyl-p-phenylenediamine (DPD) method at 515 nm (Liu et al. 2012). Nitrate (LOD 2.5 µg/L) and nitrite (LOD 1.8 µg/L) were analysed using a Dionex ICS-3000 Ion Chromatography (IC) with a suppressed conductivity detection and an IonPac AS9-HC column (Salhi and Von Gunten 1999). Ammonia concentration was determined using the indophenol colorimetric method (Verdouw et al. 1978). The indophenol method gives the total concentration of ammonia (i.e., NH<sub>4</sub><sup>+</sup> + halamines). Therefore, NH<sub>4</sub><sup>+</sup> was determined by subtracting the total oxidant concentration and decomposition of the different halamines under different experimental conditions (Allard et al. 2018b).

Gas Chromatography/Mass Spectrometry (GC/MS) was used to quantify nitrogen gas (N<sub>2</sub>), according to the method described by Vikesland and Valentine (Vikesland et al. 1996). To avoid the interference of the ubiquitous  $^{14}N_2$  present in the air,  $^{15}N$ -labelled ammonium sulfate was used in this experiment. A calibration curve for N<sub>2</sub> is presented in Figure A-5-1.

Membrane Introduction Mass Spectrometry (MIMS, Microlab Aarhus, Denmark) was applied to differentiate the different halamines and monitor <sup>15</sup>N<sub>2</sub>O. The details of the configuration of the MIMS system can be found in the literature (Kristensen et al. 2010). The MIMS inlet membrane temperature was maintained at 40 °C and the liquid sample flow rate was set to 2.2 mL/min. The mass of the parent ions were selected to monitor the different halamines and avoid interferences (Hu et al. under review-b). Molecular ions at m/z 85 (NH<sup>35</sup>Cl<sub>2</sub><sup>+</sup>), 175 (NH<sup>79</sup>Br<sup>81</sup>Br<sup>+</sup>), 131 (NH<sup>81</sup>Br<sup>35</sup>Cl<sup>+</sup>, NH<sup>79</sup>Br<sup>37</sup>Cl<sup>+</sup>) were selected to monitor NHCl<sub>2</sub>, NHBr<sub>2</sub> and NHBrCl, respectively. Standards of NHCl<sub>2</sub> and NHBr<sub>2</sub> were freshly prepared and the required solution pH was achieved by adjustment with HCl and NaOH. NH<sub>2</sub>Cl and NH<sub>2</sub>Br were not quantified by the MIMS because of interferences from NHCl<sub>2</sub> and NHBr<sub>2</sub> by MIMS according to the method described by Allard et al. (Allard et al. 2018b).  $^{15}N_2O$  was quantified by the MIMS according to the method developed by Li, et al. (Li and Blatchley 2008). The concentration of  $^{15}N_2O$  was determined by monitoring the abundance of the signal at m/z 46. A calibration curve for N<sub>2</sub>O is presented in Figure A-5-2.

X-Ray Photoelectron Spectroscopy (XPS) was employed to determine different copper valence state. To obtain an adequate amount of copper particles for the XPS analysis, a 1 L reaction solution containing 500  $\mu$ M NH<sub>2</sub>Cl, 400  $\mu$ M bromide and 1 mM Cu(II) was prepared. After 2 h reaction the solution was placed in an oven and dried at 70 °C.

#### **6.2.3 Experimental Procedures**

All experiments were conducted in the dark (flasks were wrapped in aluminium foil) under magnetic agitation at room temperature ( $24 \pm 1$  °C). Each experiment was performed in duplicate. All the reaction solutions were prepared in 20 mM borate buffer. The solution pH was adjusted to pH values typical of distribution systems (6.5, 7.5, 8.5) by the addition of acid or base solutions. The pH variation was less than 0.2 unit during the experiments.

## 6.2.3.1 Kinetic Study

All experiments were conducted in 100 mL amber bottles. Different parameters were investigated, including reaction time, Cu(II) concentration, bromide concentration and solution pH. Cu(II) was added in the buffered reaction system at 0.1, 0.2, 0.5, 1.0 and 2.0 mg/L, which were similar to concentrations reported in drinking water distribution systems ( $0.56 \pm 0.49$  mg/L) (Zietz et al. 2003). The bromide was spiked to the solutions at concentrations of 5, 10, 20 and 40  $\mu$ M (i.e., 0.4, 0.8, 1.6 and 3.2 mg/L). Reactions were initiated by the addition of NH<sub>2</sub>Cl stock solutions to the solutions containing the Cu(II) or/and bromide, at the targeted initial NH<sub>2</sub>Cl concentration of 50  $\mu$ M (3.55 mg/L as Cl<sub>2</sub>). The water samples were collected at preselected time intervals to determine the concentration of the total oxidant. MIMS was applied to follow the kinetic profiles of NHCl<sub>2</sub>, NHBr<sub>2</sub> and NHBrCl in selected experiments.

## **6.2.3.2 Product Analysis**

In order to identify the nitrogen degradation products, higher concentrations of reactant were used with initial concentrations of NH<sub>2</sub>Cl, Cu(II) and bromide of 200  $\mu$ M, 2.0

mg/L and 160  $\mu$ M, respectively. The buffered reaction solutions were kept at pH 6.5, and the samples were withdrawn after 51 h of reaction time to ensure a high consumption of the total oxidant. Four different scenarios were investigated, including NH<sub>2</sub>Cl self-decay, NH<sub>2</sub>Cl decay in presence of Br<sup>-</sup>, NH<sub>2</sub>Cl decay in presence of Cu(II) and NH<sub>2</sub>Cl decay in presence of both Br<sup>-</sup> and Cu(II). For the analysis of nitrate, nitrite and ammonia, 100 mL amber bottles were used and the reaction solutions were quenched by an excess of sodium sulfite at least 5 times the initial NH<sub>2</sub>Cl concentration. 20 mL capped amber vials with 10 mL headspace were used to determine the concentration of <sup>15</sup>N<sub>2</sub> by GC/MS, while 20 mL capped amber vials without headspace were used to determine the concentration of <sup>15</sup>N<sub>2</sub>O by MIMS.

## 6.3 Results and Discussion

# 6.3.1 Synergistic Effect of Cu(II) and Bromide on the Decomposition of the Total Oxidant and Halamines Speciation

The effect of Cu(II) and bromide on the total oxidant decomposition and the fate of the different halamines in the presence of NH<sub>2</sub>Cl at pH 6.5 are shown in Figure 6-1.



**Figure 6-1.** Synergistic effect of Cu(II) and bromide on (a) the total oxidant decomposition and (b) different halamines formation and decomposition. Experimental conditions:  $[NH_2Cl]_0 = 50 \,\mu\text{M}$ ,  $[Br^-]_0 = 40 \,\mu\text{M}$ ,  $[Cu(II)]_0 = 0.5 \,\text{mg/L}$ , 20 mM borate buffer, pH 6.5. Modelling data were simulating a chloraminated bromide-containing water without Cu(II). MIMS data compared the fate of NHBrCl with and without Cu(II).

As shown in Figure 6-1a, in the absence of Cu(II) and Br<sup>-</sup>, the total oxidant only decreased by 3% in 6 h. The addition of 0.5 mg/L Cu(II) or 40  $\mu$ M Br<sup>-</sup> slightly enhanced the decomposition of the total oxidant, leading to a decrease of 16% or 11% of the total oxidant in 6 h, respectively. These observations were consistent with

previous studies showing that Cu(II) and Br<sup>-</sup> catalysed the decay of NH<sub>2</sub>Cl (Fu et al. 2009c, Vikesland et al. 2001). When Cu(II) and Br<sup>-</sup> were present simultaneously, a significant increase of the total oxidant decomposition was observed with 65% degradation in 6 h. It was found by using the halamine model (Allard et al. 2018a), that in absence of Cu(II) and under our experimental conditions, NHBrCl was the main halamine produced accounting for 38% of the total oxidant concentration, while NHCl<sub>2</sub> only accounted for 4%, NH<sub>2</sub>Br and NHBr<sub>2</sub> was negligible after 6 h (the percentages are expressed in mole of oxidant, i.e., 1 mole of  $NH_2Cl = 1$  mole of oxidant, 1 mole of NHBrCl = 2 moles of oxidant) (Figure 6-1b). The remaining  $NH_2Cl$ accounted for 53% of the initial NH<sub>2</sub>Cl concentration based on the model simulation. This was confirmed by using the MIMS (Figure 6-1b and A-5-3), the formation of NHBrCl determined by MIMS accounted for 34% of the initial NH<sub>2</sub>Cl concentration and NHCl<sub>2</sub> accounted for 3%, no NHBr<sub>2</sub> was detected after 6 h. The MIMS experimental results were in good agreement with the model predictions. Since Cu(II) had a limited effect on NH<sub>2</sub>Cl decay, it was hypothesised that Cu(II) mainly catalysed NHBrCl degradation, resulting in an increased total oxidant decomposition. This has been confirmed experimentally by MIMS. As shown in Figure 6-1b, in presence of 0.5 mg/L Cu(II), NHBrCl was fully consumed. By comparing the experimental results (Figure 6-1a) and the kinetic modelling data (Figure 6-1b), it can be concluded that the degradation of NHBrCl accounted for a large portion of the total oxidant decay with 70% after 6 hours. NH<sub>2</sub>Cl catalytically decayed in presence of Cu(II) but to a lower extent representing 22% of the total oxidant decay (Figure 6-1a). The missing 8% might come from the degradation of NHCl<sub>2</sub> by Cu(II) (Figure A-5-3).

# **6.3.2** Effect of Cu(II) Concentration on the Decomposition of the Total Oxidant and Halamines Speciation

The effect of Cu(II) concentration from 0 to 2.0 mg/L on the decomposition of total oxidant and NHBrCl in the presence of 50  $\mu$ M NH<sub>2</sub>Cl and 40  $\mu$ M Br<sup>-</sup> at pH 6.5 are shown in Figure 6-2.



**Figure 6-2.** Effect of Cu(II) concentration on (a) the total oxidant decay in the presence of NH<sub>2</sub>Cl and bromide, and (b) NHBrCl formation and decomposition determined by MIMS. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu\text{M}$ ,  $[Br]_0 = 40 \ \mu\text{M}$ , 20 mM borate buffer, pH 6.5.

Increasing the Cu(II) concentration from 0 to 0.5 mg/L significantly enhanced the total oxidant degradation. However, when the Cu(II) concentration was increased from 0.5 to 2.0 mg/L, the decomposition rate of the total oxidant was relatively similar. NHBrCl formation and decomposition in the presence and absence of Cu(II) was monitored by MIMS (Figure 6-2b). NHBrCl was continuously formed during the 6 h reaction in the absence of Cu(II). However, the presence of 0.1 mg/L Cu(II) decreased the NHBrCl concentration significantly. For 0.5 mg/L Cu(II), almost all NHBrCl was degraded. Therefore, a further increase in Cu(II) concentration does not lead to a large decrease in total oxidant since NHBrCl was the main factor responsible for the total oxidant decay. For Cu(II) concentration greater than 0.5 mg/L the limiting factor controlling the total oxidant decay is not the Cu(II) concentration but the formation of NHBrCl. It has to be noticed that NHCl<sub>2</sub> was also formed at low concentrations (MIMS data in Figure A-5-3 and model prediction in Figure A-5-4b) and its decay was also catalysed in presence of Cu(II).

## 6.3.3 Effect of Bromide Concentration on the Total Oxidant Decay Kinetic

The effect of bromide concentration from 0 to 40  $\mu$ M on the total oxidant decomposition in the presence of 50  $\mu$ M NH<sub>2</sub>Cl and 0.5 mg/L Cu(II) at pH 6.5 is shown in Figure 6-3a.



**Figure 6-3.** Effect of bromide concentration on the total oxidant decay in the presence of NH<sub>2</sub>Cl and Cu(II). (a) Total oxidant decay as a function of time. (b) Pseudo first order rate constant ( $k_{obs}$ ) of the total oxidant decay as a function of bromide concentration. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$ ,  $[Cu(II)]_0 = 0.5 \ mg/L$ , 20 mM borate buffer, pH 6.5. Dashed lines represent the modelling result of Cu(II)-catalysed total oxidant decay.

In presence of copper, the total oxidant decomposition increased with increasing bromide concentration (Figure 6-3a). As shown by the model prediction (Figure A-5-4c), increasing the concentration of bromide increased the formation of NHBrCl. As previously demonstrated the total oxidant decay is mainly driven by the interaction between NHBrCl and Cu(II). Therefore, the rate of the total oxidant decomposition increased with increasing Br<sup>-</sup> concentration (Figure 6-3b). The pseudo first order rate constant  $k_{obs}$  of the total oxidant decay increased from 7.9 × 10<sup>-6</sup> s<sup>-1</sup> for 0 µM Br<sup>-</sup> to 4.61 × 10<sup>-5</sup> s<sup>-1</sup> for 40 µM Br<sup>-</sup> (Figure A-5-5 and 6-3b). As shown in Figure 3b,  $k_{obs}$  values were proportional to the Br<sup>-</sup> concentrations with R<sup>2</sup> = 0.9800. This suggested that the Cu(II)-catalysed total oxidant decomposition in the presence of NH<sub>2</sub>Cl and Br<sup>-</sup> was first order with respect to the total oxidant and first order respect to bromide ion. In order to predict the Cu(II)-catalysed total oxidant decay can be expressed as:

$$-d[total oxidant]/dt = k_0[total oxidant] + k_{app}[total oxidant][Br^-]$$
(1)

Where  $k_0$  represents the first order rate constant of the total oxidant decay without bromide and  $k_{app}$  represents the second order rate constant of the total oxidant decay with bromide.  $k_0$  was calculated to be  $1.023 \times 10^{-5}$  s<sup>-1</sup> (intercept of  $k_{obs}$  versus bromide concentration in Figure 6-3b).  $k_{app}$  was determined to be 0.93 M<sup>-1</sup>s<sup>-1</sup> (slope of  $k_{obs}$ versus bromide concentration in Figure 6-3b). A good fit to the experimental data was obtained for the total oxidant decay under varying bromide concentrations (Figure 6-3a).

#### 6.3.4 Effect of pH on the Decomposition of the Total Oxidant

The effect of pH from 6.5 to 8.5 on the total oxidant decomposition in the presence of  $50 \,\mu\text{M}$  NH<sub>2</sub>Cl,  $40 \,\mu\text{M}$  Br<sup>-</sup> and 0.5 mg/L Cu(II) is shown in Figure 6-4.



**Figure 6-4.** Effect of pH (6.5, 7.5, 8.5) on the total oxidant decay in the presence of NH<sub>2</sub>Cl, bromide and Cu(II). Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$ ,  $[Br^-]_0 = 0$ , 40  $\mu M$ ,  $[Cu(II)]_0 = 0.5 \ mg/L$ , 20 mM borate buffer.

As expected from the chemistry of halamines (Bousher et al. 1989, Trofe et al. 1980), the total oxidant stability decreased with decreasing pH in absence of Cu(II) with 1.2%, 3.7% and 16.2% decay for pH 8.5, 7.5 and 6.5, respectively (Figure 6-4). In the presence of Cu(II), the same trend was observed but to a higher extent with 3.3%, 23.1% and 65.4% decay for pH 8.5, 7.5 and 6.5, respectively. It can be observed that the Cu(II)-catalysed total oxidant decay (the difference between the total oxidant self-decay and experiment with Cu(II)) increased with decreasing pH. This behaviour confirms our previous finding since as shown by the model prediction without Cu(II), NHBrCl formation (Figure A-5-6a) and NH<sub>2</sub>Cl decay (Figure A-5-6b) are higher at lower pH. The enhanced total oxidant decay was mainly attributed to the higher formation of NHBrCl at lower pH and its further catalytic degradation in presence of Cu(II). NHCl<sub>2</sub> formation also increased at lower pH, but its concentration was always one order of magnitude lower than NHBrCl (Figure A-5-6c).

#### **6.3.5 Product Analysis**

To provide direct evidence of the mechanism of Cu(II)-catalysed total oxidant decay in the presence of Cu(II) and Br<sup>-</sup>, the main nitrogen decay products, nitrogen gas (N<sub>2</sub>), ammonia (NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup>), nitrous oxide (N<sub>2</sub>O) and nitrate (NO<sub>3</sub><sup>-</sup>), were quantified (Figure 6-5). A nitrogen mass balance based on the total oxidant loss is presented. The total oxidant loss is expressed as nitrogen equivalent ( $\Delta$ Total N) (Figure 6-5). No nitrite or bromate were observed during the IC analysis. Table A-5-1 summarized the molar percent recoveries of different nitrogenous by-products, and an excellent total N recovery was obtained for these experiments with 100 ± 10%.



**Figure 6-5.** Nitrogen mass balance and formation of degradation products in presence or absence of bromide and/or Cu(II). Experimental conditions:  $[NH_2Cl]_0 = 200 \ \mu M$ ,  $[Cu(II)]_0 = 2.0 \ \text{mg/L}$ ,  $[Br]_0 = 160 \ \mu M$ , 20 mM borate buffer, pH 6.5, reaction time = 51 h.  $\Delta$ Total N = loss of total N (loss of total oxidant).

For the experiment conducted with NH<sub>2</sub>Cl in absence of bromide and copper at pH 6.5, the total oxidant only decreased by 55.2  $\mu$ M after 51 h, while most of the oxidant was consumed under other experimental conditions. N<sub>2</sub> and NH<sub>4</sub><sup>+</sup> were found to be the main nitrogen decay products during NH<sub>2</sub>Cl self-decay, accounting for 59.8% and 28.1% of total N, respectively. N<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> were detected at low levels accounting for 2.4% and 1.1% of total N, respectively. These results were similar to the study of Vikesland and Valentine where NH<sub>4</sub><sup>+</sup> and N<sub>2</sub> were found to be the primary nitrogen decay products from NH<sub>2</sub>Cl self-decay (Vikesland et al. 1998). In presence of Br<sup>-</sup>, Cu(II) and Br<sup>-</sup>+Cu(II), N<sub>2</sub> and NH<sub>4</sub><sup>+</sup> were still the main nitrogen decay products. N<sub>2</sub> yields accounted for 68.8 ± 1.3% of total N and NH<sub>4</sub><sup>+</sup> for 30.2 ± 6.4%. N<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> were both formed at yields accounting for less than 2%. This is different from our previous
study where N<sub>2</sub>O and NO<sub>2</sub><sup>-</sup> were found to be the main degradation products when NH<sub>2</sub>Br was degraded by Cu(II) (Hu et al. under review-a). Overall, the presence of Br<sup>-</sup> and/or Cu(II) does not change the nitrogen decomposition products speciation significantly compared to NH<sub>2</sub>Cl self-decay. N<sub>2</sub> and NH<sub>4</sub><sup>+</sup> were the two major products, and N<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> were produced at low levels.

XPS was used to further understand the reactivity of Cu(II) and elucidate if there was a change in oxidation state during its reaction. The XPS spectra of a CuCl<sub>2</sub>(s) standard and copper particles after the reaction were obtained (Figure A-5-7). Cu 2p of CuCl<sub>2</sub> standard showed that it had two peaks at binding energy of 934.8 eV and 954.5 eV, while the copper particle sample presented similar peaks. In contrast to the reaction of bromamines with Cu(II) no change in oxidation state was observed.

As previously described, the speciation of the degradation products in our experimental conditions are similar to the degradation products formed during  $NH_2Cl$  decomposition, only the yield is higher. Therefore, the main reactions involved in  $NH_2Cl$  decomposition and the formation of degradation products (2-3) were used to suggest a possible mechanism (Valentine et al. 1988).

$$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$$
<sup>(2)</sup>

$$NH_2Cl + NHCl_2 \rightarrow N_2 + 3Cl^- + 3H^+$$
(3)

Basically,  $NH_4^+$  (or  $NH_3$ ) is formed by the degradation of  $NH_2Cl$  disproportionation and  $N_2$  by reaction of  $NH_2Cl$  with  $NHCl_2$ . Since NHBrCl is the main halamine responsible for the total oxidant decay in the presence of Cu(II), Cu(II)-induced NHBrCl decay is mainly discussed here. As shown by Trofe et al. (Trofe et al. 1980), NHBrCl is formed through reaction 4-6 and  $NH_4^+$  is released during this process.

$$\mathrm{NH}_2\mathrm{Cl} + \mathrm{H}^+ \to \mathrm{NH}_3\mathrm{Cl}^+ \tag{4}$$

$$\mathrm{NH}_{3}\mathrm{Cl}^{+} + \mathrm{Br}^{-} \to \mathrm{NH}_{3}\mathrm{Br}^{+} + \mathrm{Cl}^{-}$$
(5)

$$NH_2Cl + NH_3Br^+ \rightarrow NHBrCl + NH_4^+$$
(6)

Thereafter, similar to the reaction of  $NH_2Cl$  with  $NHCl_2$  it is hypothesised that NHBrCl reacts with  $NH_2Cl$  to form  $N_2$  through a Cu(II) catalysed process (equation 7) (Vikesland et al. 2001).

$$Cu(II)-NHBrCl + NH_2Cl \rightarrow N_2 + Br^- + 2Cl^- + 3H^+ + Cu(II)$$
(7)

It has been demonstrated that in the presence of Cu(II) a Cu(II)-NH<sub>2</sub>Cl complex is formed (Fu et al. 2009b). By analogy it is postulated that a Cu(II)-NHBrCl complex is formed. Similar to  $\delta$ -MnO<sub>2</sub> (Allard and Gallard 2013, Gallard et al. 2009) and CuO (Liu et al. 2014), the complexation of NHBrCl with the lewis acid Cu(II) increased its electrophilicity and as a consequence increased its reactivity. The complexation of NHBrCl enhanced its reactivity towards NH<sub>2</sub>Cl resulting in a catalytic formation of N<sub>2</sub> as a final product. Thereafter, bromide is released in solution and recycled leading to additional formation of NHBrCl and release of NH<sub>4</sub><sup>+</sup> (equation 6).

# **6.4 Practical Implications**

NH<sub>2</sub>Cl has been extensively applied in long drinking water systems since it is a more stable disinfectant than chlorine. However, the naturally occurring bromide can react with NH<sub>2</sub>Cl to produce different brominated-halamines, especially NHBrCl, resulting in the degradation of NH<sub>2</sub>Cl. Cu(II), released from copper pipes or added as a biocide in the distribution system, was found to enhance the decay of NHBrCl in our study. In addition, the released bromide from Cu(II)-catalysed NHBrCl decay can further react with NH<sub>2</sub>Cl, leading to an additional formation of NHBrCl and further decrease the available NH<sub>2</sub>Cl needed for disinfection in drinking water. The experimental conditions applied in this study is similar to concentrations usually encountered in real water distribution systems, i.e., Cu(II) concentration, bromide concentration and pH. Therefore, the concomitant presence of Cu(II) and bromide in chloraminated distribution systems might lead to unexpected loss of disinfectant residual. This exposes the pipeline to the potential growth of a highly pathogenic organisms like *Naegleria fowleri* (Puzon et al. 2009) that can be harmful to human health.

Based on our results, several control strategies should be proposed to maintain the disinfectant stability. Firstly, increase the water pH to reduce the formation of NHBrCl. Secondly, replace the copper pipes or disuse Cu(II) as a biocide to avoid the presence of dissolved copper in water. Additional research should be carried out to assess the

effect of Cu(II) on the formation of disinfection byproducts and toxicity during chloramination of bromide-containing waters.

# **6.5 References**

- Allard, S., Cadee, K., Tung, R. and Croué, J.-P. (2018a) Impact of brominated amines on monochloramine stability during in-line and pre-formed chloramination assessed by kinetic modelling. Science of the Total Environment 618, 1431-1439.
- Allard, S. and Gallard, H. (2013) Abiotic formation of methyl iodide on synthetic birnessite: A mechanistic study. Science of the Total Environment 463, 169-175.
- Allard, S.b., Hu, W., Le Menn, J.-B., Cadee, K., Gallard, H. and Croué, J.-P. (2018b) Method development for quantification of bromochloramine using membrane introduction mass spectrometry. Environmental Science & Technology 52(14), 7805-7812.
- Bond, T., Huang, J., Graham, N.J. and Templeton, M.R. (2014) Examining the interrelationship between DOC, bromide and chlorine dose on DBP formation in drinking water—a case study. Science of the Total Environment 470, 469-479.
- Bousher, A., Brimblecombe, P. and Midgley, D. (1989) Kinetics of reactions in solutions containing monochloramine and bromide. Water Research 23(8), 1049-1058.
- Feng, Y., Teo, W.-K., Siow, K.-S., Tan, K.-L. and Hsieh, A.-K. (1996) The corrosion behaviour of copper in neutral tap water. Part I: corrosion mechanisms. Corrosion Science 38(3), 369-385.
- Fu, J., Qu, J., Liu, R., Qiang, Z., Liu, H. and Zhao, X. (2009a) Cu (II)-catalyzed THM formation during water chlorination and monochloramination: A comparison study. Journal of Hazardous Materials 170(1), 58-65.
- Fu, J., Qu, J., Liu, R., Qiang, Z., Zhao, X. and Liu, H. (2009b) Mechanism of Cu (II)catalyzed monochloramine decomposition in aqueous solution. Science of the Total Environment 407(13), 4105-4109.
- Fu, J., Qu, J., Liu, R., Zhao, X. and Qiang, Z. (2009c) The influence of Cu (II) on the decay of monochloramine. Chemosphere 74(2), 181-186.
- Gallard, H., Allard, S., Nicolau, R., Von Gunten, U. and Croué, J.P. (2009) Formation of iodinated organic compounds by oxidation of iodide-containing waters with manganese dioxide. Environmental Science & Technology 43(18), 7003-7009.
- Hansen, K., Gylling, S. and Lauritsen, F.R. (1996) Time-and concentration-dependent relative peak intensities observed in electron impact membrane inlet mass spectra. International Journal of Mass Spectrometry and Ion Processes 152(2-3), 143-155.
- Heeb, M.B., Kristiana, I., Trogolo, D., Arey, J.S. and Von Gunten, U. (2017) Formation and reactivity of inorganic and organic chloramines and bromamines during oxidative water treatment. Water Research 110, 91-101.

- Hu, J., Qiang, Z., Dong, H. and Qu, J. (2016) Enhanced formation of bromate and brominated disinfection byproducts during chlorination of bromide-containing waters under catalysis of copper corrosion products. Water Research 98, 302-308.
- Hu, W., Allard, S., Lee, Y. and Croué, J.-P. (under review-a) Mechanistic Investigation of Bromamines Decomposition in the Presence of Cu(II).
- Hu, W., Lauritsen, F.R., Croué, J.-P. and Allard, S. (under review-b) Identification and quantification of chloramines, bromamines and bromochloramine by Membrane Introduction Mass Spectrometry (MIMS).
- Hua, G. and Reckhow, D.A. (2007) Comparison of disinfection byproduct formation from chlorine and alternative disinfectants. Water Research 41(8), 1667-1678.
- Hua, G. and Reckhow, D.A. (2012) Evaluation of bromine substitution factors of DBPs during chlorination and chloramination. Water Research 46(13), 4208-4216.
- Huang, H., Shao, K.-L., Duan, S.-Y. and Zhong, C.-Y. (2019) Effect of copper corrosion products on the formation and speciation of haloacetamides and haloacetonitriles during chlorination. Separation and Purification Technology 211, 467-473.
- Kristensen, G.H., Klausen, M.M., Hansen, V.A. and Lauritsen, F.R. (2010) On-line monitoring of the dynamics of trihalomethane concentrations in a warm public swimming pool using an unsupervised membrane inlet mass spectrometry system with off-site real-time surveillance. Rapid Communications in Mass Spectrometry 24(1), 30-34.
- Le Roux, J., Gallard, H. and Croué, J.-P. (2012) Formation of NDMA and halogenated DBPs by chloramination of tertiary amines: the influence of bromide ion. Environmental Science & Technology 46(3), 1581-1589.
- Le Roux, J., Nihemaiti, M. and Croué, J.-P. (2016) The role of aromatic precursors in the formation of haloacetamides by chloramination of dissolved organic matter. Water Research 88, 371-379.
- Li, J. and Blatchley, E.R. (2008) UV photodegradation of inorganic chloramines. Environmental Science & Technology 43(1), 60-65.
- Liu, C., Salhi, E., Croué, J.-P. and Von Gunten, U. (2014) Chlorination of iodidecontaining waters in the presence of CuO: formation of periodate. Environmental Science & Technology 48(22), 13173-13180.
- Liu, C., Von Gunten, U. and Croué, J.-P. (2012) Enhanced bromate formation during chlorination of bromide-containing waters in the presence of CuO: catalytic disproportionation of hypobromous acid. Environmental Science & Technology 46(20), 11054-11061.
- Liu, C., Von Gunten, U. and Croué, J.-P. (2013) Enhanced chlorine dioxide decay in the presence of metal oxides: Relevance to drinking water distribution systems. Environmental Science & Technology 47(15), 8365-8372.
- Liu, J., Wang, J., Zhang, J. and Mu, Y. (2019) Iodo-trihalomethanes formation during chlorination and chloramination of iodide-containing waters in the presence of Cu2+. Science of the Total Environment.
- Liu, R., Tian, C., Hu, C., Qi, Z., Liu, H. and Qu, J. (2018) Effects of bromide on the formation and transformation of disinfection by-products during chlorination and chloramination. Science of the Total Environment 625, 252-261.
- Luh, J. and Mariñas, B.J. (2012) Bromide ion effect on N-nitrosodimethylamine formation by monochloramine. Environmental Science & Technology 46(9), 5085-5092.

- Luh, J. and Mariñas, B.J. (2014) Kinetics of bromochloramine formation and decomposition. Environmental Science & Technology 48(5), 2843-2852.
- McCurry, D.L., Krasner, S.W., Von Gunten, U. and Mitch, W.A. (2015) Determinants of disinfectant pretreatment efficacy for nitrosamine control in chloraminated drinking water. Water Research 84, 161-170.
- Pan, Y. and Zhang, X. (2013) Four groups of new aromatic halogenated disinfection byproducts: effect of bromide concentration on their formation and speciation in chlorinated drinking water. Environmental Science & Technology 47(3), 1265-1273.
- Pope, P.G. (2006) Haloacetic acid formation during chloramination: role of environmental conditions, kinetics, and haloamine chemistry.
- Puzon, G.J., Lancaster, J.A., Wylie, J.T. and Plumb, J.J. (2009) Rapid detection of Naegleria fowleri in water distribution pipeline biofilms and drinking water samples. Environmental Science & Technology 43(17), 6691-6696.
- Sadiq, R. and Rodriguez, M.J. (2004) Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review. Science of the Total Environment 321(1-3), 21-46.
- Salhi, E. and Von Gunten, U. (1999) Simultaneous determination of bromide, bromate and nitrite in low μg l- 1 levels by ion chromatography without sample pretreatment. Water Research 33(15), 3239-3244.
- Schreiber, I.M. and Mitch, W.A. (2005) Influence of the order of reagent addition on NDMA formation during chloramination. Environmental Science & Technology 39(10), 3811-3818.
- Trofe, T.W., Inman, G.W. and Johnson, J.D. (1980) Kinetics of monochloramine decomposition in the presence of bromide. Environmental Science & Technology 14(5), 544-549.
- Trogolo, D. and Arey, J.S. (2016) Equilibria and speciation of chloramines, bromamines, and bromochloramines in water. Environmental Science & Technology 51(1), 128-140.
- Valentine, R.L., Jafvert, C.T. and Leung, S.W. (1988) Evaluation of a chloramine decomposition model incorporating general acid catalysis. Water Research 22(9), 1147-1153.
- Verdouw, H., Van Echteld, C. and Dekkers, E. (1978) Ammonia determination based on indophenol formation with sodium salicylate. Water Research 12(6), 399-402.
- Vikesland, P.J., Ozekin, K. and Valentine, R.L. (1998) Effect of natural organic matter on monochloramine decomposition: pathway elucidation through the use of mass and redox balances. Environmental Science & Technology 32(10), 1409-1416.
- Vikesland, P.J., Ozekin, K. and Valentine, R.L. (2001) Monochloramine decay in model and distribution system waters. Water Research 35(7), 1766-1776.
- Vikesland, P.J., Valentine, R.L. and Ozekin, K. (1996), ACS Publications.
- Zhang, H. and Andrews, S.A. (2012) Catalysis of copper corrosion products on chlorine decay and HAA formation in simulated distribution systems. Water Research 46(8), 2665-2673.
- Zietz, B.P., Dieter, H.H., Lakomek, M., Schneider, H., Keßler-Gaedtke, B. and Dunkelberg, H. (2003) Epidemiological investigation on chronic copper toxicity to children exposed via the public drinking water supply. Science of the Total Environment 302(1-3), 127-144.

Every reasonable effort has been made to acknowledge the owners of copyright material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged.

# **Chapter 7. Effect of Cu(II) on Disinfection Byproducts Formation during Chloramination**

The contents of Chapter 7 & Appendix 6 are unable to be reproduced here as they are under embargo due to current consideration for publication in the journal *Chemosphere*.

# 7.1 Introduction

Monochloramine (NH<sub>2</sub>Cl) has been widely utilized as an alternative disinfectant to chlorine in long drinking water distribution systems (Le Roux et al. 2011, Yan et al. 2018, Yang et al. 2007). Even though the formation of regulated disinfection byproducts (DBPs) during chloramination is lower than during chlorination, it can still causes potential health risk to drinking water consumers by forming its own set of DBPs (Chu et al. 2010, Hua and Reckhow 2012). Trihalomethanes (THMs) is the major class of carbonaceous DBPs (C-DBPs) produced during both chlorination and chloramination (Sakai et al. 2016), and regulated by the US Environmental Protection Agency (USEPA) (Goslan et al. 2009). However, NH<sub>2</sub>Cl may increase the formation of unregulated DBPs, such as nitrogenous DBPs (N-DBPs) (Chuang et al. 2013, Lee et al. 2007). Haloacetonitriles (HANs) and haloacetamides (HAcAms) have recently received increasing attention because they exhibit a higher toxicity than the common regulated DBPs (Bond et al. 2011, Muellner et al. 2007, Shah and Mitch 2011). Bromide is frequently detected in source waters with concentrations ranging from several µg/L to mg/L (Heller-Grossman et al. 1999, Magazinovic et al. 2004, Pan and Zhang 2013, Von Gunten 2003). During chlorination, bromide can be rapidly oxidized to bromine (HOBr), it further reacts with natural organic matter (NOM) to produce brominated DBPs (Br-DBPs), which present higher health risks than their chlorinated analogues (Hua and Reckhow 2012, Sun et al. 2009, Tian et al. 2013). It was reported that NH<sub>2</sub>Cl can react with bromide to form monobromamine (NH<sub>2</sub>Br), dibromamine (NHBr<sub>2</sub>) and bromochloramine (NHBrCl) (Allard et al. 2018, Luh and Mariñas 2014, Trofe et al. 1980). The presence of these brominated halamines was shown to promote the formation of Br-DBPs (Heeb et al. 2017, Liu et al. 2018b). Therefore, it is vital for utilities to mitigate the formation of both N-DBPs and Br-DBPs to reduce any potential health risks.

Copper piping has been prevalent in home-plumbing systems, and copper salts can also be added to the drinking water distribution systems as a biocide to ensure the safe delivery of water (Boulay and Edwards 2001, Li et al. 2007). However, the presence of copper (e.g., CuO, Cu<sub>2</sub>O, Cu<sup>2+</sup>) in potable water decreases the disinfectant stability and affect the formation and speciation of DBPs (Blatchley et al. 2003, Hu et al. 2016, Liu and Croué 2015). Cu(II) (refers to soluble copper(II)) can be found in distribution

systems at concentrations up to several mg/L (Broo et al. 1998, Zhang and Andrews 2012). It was reported that Cu(II) slightly enhanced the decay of NH<sub>2</sub>Cl in absence of DBPs precursors with second order rate constant of 0.07-0.33 M<sup>-1</sup>h<sup>-1</sup> (Fu et al. 2009b). However, Cu(II) did not affect the autodecomposition of chlorine (Liu et al. 2013). During chlorination, studies revealed that the addition of CuO/Cu(II) can promote the formation of THMs, HAAs, bromate, Br-DBPs, HANs and HAcAms (Fu et al. 2009a, Hu et al. 2016, Huang et al. 2019, Liu et al. 2013). Whereas, it was found that Cu(II) had no effect on THMs formation for resorcinol and 3,5-dihydroxybenzoic acid (Fu et al. 2009a). The presence of Cu(II) did not affect the yields of dichloroacetonitrile (DCAN) and dichloroacetamide (DCAcAm) from tryptophan and phenylalanine, respectively (Huang et al. 2019). Cu(II) can bind with functional groups in model compounds or NOM and could change their reactivity toward oxidant, leading to different DBPs formation and distribution (Hu et al. 2016, Liu et al. 2013, Zhang and Andrews 2012). In the presence of Cu(II), the formation of Cl-THMs from humic acid (HA) was enhanced by 44% during chloramination, (Fu et al. 2009a). However, to our best knowledge, little information is available on the effect of Cu(II) on N-DBPs or Br-DBPs formation during chloramination, in the presence of model compounds or NOM.

The objective of this study is to investigate the effect of Cu(II) on THMs, HANs and DCAcAm (the most representative HAcAms) formation during chloramination of different model compounds and NOM. The effects of Cu(II) concentration, reaction time, and pH on DBPs formation and speciation from selected model compounds were examined in detail. Moreover, the effects of Cu(II) concentration and bromide concentration on DBPs formation and species distribution from NOM were studied. Understanding the fate of DBPs formation in the presence of Cu(II) would provide useful information to optimise control strategies in real water distribution systems.

# 7.2 Materials and Methods

# 7.2.1 Chemicals

All chemicals used in this study were of reagent grade purity. Carboxylic acid, amino acids and phenolic compounds are important constituents of NOM (Matilainen and Sillanpää 2010), thus these three groups of chemical were used to select nine model

compounds. These model compounds were citric acid (CA, 99%), glycine (Gly, 99%), histidine (His, 99%), aspartic acid (Asp, 98%), cysteine (Cys, 98%), phenol (PhOH, 99%), resorcinol (RC, 99%), hydroquinone (HQ, 99%) and p-hydroxybenzoic acid (PHBA, 99%). They were all purchased from Sigma-Aldrich. The physicochemical properties of these model compounds are displayed in Table A-6-1. 10 mM stock solutions were prepared by dissolution of the model compounds into deionized water (18.2 M $\Omega$ ·cm, Milli-Q, Millipore). A sodium hypochlorite solution (5% active chlorine, J.T.Baker) was used as the source of chlorine. Monochloramine was synthesised by dropwise addition of equal volumes of a chlorine solution to a stirred solution of ammonium chloride at an ammonia to chlorine molar ratio of 1.2:1, and the solution pH was adjusted to 9 with NaOH. Potassium bromide (KBr,  $\geq$ 99%) and cupric chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O,  $\geq$ 99%) were dissolved into deionized water to prepare stock solutions and used as the source of bromide and Cu(II), respectively. Suwannee River NOM (Catalog No. 2R101N, International Humic Substances Society) was selected as a representative extract of natural organic matter.

Four THMs standards (chloroform (TCM), dichlorobromomethane (DCBM), dibromochloromethane (DBCM), and bromoform (TBM)), six HANs standards (monochloro-, dichloro-, trichloro-, monobromo-, dibromo-, and bromochloro-acetonitrile (MCAN, DCAN, TCAN, MBAN, DBAN, and BCAN, respectively)), and dichloroacetamide (DCAcAm) standard were purchased from Sigma-Aldrich.

#### 7.2.2 Analytical Methods

The concentration of residual oxidant was analysed by the N,N-diethyl-pphenylenediamine (DPD) method with the addition of KI using a UV-visible spectrophotometer (Cary 50) monitored at 515 nm (Federation and Association 2005). Four THMs (TCM, DCBM, DBCM and TBM), six HANs (MCAN, DCAN, TCAN, MBAN, DBAN, and BCAN) and DCAcAm were quantified using an Agilent 6890 GC equipped with a DB-1 column (J&W Scientific 30m x 0.25mm x 0.001mm), and an electron capture detector (ECD). The details of the analytical methods can be found in the literature (Liu et al. 2018a). The detection limits for the DBPs measurements were  $0.2 \mu g/L$ .

#### 7.2.3 Experimental Procedures

All experiments were performed in the dark in 125 mL capped amber bottles without headspace at room temperature ( $24 \pm 1^{\circ}$ C). Each experiment was conducted in duplicate. Reactions were initiated by the addition of an aliquot of NH<sub>2</sub>Cl stock solutions into the reaction solutions. Borate buffer was applied to maintain the pH since phosphate buffer complexed with Cu(II) and affect the reaction. After preselected time intervals, samples were collected for the determination of residual oxidant and analysis of the selected DBPs. 1.5 times molar ratio of ascorbic acid to the initial monochloramine concentration was used to quench the reaction for DBPs analysis.

#### 7.2.3.1 Model Compounds Experiments

In order to maximize the formation of DBPs, 1 mM monochloramine and 100  $\mu$ M model compounds were used in this study. Firstly, DBPs formation from nine model compounds under four different experimental conditions were investigated, including in absence of Cu(II) and bromide, in presence of Cu(II) (2.0 mg/L) or bromide (20  $\mu$ M) individually and the simultaneous presence of Cu(II) and bromide. Thereafter, based on the first set of experiments, two model compounds (hydroquinone and p-hydroxybenzoic acid) were selected due to their relative high potential to produce DBPs, and the effect of Cu(II) concentrations (0, 0.2, 0.5, 1.0, 2.0, and 5.0 mg/L), reaction time (0.5, 2, 8, 24, 48 and 72 h) and pH (6, 7, 8, and 9) were investigated. 10 mM borate buffer was used for experiments at pH 8 and 9, and 50 mM borate buffer was used for pH 6 and 7. The pH deviation for experiments at pH 7, 8 and 9 was less than 0.2 unit during the whole reaction. However, for the pH 6 experiments the pH decreased to 4.2 at the end of the reaction.

## 7.2.3.2 NOM Experiments

The Suwannee River NOM was controlled at a DOC of 7.2 mgC/L. The initial monochloramine concentration was 1 mM and the pH was maintained at 8 (10 mM borate buffer). The effect of Cu(II) concentrations (0, 0.5, 2.0 and 5.0 mg/L) and bromide concentrations (0, 1, 5, 20, 50  $\mu$ M) on DBPs formation were investigated.

# 7.3 Results and Discussion

#### 7.3.1 DBPs Formation from Different Model Compounds

Figure 7-1 shows the concentrations of THMs, HANs and DCAcAm formed from the nine model compounds during chloramination under four different experimental conditions. The residual oxidant concentrations ranged from 390 to 880  $\mu$ M after 72 h reaction (Figure A-6-1), indicating that NH<sub>2</sub>Cl concentration was always in large excess.



**Figure 7-1.** Formation of (a) THMs, (b) HANs and (c) DCAcAm during chloramination of nine different model compounds under different experimental conditions. Experimental conditions:  $[NH_2Cl]_0 = 1 \text{ mM}$ ,  $[model \text{ compound}]_0 = 100 \mu$ M,  $[Cu(II)]_0 = 2.0 \text{ mg/L}$ ,  $[Br^-]_0 = 20 \mu$ M, pH 8.0, reaction time = 72 h.

# 7.3.1.1 THMs Formation

The total THMs formation from Gly, His and Cys were low with concentrations below 15 nM under all experimental conditions. In the absence of Cu(II) and bromide, CA and amino acids yielded low levels of TCM, with concentrations less than 30 nM

during chloramination (Figure 7-1a). One exception, Asp was found to produce a relatively high level of TCM with 110 nM. However, high productions of TCM were observed with phenolic compounds (PhOH, RC, HQ and PHBA) with more than 70 nM. In particular, 890 nM of TCM was formed with RC. This result is in agreement with the hypothesis that resorcinol type structure are fast reacting THM precursors while other phenolic compounds are slow reacting THM precursors (Gallard and von Gunten 2002). With the addition of Cu(II), CA exhibited a prominent increase in TCM formation with a yield of 102%. Fu et al. also presented similar finding with a Cu(II) catalysed THMs formation from CA during chloramination (Fu et al. 2009a). However, other model compounds did not show an evident enhancement of TCM formation and HQ even experienced a decrease in TCM yield by 42%. This indicated that Cu(II) is not efficient in catalysing THMs formation during chloramination of these amino acids and phenolic compounds. The complexation of Cu(II) with HQ may even reduce the reactivity of HQ towards chloramines.

When bromide was present, the total THMs concentration increased for all the model compounds compared to the absence of bromide, which was mainly attributed to the production of brominated-THMs (Br-THMs), though chlorinated-THMs (Cl-THMs) concentration decreased from most model compounds (except RC). This result supports the findings that bromide led to the formation of brominated amines that formed Br-DBPs and decreased the formation of Cl-DBPs (Yang et al. 2007). For CA, the total THMs concentration increased vastly from 26 nM to 657 nM, while TCM decreased from 26 to 2 nM, DCBM, DBCM and TBM were produced at concentrations of 4, 155 and 496 nM, respectively. In terms of amino acids, the total THMs concentrations were negligible for Gly, His and Cys. However, Asp tended to produce the highest DCBM concentration among these model compounds with 1276 nM in the presence of bromide. After Cu(II) addition to the bromide-containing waters, the concentrations of DBCM and TBM increased during CA chloramination. On the contrary, all the other model compounds exhibited a decrease of total THMs concentrations due to the reduction of Br-THMs in the presence of Cu(II). Therefore, except for CA, Cu(II) may bind with Br-THMs precursors and reduce the formation of Br-THMs from these model compounds.

#### 7.3.1.2 HANs Formation

As displayed in Figure 7-1b, under all experimental conditions, MCAN was the main HAN species generated from CA; no HANs formation was detected for Gly; MCAN and DCAN were predominant with His, Asp and Cys; while DCAN was dominant with phenolic compounds.

It clearly shows that apart from Asp, phenolic compounds were the major precursors of HANs compared to the other model compounds. These results were consistent with the literature showing that aromatic organic compounds were important in the formation of N-DBPs.(Le Roux et al. 2016, Nihemaiti et al. 2016). In the presence of Cu(II), the concentrations of total HANs increased for CA, His, Asp, HQ and PHBA, but decreased for Cys and RC, while the concentration was similar with and without Cu(II) for PhOH. Considering the model compounds with high HANs yields, Asp showed the highest HANs formation potential with 1367 nM and a further increase in the presence of Cu(II) with 2214 nM. The MCAN and DCAN concentrations increased vastly from 6 to 85 and 216 to 838 nM for HQ with and without Cu(II), respectively. Though the total HANs concentration decreased for RC since DCAN formation was reduced, the MCAN concentration increased from 25 to 153 nM.

When bromide was present, since brominated-HANs (Br-HANs) were produced, the total HANs formation increased for most model compounds compared to without bromide, with the exception of CA yielded low concentrations of HANs under all conditions. For example, the total HANs concentration increased from 1367 to 1598 nm for Asp in the presence of bromide, due to the formation of DBAN and BCAN. The total HANs concentration of HQ increased from 222 to 300 nM. When Cu(II) was added to the bromide-containing waters, a similar behaviour to the experiment without bromide was observed for the different compounds. Even though the total HANs formation was enhanced for Asp and HQ, DBAN and BCAN concentration largely decreased in the presence of Cu(II). From the above observations, it can be seen that Cu(II) inhibited the formation of Br-HANs.

# 7.3.1.3 DCAcAm Formation

As shown in Figure 7-1c, the effect of Cu(II) on DCAM formation and variation in absence/presence of bromide for different model compounds showed a profile similar to HANs. CA and Gly were not effective DCAM precursors, with concentrations

below 15 nM under all experimental conditions. In the presence of Cu(II), DCAM formation from CA, His, Asp, HQ and PHBA were promoted, in presence or absence of bromide. However, a decrease of DCAM yield was observed for Cys and RC.

According to the above results, Cu(II) showed a significant impact on the DBPs formation and distribution for HQ and PHBA among the four phenolic compounds. Therefore, HQ and PHBA were selected for the following experiments.

### 7.3.2 DBPs Formation from HQ and PHBA



# 7.3.2.1 Effect of Cu(II) Concentration

**Figure 7-2.** Effect of Cu(II) concentration on the formation of (a) TCM, (b) HANs and (c) DCAM from HQ, and (d) TCM, (e) HANs and (f) DCAM from PHBA during chloramination. Experimental conditions:  $[NH_2Cl]_0 = 1 \text{ mM}$ ,  $[model \text{ compound}]_0 = 100 \,\mu\text{M}$ ,  $[Cu(II)]_0 = 0.5.0 \text{ mg/L}$ , pH 8.0, reaction time = 72 h.

Figure 7-2 presents the formation of DBPs with different Cu(II) concentrations (0-5 mg/L) during chloramination of HQ and PHBA. The residual oxidant concentration after 72 h is shown in Figure A-6-2. It can be seen that with increasing Cu(II) concentration, the residual oxidant concentration decreased for both HQ and PHBA. In addition, HQ consumed more chloramines than PHBA either in absence or presence of Cu(II). This suggested that HQ was more reactive with chloramines than PHBA.

As illustrated in Figure 7-2a, the formation of TCM from HQ was lower at Cu(II) concentration ranging from 0.2 to 5.0 mg/L and remained relatively stable in comparison to the experiment without Cu(II). For HPBA, similar TCM formation were observed for Cu(II) concentration from 0 to 5.0 mg/L (Figure 7-2d).

When Cu(II) concentration increased from 0 to 2.0 mg/L, DCAN concentration increased from 216 to 838 nM for HQ (Figure 7-2b) and then decrease to 642 nM for 5.0 mg/L. MCAN concentration was continuously enhanced from 6 to 151 nM with 0 to 5.0 mg/L Cu(II) (Figure 7-2c). Similar to the DCAN formation profile, the total HANs formation increased at Cu(II) concentration from 0 to 2.0 mg/L, then decreased from 2.0 to 5.0 mg/L. This was owing to the fact that DCAN was the dominant HANs species. During chloramination of PHBA, Cu(II) facilitated the production of HANs with 198 nM and 369 nM for 0 and 5.0 mg/L Cu(II), respectively (Figure 7-2e), DCAN and MCAN formation were both enhanced with increasing Cu(II) concentration. The DCAM formation of HQ and HPBA both followed their HANs (or DCAN) formation behaviour, respectively (Figure 7-2f). The TCM formation behaviour was different to that of DCAN and DCAM for HQ and PHBA, indicating that the precursors of TCM were different to that of DCAN and DCAM.

### 7.3.2.2 Effect of Reaction Time



**Figure 7-3.** Effect of reaction time on the formation of (a) TCM, (b) HANs and (c) DCAM from HQ, and (d) TCM, (e) HANs and (f) DCAM from PHBA during chloramination. Experimental conditions:  $[NH_2Cl]_0 = 1 \text{ mM}$ ,  $[model \text{ compound}]_0 = 100 \,\mu\text{M}$ ,  $[Cu(II)]_0 = 2.0 \text{ mg/L}$ , pH 8.0, reaction time = 0.5-72 h.

Figure 7-3 shows the concentrations of DBPs formation with different reaction time (0.5-72 h) during chloramination of HQ and PHBA. The residual oxidant decay as a function of reaction time are available in Figure A-6-3. Longer reaction time led to a lower residual oxidant concentration. It was found that all the DBPs formation were promoted with increasing reaction time. The effect of Cu(II) on the DBPs formation were similar for HQ and PHBA with increasing formation of DBPs in presence of copper, except for TCM. In the first 24 h, Cu(II) did not affect TCM formation for HQ, but from 24 to 72 h, Cu(II) decreased TCM yields notably compared to without Cu(II) while for PHBA an increase in TCM formation was observed in presence of copper. However, for PHBA the increase of TCM formation was insignificant at 72 h. This is probably due to some loss of TCM since TCM is volatile.

## 7.3.2.3 Effect of pH



**Figure 7-4.** Effect of pH on the formation of (a) TCM and (b) HANs from HQ, and (c) TCM and (d) HANs from PHBA during chloramination. Experimental conditions:  $[NH_2Cl]_0 = 1 \text{ mM}$ ,  $[model \text{ compound}]_0 = 100 \text{ }\mu\text{M}$ ,  $[Cu(II)]_0 = 2.0 \text{ }mg/L$ , pH 6-9, reaction time = 72 h.

The effect of pH on DBPs formation during chloramination of HQ and PHBA is presented in Figure 7-4. Compared to without Cu(II), the TCM concentration was promoted by Cu(II) at an initial pH of 6 for HQ; there was no statistical difference at pH 7; while the TCM concentration was reduced at pH 8 and 9. For PHBA, Cu(II) enhanced TCM formation at all pHs except for pH 8, where the TCM concentrations were similar.

Cu(II) increased the total HANs concentration for HQ at all pHs except for pH 9, where a significant reduction of the total HANs concentration was observed. The effect of Cu(II) on DCAN and MCAN formation under various pH followed the total HANs formation profile. For PHBA, Cu(II) reduced the total HANs concentration at pH 6 and 7, however, the total HANs concentration was enhanced at pH 8 and 9.

According to the above experiments, pH is an important factor changing the effect of Cu(II) on DBPs formation during chloramination of the model compounds.

#### 7.3.3 DBPs Formation from NOM



# 7.3.3.1 Effect of Cu(II) Concentration

**Figure 7-5.** Effect of Cu(II) concentration on the formation of (a) TCM, (b) HANs and (c) DCAM from NOM during chloramination. Experimental conditions:  $[NH_2Cl]_0 = 1$  mM,  $[NOM]_0 = 7.2$  mg/L DOC,  $[Cu(II)]_0 = 0-5.0$  mg/L, pH 8.0, reaction time = 72 h.

Figure 7-5 illustrates the changes in the DBPs formation with varying Cu(II) concentrations during chloramination of NOM. The residual oxidant concentrations presented in Figure A-6-4 shows that a higher Cu(II) concentration contributed to a slightly higher decomposition rate of the residual oxidant. All the three groups of DBPS, i.e., TCM, HANs (DCAN and MCAN) and DCAM concentration increased with increasing Cu(II) concentration from 0 to 2.0 mg/L, and then decreased with 5.0 mg/L Cu(II). However, the concentration of DBPs at 5.0 mg/L Cu(II) was still higher than in the absence of Cu(II). For example, TCM concentration increased from 138 nM to 170 nM as the Cu(II) concentration increased from 0 to 2.0 mg/L, the TCM concentration

decreased to 151 nM. Previous study demonstrated that copper corrosion products catalysed the hydrolysis of the DHAN and DHAM species (Huang et al. 2019). Therefore, there is a competition between the enhancement of DBPs formation and the hydrolysis of DBPs catalysed by copper. Based on our results, in our experimental conditions, the hydrolysis of DBPs might start to play an important role at 5 mg/L Cu(II).



# 7.3.3.2 Effect of Bromide Concentration

**Figure 7-6.** Effect of bromide concentration on the formation of (a) THMs, (b) HANs and (c) DCAM during chloramination of NOM in the absence and presence of Cu(II). Experimental conditions:  $[NH_2Cl]_0 = 1 \text{ mM}$ ,  $[NOM]_0 = 7.2 \text{ mg/L DOC}$ ,  $[Br^-]_0 = 0-50 \mu$ M,  $[Cu(II)]_0 = 2 \text{ mg/L}$ , pH 8.0, reaction time = 72 h.

Since bromide concentration can vary in source waters, it is important to understand how the change in bromide concentration affect the formation of DBPs with and without Cu(II). Figure 7-6 shows the formation and speciation of four THMs, six HANs and DCAM at different bromide concentrations during chloramination in the absence and presence of Cu(II). Figure A-6-5 shows that the residual oxidant decay rate increased with increasing bromide concentration, either in the absence or presence of Cu(II).

As shown in Figure. 7-6a, the occurrence of bromide enhanced the formation of the total THMs, this enhancement increased continuously with increasing bromide concentration either in the absence or presence of Cu(II). The total THM formation in the presence or absence of Cu(II) is relatively similar for bromide concentration ranging from 0 or 5  $\mu$ M. However, when the bromide concentration increased from 5 to 50  $\mu$ M, Cu(II) clearly reduced the yields of the total THMs. In terms of THMs species distribution, the presence of Cu(II) increased the yield of TCM but decreased the yields of TBM, DBCM and DCBM.

For HANs, increasing the bromide concentration from 0 to 50  $\mu$ M resulted in a gradual enhancement of the total HANs formation from 72 to 124 nM in the absence of Cu(II). In contrast, the presence of Cu(II) decreased the total HANs formation from 158 to 123 nM when bromide concentration increased from 0 to 50  $\mu$ M. When Cu(II) was present, the total HANs yields was always higher than the corresponding experiment without Cu(II), except for 50  $\mu$ M of bromide where the yields of HANs were similar. In the presence of Cu(II), MCAN and DCAN formation was enhanced while Br-HANs were depleted, compared to the experiments without Cu(II) for all bromide concentrations.

Bromine substitution factor (BSF) between 0 and 1 is considered as the bromine substitution degree of DBPs, and is calculated based on the molar ratio of bromine concentration incorporated into a given class of DBPs (Hua et al. 2006). In this study, BSF was determined to represent THMs and HANs speciation involving bromide in the absence and presence of Cu(II), which can be expressed by the following equation (1) and (2), respectively.

$$BSF(THMs) = \frac{3[TBM] + 2[DBCM] + [DCBM]}{3([TCM] + [DCBM] + [DBCM] + [TBM])}$$
(1)

$$BSF(HANs) = \frac{2[DBAN] + [MBAN] + [BCAN]}{3[TCAN] + 2([DCAN] + [DBAN] + [BCAN]) + [MCAN] + [MBAN]}$$
(2)

As shown in Figure A-6-6, increasing the bromide concentration increased the BSF of THMs and HANs with or without Cu(II). Meanwhile, the addition of Cu(II) decreased the BSF of THMs and HANs for all bromide concentrations. Compared to THMs, Cu(II) exerted a more evident reduction of BSF in HANs. This suggested that Cu(II) is efficient in mitigating the formation of Br-DBPs.

In the absence of Cu(II), the concentration of DCAM was stable for bromide concentration of 0 to 5  $\mu$ M, a further increase in bromide concentration from 5 to 50  $\mu$ M decreased the concentration of DCAM. In the presence of Cu(II), the DCAM production was continuously reduced with increasing bromide concentration. However, the DCAM formation with Cu(II) was always higher than without Cu(II) under the same bromide concentration conditions. It was also observed that the DCAM formation behaviour in the presence of bromide was similar to that of the DCAN, with or without copper.

According to the above observations, it is seen that during chloramination of bromidecontaining waters in the presence of NOM, Cu(II) promoted the formation of Cl-DBPs but reduced the formation of Br-DBPs. Our findings are different from other studies where it was demonstrated that Cu(II)/CuO catalysed the formation of Br-DBPs during chlorination (Hu et al. 2016, Liu et al. 2013).

# 7.4 Conclusions

In this study the effect of Cu(II) on DBPs formation and species distribution during chloramination of different model compounds and NOM was investigated. Results indicated that Cu(II) had different impact on DBPs formation with different model compounds. Under most cases, Cu(II) enhanced the formation of TCM, HANs and DCAM for hydroquinone and p-hydroxybenzoic acid. Whereas, Cu(II) decreased the formation of TCM for hydroquinone. In addition, varying the pH significantly changed the yields of DBPs and affected the catalytic effect of Cu(II) on DBPs formation. As for NOM, Cu(II) enhanced HANs and DCAM formation and decreased THMs yields. It was also found that Cu(II) is more likely to promote the formation of Cl-DBPs but reduce the formation of Br-DBPs. Further investigations should be carried out to elucidate the mechanisms on involved in DBPs formation in the presence of Cu(II).

# 7.5 References

- Allard, S., Cadee, K., Tung, R. and Croué, J.-P. (2018) Impact of brominated amines on monochloramine stability during in-line and pre-formed chloramination assessed by kinetic modelling. Science of the Total Environment 618, 1431-1439.
- Blatchley, E.R., Margetas, D. and Duggirala, R. (2003) Copper catalysis in chloroform formation during water chlorination. Water Research 37(18), 4385-4394.
- Bond, T., Huang, J., Templeton, M.R. and Graham, N. (2011) Occurrence and control of nitrogenous disinfection by-products in drinking water–a review. Water Research 45(15), 4341-4354.
- Boulay, N. and Edwards, M. (2001) Role of temperature, chlorine, and organic matter in copper corrosion by-product release in soft water. Water Research 35(3), 683-690.
- Broo, A.E., Berghult, B. and Hedberg, T. (1998) Copper corrosion in water distribution systems—the influence of natural organic matter (nom) on the solubility of copper corrosion products. Corrosion Science 40(9), 1479-1489.
- Chu, W.-H., Gao, N.-Y., Deng, Y. and Krasner, S.W. (2010) Precursors of dichloroacetamide, an emerging nitrogenous DBP formed during chlorination or chloramination. Environmental Science & Technology 44(10), 3908-3912.
- Chuang, Y.-H., Lin, A.Y.-C., Wang, X.-h. and Tung, H.-h. (2013) The contribution of dissolved organic nitrogen and chloramines to nitrogenous disinfection byproduct formation from natural organic matter. Water Research 47(3), 1308-1316.
- Federation, W.E. and Association, A.P.H. (2005) Standard methods for the examination of water and wastewater. American Public Health Association (APHA): Washington, DC, USA.
- Fu, J., Qu, J., Liu, R., Qiang, Z., Liu, H. and Zhao, X. (2009a) Cu (II)-catalyzed THM formation during water chlorination and monochloramination: A comparison study. Journal of Hazardous Materials 170(1), 58-65.
- Fu, J., Qu, J., Liu, R., Zhao, X. and Qiang, Z. (2009b) The influence of Cu (II) on the decay of monochloramine. Chemosphere 74(2), 181-186.
- Gallard, H. and von Gunten, U. (2002) Chlorination of natural organic matter: kinetics of chlorination and of THM formation. Water Research 36(1), 65-74.
- Goslan, E.H., Krasner, S.W., Bower, M., Rocks, S.A., Holmes, P., Levy, L.S. and Parsons, S.A. (2009) A comparison of disinfection by-products found in chlorinated and chloraminated drinking waters in Scotland. Water Research 43(18), 4698-4706.
- Heeb, M.B., Kristiana, I., Trogolo, D., Arey, J.S. and Von Gunten, U. (2017) Formation and reactivity of inorganic and organic chloramines and bromamines during oxidative water treatment. Water Research 110, 91-101.
- Heller-Grossman, L., Idin, A., Limoni-Relis, B. and Rebhun, M. (1999) Formation of cyanogen bromide and other volatile DBPs in the disinfection of bromide-rich lake water. Environmental Science & Technology 33(6), 932-937.
- Hu, J., Qiang, Z., Dong, H. and Qu, J. (2016) Enhanced formation of bromate and brominated disinfection byproducts during chlorination of bromide-containing waters under catalysis of copper corrosion products. Water Research 98, 302-308.

- Hua, G. and Reckhow, D.A. (2012) Evaluation of bromine substitution factors of DBPs during chlorination and chloramination. Water Research 46(13), 4208-4216.
- Hua, G., Reckhow, D.A. and Kim, J. (2006) Effect of bromide and iodide ions on the formation and speciation of disinfection byproducts during chlorination. Environmental Science & Technology 40(9), 3050-3056.
- Huang, H., Shao, K.-L., Duan, S.-Y. and Zhong, C.-Y. (2019) Effect of copper corrosion products on the formation and speciation of haloacetamides and haloacetonitriles during chlorination. Separation and Purification Technology 211, 467-473.
- Le Roux, J., Gallard, H. and Croué, J.-P. (2011) Chloramination of nitrogenous contaminants (pharmaceuticals and pesticides): NDMA and halogenated DBPs formation. Water Research 45(10), 3164-3174.
- Le Roux, J., Nihemaiti, M. and Croué, J.-P. (2016) The role of aromatic precursors in the formation of haloacetamides by chloramination of dissolved organic matter. Water Research 88, 371-379.
- Lee, W., Westerhoff, P. and Croué, J.-P. (2007) Dissolved organic nitrogen as a precursor for chloroform, dichloroacetonitrile, N-nitrosodimethylamine, and trichloronitromethane. Environmental Science & Technology 41(15), 5485-5490.
- Li, B., Qu, J., Liu, H. and Hu, C. (2007) Effects of copper (II) and copper oxides on THMs formation in copper pipe. Chemosphere 68(11), 2153-2160.
- Liu, C. and Croué, J.-P. (2015) Formation of bromate and halogenated disinfection byproducts during chlorination of bromide-containing waters in the presence of dissolved organic matter and CuO. Environmental Science & Technology 50(1), 135-144.
- Liu, C., Ersan, M.S., Plewa, M.J., Amy, G. and Karanfil, T. (2018a) Formation of regulated and unregulated disinfection byproducts during chlorination of algal organic matter extracted from freshwater and marine algae. Water Research 142, 313-324.
- Liu, R., Tian, C., Hu, C., Qi, Z., Liu, H. and Qu, J. (2018b) Effects of bromide on the formation and transformation of disinfection by-products during chlorination and chloramination. Science of the Total Environment 625, 252-261.
- Liu, S.-g., Zhu, Z.-l., Tan, X.-c., Feng, X.-h., Huang, Z.-y., Qiu, Y.-l. and Zhao, J.-f. (2013) The influence of Cu (II) on the formation and distribution of disinfection by-products during the chlorination of drinking water. Water, Air, & Soil Pollution 224(4), 1493.
- Luh, J. and Mariñas, B.J. (2014) Kinetics of bromochloramine formation and decomposition. Environmental Science & Technology 48(5), 2843-2852.
- Magazinovic, R.S., Nicholson, B.C., Mulcahy, D.E. and Davey, D.E. (2004) Bromide levels in natural waters: its relationship to levels of both chloride and total dissolved solids and the implications for water treatment. Chemosphere 57(4), 329-335.
- Matilainen, A. and Sillanpää, M. (2010) Removal of natural organic matter from drinking water by advanced oxidation processes. Chemosphere 80(4), 351-365.
- Muellner, M.G., Wagner, E.D., McCalla, K., Richardson, S.D., Woo, Y.-T. and Plewa, M.J. (2007) Haloacetonitriles vs. regulated haloacetic acids: are nitrogencontaining DBPs more toxic? Environmental Science & Technology 41(2), 645-651.

- Nihemaiti, M., Le Roux, J., Hoppe-Jones, C., Reckhow, D.A. and Croué, J.-P. (2016) Formation of haloacetonitriles, haloacetamides, and nitrogenous heterocyclic byproducts by chloramination of phenolic compounds. Environmental Science & Technology 51(1), 655-663.
- Pan, Y. and Zhang, X. (2013) Four groups of new aromatic halogenated disinfection byproducts: effect of bromide concentration on their formation and speciation in chlorinated drinking water. Environmental Science & Technology 47(3), 1265-1273.
- Sakai, H., Tokuhara, S., Murakami, M., Kosaka, K., Oguma, K. and Takizawa, S. (2016) Comparison of chlorination and chloramination in carbonaceous and nitrogenous disinfection byproduct formation potentials with prolonged contact time. Water Research 88, 661-670.
- Shah, A.D. and Mitch, W.A. (2011) Halonitroalkanes, halonitriles, haloamides, and N-nitrosamines: a critical review of nitrogenous disinfection byproduct formation pathways. Environmental Science & Technology 46(1), 119-131.
- Sun, Y.-X., Wu, Q.-Y., Hu, H.-Y. and Tian, J. (2009) Effect of bromide on the formation of disinfection by-products during wastewater chlorination. Water Research 43(9), 2391-2398.
- Tian, C., Liu, R., Guo, T., Liu, H., Luo, Q. and Qu, J. (2013) Chlorination and chloramination of high-bromide natural water: DBPs species transformation. Separation and Purification Technology 102, 86-93.
- Trofe, T.W., Inman, G.W. and Johnson, J.D. (1980) Kinetics of monochloramine decomposition in the presence of bromide. Environmental Science & Technology 14(5), 544-549.
- Von Gunten, U. (2003) Ozonation of drinking water: Part II. Disinfection and byproduct formation in presence of bromide, iodide or chlorine. Water Research 37(7), 1469-1487.
- Yan, M., Roccaro, P., Fabbricino, M. and Korshin, G.V. (2018) Comparison of the effects of chloramine and chlorine on the aromaticity of dissolved organic matter and yields of disinfection by-products. Chemosphere 191, 477-484.
- Yang, X., Shang, C. and Westerhoff, P. (2007) Factors affecting formation of haloacetonitriles, haloketones, chloropicrin and cyanogen halides during chloramination. Water Research 41(6), 1193-1200.
- Zhang, H. and Andrews, S.A. (2012) Catalysis of copper corrosion products on chlorine decay and HAA formation in simulated distribution systems. Water Research 46(8), 2665-2673.

Every reasonable effort has been made to acknowledge the owners of copyright material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged.

# **Appendix 1**



**Figure A-1-1.** Representative mass spectra of a solution of monochloramine in presence of bromide: Evidence of NHBrCl formation.  $[NH_2Cl] = 400 \ \mu M$ ,  $[Br] = 4 \ mM$ , pH 6, 10 mM phosphate.



**Figure A-1-2.** Modeling of the formation of NHBrCl from reaction between HOBr and NH<sub>2</sub>Cl for 10 min. [HOBr] =  $[NH_2Cl] = 100 \mu M$ ; Phosphate buffer = 10 mM; pH 5 to 8.



**Figure A-1-3.** Modeling of the formation of NHBrCl from reaction between HOBr and NH<sub>2</sub>Cl for 10 min. [HOBr] =  $[NH_2Cl] = 50-300 \ \mu\text{M}$ ; Phosphate buffer = 10 mM, pH 6.



**Figure A-1-4.** Variation of  $[NHBrCl]_{max}/[NH_2Cl]_0$  depending on the pH and  $[NH_2Cl]_0$  from 0.125 to 1.25 mM with  $[Br^-] = 5$  mM (ratio 0.025 to 0.25).















**Figure A-1-5.** Modelling of oxidants for all experimental conditions used in this study.  $[NH_2Cl]_0 0.2$  to 5mM,  $[Br]_0 0.5$  to 5 mM and pH 5 to 6.2.



**Figure A-1-6.** Percentage of NHBrCl remaining in solution for different pH after 30 min. Modeling by Kintecus using Br<sup>-</sup>/NH<sub>2</sub>Cl ratio = 1; Phosphate buffer 10 mM; [Br<sup>-</sup>] =  $[NH_2Cl] = 5 \text{ mM}$  at pH 6.



**Figure A-1-7.** Bromochloramine decomposition at different pHs. Modelling by Kintecus using  $Br^{-}/NH_2Cl$  ratio = 1; Phosphate buffer 10 mM;  $[Br^{-}] = [NH_2Cl] = 5$  mM.

Every reasonable effort has been made to acknowledge the owners of copyright material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged.

# Appendix 2

Table A-2-1. Main water quality parameters

Real Water	pН	DOC (mg/L)	TN (mg/L)	Chloride (mg/L)	Bromide (mg/L)
Surface water 1 (SW1)	8.0	0.98	0.16	16	0.08
Surface water 2 (SW2)	6.7	0.34	0.09	24	0.986
Seawater (SW3)	7.7	NA	NA	69816	73.5

 Table A-2-2.
 Fragmentation of the different halamines in the mass spectrometer

NH <sub>2</sub> Cl			
Parent ions	m/z	Possible fragments	m/z
$NH_2{}^{35}Cl^+$	51	NH <sup>35</sup> Cl <sup>+</sup>	50
		$N^{35}Cl^{+}$	49
		<sup>35</sup> Cl <sup>+</sup>	35
		$\mathrm{NH}_{2}^{+}$	16
		$\rm NH^+$	15
$NH_2{}^{37}Cl^+$	53	NH <sup>37</sup> Cl <sup>+</sup>	52
		$N^{37}Cl^+$	51
		<sup>37</sup> Cl <sup>+</sup>	37
		$\mathrm{NH}_{2}^{+}$	16
		$\mathrm{NH}^+$	15
NHCl <sub>2</sub>			
Parent ions	m/z	Possible fragments	m/z
$NH^{35}Cl_2{}^+$	85	$N^{35}Cl_{2}^{+}$	84
		NH <sup>35</sup> Cl <sup>+</sup>	50
		$N^{35}Cl^{+}$	49
		<sup>35</sup> Cl <sup>+</sup>	35
		$\rm NH^+$	15
$1H^{35}Cl^{37}Cl^{+}$	87	$N^{35}Cl^{37}Cl^+$	86
		NH <sup>37</sup> Cl <sup>+</sup>	52
		$N^{37}Cl^+$	51
		NH <sup>35</sup> Cl <sup>+</sup>	50
		$N^{35}Cl^{+}$	49
		<sup>37</sup> Cl <sup>+</sup>	37
		<sup>35</sup> Cl <sup>+</sup>	35
		$\rm NH^+$	15
$NH^{37}Cl_2^+$	89	$N^{37}Cl_2^+$	88
		NH <sup>37</sup> Cl <sup>+</sup>	52
		$N^{37}Cl^+$	51
		<sup>37</sup> Cl <sup>+</sup>	37
		NH <sup>+</sup>	15

NH <sub>2</sub> Br			
Parent ions	m/z	Possible fragments	m/
$NH_2^{79}Br^+$	95	NH <sup>79</sup> Br <sup>+</sup>	94
		$N^{79}Br^+$	93
		$^{79}{ m Br^{+}}$	79
		$\mathrm{NH}_{2}^{+}$	16
		$\mathbf{NH}^+$	15
$NH_2^{81}Br^+$	97	$NH^{81}Br^+$	96
		$N^{81}Br^+$	95
		$^{81}\mathrm{Br}^{+}$	8
		$\mathrm{NH}_{2}^{+}$	10
		$\mathbf{NH}^+$	1.
NHBr <sub>2</sub>			
Parent ions	m/z	Possible fragments	m/
$NH^{79}Br_2^+$	173	$N^{79}Br_{2}^{+}$	17
		$^{79}{ m Br_2^+}$	15
		NH <sup>79</sup> Br <sup>+</sup>	94
		$N^{79}Br^+$	93
		$^{79}{ m Br^{+}}$	79
		$NH^+$	1.
$\mathbf{NH}^{79}\mathbf{Br}^{81}\mathbf{Br}^{+}$	175	N <sup>79</sup> Br <sup>81</sup> Br <sup>+</sup>	17
	170	$^{79}{ m Br}^{81}{ m Br}^+$	16
		$NH^{81}Br^+$	96
		$N^{81}Br^+$	94
		NH <sup>79</sup> Br <sup>+</sup>	94
		$N^{79}Br^+$	03
		81 Br <sup>+</sup>	2.
		79 <b>B</b> r <sup>+</sup>	70
		DI NUI+	14
$NII81D_{m} +$	177	ΝΠ N181D# +	1. 17
	1//	$1N^{**}DI_2^{*}$	1/
		$\mathbf{DI}_2^*$	10
			90
			93
		°'Bt	8
NHD-CI		NH'	12
NHBFCI Derent ions	m/7	Dossible fragments	m
1100000000000000000000000000000000000	129	$N^{79}Br^{35}C1^+$	12
I DI CI	127	$NH^{79}Br^+$	94
		$N^{79}Br^+$	03
		79 <b>B</b> r <sup>+</sup>	9. 70
		NILI35C1+	15 51
		NI35C1+	50
			49
			55
NIL181D 25-01	101		15
NH°1Br <sup>33</sup> Cl <sup>+</sup>	131	N° <sup>1</sup> Br <sup>55</sup> Cl <sup>+</sup>	13
		A ** *01	~

		$N^{81}Br^+$	95
		$^{81}\mathrm{Br}^{+}$	81
		NH <sup>35</sup> Cl <sup>+</sup>	50
		$N^{35}Cl^+$	49
		$^{35}Cl^{+}$	35
		$\mathbf{NH}^+$	15
$NH^{79}Br^{37}Cl^+$	131	$N^{79}Br^{37}Cl^+$	130
		NH <sup>79</sup> Br <sup>+</sup>	94
		$N^{79}Br^+$	93
		$^{79}{ m Br^{+}}$	79
		NH <sup>37</sup> Cl <sup>+</sup>	52
		$N^{37}Cl^+$	51
		$^{37}Cl^{+}$	37
		$\mathbf{NH}^+$	15
$NH^{81}Br^{37}Cl^+$	133	$N^{81}Br^{37}Cl^+$	132
		$NH^{81}Br^+$	96
		$N^{81}Br^+$	95
		$^{81}{ m Br^{+}}$	81
		NH <sup>37</sup> Cl <sup>+</sup>	52
		$N^{37}Cl^+$	51
		<sup>37</sup> Cl <sup>+</sup>	37
		$\rm NH^+$	15

Table A-2-3. Reproducibility of chloramines and bromamines

	5 μM NH2Cl		2 μM NHCl2		10 μM NH2Br		4 μM NHBr2	
Sample number	MIMS respons e (pA)	Calculated concentrati on						
		(μM)		(μM)		(μM)		(μM)
1	6.606	5.042	9.400	2.083	4.236	9.265	6.100	3.502
2	6.748	5.150	8.679	1.923	4.52	9.886	6.617	3.799
3	6.632	5.062	8.981	1.990	4.721	10.326	6.870	3.944
4	6.883	5.253	8.563	1.897	4.496	9.834	7.119	4.087
5	6.394	4.880	9.267	2.053	4.434	9.698	7.175	4.119
6	6.738	5.143	8.836	1.958	4.696	10.271	7.502	4.307
7	6.551	5.000	9.257	2.051	4.901	10.720	7.393	4.244
8	6.325	4.827	9.139	2.025				
9	6.213	4.742	8.605	1.906				
10	6.422	4.901	9.545	2.115				
Averag	6.551	5.000	9.027	2.000	4.527	10.000	6.968	4.000
e	$\pm 0.211$	± 0.161	$\pm 0.347$	$\pm 0.077$	$\pm 0.218$	$\pm 0.478$	$\pm 0.486$	$\pm 0.279$



**Figure A-2-1.** Representative MIMS response for chloramines and bromamines standards. (a) NH<sub>2</sub>Cl, (b) NHCl<sub>2</sub>, (c) NH<sub>2</sub>Br, (d) NHBr<sub>2</sub>.


**Figure A-2-2.** Comparison of direct UV measurements ( $\epsilon_{NHBrCl,320nm}$ = 304 M<sup>-1</sup>cm<sup>-1</sup>) and MIMS response (m/z 131) for determination of NHBrCl at different experimental conditions and days. Experimental conditions: pH 6, 10 mM phosphate buffer, MIMS response were recorded after background subtraction. (a) 200 µM NH<sub>2</sub>Cl + 2 mM Br<sup>-</sup>, (b) 200 µM NH<sub>2</sub>Cl + 4 mM Br<sup>-</sup>. (c) MIMS calibration curves for NHBrCl obtained at two different days, concentration range: 10-55 µM (black symbols), 15-60 µM (red symbols).



**Figure A-2-3.** Speciation of halamines during in-line chloramination. Experimental conditions: [HOCl] = 42  $\mu$ M (3 mg Cl<sub>2</sub>/L) for 4 min followed by addition of [NH<sub>3</sub>] = 51  $\mu$ M (863  $\mu$ g/L), [Br-] = 5  $\mu$ M (400  $\mu$ g /L), pH 8, 15 h.



**Figure A-2-4.** Speciation of halamines during pre-formed chloramination. Experimental conditions:  $[NH_2Cl] = 42 \ \mu M \ (3 \ mg \ Cl_2/L), \ [NH_3] = 8 \ \mu M \ (136 \ \mu g/L), \ [Br-] = 5 \ \mu M \ (400 \ \mu g \ /L), \ pH \ 8, \ 72 \ h.$ 



**Figure A-3-1.** NH<sub>2</sub>Cl decomposition and NHCl<sub>2</sub> formation at (a) pH 8 and (b) pH 6.5 predicted by Kintecus model. Experimental conditions:  $[NH_2Cl]_0 = 50 \mu M$ .



**Figure A-3-2.** Released soluble copper determined by AAS under different CuO concentrations. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$ ,  $[Br]_0 = 40 \ \mu M$ , pH 6.5, borate buffer = 20 mM.



**Figure A-3-3.** Effect of CuO on NHCl<sub>2</sub> decomposition during the reaction of NH<sub>2</sub>Cl with bromide. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$ ,  $[Br^-]_0 = 20 \ \mu M$ ,  $[CuO]_0 = 0.05 \ g/L$ , pH 6.5, borate buffer = 20 mM.



**Figure A-3-4.** Model prediction of total oxidant and NHBrCl for NH<sub>2</sub>Cl decomposition in the presence of different bromide concentrations. (a) Total oxidant decay in the presence of 0.05 g/L CuO determined by the experiments (solid symbols) and total oxidant decay in the absence of CuO determined by the modelling (dashed lines); (b) modelling of NHBrCl formation and decomposition. Experimental conditions:  $[NH_2Cl]_0 = 50 \,\mu\text{M}$ ,  $[Br^-] = 0.80 \,\mu\text{M}$ , pH 6.5.



**Figure A-3-5.** Pseudo first order kinetic model for the total oxidant decomposition with different bromide concentration in the presence of CuO. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$ ,  $[Br^-] = 0.80 \ \mu M$ ,  $[CuO] = 0.05 \ g/L$ , pH 6.5, borate buffer = 20 mM.



**Figure A-3-6.** Model predictions for the kinetic of the total oxidant and the different halamines in the presence of NH<sub>2</sub>Cl and bromide at different pHs. (a) The total oxidant decay determined by experiment and modelling; (b) NHBrCl formation (modelling); (c) NHCl<sub>2</sub> formation (modelling). Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$ ,  $[Br^-] = 5 \ \mu M$ , pH 6.5-8.0.

Cu(II) (mg/L)	N <sub>2</sub> (%)	N <sub>2</sub> O (%)	NO <sub>2</sub> <sup>-</sup> (%)	<b>NO</b> <sup>2</sup> <sub>3</sub> (%)	Total (%)			
0	76.5	11.6	15.2	6.0	109.2			
1.0	11.6	29.5	51.8	5.5	98.3			
2.0	6.6	36.1	38.7	4.5	86.0			
5.0	6.0	48.1	24.0	2.6	80.6			

Table A-4-1. Molar percent recoveries of the different nitrogen species

**Text A-4-1.** Since total bromamine were synthesised by using a high excess of ammonium (NH<sub>4</sub>Cl or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) which was 1000 times the HOBr concentration, the chloride or sulfate concentrations were 50 and 25 mM in solutions, respectively. The high concentration of chloride interfered with the analysis of nitrite (a potential degradation product of monobromamine) by ionic chromatography. Therefore, NH<sub>4</sub>Cl couldn't be used for the mechanistic investigation. However, sulfate was free of interference for nitrite analysis. In the absence of Cu(II), there was no discrepancy between chloride and sulfate on total bromamine decomposition (Figure A-4-1). Nevertheless, the total bromamine decomposition decreased in presence of sulfate compared to chloride when 5.0 mg/L Cu(II) was present. It was shown previously that the presence of sulfate hindered the chlorine decay in the presence of CuO (Liu et al. 2013). It is hypothesised that complexation reactions between Cu(II) and sulfate reduced the amount of available Cu(II) to react with total bromamine and decrease the total bromamine decomposition.



**Figure A-4-1.** Impact of chloride and sulfate on total bromamine decomposition. Experimental conditions: [total bromamine]<sub>0</sub> = 50  $\mu$ M, pH = 7.5, the total bromamine concentration was determined with the DPD method and the pH was regulated by automatic titration. Solid lines: NH<sub>4</sub>Cl/Br molar ratio = 1000:1. Dashed lines: (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/Br molar ratio = 500:1.



Figure A-4-2. Calibration curve for  ${}^{15}N_2$  (m/z 30) analysis by GC/MS



Figure A-4-3. Calibration curve for  ${}^{14}N_2O$  (m/z 44) analysis by MIMS



**Figure A-4-4.** Effect of pH on bromamines speciation during its self-decomposition determined by UV scan. (a) monobromamine decomposition as a function of time, (b) dibromamine decomposition as a function of time. Experimental conditions: [total bromamine]<sub>0</sub> = 50  $\mu$ M, NH<sub>4</sub>Cl/Br molar ratio = 1000:1. The pH was regulated by automatic titration.



**Figure A-4-5.** Pseudo-first-order linearisation for total bromamine decomposition at different Cu(II) concentration. Experimental conditions: [total bromamine]<sub>0</sub> = 50  $\mu$ M, pH = 7.5, NH<sub>4</sub>Cl/Br molar ratio = 1000:1, the total bromamine concentration was determined with the DPD method and the pH was regulated by automatic titration.



**Figure A-4-6.** Effect of pH on total bromamine decomposition (a) without Cu(II), and (b) with Cu(II). Experimental conditions: [total bromamine]<sub>0</sub> = 50  $\mu$ M, [Cu(II)] = 2.0 mg/L, NH<sub>4</sub>Cl/Br molar ratio = 1000:1, pH ranging from 6.0 to 8.5, the total bromamine concentration was determined with the DPD method and the pH was regulated by automatic titration.





**Figure A-4-7.** Pseudo-first order linearisation for total bromamine decomposition at different pHs in the presence and absence of Cu(II). Experimental conditions: [total bromamine]<sub>0</sub> = 50  $\mu$ M, NH<sub>4</sub>Cl/Br molar ratio = 1000:1, pH 6.0-8.5, the total bromamine concentration was determined with the DPD method and the pH was regulated by automatic titration.



**Figure A-4-8.** MIMS response for total bromamine decomposition products in the presence of different Cu(II) concentration. (a)  ${}^{15}N_2O$  (m/z 46); (b)  ${}^{15}NO_2$  (m/z 47). Experimental conditions: [Total bromamine]<sub>0</sub> = 200 µM, borate buffer = 20 mM, pH = 9.2, ( ${}^{15}NH_4$ )<sub>2</sub>SO<sub>4</sub>/Br molar ratio = 50:1.



**Figure A-4-9.** Cu 2p XPS spectra of CuCl<sub>2</sub> standard and copper particles from the bromamine reaction. Experimental conditions: [Total bromamine]<sub>0</sub> = 500  $\mu$ M, [Cu(II)]<sub>0</sub> = 1 mM, without buffer, pH = 8.0, NH<sub>4</sub>Cl/Br molar ratio = 100:1. The aqueous phase was evaporated at 70 °C.

#### Reference

Liu, C., Von Gunten, U. and Croue, J.-P. (2013) Chlorination of bromide-containing waters: Enhanced bromate formation in the presence of synthetic metal oxides and deposits formed in drinking water distribution systems. Water Research 47(14), 5307-5315.

Experimental conditions	N <sub>2</sub> (%)	NH <sub>4</sub> <sup>+</sup> (%)	N2O (%)	NO <sub>3</sub> (%)	Total (%)
Self-decay	59.8	28.1	2.4	1.1	91.4
Br	71.5	36.6	0.3	0.6	109.0
Cu(II)	67.5	23.8	1.6	1.0	93.9
Br-+Cu(II)	70.0	31.7	1.4	0.9	104.0

Table A-5-1. Molar percent recoveries of the different nitrogen species



Figure A-5-1. Calibration curve for  ${}^{15}N_2$  (m/z 30) analysis by GC/MS



Figure A-5-2. Calibration curve for  ${}^{14}N_2O$  (m/z 44) analysis by MIMS



**Figure A-5-3.** Effect of Cu(II) concentration on NHCl<sub>2</sub> formation and decomposition determined by MIMS. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$ ,  $[Br^-]_0 = 40 \ \mu M$ , 20 mM borate buffer, pH 6.5.



**Figure A-5-4.** Model prediction for the effect of bromide concentration on the different halamines formation in the presence of NH<sub>2</sub>Cl. (a) NH<sub>2</sub>Cl; (b) NHCl<sub>2</sub>; (c) NHBrCl. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu\text{M}$ , pH 6.5.



**Figure A-5-5.** Pseudo first order kinetic model for total oxidant decomposition with different bromide concentration. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$ ,  $[Cu(II)]_0 = 0.5 \ mg/L$ , 20 mM borate buffer, pH 6.5.



**Figure A-5-6.** Model prediction for the effect of pH on the different halamines formation in the presence of bromide. (a) NH<sub>2</sub>Cl; (b) NHCl<sub>2</sub>; (c) NHBrCl. Experimental conditions:  $[NH_2Cl]_0 = 50 \ \mu M$ ,  $[Br^-]_0 = 40 \ \mu M$ .



**Figure A-5-7.** Cu 2p XPS spectra of CuCl<sub>2</sub> standard and copper particles obtained from the reaction. Experimental conditions:  $[NH_2Cl]_0 = 500 \ \mu M$ ,  $[Br^-]_0 = 400 \ \mu M$ ,  $[Cu(II)]_0 = 1 \ mM$ , pH 6.5. The aqueous phase was evaporated at 70 °C.

Model compound	Abbreviation	Classification	Structure	Molar mass (g mol <sup>-1</sup> )	Log Kow	pKa
Citric acid	CA	Carboxylic acid		192.12	-1.64	3.13, 4.76, 6.40
Glycine	Gly	Amino acid	H <sub>2</sub> N OH	75.07	-3.21	2.34, 9.60
Histidine	His	Amino acid	N N NH2 NH2	155.16	-3.32	1.78, 5.97, 8.97
Aspartic acid	Asp	Amino acid		133.10	-3.89	1.92, 3.87, 9.87
Cysteine	Cys	Amino acid		121.16	-2.49	1.71, 8.33, 10.78
Phenol	PhOH	Phenolic	OH	94.11	1.46	9.99
Resorcinol	RC	Phenolic	ОН	110.11	0.80	9.30, 11.06
Hydroquinone	HQ	Phenolic	OH OH	110.11	0.59	9.96
P- Hydroxybenzoic acid	РНВА	Phenolic/ Carboxylic acid	OH	138.12	1.58	4.54

 Table A-6-1. Physicochemical properties of model compounds



**Figure A-6-1.** Residual oxidant after 72 h chloramination of nine different model compounds under different experimental conditions. Experimental conditions:  $[NH_2Cl]_0 = 1 \text{ mM}$ ,  $[model \text{ compound}]_0 = 100 \mu \text{M}$ ,  $[Cu(II)]_0 = 2.0 \text{ mg/L}$ ,  $[Br^-]_0 = 20 \mu \text{M}$ , pH 8.0, reaction time = 72 h.



**Figure A-6-2.** Effect of Cu(II) concentration on the residual oxidant decay during chloramination of HQ and PHBA. Experimental conditions:  $[NH_2Cl]_0 = 1 \text{ mM}$ ,  $[model \text{ compound}]_0 = 100 \,\mu\text{M}$ ,  $[Cu(II)]_0 = 0-20 \text{ mg/L}$ , pH 8.0, reaction time = 72 h.



**Figure A-6-3.** Effect of reaction time on the residual oxidant decay during chloramination of HQ and PHBA. Experimental conditions:  $[NH_2Cl]_0 = 1 \text{ mM}$ ,  $[model \text{ compound}]_0 = 100 \,\mu\text{M}$ ,  $[Cu(II)]_0 = 2.0 \text{ mg/L}$ , pH 8.0, reaction time = 0.5-72 h.



**Figure A-6-4.** Effect of Cu(II) concentration on the residual oxidant decay during chloramination of NOM. Experimental conditions:  $[NH_2Cl]_0 = 1 \text{ mM}$ ,  $[NOM]_0 = 7.2 \text{ mg/L DOC}$ ,  $[Cu(II)]_0 = 0.5.0 \text{ mg/L}$ , pH 8.0, reaction time = 72 h.



**Figure A-6-5.** Effect of bromide concentration on the residual oxidant decay during chloramination of NOM. Experimental conditions:  $[NH_2Cl]_0 = 1 \text{ mM}$ ,  $[NOM]_0 = 7.2 \text{ mg/L DOC}$ ,  $[Br^-]_0 = 0.50 \mu M$ ,  $[Cu(II)]_0 = 2.0 \text{ mg/L}$ , pH 8.0, reaction time = 72 h.



**Figure A-6-6.** Effect of Cu(II) on the BSF variation of (a) THMs and (b) HANs during chloramination of NOM. Experimental conditions:  $[NH_2Cl]_0 = 1 \text{ mM}$ ,  $[NOM]_0 = 7.2 \text{ mg/L DOC}$ ,  $[Br^-]_0 = 0.50 \mu M$ ,  $[Cu(II)]_0 = 2.0 \text{ mg/L}$ , pH 8.0, reaction time = 72 h.

