Simultaneous time-resolved aqueous haloamine measurement empowers robust kinetic model analysis

Lynn Katz
lynnkatz@mail.utexas.edu

University of Texas at Austin

Samuel Brodfuehrer
https://orcid.org/0000-0002-7261-0495

University of Texas at Austin

Daniel Blomdahl
University of Texas at Austin

David Wahman
United States Environmental Protection Agency
https://orcid.org/0000-0002-0167-8468

Gerald Speitel
University of Texas at Austin

Pawel Misztal
University of Texas at Austin

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Abstract

We demonstrate the first application of Proton Transfer Time-of-Flight Mass Spectrometry (PTR-ToF-MS) for monitoring kinetics of disinfectant decay in water with 1 to 3 orders of magnitude greater sensitivity than other analytical methods. Chemical disinfection inactivates pathogens during water treatment and prevents regrowth as water is conveyed in distribution system pipes, but it also causes formation of toxic disinfection by-products (DBPs). Analytical limits have hindered kinetic models which aid in ensuring water quality and protecting public health by predicting disinfectant DBPs formation. PTR-ToF-MS, designed for measuring gas phase concentrations of organic compounds, was able to simultaneously monitor aqueous concentrations of five haloamines relevant to chloramine disinfection under drinking water relevant concentrations. This novel application to aqueous analytes opens a new range of applications for PTR-ToF-MS.

1. Introduction

The adoption of drinking water disinfection with free chlorine in the early 20th century has made incidences of waterborne disease outbreaks rare in the United States (U.S.). However, the ability to predict the decay of disinfectants and formation of toxic disinfection byproducts (DBPs) has remained a vexing issue for water utilities. A recent paper indicated that 9–45 million Americans are affected annually by health-based water quality violations particularly in rural and minority communities. Most of the violations are due to coliform bacteria (37%) and DBP rule violations (25%), both of which are linked to issues with disinfection practices. A common way to address these issues is to use chloramines as secondary disinfectants because they form fewer regulated DBPs and persist longer in water distribution systems. Considerable work has been done since the 1980s to develop robust kinetic models for chloramine decay and DBP formation in drinking water, but an aspect that has remained elusive and is emerging as an issue in such models is the role of bromide (Br) which is common in source waters. The presence of Br in chloraminated waters leads to the formation of brominated haloamines (brominated analogues of chloramines) and brominated DBPs which are more toxic than their chlorinated counterparts and are often the driver of overall human toxicity (less abundant but more toxic DBPs form). With increasing total dissolved solid concentrations in freshwaters and the use of alternative water sources with higher Br concentrations (e.g. seawater, municipal wastewater), accurate measurements of haloamines are needed to develop reliable models for the formation and transformation of brominated species in drinking water. The objectives of this work are to i) demonstrate that proton transfer time of flight mass spectrometry (PTR-ToF-MS) can be used to measure concentrations of trace volatile analytes in the liquid phase and ii) to show the methodology can be used to monitor haloamine reactions in real time to expand our knowledge and prediction capabilities of haloamine formation and decay.

Most U.S. drinking water plants utilize two disinfection periods: primary for inactivating microorganisms and secondary for maintaining water quality and preventing (re)growth of pathogens in water distribution
systems and premise plumbing. Chloramines are generally formed by first adding free chlorine (prechlorination) for primary disinfection followed by ammonia to form chloramines which are used as secondary disinfectants. For pH ranges typical of drinking water (pH 7 to 9), monochloramine (NH₂Cl) is the most abundant chloramine species; dichloramine (NHCl₂) also forms but at lower concentrations.

In Br⁺ containing waters, prechlorination oxidizes Br⁻ to free bromine. Subsequently, when ammonia is added to form chloramines, a dynamic mixture of five haloamines forms: NH₂Cl, NHCl₂, monobromamine (NH₂Br), dibromamine (NHBr₂), and bromochloramine (NHBrCl). The formation of NH₂Br, NHBr₂, and NHBrCl is undesired compared to NH₂Cl and NHCl₂ because they decay faster and form greater concentrations of brominated DBPs. The relevant reaction kinetics among the five haloamines and in waters containing natural organic matter (NOM, the precursor to DBPs) are complex and incompletely understood, and yet are a prerequisite for developing mechanistic kinetic models to understand disinfectant residual maintenance, minimize brominated DBP formation, and manage water distribution systems in a manner that ensures public health. A better understanding of the formation of brominated DBPs is urgently needed, because recent work has shown that unregulated DBPs, such as brominated haloacetonitriles are the major drivers of toxicity in drinking water, the U.S. EPA is currently considering expanding the DBP rule to specifically regulate brominated haloacetic acids.

A major limitation to the study of chloramine chemistry has been the lack of an analytical method that can in real time accurately measure all relevant haloamines (some rapidly form and decay) at concentrations relevant to drinking water. Current analytical methods for measuring haloamines are ultraviolet-visible (UV-Vis) spectroscopy, a combination of colorimetric tests, and membrane introduction mass spectrometry (MIMS). UV-Vis spectroscopy has been used to study haloamine chemistry but requires concentrations much higher than seen in drinking water and overlapping UV spectra make it difficult to resolve quantitatively the several species present in solution. The indophenol and total chlorine DPD colorimetric methods are widely employed by water utilities. While these two methods are often used in combination, the results can be confounding; the indophenol method specifically measures NH₂Cl, whereas the total chlorine DPD method measures the total oxidant concentration which, in the case of chloraminated waters, is the total haloamine concentration on a halogen basis ([NH₂Cl] + 2[NHCl₂] + [NH₂Br] + 2[NHBrCl] + 2[NHBr₂]). MIMS uses a semipermeable hydrophobic membrane that rejects water to introduce dissolved analytes to a mass spectrometer that identifies and quantifies analytes based on their mass to charge ratio (m/z). MIMS configurations generally use an electron ionization source which generates many fragment ions from the parent molecule. In haloamine systems, this fragmentation results in dihaloamines (NHCl₂, NHBr₂, and NHBrCl) interfering with the quantification of monohaloamines (NH₂Cl and NH₂Br). Fragmentation has made the simultaneous monitoring of all five haloamines with this technique impossible when there are relatively large concentrations of the three brominated haloamines, particularly NHBrCl because it interferes with both NH₂Cl and NH₂Br.
PTR-ToF-MS is an analytical technique that uses chemical ionization with hydronium ion (H$_3$O$^+$) to measure gas phase volatile organic compounds (VOCs) as well as inorganic compounds at single parts per trillion concentrations. Chemical ionization is a “soft ionization” process that results in significantly less fragmentation than electron ionization commonly used with MIMS because less energy is imparted on the parent compound when it is ionized. One group of researchers utilized H$_3$O$^+$ as a chemical ionization source in conjunction with MIMS and found that chloramines and NH$_2$Br degraded significantly within the membrane such that the signals for the parent compounds were weaker than those of decay products; an issue that negated the advantages of chemical ionization when used in conjunction with MIMS. PTR-ToF-MS has been used to measure chloramines in the air at indoor pools and following cleaning with ammonia and chlorine-based cleaners. Selected ion flow tube mass spectrometry, a similar technology to PTR-ToF-MS that is orders of magnitude less sensitive, has been used to detect and characterize NH$_2$Cl, NHCl$_2$, and NH$_2$Br in human breath. The impressive sensitivity of PTR-ToF-MS for measuring gas phase compounds has the potential for correlating gas and aqueous concentrations of haloamines.

In this work, we demonstrate expanded functionality of PTR-ToF-MS by being the first to use it to examine drinking water relevant concentrations of haloamines in real time, thus enabling us to simultaneously quantify aqueous concentrations of haloamines as they form and decay. The data acquired using PTR-ToF-MS enables estimation of relevant kinetic parameters, assessment of relevant competing reactions, and validation of any already developed kinetic model. More generally, we show that PTR-ToF-MS can be used to measure concentrations of trace volatile analytes in a liquid phase via headspace analysis, thereby exposing the potential for a wide range of new applications.

2. Main Text

2.1 Mass spectra of haloamines using PTR-ToF-MS

The protonated molecular ions used for quantification of haloamines were m/z 51.995 (NH$_2$ClH$^+$), 85.956 (NHCl$_2$H$^+$), 95.944 (NH$_2$BrH$^+$), 131.903 (NHBrClH$^+$), and 175.852 (NHBr$_2$H$^+$) because they were the dominant ions. In the mass spectrum for each haloamine (Fig. 1), the protonated molecular ion for acetone, C$_3$H$_6$OH$^+$ (m/z 59.049), and acetic acid, C$_2$H$_4$O$_2$H$^+$ (m/z 61.028), are present because they are ubiquitous in the ambient air of indoor spaces and captured due to the open headspace sampling method utilized in this work. PTR-ToF-MS sampling of ambient air in the laboratory contained peaks corresponding to acetone and acetic acid (Fig. S1). Additionally, the NHCl$_2$ and NHBrCl mass spectra (Fig. 1B and 1D) have significant peaks of the protonated ion of acetic acid because those experiments were buffered with acetate and performed at pH 4 and 5, respectively.

The mass spectrum for NH$_2$Br featured the molecular ions NH$_2$$^{79}$BrH$^+$ (m/z 95.944) and NH$_2$$^{81}$BrH$^+$ (m/z 97.942) (Fig. 1C). The mass spectrum for NHBr$_2$ (Fig. 1E) additionally revealed the expected molecular
ions $\text{NH}^{79}\text{Br}_2\text{H}^+ (m/z 173.854)$, $\text{NH}^{79}\text{Br}^{81}\text{BrH}^+ (m/z 175.852)$, and $\text{NH}^{81}\text{Br}_2\text{H}^+ (m/z 177.851)$, as well as the molecular ions of many potential fragment ions, including $\text{NH}^{79}\text{BrH}^+ (m/z 94.936)$, $\text{NH}^{81}\text{BrH}^+ (m/z 96.935)$, $\text{Br}^{79}_2^+ (m/z 157.837)$, $\text{Br}^{79}_2\text{Br}^{81}^+ (m/z 159.834)$, $\text{Br}^{81}_2^+ (m/z 161.832)$, $\text{NH}^{79}\text{Br}_2^+ (m/z 172.842)$, and $\text{NH}^{79}\text{Br}^{81}\text{Br}^+ (m/z 174.842)$. With MIMS, the signals for $\text{Br}^{79}_2^+$ ions have been two$^{29}$ and tenfold$^{30}$ as high as the signal for $\text{NHBr}_2$, while with PTR-ToF-MS, it is only a tenth of $\text{NHBr}_2$ highlighting the cleaner mass spectrum obtained with PTR-ToF-MS versus MIMS. Additional discussion about the mass spectra of the other haloamines is presented in the Supplementary Material (Section S2.1).

The expected isotopic ratios and characteristic mass defects of the haloamines detected by the PTR-ToF-MS led to high confidence of ion identification (within > 1 mDa mass accuracy). The high resolution (5 decimal points, simplified by rounding to 3 decimal points in this work) m/z for molecular and fragment ions as well as the relative mass error (Eq. 1) for all five haloamine isotopes were quantified (Table 1). The average mass deviation for the haloamines detected was $4.73 \pm 2.14$ ppm which shows high confidence of ion identification because ions with similar mass values can be resolved separately.
Table 1  
Protonated parent ions detected by PTR-ToF-MS and their mass defects compared to exact values. Dominant ions in bold. The trihaloamine species were detected but not quantified.

<table>
<thead>
<tr>
<th>Haloamine</th>
<th>Ion Formula</th>
<th>Isotopic Ratio</th>
<th>Exact m/z</th>
<th>Detected m/z</th>
<th>Mass Error (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monochloramine</td>
<td>$\text{NH}_2^{35}\text{ClH}^+$</td>
<td>1.00</td>
<td>51.99485</td>
<td>51.9945</td>
<td>6.73</td>
</tr>
<tr>
<td></td>
<td>$\text{NH}_2^{37}\text{H}^+$</td>
<td>0.32</td>
<td>53.99190</td>
<td>53.9919</td>
<td>0.00</td>
</tr>
<tr>
<td>Dichloramine</td>
<td>$\text{NH}^{35}\text{Cl}_2\text{H}^+$</td>
<td>1.00</td>
<td>85.95588</td>
<td>85.9564</td>
<td>6.05</td>
</tr>
<tr>
<td></td>
<td>$\text{NH}^{35}\text{Cl}^{37}\text{ClH}^+$</td>
<td>0.64</td>
<td>87.95293</td>
<td>87.9524</td>
<td>6.03</td>
</tr>
<tr>
<td>Monobromamine</td>
<td>$\text{NH}_2^{79}\text{BrH}^+$</td>
<td>1.00</td>
<td>95.94434</td>
<td>95.9438</td>
<td>5.63</td>
</tr>
<tr>
<td></td>
<td>$\text{NH}_2^{81}\text{BrH}^+$</td>
<td>0.97</td>
<td>97.94229</td>
<td>97.9422</td>
<td>0.92</td>
</tr>
<tr>
<td>Bromochloramine</td>
<td>$\text{NH}^{35}\text{Cl}^{79}\text{BrH}^+$</td>
<td>0.77</td>
<td>129.90537</td>
<td>129.904</td>
<td>10.55</td>
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<tr>
<td></td>
<td>$\text{NH}^{37}\text{Cl}^{79}\text{BrH}^+$</td>
<td>1.00</td>
<td>131.90309</td>
<td>131.903</td>
<td>0.68</td>
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<tr>
<td></td>
<td>$\text{NH}^{35}\text{Cl}^{81}\text{BrH}^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{NH}^{37}\text{Cl}^{81}\text{BrH}^+$</td>
<td>0.24</td>
<td>133.90037</td>
<td>133.9</td>
<td>2.76</td>
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<tr>
<td>Dibromamine</td>
<td>$\text{NH}^{79}\text{Br}_2\text{H}^+$</td>
<td>0.51</td>
<td>173.85485</td>
<td>173.854</td>
<td>4.89</td>
</tr>
<tr>
<td></td>
<td>$\text{NH}^{79}\text{Br}^{81}\text{BrH}^+$</td>
<td>1.00</td>
<td>175.85280</td>
<td>175.852</td>
<td>4.55</td>
</tr>
<tr>
<td></td>
<td>$\text{NH}^{81}\text{Br}_2\text{H}^+$</td>
<td>0.49</td>
<td>177.85075</td>
<td>177.851</td>
<td>1.41</td>
</tr>
<tr>
<td>Acetone</td>
<td>$\text{C}_3\text{H}_6\text{OH}^+$</td>
<td>$-$</td>
<td>59.04914</td>
<td>59.0492</td>
<td>1.02</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>$\text{C}_2\text{H}_4\text{O}_2\text{H}^+$</td>
<td>$-$</td>
<td>61.02840</td>
<td>61.0284</td>
<td>0.00</td>
</tr>
<tr>
<td>Trichloramine</td>
<td>$\text{N}^{35}\text{Cl}_3\text{H}^+$</td>
<td>1.00</td>
<td>119.90700</td>
<td>119.9169</td>
<td>82.63</td>
</tr>
<tr>
<td></td>
<td>$\text{N}^{35}\text{Cl}_2^{37}\text{ClH}^+$</td>
<td>0.96</td>
<td>121.96000</td>
<td>121.914</td>
<td>377.66</td>
</tr>
<tr>
<td>Tribromamine</td>
<td>$\text{NH}^{79}\text{Br}_3\text{H}^+$</td>
<td>0.34</td>
<td>251.76500</td>
<td>251.7654</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>$\text{NH}^{79}\text{Br}_2^{81}\text{BrH}^+$</td>
<td>1.00</td>
<td>253.76300</td>
<td>253.7633</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>$\text{NH}^{79}\text{Br}^{81}\text{Br}_2\text{H}^+$</td>
<td>0.97</td>
<td>255.76100</td>
<td>255.7613</td>
<td>1.05</td>
</tr>
</tbody>
</table>
As expected, the mass spectra acquired using PTR-ToF-MS were simpler, had fewer fragment ions, and contained more distinct peaks for parent ions than those captured using MIMS. Fragment ions still formed even though chemical ionization with \( \text{H}_3\text{O}^+ \) is a much lower energy process than electron ionization. Some fragments were likely formed due to impurities in the chemical ionization process which results in the small formation of \( \text{O}_2^+ \) as part of the ionization gas which imparts more energy than \( \text{H}_3\text{O}^+ \). The impact of the fragment ions from \( \text{NHCl}_2, \text{NHBrCl}, \) and \( \text{NHBr}_2 \) on the quantification of \( \text{NH}_2\text{Cl} \) and \( \text{NH}_2\text{Br} \) is further explored in Section 3.3.

2.2 Calibration curves and detection limits for haloamines using PTR-ToF-MS

Calibration curves (Fig. S2) for each haloamine were successfully developed (see discussion in Section S2.2) which demonstrates that PTR-ToF-MS can be used to effectively quantify aqueous haloamine concentrations with headspace measurements at drinking water relevant concentrations. More broadly the results show that PTR-ToF-MS can be used to measure aqueous concentrations, which no other studies have previously attempted. This opens the potential for much broader applications of PTR-ToF-MS technology to quantify low concentrations of volatile compounds in aqueous solutions.

The level of detection (LOD) and level of quantification (LOQ) using PTR-ToF-MS were determined for each haloamine (Table S1). The LOD and LOQ were estimated by the method of blank determination where the average haloamine concentration of ten sample blanks plus three and ten times the standard deviation, respectively for LOD and LOQ. The LODs of \( \text{NH}_2\text{Cl}, \text{NHCl}_2, \text{NH}_2\text{Br}, \text{NHBrCl}, \) and \( \text{NHBr}_2 \) were 0.90, 0.0023, 0.059, 0.0086, and 0.00072 µM. The LOQs of \( \text{NH}_2\text{Cl}, \text{NHCl}_2, \text{NH}_2\text{Br}, \text{NHBrCl}, \) and \( \text{NHBr}_2 \) were 1.1, 0.0045, 0.092, 0.016, and 0.0016 µM. The lowest LODs determined with MIMS for \( \text{NH}_2\text{Cl}, \text{NHCl}_2, \text{NH}_2\text{Br}, \text{NHBrCl}, \) and \( \text{NHBr}_2 \) were 0.48, 0.24, 1.44, 2.51, and 0.84 µM respectively. PTR-ToF-MS has LODs 1 to 3 orders of magnitude lower than MIMS for all haloamines except \( \text{NH}_2\text{Cl} \). The improved sensitivity for the haloamines other than \( \text{NH}_2\text{Cl} \) is particularly important because they are present at much lower concentrations than \( \text{NH}_2\text{Cl} \) in chloraminated waters.

2.3 Impact of dihaloamine fragments on quantification of monohaloamines

The dihaloamines \( \text{NHCl}_2, \text{NHBrCl}, \) and \( \text{NHBr}_2 \) have been shown to form fragments (Section 3.1) that contribute to the molecular ions for \( \text{NH}_2\text{Cl} \) (m/z 51.995) and \( \text{NH}_2\text{Br} \) (m/z 95.944). The contribution from dihaloamines to the fragments at m/z 51.995 and 95.944 must be accounted for to ensure all haloamines are accurately quantified in a mixture. A set of interference calibration curves was developed...
to account for contribution of the fragment ions from NHCl₂, NHBrCl, and NHBr₂ to those two m/z values (Fig. 2). All the interference calibration curves were fit linearly ($R^2 > 0.92$) with an intercept of zero, except for NHCl₂ (Fig. 2A). The nonzero intercept for NHCl₂ is likely due to small amounts of HOCl (which can be present at the low pH value of 4 that NHCl₂ was formed in this work) being ionized and interfering at m/z 51.995. This phenomenon did not impact the NHBrCl interference calibration curve (Fig. 2B) because less HOCl would be present at the higher pH of 5 and HOCl would rapidly react with Br⁻ present in the NHBrCl solutions.

PTR-ToF-MS has much lower levels of fragmentation than MIMS, which makes it a more viable option for collecting robust kinetic data of haloamines. The contribution of 10 µM of dihaloamines to the signals of monohaloamines for PTR-ToF-MS and MIMS is compared in Table 2. The fragments formed during chemical ionization using PTR-ToF-MS are approximately 2 to 20% of those formed from electron ionization by MIMS. The much lower level of fragmentation of NHBrCl and NHBr₂ is particularly important because these dihaloamines can be present in much greater concentrations than NHCl₂ in solutions containing Br⁻.

Table 2

<table>
<thead>
<tr>
<th>Dihaloamine</th>
<th>NH₂Cl</th>
<th>NH₂Br</th>
<th>NH₂Cl</th>
<th>NH₂Br</th>
<th>NH₂Cl</th>
<th>NH₂Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>NHCl₂</td>
<td>0.3 µM</td>
<td>-</td>
<td>17 µM</td>
<td>-</td>
<td>5.2 µM</td>
<td>-</td>
</tr>
<tr>
<td>NHBrCl</td>
<td>3.2 µM</td>
<td>1.4 µM</td>
<td>50 µM</td>
<td>7.8 µM</td>
<td>NM*</td>
<td>NM*</td>
</tr>
<tr>
<td>NHBr₂</td>
<td>-</td>
<td>3.4 µM</td>
<td>-</td>
<td>28 µM</td>
<td>-</td>
<td>21 µM</td>
</tr>
</tbody>
</table>

* Not measured (NM)

2.4 Effectiveness of PTR-ToF-MS at monitoring dynamic aqueous haloamine kinetics

While the preceding discussion highlighted the ability to accurately measure haloamine compounds at environmentally relevant concentrations, a primary goal of this work is to demonstrate the potential for this method to guide model development and predict haloamine formation and decay. Two kinetic experiments were performed, with and without NOM (the major precursor to DBPs found in all source water), to evaluate the effectiveness of using PTR-ToF-MS to measure haloamines in a dynamic mixture. Experiments were designed to simulate the chloramination process used in practice; chloramines are commonly formed with prechlorination followed one minute later by ammonia addition to form chloramines. During each experiment, PTR-ToF-MS was used to simultaneously monitor the five
haloamine concentrations. The indophenol and total chlorine DPD colorimetric methods were also used to measure NH$_2$Cl and total haloamine ([NH$_2$Cl] + 2[NHCl$_2$] + [NH$_2$Br] + 2[NHBrCl] + 2[NHBr$_2$]) concentrations, respectively.

The effectiveness of using PTR-ToF-MS for monitoring haloamine concentrations was assessed by comparing the results to the colorimetric methods in both kinetic experiments. The NH$_2$Cl and total haloamine concentrations measured using PTR-ToF-MS were in good agreement with those determined with the established colorimetric methods with differences ranging from 0.4 to 3.7 µM (4.1 to 13%) for the experiment without NOM (Fig. 3A) and 0.03 to 6.2 µM (0.1 to 37%) for the experiment with NOM (Fig. 3B). The consistency between the two total haloamine measurements shows that the mass balance on the haloamines measured using PTR-ToF-MS is correct. Accurate NH$_2$Cl measurements highlight the ability to account for fragment ions because the most significant impact of fragmentation occurs when NHBrCl interferes with NH$_2$Cl quantification (Table 2), and NHBrCl forms rapidly during the kinetic experiments (Fig. 4). Additionally, the consistency between the PTR-ToF-MS and colorimetric method measurements in the NOM experiment shows that a low concentration (2 mg/L as C) of organic carbon, typical of natural waters, does not significantly impact or interfere with the PTR-ToF-MS method for quantifying haloamines.

### 2.5 Implications for existing haloamine models

The kinetic experiment monitored by PTR-ToF-MS shows that, in the absence of NOM, the concentrations of the various haloamines changed substantially during the short 30-minute experiments (Fig. 4). NH$_2$Cl and NH$_2$Br were rapidly consumed to form NHBrCl and NHBr$_2$ and the dihaloamines then decayed. NHCl$_2$ was excluded from Fig. 4 because it was present at very low concentrations (< 0.1 µM) and did not change substantially. The experimental data were also compared to the most widely used haloamine model (Fig. 4, Table S2) and another model developed by Pope using MIMs (Fig. S3, Table S3). The two kinetic models yield similar simulated concentrations of haloamines; therefore, we will focus on the comparison to the kinetic model developed by Luh and Mariñas (L&M model) $^{18}$.

Substantial discrepancies are apparent between the L&M model and the data collected using PTR-ToF-MS, which highlights the significant deficiencies in existing kinetic models to describe haloamine formation and decay at conditions representative of actual chloramine application to drinking water (e.g., pH 7–9, < 4 mg Cl$_2$/L, and chloramines formed with a prechlorination step). The model greatly underpredicts NH$_2$Cl decay and NHBrCl formation, while also overpredicting NHBr$_2$ formation. The predicted dominant brominated haloamine was NHBr$_2$ while the PTR-ToF-MS data showed that NHBrCl was the dominant brominated haloamine after the first two minutes. Therefore, if one relied on the L&M model to understand brominated DBP formation, the model estimated dominant brominated haloamine, NHBr$_2$, could be incorrectly associated with DBP formation instead of NHBrCl.
The differences between the L&M model and PTR-ToF-MS data reflect the limitations of current analytical methods, which required Luh and Mariñas to perform experiments at conditions atypical of chloramination. They combined NH$_2$Cl (at a concentration more than threefold higher than the highest allowable chloramine concentration of 4 mg Cl$_2$/L in drinking water) with a fivefold excess of Br$^-$ to form NHBrCl (example shown in Fig. S4). This approach resulted in a set of reactions that applies to their experimental conditions but does not translate to more representative chloramination conditions as exhibited in Fig. 4. PTR-ToF-MS can overcome the previous issues by providing more representative experimental data to develop a truly comprehensive haloamine kinetic model for guiding and optimizing disinfection practices when using chloramines. Additionally, PTR-ToF-MS can monitor the relevant haloamine species when NOM is present which is advantageous for studying haloamine reactions with NOM that lead to DBP formation (Fig. S5).

3. Conclusion

The use of PTR-ToF-MS to sample the headspace of an aqueous solution and directly correlate that to dissolved concentrations opens a wide range of new potential uses for this analytical technology. Many VOCs from anthropogenic sources (e.g. petroleum products, plastics, solvents, paints, adhesives, refrigerants) end up in ground, surface, and drinking waters$^{32,33}$. Measurement of VOCs in water generally requires sample preparation (e.g., extractions, concentrating), separation by gas chromatography, and then quantification via mass spectrometry, flame ionization detection, or electron capture detection$^{34}$. Headspace sampling utilizing PTR-ToF-MS has the potential to significantly simplify analysis of VOCs in water and increase sample throughput and improve sensitivity. Additional work is necessary to test the effectiveness of PTR-ToF-MS for the wide range of VOCs in water, but the work in this study demonstrated a proof of concept that rapid, sensitive headspace sampling can be used to directly determine aqueous concentrations of volatile analytes in real time.

The novel haloamine kinetic data collected in this work highlights a particularly useful application of PTR-ToF-MS because not only are aqueous concentrations being measured but reactions kinetics are being assessed in real-time. The data demonstrated major deficiencies in existing kinetic models, illustrating their limited usefulness in predicting disinfectant residual maintenance and DBP formation, and more broadly as tools for managing water distribution systems. Because PTR-ToF-MS allows simultaneous, real-time measurement of the five important haloamines, future experimental work and modeling will be able for the first time to evaluate kinetic models for all important species. Additionally, this method has the potential to also study the simultaneous formation of DBPs which would provide even greater insight into the formation mechanisms of DBPs. Such a study would allow revisions to existing kinetic models to close fundamental knowledge gaps, thereby enabling a better understanding of Br$^-$ impacted waters and providing more robust predictive tools for managing drinking water treatment plants and distributions systems.

4. Disclaimer
The research presented was not performed or funded by EPA and was not subject to EPA’s quality system requirements. The views expressed in this article are those of the author(s) and do not necessarily represent the views or the policies of the U.S. Environmental Protection Agency. Any mention of trade names, manufacturers or products does not imply an endorsement by the United States Government or the U.S. Environmental Protection Agency. EPA and its employees do not endorse any commercial products, services, or enterprises.

Methods

6.1 Synthesis of haloamines

Reagent grade chemicals and ultrapure water (18.2 MΩ·cm, Milli-Q, Millipore) were used to prepare all stock haloamine solutions and dilutions and wrapped in foil to protect against UV induced decay. The haloamines were made by combining hypochlorite (OCl) or hypobromite (OBr) with ammonia chloride (NH4Cl) at various halogen to nitrogen ratios (X2/N) and pH values. A 4.99% sodium hypochlorite solution (NaOCl) solution was used to make hypobromite ion (OBr) solutions. The OCl concentration was determined before use by measuring the absorbance on a Hach DR6000 Spectrophotometer (Hach Company, Loveland, CO) at 292 nm, using a molar absorptivity ($\varepsilon_{\text{OCl-},292\text{nm}}$) of 362 M$^{-1}$cm$^{-1}$\textsuperscript{35}. The OBr stock solution was prepared by combining OCl with Br at a Br/Cl molar ratio of 1.05. The exact OBr stock solution concentration was determined by monitoring the absorbance for OBr at 329 nm ($\varepsilon_{\text{OBr-},329\text{nm}}$ = 332 M$^{-1}$cm$^{-1}$\textsuperscript{36}).

The NH$_2$Cl stock solution was prepared by adding OCl dropwise to a well-mixed pH 9 ammonia solution at a Cl$_2$/N molar ratio of 0.6. The NH$_2$Cl stock solution concentration was determined by measuring the absorbance at 243 nm ($\varepsilon_{\text{NH}_2\text{Cl},243\text{nm}} = 461$ M$^{-1}$cm$^{-1}$\textsuperscript{37}). The NHCl$_2$ stock solution was prepared by buffering a NH$_2$Cl solution with 10 mM acetate and rapidly dropping the pH to 4. The NHCl$_2$ solution was aged for at least 4 hours to maximize formation of NHCl$_2$. The NHCl$_2$ and NH$_2$Cl concentrations were determined by reconciling overlapping UV spectra at 243 ($\varepsilon_{\text{NH}_2\text{Cl},243\text{nm}} = 461$ M$^{-1}$cm$^{-1}$ and $\varepsilon_{\text{NHCl}_2,243\text{nm}} = 235$ M$^{-1}$cm$^{-1}$) and 294 nm ($\varepsilon_{\text{NH}_2\text{Cl},294\text{nm}} = 15$ M$^{-1}$cm$^{-1}$ and $\varepsilon_{\text{NHCl}_2,294\text{nm}} = 282$ M$^{-1}$cm$^{-1}$).

The NH$_2$Br stock solution was prepared by combining ammonia and OBr solutions at a Br$_2$/N molar ratio of 1:1000 at pH 9 (the large excess of ammonia buffered the solution). The NHBr$_2$ stock solution was prepared by combining ammonia and OBr at a Br$_2$/N molar ratio of 1:2 at pH 7.2 in 10 mM phosphate buffer. The NH$_2$Br and NHBr$_2$ concentrations in each stock solution were determined by reconciling overlapping UV spectra at 232 ($\varepsilon_{\text{NH}_2\text{Br},232\text{nm}} = 82$ M$^{-1}$cm$^{-1}$ and $\varepsilon_{\text{NHBr}_2,232\text{nm}} = 2000$ M$^{-1}$cm$^{-1}$) and 278 nm ($\varepsilon_{\text{NH}_2\text{Br},278\text{nm}} = 425$ M$^{-1}$cm$^{-1}$ and $\varepsilon_{\text{NHBr}_2,278\text{nm}} = 715$ M$^{-1}$cm$^{-1}$\textsuperscript{38}).

The NHBrCl stock solution was prepared by combining a NH$_2$Cl solution with HOBr at a NH$_2$Cl/HOBr molar ratio of 3:2 at pH 5 in 10 mM acetate buffer. At these conditions, NHBrCl will rapidly form and is
sufficiently stable for analysis within minutes\textsuperscript{39}. The NHBrCl concentration was equal to the HOBr added, and the NH\textsubscript{2}Cl concentration was equal to half the NHBrCl concentration.

6.2 PTR-ToF-MS operating parameters and sampling procedure

A Vocus 2R PTR-ToF-MS (Aerodyne, Inc., Billerica, MA, USA) was used to measure haloamine concentrations. The internal parameters used in PTR-ToF-MS greatly impact ion sensitivities and detection transmission efficiencies\textsuperscript{40}. The following optimized parameters were used: focused ion molecule reaction (FIMR) pressure = 2.3 mbar, FIMR temperature = 120 °C, big segmented quadrupole (BSQ) voltage = 275 V, H\textsubscript{3}O\textsuperscript{+} ion source flow rate = 15 sccm, FIMR front voltage = 650 V, FIMR rear voltage = 25 V. These settings resulted in E/N = 155 Td, where E is the electrical field strength and N is the gas number density, which is sufficiently high to prevent excessive water clusters in high humidity samples. The PTR-ToF-MS parameters used in this study are commonly used in studies\textsuperscript{41,42} but were further optimized in the current work for NH\textsubscript{2}Cl, NHCl\textsubscript{2}, and NH\textsubscript{2}Br signals by adjusting FIMR parameters including temperature.

Headspace sampling was used to measure haloamine concentrations in standards for calibration curves and samples from kinetic experiments. 5 mL of a solution was pipetted from a bulk standard or experiment into a 2 dram (7.4 mL) screw-top vial (Fisherbrand vial N51A, Fisher Scientic, Inc.), and a \textfrac{1}{4}-inch Teflon line (length of ~20 cm) was connected to the Vocus inlet and held 1 cm above the liquid surface of the solution (it took approximately 30 seconds to transfer samples for measurement on the PTR-ToF-MS). The Teflon line was held in the vial until the Vocus signal stabilized, approximately 15-20 seconds. The PTR-ToF-MS was operated at 1 Hz time resolution and with sufficient flow pressure (using a LI-COR 850 CO\textsubscript{2} monitor as a pump downline) to result in <1 second response time. All standard headspace measurements were completed in at least triplicate except in the case of NHBr\textsubscript{2} which will be discussed later.

Data processing of the Vocus concentration data was done using PTRwid (version v_003_jul_01_2021) with the configuration file customized to cause all five haloamines and their halogen isotopes to be added to the unified mass list\textsuperscript{43}. The protonated m/z ratio (as measured by the Vocus) of the isotopes of each haloamine, volatile buffer, and acetone are shown in Table 1. The PTRwid data processing resulted in a concentration time series at 1 Hz time resolution which was further analyzed using MATLAB (Mathworks, Portola Valley, CA, USA). Headspace sampling was performed until a consistent mass spectrum was observed for 15-20 seconds.

6.3 Calibration curves
The NH$_2$Cl, NHCl$_2$, and NH$_2$Br stock solutions were used to make a series of dilutions to make standards for calibration or the mass spectrometer. The NHBrCl standards were made by combining NH$_2$Cl and HOBr for each individual standard. NHBr$_2$ is inherently unstable and rapidly decays so it was impossible to make a series of standards diluted from a stock solution. Therefore, the standard curve for NHBr$_2$ was made by simultaneously monitoring the decaying concentration of the NHBr$_2$ stock solution using UV-Vis spectroscopy and then immediately pipetting a sample for analysis. This procedure was then repeated every few minutes on the decaying NHBr$_2$ solution to obtain the data needed to make the NHBr$_2$ calibration curve.

### 6.4 Kinetic experiments

Two kinetic experiments, one without NOM and one with NOM, were performed to assess the effectiveness of using PTR-ToF-MS to measure haloamine mixtures undergoing formation and decay. To maximize brominated haloamine formation, prechlorination used Br$^-$ and free chlorine concentrations at the upper range that occurs in drinking water treatment before ammonia addition to form haloamines. For the experiment without NOM, a solution of 2 mg/L as Br (25 μM) in 10 mM phosphate buffer at pH 7.2 was prepared and dosed with 4 mg/L as Cl$_2$ of free chlorine (56 μM). The solution was mixed for 1 minute, the median prechlorination duration, and then ammonia was added at a Cl$_2$/N molar ratio of 0.6 to form haloamines. The same procedure was repeated for the experiment with NOM except that 2 mg/L as C of Upper Mississippi River NOM (International Humic Substance Society, St Paul, MN, USA) was also present in solution before free chlorine addition. Ammonia addition initiated the start of a kinetic experiment because within milliseconds the monohaloamines, NH$_2$Cl and NH$_2$Br, form.

Monitoring continued for 30 minutes using PTR-ToF-MS as well as the indophenol and total chlorine DPD colorimetric methods. Samples were continuously taken from the bulk sample and put in the screw-top vials to be analyzed by the PTR-ToF-MS and samples were taken at approximately 2, 10, 20, and 30 minutes to be analyzed using the colorimetric methods.

### References


21. Pope, P. G. Haloacetic acid formation during chloramination: role of environmental conditions, kinetics, and haloamine chemistry. (University of Texas at Austin, 2006).


29. Pope, P. G. Haloacetic acid formation during chloramination: role of environmental conditions, kinetics, and haloamine chemistry. (University of Texas at Austin, 2006).

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**Figures**
Figure 1

Representative PTR-ToF-MS mass spectra for each haloamine: a) 200 μM NH₂Cl, b) mixture of 200 μM NHCl₂ and 20 μM NH₂Cl, c) 50 μM NH₂Br, d) mixture of 200 μM NHBrCl and 100 μM NH₂Cl, and e) 116 μM NHBr₂.

a The NHCl₂ standard is present in solution with NH₂Cl
Synthesis of a high purity aqueous solution of NHBrCl is impossible, so it must be present in solution with NH₂Cl.

**Figure 2**

Interference from dihaloamines on monohaloamines: a) NHCl₂ fragments interfering with NH₂Cl quantification (m/z = 51.995), b) NHBrCl fragments interfering with NH₂Br quantification (m/z = 51.995), c) NHBr₂ fragments interfering with NH₂Br quantification (m/z = 95.944), and d) NHBrCl fragments interfering with NH₂Br quantification (m/z = 95.944).
Figure 3

Measured concentrations of total haloamines and monochloramine during kinetic experiment using PTR-ToF-MS (V) and colorimetric (C) methods. pH 7.2, 10 mM phosphate buffer, and \([\text{Br}^-] = 2 \text{ mg/L as Br}^-\) (25 µM) dosed with \([\text{HOCl}] = 4 \text{ mg/L as Cl}_2^-\) (56 µM) for 1 minute followed by addition of \([\text{NH}_3] = 1.3 \text{ mg/L as N}\) (93 µM).  

a) without NOM  
b) \([\text{NOM}] = 2 \text{ mg/L as C}\).
Figure 4

Comparison of Luh and Mariñas model (dashed lines) to measured haloamine concentrations during the kinetic experiment using PTR-ToF-MS. pH 7.2, 10 mM phosphate buffer, and [Br] = 2 mg/L as Br (25 μM) dosed with [HOCl] = 4 mg/L as Cl₂ (56 μM) for 1 minute followed by addition of [NH₃] = 1.3 mg/L as N (93 μM). a) 0-30 μM concentration range b) 0-15 μM concentration range.
Supplementary Files

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