A comparison of sodium sulfite, ammonium chloride, and ascorbic acid for quenching chlorine prior to disinfection byproduct analysis

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ABSTRACT

This study compared 3 commonly used quenching agents for dechlorinating samples prior to disinfection byproduct (DBP) analysis under typical drinking water sampling conditions for a representative suite of chlorination byproducts. Ascorbic acid and sodium sulfite quenched the residual free chlorine to below detection within 5 seconds. Ammonium chloride did not quench the chlorine to below detection with up to a 70% molar excess, which agrees with published ammonium chloride-chlorine chemistry. With respect to the DBPs, ascorbic acid worked well for the trihalomethanes and haloacetic acids, except for dibromoiodomethane, which exhibited 2.6–28% error when using ascorbic acid compared to non-quenched control samples. Sodium sulfite also worked well for the trihalomethanes (and performed similarly to ascorbic acid for dibromoiodomethane) and was the best performing quenching agent for MX and the inorganic DBPs, but contributed to the decay of several emerging DBPs, including several halonitromethanes and haloacetamides. Ammonium chloride led to considerable errors for many DBPs, including 27–31% errors in chloroform concentrations after 24 hours of storage. This work shows that ascorbic acid is suitable for many of the organic DBPs analyzed by gas chromatography-electron capture detection and that sodium sulfite may be used for simultaneous chlorite, chlorate, and bromate analysis.

Key words | ammonium chloride, ascorbic acid, chlorine, disinfection byproducts, sodium sulfite

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HIGHLIGHTS

- Low ascorbic acid and sodium sulfite doses quenched chlorine within 5 seconds.
- Ascorbic acid had minimal effect on most of the organochlorine byproducts tested.
- Sodium sulfite was the best-performing quenching agent for the inorganic byproducts.
- Ammonium chloride led to errors for chloroform and several nitrogenous byproducts.
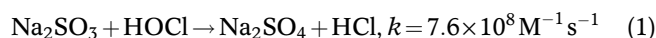
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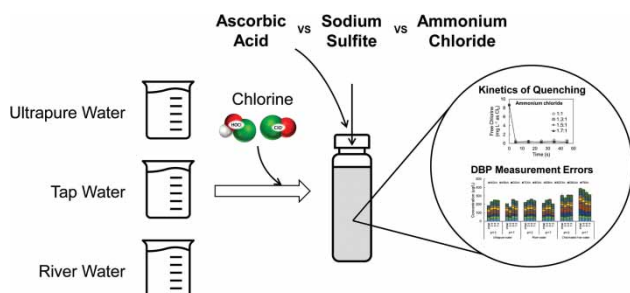
INTRODUCTION

The chlorination of drinking water can lead to the formation of a variety of disinfection byproducts (DBPs). Several of the more conventional DBPs, including trihalomethanes and haloacetic acids, are regulated in regions across North America, and many of the more recently identified compounds, including haloacetamides and halofuranones, are under scrutiny due to higher toxicity than regulated DBPs (U.S. EPA 2006; MECP 2016; Wagner & Plewa 2017). When sampling for DBPs, residual chlorine is typically removed to prevent ongoing DBP formation during transport and sample storage. To that end, a chlorine quenching agent is added to the samples. That quenching agent should rapidly eliminate the residual chlorine, and it should also have no impact on measured DBP concentrations either through reacting with the DBP or interfering with the analytical method.

EPA Method 551.1 and *Standard Methods* recommend the use of ammonium chloride to quench chlorine prior to analysing the majority of organohalide DBPs (APHA 1995; U.S. EPA 1995). As discussed elsewhere, this is because of DBP instability found in a number of studies from the 1980s when using sodium sulfite (Wang *et al.* 2016). Still, ammonium chloride has been found to lead to the formation or decay of DBPs from several classes, including the haloacetic acids (Hong *et al.* 2008), haloacetamides (Ding *et al.* 2018), and halonitromethanes (Liew *et al.* 2012). Ascorbic acid has been studied as a potential alternative (Krasner *et al.* 1989; Peterka 1998; Urbansky 1999), and it has recently been used in surveys of both conventional and emerging
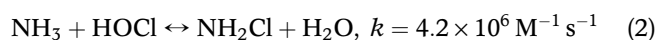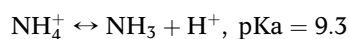
DBPs (Weinberg *et al.* 2002; Fang *et al.* 2010; Farré *et al.* 2013; Chuang *et al.* 2019; Mian *et al.* 2019).

All three of these quenching agents react with free chlorine through known pathways, as shown in Equations (1)–(3), and each can reduce chlorine to non-detectable levels (Fogelman *et al.* 1989; Jafvert & Valentine 1992; Folkes *et al.* 1995).

Sodium sulfite

$$Na_2SO_3 + HOCl \rightarrow Na_2SO_4 + HCl, k = 7.6 \times 10^8 \, M^{-1} \, s^{-1} \quad (1)$$

Ammonium chloride

$$NH_4^+ \leftrightarrow NH_3 + H^+, \ pKa = 9.3$$

$$NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O, \ k = 4.2 \times 10^6 \, M^{-1} \, s^{-1} \quad (2)$$

Ascorbic acid

$$C_6H_8O_6 + HOCl \rightarrow C_6H_6O_6 + HCl + H_2O,$$
$$k = 6 \times 10^6 \, M^{-1} \, s^{-1} \quad (3)$$
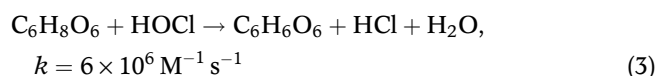
Basu & De Souza (2011) showed that for several quenching agents, organic and inorganic matter may influence the speed and completeness of chlorine quenching. For ascorbic acid and sodium bisulfite, dechlorination was inhibited to varying degrees in the presence of 20 mg L^{-1} total organic carbon (TOC) or 5 NTU of inorganic particulate matter, with decreased dechlorination rates and lower overall

removal of total chlorine, particularly at low quenching agent doses (e.g. equal molar concentrations as chlorine). In contrast, sodium thiosulfate was not affected by the presence of organic matter at those same low doses. In other words, different quenching agents may have varied performance in waters with different organic and inorganic matter characteristics, which highlights a need to understand the suitability of the quenching agent(s) under water quality conditions similar to those of the sampling site.

A quenching agent should also have minimal impact on measured DBP concentrations. This impact can take several forms, including the quenching agent leading to the decay of one or more DBPs, leading to the formation of DBPs, decreasing extraction efficiency, or producing a signal that interferes with the analyte of interest. The literature contains several examples of such undesirable effects. For example, Croué & Reckhow (1989) describe that trichloronitromethane (chloropicrin) quickly decays to dichloronitromethane in the presence of sodium sulfite ($k = {\sim}85$ M^{-1} s^{-1} at 20 °C), and Kristiana *et al.* (2014) observed that among 5 quenching agents, the use of ascorbic acid uniquely resulted in the near-complete absence of chlorite within 24 hours, possibly because of a redox reaction between the two or ascorbic acid interfering with the ion chromatographic analysis. Regardless of the type of interference, these collective effects ultimately result in an error in the final measured DBP concentration. While there have been efforts to understand this error for some DBPs and common quenching agents, there is limited information for many emerging DBPs. Furthermore, much of the existing literature focusses on individual classes of DBPs, which precludes the possibility of identifying a 'universal' quenching agent that can be used to streamline the analysis of all DBPs quantified using the same analytical method (e.g. organic DBPs analyzed with gas chromatography and electron capture detection, or inorganic DBPs analyzed with ion chromatography).

In response, the objective of this study was to directly compare ascorbic acid, sodium sulfite, and ammonium chloride for dechlorinating samples prior to DBP analysis under conditions (pH, TOC) representative of drinking water sampling. The speed and extent of dechlorination for each candidate was tested for a typical drinking water sample and compared to reported findings. Then, the overall error caused by each quenching agent on measured DBP concentrations was assessed for a group of DBPs representing a cross-section of those that can form during chlorination. This select group was made to include compounds that are routinely regulated; compounds that are typically included in studies or surveys of emerging DBPs; and a mix of chlorinated, brominated, and iodinated species, while maintaining the ability to clearly distinguish each DBP during chromatographic separation and analysis.

METHODS

Waters and chemicals

All samples were prepared in either Milli-Q® water, City of Toronto tap water (pH 7.16, TOC = 2.1 mg L^{-1}, chloramine residual = 1.69 mg-Cl$_2$ L^{-1}), or untreated Otonabee River water (pH 8.0–8.2, TOC = 5.0–5.2 mg L^{-1}), as specified. Reagent grade sodium hypochlorite (10–15%) was used to adjust chlorine concentration, and sulfuric acid (assay: 90–98%) was used to lower pH. All other reagents were of analytical grade or higher.

Experimental procedures

Quenching kinetics

EPA Method 551.1 and *Standard Methods* recommend using large doses of the quenching agent, at molar concentrations in the order of 10–100× the residual chlorine concentration under typical disinfection conditions (APHA 1995; U.S. EPA 1995). However (and with the exception of ammonium chloride), lower doses are becoming more common in DBP monitoring and research, in the order of 1.2–2× the residual chlorine concentration, to minimize any potential impact of the quenching agent on DBP analysis (Reckhow & Singer 1990; Weinberg *et al.* 2002; Worley *et al.* 2003; Liew *et al.* 2012; Kristiana *et al.* 2014). In this work, each quenching agent was added at molar quenching agent-to-chlorine ratios from 1:1 to 1.7:1 to align with the more modern convention. All ratios given to describe the amount of quenching agent used will refer to the molar quenching agent-to-chlorine ratio. To investigate the speed and

completeness of quenching, sodium sulfite, ascorbic acid, or ammonium chloride was added to sample bottles containing tap water and approximately 9 mg L^{-1} of free chlorine as Cl$_2$. This high chlorine concentration was used to represent the higher end of doses that might be considered or studied in the context of drinking water disinfection or (advanced) oxidation, and to ensure that residual chlorine concentrations could be accurately measured after high (near 2-log) levels of dechlorination. The residual free chlorine concentration was measured immediately after adding the quenching agent (5 seconds) and at 10 second intervals thereafter. Samples were stirred while the quenching agent was being added and during sampling.

Impact on DBPs

Each of the DBPs listed in Table 1 was spiked into Milli-Q$^®$ water at the concentration shown. The DBPs were divided into 3 groups and each group was spiked into a separate Milli-Q$^®$ water sample. This was done to facilitate distinguishing each compound during the analysis. The groups were: (1) THM$_4$, HAA$_9$, HANs, HNMs, inorganics, and MX; (2) iodinated THMs and iodinated HAAs; and (3) HAMs and HALs. Separate samples then received 1 of 7 treatments: (1–3) samples were spiked with freshly-prepared sodium sulfite, ascorbic acid, or ammonium chloride, respectively, such that the molar ratio would be 1.5:1 if there were 10 mg L^{-1} of free chlorine in the sample, just greater than the 9 mg L^{-1} used to investigate the quenching kinetics; (4–6) samples were spiked with 10 mg L^{-1} of free chlorine and then with sodium sulfite, ascorbic acid, or ammonium chloride, respectively, at a 1.5:1 ratio; or (7) no quenching agent or chlorine (unquenched control). The samples were then stored, headspace-free, in the dark at 4 °C. The DBP concentrations were measured over the next 7 days (samples were stored in separate vials corresponding to each storage time to ensure that the samples remained headspace-free). Based on those measured concentrations, the best performing quenching agent for each DBP was selected and used in a similar experiment in Otonabee River water, representing a more complex drinking water sample matrix, to confirm the results in Milli-Q$^®$ water and to test for any matrix effects

Table 1 | Monitored DBPs

Trihalomethanes (THMs), 50 µg L^{-1} each		Inorganics, 100 µg L^{-1} each
Trichloromethane (TCM)	Triiodomethane (TIM)	Chlorite
Bromodichloromethane (BDCM)	Dibromoiodomethane (DBIM)	Chlorate
Dibromochloromethane (DBCM)	Bromodiioodomethane (BDIM)	Bromate
Tribromomethane (TBM)	Dichloroiodomethane (DCIM)	
Haloacetic Acids (HAAs), 50 µg L^{-1} each		**Haloacetonitriles (HANs), 10 µg L^{-1} each**
Chloroacetic acid (MCAA)	Bromodichloroacetic acid (BDCAA)	Trichloroacetonitrile (TCAN)
Dichloroacetic acid (DCAA)	Chlorodibromoacetic acid (CDBAA)	Dichloroacetonitrile (DCAN)
Trichloroacetic acid (TCAA)	Iodoacetic acid (IAA)	Bromochloroacetonitrile (BCAN)
Bromoacetic acid (MBAA)	Diiodoacetic acid (DIAA)	**Halonitromethanes (HNMs), 10 µg L^{-1} each**
Dibromoacetic acid (DBAA)	Bromoiodoacetic acid (BIAA)	Trichloronitromethane (TCNM)
Tribromoacetic acid (TBAA)	Chloroiodoacetic acid (CIAA)	Bromodichloronitromethane (BDCNM)
Bromochloroacetic acid (BCAA)		Dibromochloronitromethane (DBCNM)
Haloacetamides, 50 µg L^{-1} each	**Halofuranones, 40 ng L^{-1} each**	**Haloacetaldehydes (HALs), 50 µg L^{-1} each**
Dibromoacetamide (DBAM)	3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX)	Dichloroacetaldehyde (DCAL)
Trichloroacetamide (TCAM)		Tribromoacetaldehyde (TBAL)

on the performance of that quenching agent. All experiments were performed in duplicate.

Analytical methods

Free chlorine was measured using the DPD method (HACH DR/2500 spectrophotometer and Permachem reagent packs, HACH, Toronto, Canada). pH was measured using a pH meter (Orion Star A111, Thermo Scientific). The THMs, HANs, HNMs, HALs, and HAMs were extracted using liquid-liquid extraction and analyzed using gas chromatography-electron capture detection (GC-ECD; Agilent 7890B Series Gas Chromatograph, DB 5.625 capillary column, 1225631, Agilent Technologies Canada Inc., Mississauga, ON, Canada), with 1,2-dibromopropane as an internal standard, according to EPA Method 551.1 (U.S. EPA 1995). The HAAs were extracted and analyzed according to Standard Method 6251B (APHA 1995), using 2,3,4,5-tetrafluorobenzoic acid as an internal standard and the same GC-ECD equipment. The halofuranone MX was extracted and analyzed with solid phase extraction and gas chromatography-mass spectrometry following the methods described by Mian *et al.* (2019), using a Varian 3800 GC paired with a 4000 MS and equipped with a DB-1701 column (30 m × 0.25 mm × 0.25 μm ID, Agilent Technologies Canada Inc., Mississauga, ON). The inorganic DBPs were analyzed using a Dionex ICS-5000 + DC ion chromatograph based on EPA Method 300.1 (U.S. EPA 1997). All samples were analyzed in duplicate.

RESULTS AND DISCUSSION

Kinetics of quenching

The kinetics of the reaction between chlorine and the 3 quenching agents are illustrated in Figure 1. All quenchers

reduced the chlorine concentration by at least 85% within 5 seconds at a 1:1 ratio. However, only ascorbic acid was able to quench chlorine to below the detection limit (0.1 mg L^{-1}) at this ratio. This effectiveness from ascorbic acid was expected, as it has previously been reported to react very quickly with chlorine, quenching to below detection in <1 second in ultrapure water (Folkes *et al.* 1995). In comparison, sodium sulfite required between a 20 and 30% molar excess to quench chlorine to below detection (doing so within 5 seconds), and ammonium chloride did not quench chlorine to below detection for any of the molar ratios tested (discussed subsequently).

Table 2 lists theoretical dechlorination times for each quenching agent calculated based on reported reaction rate coefficients, and a 1:1 molar ratio. According to the rates from Folkes *et al.* (1995) and Fogelman *et al.* (1989) (~6 × 10^6 M^{-1} s^{-1} for ascorbic acid and 7.9 × 10^8 M^{-1} s^{-1} for sodium sulfite, respectively), sodium sulfite was expected to be a faster quenching agent than ascorbic acid. However, there is some disagreement in reported rate coefficients. Hermant & Basu (2013) measured dechlorination rates in a synthetic water at molar ratios from 0.56:1 to 5.6:1 and found sodium sulfite to be the slower quenching agent (they observed smaller rate coefficients overall: 1.36 × 10^{-6} M^{-1} s^{-1} for ascorbic acid and 135 M^{-1} s^{-1} for sodium sulfite). They also found that at molar ratios up to 1.7:1, sodium sulfite did not completely quench the residual chlorine, unlike ascorbic acid, which quenched completely when present at molar concentrations equal to or greater than chlorine.

There are several possible explanations for the disagreement in reported quenching rates. The different studies used different experimental setups to measure the rates: stopped-flow spectrophotometry by Folkes *et al.* (1995), which is reported to underestimate rates for fast reactions (e.g. 1st order constants >300 s^{-1}) (Owens
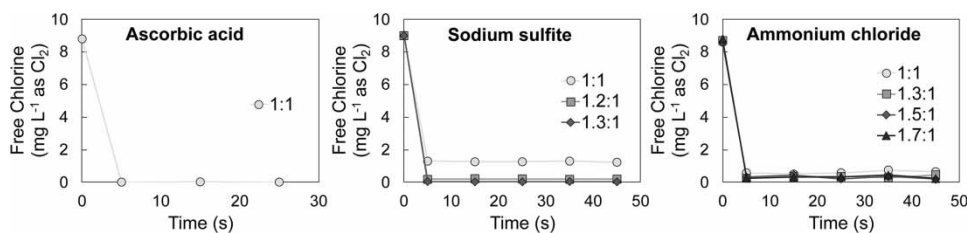
Figure 1 | Speed with which the 3 quenching agents react with free chlorine at several molar quenching agent-to-chlorine ratios (City of Toronto tap water, pH 7.16).

Table 2 | Free chlorine half life ($t_{1/2}$) and time to reduce chlorine to below 0.1 mg L^{-1} ($t_{< \, 0.1 \, mg \, L^{-1}}$) for ascorbic acid, sodium sulfite, and ammonium chloride based on published rate coefficients

Quenching agent	Time (s)		Source
	$t_{1/2}$	$t_{<0.1 \, mg \, L^1}$	
Ascorbic acid	0.00171	0.164	Folkes *et al.* (1995)
	46.7	92.3	Hermant & Basu (2013)
Sodium sulfite	0.0000135	0.00134	Fogelman *et al.* (1989)
	58.4	5,730	Hermant & Basu (2013)
Ammonium chloride	0.313	19.2	Jafvert & Valentine (1992)

et al. 1980); pulsed-accelerated-flow spectroscopy for Fogelman *et al.* (1989), which is capable of measuring faster reactions than stopped-flow systems can (Nemeth *et al.* 1987), and a flow loop with a chlorine analyzer for Hermant & Basu (2013). The water matrix is also known to be an influencing factor on measured reaction rates. There are numerous studies discussing the inhibitory effects of organic matter on dechlorination (Helz & Nweke 1995; Maccrehan *et al.* 1998; Yonkos *et al.* 2001), and (as mentioned earlier) Basu & De Souza (2011) showed that inorganic matter may slow ascorbic acid and sodium sulfite dechlorination, depending on the quenching agent-to-chlorine ratio. It may also be that dissolved oxygen oxidizes some sodium sulfite and ascorbic acid with the assistance of unknown natural catalysts in the water samples (at different rates) before they can react with chlorine, decreasing the speed at which chlorine is reduced and lowering the apparent rate coefficient between the quencher and chlorine (U.S. EPA 2000). It is not clear that this was the case in the current work, though, as the reaction between oxygen and sulfite is thought to proceed relatively slowly with a half life of several hours to days (Wilkinson *et al.* 1993).

When ammonium chloride is used as a quenching agent, the chloramines formed in the reaction between hypochlorous acid and ammonia exist in equilibrium with free chlorine. As a result, some free chorine will always remain in solution. Thus, ammonium chloride did not quench the chlorine to below detection at any of the molar ratios tested, and a 0.58–0.75 mg L^{-1} free chlorine residual remained after 5 seconds when the chlorine was quenched at a 1:1 ratio. This agrees with the 0.70 mg L^{-1} remaining after 5 seconds calculated using the chlorine-

ammonia model proposed by Jafvert & Valentine (1992). To compensate for this effect, a high dose of ammonium chloride is typically recommended in order to shift the equilibrium towards chloramines and reduce the free chlorine residual (e.g. 250 mg-NH$_4$Cl L^{-1}, or a molar ratio to chlorine in the range of 30–300:1; APHA 1995). Ultimately, the results show that both ascorbic acid and sodium sulfite are capable of rapidly reducing the chlorine to below detection, though sodium sulfite may require a molar excess depending on the water matrix. Ammonium chloride would require a molar excess beyond the 1.7:1 tested in this study.

Effects of quenching agents on disinfection byproducts

The next step was to investigate how the quenching agents affect measured concentrations of DBPs that are spiked into the sample water. In Figure 2, the concentrations of DBPs in a control sample with only the DBPs (unquenched) is compared to concentrations in samples receiving the DBPs and one of three quenching agents, and also to samples receiving the DBPs, chlorine, and then a quenching agent. The concentrations presented are after 1 and 7 days of storage. Figure 2 is intended to give a high-level view of the effects of each quenching agent on different classes of DBPs. Sections 3.2.1–3.2.3 describe the notable observations for individual DBP species.

The performance of each quencher, or the effect it had on measured concentrations, is assessed in 2 ways. First, the effect is described in terms of the percent error of the concentration in the quenched sample from that in the unquenched control. Percent error (%E) was calculated
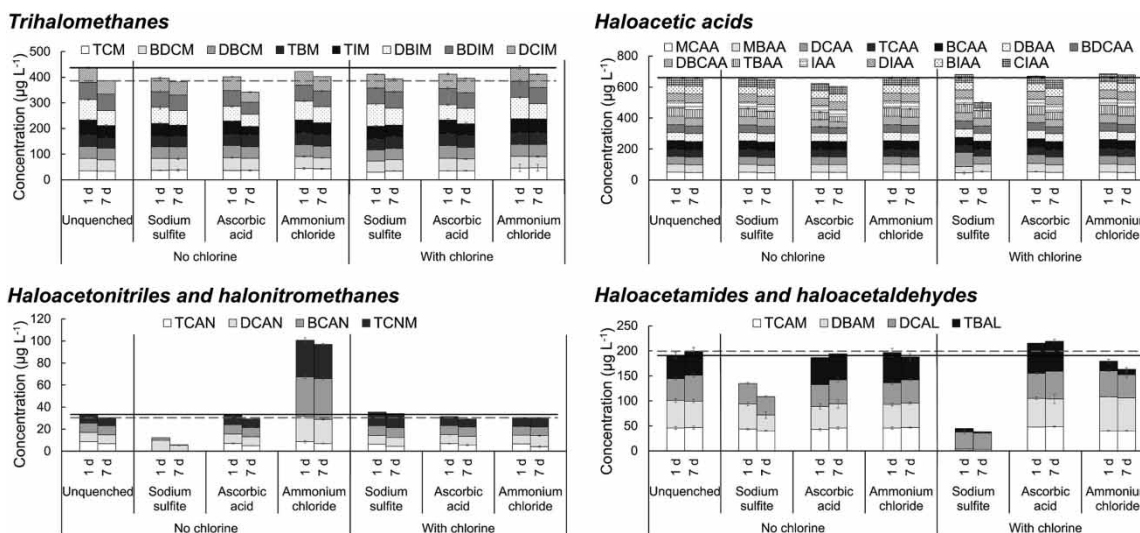
Figure 2 │ Effects of quenching agents on THM, HAA, HAN, HNM, HAM, and HAL concentrations after 1 and 7 days of storage, either without or with chlorine added prior to the quenching agent (conducted in Milli-Q® water). The error bars represent the standard deviation of 2 samples, and horizontal black and dashed grey lines represent 0%E after 1 day and 7 days, respectively (for the group of DBPs). The black and grey lines for the haloacetic acids overlap.

according to Equation (4), where $C_{x,y}$ is the concentration of DBP x with chlorine condition y (0 or 10 mg L^{-1}) and $C_{unquenched,x}$ is the concentration of DBP x in the unquenched control, all for a given storage time t.

$$\%E_{x,y,t} = \left| \frac{C_{x,y} - C_{unquenched,x}}{C_{unquenched,x}} \right|_t \times 100\% \qquad (4)$$

Second, statistical inference was made using a two-sample t-test ($\alpha = 0.05$) assuming unequal variances to assess the difference in means between unquenched and quenched samples (for each quenching agent, with or without chlorine), at a given storage time. This analysis was conducted for each DBP using MATLAB®, and the complete results may be found in the Supplementary Material.

To be clear, this work is not an assessment of the stability of the DBPs. Several DBPs are known to be unstable in aqueous solution, susceptible to neutral/base-catalyzed hydrolysis or to chlor(am)ine attack. Rather, this work is an assessment of the effect that each quenching agent has on the measured concentration of the DBP. If a quenched sample has a low %E, it means that the quenching agent had little impact on the measured concentration compared to a sample without a quenching agent.

Ascorbic acid

Ascorbic acid did not considerably affect the majority of organochlorine DBPs tested, and it worked particularly well for the conventional THMs and HAAs. Errors for the THM4 were generally minor (%E = 0.1–5.5% after 1 day, 1.1–13.9% after 7 days) and were comparable to the best results of the other 2 quenchers. There were larger errors for the iodinated THMs. For example, all iodinated THM concentrations were 20–30% smaller than in the control after 7 days when reacting with ascorbic acid alone. Moreover, there was significant evidence to suggest that ascorbic acid affected the concentration of DBIM, which was 26–28% less than in the control after 1 day. However, ascorbic acid still had the lowest overall THM percent error of the 3 quenchers after 1 day of storage (6.1–8.3%) and after 7 days when quenched in the presence of chlorine (5.5%).

Likewise, there were only minor errors for total HAAs when quenched in the presence of chlorine (%E = 2.7–3.1%). Ascorbic acid did, however, lead to the largest overall HAA errors when no chlorine was used (%E = 5.8% after 1 day and 8.3% after 7 days). This was driven by relatively large decreases in BDCAA, DBCAA, and TBAA concentrations (%E = 11.8–38.3%), and decreases in DIAA, BIAA, and CIAA concentrations, which were found to be statistically significant after 7 days of storage (%E = 5.6–9.3). This

suggests that ascorbic acid may be suitable for quenching chlorine prior to HAA analysis when using low quenching agent doses that leave minimal residual ascorbic acid.

Ascorbic acid also worked well for many of the emerging DBPs. The HANs, TCNM, TCAM, and DCAL were all similar in concentration to the controls (regardless of whether chlorine was present). For example, in samples without chlorine, TCNM concentrations were $7.9 \, \mu g \, L^{-1}$ vs. $8.8 \, \mu g \, L^{-1}$ after 1 day and $7.3 \, \mu g \, L^{-1}$ vs. $7.7 \, \mu g \, L^{-1}$ after 7 days in the unquenched vs. ascorbic acid samples.

Ascorbic acid did lead to measurement issues for certain compounds. In particular, the brominated HNM, HAM, and HAL species all had sizable errors. The brominated HNMs were measured at concentrations as much as $+7\times$ higher than in the unquenched controls (Figure S1), DBAM concentrations were 8.9–16.4% lower in samples quenched with ascorbic acid alone, and TBAL concentrations were 10–30% higher in samples with ascorbic acid. These compounds are, however, generally known to be unstable or troublesome to analyze (their analyses giving imprecise results) (Liew *et al.* 2012; Kristiana *et al.* 2014; Ding *et al.* 2018). This is reflected in the current work where, for example, neither the errors for the brominated HAMs nor HALs were found to be statistically significant because of the relatively large standard deviations for those DBP measurements (Table S1). The errors seen in this study may not be due to ascorbic acid, but rather the analytical issues with those particular compounds. Lastly, no chlorite was detected in any sample quenched with ascorbic acid (Figure S2), which agrees with other results (Kristiana *et al.* 2014). Ultimately, ascorbic acid could serve as a common quencher for the organochlorine DBPs analyzed with GC-ECD, but there are select DBPs within that group for which errors would be expected.

Sodium sulfite

Sodium sulfite functioned well for some DBP classes, but adversely affected the measurement of many organic DBPs. Sodium sulfite alone did not have an appreciable effect on HAA concentrations. However, when samples were quenched with sodium sulfite in the presence of chlorine, MCAA, MBAA, BCAA concentrations were all noticeably lower than in the controls after 1 day (%E =

9.1–23%), while DCAA increased from $51 \, \mu g \, L^{-1}$ in the control to $91 \, \mu g \, L^{-1}$ in the quenched sample over the same period. After 7 days, these errors (and those for the rest of HAA9) were similar to those from the other quenching agents, but all 4 iodinated HAAs had decreased relative to the control: by 27 and 72% for CIAA and BIAA, and to non-detect and near non-detect levels for IAA and DIAA. Several other compounds were also completely (or nearly) eliminated in the presence of sodium sulfite. Specifically, TCAN, BCAN, TCNM, DBCNM, and TBAL, in addition to the HAMs, which were reduced to near non-detection levels in samples that had been chlorinated prior to quenching with sodium sulfite.

As mentioned, sodium sulfite did work well for certain classes. Errors for THM4 were minor (%E = 4.2%–9.7%), and errors for most of the iodinated THMs were comparable to those from the other 2 quenching agents (including the decrease observed for DBIM with ascorbic acid). Sodium sulfite did not have a significant effect on any inorganic DBP, and it was the best performing quenching agent for the halofuranone MX, as shown in Figure 3. Therefore, it appears that sodium sulfite can be used for most THMs, the inorganics, and MX.

Ammonium chloride

Ammonium chloride led to increases in concentration of certain traditional DBPs and enhanced the decay of several less-stable compounds. While the HAAs and the majority of
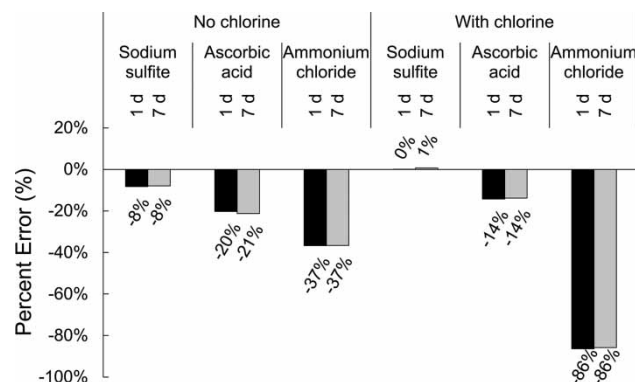
Figure 3 | Effects of the 3 quenching agents on MX concentrations ($C_0 = 40 \, ng \, L^{-1}$) after 1 and 7 days of storage, either without or with chlorine ($10 \, mg \, L^{-1}$) added prior to the quenching agent, relative to a control receiving neither a quencher nor chlorine (conducted in Milli-Q® water).

the THMs had small errors or were similar in concentration to the other quenchers, TCM concentrations were 27–31% higher in samples quenched with ammonium chloride compared to the control after 1 day (35 $\mu g\,L^{-1}$ in the control vs. 44–46 $\mu g/L$ in the ammonium chloride-quenched samples). Since the only organics present in the ultrapure water were the other DBPs, the additional TCM would have formed as the end product of residual chlor(am)ine degrading the other DBPs. Additional work would be needed to identify the specific precursor DBPs, but general information on DBP-DBP transformations has been reported elsewhere (Glezer *et al.* 1999). Given that maximum THM concentrations are regulated in many regions, and that TCM is typically the most abundant THM (Richardson *et al.* 2007), the increases in TCM concentration from ammonium chloride observed here can be problematic.

Ammonium chloride also led to appreciable changes in HAN and HNM concentrations vs. the control (and statistically significant changes for 4 of the 6 HANs and HNMs). DCAN, TCNM, and BCAN all increased when in the presence of ammonium chloride alone, and TCAN, BDCNM, and DBCNM decreased when ammonium chloride was used to quench chlorine. On average, the HAN and HNM percent errors were 175 and 135% in the unquenched samples after 7 days when no chlorine was present and were 24 and 72% when chlorine was present.

In the absence of chlorine, ammonium chloride did not lead to any statistically significant differences for the HAMs or HALs. With chlorine, TCAL and TBAL concentrations were 10–77% smaller than in the unquenched controls, which may be due to instability of these compounds in the presence of residual chlor(am)ine (Liew *et al.* 2012; Gao *et al.* 2020). The initial (spiked) concentration of each HAN, HNM, HAM, and HAL was at least 31-, 7.9-, 25-, and 49-times its detection limit, respectively, so the errors are not expected to be the result of the DBP concentrations being close to the detection limits. Finally, errors for the inorganics were small or comparable to the other quenching agents, and ammonium chloride was the worst performing quenching agent for MX (Figure 3).

Based on its effects on the compounds discussed, ammonium chloride is not suitable as a universal quencher at the low ammonium chloride doses used in this study.

Again, EPA Method 551.1 and *Standard Methods* recommend using large molar excesses of ammonium chloride (APHA 1995; U.S. EPA 1995). If the DBP errors observed with ammonium chloride are the result of the trace amounts of chlorine remaining in solution (due to incomplete quenching by ammonium chloride), and not due to the instability of the DBPs in the presence of ammonium chloride itself, using ammonium chloride at larger doses than those used in this study may improve its suitability.

Matrix effects in untreated river water

The previous analysis in pure water ignores any potential matrix effects from the interaction between the quenching

Table 3 | DBPs analyzed by using GC-ECD for which ascorbic acid may not be suitable

DBP	Explanation
Dibromoiodomethane (DBIM)	Significant errors for ascorbic acid. Ammonium chloride led to the smallest errors.
Bromodichloronitromethane (BDCNM)	Relatively large errors for all quenching agents. No suitable quencher was identified. Ammonium chloride may be effective at higher quenching agent doses.
Dibromochloronitromethane (DBCNM)	Relatively large errors for all quenching agents. No suitable quencher was identified. Ammonium chloride may be effective at higher quenching agent doses.
Dibromoacetamide (DBAM)	Relatively large errors for all quenching agents. Ascorbic acid marginally outperformed the others, but ammonium chloride may be effective at higher quenching agent doses
Tribromoacetaldehyde (TBAL)	Relatively large errors for all quenching agents. No suitable quencher was identified. Ammonium chloride may be effective at higher quenching agent doses.

agent and a typical drinking water sample matrix. To explore these effects, the more widely regulated DBPs, the THMs (THM4 plus the iodinated species), HAA9, and the 3 inorganics, were spiked into river water along with the best quencher according to the pure water results. The concentration of each DBP was analyzed over 7 days, in comparison to a control receiving no quenching agent.

Ascorbic acid was chosen for the THMs and HAAs, and sodium sulfite for chlorite, chlorate, and bromate. All DBPs were unaffected by their chosen quenching agent. None of the quenching agents were found to adversely affect DBP concentrations (Figures S3, S4, S5, and S6). There was minimal interaction between quenching agent and byproduct over the 7 days of storage, nor was there evidence of interactions with products of reactions between quenching agent and (in)organic matter in the water (see Supplementary Material).

CONCLUSIONS

Ascorbic acid had the best overall performance for the organic DBPs analyzed with GC-ECD, acknowledging that there were certain emerging (often brominated) species that showed large errors (relative to the more conventional DBPs) in the presence of ascorbic acid (Table 3). In most cases, none of the quenching agents performed well for those compounds, and the errors may just be related to the inherent instability or analytical challenges of those compounds. Sodium sulfite is recommended for the inorganic DBPs and was the best performing quenching agent for MX.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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