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Factors affecting atrazine concentration and quantitative determination in chlorinated water

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ABSTRACT

Although the herbicide atrazine has been reported to not react measurably with free chlorine during drinking water treatment, this work demonstrates that at contact times consistent with drinking water distribution system residence times, a transformation of atrazine can be observed. Some transformation products detected through the use of high performance liquid chromatography–electrospray mass spectrometry are consistent with the formation of *N*-chloro atrazine. The effects of applied chlorine, pH, and reaction time on the transformation reaction were studied to help understand the practical implications of the transformation on the accurate determination of atrazine in drinking waters. The errors in the determination of atrazine are a function of the type of dechlorinating agent applied during sample preparation and the analytical instrumentation utilized. When a reductive dechlorinating agent, such as sodium sulfite or ascorbic acid is used, the quantification of the atrazine can be inaccurate, ranging from 2-fold at pH 7.5 to 30-fold at pH 6.0. The results suggest HPLC/UV and ammonium chloride quenching may be best for accurate quantification. Hence, the results also appear to have implications for both compliance monitoring and health effects studies that utilize gas chromatography analysis with sodium sulfite or ascorbic acid as the quenching agent.

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1. Introduction

Atrazine is one of the most widely applied herbicides in the United States (US) and worldwide with about 34,000 metric tons used annually in the US alone [1,2]. While atrazine is no longer used in countries in the European Union (EU), related compounds are utilized. Due to concerns about human health effects resulting from exposure to contaminated drinking water, atrazine in drinking water is currently regulated in the US under the Safe Drinking Water Act, as amended, at 3 μg/L [3,4]. The regulation stipulates that monitoring occur at the treatment plant; however, the concentrations of atrazine (and other regulated substances) may change during the time they travel between the treatment plant and the point of use (e.g. the consumers' tap). Reasons for this potential change in concentration include interaction (e.g. adsorption) with distribution system components, reaction with the biofilms present in the distribution systems, and reaction with residual disinfectants.

Previous work has suggested that atrazine will not react measurably with chlorine during water chlorination [5–9] at treatment plants. The chlorine reactivity of atrazine continues to be of interest. For example, recently chlorination of eight selected triazine pesticides, including atrazine, was studied for chlorine contact times consistent with drinking water treatment plants. Only sulfur containing triazines were observed to react to form sulfur oxidation products such as sulfoxides and sulfones [10,11], and no reactivity of atrazine was reported [9]. Another recent study reported the stability of atrazine and its degradation products for various storage conditions [12]. Among these, two sets of storage conditions in chlorinated water were investigated. Under one set of conditions, both the concentrations of atrazine and its degradates decreased significantly after 2 days of storage, with greater loss in concentration up to 14 days. In the other, only the degradates, not atrazine itself, were observed to decrease in concentration over the course of the experiment. The chlorine reaction products were not reported.

The molecular structure of atrazine suggests that it is possible that chlorine could react with the two amine groups of atrazine. The formation of *N*-chloro compounds has been reported with primary amines [13,14], amino acids [15,16], aldicarb [17], and others [18–22]. The reaction mechanism for the formation of *N*-chloro

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compounds has also been studied in great detail [13,18,23–25]. For instance, the overall mechanism for primary and secondary amines is by itself straightforward, with the chlorine atom of the hypochlorous group interacting with the lone electron pair of the amine. An interesting aspect of this reaction is the role of water in assisting the mechanism through hydrogen bonding to the nitrogen [24]. The mechanism for tertiary amine chlorination is more involved, since hydrogen bonding does not occur. These studies suggest that the reaction of atrazine and chlorine is possible and lead to question of why *N*-chlorination of atrazine has not been specifically reported (to the best of our knowledge).

In this regard, *N*-chloro compounds have been reported to be reduced by ascorbic acid or sulfite-based reductant, leading to reformation of the original compound present before chlorination [17,20,26–28]. Building upon this point, it is useful to consider that common analytical methods for the determination of atrazine frequently employ a sulfite-based reducing agent. Five analytical methods are currently EPA approved for atrazine [29,30]. All these methods except Method 551.1 specify reductive dechlorinating agents, although Method 551.1 is more commonly used for the analysis of disinfection byproducts, such as trihalomethanes, than it is for atrazine analysis. Methods 507 and 525.2 are commonly selected for analysis of atrazine because these methods allow for simultaneous determination of many additional herbicides and pesticides.

Thus, if the analogous *N*-chloro atrazine were to form during chlorination of drinking water, it could then be dechlorinated in the presence of the strong reducing agents often used during analysis, leaving the parent atrazine in solution. This would then disguise the original transformation, leading to errors in the analytical determination and subsequent reporting of atrazine concentration. This may explain the previous results regarding water chlorination of atrazine [5–8].

Therefore, the focus of this work is to better understand the largely unreported yet not unexpected behavior of atrazine in the presence of chlorine for conditions that are representative of drinking water distribution systems. Also, the choice of dechlorinating agents and analytical techniques will be evaluated to determine if they can promote or interfere with the accurate determination of atrazine. Implications of these findings regarding the exposure of the public to atrazine and other related compounds will be discussed.

2. Materials and methods

2.1. Reagents

Deionized water from a Milli-Q Millipore (Bedford, MA) water system was used with monobasic (ACS grade, GFS Chemicals, Columbus, OH) and dibasic phosphate reagents (ACS grade, Fisher Scientific, Fair Lawn, NJ) to produce the buffer solutions from pH 5.5 to 7.5. Boric acid (ACS, Fisher Scientific, Fair Lawn, NJ) solutions adjusted with sodium hydroxide in Milli-Q water provided the buffers for the pH 8.5 and 9.5 studies. Chlorinated tap water, derived from a surface water source, was collected from a laboratory tap flushed without aeration for several minutes.

A stock solution prepared with crystalline atrazine (98% pure, Supelco, Bellefonte, PA) was made to 1000 ppm in methanol (Optima, Fisher Scientific, Fair Lawn, NJ) for use in all the experiments. A similar approach was utilized to prepare a stock solution of desethyl atrazine (ChemService, West Chester, PA). A 4% chlorine solution of sodium hypochlorite (Sigma–Aldrich, Milwaukee, WI) was used for chlorine dosing. Three different chlorine-quenching solutions in 10-fold molar excess to the dosed chlorine concentration were prepared using powdered ammonium chloride (USP/FCC, Fisher Scientific, Fair Lawn, NJ), powdered sodium sulfite (ACS, Fisher Scientific, Fair Lawn, NJ), and powdered L-ascorbic acid (ACS, Sigma–Aldrich, St. Louis, MO) were mixed with Milli-Q water to 500 ppm.

2.2. Experimental procedure

Appropriate amounts of methanolic atrazine stock solution were dispensed into a clean, dry Erlenmeyer flask to achieve the target concentrations, and the methanol was allowed to completely evaporate, leaving a specific mass of solid atrazine inside the flask. Buffer solutions at the desired pH were added to the Erlenmeyer flask, and mixed thoroughly with a stir bar, usually overnight to dissolve the atrazine deposit. The resulting solution was then divided into 125 mL brown amber glass bottles. Half of the bottles containing the atrazine sample were dosed with chlorine to the desired concentration, and the other half were not dosed so that they could act as controls for atrazine loss (e.g. via adsorption or hydrolysis). In addition, blank control solutions were prepared by dosing atrazine-free buffer with chlorine. The bottles were stored at room temperature. Duplicate bottles from each type of the sample, atrazine control, and blank control were analyzed at the desired time-steps, which ranged from 1 h to 28 days. Free and total chlorine readings from the sample and the blank control were taken immediately after opening the bottles via the *N*,*N*-diethyl-1,4 phenylenediamine sulfate (DPD) method using AccuVac vials (Hach, Loveland, CO).

2.3. Instrumental analysis

For GC/MS analysis, a 20 mL aliquot of the sample was added to a 40 mL disposable glass vial to which 3 g of sodium chloride had been added. Ten-fold stoichiometric excess of either sodium sulfite, ascorbic acid, or ammonium chloride quenching agent was then added. One milliliter of solution was transferred to HPLC autosampler vials, and the remainder was extracted with 3 mL of methyl *t*-butyl ether (99+%, PRA grade, Aldrich Chemical Co. Inc., Milwaukee, WI) spiked with 1,2,3-trichloropropane (99+%, Acros Organics, NJ) as an internal standard for GC/MS analysis. One microliter of each extract was injected into a Varian Star 3400 CX gas chromatograph equipped with a Varian Saturn 2000 mass spectrometer and a Varian 8200 CX Auto sampler (Palo Alto, CA). An Equity DB5, 0.32 mm ID, 30 m column was used for all analyses. The 15.25 min temperature ramp program utilized a 270 °C injector temperature, a 2 min hold time at 45 °C, a ramp at 20 °C/min to a final temperature at 230 °C, and a 4 min hold time at 230 °C. Ultra high purity helium was used as the carrier gas.

An Agilent 1100 HPLC/UV (Palo Alto, CA) system with an auto sampler was utilized for aqueous samples. The photodiode array detector was scanned across its entire range. It was equipped with an Agilent ZORBAX Eclipse XDB-C18 (Palo Alto, CA), 3.0 mm × 250 mm, 5 μm column. Isocratic elution used a mixture of 60% HPLC grade acetonitrile (Fisher Scientific, Fair Lawn, NJ) with 40% 10 mM, filtered, ammonium acetate (HPLC grade, Fisher Scientific, Fair Lawn, NJ) mixture at a flow rate of 0.5 mL/min with a 20 min run time. Injection volume was held constant at 10 μL. For mass spectrometric detection (HPLC/MS), a Finnigan MAT TSQ-700 (San Jose, CA) equipped with a standard Finnigan electrospray interface was used. Similar chromatographic conditions to the Agilent HPLC/UV instrument were used, and manual injections were made with a Rheodyne (Rohnert Park, CA) model 7725 injector into a Waters 600 (Milford, MA) HPLC. Mass spectra were acquired by scanning Q3 over appropriate mass ranges in positive ion mode.

3. Results and discussion

3.1. Transformation of atrazine by free chlorine

Fig. 1 illustrates the transformation of atrazine in the presence of free chlorine. The upper chromatogram is from an atrazine solution that reacted with chlorine for 1 h, and the middle chromatogram is from an atrazine solution that reacted with chlorine for 7 days. No quenching agent was used on either sample. The peak area of the atrazine after 7 days was not quantifiable within experimental error, but may be estimated to be less than 99% of the peak area from the 1 h reaction. In addition, two small peaks are observed in the chromatogram of the 7-day reaction sample at a column retention time of around 22 and 23 min, respectively. This sample was further analyzed by HPLC–ESI-MS to characterize the compounds corresponding to these later peaks. As shown in Fig. 1, ions were observed for these peaks with m/z ratios consistent with *N*-chloro compounds, possibly formed via chlorine's reaction with the two amine groups of atrazine, as discussed in detail in the introduction. The HPLC–ESI-MS identification is considered tentative because no independent standard of the compound is available. Indeed, the synthesis of *N*-chloro compounds typically involves aqueous chlorination of the parent amine, which is the same process occurring in drinking water treatment with chlorine. This dilemma in standard preparation has resulted in the identities of *N*-chloro compounds being tentatively reported but supported by supplemental information. Such supplemental information has included liquid chromatography retention times consistent with the parent compound and also that, in all tested cases, *N*-chloramine reverse phase retention was reported to be greater than the parent amine [20]. Other supplemental information includes mass spectral data consistent with proposed structures [18,23], and selective reactivity of *N*-chloro compounds with reducing agents [17,27,28,31]. Of particular relevance here is that the identity of *N*-chloro alicarb was confirmed via observation of its reaction with sulfite to form aldicarb, combined with liquid chromatography/mass spectrometry data [17].

Thus, to support the tentative identification of *N*-chloro atrazine compounds in Fig. 1, sulfite reducing agent was added to the solution containing the tentatively identified *N*-chloro compounds, which resulted in a chromatogram containing a single peak with the same retention time and the same area as the original atrazine solution. This is particularly meaningful because the sum of the peak areas of the two small peaks is different than the peak area of the original atrazine (Fig. 1). There are several possibilities for this. One is that the molar extinction coefficient(s) of the *N*-chloro compound(s) are smaller than atrazine. Chlorine degradation of the triazine ring could reduce its ability to act as a chromophore; however, typically a more powerful oxidant such as ozone is required to degrade the triazine ring [6,32,33]. Alternatively, the chlorination reaction may produce multiple products, possibly *N*-chloro compounds other than the two depicted in Fig. 1 that cannot be resolved under the liquid chromatographic conditions utilized. This is not unexpected since some *N*-chloro compounds have presented chromatography challenges [34], especially if multiple chlorine atoms are present. In any case, the area of the peak observed after addition of the reducing agent was the same within experimental error as the original peak area, suggesting quantitative regeneration of the original atrazine (Table 1).

3.2. Effects of dechlorinating agents on the quantitative determination of atrazine

As mentioned above, *N*-chloro compounds have been shown to be dechlorinated by the common reducing agent sulfite [20].

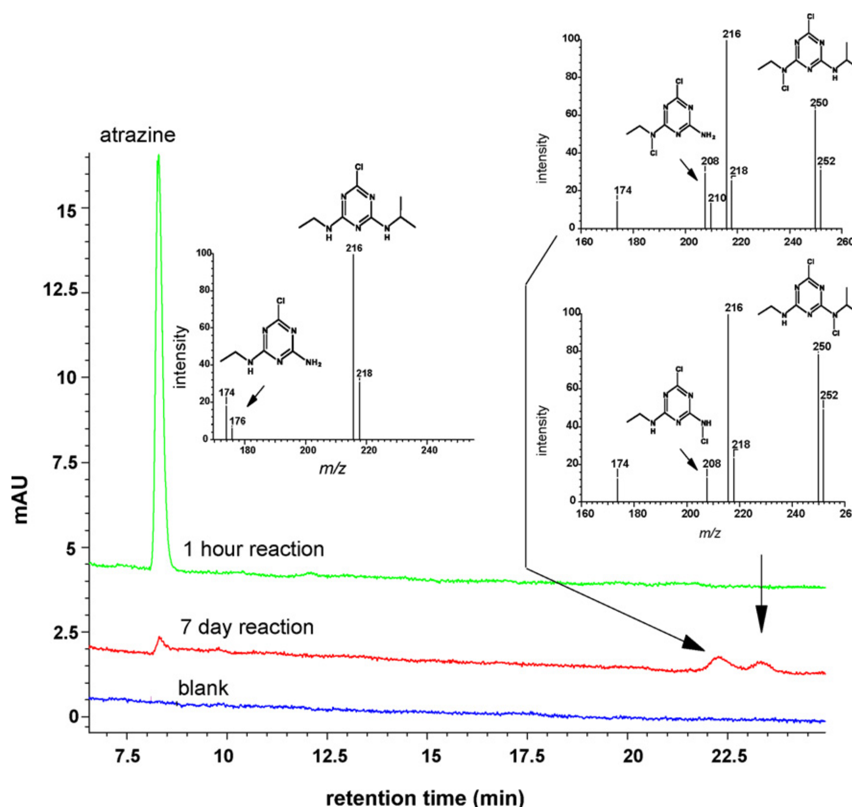

Fig. 1. HPLC/UV chromatograms of a 1 ppm atrazine solution reacted at pH 5.5 for the amount of time indicated. The chromatograms are graphically offset for illustrative purposes; the initial baseline magnitude for all samples were similar. The ESI-MS spectra are shown as insets, along with proposed structures of the non-protonated forms. Due to the low concentrations of reaction products between 22 and 23 min, the isotopic peaks at m/z 176 and 210 were below the set noise threshold.

Table 1
Effect of dechlorinating agent. Analysis was performed by HPLC/UV. 1 ppm atrazine and 3.3 ppm sodium hypochlorite were allowed to react at pH 5.5 for the times indicated. The error is reported as $x \pm \sigma_{n-1}$, with $n = 3$.

Dechlorinating agent	Atrazine concentration (ppm) determined after 1 h reaction (mg/L)	Atrazine concentration (ppm) determined after 7-day reaction (mg/L)
None	0.91 ± 0.05	Not quantifiable
Ammonium chloride	0.92 ± 0.01	Not quantifiable
Sodium sulfite	0.95 ± 0.01	0.94 ± 0.01
Ascorbic acid	0.92 ± 0.02	0.86 ± 0.01

Dechlorinating agents are added to water samples to halt chlorine reactions during kinetic studies, and they also prevent analytical difficulties such as contact of free chlorine with analytical columns, which can shorten column life and result in other analytical problems. There are two main types of dechlorinating agents used in analytical methods for water analysis. One type uses compounds that reduce chlorine, such as sodium sulfite, sodium thiosulfate, and ascorbic acid. The other type of dechlorinating agent, such as ammonium chloride, acts by combining with the chlorine, preventing its further reaction.

Table 1 shows the differences in the determined atrazine concentrations as a function of dechlorination agent for atrazine samples exposed to chlorine for 1 h and 7 days. As can be seen, the use of different dechlorination agents affected the quantitative analytical result of aqueous atrazine samples exposed to free chlorine. After reacting for 1 h, regardless of dechlorinating agent, the determined concentrations were generally similar to each other and to the initial atrazine concentration, within experimental error at the 95% confidence level. This is similar to previous reports that atrazine and other triazine compounds are unaffected by reaction with chlorine on an actual drinking water treatment plant's residence time scale [5–8]. However, after 7 days of reaction, the potential residence time within some distribution systems, the concentration of atrazine for samples unquenched and quenched with ammonium chloride was not quantifiable within experimental error, whereas the atrazine concentration for those samples quenched with sodium sulfite or ascorbic acid were more similar to the initial concentration. These results suggest that atrazine can be significantly transformed by the presence of a chlorine residual, and that sodium sulfite and ascorbic acid at typical quenching doses can quantitatively convert the transformation products back to the parent atrazine, presumably by chemical reduction. This may help explain the observation in a recent work in which atrazine was reported to not react with chlorine; sodium sulfite was utilized [9].

Although these reactions were conducted at a pH of 5.5, which is not typically seen in drinking water systems, they are presented here for illustrative purposes. Additional work at more representative pH values are presented below with a discussion on the potential implications regarding estimates of exposures of pesticides and their chlorinated transformation products/degradates.

3.3. *Effects of the instrumental technique on quantitative determination of atrazine*

Both GC/MS and HPLC/UV were used to analyze the same reaction mixture after quenching. GC/MS was initially investigated as a means to reach lower quantification levels. Notable differences were observed between GC and LC chromatograms with regard to the quantification of atrazine. Importantly, in the LC chromatogram (Fig. 1), the area of the atrazine peak decreases, corresponding to essentially complete disappearance of atrazine from solution after a chlorine reaction time of 7 days. By contrast, the GC/MS chromatogram in Fig. 2 shows that the sample chlorinated for 7 days still had an instrumental response about half that of the non-chlorinated sample. This suggests that some reaction between chlorine and atrazine had occurred, but additional details of the reaction are unclear from the GC/MS data. One clue is that the chlorinated sample also produced a long tailing feature between 11.5 and 12.5 min. This suggests a number of possibilities. First, the transformation products may not be gas chromatographically resolved from the atrazine. Another possibility is that the transformation products are thermally unstable and degraded by the heat of the GC injector, reforming atrazine in the injector port. Given the instability of the transformation products to reduction, as shown in Table 1, it is conceivable that they are also thermally labile, especially if they are *N*-chloro compounds as discussed above, perhaps due to weaker bonding, similar to that reported for some *N*-chloro bonds [35,36]. Both of these possibilities are related to the GC separation, so regardless of the physical cause, the end result is that poor quantification may occur if GC is utilized under these conditions, especially if a reducing agent is used to quench the reaction prior to analysis. Accordingly, these results may also apply to the approved EPA methods for determination of atrazine, which all rely on GC separation [29,30].

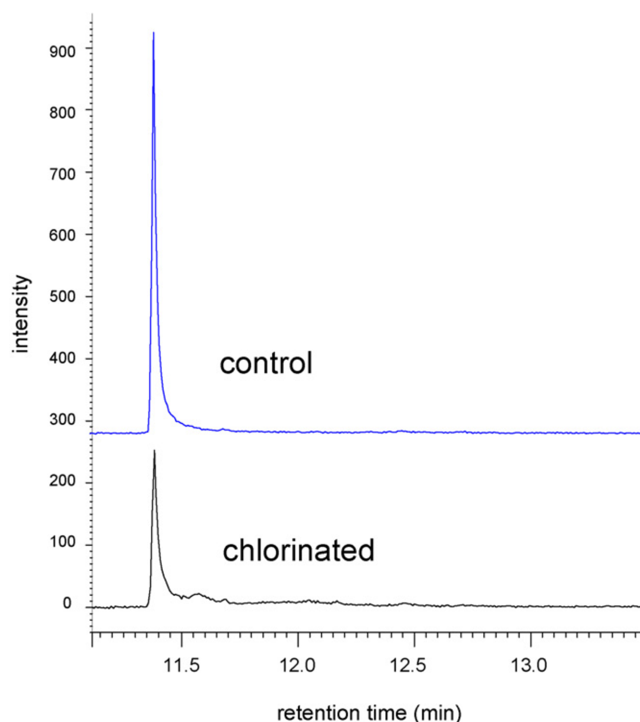

Fig. 2. GC/MS chromatograms of a 1 ppm atrazine solution reacted at pH 5.5 for 7 days. The chlorinated sample was unquenched. The two chromatograms are offset for graphical purposes. The original baseline values were similar, but the relative vertical scales are the same. The mass spectrum (not shown) corresponding to the sharper peak at 11.4 min (in both the control and chlorinated cases) and the broader peak at 11.6 min (in the chlorinated case) both resemble that of atrazine and are otherwise unremarkable.

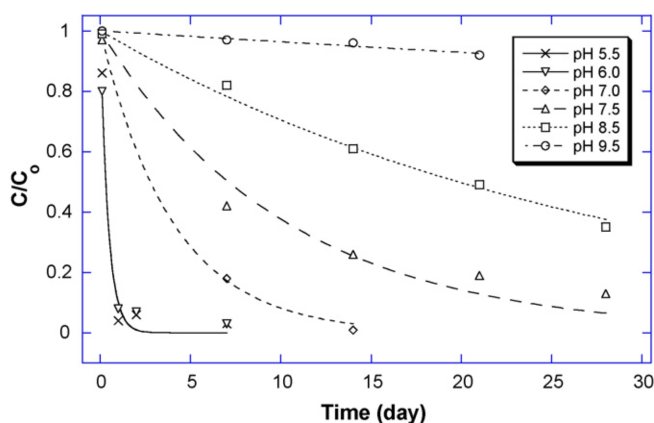

Fig. 3. Plot of change in concentration versus time as a function of pH. The curves are the best fit of the data to first order loss of atrazine. Note that the best fit curves for pH 5.5 and 6 overlap. The initial atrazine concentration (C_0) was 1 mg/L, with an initial 10-fold molar excess of chlorine. The chlorine residual was quenched with ammonium chloride in 10-fold molar excess to the chlorine. 0.1 M phosphate or borate buffer was utilized, as appropriate for pH.

3.4. Exploration of reaction kinetics at various experimental conditions

To relate the findings presented above to the determination of atrazine under more common drinking water conditions, the kinetics of the atrazine transformation were explored through observing the loss of atrazine upon reaction with chlorine at several pHs ranging from pH 5.5 to 9.5, reaction times up to 28 days, and various chlorine and atrazine concentrations. These conditions are reasonable given that the secondary MCL for drinking water specifies that the pH should be in the range of the 6.5–8.5 [4]. While 28 days is an extreme residence time, it is conservative in that it covers the range of water ages in distribution systems. Also, lower chlorine and atrazine concentrations than those in the work discussed above were employed in order to be more representative of actual drinking water systems.

Experiments varying initial chlorine from 0.2 to 4 mg/L, and atrazine concentrations from 10 to 1000 μg/L, were conducted with HPLC/UV detection to determine reaction order by method of initial rates. The reaction order was calculated as 1.1 ± 0.1 for chlorine and 1.02 ± 0.06 for atrazine, respectively. The overall reaction order was determined to be 2.1 ± 0.1. Note that these reaction order results, corresponding to the reaction being first order with respect to both reactants and second order overall, are consistent with previous research on the formation of an *N*-chloro compound [19].

Fig. 3 plots the decrease in measured atrazine concentration as a function of time. As the initial chlorine was present in 10-fold molar excess over the initial atrazine, the observed decreases in atrazine were curve fit to a first order reaction kinetic model, and the results are presented in Table 2. The value of the half-life calculated under these experimental conditions is influenced by a number of experimental errors, as well as uncertainties in the mechanism of the reaction. Thus, the values in Table 2 should be viewed as approximations. One observation from Table 2 is that the half-life decreases with decreasing pH, which is consistent with HOCl being the chief reactive chlorine species, since p*K*a of HOCl is about 7.5 [19]. Further analysis of this trend, along with additional, targeted experiments may help better elucidate the precise reaction mechanism of the atrazine transformation, which is beyond the scope of this paper. This is the expected behavior if HOCl is considered to be the reactive species in many chlorination reactions, including the formation of chloramines [19].

The results above show that the reaction of chlorine with atrazine is a minor issue at a high pH (9.5), while at a lower pH (5.5) it is much faster, with atrazine reacting completely within experimental error. The results at intermediate pH values suggest that atrazine reactivity, although not complete, could substantially influence attempts to estimate the health risk associated with atrazine present in chlorinated distribution system waters. Namely, the health effects trade-off would have to be determined between atrazine and its *N*-chloro byproduct. The data presented here are a brief kinetic analysis for a range of reaction conditions of interest to drinking water. A more exhaustive kinetic analysis could be performed to elucidate more details about the atrazine transformation kinetics and mechanism. Likewise, it would be possible to perform more detailed studies to provide additional support to the tentative identification of the reaction products. However, the results are sufficient to discuss the practical implications of the interrelated roles of dechlorinating agent, instrumental technique, and reaction kinetics during analysis of drinking water for atrazine.

3.5. Implications for determining atrazine in drinking water

Table 3 shows, as a function of pH, the ratio of the concentration of atrazine determined when sodium sulfite is used as a quenching agent to the concentration of atrazine determined when ammonium chloride is used for the same purpose. Thus, the values in Table 3 can be thought of as representing the factor by which atrazine determination may be misreported if sodium sulfite, instead of ammonium chloride, is used to quench a 7-day reaction between chlorine and atrazine. In general, this factor becomes greater with decreasing pH. At pHs of 5.5 and 6.0, the factor between quenching agents is nearly 30-fold, whereas at pHs of 7.0 and 7.5, it is approximately 2-fold. Above pH 7.5, the factor drops to being indistinguishable from experimental difference.

Although almost no distribution system would see water with a pH of 6.0 or below, results presented in Tables 2 and 3 imply that, at a more reasonable pH of between 6.0 and 7.5, analytical methods that utilize sodium sulfite and ascorbic acid may result in atrazine determinations that do not accurately reflect the actual concentration of atrazine in the water. For example, suppose that a method utilizing sodium sulfite was used to determine an atrazine

Table 2
Half-lives of observed atrazine loss in the presence of excess chlorine at several pHs, calculated for the data shown in Fig. 3. The uncertainty listed for the half-life and value for R^2 is based on the standard error in the curve fit in Fig. 3.

pH	Half-life (days)	R^2
5.5	0.30 ± 0.07	0.977
6.0	0.30 ± 0.04	0.988
7.0	2.8 ± 0.1	0.999
7.5	7.1 ± 0.1	0.966
8.5	20 ± 1	0.997
9.5	190 ± 10	0.952

Table 3
Ratio of concentration of atrazine determined following quenching with sodium sulfite ($C_{\text{sodium sulfite}}$) to concentration determined following quenching with ammonium chloride ($C_{\text{ammonium chloride}}$). The reaction time was 7 days for a 1 mg/L solution of atrazine dosed with a 10-fold molar excess of chlorine. The propagated error is reported as $x \pm \sigma_{n-1}$, with $n = 3$.

pH	$C_{\text{sodium sulfite}}/C_{\text{ammonium chloride}}$
5.5	27 ± 7
6.0	32 ± 6
7.0	4.5 ± 0.4
7.5	1.8 ± 0.1
8.5	0.99 ± 0.03
9.5	0.98 ± 0.02

value of 5.0 ppb in the distribution system. This value is clearly over the regulatory limit of 3.0 ppb. However, Table 3 suggests, if ammonium chloride were used for dechlorination, the actual concentration could be within compliance limits (under 3 ppb), albeit there would be a sizable, unreported, *N*-chloro atrazine byproduct present that could be a health concern unto itself. Thus, Table 3 suggests that using sodium sulfite instead of ammonium chloride during analysis would lead a consumer or exposure researcher to think that the true atrazine concentration was above the regulatory limit. Although the current method with a sulfite quenching agent is conservative, no knowledge of the chlorination products of atrazine or their concentrations would be obtained if sulfite was used.

Accordingly, in order to better characterize both the concentration of atrazine and its transformation products, it may be prudent in studies that investigate atrazine exposure to utilize ammonium chloride as the quenching agent in conjunction with HPLC quantification in order to accurately quantify the parent atrazine. It may also be desirable to split the sample and dechlorinate one part with sodium sulfite and the other with ammonium chloride. The ammonium chloride sample would yield the true atrazine concentration, while the difference between the two would yield the total amount of atrazine oxidized by chlorine, or at least the amount of atrazine transformed into byproducts that are reduced back to atrazine by the presence of sodium sulfite. The ultimate success of this suggestion depends on the mechanism of atrazine transformation in the particular water, which requires additional study to elucidate if the transformation and reformation of the parent atrazine occurs quantitatively and reproducibly. For studies at water treatment plants, determining atrazine with ammonium chloride quenching before and after chlorine is applied could reveal similar information, assuming that the atrazine concentration in the influent was stable and that the atrazine was not lost by other mechanisms such as adsorption, complexation, and so forth. At the very least, a paired pre- and post-chlorination sample could add additional information that may be useful in understanding the fate of atrazine.

It should be mentioned again that the conditions of greater atrazine transformation, namely pHs ≤ 7.5 and longer residence times, may not occur for all drinking water distribution systems. However, straightforward considerations indicate that some source waters contaminated with atrazine may be impacted, especially for those treatment plants which perform chlorination at lower pH. (These plants prefer this because the microbial efficiency of chlorine disinfection is thought to be greater for the HOCl form of chlorine present at low pHs [19]. The plant then raises the pH for corrosion control prior to distribution.) One resource for estimating the number of systems that may be affected is EPA's Information Collection Rule (ICR) database [37]. The ICR database includes water quality results, including pH, from public water systems each serving at least 100,000 people. Of 974 possible entries for pH values at average distribution residency times for surface water systems that utilize with chlorine, there are 396 entries with pH ≤ 7.5. Of these, the average system residency time is 2.7 days with an average maximum residency time of 5.5 days. The ICR database does not include the population served as a function of residency time, although it should be noted that the population served by the utilities in the categories above represents tens of millions of customers. More importantly, it should be pointed out that the practices of these large utilities probably are more prevalent in the many more numerous smaller utilities that were not included in the ICR. In fact, these smaller utilities often have fewer resources, so may be less likely to adjust the pH of their water. Thus, it is conceivable that an appreciable amount of atrazine transformation occurs, resulting in a misreporting of distributed atrazine levels for a large number of consumers. This situation might be especially pronounced for locations where higher atrazine concentrations are present in the source water, and a recent report indicates concentrations as high as 86 μg/L produced after run-off producing rainfall [31]. Consequently, the potential exists for unnecessary treatment steps being required to remove parent atrazine to below regulated levels.

Drinking water systems that do meet the conditions conducive to atrazine transformation, or have portions of their distribution systems in which longer residence times are common, may wish to consider the data presented above and perform additional experiments. Note that the data presented here may not be comprehensive for the many similar types of conditions affecting atrazine determination/transformation. Therefore, for any particular water, it would be worthwhile to investigate if atrazine analysis is affected in the manner described above. Namely, other substances found in a particular drinking water sample, i.e. the drinking water matrix, might influence the reaction. As a preliminary investigation, local chlorinated tap water derived from a surface water source was fortified with atrazine at pH 7.5. Compared to a similar solution prepared from deionized water, the transformation of atrazine observed was not distinguishable from experimental error.

3.6. Additional implications for exposure to atrazine and related compounds

The data presented above suggest that previous studies may have overlooked the chlorination transformation of atrazine, either as a result of the instrumental technique utilized or the choice of dechlorinating agent [5–8]. This, in turn, may have regulatory implications with regard to human exposure as described in the Food Quality Protection Act (FQPA) and in compliance monitoring as mentioned in the Safe Drinking Water Act (SDWA). With regard to SDWA, the regulated compound is atrazine. The FQPA requires that public exposure to pesticides be considered from all sources, so exposure to pesticide transformation products could be considered by the FQPA. Thus, the effects on human health to potential exposure to atrazine chlorine transformation products, not just the parent atrazine, in drinking water may be important. Specifically, human exposure estimates to atrazine may be affected by errors in atrazine determination, if the *N*-chloro compounds are not considered.

With regards to the potential health effects, it should be noted that several, but not all, triazine compounds are considered to have a "common mechanism of toxicity" since they act the same way in the body–that is, the same toxic effect occurs in the same organ or tissue by essentially the same sequence of major biochemical events [38]. Thus, a detailed study may be required to determine if atrazine chlorination products share a common mechanism of toxicity with atrazine. In this regard, it should be noted that the triazine compounds that are considered to have a "common mechanism of toxicity" are all s-chlorotriazines, whereas other triazine compounds do not share the toxicity profile of the former group [38]. The *N*-chloro atrazine inherently retains the s-chlorotriazine group, so it may too have a common mechanism of toxicity as atrazine.

Atrazine is one of several triazine compounds in use today, and triazine compounds are metabolized by microorganisms in the environment. These triazine compounds and metabolic products may react similarly with chlorine, resulting in potential difficulties in their determination as well. Examination of the structures of these compounds suggest that, if *N*-chloro compounds are formed, the mechanism of formation of these *N*-chloro compounds might be less hindered, possibly resulting in a higher kinetic transformation rate than showed herein, and potentially increasing the number of drinking water systems in which the analytically confounding conditions discussed above may be applicable. Indeed, preliminary experiments similar to those described above indicate that the half-life for the reaction of desethyl atrazine with chlorine is 1.2 ± 0.1 days at pH 7.5. This is about a 6-fold decrease in half-life

as compared to atrazine (Table 2). It is worthwhile to note the data presented in a study of atrazine and its degradates during storage in the presence of chlorine [12]. Namely, it could be inferred that the reaction of desethyl atrazine with chlorine is between two and four times more rapid than for atrazine, depending on the water conditions. The similarity in reaction rate trends is consistent with the observations in this manuscript, which show the water conditions significantly influence the reaction rate.

Finally, these results may also be applicable to the analytical determination of other compounds that may potentially form *N*-chloro compounds, in addition to the triazine compounds discussed above. These types of compounds are not only of interest for the Safe Drinking Water Act and the Food Quality Protection Act, but can also be of importance in the event of the intentional contamination of water. Indeed, studies have been reported which may reflect the interaction of compounds such as nicotine and glyphosate with chlorine in drinking water [21,22,39]. In addition, the formation and subsequent discharge into the environment of stable chloramines may also be important following chlorination of wastewater [20,40,41].

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