Journal of Chromatography A, 1217 (2010) 676–682

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Factors affecting atrazine concentration and quantitative determination in chlorinated water

Karen A. Wulfeck-Kleier[a], Michael D. Ybarra[a], Thomas F. Speth[a], Matthew L. Magnuson[b,*]

[a] National Risk Management Research Laboratory/Water Supply and Water Resources Division, US Environmental Protection Agency, 26 West Martin Luther King Drive, Cincinnati, OH 45268, USA
[b] National Homeland Security Research Center/Water Infrastructure Protection Division, US Environmental Protection Agency, 26 West Martin Luther King Drive, Cincinnati, OH 45268, USA

ARTICLE INFO

Article history:
Received 26 October 2009
Received in revised form
30 November 2009
Accepted 1 December 2009
Available online 5 December 2009

Keywords:
Triazine
Atrazine
Quantitative analysis
Chloramine
Drinking water
Chlorine

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.

Published by Elsevier B.V.

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

* Corresponding author. Tel.: +1 513 569 7321; fax: +1 513 487 2559.
E-mail address: magnuson.matthew@epa.gov (M.L. Magnuson).

0021-9673/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.chroma.2009.12.012

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.