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# Oxidation of cyanobacterial neurotoxin beta-N-methylamino-L-alanine (BMAA) with chlorine, permanganate, ozone, hydrogen peroxide and hydroxyl radical

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ABSTRACT

Beta-N-methylamino-L-alanine (BMAA), a new cyanobacterial neurotoxin produced by more than 20 genera of cyanobacteria, has been associated with amyotrophic lateral sclerosis/parkinsonism–dementia complex (ALS/PDC) or Alzheimer's disease. Although BMAA has been shown to be removed in drinking water treatment plants (DWTPs), studies regarding the reactions between BMAA and the commonly used oxidants in DWTPs are limited to chlorine under specific conditions. In this study, the reaction kinetics between BMAA and five oxidants commonly used in DWTPs, including chlorine, potassium permanganate, ozone, hydrogen peroxide and hydroxyl radical were investigated. The oxidation of BMAA by chlorine, ozone or OH radical followed the second order reaction rate law, and the reaction rate was in the order of OH radicals > ozone >> chlorine. The rate constants increased by 20 times from $2 \times 10^3\ M^{-1}s^{-1}$ at pH 5.8 to $4.93 \times 10^4\ M^{-1}s^{-1}$ at pH 7, and kept in a relatively stable level at pH 7–9.5; rate constants of OH radicals were $1.11 \times 10^8\ M^{-1}s^{-1}$ at pH 6.5 and $5.51 \times 10^9$- $1.35 \times 10^{10}\ M^{-1}s^{-1}$ at pH > 6.5. For both permanganate and $H_2O_2$ only, the removal of BMAA was negligible. The pH dependency of chlorine and the OH radical may be attributed to the neutral form of BMAA with free lone pair electrons readily to be attacked by oxidants. However, for ozonation of BMAA, the rate constants were $1.88 \times 10^6$–$3.72 \times 10^{10}\ M^{-1}s^{-1}$, with a linear dependency on pH, implying that the hydroxide concentration governs the reaction. In addition, the rate of BMAA degradation was found to be slower in natural water if compared with that in deionized water.



## 1. Introduction

The blooming of cyanobacteria has become a global phenomenon in recent years because of eutrophication of many lakes and reservoirs. Since many cyanobacteria are producers of cyanotoxins and taste and odor (T&O) compounds, excess growth of cyanobacteria may deteriorate the water quality of water resources, posing risk to public health and endangering public perceptions of drinking water. Therefore, removal of cyanotoxins, such as microcystins, cylindrospermopsin, saxitoxin, and anatoxins, and T&O compounds, such as geosmin and 2-methylisoborneol, in drinking water treatment processes has been well documented (Lin et al., 2009; Rodríguez et al., 2007b; Zamyadi et al., 2013).

Recently, a novel neurotoxin, *β-N*-methylamino-*L*-alanine (BMAA) (Cox et al., 2005), produced by many genera of cyanobacteria, has received high attention because of its association with amyotrophic lateral sclerosis/parkinsonism–dementia complex (ALS/PDC) or Alzheimer's disease (Bradley et al., 2013; Murch et al., 2004; Pablo et al., 2009). In addition, the cyanotoxin has been proved to be neurotoxic to chicks, rats, and monkeys (Bell, 2009), and may be incorporated into the brain, where it recycles, causing slow neurodegeneration (Murch et al., 2004; Rao et al., 2006). BMAA has been detected in many water resources, including Lake Winnipeg, Manitoba, Canada (Bishop et al., 2018), 6 of the 12 studied reservoirs in Nebraska, USA (Al-Sammak et al., 2014), and 1 of the 3 studied water sources in South Africa (Esterhuizen-Londt and Downing, 2011). Considering the occurrence in water resources and toxicity to human health, understanding the removal of BMAA in water treatment processes is thus needed for better management of cyanotoxin-relevant drinking water quality.

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Although conventional water treatment processes, including sedimentation, flotation, and filtration, can remove cyanobacterial cells and intra-cellular cyanotoxins from water, the processes cannot effectively remove dissolved contaminants (Newcombe and Nicholson, 2004; Pietsch et al., 2002). Chemical oxidation processes, however, have been applied in water treatment for the removal of extracellular cyanotoxins. Westrick et al. reviewed and summarized the effectiveness and application of six oxidants, including chlorine, chloramine, chlorine dioxide, permanganate, ozone, and hydroxyl radial (·OH), for the destruction of four conventional cyanotoxins, including microcystin, anatoxin-a, cylindrospermopsin, and saxitoxin (Westrick et al., 2010). Among these oxidants, chlorine is the most commonly used oxidant in drinking water systems, for which the reactions between chlorine and conventional cyanotoxins have been extensively documented (Acero et al., 2005; Rodríguez et al., 2007b, 2008). Chlorine may react with organic compounds on the moieties of activated aromatic and neutral amine groups (Rodríguez et al., 2007b). Potassium permanganate ($KMnO_4$), ozone, and hydroxyl radicals are three other oxidants commonly used in drinking water treatment. The reactions between permanganate and organic compounds are known to include electron exchange, hydrogen abstraction, and oxygen donation (Rodríguez et al., 2007a), while the reactions with ozone may involve attacks on alkene groups as well as activated aromatic and neutral amine groups (Von Gunten, 2003; Westrick et al., 2010). In the case of hydroxyl radicals, the reactions with organic compounds involve random attacks on carbon-hydrogen bonds (Westrick et al., 2010). Since BMAA is considered to be a new cyanotoxin, unlike conventional cyanotoxins, reactions between BMAA and the oxidants used in water treatment processes have been rarely studied, with only one study focusing on reactions with chlorine (Chen et al., 2017).

Chen et al. (2017) studied the reaction mechanisms/kinetics and formation of intermediates between BMAA and chlorine. In their report, four chlorinated intermediates, each with one or two chlorines, were identified, where the intermediates were possibly converted back to BMAA under a reducing condition (Chen et al., 2017). The reaction pathway of BMAA and chlorine has been shown to occur in three steps, where it was studied for the reaction kinetics at pH 5.5 and 7.0 in deionized water (Chen et al., 2017), with the scheme being shown in SI Scheme S1. The three reaction steps include reaction of BMAA and free chlorine to form chlorinated BMAA, autodecomposition of chlorinated BMAA, and the reaction of chlorinated BMAA with free chlorine.

In Chen et al. (2017), the reactions between chlorine and BMAA were only studied in deionized water under acidic and neutral conditions. However, in natural waters, particularly in those with high algae/cyanobacteria concentrations, the pH value is usually higher than 8.0 (Xie et al., 2003). Since the dominant species of chlorine at pH < 8.0 is HOCl, whereas $OCl^-$ dominates at pH 8.0–10.0 (Aieta et al., 1984), it is necessary to study the reaction between BMAA and chlorine at pH values higher than 8.0. In addition, natural water contains natural organic matter (NOM) and ions (Boyle et al., 1977; Sholkovitz, 1976), so it is also necessary to understand the impact of the water matrix on the BMAA and chlorine reaction in natural water.

In light of the shortage of current literature on BMAA removal, the aims of this study are (1) to examine the reaction kinetics during BMAA chlorination processes in natural water and under alkaline conditions, (2) to understand the removal of BMAA by different oxidants, including $KMnO_4$, ozone, $H_2O_2$ and hydroxyl radical, and (3) to elucidate the effect of pH and water matrix on the reactions between these oxidants and BMAA.

## 2. Materials and methods

### 2.1. BMAA analyses

The quantification of BMAA was performed using a liquid chromatograph (UltiMate 3000 HPLC, Thermo Scientific, USA), coupled to a tandem mass spectrometer (MS/MS) (TSQ Quantum Ultra, Thermo Scientific, USA). A HILIC column (2.7 μm, 4.6 mm × 150 mm I.D., Capcell Core PC, Shisido, Japan) was used in this analysis for which the flow rate was set at 0.25 mL-min$^{-1}$. The gradient came with mobile phase A (0.1% formic acid) 15% and mobile phase B (ACN + 0.1% formic acid) 85% for 1.5 mins. Then, the mobile phase B was decreased to 30% in 2 mins, held at 30% for 7 min, and finally returned to 85% until the process was terminated at 20 min.

To identify BMAA, the MS/MS system was operated under the positive ion mode, and three SRM transitions of *m/z* were monitored, 119.1 > 44.0 amu (collision energies (CE) = 14 eV), 119.1 > 88.0 amu (CE = 11 eV), and 119.1 > 102.1 amu (CE = 9 eV). The ion source parameters were optimized with the parameters being set as spray voltage = 3500 V, vaporizer temperature = 300 °C, and capillary temperature = 280 °C. Nitrogen was used as the sheath gas, with a pressure = 20 psi, the aux gas pressure = 40 psi, and argon collision gas pressure = 1.5 mTorr.

### 2.2. Chlorination experiments

A batch reaction was used for the chlorination experiments in this study, with 500-mL glass vessels used as the reactors. A stock solution of BMAA, ≥ 97% purity (Sigma-Aldrich, USA), was prepared at 250 mg/L before use. Two types of natural water were collected from Lan Tan Reservoir, Chiayi, Taiwan (LT water, Total organic carbon (TOC) = 1.4 mg/L) and Cheng Kung Lake (TOC = 12.7 mg/L), Tainan, Taiwan. The two natural waters and deionized water (Milli-Q, USA) were used as the studied water matrix. For the chlorination experiments, the pH of the deionized water was adjusted to 6.5, 9.0, and 9.5 using sodium hydroxide (GR Grade, Showa Chemical, Japan), while that of the two natural waters was not adjusted. Both chlorine and BMAA dosages were set at 0.5–5 mg/L in the chlorination experiments. Ascorbic acid (≥99% purity, Acros Organics, USA) was used as the reductant for the kinetic experiments of chlorine and chlorinated-BMAA. The difference of pH values before and after the experiments were all less than 0.2, suggesting that the pH values were stable during the oxidation process.

### 2.3. Competition experiments

Based on the preliminary experiments, the oxidation of BMAA by ozone and chlorine were completed very fast. BMAA was either disappeared or remained constant after 1 min. The reaction kinetics could not be obtained through direct measurement of the BMAA concentration. Therefore, competition experiments were conducted for the reaction kinetics of BMAA with chlorine and with ozone, following a similar approach to that reported in Shah et al. (2006) and Chen et al. (2017) (Chen et al., 2017; Shah et al., 2006). The reactions between BMAA and chlorine (or ozone) can be described by a second-order reaction as

$$\ln\frac{C_{reactant}}{C_{reactant_0}} = -K_{app}\int C_{oxidant}dt \quad (1)$$

where $C_{reacant}/C_{reactanto}$ is the ratio of the BMAA or competitor concentration at time t relative to the initial concentration;