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# Removal of microcystin-LR by free chlorine: Identify of transformation products and disinfection by-products formation

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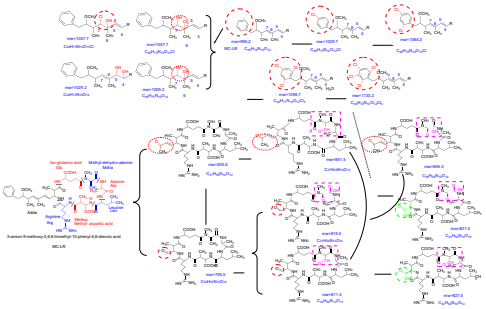
## HIGHLIGHTS

- The occurrence of MC-LR in surface water were detected in the Yangtze River Delta region of China.
- 16 different intermediate products were identified during chlorination.
- Chlorination of MC-LR contributed to the formation of C-DBPs and N-DBPs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Worldwide, the increasing occurrence of microcystin-LR (MC-LR) in water bodies used as source waters for drinking water has become an important public health issue. The present study surveying the MC-LR concentration of natural water in water resources from the Yangtze River Delta region of China was performed from 2013 to 2014. Many of the samples analyzed were found to have high concentration. The highest concentration of MC-LR was 27.79 μg/L, which was observed at Xijiu River in August of 2013. MC-LR is chemically stable, but disinfection by chlorine is known to reduce concentration of MC-LR. In this work, behavior of MC-LR with regard to chlorine has been studied. The decomposition of MC-LR followed first-order kinetics with average first-order constants of about $1.90 \times 10^{-4}$ $s^{-1}$ of a [Chlorine]:[MC-LR] molar ratio of 20:1. The Mdha amino acid in the cyclic structure, the diene bonds and benzene ring in the Adda side chain were the reacted sites of MC-LR. The intermediates and byproducts formed during the chlorination of MC-LR and the probable degradation pathway were investigated, 16 different intermediates were found. Furthermore, the formation potential of carbonaceous disinfection by-products (C-DBPs) and nitrogenous disinfection by-products (N-DBPs) were detected by GC/MSMS.



## 1. Introduction

Microcystin-LR (MC-LR) is frequently detected in surface water, which extremely stable even in extreme environments, such as high temperature or low pH. Therefore, MC-LR may persist for months or years in natural waters, which have also been linked to the high incidence of liver cancer in areas of China where populations are largely dependent on surface drinking water [1,2]. The damage to liver is a inhibition of protein phosphatases 1 and 2 A, causes massive hepatic hemorrhage [3]. It is a cyclic heptapeptide containing five amino acids invariant in all microcystins, and two additional amino acids, Leucine at position 2 and Arginine at position 4, which are designated "L" and "R", respectively. Adda group is one of the key components for biologic activity linked

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with the Adda side chain, which is largely responsible for their toxicity. The World Health Organization guidelines adopted a provisional guideline value for MC-LR of 1.0 μg/L in drinking water [4]. Because of anthropic pressure, the cyanobacterial blooms phenomenon is drastically increasing in temperate countries, and climate change may also raise its occurrence and magnitude, thus increasing the potential exposure to algal toxins. Recently, studies in several European and Asian countries revealed that microcystins were present in samples investigated [5–7]. MC-LR is commonly investigated in China, however, few papers that reported the results of the MC-LR concentration of drinking water for Yangtze River Delta region in a year-long period [8–11]. In this study, water samples were collected at 6 sampling sites supplied from drinking water resources, where sampling sites located at Xijiu River, Hengshan Reservoir, Youche Reservoir, Taihu Lake, Yangtze River and Huangpu River. Fig. 1 summarizes the occurrence of MC-LR and the range of concentrations detected in water samples.

The conventional water treatment processes have been proven to be unreliable for the removal of MC-LR. Numerous efforts have been devoted to characterize the fate of MC-LR in various water treatment technologies, such as ozonation, chlorination, chloramination, photocatalysis, photoelectrocatalytic, potassium permanganate, potassium ferrate and electrochemical oxidation have been studied by some researchers [12–17]. However, the use of photocatalysis may oxidize contaminants in a long period of time and permanganate may lead to secondary pollution, which can adversely affect the quality of the treated water. Chloramine is not capable of oxidizing microcystins [18]. It was suggested that MC-LR can be easily decomposed by chlorination, which is a strong oxidant widely used to ensure water disinfection. Tsuji et al. showed that a chlorine dose of 2.8 mg/L for a contact time of 30 min was sufficient for 99% oxidation of MC-LR [19]. Similarly, Sorlini et al. showed that chemical oxidation with sodium hypochlorite shows a yield of 80% with a concentration of 3 mg$Cl_2$/L with a consequent reduction of MC-LR concentration from 10 to 1.5–2 μg/L [20]. Rodríguez suggested that chlorination of MC-LR can reach to 90% in 10 min with an initial MC-LR concentration of 2.5 mg/L [21]. Acero et al. reported that MC-LR is easily reduced to below 1 μg/L when the initial concentration of chlorine was higher than 2 mg/L, in this surface water [22]. It is generally admitted that chlorination was effective in the oxidation of MC-LR. The rate constant for the reactions of MC-LR with chlorine has been investigated in previous studies. Acero et al. suggested that the apparent second-order rate constant at 20°C and pH 8 was found to be 33 $M^{-1}\,s^{-1}$ [23]. Xagoraraki et al. observed the inactivation rate was 0.05 $min^{-1}$ at pH 7.5, temperature on 20°C, initial MC-LR concentration 1.87 μg/L and average free chlorine concentration of 2.9 mg/L [24]. Ho et al. determined that chlorination values of CT up to 25 mg min/L were required for oxidation of all microcystin analogues to below the World Health Organization guideline value of 1.0 μg/L [25]. The CT value is calculated by determining the area under a graph of chlorine concentration vs time. MC-LR is efficiently transformed by chlorine and the chlorinated by-products produced immediately while the adding of chlorine. Chlorination by-products of MC-LR have been mentioned in some studies. The first byproduct has been identified as dihydroxy-microcystin, through the chlorination of double bond of the Adda group [19]. Huang et al. reported that the products with mass-to-charge ratio ($m/z$) of 1047 and 1029 were identified, considering with monochloro-hydroxy-MC-LR and dihydroxy-MC-LR respectively [26]. Merel et al. identified four by products as well as their isomers: monochloro-microcystin, monochloro-dihy droxy-microcystin, dichloro-dihydroxy-microcystin and trichloro-hydroxy-microcystin, with respectively mass/charge ratio ($m/z$) of 1029.516, 1063.521, 1097.481 and 1115.448 [27]. Additionally, a negative consequence of chlorine application for oxidation purposes is the formation of disinfection by produces (DBPs). These DBPs are considered as a potential and important source of endocrine-disruption and some have been identified as probable human carcinogens [28]. Therefore, in the present work the kinetics of MC-LR oxidation by chlorine was studied and characterization of reaction products by LC-MSMS. In addition, efforts have been made to determine the identities of DBPs species, containing C-DBPs and N-DBPs. The disinfection byproducts were tested with GC-MSMS, which is essential for understanding and optimizing chlorine for oxidative removal of MC-LR.

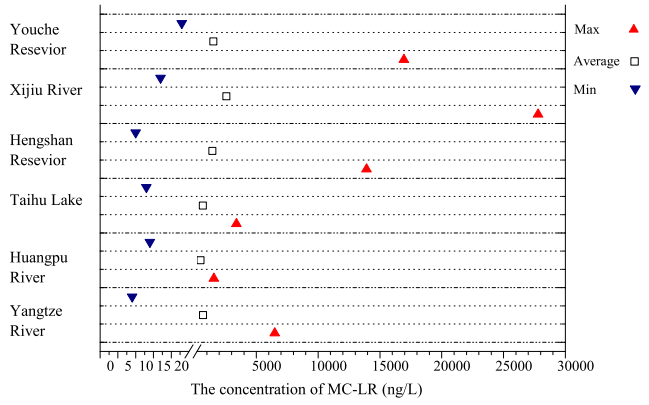


**Fig. 1.** The concentration of MC-LR at the sample locations (Youche Reservoir, Xijiu River, Hengshan Reservoir, Taihu Lake, Yangtze River and Huangpu River).

## 2. Materials and methods

### 2.1. Materials and reagents

MC-LR prepared in pure methanol with a molecular weight of 995.2 Da was purchased from agro-environmental protection institute, ministry of agriculture, China. This solution was further diluted by methanol solution to 20 μg/L as the working stock solution. Hypochlorous acid stock solution (about 2.0 g$Cl_2$/L) was prepared diluting a commercial bleach solution (Sinopharm Chemical Reagent Co., Ltd., China) in Milli-Q water and standardized by the DPD (N,N-diethyl-p-phenylenediamine, Sigma, >99%) colorimetric method [29]. The flask was then sealed and stored at 4°C prior to use. Formic acid (HPLC grade) and sodium hypochlorite (5% chlorine) were from Sinopharm Chemical Reagent Co., Ltd (China). DBPs standard solutions were purchased from Sigma–Aldrich (USA). Working solutions was obtained from a Milli-Q System (Waters, Millipore) with a specific resistance of 18MU cm. Organic solvents and other chemicals used in the analysis, Either HPLC or analytical grade, were supplied from Sigma–Aldrich (USA).

### 2.2. Experimental procedures

Chlorination experiments were carries under pseudo-first-order conditions, adding the volume of hypochlorous acid stock solution needed to ensure different [chlorine]/[MC-LR] molar ratio. MC-LR solution (20 μg/L) was prepared in 40 mL amber vials with Teflon caps. The experiments were started after addition of an aliquot of the chlorine stock solution into the reactor while stirring (for 5 s). At fixed time interval, 0.8 mL of samples was rapidly transferred with a syringe into a LC-MSMS vial containing sodium thiosulfate to stop the reaction, which molar is 120% of chlorine. Experiments were conducted at ambient temperature 20 ± 2°C. The chlorine concentration applied to exam DBPs groups was 3 mg/L with a MC-LR concentration of 20 μg/L. After reacting for