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Review

An overview of the accumulation of microcystins in aquatic ecosystems

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ABSTRACT

Cyanotoxins produced by toxic cyanobacteria pose a major, worldwide environmental threat to freshwater ecosystems. Microcystins (MCs) are considered to be the most hazardous groups. Indeed, some of the largest aquatic ecosystems on the earth are being contaminated with MCs. Questions have arisen regarding their transfer and bioaccumulation in natural environment. This review summarizes the present state of knowledge regarding toxic cyanobacteria and MCs, with a specific focus on their distribution in different components of aquatic ecosystems. Their accumulation in water columns, aquatic animals, plants, and sediments is summarized. MCs have been contaminating all areas of the aquatic ecosystems. Of these, the water column was the most contaminated with MCs and served as an intermediate transmission substation. Via this route, MCs could enter to other stations such as sediment, animals, aquatic and terrestrial plants. Therefore, the use of water contaminated with MCs may induce food chain contaminations with considerable health risks.

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1. Introduction

The occurrence of toxic cyanobacteria blooms associated with their toxins in aquatic ecosystems has become a worldwide problem (Preece et al., 2017). The impacts of these toxins on human health have been exacerbated as a result of increased nutrient loading and climate change (Preece et al., 2017). Among cyanotoxins, microcystins (MCs) with their hepatotoxic and tumor-promoting activities, are the most common and are considered to be one of the most hazardous groups (Li et al., 2017). MCs can be produced by numerous genera, *Anabaena* (*Dolichospermum*), *Aphanizomenon, Microcystis, Planktothrix* and more rarely by

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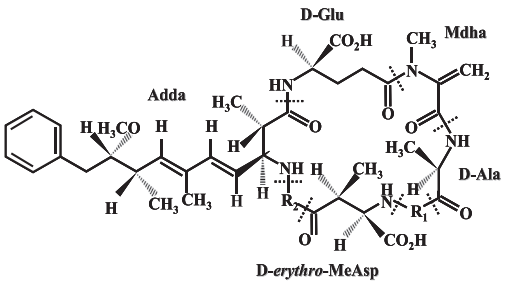
Anabaenopsis, Aphanocapsa, Cylindrospermopsis, Fischerella, Gleotrichia, Gomphosphaeria, Hapalosiphon, Nodularia, Nostoc, Phormidium, Pseudanabaena, Synechococcus, in which *Microcystis* genus has been reported as the most common bloom forming and the main producer of MCs in freshwater ecosystems (Preece et al., 2017). MCs contain seven peptide-linked amino acids, with the two terminal amino acids of the linear peptide being condensed (joined) to form a cyclic compound. As a group of cyclic heptapeptides, MCs share a general structure of cyclo-(D-alanine-R_1-D-MeAsp-R_2-Adda-D-glutamate-Mdha) in which R_1 and R_2 are variable L-amino acids, D-MeAsp is D-erythro-β-methylas-partic acid, and Mdha is N-methyldehydroalanine (Preece et al., 2017). Among MCs congeners, the three most predominant ones are MC-LR, MC-RR and MC-YR, in which MC-LR is the most toxic one (Li et al., 2017). The R1, R2 variable amino acids for MC-LR, MC-RR and MC-YR are leucine (L), arginine (R) and tyrosine (Y) (Fig. 1). The amino acid Adda, or (2S,3S,8S,9S)-3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid, which present in all variants, is crucial for the toxicity of MCs molecules. Over 100 structure variants have been reported so far (Li et al., 2017).

The ecological risk of MCs in the aquatic ecosystems is a growing concern. Toxic effects of MCs on animals and plant have been extensively studied and reviewed (Corbel et al., 2014; Chen et al., 2016; Elisabete et al., 2016; Machado et al., 2017; McLellan and Manderville, 2017). Target molecules of MCs appear to be the same in both animals and higher plants. In mammal cells, MCs able to enter in hepatocyte cell membranes through active uptake by multispecific organic-anion transporting polypeptides (OATP) and concentrate mainly in liver (McLellan and Manderville, 2017). However, the specific transporters of these in vegetable organisms are not known. It is suggesting that peptide transporters might potentially be involved in the transport of MCs in higher plants (Machado et al., 2017). The inhibition of protein phosphatases (PP) 1 and PP2A is widely assumed as the principal mechanism of toxicity of MCs, however recently studies found that MCs modulate PPs activity not only by direct inhibition of their activity, but also by regulating their expression (Chen et al., 2016; Elisabete et al., 2016). While PPs serve as a regulator to maintain homeostasis in the cell, inhibition of PPs leads to hyperphosphorylation, causing severe cell damage (Chen et al., 2016). This is a major post-transitional modification which can result in excessive signaling and may lead towards cell proliferation, cell transformation and tumor promotion (Elisabete et al., 2016). Besides inhibition of PPs, oxidative stress produced by reactive oxygen species (ROS) such as superoxide anion ($O_2^{\bullet -}$), hydrogen peroxide (H_2O_2) and hydroxyl radical ($HO^{\bullet}$) may play an important biochemical mechanism of MCs toxicity in both mammal and plant cells (Elisabete et al., 2016).

For many years, the occurrence of cyanobacterial blooms associated with MCs in drinking water has resulted in a number of public health events. Exposure to these toxins can lead to liver failure in wild animals, livestock and aquatic organisms, as well as human illnesses and deaths. The most well-known occurrence of a harmful effect of MCs is sometimes referred to as “the Caruaru Incident”. This event represents the first confirmed 70 deaths at a hemodialysis center as a result of direct exposure to MCs (Pouria et al., 1998). Ueno et al. (1996) also reported that human chronic exposure to MCs via consumption of drinking water contaminated with MCs has increased risks of primary liver cancer in humans in the eastern region of China. In a study by Chen et al. (2009a), a human population (in China) was chronically exposed to MCs via consumption of contaminated aquatic organisms. The authors reported that there was a positive relationship between the MCs concentration in serum samples and major liver biochemical indices, confirming hepatocellular damage. Many deaths of terrestrial and aquatic animals due to acute exposed to MCs have been reported. As a preventive step to reduce risks caused by MCs, the WHO recommends a provisional guideline value of 1 $\mu g\,l^{-1}$ for MC-LR concentration in drinking water and a chronic tolerable daily intake (TDI) of 0.04 $\mu g\,kg^{-1}$ body mass per day for human consumption (Li et al., 2017).

Bioaccumulation and distribution of MCs in different aquatic organisms has been extensively studied and reviewed (Martins and Vasconcelos, 2009; Ferrão-Filho and Kozlowsky-Suzuki, 2011; Corbel et al., 2014; Machado et al., 2017; Preece et al., 2017). Such



	R_1	R_2
microcystin-RR	arginine	arginine
microcystin-LR	leucine	arginine
microcystin-YR	tyrosine	arginine

Fig. 1. Chemical structure of the three most common microcystin (MC) analogs (MC-LR, - RR, -YR).

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