



Spatiotemporal distribution and potential risk assessment of microcystins in the Yulin River, a tributary of the Three Gorges Reservoir, China

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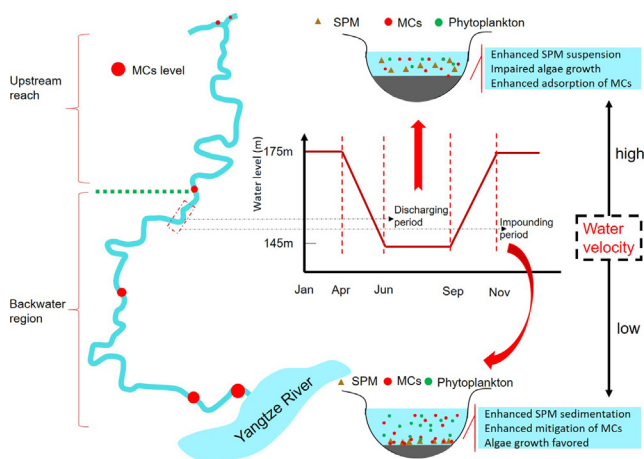
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GRAPHICAL ABSTRACT

Highlights

- MCs concentration in the Yulin River are sensitive to hydrodynamics condition.
- Suspended particulate matter (SPM) plays a vital role in reduction of MCs.
- MC-LR is of highly adverse risk to benthonic invertebrates.
- Alternation of hydrodynamics migrated the SPM absorbed MCs to the sediment.



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ABSTRACT

Microcystins (MCs) pose potential threat for both aquatic organisms and humans, whereas their occurrence in response to hydrodynamic alterations are not clearly understood. Here, spatiotemporal variations of dissolved MC-RR and MC-LR were evaluated monthly in 2016 in the Yulin River, a tributary of the Three Gorges Reservoir (TGR). The environmental factors that linked to MCs concentration were discussed. The results revealed that MC-RR maximumly reached 3.55 $\mu\text{g/L}$, and the maximum MC-LR concentration exceeded the threshold value of 1.0 $\mu\text{g/L}$ recommended by the WHO. MCs concentrations were higher during the flood season and decreased from the estuary to the upstream reach of the Yulin River. Ecological risk assessment confirmed that MC-LR had significant adverse effects on the benthonic invertebrates *Potamopyrgus antipodarum*. MCs content in the sediment was 1.70- to 20-fold higher than

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that in suspended particulate matter (SPM). The impacts of environmental factors on the MCs profile differed between flood and dry seasons and the longitudinal differences of MCs were determined by the longitudinal profile of water velocity and SPM content, which were affected by TGR operations. This study suggested that the occurrence of MCs in the Yulin River were influenced by hydrologic regime in TGR.

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1. Introduction

The Three Gorges Project (TGP) is the world's largest hydroelectric power plant and the most important water control project built in China on the Yangtze River [1]. Since the initial impoundment of the huge project in June 2003, the Three Gorges Reservoir (TGR) has annually altered from a natural river to a channel-type reservoir. It was revealed that after impoundment, the hydrodynamic conditions of these tributaries have largely changed [2,3], and the increasing abundance and biomass of phytoplankton assemblages dominated by *Microcystis* have been widely reported [4,5]. Many strains of *Microcystis* produce microcystins (MCs) [6], which can cause acute liver damage and promote tumor production and are linked to neurological disorders [7–9], therefore, they are highly toxic to wildlife and livestock as well as humans [10]. To date, at least 100 MCs have been structurally characterized, among which microcystin-LR (MC-LR) is the most toxic and abundant, followed by microcystin-RR (MC-RR) [11,12]. The World Health Organization (WHO) has therefore established a provisional drinking water guideline value of 1.0 µg/L for MC-LR [13].

Numerous efforts have been made worldwide to identify factors that affect MCs occurrence in freshwater systems. Previous studies have contributed to a widely accepted model that environmental factors may contribute to MCs concentrations via two main pathways: i) by enhancing the abundance of MCs-producing strains within a population and ii) by induction of MCs production by toxigenic strains [14]. Several studies have addressed the factors that influence the proliferation and toxin production of *Microcystis*, such as increased nutrient loading and the stoichiometric ratio of nitrogen (N) and phosphorus (P) [15]. In the absence of nutrient limitation, temperature is often considered the most important determinant for toxin-producing cyanobacteria in freshwater [16]. In complex aquatic systems, the conditions that induce toxin production are usually the sum of a variety of factors. In addition to the release of MCs by toxic cyanobacteria, there are multiple approaches that could impair the dissolved MCs levels in natural aquatic environments and five pathways have been proposed, including (1) dilution, (2) adsorption by sediment or suspended particulate matter (SPM), (3) thermal decomposition, (4) photolysis and (5) biological degradation [17–19]. Therefore, the measured dissolved MC concentration in a natural aquatic environment is the consequence of MCs production by cyanobacterial species vs. MCs removal by physical, chemical, and biological approaches. These two factors are largely associated with water hydrological conditions.

Recently, it was shown that environmental disturbances trigger apparent and abrupt switches from a non-cyanobacterial taxadominated state to a cyanobacteria-dominated state associated with a return to cyanobacteria dominance, hence increasing the risk of MCs [20,21]. Zhou et al. also revealed that under turbulent conditions, MCs concentrations significantly increase and reach a maximum level 3.4 times higher than in calm water [22]. On the other hand, it has also been demonstrated that SPM contributes to a reduction of pollutants in water [23], which could be remarkably enhanced when the SPM content increases as a result from water turbulence. These physical disturbances strongly affect the nutri-

ent levels. Specifically, the nutrients levels in the surface waters are strongly dependent on the stability of the water column or the turbulent state, which could be influenced by wind waves or hydrodynamic conditions, this has also been suggested to play a vital role in the formation and persistence of toxin producing cyanobacterial blooms [24].

Given its influence on SPM activity and nutrient levels, hydrodynamic conditions could be a key environmental factor regulating MCs concentration. The construction of a dam will alter the load or state of SPM in the water body [25], potentially reducing underwater light intensity, changing the temperature, and adsorbing contaminants [26]. Such processes contribute to the reduction of MCs concentrations in the water column. In general, the available data indicate that dissolved MCs are impacted by a variety of parameters, however, the response of MCs concentrations to an changed hydrological conditions has been studied on a relatively limited scale. In fact, river damming brings risks for environmental concerns from multiple ways. First, the decreased water velocity favors lake-type phytoplankton growth such as *Microcystis* and *Chlorophyta*. Second, the decreased water velocity is also associated with the migration of SPM from the water phase to sediment, which may impair its adsorption of pollutants. Third, damming of the river substantially reduces the transport of SPM from a river system to its downstream area, which contributes to the accumulation of pollutants, etc. However, to date, literature regarding the impact of varied hydrodynamic conditions, caused by river damming, on pollutants' fates through the abovementioned three approaches are lacking.

Against this background, we investigated the spatiotemporal profile of dissolved MCs in the Yulin River, an upstream tributaries of the TGR, and clarified the linkage between MCs concentrations and environmental factors in response to the hydrodynamic alterations caused by TGR operation, in the course of an entire year. Based on our results, we assessed the ecological risk of MCs and analyzed the impact of environmental factors on MCs concentrations. This study was done to work towards providing critical information regarding the impacts of the TGR operation on MCs concentrations in tributaries.

2. Materials and methods

2.1. Chemicals and reagents

MC-LR and MC-RR standards were provided by the Express Technology Company (Beijing, China). HPLC-grade methanol, which was used as the mobile phase, was obtained from Fisher (Loughborough, UK). Ultrapure reagent water was obtained using a Millipore Advantage A10 ultrapure water system (Billerica, MA, USA).

2.2. Study sites

The Yulin River (106°27'30"–106°57'58"E, 29°34'45"~30°07'22" N) is one of the tributary rivers in the higher reaches of the TGR. It is approximately 218.2 km long and has a total watershed area of 3861 km². Since the impoundment

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