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Effects of light, microorganisms, farming chemicals and water content on the degradation of microcystin-LR in agricultural soils

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ABSTRACT

An experiment was conducted to investigate the effect of farming activities on microcystin-LR (MC-LR) degradation in soils. Three farming activities were assessed: 1) fertilization via addition of different nitrogen sources and organic matter; 2) pesticide application by addition of different commercial pesticides; and 3) irrigation by addition of different amount of water. The contribution of the two major degradation processes of MC-LR in soils, photodegradation and biodegradation, were also evaluated. MC-LR was added into the soil samples to create a concentration of 500 μg kg^{-1} for each treatment. Results showed that natural degradation of MC-LR in soils was mainly by biodegradation rather than photodegradation. MC-degradation was stimulated by the addition of $NaNO_3$ and humic acid, whereas degradation was inhibited by addition of NH_4Cl, glucose, and glycine. Application of high concentrations of glyphosate and chlorothalonil significantly inhibited the degradation of MC-LR in soils and the half-life was almost twice as long as the control. No significant effect was found by addition of $CO(NH_2)_2$ and dimethoate. Both low (10%) and high water content (60%) could lead to inhibition of MC-LR degradation. Results from our study help to inform farm practices that could alleviate contamination by MC-LR in agroecosystems.

1. Introduction

Microcystins (MCs) are frequently produced by some bloom-forming cyanobacteria, mainly *Microcystis*, *Anabaena, Nostoc* and *Oscillatoria*, in eutrophic fresh water lakes (Chen et al., 2016). Owing to MCs' potential carcinogenicity, they can negatively affect both public health and fundamental ecological processes (Rastogi et al., 2014; Zhao et al., 2016). More than 200 different structural analogues of MCs, with a range of molecular weights from 882 to 1116 Da, have been identified from cyanobacterial blooms and cultures (Zastepa et al., 2015; Spoof and Catherine, 2017). Microcystin-LR is the most common and potent analogue, followed by microcystin-RR and microcystin-YR (Chen et al., 2016). The World Health Organization (WHO) proposed a safety guideline of 1.0 μg L^{-1} MC-LR for drinking water (Falconer, 1999). However, total MCs concentrations in surface waters vary from less than 1 μg L^{-1} to 29,000 μg L^{-1} (Spoof et al., 2003; Billiam et al., 2006; Nasri et al., 2008; Giannuzzi et al., 2011; Liu et al., 2011). The highest concentrations of MCs come from very dense cyanobacterial biomass, but their concentration in most of the water samples is less than 100 μg L^{-1} (Lindholm and Meriluoto, 1991; Jones and Orr, 1994; Lahti et al., 1997).

Due to their cyclic structure, MCs have a high chemical stability in the natural environment. Although MCs are produced in aquatic ecosystems, irrigation with cyanobacteria-containing water can bring MCs to agricultural soils; in addition, cyanobacterial blooms can be used as organic fertilizer after being intentionally harvested from lakes (Liu et al., 2008; Saqrane et al., 2009; Chen et al., 2010a, 2012). Once MCs are present in the soil, they can be removed according to various processes (e.g., photolysis, hydrolysis or microbial degradation) (Corbel et al., 2014a). Moreover, microbial activity is thought to be the major degradation process for MCs in soil ecosystems (Miller and Fallowfield, 2001; Chen et al., 2006; Rastogi et al., 2014). To the best of our knowledge, no previous studies concerning photodegradation of MCs in soils have been reported. Normally, MCs are stable in water under natural sunlight, but can rapidly be degraded under ultraviolet radiation (UVR). Tsuji et al. (1995) reported that about half of MC-LR was degraded after a 10 min exposure to 1.47 W m^{-2} UVR, whereas complete degradation was measured after a 10 min exposure to 25.50 W m^{-2} UVR. Moreover, MCs can be rapidly degraded following exposure to UVR near the absorption maximum (238 nm) by

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isomerisation or intramolecular reaction (photosensitized reactions) in the presence of pigments or humic substances (Tsuji et al., 1995; Kaya and Sano, 1998).

Biodegradation of MCs in the environment has been widely studied. Environmental factors, such as nutrient conditions (Chen et al., 2010b; Li et al., 2011), oxygen status (Holst et al., 2003) and temperature (Park et al., 2001; Chen et al., 2010b) are reported to affect the biodegradation rate of MCs. In aquatic systems, MCs have been shown to be readily degraded by bacteria with MC half-lives ranging from approximately 1 to 14 d (Edwards et al., 2008; Chen et al., 2008). However, studies on the biodegradation of MCs in soils are rare. Chen et al. (2006) reported that the half-life of MCs degradation in soils ranged from 6.0 to 17.1 days for MC-LR, 7.9–17.8 days for MC-RR, and 7.1–10.2 days for MC- Dha7 LR. High organic carbon content in soils favored MCs degradation (Chen et al., 2006). Miller and Fallowfield (2001) found that MC-LR could be completely degraded within 10–16 d in two of three tested soils. Soils with higher microbial activity favored the degradation of MC-LR.

It is suggested that the adsorption of MCs in soils is generally low, which can potentially result in higher bioavailability in plant-soil systems (Machado et al., 2017). Moreover, Eynard et al. (2000) indicated that soil was unable to protect groundwater from surface water that contains cyanotoxins. Consequently, degradation of MCs in soils is very important to protect plant-soil system and groundwater from MCs contamination. Farming activities, such as fertilizing, pesticide spraying and irrigation can have a significant impact on the soil microbial community (Atlas et al., 1978; Bollen, 2003; Paul et al., 2003; Dai, 2007; Tejada et al., 2014). However, to the best of our knowledge, no previous work has assessed the effect of different farming activities on MCs degradation in soils. In the present study, first we evaluated the contribution of photodegradation and biodegradation in the MC-degradation process. Then we assessed the effect of three different farming practices on MC-LR degradation. 1) the impact of fertilizers by addition of carbamide, ammonia chloride, sodium nitrate, glucose, glycine and humic acid at different concentrations; 2) the impact of pesticide application by addition of dimethoate, glyphosate and chlorothalonil at different concentrations; and 3) the impact of water content by incubation of soils under different water content (10%, 20%, 30% and 60%). Results from this study provide insights into the impact of farming activities on MC-LR degradation, and provide guidance regarding the alleviation of MC-LR contamination in agricultural soils.

2. Materials and methods

2.1. Toxins and chemicals

The MC-LR standard used in the present study was purchased from Taiwan Algal Science Inc. (≥ 95% purity, Lot No.: L1101003, CAS No.: 101043–37-2) and stored at − 25 °C. HPLC-grade methanol was used as the mobile phase in HPLC analysis. Technical grade pesticides were used in the present study (dimethoate, purity ≥ 97.5%; glyphosate, purity ≥ 98%; chlorothalonil, purity ≥ 99.7%). All other chemicals were of analytical grade.

2.2. Soil collection and characterization

Farmland soils (0–15 cm) that were not previously exposed to MCs were collected from the lakeside of Lake Taihu at Suzhou. After being taken back to the laboratory, the soil samples were homogenized and passed through a 2-mm sieve to sift out roots and other large debris. A portion of each soil sample was used for physico-chemical analysis after being air-dried at 25 °C for 48 h (Sparks et al., 1996). Physicochemical properties included the following: 27.9% sand, 31.0% silt, 41.2% clay, pH 7.46, 9.91 g organic matter kg^{-1} soil, 0.78 g total nitrogen kg^{-1} soil, 15.4 mg available P kg^{-1} soil, and 150 mg available K kg^{-1} soil. The remaining soil sample was kept fresh at 4 °C for degradation experiments.

2.3. Degradation study for MC-LR

2.3.1. Impact of light and microorganisms

MC-LR degradation experiments were conducted in a series of 100-mL pots. Each of the pots was filled with 50 g soil. Four treatments were applied: (1) MC-LR application and incubation in the light (Light treatment); (2) MC-LR application and incubation in the dark (Dark treatment); (3) MC-LR application, 2% azide (w/v) solution, which has been shown previously to kill soil microorganisms (Miller and Fallowfield, 2001), and incubated in the light (Sterile light treatment); (4) MC-LR application, 2% azide (w/v) solution, and incubation in the dark (Sterile dark treatment).

Soil samples (4 kg) were artificially contaminated by spiking the MC-LR solution to give a final concentration of 500 μg kg^{-1}. After thoroughly mixed with a rotary mixer (Philips handmixer, HR1570) to assure uniform MC-LR distribution, the soil sample was subjected to different treatments (the same below in 2.3.2, 2.3.3 and 2.3.4). Soil samples in the light treatment were incubated in a growth chamber under natural sunlight (temperature: 30 °C; relative humidity: 70%). All other samples were incubated under the same conditions in the dark. To avoid excessive water evaporation from soil, pots were covered with porous plastic film. All experiments were carried out in duplicate for 18 days.

The moisture content of soil was brought to 60% of the maximum water holding capacity (WHC) in treatments described in Sections 2.3.1, 2.3.2 and 2.3.3, whereas the water content of soils described in Section 2.3.4 was set as needed. The water content in all treatments was kept constant by amending as needed after daily weighing. For each treatment, 4 g soil was sampled every three days and stored at − 40 °C for MC-LR analysis.

The specific design of the experiments was showed in the diagram (Fig. S1).

2.3.2. Impact of fertilizers

Fifty grams of soils were placed in a series of pots (same as above). Each soil sample was further enriched by spiking with different fertilizers to give a final concentration as needed. The recommended application rate for N fertilizer in a vegetable field near Taihu Lake is about 60 kg ha^{-1}. Assuming that the soil weight is 1.5 × 105 kg ha^{-1} at the effective soil depth of 10 cm (GB/T 31270.1-2014), 60 kg ha^{-1} corresponds to 400 mg N kg^{-1} dry soil, so the three different levels of N fertilizer in the present study represent 0.5, 1 and 2 times the concentration of the recommended rate, 200, 400 and 800 mg N kg^{-1} dry soil, respectively. The levels of organic fertilizer were set similarly to N fertilizer. The impact of different fertilizers on MC-LR degradation was investigated by addition of $CO(NH_2)_2$ (0, 200, 400, 800 mg N kg^{-1} dry soil), NH_4Cl (0, 200, 400, 800 mg N kg^{-1} dry soil), $NaNO_3$ (0, 200, 400, 800 mg N kg^{-1} dry soil), glucose (0, 200, 400, 800 mg kg^{-1} dry soil), glycine (0, 200, 400, 800 mg kg^{-1} dry soil) and humic acid (0, 200, 400, 800 mg kg^{-1} dry soil). The dark treatment described in Section 2.3.1 also served as the control treatment for this fertilizer experiment.

2.3.3. Impact of pesticides

The impact of different pesticides on MC-LR degradation was investigated by addition of dimethoate, (50, 100, 200 mg kg^{-1} dry soil), glyphosate (0, 25, 50, 100 mg kg^{-1} dry soil), and chlorothalonil (0, 5, 10, 20 mg kg^{-1} dry soil) to pots containing 50 g of soil. The rates represent 0.5, 1 and 2 times the concentration of the highest recommended rate. The dark treatment described in Section 2.3.1 also served as the control treatment for this pesticide experiment.

2.3.4. Impact of water content

The impact of water content on MC-LR degradation was studied by incubation of pots containing 50 g of soil with 10%, 20%, 30% and 60%