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Microcystin Concentrations in the Nile River Sediments and Removal of Microcystin-LR by Sediments During Batch Experiments

Zakaria A. Mohamed, Hassan M. El-Sharouny, Wafaa S. Ali

Department of Botany, Faculty of Science, Sohag University, Sohag, 82524, Egypt

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Abstract. During the present study, microcystin (MCYST) concentrations in the Nile River and irrigation canal sediments, Egypt, were investigated during the period January–December 2001. Batch experiments were also conducted to confirm the adsorption of MCYSTs on these sediments. The results of field study showed that MCYST concentrations in the sediments were correlated with total count of cyanobacteria, particularly *Microcystis aeruginosa*, and MCYST within phytoplankton cells in most sites. No detectable levels of MCYSTs were found in the cell-free water of all studied sites in the Nile River and irrigation canals during the entire study period. The data obtained from batch adsorption experiments confirmed the capability of the Nile River and irrigation canal sediments for MCYST adsorption; and that adsorption was sediment weight-dependent and thus fitted the Freundlich adsorption isotherm. The results also revealed that both adsorption capacity (K_f) and intensity (1/n) varied significantly with clay and organic matter contents of these sediments. The results of present study have two implications. First, the presence of cyanobacterial toxins in freshwater sediments can affect benthic organisms inhabiting these sediments, and thus it should be considered during biological monitoring of rivers and streams. Second, the ability of freshwater sediments to adsorb cyanobacterial toxins suggests that bank filtration could be used in developing countries (*e.g.*, Egypt), which require an inexpensive and low-maintenance method for removing these toxins from drinking water.

Toxic cyanobacteria have been reported to cause dense water blooms in eutrophic surface waters, particularly in temperate regions worldwide (Codd 1995). Recently, toxic cyanobacteria have been investigated in Egyptian freshwaters, especially in the Nile River, the major source for drinking water in Egypt (Brittain *et al.* 2000; Mohamed and Carmichael 2000; Mohamed 2001, 2002). Cyanobacteria produce two main types of toxins: cyclic peptide hepatotoxins and alkaloid neurotoxins (Carmichael 1992, 1997). Of particular importance are the hepatotoxic cyclic peptides called microcystins (MCYSTs), which are commonly found in freshwaters (Carmichael 2000). MCYSTs have received attention in many countries after the report of Jochimsen *et al.* (1998) of the deaths of 50 patients exposed to MCYST-LR-contaminated water during dialysis treatment.

MCYSTs are cyclic heptapeptides produced by several species of commonly occurring cyanobacteria such as *Microcystis*, *Anabaena*, and *Oscillatoria* (Carmichael 1997, 2000). MCYSTs are usually confined within cyanobacterial cells, but during bloom senescence and cell lysis, they are released into the surrounding water (Tsuji *et al*. 1996, 2001). On entering the surround water, they may undergo five natural routes of detoxification: (1) dilution by uncontaminated water masses, (2) adsorption on particulate materials, (3) temperature and pH–dependent decomposition, (4) photolysis, and (5) biodegradation (Harada and Tsuji 1998). The potential for these toxins to impact adversely on human health requires that these toxins be removed from water supplies prior to use (Miller *et al.* 2001).

Many strategies such as chlorination (Nicholson *et al*. 1994), ozonation (Rositano *et al.* 1998), adsorption to activated carbon (Lambert *et al.* 1996; Mohamed *et al.* 1999), nanofiltration (Muntisov and Trimboli 1996), and ultraviolet radiation (Tsuji *et al.* 1995) have been investigated for the removal of cyanobacterial toxins from water. However, these techniques had some disadvantages, because most of them are expensive and needs a high level of maintenance. Therefore, an inexpensive and low-maintenance method such as filtration through soil and sediments would be the suitable technique in developing countries.

Many studies have been reported on the adsorption of MCYSTs to sediments (Rapala *et al.* 1994; Harada and Tsuji 1998; Kiyomi *et al*. 2000) and clay particles (Morris *et al.* 2000; Miller *et al*. 2001). However, these studies were performed only in batch experiments, and only a few studies have been carried out on the adsorption of MCYSTs on sediments in the natural environment (Tsuji *et al.* 2001; Babica *et al*. 2006; Chen *et al.* 2006a, 2006b; Ihle *et al.* 2006). To assess the health implications, it is very important to pursue MCYSTs under field conditions (Tsuji *et al*. 2001). Therefore, the present study aimed at investigating the seasonal variation of MCYST concentrations in sediments of the Nile River and irrigation canals for the first time in Egypt, and to confirm the

Correspondence to: Zakaria A. Mohamed; *email:* mzakaria_99@yahoo.com

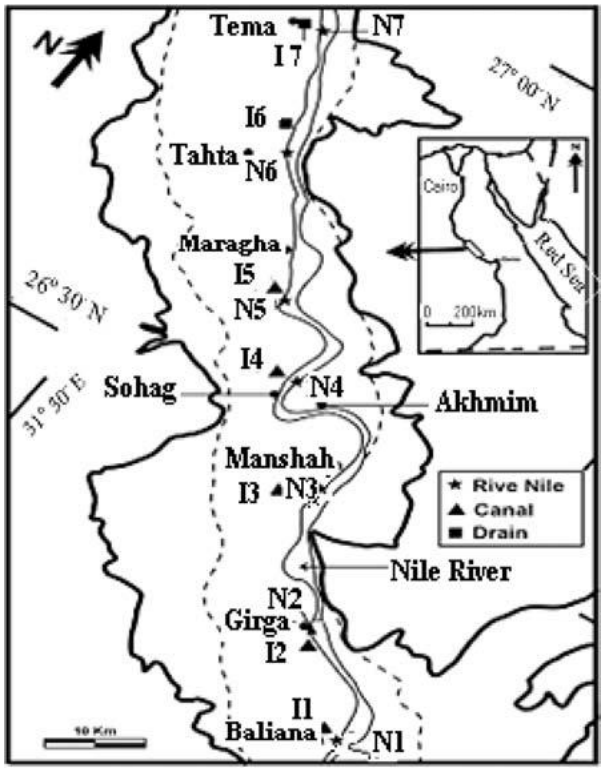

Fig. 1. A map showing the location of studied sites in the Nile River (N1–N7) and irrigation canals (I1–I7)

capability of these sediments for adsorption of MCYSTs during batch experiments.

Materials and Methods

Sample Collection

Water samples were collected once every month from the Nile River and irrigation canals (January 2001 to December 2001) at seven sites in different cities (from Baliana to Tema) in the Sohag district (Fig. 1). Samples were collected in the mid-morning to early afternoon with a phytoplankton net (25 μm in diameter). The pH of water samples was measured using a pH-meter (WPYE-290). At the same time as water sampling, sediment samples were taken at a depth of 2 m from the surface of the water using an undisturbed core sampler. Each sediment sample was collected from the first 10 cm and homogenized. All sediment samples were freeze-dried and used for toxin analysis and adsorption experiments. Phytoplankton samples were preserved in acid Lugol's solution for enumerating the density of cyanobacteria. Cyanobacterial species in preserved samples were counted in a hemocytometer or a Sedgewick–Rafter counting chamber using an Olympus binuclear light microscope. The counts were expressed as an organism per liter of the original water of the Nile River or irrigation canals. Cyanobacterial species were identified according to Prescott (1978).

Toxin Analysis

Water samples. After sampling, 500-ml water samples were filtered through a glass microfiber filter GF/C. The retained phytoplankton were extracted in 5-ml 95% methanol at room temperature (25 ± 2°C) and dim light for 24 h with shaking. The extract was filtered through GF/C filter papers, and the filtrate was evaporated until dryness. The residue was re-dissolved in 1 ml distilled water and tested for toxicity using enzyme-linked immunosorbent assay (ELISA) according to Carmichael and An (1999). The filtrates of water samples were passed through C18 cartridges and eluted with 80% methanol. The eluted fraction was evaporated to dryness. The residue was re-dissolved in 1 ml distilled water and tested for MCYSTs by the ELISA procedure as outlined above.

Microcystis cultures. Because *Microcystis aeruginosa* was the most dominant species among cyanobacteria present in the water samples during the period of study, isolates of *M. aeruginosa* from selected water samples, where heavy bloom of this species was present, were grown and scaled up in BG-11 medium at 25 ± 2°C and continuous light of 24 μmol m^{-2} s^{-1} light intensity for 3 weeks. The harvested cells were extracted by solid phase extraction according to the method used by Carmichael and An (1999). Briefly, 1 g of freeze-dried cells was extracted three times with a methanol-*n*-butanol-water mixture (4:1:15) overnight at room temperature while stirring or with sonicator, and then centrifuged for at 10,000 *g* for 10 minutes. The supernatants were combined, and blown with sterilized air to remove organic solvents. The residue was diluted in distilled water, and filtered through GF/C filter paper or centrifuged at 10,000 *g*. The filtered fraction was passed through C-18 cartridges, and the toxin was then eluted with two volumes of 80% methanol. The eluted fraction was evaporated to dryness. The residue was re-dissolved in 1 ml distilled water and tested for MCYSTs by the ELISA procedure as outlined above. To investigate the toxin profile of *M. aruginosa* isolates, the eluted fractions of solid phase extraction in methanol were applied to Perkin Elmer high-performance liquid chromatography (HPLC) with a photodiode array UV/Vis detector at 238 nm using a Bondapak C18 column. The mobile phase was acetonitrile (pH adjusted to 2 using trifluoroacetic acid) at room temperature and flow rate of 1 ml min^{-1}. The HPLC analysis was carried out in Cairo University.

Sediments. MCYSTs in freeze-dried sediments collected during this study were extracted with an extraction system: 5% acetic acid in 0.1% trifluoroacetic acid–methanol according to Harada (1996) and Babica *et al*. (2006) and as follows; a 100-ml extraction solvent system was added to 10 g of each sediment sample. The samples were shaken for 24 h in a Lab-Line incubator-shaker, and filtrated through GF/C filter papers. The filtrates were evaporated to dryness, and the residues were re-dissolved in 1 ml distilled water and tested for MCYSTs by the ELISA procedure as outlined above. The toxin concentration in the sediments was expressed as micrograms MCYSTs per gram freeze-dried sediments.

Batch adsorption experiment. To confirm the capability of sediments for MCYST adsorption, 14 freeze-dried sediment samples were selected from samples collected during the field study from different sites in the Nile River and irrigation canals, and used in batch experiments. The organic matter content of the sediments was determined by the titrimetric dichromate redox method of Tiessen and Moir (1993). Particle size analysis was carried out on sediment samples according to the method of Sheldrick and Wang (1993). The isotherm experiments were performed in the laboratory as follows: Pure MCYST-LR at concentration of 2 mg/L was dissolved in filtered and sterilized Nile River water (pH 8), and divided into subsamples, 50 ml each. The subsamples were placed in 100 ml-glass bottles, each containing different amounts (0.5, 1, 2, and 4 g) of each sediment sample. Control contained sterilized Nile River water without sediment. All batch adsorption experiments were conducted in triplicate. The bottles were shaken for 24 h in a Lab-Line incubator-shaker at

25°C. The samples were then filtered through GF/C (Whatman) to remove the sediments suspended in the solution.

Determination of adsorption isotherms. The concentration of non-adsorbed MCYST at equilibrium was determined in the filtrate by ELISA. Controls containing no sediment were used to determine the concentration of MCYST in solution at equilibrium. The isotherm data were characterized by the nonlinear Freundlich equation:

$$Q = K_f C_f^{1/n}$$

where $Q = (C_i - C_f)$ is the MCYST concentration adsorbed on sediment in μg/g.

C_f = is the equilibrium concentration of MCYST (μg/L) in the solution (not-adsorbed)

C_i = is the initial concentration of MCYST in the solution (μg/L).

K_f = is Freundlich adsorption coefficient (L g^{-1}) that provides an indication of the adsorption capacity of the sediment.

n = is the linearity exponent that provides an indication of the intensity of the adsorption.

The adsorption isotherms (K_f and 1/n), which define the adsorption properties of a contaminant to the sediments (Oliver *et al.* 1996), were obtained by plotting log Q as a function of log C_f. In order to evaluate the extraction efficiency of the extraction system (5% acetic acid in 0.1% trifluoroacetic acid–methanol), MCYSTs adsorbed on the sediments during adsorption isotherm experiments were extracted by this extraction system. The recovered MCYSTs were determined by the ELISA procedure as outlined above.

Statistical Analysis

The values of all parameters determined during the present study are the means of three readings. Spearman rank correlation coefficients were used to measure the degree of association between MCYST concentrations in the sediments, and total count of cyanobacteria, number of *M. aeruginosa*, and MCYSTs within phytoplankton cells in the water samples. The capacity differences for the adsorption of MCYST-LR with different sediments were calculated by one-way analysis of variance (ANOVA). The differences were considered significant at $p < 0.05$.

Results

Seasonal Variation of Total Count of Cyanobacteria, MCYSTs Within Phytoplankton Cells, and MCYSTs in the Sediments

During the present study, the total count of cyanobacteria as an average showed a great variation in the Nile River and irrigation canals along the study period ($p < 0.01$). This count was higher in summer and autumn than in winter and spring, and correlated with the count of the most dominant cyanobacterium *Microcystis aeruginosa* ($r = 0.99$) (Fig. 2 and 3). On the average this species represented 69.7–71.1% of the total count of cyanobacteria in the Nile River and 41.66–71.1% in the irrigation canals during the period of study (Fig. 2). On the other hand, the total count of cyanobacteria did not correlate with other species of cyanobacteria, which had low percentages in most sites ($r < 0.2$) (Fig. 2) However, the total count of cyanobacteria had significant correlation ($r > 0.8$) with the count of certain species in the sites not containing *M. aeruginosa* (*e.g.*, sites I3, I6, I7, N5). These species were *Anabaena circinalis*, *Oscillatoria angutissima*, *Oscillatoria limnetica*, and *Oscillatoria tenuis*.

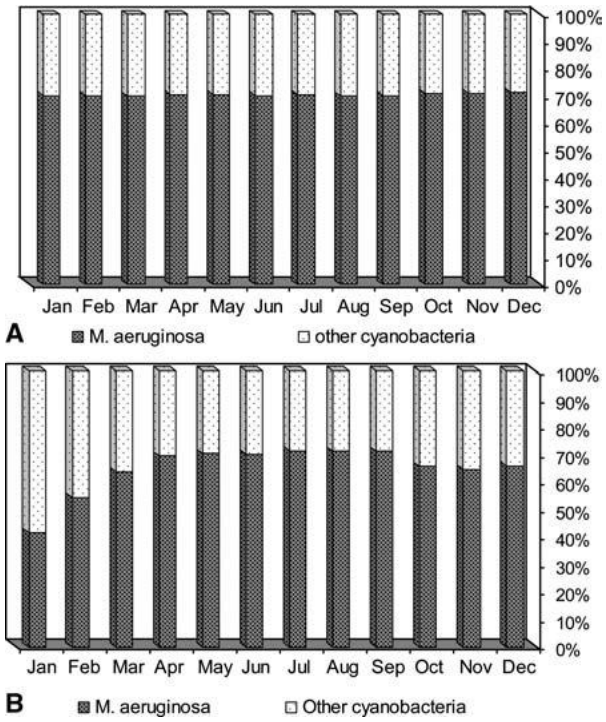

Fig. 2. Seasonal variation in percentages (%) of *Microcystis aeruginosa* and other cyanobacteria in the Nile River **(A)** and irrigation canals **(B)** in Egypt during the period of study

MCYST concentrations within phytoplankton cells as averages showed seasonal variation in the Nile River and irrigation canal sites ($p < 0.05$) during the period of study. The highest concentrations were recorded in summer and autumn (Fig. 3), and correlated with the total count of cyanobacteria ($r > 0.9$) and the count of *M. aeruginosa* ($r > 0.7$). MCYST concentrations as averages in the Nile River and irrigation canal sediments, as determined by ELISA, varied greatly during the period of study ($p < 0.01$), with highest amounts obtained during summer and autumn (Fig. 3). They ranged from 0.039 to 0.092 μg g^{-1} in the Nile River sediments and from 0.039 to 0.066 μg g^{-1} in the irrigation canal sediments. However, no detectable levels of MCYSTs were found in the sediments collected from all sites studied during the period from January to March 2001. The results also showed that MCYST concentrations in the sediments had significant correlations with MCYSTs within phytoplankton cells ($r > 0.6$), the total count of cyanobacteria ($r > 0.66$), and the count of *M. aeruginosa* ($r > 0.6$) in the Nile River and irrigation canals (Fig. 3). The statistical ANOVA did not reveal any significant difference in pH values (7.2–8.5) among sites studied in the Nile River and irrigation canals during the period of study ($p > 0.1$). In addition, no significant correlation was observed between MCYST concentrations in the sediments and pH values of water samples in most sites studied. During all of the study period, no detectable levels of MCYSTs were found in

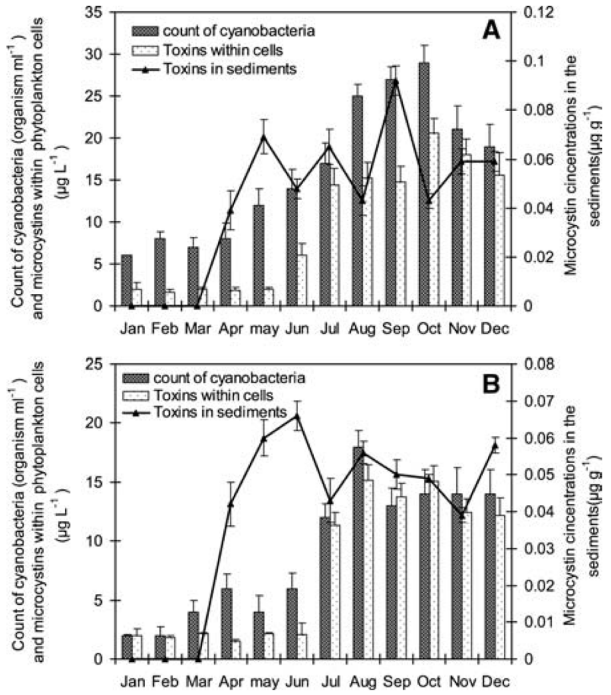

Fig. 3. Seasonal variation in total count of cyanobacteria (organism L^{-1}), microcystin concentrations within phytoplankton cells (µg L^{-1}) of water samples, and microcystin concentrations in the sediments (µg g^{-1}dry sediments) in the Nile River **(A)** and irrigation canals **(B)** in Egypt during the period of study

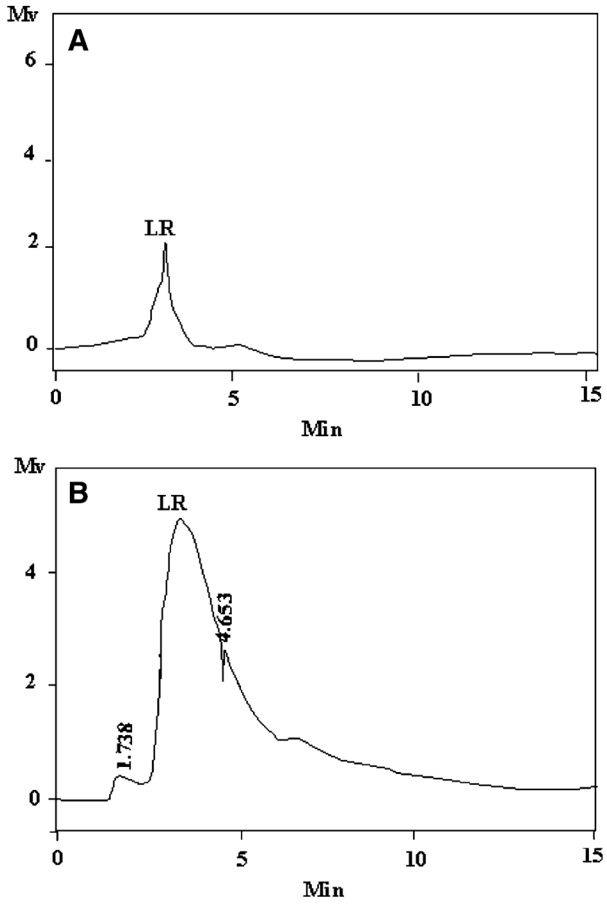

Fig. 4. High-performance liquid chromatography chromatograph of **(a)** standard microcystin-LR and **(b)** the methanolic fraction of batch culture of *Microcystis aeruginosa* isolated from the Nile River during the period of study

the cell-free water of all sites in the Nile River and irrigation canals (therefore, data not shown).

Because of the abundance of *M. aeruginosa* in all sites during the present study and its intimate relationship with MCYST production worldwide, the toxins produced by this species were isolated and characterized. The toxin content in this cyanobacterium as determined by ELISA was 250 µg MCYST/g dry weight. The HPLC analysis revealed one peak corresponding to microcystin-LR (MCYST-LR) when compared to standards at a level of 440 µg g^{-1} dry weight (Fig. 4).

Batch Adsorption of MCYSTs on Sediments

The data obtained from laboratory experiments of adsorption of MCYST-LR on sediments collected from the Nile River and irrigation canals showed that these sediments are capable of adsorption of MCYST-LR, and that adsorption was sediment weight–dependent and thus fitted the Freundlich adsorption isotherms. The results also revealed that sediments from two sites (N3 and N4) in the Nile River and two sites (I4 and I6) in the irrigation canals had larger binding capacities (K_f values) and binding intensities (1/n) than sediments from other sites (Table 1). Furthermore, K_f values differed significantly ($p < 0.05$) among sediments of different sites (Table 1), and correlated with clay ($r = 0.63$) and organic matter ($r = 0.45$). On the other hand, K_f values did not show any significant correlation with either sand ($r = 0.026$) or silt ($r = 0.08$) contents of these sediments (Tables 1 and 2). The results also showed that recovery rates of MCYST-LR from spiked sediments extracted with 5% acetic acid in 0.1 % trifluoroacetic acid–methanol were 56–76% for the Nile River sediments and 58–76% for irrigation canal sediments (Table 1). These recovery rates did not show any clear correlation with the contents of organic matter, sand, silt, or clay of the sediments used ($r < 0.1$).

Discussion

Adsorption of MCYSTs released from cyanobacteria on the sediments contributes to the detoxification of these toxins in the natural environment (Harada 1996; Tsuji *et al.* 2001; Babica *et al.* 2006; Chen *et al.* 2006a, 2006b; Ihle *et al.* 2006). During our study on the seasonal variation of MCYSTs in the sediments of the Nile River and irrigation canals in Egypt, MCYSTs were detected in these sediments at considerable concentrations, and these concentrations varied significantly among studied sites. This variation could be attributed to the difference in the physicochemical properties of these sediments (Miller *et al.* 2001). This explanation was confirmed later during our batch experiments by studying the relationship between binding capacities (K_f values) of the sediments for

Table 1. Freundlich adsorption coefficients and recovery (%) of MCYST-LR across sediments collected from different sites in the Nile River and irrigation canals in Egypt

Sediments	Adsorption isotherms			% MCYST-LR recovery
	K_f	1/n	r^2	
Nile River sediments				
N1	25.5	0.19	0.777	56
N2	28.8	0.22	0.96	58
N3	125.9	1.4	0.975	68
N4	100	1.1	0.872	76
N5	25.7	0.14	0.952	78
N6	43.7	0.5	0.975	61
N7	50.1	0.55	0.981	78
Irrigation canal sediments				
I1	21.4	0.07	0.11	58
I2	56.1	0.73	0.962	64
I3	76	0.88	0.894	68
I4	100	1.4	0.956	76
I5	25.7	0.13	0.111	59
I6	125.9	1.45	0.98	57
I7	25.5	0.19	0.927	62

MCYST-LR microcystin-LR.

Table 2. Soil texture and organic matter contents of sediments from studied sites in the Nile River (N1–N7) and irrigation canals (I1–I7) used in batch adsorption experiments

Site/month	Clay (%)	Sand (%)	Silt (%)	Organic matter (%)
N1/12	3.35 ± 0.2	95.22 ± 4.2	1.43 ± 0.5	0
N2/12	2.98 ± 0.2	52.29 ± 2.7	44.73 ± 1.5	1.88 ± 0.2
N3/12	23.19 ± 1.6	7.67 ± 0.8	69.14 ± 3.1	5.97 ± 0.4
N4/9	8.84 ± 0.4	47.10 ± 3.1	44.06 ± 2.3	1.01 ± 0.1
N5/9	0.74 ± 0.1	61.49 ± 3.2	37.77 ± 1.8	0.4 ± 0.05
N6/12	0.91 ± 0.1	77.48 ± 2.2	21.61 ± 1.6	1.74 ± 0.1
N7/12	17.98 ± 1.2	12.54 ± 1.1	69.48 ± 2.6	2.62 ± 0.3
I1/12	5.16 ± 0.7	14.20 ± 1.5	80.64 ± 3.7	2.82 ± 0.3
I2/12	13.26 ± 1.3	18.50 ± 1.7	68.24 ± 3.	2.88 ± 0.7
I3/12	14.19 ± 1.4	10.46 ± 1	75.35 ± 5.2	2.95 ± 0.3
I4/12	3.39 ± 0.8	61.30 ± 3.6	35.31 ± 2.5	2.68 ± 0.2
I5/11	15.5 ± 1.4	12.24 ± 1.4	72.26 ± 3.4	1.41 ± 0.1
I6/12	30.03 ± 2.3	15.70 ± 1.3	54.27 ± 2.5	2.08 ± 0.1
I7/10	7.47 ± 1	22.52 ± 1.7	70.01 ± 3.2	3.35 ± 0.4

MCYST-LR, and clay, sand, silt, and organic matter contents of these sediments.

In addition, MCYSTs in the sediments correlated with the total count of cyanobacteria, particularly *M. aeruginosa*, and MCYSTs within phytoplankton cells during the present study. This finding is expected and coincides with the hypothesis that healthy bloom populations produce little extracellular toxin in the water (Chorus and Bartram 1999), and thereby the available toxins adsorbed on sediments are low in quantity. Recently, Ihe *et al*. (2006) reported that MCYSTs produced during the pelagic phase of *Microcystis* are preserved in the sediments after sedimentation out of the pelagic zone. MCYST concentrations detected in the Nile River and irrigation canal sediments (0.039–0.092 μg g^{-1} dry sediments) during the present study can be compared to their concentrations detected in the natural sediments in other countries. Tsuji *et al*. (2001) detected MCYSTs in Japanese lake sediments at concentrations 0.08–2.33 μg g^{-1}. Another study found lower MCYSTs in sediments from prawn farm, New South Wales, Australia at concentrations 0.0005–0.0041 μg g^{-1} (Kankaanpää *et al*. 2005). Recently, Babica *et al*. (2006) detected MCYSTs in sediments from Brno reservoir in Czech Republic at concentrations ranged from 0.003 to 0.38 μg g^{-1} as detected by ELISA. However, the actual concentration of MCYSTs adsorbed on the natural sediments depends strongly on the solvent used for extracting MCYSTs from these sediments. Recoveries of MCYST-LR spiked with the Nile River and irrigation canal sediments and extracted with 5% acetic acid in 0.1% trifluoroacetic acid–methanol (56–76%) are well comparable with recovery rates for MCYST-LR (55.3–77.8%) spiked with Brno reservoir (Czech Republic) sediments extracted by the same procedure (Babica *et al*. 2006). However, they were higher than recovery rates of total MCYSTs (32.3–56.8%) from Brno reservoir sediments during the same study of Babica *et al*. (2006). The latter authors also found differences in the extraction efficiencies of MCYST variants, which decrease with the increasing hydrophobicity of MCYSTs, where the highest recovery rates (55.3–77.8%) were obtained with MCYST-LR followed by MCYST-YR (44.1–59.5%) and MCYST-RR (20–38.8%). Therefore, the authors deduced that the very low recovery rate of one MCYS variant (*e.g*., MCYST-RR) will dramatically reduce the total recovery rate from sediments. Hence, the results of recovery rates obtained during our study along with those obtained by Babica *et al*. (2006) suggest that the solvent system (5% acetic acid in 0.1% trifluoroacetic acid–methanol) is most efficient to extract MCYSTs from Natural sediments. However, more recently, Chen *et al.* (2006a) reported that this extraction method showed low recovery rates for MCYSTs, particularly the most hydrophilic MCYST-RR, when compared to the extraction solvent (0.1 M EDTA–0.1M $Na_4P_2O_7$-0.1% TFA) which was effective to extract over 90% of MCYSTs from sediments.

No detectable levels of MCYSTs were found either in the cell-free water of the Nile River and irrigation canals during the entire period of our study, or in the sediments during the period from January to March. These two findings may indicate the existence of other routes of MCYST detoxification in the natural environment, besides adsorption on sediments. The first may be due to the dilution of the toxin in the Nile River water, whereas the second would be due to the biological degradation of these toxins by microbes present in the sediments under the most suitable conditions during this period (Harada 1996; Christoffersen *et al*. 2002; Holst *et al.* 2003).

The use of batch adsorption techniques is conventionally the first step in examining the fate of contaminants in the environment and can therefore be used as an initial step in evaluating the effectiveness of bank filtration as a toxin removal strategy (Miller *et al*. 2001). In the present study, the results of batch experiments confirmed the ability of sediments from the Nile River and irrigation canals in Egypt to adsorb the highly hepatotoxic MCYST-LR. Furthermore, this study revealed a significant correlation between adsorption capacities (K_f values) and organic matter and clay contents of these sediments. These results agree totally with previous studies demonstrating the significance of both organic matter and clay in the binding of MCYSTs to sediments (Donati *et al*. 1994; Rapala *et al.* 1994; Lambert *et al*. 1996; Morris *et al*. 2000; Miller *et al*. 2001). However, Chen *et al*. (2006b) reported that the sorption

behavior of MCYSTs on the soils did not depend on the total organic matter in the soil, but on the content of the clay in the soils. These authors attributed the importance of clay to the presence of metal ions in the clay surfaces with which MCYSTs can chelate through nitrogen and oxygen atoms found in their structure. Babica *et al*. (2006) also reported that the sorption of MCYSTs onto inorganic materials such as clay minerals is probably a more important process than interactions of MCYSTs with organic sediment matter. Previously, the mechanism of MCYST adsorption on the sediment was suggested by Harada (1996), who reported that during MCYST adsorption on sediment, the hydrophilic part such as the arginine and glutamic acid moieties would tightly interact with the sediments. In contrast, the hydrophobic part such as Adda (3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-(4E),(6E)-dienoic acid) is not strongly bound to the sediments; therefore, it can be oxidized by ozone during water treatment. In this respect, Tsuji *et al*. (2001) reported that the hydrophilic MCYST-RR is more tightly adsorbed on the sediments than the hydrophobic MCYST-LR. In our study, we used MCYST-LR only during the batch experiment, because it was the most common toxin produced by the dominant cyanobacterium *M. aeruginosa* in the Nile River and irrigation canals. Previously, Morris *et al*. (2000) reported the adsorption of MCYST-LR by natural clay particles and suggested that this property can be used for the elimination of MCYSTs from drinking water.

Solution pH has been shown to affect the adsorption of MCYSTs on soil particles (Miller *et al*. 2001). In contrast, the results of our field study did not reveal a significant correlation between MCYST concentrations in the sediments and pH values of water samples at studied sites. This may be attributed to the absence of significant variation in pH values of water samples at sites studied during all the period of study, because the pH values ranged between 7.2 and 8.5. Therefore, our batch experiments were conducted only at pH 8 (the most common pH of the Nile River water). Also, biological degradation of MCYSTs by microbes present in the sediments was not taken into consideration during the design of our batch experiments because of long half-lives of 3 to 9 days of microbial degradation of MCYSTs (Jones and Orr 1994; Jones *et al.* 1994; Lam *et al*. 1995; Cousins *et al*. 1996). Therefore, the 24-h time period of mixing in our batch experiments is not sufficient for toxin loss by microbial degradation.

Conclusion

The results of our study showed for the first time that MCYSTs can be adsorbed and seasonally varied in the Nile River and irrigation canal sediments in Egypt as a route of detoxification in the natural environment. Furthermore, the results of batch experiments confirmed that these sediments had high capacities (K_f values) for MCYST adsorption, and that these capacities had a positive correlation with clay and organic matter contents of these sediments. The findings of this study have two implications. First, the presence of these potent toxins in freshwater sediments can affect benthic organisms inhabiting these sediments (Montagnolli *et al.* 2004). Hence, they should be considered during biological monitoring of rivers and streams. Second, the ability of sediments to adsorb cyanobacterial toxins suggests that bank filtration (the movement of water either naturally or artificially through the riverbed and/or aquifer material) could be used in developing countries (*e.g.*, Egypt), which require an inexpensive and low maintenance method for removing these toxins from drinking water.

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