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Laboratory simulated transport of microcystin-LR and cylindrospermopsin in groundwater under the influence of stormwater ponds: implications for harvesting of infiltrated stormwater

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Abstract Water shortages in the southeastern United States have led to a need for more intensive management and usage of stormwater for beneficial uses such as irrigation. Harvesting of infiltrated stormwater from horizontal wells in sandy aquifer sediments beneath stormwater ponds has emerged as an alternative in need of evaluation. Cyanobacteria may proliferate in stormwater ponds; cyanotoxins produced by these organisms represent potential public health concerns. Results of two, saturated flow, sand column experiments indicate breakthrough of microcystin-LR (MCLR) and cylindrospermopsin (CYL) within 1–2 pore volumes indicating little removal attributable to sorption. Concentration-based MCLR removal efficiencies up to 90% were achieved, which we hypothesize were predominantly due to biodegradation. In contrast, CYL removal efficiencies were generally less than 15%. On the basis of these results, removal of sandy soil in the stormwater pond bottom and addition of sorption media with greater binding affinities to cyanotoxins may enhance natural attenuation processes prior to water withdrawal.

Key words cyanotoxin; natural attenuation; ELISA; stormwater management; water harvesting

INTRODUCTION

As the demand for freshwater increases throughout the world to meet both public supply and irrigation needs, stormwater is increasingly being managed as a resource by operation of stormwater ponds to harvest water for beneficial uses. Withdrawal of water from horizontal wells beneath stormwater ponds is one method used to harvest water of sufficient quality for the intended use. Cyanobacteria may proliferate in stormwater ponds; cyanotoxins produced by these organisms represent potential public health concerns (Abbott *et al.*, 2009). Wanielista *et al.* (2006) report that cyanobacteria and the hepatotoxic microcystins were present in 15 central Florida, USA, stormwater ponds where all had detectable levels of microcystin with concentrations ranging from 0.04 to 1.6 μg/L. A variety of other cyanotoxins – including cylindrospermopsin, anatoxin-a, and lyngbyatoxin – have been detected in Florida rivers, natural lakes, and reservoirs (Burns *et al.*, 2002; Abbott *et al.*, 2009).

The objective of a recent study discussed herein was to investigate the potential for transport of microcystin-LR (MCLR) and cylindrospermopsin (CYL) in groundwater by using two vertical, downflow columns packed with sand to simulate typical stormwater pond sediment in Florida, USA. Breakthrough and toxin recovery of MCLR and CYL were evaluated on the basis of concentration and mass. Water samples were evaluated for toxins by enzyme linked immunosorbent assay (ELISA) and a sample subset by liquid chromatography triple quadrupole mass spectrometry (LC/MS/MS).

EXPERIMENTAL METHODS

Two identical columns were constructed of cast acrylic tubes (150 cm tall, 29 cm inside diameter, Fig. 1). Six sampling ports were installed at depths of 15, 30, 46, 61, 91, and 140 cm along each column. The columns were packed with air-dried, poorly graded, clean sand (0.2 mm median grain size). Sand was compacted to a dry bulk density of approx. 1.6 g/cm^3 and an inter-particle porosity of 0.41.

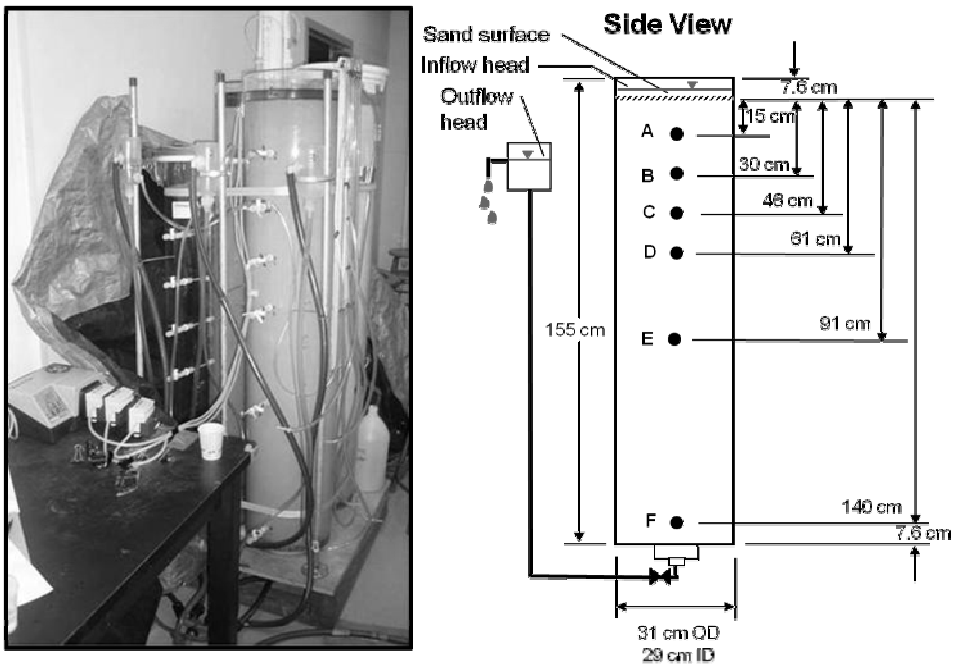

Fig. 1 Sand columns.

Two column experiments of 3-day and 10-day duration were performed. Natural stormwater spiked with commercially available cyanotoxin standards (Abraxis, LLC, Warminster, PA) was continuously applied to both columns for the duration of each experiment. MCLR ($C_{40}H_{74}N_{10}O_{12}$, molecular weight 995 g/mol) has log octanol/water distribution ratios (log D_{ow}) less than zero for pH values greater than 6 (Gert-Jan de Maagd *et al*., 1999), suggesting hydrophilic behaviour in common freshwater environments. For CYL ($C_{15}H_{21}N_5O_7S$, molecular weight 438 g/mol), log D_{ow} values are not available, although Wormer *et al*. (2008) report CYL is more water soluble

than microcystins. For the 3-day experiment, both columns were run simultaneously using stormwater spiked to yield a MCLR concentration of 3.9 µg/L with sampling intervals of 0.5–14 h. For the 10-day experiment, both columns were run simultaneously using stormwater spiked to yield a MCLR concentration of 2.2 µg/L and a CYL concentration of 0.5 µg/L with sampling intervals of 0.5–48 h. Columns were operated in a gravity-feed manner.

Samples were collected from each sampling port, as well as from the ponded water at the top of each column (Fig. 1). Replicate samples were not collected because duplicate columns were operated. Samples were filtered upon collection using 0.45 µm glass-microfiber syringe filters and quantitatively analysed using commercially available ELISA kits (Microcystin-ADDA and Cylindrospermopsin kits, Abraxis, LLC, Warminster, PA). The detection limit for each ELISA is 0.1 µg/L (MCLR) and 0.04 µg/L (CYL). All samples were analysed in duplicate; quality control samples were analysed with each run, consisting of at least one blank and 5–7 control samples of known concentration. To confirm results by ELISA, a subset of samples was analysed using LC/MS/MS with a reporting limit of 0.01 µg/L (Loftin *et al.*, 2008).

EXPERIMENTAL RESULTS

Results of both column experiments indicate the potential for substantial removal of MCLR and limited removal of CYL during saturated flow through sand. ELISA results indicate relatively conservative transport of MCLR and CYL at breakthrough, followed by substantial declines in MCLR and little or no decline in CYL (Fig. 2). Reasons for MCLR concentrations greater than the influent concentration are not clear, but may be due in part to variability in the ELISA technique. Results from control samples indicate that 95% had percent recoveries ranging from 77 to 133%. Nevertheless, the shapes of the MCLR breakthrough curves are consistent for both columns and both the 3-day and 10-day experiments. Breakthrough occurred between 1 and 2 pore volumes for each toxin, indicating both MCLR and CYL were moving at or slightly slower than the pore-water velocity suggesting little sorption (Fig. 2).

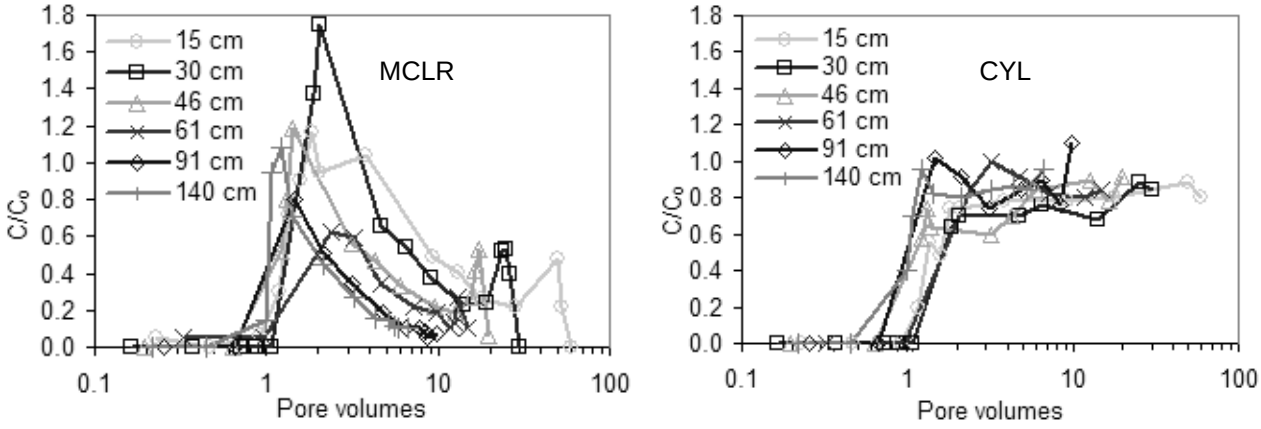

Fig. 2 Dimensionless breakthrough curves for the 10-day experiment for MCLR and CYL based on measured concentrations (C) at each sampling port and respective influent concentrations (C_o) and a sand porosity of 0.41. One pore volume corresponds to the following elapsed times at each sampling port: 2.2 h at 15 cm, 4.5 h at 30 cm, 6.9 h at 46 cm, 9.3 h at 61 cm, 15 h at 91 cm, and 23 h at 140 cm.

Concentration-based MCLR removal efficiencies up to 90% and mass-balance based removal efficiencies up to 70% were achieved (Fig. 3), which we hypothesize were predominantly due to biodegradation. Biological activity in the columns was suggested by continuous formation of a biofilm layer on the sand surface that was well established (1–2 mm thick) by day 4 of the experiment. Dissolved oxygen (DO) concentrations dropped dramatically after day 3 in the upper 60 cm of sand, decreasing from 5–6 mg/L to 0.2–0.6 mg/L during the experiment. DO was relatively constant in the lower 60 cm of the columns at less than 1.5 mg/L. The lowest MCLR concentrations occurred in the upper 60 cm of sand, consistent with the zone of suspected microbial activity. Biofilm development occurred, but to a lesser degree, during the 3-day experiment and columns remained aerobic, which was consistent with MCLR removal efficiencies about half those experienced after 10 days. LC/MS/MS results confirmed the reductions in MCLR given by ELISA. In contrast, both concentration-based and mass-balance based CYL removal efficiencies were generally less than 15% (Fig. 3).

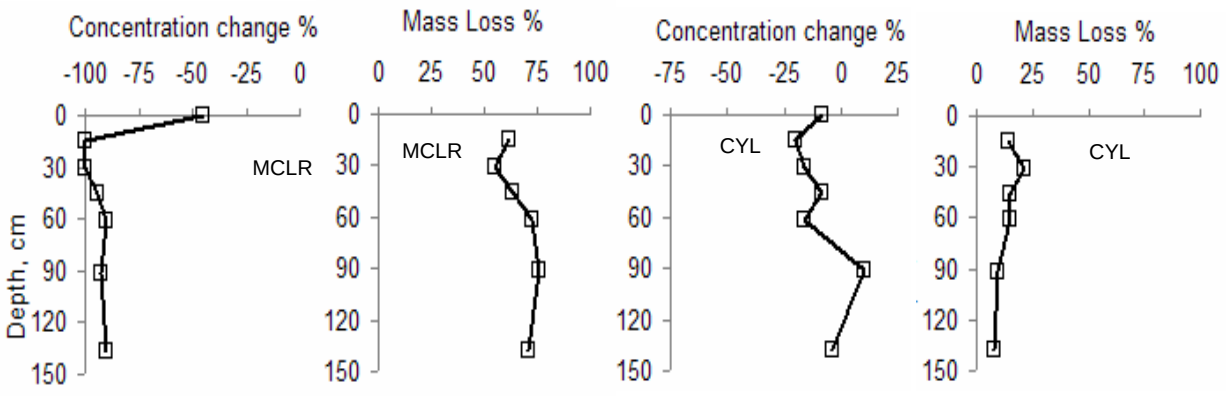

Fig. 3 Concentration-based and mass-based removal efficiencies by depth below sand surface for the 10-day experiment for MCLR and CYL.

CONCLUSIONS

The following conclusions may be drawn: (1) sandy systems provide little cyanotoxin removal attributable to sorption; (2) biodegradation may play a key role in MCLR reduction; and (3) harvested water may be impacted in sandy systems by MCLR and CYL present in stormwater. Grützmacher *et al*. (2002) reported similar results during slow sand filtration (80 cm thick filter bed), noting not only negligible adsorption but also the formation of a biofilm postulated to be the location of most of the microcystin degradation. However, little research is available on CYL removal by filter media, and results of this study suggest that management decisions cannot be based solely on the study of one cyanotoxin. Stormwater pond construction practices might be improved by the removal of sandy soil in the pond bottom and addition of sorption media to retard cyanotoxin transport, thus providing greater opportunity for sorption and potential biodegradation. Further research is needed to determine the effectiveness of a biologically active sorption media for cyanotoxin removal, including investigation of the differing response of different cyanotoxins to a chosen management strategy.

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