The adsorption of cyanobacterial hepatoxins as a function of soil properties

Megge J. Miller, John Hutson and Howard J. Fallowfield

ABSTRACT

Cyanobacterial hepatotoxins present a risk to public health when present in drinking water supplies. Existing removal strategies, although efficient, are not economically viable or practical for remote Australian communities and developing nations. Bank filtration is a natural process and a potential low cost, toxin removal strategy. Batch studies were conducted in 12 texturally diverse soils to examine the soil properties influencing the adsorption of the cyanobacterial hepatotoxins, microcystin-LR and nodularin. Sorption isotherms were measured. Freundlich and linear isotherms were observed for both toxins with adsorption coefficients not exceeding $2.75 \, \text{l kg}^{-1}$ for nodularin and $3.8 \, \text{l kg}^{-1}$ for microcystin. Significant positive correlations were identified between hepatotoxin sorption and clay and silt contents of the soils. Desorption of toxins was also measured in three different soils. Pure nodularin and microcystin-LR readily desorbed from all soils.

Key words | adsorption, bank filtration, drinking water, cyanobacterial hepatotoxins, soil aquifer filtration

Megge J. Miller
Department of Environmental Health, School of
    Medicine,
Faculty of Health Science, Flinders University,
GPO Box 2100, Adelaide 5001, Australia

John Hutson
Department of Earth Sciences,
Faculty of Science and Engineering, Flinders
    University,
GPO Box 2100, Adelaide 5001, Australia

Howard J. Fallowfield (corresponding author)
Department of Environmental Health, School of
    Medicine,
Faculty of Health Science, Flinders University,
GPO Box 2100, Adelaide 5001, Australia
Tel: +61-8-8204 5730,
Fax: +61-8-8204 5226,
E-mail: Howard.Fallowfield@flinders.edu.au

INTRODUCTION

Cyanobacteria are common in temperate regions worldwide (Carmichael et al. 1985; Codd 1995). Public health concerns arise when cyanobacteria produce toxins that compromise the quality of drinking and recreational waters. The cyanobacterial hepatotoxins, microcystin-LR and nodularin, are known to inhibit protein phosphatases 1 and 2A (MacKintosh et al. 1990; Yoshizawa et al. 1990; Eriksson et al. 1990), which results in tumor promotion in experimental animals (Nishiwaki-Matsushima et al. 1992; Ohta et al. 1994). Chronic adverse health effects may occur in populations that use hepatotoxin contaminated water for drinking or recreational purposes (Hrudey et al. 1994). The potential for the hepatotoxins to adversely effect human health was recently highlighted by the death of 50 patients in a Brazilian hospital who received microcystin contaminated water as a part of their renal dialysis treatment (Jochimsen et al. 1998).

Conventional techniques for the removal of cyanobacterial hepatotoxins from water are often expensive, highly

dependent on existing infrastructure and technically demanding. There is a need in developing countries and in remote communities for a low cost, easily maintained toxin removal strategy. Bank filtration is a possible technique for removing cyanobacterial toxins from drinking water supplies. Bank filtration is the natural and/or induced movement of water through aquifer material. Once present in the environment, the toxins, or indeed any xenobiotic, can be transported through the soil water ultimately entering an aquifer, degraded by micro-organisms or bound to organic and/or mineral fractions of the soil material. The retention of organic compounds by soil particles is dependent upon the functional groups of the compound and the characteristics of the soil. Both microcystin-LR and nodularin molecules contain hydrophilic functional groups such as carboxylic acid and amino groups. The toxins also contain a unique, relatively hydrophobic portion termed Adda (3-amino-9-methoxy-

2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid). Several soil parameters can affect the adsorption of organic compounds to soils. These factors usually act in combination to influence adsorption processes. Soils with relatively high clay and organic carbon (OC) contents tend to enhance adsorption of pesticides in laboratory experiments (Hance 1988; Oliver *et al.* 1996).

Several studies have investigated the persistence of cyanobacterial toxins in the environment. Rapala *et al.* (1994) demonstrated that losses of microcystin-LR were partially attributable to adsorption to lake sediments. This finding was supported by Lahti *et al.* (1996) who reported a 97.5–99.5% reduction in microcystin-LR levels in soil and sediment column studies. Neither of these studies quantified the soil/sediment pH, organic carbon (OC) content or soil texture, making it difficult to determine the factors, which influenced the adsorption of microcystin-LR to soil and/or sediment. The fate of microcystins in artificial recharge of groundwater and in bank filtration was recently examined (Lahti *et al.* 1998). However, the methods did not enable any conclusions to be made regarding processes influencing adsorption, as the soil properties were not quantified and toxin extraction methods from soil particles were not validated.

The movement of toxic organic chemicals through soils governs their potential to enter the groundwater and/or food chains and cause adverse effects to humans and the ecosystem (Beck *et al.* 1993). A detailed understanding of the factors that influence the fate and transport of a particular contaminant is required to enable the assessment of the efficiency of bank filtration as a removal strategy for cyanobacterial toxins. The purpose of this study was to examine sorption of microcystin-LR and nodularin in a wide range of soils and to determine whether or not sorption was related to soil properties.

MATERIALS AND METHODS

Soil collection and analysis

Soils were collected from twelve sites in the Willunga Basin and Lake Alexandrina region of South Australia. Sample sites were chosen with the aim of collecting a wide range of different soil textural types according to the texture classification system of Marshall (1947). Once collected, all soil samples were stored in the dark at 4°C until used in the experiments.

The organic carbon content of the soils was determined by the titrimetric dichromate redox method (Tiessen & Moir 1993). Particle size analysis was performed on the soil samples using the pipette method (Sheldrick & Wang 1993) and soil pH was measured in distilled water (Rowell 1994).

Cyanobacterial toxins and toxin analysis

Cyanobacterial toxins, nodularin and microcystin-LR, were extracted in methanol from harvested mass cultures of *Nodularia spumigena* and *Microcystis aeruginosa*, respectively. The extracts were dried under a constant stream of nitrogen at 50°C and resuspended in distilled water (Miller *et al.* 2001). Nodularin and microcystin concentrations together with the internal standard tolbutamide used in the batch studies were quantified using reversed phase high performance liquid chromatography (HPLC) and detection at 240 nm, using a UV-VIS detector (Shimadzu SPD-10AV) by the methods described by Miller *et al.* (2001). The toxin concentrations were calculated by reference to authentic standards (microcystin-LR, 98% purity, Sigma; nodularin, >95% purity, Calbiochem) and determined quantitatively by peak area ratio (toxin:tolbutamide), following the construction of a standard line for each toxin.

Batch adsorption experiments

Adsorption isotherms were determined using the method described by Miller *et al* (2001). Soil (10 g) was added to 250 ml Erlenmeyer flasks containing 50 ml of aqueous toxin extract (0.1 – 2.5 mg l^{-1}) and mixed for 24 h. Both linear and non-linear (Freundlich) sorption isotherms were fit to the sorption data. Linear adsorption isotherms are described by:

$$S = kd.C_{eq}, \tag{1}$$

and non-linear adsorption isotherms by

$$S = k_f.C_{eq}^n \tag{2}$$

where,

S   is the amount of toxin adsorbed per unit of soil (mg kg^{-1}),

C_{eq} is the concentration of toxin in solution after 24 hours mixing (mg l^{-1}),

k_d is the linear distribution coefficient ($l\,kg^{-1}$),

k_f is the Freundlich adsorption coefficient ($l\,kg^{-1}$), and

n is a linearity exponent.

The experimental data obtained from the batch studies were plotted on a decimal scale (k_d) and also $\log_{10}$ normalised scale (k_f). The adsorption isotherm with the highest statistical significance was chosen to describe the adsorption processes occurring in each soil.

Both linear and non-linear isotherms were observed. For comparison purposes the concentration of sorbed toxin in equilibrium with a solution concentration of $2.5\,mg\,l^{-1}$ and $0.1\,mg\,l^{-1}$ was calculated. A concentration of $2.5\,mg\,l^{-1}$ although only occasionally found during bloom conditions was chosen as a worse case scenario. The concentration of $0.1\,\mu g\,l^{-1}$ is one tenth of the guideline value for long term exposure to microcystin-LR (World Health Organisation 1998). The relationship between various soil parameters and the concentration of sorbed toxin at both of the chosen equilibrium concentrations were investigated using regression analyses.

Desorption experiments

Three soils (McLaren Flat, Lakes Plains and Hallett Cove), which have diverse particle size distributions, were chosen for the desorption experiments. Pure nodularin and microcystin-LR solutions at concentrations of 0.1, 0.25, 0.5, 1.0 and $2.5\,mg\,l^{-1}$ were prepared in distilled water. Soil (1 g) was added to polypropylene centrifuge tubes containing toxin solution (5 ml) and mixed for 24 hours using an end-on-end mixer (Nutator). Equilibrations were performed in triplicate. Previous work had demonstrated that there was no significant difference between orbital mixing and end-on-end mixing at a soil:toxin solution ratio of 1:5 (w/v). After centrifuging at $1600\,g$ for 25 minutes supernatant solution (1 ml) was removed for toxin analysis using HPLC. The remaining supernatant ($<4\,ml$) was removed and distilled water (5 ml) was added to the soil. The tube was vortexed to re-suspend the soil and initiate desorption. Each tube was mixed for 24 hours and the procedure detailed above was repeated until toxin was no longer detectable ($<0.016\,mg\,l^{-1}$).

Statistical analysis

Adsorption isotherms were calculated for each soil/toxin combination. The relationship between soil properties and the absolute amount of toxin adsorbed at equilibrium concentrations (C_{eq}) of $2.5\,mg\,l^{-1}$ and $0.1\,\mu g\,l^{-1}$, were determined by linear and multiple regression analyses (using Statistica software). The level of statistical significance for all statistical tests was accepted at $p < 0.05$.

RESULTS

Soil analysis

Most of the soils were sandy, with 8 of the 12 soils possessing sand contents above 70%, as shown in Table 1. The Hallett Cove soil had the highest sand content of 98.5%. Within these 8 soils, the pH, organic carbon and clay contents varied considerably. For example, Milang soil had

Table 1 | Physico-chemical properties of soils from the Willunga Basin and Lake Alexandrina regions of South Australia

Site	pH	OC (%) (Organiccarbon)	Clay (%)	Silt (%)	Sand (%)
Strathalbyn	8.07	5.30	10.08	6.17	76.20
Milang	8.29	0.08	0.25	ND	96.50
Lakes Plains	8.89	0.50	16.10	29.55	53.25
Langhorne Creek	7.06	11.12	41.05	31.60	18.15
Belvidere	8.15	0.09	7.96	2.42	88.99
Meadows	6.07	3.29	8.13	10.20	74.30
Kuipto	5.33	2.59	5.65	33.75	57.80
Aldinga	8.68	3.69	13.60	12.00	66.35
McLaren Flat	6.38	2.86	2.91	8.73	81.45
Blewett Springs	6.73	3.25	6.41	5.45	79.85
Onkaparinga River	8.30	0.92	0.73	1.92	92.85
Hallett Cove	9.25	0.02	ND	ND	98.45

ND = none detected

minimal clay and OC contents, while McLaren Flat had a relatively high OC content (2.86%).

Batch adsorption experiments

Table 2 shows the linear and non-linear adsorption coefficients for each site and toxin. Nodularin sorption, in the Milang soil and microcystin sorption in the Belvidere soil was variable and non-reproducible, and were excluded from the toxin data sets.

Five of the twelve soils Hallett Cove (Figure 1), Onkaparinga River (Figure 2), Aldinga (Figure 3), Langhorne Creek (Figure 4) and Belvidere (Figure 5), demonstrated non-linear adsorption of nodularin. The k_f values ranged from $0.22\,l\,kg^{-1}$ for Belvidere and Hallett Cove soils to $2.75\,l\,kg^{-1}$ in Langhorne Creek soil (Table 2). The remaining sites displayed linear adsorption processes for nodularin, with k_d values ranging from $0.2\,l\,kg^{-1}$ in McLaren Flat soil to $2.59\,l\,kg^{-1}$ in soil from Lakes Plains.

Table 2 | Adsorption coefficients for nodularin (k_{nod}) and microcystin-LR (k_{mic}) in soils from the Willunga Basin and Lake Alexandrina regions of South Australia

Site	k_{nod} (L kg^{-1})	k_{mic} (L kg^{-1})
Strathalbyn	1.00	0.97
Milang	NS	0.46 (n = 0.53)†
Lakes Plains	2.59	3.80 (n = 0.8)†
Langhorne Ck	2.75 (n = 0.72)†	3.16 (n = 0.83)†
Belvidere	0.22 (n = 0.61)†	NS
Meadows	1.21	1.32
Kuipto	1.30	1.35
Aldinga	1.74 (n = 0.72)†	1.36
McLaren Flat	0.20	0.21
Blewett Springs	0.42	1.24
Onkaparinga River	0.39 (n = 0.59)†	1.84
Hallett Cove	0.22 (n = 0.76)†	0.31

NS = not significant (the isotherm regression had $p > 0.05$)
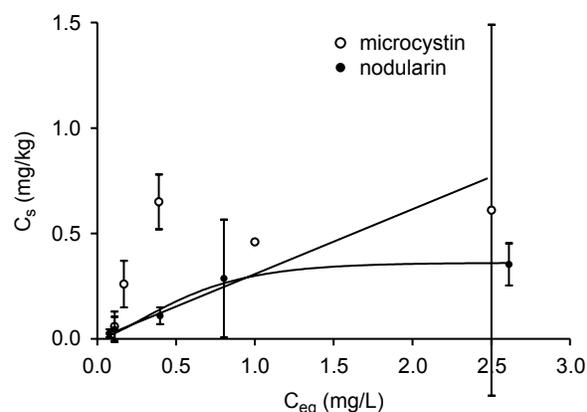†Freundlich adsorption isotherm, with linearity exponent (n) in parentheses

Figure 1 | Sorption isotherms for microcystin and nodularin, in Hallett Cove soil.

Non-linear adsorption of microcystin was observed in three of the soils, Milang, Lakes Plains and Langhorne Creek. The soil from Lakes Plains (Figure 6) had the highest non-linear sorption coefficient for microcystin, with a k_f of $3.8\,l\,kg^{-1}$ and Milang (Figure 7) had the lowest k_f of $0.46\,l\,kg^{-1}$. Microcystin-LR sorption across the remaining sites was linear and the k_d values were similar (Table 2).

Because some sorption was non-linear, the influence of soil properties on toxin sorption could not be directly compared by examining only k_d and k_f values. To enable comparisons across the 12 soils, isotherms for both toxins were normalised to the total amount of toxin sorbed (C_s) at two equilibrium solution concentrations. Table 3 shows the equations of the statistically significant simple regressions when C_{eq} was $2.5\,mg\,l^{-1}$ and $0.1\,\mu g\,l^{-1}$. When the absolute
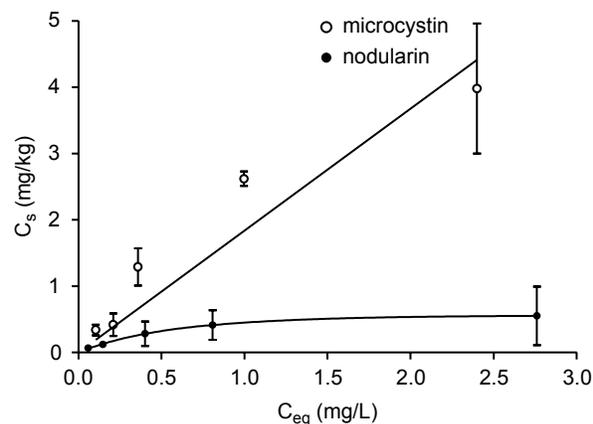

Figure 2 | Sorption isotherms for microcystin and nodularin in soil from the banks of the Onkaparinga River.
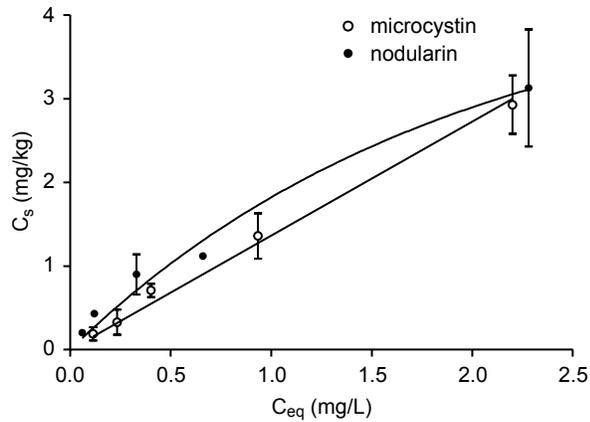
Figure 3 │ Sorption isotherm for nodularin and microcystin in Aldinga soil.

Figure 5 │ Freundlich adsorption isotherm for nodularin sorption at Belvidere. The regression for microcystin sorption was not statistically significant ($p > 0.1$).

amount of toxin adsorbed at C_{eq} of 2.5 mg l^{-1} was regressed against the various soil parameters, the clay and silt contents produced significant positive correlations for both nodularin and microcystin. In contrast, there was a strong negative influence ($p < 0.009$) of sand content on the amount adsorbed for both toxins. Regressions of the amount of toxin sorbed for both of the hepatotoxins against soil pH and OC content were not statistically significant when C_{eq} was 2.5 mg l^{-1}.

No significant simple or multiple correlations were observed for microcystin-LR sorption with any of the soil parameters at $C_{eq} = 0.1 \,\mu g \; l^{-1}$. When the amount of nodularin sorbed at C_{eq} of 0.1 μg l^{-1} was plotted against the soil parameters in a simple regression, the only significant correlations were against OC and clay contents. Comparing this observation with the results obtained for
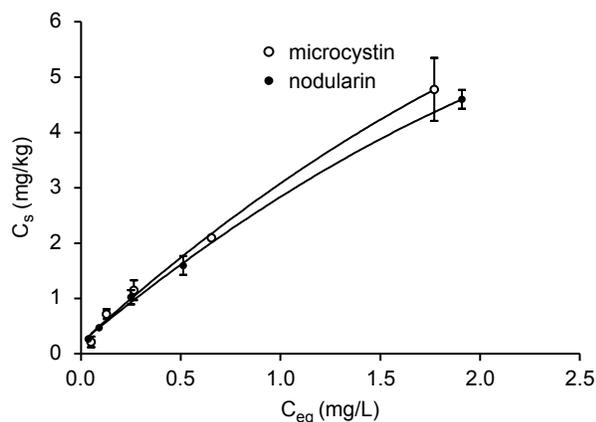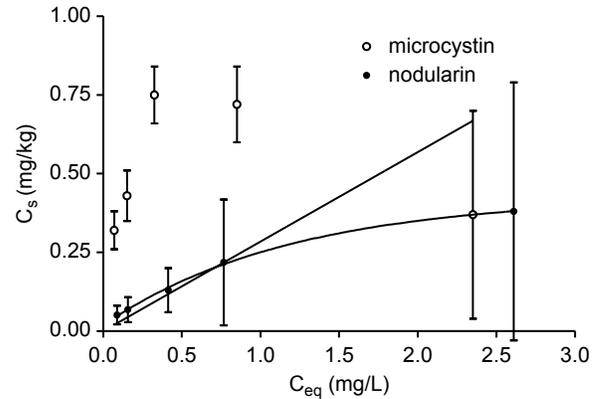
nodularin regressions when $C_{eq} = 2.5$ mg l^{-1}, suggests that at lower concentrations, the soil OC content was important for the adsorption of nodularin. Further regression analyses between nodularin sorption at various C_{eq} values and the OC contents for the 11 soils showed that when the C_{eq} was 0.1 mg l^{-1}, the highest level of significance was obtained. At higher concentrations the p value diminished and clay became the dominant factor determining nodularin sorption to soil.

Multiple regression analysis using nodularin as the test toxin at C_{eq} of 2.5 mg l^{-1} produced significant relationships for each soil parameter combination possible, except soil pH and OC. The silt and sand contents contributed the most to the level of significance in almost all of the nodularin multiple regression analyses containing these parameters (Table 3).
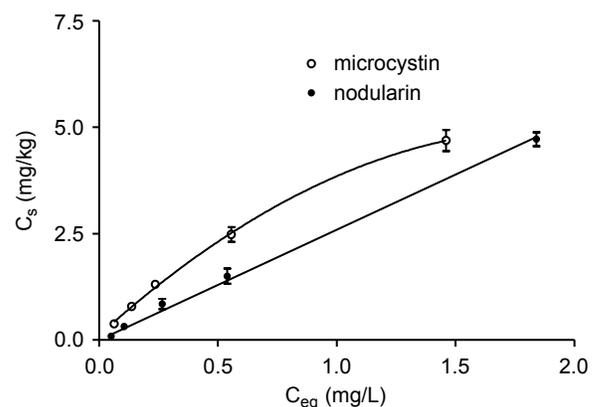

Figure 4 │ Sorption isotherms for microcystin and nodularin in Langhorne Creek soil.

Figure 6 │ Sorption isotherms for nodularin and microcystin in Lakes Plains soil.
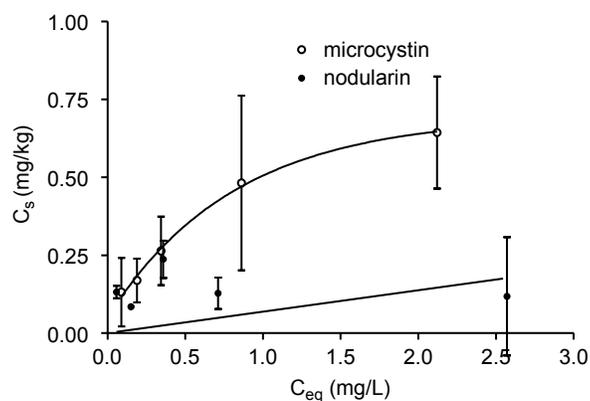
Figure 7 | Sorption isotherm for microcystin in Milang soil. The isotherm for nodularin sorption was not statistically significant.

Multiple regression analyses of the absolute amount of microcystin adsorbed at the equilibrium concentration of $2.5 \, \text{mg l}^{-1}$ plotted against the soil properties gave several statistically insignificant combinations (Table 3). The combinations of OC/silt, soil pH/OC and soil pH/clay content against microcystin sorption were all not significant. All other possible combinations were statistically significant ($p < 0.05$). For microcystin sorption, the sand and clay contents were the factors that contributed to the level of significance in the multiple regression analyses.

Multiple regression analyses of clay/soil pH, clay/silt and clay/sand against nodularin sorption at C_{eq} $2.5 \, \text{mg l}^{-1}$ were significant and the equations for each multiple regression are given in Table 3. Clay content was the parameter that contributed most to the level of significance observed for the amount of nodularin sorbed in these analyses. All other possible combinations in the analysis were not significant.

Desorption experiments

Desorption of pure nodularin (Figure 8) and microcystin (not shown) was similar in the McLaren Flat and Hallett Cove soils. Two concentrations (initial solution concentrations: $1.0 \, \text{mg l}^{-1}$ and $0.25 \, \text{mg l}^{-1}$) were chosen to monitor the toxin desorption over time, after a 24 hour adsorption phase. Figure 8 appears to show that the total amount of nodularin desorbed exceeded the amount adsorbed in McLaren Flat and Hallett Cove soils. Similar data was obtained for

Table 3 | Regression equations of significant correlations ($p < 0.05$) between the amount of cyanobacterial hepatotoxins adsorbed (C_s, expressed as mg kg^{-1}) and physico-chemical properties of the 11 soils studied, when $C_{eq} = 2.5 \, \text{mg L}^{-1}$ and $C_{eq} = 0.1 \, \mu\text{g L}^{-1}$. Soil parameters in parentheses are expressed as % of soil composition

Regression Equation

$C_{eq} = 2.5 \, mg \, L^{-1}$

NODULARIN

$C_s = 0.13 \, (\text{clay}) + 1.08$

$C_s = 0.14 \, (\text{silt}) + 0.66$

$C_s = 8.09 - 0.08 \, (\text{sand})$

$C_s = 0.395 \, (\text{pH}) - 0.085 \, (\text{sand}) + 5.55$

$C_s = 0.06 \, (\text{OC}) + 0.13 \, (\text{silt}) + 0.56$

$C_s = 0.0002 \, (\text{pH}) + 0.00008 \, (\text{clay}) - 0.003$

$C_s = 0.0001 \, (\text{clay}) - 0.00003 \, (\text{silt}) + 0.0003$

$C_s = 0.0001 \, (\text{clay}) - 0.00003 \, (\text{sand}) + 0.008$

MICROCYSTIN

$C_s = 0.14 \, (\text{clay}) + 2.00$

$C_s = 0.13 \, (\text{silt}) + 1.71$

$C_s = 8.83 - 0.076 \, (\text{sand})$

$C_s = 0.57 \, (\text{pH}) - 0.08 \, (\text{sand}) + 5.20$

$C_s = 0.08 \, (\text{clay}) + 0.079 \, (\text{silt}) + 1.56$

$C_{eq} = 0.1 \, \mu g \, L^{-1}$

NODULARIN

$C_s = 0.00023 \, (\text{OC}) + 0.00018$

$C_s = 0.00007 \, (\text{clay}) + 0.00011$

microcystin desorption. The apparent peak in desorption at 48 hours was likely a consequence of the inability to remove all of the interstitial solution from the soil matrix following centrifugation. What is important to note, however, is that the majority of nodularin and microcystin was desorbed within the first 24 hours following adsorption and no toxin was detectable in solution after 72 hours of the experiment. The
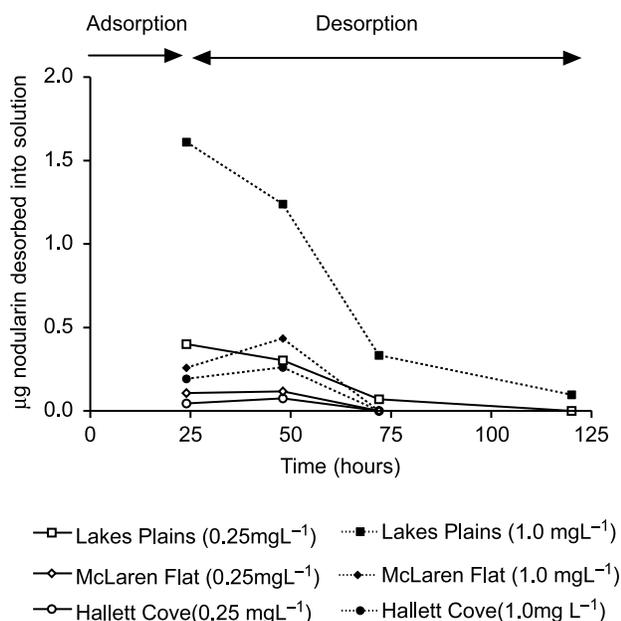
Figure 8 | Desorption of pure nodularin in three soils after an adsorptive phase in the first 24 hours of the experiment. The values given in the figure legend are the concentrations of nodularin in solution before the addition of the soil. The first point at 24 hours is the amount of nodularin bound to the soil, while the remainder of the points are the μg of nodularin in solution after each desorption step.

high clay soil of Lakes Plains desorbed both toxins over a longer time scale than the sandier soils, which suggests that the toxins were more strongly retained at this site. All of the nodularin was desorbed within 144 hours and microcystin was desorbed within 120 hours. Mass balance calculations indicated that negligible amounts of toxins remained bound to the three soils.

DISCUSSION

The results reported above suggest that there are a number of factors that will influence the efficacy of bank filtration for the removal of cyanobacterial toxins from drinking water. There appeared to be little difference between the adsorption coefficients of nodularin and microcystin. Non-linear adsorption processes occurred more often in the soils in the presence of nodularin than microcystin. The adsorption coefficients obtained in this study, although quite low, were similar to those reported for other organic contaminants. Pusino *et al.* (1992) reported Freundlich coefficient (k_f) values of

between 0.98 and 16.78 $l\ kg^{-1}$ for metolachlor in three texturally diverse soils. The lowest k_f was in a sandy soil, whilst the high k_f value was recorded in the soil containing 16% OC and 14.6% clay. Richey *et al.* (1997) reported k_d values of between 0.17 and 20 $kg\ l^{-1}$ for trifluoroacetate across twenty different soil horizons, with the lowest k_d values reported in the soils with the highest sand contents. This trend was also noted in the current study. The sites with the highest sand contents at Milang and Hallett Cove had the lowest adsorption coefficients for microcystin. Hallett Cove and Belvidere soils produced the equal lowest k_f value of 0.22 $l\ kg^{-1}$ for nodularin.

Many studies examining the adsorption of organic compounds to soils have identified the OC content as one of the most important factors governing adsorption (McGrath 1996; Kuwatsuka & Yamamoto 1997). Borisover and Graber (1997) concluded from thermodynamic analysis of a variety of hydrophobic and hydrophilic organic compounds, that solutes can interact with soil OC via the formation of hydrogen bonds. The OC contents of the soils in the current study were variable, ranging from 0.02 to 11.12%. However, regression analysis of toxin sorption against soil OC at $C_{eq} = 2.5\ mg\ l^{-1}$ did not result in significant correlations. This suggests that nodularin and microcystin do not partake in significant hydrogen bonding with soil OC at this concentration. However, at lower concentrations ($<0.1\ mg\ l^{-1}$) the soil OC had a significant influence on nodularin sorption. This suggests that perhaps there were a limited number of sites for nodularin adsorption to soil OC. At the lower concentrations the toxin can bind to OC, but as the nodularin concentration increases the OC binding sites become saturated and the clay binding sites may then be utilised for binding nodularin. The affinity of nodularin and microcystin for soil OC and clay binding sites requires further investigation.

The factors that were significantly correlated with toxin sorption (at $C_{eq} = 2.5\ mg\ l^{-1}$), were clay, silt and sand contents. Clay has long been recognised for its ability to enhance adsorption of organic compounds to soil (Hayes *et al.* 1972; Cox *et al.* 1995). Although the types of clay particles present were not identified in the current study, the results from the regression analysis at both of the C_{eq}

concentrations suggest it is likely that the clays are adsorptive of the large hepatotoxins. Zielke *et al.* (1989) state that clays in the presence of water (i.e. highly hydrated), as in the case for bank filtration, possess hydroxyl groups at the edge of the particle and may act as binding sites for ligand exchange. Alternatively, under the correct thermodynamic conditions, the hydroxyl groups can react with functional groups on the toxin molecule, such as the carboxylic acid group. These reactions are two of many that are possible resulting in the binding of toxin molecules to clay particles. However, this project did not aim to examine the thermodynamics of binding reactions, therefore it is difficult to conclude with certainty, which reactions occurred. Another possible explanation for the enhanced toxin adsorption in soil with high clay contents is that clay soils intrinsically possess higher surface areas. The larger surface area means that there are more sites available for adsorption.

The negative relationship between sand content and toxin sorption was to be expected as sand contains few reactive functional groups that can partake in adsorption processes. In addition, sand has a smaller surface area than clay soils and therefore, fewer adsorption sites. Most of the soils used in this study were sandy, except for the Lakes Plains, Langhorne Creek and Kuipto sites. These sites generally had the highest adsorption coefficients both for nodularin and microcystin. The high sand content of the majority of the soils explains why the adsorption coefficients were low.

Desorption experiments are useful to determine how tightly bound a contaminant is to soil and hence its availability for degradation (Scow *et al.* 1995). Pure nodularin and microcystin were adsorbed to three soils and then desorption was monitored over 72 to144 hours. Under the conditions used in this experiment, McLaren Flat and Hallett Cove soils did not retain either toxin for longer than 72 hours, possibly due to the low clay contents of these soils (<2.91%). The Lakes Plains site (clay content: 16.1%) retained the toxin over a longer time frame, confirming that the clay could be the main toxin binding component of the soil. All three sites had reversible binding of nodularin and microcystin, which suggests that the toxin would be available for microbial degradation.

REFERENCES

Beck, A., Johnston, A. & Jones, K. 1993 Movement of nonionic organic chemicals in agricultural soils. *Crit. Rev. Environ. Sci. Tech.* **23**, 219–248.

Borisover, M. D. & Graber, E. R. 1997 Specific interactions of organic compounds with soil organic carbon. *Chemosphere.* **34**, 1761–1776.

Carmichael, W. W., Jones, C. L. A., Mahmood, N. A. & Theiss, W. C. 1985 Algal toxins and water-based diseases. *CRC Crit. Rev. Environ. Control.* **15**, 275–313.

Codd, G. A. 1995 Cyanobacterial toxins: occurrence, properties and biological significance. *Wat. Sci. Tech.* **32**(4), 149–156.

Cox, L., Hermosin, M. C. & Cornejo, J. 1995 Adsorption and desorption of the herbicide thiazafluron as a function of soil properties. *Intl. J. Environ. Analyt. Chem.* **58**, 305–314.

Eriksson, J. E., Toivola, D., Meriluoto, J. A. O., Karaki, H., Han, Y. G. & Hartshorne, D. 1990 Hepatocyte deformation induced by cyanobacterial toxins reflects inhibition of protein phosphatases. *Biochem. Biophys. Res. Commun.* **173**, 1347–1353.

Hance, R. J. 1988 Adsorption and bioavailability. *Environmental Chemistry of Herbicides*, Volume 1. (ed. R. Grover), pp. 1–19. CRC Press Inc, Boca Raton, FL.

Hayes, M. H. B., Lundie, R. P. & Stacey, M. 1972 Interaction between organophosphorus compounds and soil materials. I. Adsorption of ethyl methyl phosphonofluoridate. *Pesticide Sci.* **31**, 619–625.

Hrudey, S. E., Lambert, T. W. & Kenefick, S. L. 1994 Health risk assessment of microcystins in drinking water supplies. In *Toxic Cyanobacteria- A Global Perspective* (ed. M. Burch), pp. 7–12. Australian Centre for Water Quality Research, Adelaide.

Jochimsen, E. M., Carmichael, W. W., Cardo, D. M., Cookson, S. T., Holmes, C. E. M., Antunes, B. C., Filho, D. A. M., Lyra, M. D., Barreto, V. S., Azevedo, S. M. F. O. & Jarvis, W. R. 1998 Liver failure and death after exposure to microcystins at a haemodialysis centre in Brazil. *New Eng. J. Med.* **338**, 873–878.

Kuwatsuka, D. S. & Yamamoto, I. 1997 Relationships between soil properties and sorption behaviour of the herbicide halosulfuron-methyl in selected Japanese soils. *Pesticide Sci.* **22**, 288–292.

Lahti, K., Vaitomaa, J., Kivimaki, A. L. & Sivonen, K. 1998 Fate of cyanobacterial hepatotoxins in artificial recharge of groundwater and in bank filtration. In *Artificial Recharge of*

Groundwater (ed. J. H. Peters), pp. 211–216. Balkema, Rotterdam.

Lahti, K., Kilponen, J., Kivimaki, A. L. & Erkomaa, K. 1996 Removal of cyanobacteria and their hepatotoxins from raw water in soil and sediment columns. Artificial recharge of groundwater NHO-Report No 38. *Proceedings of an International Symposium* (eds. A. L. Kivimaki & T. Suokka), pp. 187–195. Nordic Hydrological Program, Helsinki, Finland.

MacKintosh, C., Beattie, K. A., Klumpp, S., Cohen, P. & Codd, G. A. 1990 Cyanobacterial microcystin-LR is a potent inhibitor of protein phosphatases 1 and 2A from both mammals and higher plants. *FEBS Letts.* **264**, 187–192.

Marshall, T. J. 1947 Mechanical composition of soil in relation to field description of texture. *Coun. Sci. Ind. Res. Aust.*, 224.

McGrath, D. 1996 A note on the adsorption characteristics of organic pollutants in Irish soils. *Irish. J. Agricul. Food Res.* **35**, 55–61.

Miller, M. J., Critchley, M. M., Hutson, J. & Fallowfield, H. J. 2001 The adsorption of cyanobacterial hepatotoxins from water onto soil during batch experiments. *Water Res.* **35**, 1461–1468.

Nishiwaki-Matsushima, R., Ohta, T., Nishiwaki, S., Suganuma, M., Kohyama, K., Ishikawa, T., Carmichael, W. W. & Fujiki, H. 1992 Liver tumor promotion by cyanobacterial cyclic peptide toxin microcystin-LR. *J. Cancer Res. Clin. Oncol.* **118**, 420–424.

Ohta, T., Sueoka, E., Iida, N., Komori, A., Suganuma, M., Nishiwaki, R., Tatematsu, M., Kim, S-J., Carmichael, W. W. & Fujiki, H. 1994 Nodularin, a potent inhibitor of protein phosphatases 1 and 2A, is a new environmental carcinogen in male F344 rat liver. *Cancer Res.* **54**, 6402–6402.

Oliver, Y.M., Gerritse, R.G., Dillon, P.J., Smettem, K.R.J., 1996 *Fate and Mobility of Stormwater and Wastewater Contaminants in Aquifers 2. Adsorption Studies for Carbonate Aquifers*, Centre for Groundwater Studies Report No. 68, South Australia.

Pusino, A., Weiping, L. & Gessa, C. 1992 Influence of organic matter and its clay complexes on metolachlor adsorption on soil. *Pesticide Sci.* **36**, 283–286.

Rapala, J., Lahti, K., Sivonen, K. & Niemela, S. I. 1994 Biodegradability and adsorption on lake sediments of cyanobacterial hepatotoxins and anatoxin-a. *Letts Appl. Micro.* **19**, 423–428.

Richey, D. G., Driscoll, C. T. & Likens, G. E. 1997 Soil retention of trifluoroacetate. *Environ. Sci. Technol.* **31**(6), 1723–1727.

Rowell, D. L. 1994 *Soil Science: Methods and Applications*. Longman Scientific and Technical, New York.

Scow, K. M., Fan, S., Johnson, C. & Ma, G. M. 1995 Biodegradation of sorbed chemicals in soil. *Environ. Health Perspect.* **103**, 93–95.

Sheldrick, B. H. & Wang, C. 1993 Particle size distribution. In *Soil Sampling and Methods of Analysis* (ed. M. R. Carter), pp. 499–511. Lewis Publishers, USA.

Tiessen, H. & Moir, J. O. 1993 Total and organic carbon. In *Soil Sampling and Methods of Analysis* (ed. M. R. Carter), pp. 187–199. Lewis Publishers, USA.

World Health Organisation 1998 *Guidelines for Drinking Water Quality. Addendum to Volume 2, Health Criteria and Other Supporting Information*, 2nd Edition. World Health Organisation, Geneva.

Yoshizawa, S., Matsushima, R., Watanabe, M. F., Harada, K., Ichihara, A., Carmichael, W. W. & Fujiki, H. 1990 Inhibition of protein phosphatases by microcystis and nodularin associated with hepatotoxicity. *J. Cancer Res. Clin. Oncol.* **116**, 609–614.

Zielke, R. C., Pinnavaia, T. J. & Mortland, M. M. 1989 Adsorption and reactions of selected organic molecules on clay mineral surfaces. In *Reactions and Movement of Organic Chemicals in Soils* (eds. B. L. Sawhney & K. Brown), pp. 81–97. Soil Science Society of America Inc., Wisconsin.

Available online September 2005