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Sorption of the cyanobacterial toxins cylindrospermopsin and anatoxin-a to sediments

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ABSTRACT

The occurrence of the cyanobacterial toxins anatoxin-a (ATX) and cylindrospermopsin (CYN) in surface waters has been reported throughout the world. Beside degradation, sorption is an important pathway for toxin elimination if these resources are used for drinking water production via sediment passage. However, to date studies that systematically investigated sorption of these toxins onto sediments are lacking. Therefore, the aim of our work was (i) to determine the adsorption coefficients of ATX and CYN according to the Freundlich and Langmuir model for sediments of various textures and (ii) to derive sorption-relevant sediment characteristics. We determined sorption parameters in air-dried samples of eight differently textured sediments using batch experiments. Results for both toxins showed best fits with the Langmuir model. Organic C proved to be the main sediment parameter determining CYN sorption. There was no or little CYN sorption on sandy and silty sediments (0–39 μg kg^{-1}), respectively, presumably due to charge repulsion from the negatively charged surfaces. Sorption of ATX (max. sorbent loading ranging from 47 to 656 μg kg^{-1}) was much stronger than that of CYN (max. sorbent loading ranging from 0 to 361 μg kg^{-1}) and predominantly controlled by clay and to a minor degree also by organic C and silt. While ATX sorption to most sediments occurred mainly through cation exchange this mechanism played only a minor role in CYN sorption to organic C. Hence, high mobility for CYN and moderate mobility for ATX during sediment passage has to be expected.

1. Introduction

Anatoxin-a (ATX) and cylindrospermopsin (CYN) are toxins produced by certain cyanobacteria (ATX: Edwards et al., 1992; Sivonen et al., 1989; CYN: Ohtani et al., 1992; Falconer, 2005; Preußel et al., 2006). They are known to have a range of effects on human health such as tissue damage (liver, lung, gut) and cell necrosis (CYN: Hawkins et al., 1997), as well as damage to the nervous and respiratory systems (ATX: Thomas et al., 1993).

Anatoxin-a is an alkaloid toxin with a molecular weight of 165 g mol^{-1} (Fig. 1a). Despite its worldwide distribution it seems not to occur as frequently as microcystins and cylindrospermopsin (Osswald et al., 2007; Hedman et al., 2008). The screening of 78 German water bodies yielded maximum total ATX concentration (i.e. intracellular and extracellular) of up to 13.1 μg L^{-1}, but higher concentrations can be expected during bloom situations (Bumke-Vogt et al., 1999). The highest anatoxin-a concentration found was 1750 μg L^{-1} (Hedman et al., 2008). Anatoxin-a was shown to decompose

Abbreviations: ATX, anatoxin-a; CYN, cylindrospermopsin; OC, organic carbon; CEC, cation exchange capacity.

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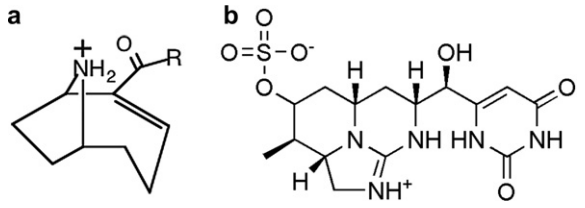

Fig. 1 – Molecular structure of (a) Anatoxin-a and (b) Cylindrospermopsin.

under the influence of light and alkaline pH (Stevens and Krieger, 1991) and to adsorb on lake sediments (Rapala et al., 1994).

Cylindrospermopsin is an alkaloid toxin with a cyclic guanidine moiety bridged to a hydroxymethyluracil group and a molecular weight of 415 g mol^{-1} mol^{-1} (Chiswell et al., 1999; Fig. 1b). Cylindrospermopsin has been detected in many water bodies throughout the world with concentrations in subtropical regions of Australia in the range of up to120 μg L^{-1} (Shaw et al., 1999; McGregor and Fabbro, 2000) and in European freshwaters with maximum concentrations between 9 and 18 μg L^{-1} (Bogialli et al., 2006a; Quesada et al., 2006; Rücker et al., 2007). Due to its chemical stability and slow degradation (Chiswell et al., 1999) CYN shows a high persistence in many water bodies (Wormer et al., 2008). Sorption to sandy sediments with a content of fines of 1% and 4% was found to be negligible (Klitzke et al., 2010).

If toxin contaminated surface waters are used as drinking water reservoirs, efficient elimination has to be ensured. Beside degradation, dilution and physical straining, sorption is an important process for contaminant removal during drinking water (pre-) treatment methods (Grützmacher et al., 2010) such as river bank filtration, artificial groundwater recharge, and slow sand filtration. The properties and structure of the toxins together with sediment texture determine their sorption capacity. While CYN is very hydrophilic and carries both a positive and a negative charge at neutral pH (Meriluoto and Spoof, 2008) ATX occurs as cation below pH 9.6 (pk_a: 9.6; Devlin et al., 1977). The adsorption of both organic zwitterions to soils and soil minerals (Carrasquillo et al., 2008) as well as the adsorption of organic cations onto clays (Narine and Guy, 1981) and sediments (Brown and Combs, 1985) are well documented phenomena. Burns et al. (2009) found strong sorption of the cyanobacterial toxin saxitoxin, which occurs as protonated ion below pH 8.2, to clays and sediments. As a cation bridging mechanism has been reported for other organic zwitterions to enhance sorption to organic matter (MacKay and Canterburry, 2005), we hypothesize higher CYN sorption in the presence of divalent cations such as Ca.

In order to gain a better understanding of the role of toxin removal by adsorption during sediment passage the objective of this study was to (i) determine the adsorption coefficients of CYN and ATX according to the Freundlich and Langmuir model for sediments of various textures and to (ii) derive relevant sediment and hydrochemical characteristics which control CYN and ATX sorption.

2. Material and methods

To determine adsorption isotherms batch experiments were conducted with sediments of varying texture as outlined in the procedure of the OECD guideline 106 (OECD, 1997).

2.1. Materials

2.1.1. Sediments

We investigated 10 sediments of hydromorphic character from ponds (KHW, SRW), streams (Newel), aquifers (GW, Müggel), slow sand filter ponds (UBA), the G_r-horizon of a gley soil (Kyll), and three types of soils (NM, Mergel, Organic mud). With the exception of the three soils their sampling locations showed saturated conditions for most of the time during the year. Their origin and hydromorphic condition are summarized in Table 1 in the supplementary material. The physical parameters of the sediments (grain size distribution, water loss at 105 °C and loss on ignition at 550 °C) are displayed in Table 1, several chemical parameters (i.e. organic carbon (OC) content, C/N-ratio, pH_{CaCl_2}, potential cation exchange capacity (CEC_{pot}), and effective cation exchange capacity (CEC_{eff})) are shown in Table 2.

2.1.2. Chemicals

All solutions were made up in deionised water. For preparing a 0.01 M $CaCl_2$ solution (ionic strength I = 0.03 M) $CaCl_2 \times 2H_2O$ was used, the 0.03 M KCl solution (I = 0.03 M) was produced with KCl (both chemicals were obtained from Merck, Germany). Stock solutions of ATX were prepared using anatoxin-a-fumarate (Tocris, United Kingdom). Pure cylindrospermopsin (purchased from Dr. A. Humpage, Australian Water Quality Centre, Salisbury, Australia) was quantified using the extinction coefficient published by Sano et al. (2008). All stock solutions were made up in 0.01 M $CaCl_2$ solution and 0.03 M KCl solution, respectively.

2.2. Methods

2.2.1. Batch experiments

Prior to the main sorption experiment, preliminary experiments were conducted to identify appropriate (i) solid-solution

Table 1 – Physical sediment parameters (n.d.: not determined).

Sediments	Clay [%]	Silt [%]	Sand [%]	Water content [%]	Loss on ignition [%]
UBA	1	0	99	21.3	0.1
GW	2	2	96	8.1	0.6
NM	3	1	96	19.6	1.6
Mergel	2	9	89	7.6	0.0
Organic mud	n.d.	n.d.	n.d.	73.1	83.5
Organic mud-1	15	51	33	48.6	11.0
Müggel	9	17	74	15.5	0.9
KHW	6	14	80	46.7	6.2
Kyll	6	46	48	17.5	1.7
Newel	36	52	12	36.2	7.1
SRW	27	46	27	30.3	4.2