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Cylindrospermopsin degradation in sediments – The role of temperature, redox conditions, and dissolved organic carbon

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ABSTRACT

One possible consequence of increasing water temperatures due to global warming in middle Europe is the proliferation of cylindrospermopsin-producing species from warmer regions. This may lead to more frequent and increased cylindrospermopsin (CYN) concentrations in surface waters. Hence, efficient elimination of CYN is important where contaminated surface waters are used as a resource for drinking water production via sediment passage. Sediments are often characterized by a lack of oxygen and low temperature (i.e. approx. 10 °C). The presence of dissolved organic carbon (DOC) is not only known to enhance but also to retard contaminant degradation by influencing the extent of lag phases. So far CYN degradation has only been investigated under oxic conditions and at room temperature. Therefore, the aim of our experiments was to understand CYN degradation, focusing on the effects of i) anoxic conditions, ii) low temperature (i.e. 10 °C) in comparison to room temperature (23 ± 4 °C) and iii) DOC on lag phases. We used two natural sandy sediments (virgin and preconditioned) and surface water to conduct closed-loop column experiments. Anoxic conditions either inhibited CYN degradation completely or retarded CYN breakdown in comparison to oxic conditions ($T_{1/2}$ (oxic) = 2.4 days, $T_{1/2}$ (anoxic) = 23.6 days). A decrease in temperature from 20 °C to 10 °C slowed down degradation rates by a factor of 10. The presence of DOC shortened lag phases in virgin sediments at room temperature but induced a lag phase in preconditioned sediments at 10 °C, indicating potential substrate competition. These results show that information on physico-chemical conditions in sediments is crucial to assess the risk of CYN breakthrough.

1. Introduction

Cylindrospermopsin (CYN) is an alkaloid cyanobacterial toxin (Chiswell et al., 1999), which has been found in almost all continents. In Europe, CYN findings were reported in concentrations between 9 and 18 μg L^{-1} (Bogialli et al., 2006; Quesada et al., 2006; Rücker et al., 2007). However, increased lake water temperatures due to global warming may lead to enhanced proliferation of Nostocales cyanobacteria (Jöhnk et al., 2011) – to which most of the cylindrospermopsin-producing species belong – and thus to a higher abundance of CYN in middle Europe in the future.

Abbreviations: CYN, cylindrospermopsin; DOC, dissolved organic carbon.

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In contrast to the well studied microcystins, a large fraction of CYN concentrations (68–98%) occurs extracellularly, with peak concentrations in the water body toward the end of a bloom (Chiswell et al., 1999; 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 (Wörmer et al., 2008). These findings may have important implications for water authorities if concentrations in surface waters are in a health-relevant range (e.g. $>1\,\mu g\,L^{-1}$, as proposed by Humpage and Falconer, 2003 for drinking water). Hence, effective elimination of CYN has to be ensured if contaminated surface waters are used for drinking water production via sediment passage.

Riverbank filtration, artificial groundwater recharge and slow sand filtration are common methods for the natural (pre-)treatment of drinking water. Sediment passage may decrease toxin concentrations by dilution, adsorption and microbial degradation. These elimination processes are affected by several parameters such as sediment texture, hydrochemical conditions (i.e. pH, concentrations and type of dissolved organic matter (DOM), flow settings as well as by biotic and abiotic conditions governing microbial degradation).

Previous studies have shown CYN to degrade during sediment contact at oxic conditions and at room temperature (Klitzke et al., 2010). Everson et al. (2009) postulate reduced temperatures to lead to slower CYN degradation in the water due to lower microbial activity. In aquifers, temperature often fluctuates around 10 °C. Few investigations report temperature to affect the elimination of the cyanobacterial toxin microcystin. Grützmacher et al. (2007) found microcystin removal in a saturated sediment column to be higher in temperature ranges between 16 and 32 °C than at temperatures below 11 °C. Similarly, Wang et al. (2007) observed biodegradation of microcystin-LR in granular activated carbon filters to be temperature-dependent. However, at the moment, no data for temperature-dependent degradation of CYN in soils or sediments exist.

In a previous study conducted at room temperature, we could demonstrate that the presence of DOM enhances CYN degradation (Klitzke et al., 2010). However, this work did not address whether this effect would also play a significant role (i) at 10 °C, which is a temperature range often encountered in aquifers as well as (ii) in virgin sediments, where CYN degradation only starts after a lag phase (Klitzke et al., 2010).

Redox conditions in saturated sediments are often anoxic. Under such conditions, the elimination of many organic contaminants is often decelerated (for instance Czajka and Londry, 2006; Grützmacher et al., 2010). Everson et al. (2009) presume slow breakdown rates for CYN in the water in the absence of oxygen. They suppose this condition to inhibit the microbial activity associated with CYN degradation. However, so far, this effect has not been studied for CYN in contact with sediments. As microcystin degradation in sediments was shown to be slowed down under anoxic conditions in comparison to oxic conditions (Grützmacher et al., 2010) we also presume CYN degradation to be decelerated in an anoxic environment. Therefore, the aim of the work presented here was to fill the knowledge gaps on the impact of temperature, redox conditions and DOC on CYN degradation. To complement to the body of existing information, first results on CYN degradation (i) at 10 °C with and without DOC, (ii) in virgin sediments with and without DOC, and (iii) under reducing conditions are presented.

2. Material and methods

2.1. *Origin and characterization of sediments, waters and CYN used in the experiments*

A filter sand was obtained from one of the slow sand filters of the Federal Environment Agency's facility for technical-scale slow sand and bank filtration experiments (SIMULAF) in Berlin, Germany. The sediment texture was classified as medium sand with a content of fines and C_{org} of 1% and 0.7%, respectively. To study CYN degradation under reducing conditions, we additionally used a groundwater sediment, obtained from an aquifer north of Berlin (2.6–4.4 m below top ground surface). The sediment texture was medium-sandy fine sand with a content of fines and C_{org} of 4% and 0.04%, respectively. We used both "virgin" (i.e. sediments did not have any previous contact to CYN) and preconditioned sediments (i.e. after CYN exposure through previous experiments). The groundwater sediment stems from the same sample batch as the one used for the study in Klitzke et al. (2010). The filter sand was sampled at the same location but later than the one used in Klitzke et al. (2010), i.e. in April 2009 as opposed to July 2008. The surface water used in the experiments was obtained from the reservoir feeding the slow sand filters and was filtered through a 1.2 μm membrane (ME28, Schleicher & Schüll, Germany). The water does not have any previous history of CYN-producing cyanobacteria. Water pH amounted to 8.0 ± 0.2 and conductivity to $940\,\mu S\,cm^{-1} \pm 40\,\mu S\,cm^{-1}$. For the experiments conducted under anoxic conditions, we used anoxic groundwater that was extracted on-site from a quaternary aquifer.

Pure cylindrospermopsin (Alexis Chemicals, Germany) was used as standard material. In two experimental set-ups (denoted with "+ DOC", Table 1), dissolved organic carbon (DOC) was added to the CYN solution by dissolving natural organic matter (NOM) obtained by reverse osmosis from a Norwegian drinking water reservoir (1R108N Nordic Reservoir NOM, International Humic Substance Society).

2.2. *Column experiments*

The columns were made of quartz glass (inner diameter: 4.5 cm, length 18 cm) and were closed by teflon plugs at both ends. After filling the columns with the respective sediment, water was flushed through from the bottom to the top of the columns for at least 24 h prior to the beginning of the experiment. Sorption of CYN onto column material was tested in preliminary experiments and can hence be ruled out (data not shown). Retention of CYN by the respective sediments was found to be negligible (Klitzke et al., 2010). All experiments were conducted in duplicate.

Cylindrospermopsin degradation was determined in closed-loop column experiments (Fig. 1). After the outflow of the column, an online-probe was installed to record the redox potential of the solution. The presented values are corrected for the standard potential of the redox probe at 20 °C