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Occurrence and elimination of cyanobacterial toxins in drinking water treatment plants☆

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Abstract

Toxin-producing cyanobacteria (blue-green algae) are abundant in surface waters used as drinking water resources. The toxicity of one group of these toxins, the microcystins, and their presence in surface waters used for drinking water production has prompted the World Health Organization (WHO) to publish a provisional guideline value of 1.0 μg microcystin (MC)-LR/l drinking water. To verify the efficiency of two different water treatment systems with respect to reduction of cyanobacterial toxins, the concentrations of MC in water samples from surface waters and their associated water treatment plants in Switzerland and Germany were investigated. Toxin concentrations in samples from drinking water treatment plants ranged from below 1.0 μg MC-LR equiv./l to more than 8.0 μg/l in raw water and were distinctly below 1.0 μg/l after treatment. In addition, data to the worldwide occurrence of cyanobacteria in raw and final water of water works and the corresponding guidelines for cyanobacterial toxins in drinking water worldwide are summarized.

Keywords: Microcystin; Ozonation; Cyanobacteria; TOC; *Planktothrix rubescens*; *Microcystis aeruginosa*

Introduction

The majority of the populations in industrialized countries are dependent on drinking water from public or private water suppliers. These water treatment plants are required to guarantee the drinking water quality according to the respective national drinking water guidelines. These guidelines address microbial (e.g., *E. coli*, coliforme bacteria) and chemical (e.g., cyanides, pesticides) parameters as health-relevant endpoints and indicator parameters (smell, taste, conductivity) as a quality control for the proper functioning of the water treatment plants (Schmitz, 2001). Guidelines for cyanobacterial toxins in water exist in several countries worldwide (Table 1). Most of these countries have a history of problems with cyanobacterial contamination in drinking water reservoirs and they may serve as examples for the rest of the world. In Europe, cyanobacterial toxins are not yet clearly regulated. However, in the European Water Framework Directive (2000) (2000/60/EC), which characterizes high-priority water pollutants, toxin-producing cyanobacteria (blue-green algae) have been specifically highlighted as potential key hazardous pollutants. The harmful potential of cyanobacterial toxins for the population is appreciated in many European countries and has been described in many publications (Funari et al., 2000; Hitzfeld et al., 2000b; Thebault et al., 1995; Vasconcelos, 1999). The fact that cyanobacteria are able to exist even in hot springs in volcanic regions (Ward et al., 1998) and in cold and hot deserts such as Antarctica (Hitzfeld et al., 2000a; Wynn-Williams, 2000) or the Atacama desert (Wynn-Williams, 2000) underlines the omnipresence of these organisms. Cyanobacteria are ubiquitous in surface waters worldwide and many species including *Microcystis*, *Nodularia*, *Cylindrospermopsis*, *Anabaena*, and *Aphanizomenon* are known to produce toxins such as microcystins (MC), nodularins, cylindrospermopsins, anatoxins, and paralytic shellfish poisons (Landsberg, 2002). However, due to a paucity of toxicity data for other

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Table 1
Guideline values for toxic cyanobacterial secondary metabolites

	Microcystins	PSPs	Anatoxin-a	Cylindrospermopsin	
Australia	lifetime exposure: 1.3 μg/l brief period: 10 μg/l	3.0 μg/l (suggested for brief period)	mentioned in guideline (w/o value)	mentioned in guideline (w/o value)	(Fitzgerald et al., 1999; NHMRZ/ARMCANZ, 2001)
Brazil	1.0 μg/l	3.0 μg/l (suggested)	–	15 μg/l (suggested)	(Azevedo, 2001)
Canada	1.5 μg/l	–	–	–	(Health Canada, 2003)
France	1.0 μg/l	–	–	–	(France, 2001)
European Drinking Water Directive, 1998	0.1 μg/l (default value)[a]	0.1 μg/l (default value)[a]	0.1 μg/l (default value)[a]	0.1 μg/l (default value)[a]	(Schmidt et al., 2002)
New Zealand	1.0 μg/l	1.0 μg/l	3.0 μg/l [1.0 μg/l for anatoxin-a(s) + homoanatoxin]	3.0 μg/l	(Ministry of Health, 2002)
Oregon (USA)	1.0 μg/g (health food)	–	–	–	(Gilroy et al., 2000)
WHO	1.0 μg/l (provisional)	–	–	–	(WHO, 1998)

[a] The value of 0.1 μg/l was originally used for pesticides, but nowadays it is applied as a provisional value for other toxins whose character is unknown or as a quality target designed to be well below the concentration derived from health criteria (Schmidt et al., 2002).

toxins including the >80 other MC congeners, the World Health Organization (WHO, 1998) has set a provisional guideline value for MC-LR (L: lysine, R: arginine) of 1.0 μg/l drinking water (Table 1). Microcystins and nodularins have a high acute toxicity with LD50's ranging from 36 to 122 μg/kg in mice and rats i.p. or i.v. (Dawson, 1998; Sivonen et al., 1989) and have also been implicated in tumor promotion in both liver (Ito et al., 1997) and colon (Humpage et al., 2000). Nodularins and MCs are also suspected to induce liver carcinogenesis (Ohta et al., 1994; Zegura et al., 2003). The inhibition of protein phosphatase enzymes seems to be responsible for the toxicity of both substances, but additional mechanisms are likely.

Humans may come into contact with cyanobacterial toxins through ingestion or dermal contact with cyanobacteria and their respective toxins. Possible pathways for exposure are during recreational activities (Chorus et al., 2000; Pilotto et al., 1997), by ingestion of contaminated agricultural products (Abe et al., 1996; Codd et al., 1999; McElhiney et al., 2001), cyanobacterial health foods (Gilroy et al., 2000), or contaminated shellfish (Eriksson et al., 1989) and fish (Ernst et al., 2001). It is becoming increasingly clear that almost every part of the world depending on drinking water from surface waters, has or will encounter problems with toxic cyanobacteria in its drinking water system (Tables 2 and 3), due to the ubiquitous presence in raw water feeding into water treatment plants. Thus, water treatment systems must eliminate cyanobacteria and their toxins from the raw water. Conventional water treatment with only a filtration step (Grützmacher et al., 2002) or with an additional flocculation step (Lambert et al., 1996) has been shown to be ineffective in removing dissolved microcystins from water. Flocculation with an appropriate concentration of flocculent is suitable only for removing cyanobacterial cells from water. However, the possibility of cell lysis could lead to an increase in extracellular toxin concentration, which cannot be eliminated by the methods mentioned. Furthermore, intact cells have been observed in final water after the whole treatment train (Lepistö et al., 1994). In ozonation water treatment processes, both ozone and OH radicals work as oxidizing agents (Staehelin and Hoigné, 1985). Preozonation with 0.5–1.5 mg/l aims to inactivate bacteria (Lee and Deininger, 2000), viruses, and protozoa, and to detoxify harmful compounds such as phenols, polycyclic aromatics, and microcystins. Undesirable taste-and-odor substances are also eliminated. Furthermore, other natural organic matter is modified to products that are more easily adsorbed and filtered (Siddiqui et al., 1997). Subsequent to ozonation two-layer filters (pumice/quartz-sand) remove the majority of the organic substances (e.g., cyanobacterial cells) and thus act as a mechanical rough cleaning step. This function makes backwashing at regular intervals necessary to avoid saturation and clogging of the filters and consequently a breakthrough of cyanobacterial cells. Intermediate ozonation with ~0.5 mg/l is necessary to guarantee the elimination of harmful substances including cyanobacterial toxins, which survive the preceding treatment steps. Furthermore, intermediate ozonation improves particle removal in the subsequent filter system (Becker and O'Melia, 2001). Activated carbon eliminates the surplus ozone, adsorbs hydrophobic compounds, and acts as substrate for bacteria, which mineralize most of the organic by-products (ketones, aldehydes, acids) produced by the ozonation step (Lambert and Graham, 1995; Von Gunten, 1998). Thus, activated carbon filters act as biofilms that potentially metabolize organic compounds; however, they also show a significantly impaired ability to adsorb toxins. Moreover, biodegradation of microcystins by the biofilm does not seem to occur (Falconer et al., 1989; Lambert et al., 1996). The last