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# Fate of toxic cyanobacterial genera from natural bloom events during ozonation

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ABSTRACT

Intense accumulation of toxic cyanobacteria cells inside plants, unsuccessful removal of cells and consequent breakthrough of cells and toxins into treated water have been increasingly documented. Removal or destabilisation of cells in the pre-treatment stage using pre-ozonation could be an efficient practice as ozonation has been proven to be effective for the removal of cells and toxins. However, several unknowns including the ozone demand, the potential release of cell-bound toxins and organic matter and their impact on treatment train needs to be addressed. The general objective of this work was to study the impact of direct ozonation on different potentially toxic cyanobacteria genera from natural blooms. Water samples from five cyanobacterial bloom events in Lake Champlain (Canada) were ozonated using 2–5 mg/L $O_3$ for a contact time of maximum 10 min. Cyanobacterial taxonomic enumeration, cyanotoxins, organic matter and post-chlorination disinfection by-product formation potential analyses were conducted on all samples. *Anabaena*, *Aphanizomenon*, *Microcystis* and *Pseudanabaena* were detected in bloom water samples. Total cell numbers varied between 197,000 and 1,282,000 cells/mL prior to ozonation. Direct ozonation lysed (reduction in total cell numbers) 41%–80% of cells and reduced released toxins to below detection limits. *Microcystis* was the genus the least affected by ozonation. However, DOC releases of 0.6–3.5 mg/L were observed leading to maximum 86.92 μg/L and 61.56 μg/L additional total THMs (four trihalomethanes) and $HAA_6$ (six haloacetic acids) formation, respectively. The results of this study demonstrate that vigilant application of pre-ozonation under certain treatment conditions would help to avoid extreme toxic cells accumulation within water treatment plants.



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## 1. Introduction

Cyanobacteria and their associated toxins have been increasingly detected in drinking water sources and at the water intake of water treatment plants. The increase of global temperature caused by climate change affects the timing of blooms and favours the dominance of cyanobacteria, especially in nutrient rich environments (Elliott, 2012; Paerl and Paul, 2012). Certain cyanobacteria genera, e.g. *Anabaena*, *Aphanizomenon*, *Microcystis* and *Pseudanabaena*, are producers of several potent toxins. Microcystins with over 60 known analogues are the most commonly detected group of cyanotoxins, but the list of known cyanotoxins also includes saxitoxins, anatoxins, cylindrospermopsin and others (van Apeldoorn et al., 2007; Merel et al., 2013a). The human health effects of these toxins include gastroenteritis, cytotoxicity, liver damage and hepatotoxicity, and neurotoxic effects (van Apeldoorn et al., 2007; Corbel et al., 2014; Lévesque et al., 2014).

In response to the human health effects of cyanobacterial toxins, water regulatory authorities around the world have introduced cyanotoxin standards, and cyanobacteria threshold alert levels and management plans. The World Health Organisation (WHO) and several countries have issued guideline values ranging from 1.0 to 1.5 μg/L of microcystin-LR (MC-LR) in potable water (Chorus and Bartram, 1999; Merel et al., 2013b). Furthermore, WHO proposed two cyanobacteria alert levels for management of drinking sources: 2000 and 100,000 cells/mL titled WHO Alert Level 1 and 2, respectively (Chorus and Bartram, 1999).

Despite the recent scientific and technical advances in the treatment of potentially toxic cyanobacteria and cyanotoxins, new treatment challenges related to their accumulation in treatment plants have been identified in recent years. The presence of toxic blooms at the intake of water treatment plants can lead to the accumulation of toxic cyanobacteria cells within certain processes, e.g. sludge bed of sedimentation tanks, filter media, and sludge thickeners. Unless properly managed, this accumulation has the potential to release toxins (Zamyadi et al., 2012b). Recycling within the treatment plant could result in the breakthrough of toxins into treated water. Such risk has recently been documented in a full scale water treatment plant, as the passage of toxins, toxic cells and cell debris in filtered water hindered chlorination and resulted in the breakthrough of 2.47 μg/L total microcystins, surpassing the WHO and Quebec (Canada) provincial water quality standards in the treated drinking water (Zamyadi et al., 2012b). The accumulation of cells in sludge blanket of sludge bed clarifiers and in the sludge of sedimentation tanks constitutes a risk for toxin release that must be considered for sludge treatment and supernatant disposal or recycling.

Even in the case of non-toxic blooms, the accumulation of high densities of algal or cyanobacterial cells in the treatment plants can cause process malfunction and loss of compliance (Kommineni et al., 2009; Zamyadi et al., 2012b). Inefficient coagulation and the propensity of cyanobacteria cells to float have been shown to lead to the breakthrough of cyanobacteria cells in settled water (Kommineni et al., 2009; Hu et al., 2014). The accumulation of cyanobacteria cells in filters affects head loss development and decreases filter productivity; it also represents a potential for toxin accumulation and release and concerns about the treatment, disposal and recycling of filter backwash water (Kommineni et al., 2009; Zamyadi et al., 2012b, 2013b). Additionally, the removal by coagulation and filtration is species dependent (Henderson et al., 2010; Zamyadi et al., 2013b) and is affected by the presence of cell debris and of algal organic matter (both internal and external) (Henderson et al., 2010).

The removal of several classes of cyanotoxins by oxidants such as chlorine, ozone, chloramines, potassium permanganate and chlorine dioxide has been widely studied in recent years and the impact of major water quality parameters (e.g. organic matter, pH, temperature) thoroughly investigated (Miao and Tao, 2009; Miao et al., 2010; Al Momani and Jarrah, 2010; Merel et al., 2013b). Ozonation and advanced oxidation using $OH^{\bullet}$ are recognised as most effective as they readily oxidise microcystins to non-toxic degradation products (Rositano et al., 1998, 2001; Brookes et al., 2006; Onstad et al., 2007; Rodriguez et al., 2007). The efficiency of both molecular and radical ozone to degrade cyanotoxins has been evaluated at laboratory scale using standard cyanotoxin concentrates spiked in buffered ultrapure or natural water (Onstad et al., 2007; Al Momani and Jarrah, 2010). Although it is possible to predict the kinetics of the oxidation of free toxins, cyanotoxins are mainly present as cell bound and the extent of the oxidation of cell bound toxins is determined to the rate of their release from damaged cyanobacteria cells (Daly et al., 2007; Coral et al., 2013; Wert et al., 2014). Cell bound organic matter may also induce oxidant agent demand influencing the efficiency of toxin oxidation.

Pre-ozonation of cells may improve their removal by sedimentation and filtration because of changes in the external cell structure, excretion of polymeric materials and degradation of the released extracellular organic matter (EOM). A recent publication highlighted the benefit of pre-ozonation to reduce the potential of cyanobacterial cell accumulation within sludge bed of sedimentation tanks in a treatment plant with low risk of cyanobacterial presence at the source (Zamyadi et al., 2013a). However, the available information with regard to pre-ozonation and/or direct ozonation of potentially toxic cyanobacteria cells in this field is limited. Several questions regarding the release of cell-bound compounds (e.g. toxins, taste and odour compounds and organic matter) and their impact on efficiency of following treatment processes (e.g. contribution of cellular organic matter to the pool of disinfection by-products precursors) remain unknown.

The general objective of this work was to study the impact of direct ozonation of different potentially toxic cyanobacteria genera. The specific objectives of this study were: (1) to assess the impact of present cyanobacteria genera and variations in dominant genera on ozonation capacity to cause cell lysis, (2) to demonstrate the impact of direct ozonation on cell integrity and the release of cellular organic matter in natural bloom samples, (3) to investigate the fate of cell-bound toxins during ozonation of cells from natural bloom events, and (4) to assess the potential application of direct ozonation as an operational solution to prevent cells breakthrough into the plants and their consequent accumulation. To the best of our knowledge,