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Fate of toxic cyanobacterial cells and disinfection by-products formation after chlorination

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ABSTRACT

Drinking water sources in many regions are subject to proliferation of toxic cyanobacteria (CB). Chlorination of source water containing toxic cyanobacterial cells for diverse treatment purposes might cause cell damage, toxin release and disinfection by-products (DBP) formation. There is limited information available on chlorination of different toxic CB cells and DBP formation potentials. This work: (1) determines the extent of lysis and toxins/taste and odor compound release in chlorinated natural water from CB cells (*Anabaena circinalis*, *Microcystis aeruginosa*, *Cylindrospermopsis raciborskii*, and *Aphanizomenon issatsckenka*) from laboratory cultures and natural blooms; (2) assesses the rates of oxidation of toxins by free chlorine under environmental conditions; (3) studies the DBP formation associated with the chlorination of CB cell suspensions. With chlorine exposure (CT) value of <4.0 mg min/L >60% cells lost viability causing toxin release. Cell membrane damage occurred faster than oxidation of released toxins. Kinetic analysis of the oxidation of toxins in natural water revealed significant differences in their susceptibility to chlorine, saxitoxins being the easiest to oxidize, followed by cylindrospermopsin and microcystin-LR. Furthermore, concentrations of trihalomethanes and haloacetic acids (<40 μg/L) and N-nitrosodimethylamine (<10 ng/L) as chlorination by-products were lower than the guideline values even at the highest CT value (220 mg min/L). However, the DBP concentrations in environmental bloom conditions with very high cell numbers were over the guideline values.

1. Introduction

The effects of global climate change, particularly changes in water temperature and nutrient loads, appear to enhance the proliferation of potentially toxic cyanobacteria (CB) in drinking water (DW) sources in many parts of the world (Elliott et al., 2006; Jöhnk et al., 2008; Paul, 2008). The increasing frequency and intensity of toxic CB blooms in DW sources and detection of cyanotoxins in drinking water treatment plants (WTP) intakes and treated water is causing several major challenges for DW production and water reuse (Lahti et al., 2001; Svrcek and Smith, 2004; Merel et al., 2010b; McQuaid et al., 2011). Many cyanotoxins have been identified, with different degrees and mechanisms of human toxicity. Neuro- and hepatotoxicity are the major mechanisms reported to date, with some toxins displaying tumour promoting, and even

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carcinogenic properties. In addition, some CB species produce several different toxins, and the toxins produced by a particular species can vary between geographical regions (Svrcek and Smith, 2004; Humpage, 2008; Newcombe et al., 2010). The main toxins of interest, the CB species producing these toxins, and their toxicity for humans are summarized in the supplementary data (SD) section (Table SD-S1 and Figure SD-S2).

The presence of CB can also cause process disturbances in WTP using filtration, such as excessive head loss development, short filter runs and increased coagulant demand (Mouchet and Bonnelye, 1998; Merel et al., 2010b). It has been suggested that the accumulation of CB cells in certain treatment processes (e.g. sludge bed of sedimentation tank, surfaces of clarifiers and filters) can be associated with significant toxin release during treatment and raises concerns about the effectiveness of post-oxidation (Pietsch et al., 2002). The release of CB metabolites during treatment has also raised issues of taste and odor (T&O) materials, e.g. geosmin and 2-methylisoborneol (MIB) (SD section: Figure SD-S3), which are aesthetically unpleasant (Lin et al., 2009; Hobson et al., 2010), trihalomethanes (THM), haloacetic acids (HAA) and N-nitrosodimethylamine (NDMA) precursors (El-Dib and Ali, 1994; Graham et al., 1998), assimilable carbon (Mouchet and Pourriot, 1992), and oxidant demand (Merel et al., 2010b).

In many smaller regional and remote water supplies and in developing countries, efficient filtration processes are often not available for DW treatment. This situation could lead to the chlorination of raw water containing potentially toxic CB cells. Furthermore, pre-oxidation ahead of filtration is commonly used in water treatment for many purposes, including the reduction of algal cells and filter cycle optimization (Mouchet and Bonnelye, 1998; Chen and Yeh, 2005). The susceptibility to lysis of CB subjected to chlorination is influenced by the species present, the physiological state of the cells, e.g. the growth phase (Pietsch et al., 2002; Meriluoto and Codd, 2005; Lin et al., 2009), and the conditions of oxidation. It has been documented that during chlorination of a cyanobacterial suspension, the rate of toxin release is determined by the rate of the loss of membrane integrity (Daly et al., 2007; Zamyadi et al., 2010).

Chlorine can effectively oxidize different cyanotoxins under specific conditions (Ho et al., 2006,2009). For the confident application of chlorine to CB cell suspensions, the important parameters to consider are the concentration of chlorine, the CB cells and/or toxin contact time with chlorine and relevant oxidation conditions (pH, temperature, and hydraulic mixing). The exposure to the oxidant is most often expressed in CT, the residual concentration of the oxidant multiplied by time (Ho et al., 2006). Oxidation of the released intracellular toxins will follow the oxidation kinetics established for dissolved toxins, if sufficient residual oxidant is still present at the moment of release (Daly et al., 2007; Zamyadi et al., 2010).

Cell lysis may also lead to a release of cell-bound particulate and dissolved organic carbon (DOC) that exert a significant chlorine demand and contribute to the disinfection by-products (DBP) precursor pool (Fang et al., 2010). Laboratory experiments in controlled conditions using culture stocks suggest that oxidant demand from the cells and the released cell-bound organics can easily be met with cell numbers <47,000 cells/mL and proper accounting of the chlorine demand of the culture media (Zamyadi et al., 2010). Published results on chlorine demand and DBP formation potential of cyanobacterial suspensions should be assessed in the light of:

- The differences between algal and cyanobacterial cell composition (e.g. cell membrane). Within a particular phylum, the species can vary significantly in terms of their morphology (SD section: Figure SD-S4) and the composition and quantity of excreted organic matter (Henderson et al., 2008).
- The quantity and composition of organic compounds associated with the cells exposed to chlorine. CB cells contain a wide range of intracellular compounds, those released due to autolysis of cells, often referred to as extracellular organic matter (EOM) and those released by compromised lysis, referred to as internal organic matter (IOM) (Fang et al., 2010). The conditions of testing in the laboratory determine the density of cells and the accumulation of EOM, and significant accumulation can occur in batch cultures (Hoyer et al., 1985; Nguyen et al., 2005). EOM release varies widely with the cell growth phase. The organic composition and character of EOM and IOM compounds in CB cells will determine its reactivity to chlorine (Bond et al., 2009; Huang et al., 2009). Furthermore in natural conditions, the background DOC concentrations range widely (1–50 mg/L) depending on the organic matrix (Thurman, 1985) and these will also have an impact on the chlorine reactivity of the system.
- The concentration of chlorine applied to the cells and used for the DBP testing. Typically industry dosages are low (<1.5 Cl_2:DOC ratio) as opposed to more aggressive dosages applied in laboratory tests (1.7–5 Cl_2:DOC ratio) to oxidize dense cell suspensions and to determine DBP formation potential (Wardlaw et al., 1991; Nguyen et al., 2005; Daly et al., 2007). Typical pre-chlorination doses vary between 0.25 and 2 mg/l and are adjusted according to water quality parameters (e.g. ammonia concentrations) and the water quality goals to be achieved (e.g. manganese removal and plant hygiene) (Agence Française de Sécurité Sanitaire des Aliments and Agence Française de Sécurité Sanitaire de l'Environnement et du Travail, 2006).

Results from limited information on the impact of chlorination of cell-bound toxins and resulting DBP formation are contradictory (Huang et al., 2009; Zamyadi et al., 2010). Table 1 summarizes the chlorination conditions and DPB yields reported from various laboratory trials using cultured strains under a range of chlorination conditions. The diversity of chlorination conditions and the accumulation of EOM in the culture media limit our ability to extend these yields to full scale operations. Consequently, there is a need to better understand the limitations of the oxidation of CB cells and their toxins in natural water, subsequent toxin release and oxidation, and the DBP formation. The objectives of this research were: (1) to determine the extent of lysis and toxins/T&O compounds release in chlorinated natural water from CB cells from laboratory cultures and natural blooms; (2) to assess the rates of oxidation of toxins by free chlorine in environmental conditions; (3) to study the DBP formation associated with the chlorination of CB cell suspensions. To the best of our