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Characterisation of algogenic organic matter during an algal bloom and its implications for trihalomethane formation

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ABSTRACT

It is predicated that algal blooms will become an increasing problem under changing climatic conditions. This is particularly concerning for the potable water treatment industry since algogenic organic matter (AOM) in surface waters supplying water treatment works (WTWs) can cause a number of treatment issues. However, whilst previous studies have shown that AOM is distinct from terrigenous, humic-dominated organic matter, limited information exists relating to changes in the character of AOM during different algal growth phases. In this study, reservoir water containing dissolved organic carbon (DOC) dominated by humic material was enriched with nutrient medium to create an algal bloom. Over the course of the algal bloom, DOC was characterised using XAD-fractionation and UV absorbance measurements. In addition, the reactivity of DOC with chlorine both before and after XAD-fractionation was assessed using trihalomethane formation potential (THMFP) and bromine incorporation measurements to monitor whether THM yield and speciation varied between different growth phases. Characterisation of DOC during the algal bloom indicated a shift towards more hydrophilic, aliphatic (low specific UV absorbance; SUVA) DOC with the release of extracellular organic matter (EOM) and later intracellular organic matter (IOM) during cell lysis. XAD-fractionation results suggest that algae produce predominantly hydrophilic neutral (HPIN) DOC. In contrast to some existing research, our study shows a marked change in DOC reactivity over time with a reduction in standardised THMFP (STHMFP) and the initial rate of THM formation observed as the algal bloom progressed. However, bromine incorporation increased with culture age.

1. Introduction

Algogenic organic matter (AOM), consisting of cells, extracellular organic matter (EOM; released from algal cells by diffusion) and intracellular organic matter (IOM; released from senescent algal cells during cell lysis), causes a number of issues in potable water treatment. These substances may contribute taste and odour, elevate total organic carbon (TOC) levels, increase coagulant and chlorine demand, cause membrane fouling and lead to an increase in potentially-harmful disinfection by-products (DBPs) such as trihalomethanes (THMs) (Bernhardt et al., 1991; Nguyen et al., 2005; Li et al., 2012). Some species of algae also produce toxic metabolites which present a public health risk (Žegura et al., 2011). The frequency and duration of algal blooms is predicted to increase as a result of climate change (Ritson et al., 2014). Thus, developing a better

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understanding of the changes in water quality and treatability during these episodes is important in allowing water treatment companies to adapt to a future treatment scenario.

Within the DOC pool, AOM shows a number of differences from natural organic matter (NOM) of terrigenous origin. Firstly, AOM has a higher nitrogen content than humic material due to its proteinaceous origin; TOC/TON ratios are reported as follows: NOM $\gg$ EOM > IOM $\approx$ algal cells (Fang et al., 2010). In addition, AOM is more biodegradable and is characterised by lower molecular weights (MWs) (Leenheer and Croue, 2003; Nguyen et al., 2005; Fang et al., 2010). XAD-fractionation and specific UV absorbance (SUVA) measurements suggest that AOM tends to contain more hydrophilic and less aromatic carbon (Her et al., 2004; Leloup et al., 2013; Zhou et al., 2014). AOM characteristics also change as an algal bloom progresses through a series of growth phases (typically: lag phase, exponential growth phase, stationary phase and death phase). EOM is mostly released during the exponential growth phase and is composed of lower MW compounds such as glycolic and amino acids. IOM, released from senescent cells, mostly during the death phase, is composed of higher MW products such as polysaccharides (Huang et al., 2009).

Though algal cells tend to be associated with higher THM formation potential (THMFP), standardised for carbon concentration (STHMFP) than IOM and EOM (Yang et al., 2011), coagulation-flocculation is generally effective in removing algal cells during water treatment (Henderson et al., 2010). Therefore, EOM and IOM represent the main algogenic THM precursors in potable water treatment. Under standardised chlorination conditions, the STHMFP of AOM varies between algal species, though contradictory results have been reported with regard to the relative reactivity of blue–green algae vs. green algae vs. diatoms (Plummer and Edzwald, 2001; Nguyen et al., 2005). Few studies have compared STHMFP values during different algal growth phases and contradictory results have been reported with regard to the reactivity of AOM as an algal bloom progresses. Nguyen et al. (2005) and Huang et al. (2009) concluded that DOC reactivity (STHMFP) did not vary significantly as a function of growth phase but only Huang et al. (2009) measured STHMFP during the death phase when large amounts of IOM are released into solution. Conversely, Yang et al. (2011) reported TOC and THMFP data that suggested a peak in STHMFP during the exponential growth phase. Furthermore, there are very limited data available for THM formation rates during different growth phases – an important consideration in a potable water treatment context since residence times of water in distribution systems are generally much shorter than the 7 d incubation periods typically used in the measurement of STHMFP. The speciation of THMs and particularly, the percentage of brominated THMs (BrTHMs) formed, is also reported to vary between species of algae and according to growth phase as a result of changing AOM character (Huang et al., 2009; Yang et al., 2011) although there remains limited research in this area. This issue is important since BrTHMs are reported to be more carcinogenic than $CHCl_3$ (Richardson et al., 2007). To our knowledge, bromine incorporation of individual XAD fractions during chlorination has not yet been assessed during an algal bloom.

In this study, an algal bloom was generated in the laboratory using water collected from an upland drinking water reservoir by enriching with nutrient medium. A natural sample, as opposed to a pure algal culture was used to more accurately reflect field conditions and therefore better represent the water treatment scenario. Quantification and characterisation of DOC including XAD-fractionation and THMFP measurements were undertaken during the different growth phases. The data were used to assess how STHMFP, THM formation rate and bromine incorporation varied with algal growth phase and compared with the raw reservoir water.

2. Methods

2.1. Site description and sample collection

The water used in the study was collected from a UK upland drinking water reservoir. Its catchment comprises extensive areas of peatland (32%) and grassland (38%) as well as mainly-coniferous forest plantations (30%) (Cohen, 2009). Although algal populations are normally low in this reservoir, the drinking water provider has observed increased algal biomass in late spring/early summer. For this study, 10 L of water was collected from the surface (0–1 m depth) of the reservoir in May 2013 and transported immediately to the laboratory. Since the composition of natural surface water tends to fluctuate through time, the use of a natural sample in this study raises issues about repeatability. However, the use of this method was necessary to ensure that microbiological processes more accurately reflected those of a drinking water reservoir. In order to enable an appropriate comparison with existing research findings, we also sought to identify the species present in the algal bloom.

2.2. Cultivation and measurement of algae

A 30% Bold Basal medium with threefold nitrogen and vitamins (3N-BBM+V) (CCAP, UK) was made using 10 L of reservoir water. During a preliminary study, chlorophyll-*a* measurements indicated that this nutrient concentration was sufficient to produce an algal bloom. The solution was transferred to a 15 L glass jar, placed in a naturally-lit area of the laboratory and provided with aeration *via* an air pump connected to a ceramic air stone.

Algal population density was monitored by measuring chlorophyll-*a* concentration. These measurements were plotted over time and used to decide on the timing of the collection of larger sub-samples to represent distinct growth phases. For chlorophyll-*a* measurement, a 20 mL sub-sample was filtered through a Whatman GF/C filter which was then placed