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Carbonaceous and nitrogenous disinfection by-product formation from algal organic matter

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HIGHLIGHTS

- AOM contains predominantly (52–81%) hydrophilic organic matter.
- AOM forms significant amounts of carbonaceous and nitrogenous DBPs.
- Cyanobacteria *Microcystis aeruginosa*-AOM forms more HAN than other algae studied.
- Growth phase of algae has greater impact on DBP formation than its taxonomic group.
- Correlations between DBPFP and specific AOM chemical attributes are generally weak.

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ABSTRACT

Seasonal algal blooms in drinking water sources release intracellular and extracellular algal organic matter (AOM) in significant concentrations into the water. This organic matter provides precursors for disinfection by-products (DBPs) formed when the water is subsequently chlorinated at the final disinfection stage of the potable water treatment process. This paper presents results of AOM characterisation from five algal species (three cyanobacteria, one diatom and one green) alongside the measurement of the DBP formation potential from the AOM of six algal species (an additional diatom). The character was explored in terms of hydrophilicity, charge and protein and carbohydrate content. 18 DBPs were measured following chlorination of the AOM samples: the four trihalomethanes (THMs), nine haloacetic acids (HAAs), four haloacetonitriles (HANs) and one halonitromethane (HNM).

The AOM was found to be mainly hydrophilic (52 and 81%) in nature. Yields of up to 92.4 μg mg^{-1} C carbonaceous DBPs were measured, with few consistent trends between DBP formation propensity and either the specific ultraviolet absorbance (SUVA) or the chemical characteristics. The AOM from diatomaceous algae formed significant amounts of nitrogenous DBPs (up to 1.7 μg mg^{-1} C). The weak trends in DBPFP may be attributable to the hydrophilic nature of AOM, which also makes it more challenging to remove by conventional water treatment processes.

1. Introduction

Chlorination of drinking water is known to cause the formation of disinfection by products (DBPs) which are a health concern (Richardson, 2003). Carbonaceous DBPs (C-DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) are formed when the organic matter (OM) in the water reacts with chlorine. THMs are widely regulated at 80, 100, 100 and 250 μg L^{-1} for the sum of four THMs in the USA, Europe, Canada and Australia respectively (US EPA, 1998; Health Canada, 2012; EU Council Directive, 1998; NHMRC NRMMC, 2011). Nitrogenous DBPs (N-DBPs) such as haloacetonitriles (HAN) and halonitromethanes

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Abbreviations

AOM	algal organic matter
BCAA	bromochloroacetic acid
BDCAA	bromodichloroacetic acid
C-DBPs	Carbonaceous DBPs
DBAA	dibromoacetic acid
DBCAA	dibromochloroacetic acid
DBPs	disinfection by-products
DCAA	dichloroacetic acid
DCAN	dichloroacetonitrile
DOC	dissolved organic carbon
DWI	Drinking Water Inspectorate
DXAA	dihalogenated acetic acids
ECD	electron capture detection
EOM	extracellular organic matter
GC	gas chromatography
HAAs	haloacetic acids
HANs	haloacetonitriles
HNMs	halonitromethanes
HPI	hydrophilic organic fraction
HPO	hydrophobic organic fraction
IC	inorganic carbon
MBAA	monobromoacetic acid
MCAA	monochloroacetic acid
MXAA	monohalogenated acetic acids
N-DBPs	Nitrogenous DBPs
NOM	natural organic matter
OM	organic matter
SUVA	specific ultraviolet absorbance
TBAA	tribromoacetic acid
TC	total carbon
TCAA	trichloroacetic acid
TCAN	trichloroacetonitrile
TCM	trichloromethane
TCNM	trichloronitromethane
THMs	trihalomethanes
TPI	transphilic organic fraction
TXAA	trihalogenated acetic acids
USEPA	United States Environmental Protection Agency
UV_{254}	ultraviolet absorbance at 254 nm
WHO	World Health Organisation

(HNM) are also of health concern and have been shown to be more cytotoxic and genotoxic than C-DBPs (Plewa et al., 2002). They are not regulated but some (dichloroacetonitrile and dibromoacetonitrile at 20 and 70 μg L^{-1} respectively) are incorporated in the WHO drinking water guidelines (WHO, 2006). Although in the EU THMs are the only chlorinated DBPs regulated, the approach to meeting the regulation is becoming risk based; regulations make clear the duty to minimise DBPs as a whole.

The most studied type of OM is terrestrial or natural organic matter (NOM) which varies seasonally by, for example, leaching from soil (Thibodeaux and Aguilar, 2005). Advances in water treatment and an understanding of NOM behaviour have enabled sufficient and enhanced removal of organic DBP precursors to minimise DBP formation. The seasonality of the NOM quantities and character can be addressed with enhanced coagulation controlled through UV_{254} (Fabris et al., 2013) and zeta potential (Sharp et al., 2006) monitoring. The yield of DBPs (μg/mg C or μg/UV254) from NOM has been shown to correlate with dissolved organic carbon (DOC) and UV absorbance at 254 nm (UV254); reported yield values for THMs and HAAs have ranged from 61 to 124 μg/mg C across various studies (Table 2).

A less extensively studied source of OM is from algae, generating dissolved organic carbon (DOC) levels of 1–25 mg L^{-1} (Nguyen et al., 2005) from algal organic matter (AOM) (Pivokonsky et al., 2014). Besides contributing to the organic carbon content in water, algal cells contain organic nitrogen in the form of polysaccharides, proteins, peptides, amino sugars and other trace organic acids (Huang et al., 2009). AOM arises (a) extracellularly via metabolic excretion, forming extracellular organic matter (EOM) or (b) intracellularly due to autolysis of cells, forming intracellular organic matter (IOM). AOM is known to comprise proteins, neutral and charged polysaccharides, nucleic acids, lipids and small molecules, of which polysaccharides can comprise up to 80–90% of the total release. The IOM proportion increases with increasing age of the algae system (Henderson et al., 2008). EOM and IOM are of interest when studying the DBPs formed when algae arises in source waters, since they may be recalcitrant to water treatment (Henderson et al., 2010).

The study of THM and HAA formation from AOM (Wachter and Andelman, 1984; Schmidt et al., 1998; Nguyen et al., 2005; Huang et al., 2009; Zhou et al., 2014) has generally been focused on the chlorination of water containing algal cells (Hong et al., 2009; Huang et al., 2009; Liao et al., 2015). Both algal cells and AOM can potentially generate significant amounts of THMs and HAAs. There has also been some work on the formation of nitrogenous DBPs, such as HANs, from chlorination of algal cells and/or AOM and its fractions (Oliver, 1983; Fang et al., 2010; Zhou et al., 2014). As with NOM, AOM can be fractionated according to both size and chemistry, with studies indicating the hydrophilic (HPI) chemical fraction to dominate over the transphilic (TPI) and hydrophobic (HPO) fractions regardless of the status of growth in the cell life cycle (Table 1). Studies of fraction yield, the mass of chlorinated DBP formed per unit mass of organic carbon in μg DBP per mg C, indicate similar DBP formation trends in AOM as reported for NOM, the most reactive fractions being those at higher molecular weight (Lui et al., 2012) and hydrophobicity (Zhou et al., 2014).

A summary (Table 2) of overall trends in yield for the C-DBPs indicate a number of key facets:

a) The most abundant data relate to THMs, and trichloromethane (TCM) specifically;
b) The reported TCM yield value for a single species (*Microcystis aeruginosa*) varies by more than a factor of two across the five studies;
c) Most studies have been based on one or two species, rather than a wider range;
d) The chlorination conditions adopted vary between the studies with respect to the to Cl_2:C ratio and exposure time;

Table 1
% distribution of AOM between the three chemical fractions, *Microcystis aeruginosa*.

Growth phase	HPO	TPI	HPI	Reference
Exponential	27	4	69	Pivokonsky et al., 2014
Exponential	24	9	67	Zhou et al., 2014
Exponential	2	23	75	Leloup et al., 2012
Stationary	20	19	61	Leloup et al., 2012
Stationary	42	6	52	Qu et al., 2012
Stationary	24	17	59	Henderson et al., 2008