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

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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.

Keywords

Algae, trihalomethanes, haloacetic acids, haloacetonitriles, characterisation

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

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 (USEPA, 1998, Health Canada, 2012, EU, 1998, NHMRC, 2011). Nitrogenous DBPs (N-DBPs) such as haloacetonitriles (HAN) and halonitromethanes (HNM) are also of health concern and have been shown to be more cytotoxic and genotoxic than C-DBPs (Plewa, 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, 2016). 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, 2008; Huang et al. 2009; Laio 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

131 as reported for NOM, the most reactive fractions being those at higher molecular weight (Lui
132 et al, 2012) and hydrophobicity (Zhou et al, 2014).

133

134 **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, 2013
Stationary	20	19	61	Leloup et al, 2013
Stationary	42	6	52	Qu et al, 2012
Stationary	24	17	59	Henderson et al, 2008

135

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

137 a) The most abundant data relate to THMs, and trichloromethane (TCM) specifically;

138 b) The reported TCM yield value for a single species (*Microcystis aeruginosa*) varies by more
139 than a factor of two across the five studies;

140 c) Most studies have been based on one or two species, rather than a wider range;

141 d) The chlorination conditions adopted vary between the studies with respect to the to Cl_2:C
142 ratio and exposure time;

143 e) The limited data available suggests that the phase of the growth cycle may also influence
144 both the amount and the yield of the DBP generated.

145

146 Interpretation of the available literature data across different studies is challenged by the
147 different experimental conditions adopted, the differing fractions of the algal matter studied,
148 and the limited scope of the studies in terms of the number of species investigated
149 (predominantly one or two). It is of interest to establish whether any trends or patterns if DBP
150 formation, and yield specifically, exist for AOM across different algal species. AOM is of
151 practical interest since the algal solids are retained by the filtration process, the dissolved AOM
152 component being the fraction subjected to final chlorination. Both C- and N-DBP formation is
153 considered from AOM of six algal species at the onset of the stationary phase. Characterisation

encompasses hydrophilicity, charge, protein and carbohydrate content, with a view to linking character to DBP formation potential with reference to THMs, HAAs, HANs and one HNM (trichloronitromethane, TCNM).

Table 2: Summary of selected published chlorinated DBP yield data

Algal species	TCM	DCAA	TCAA	Cl_2:C	*t,* h	Reference
	($\mu g\ mg^{-1}$ C)					
Anabaena flos-aquae[1] [a]	35	26	22	-[4]	168	Huang et al., 2009
Anabaena flos-aquae[1] [a]	18	-	-	1.4	24	Wachter & Andelman, 1984
Cyclotella meneghiniana [b]	29	-	-	11	72, 168	Laio et al, 2015
Chaetoceros mulleri [a]	29	-	-	5	168	Nguyen et al. 2005
Chlamydomonas sp.[b]	25	213	67	20	120	Lui et al, 2012
Microcystis aeruginosa [b]	61	-	-	-[4]	168	Huang et al. 2009
Microcystis aeruginosa[1] [a]	35	42	24	-[4]	168	Huang et al., 2009
Microcystis aeruginosa[2] [a]	16	11	-	5	72	Fang et al., 2010
Microcystis aeruginosa[1][a]	27	11	11	3	72	Qi et al, 2016
Microcystis aeruginosa [b]	21	-	-	7.1	72, 168	Laio et al, 2015
Microcystis aeruginosa[1,3] [a]	33	-	-	5	72	Zhou et al, 2014
Nitzschia sp. [b]	48	25	19	10	96	Hong et al, 2008
Oscillatoria sp. [b]	26	34	39	10	96	Hong et al, 2008
Oscillatoria prolifera [a]	30	-	-	5	168	Nguyen et al. 2005
Scenedesmus quadricauda [a]	48	35	23	5	168	Nguyen et al. 2005
Scenedesmus quadricauda [b]	64	-	-	5	168	Nguyen et al. 2005

Cl_2:C chlorine:carbon mass ratio; *t* chlorination time; [1]Exponential growth phase; [2]Stationary growth phase; [3]HPO fraction; [4]>0.5 mg/L residual; [5]20 mg/L; [a] – AOM, [b] – algal cells

2 Materials and methods

2.1 Algal cultivation

Freshwater algae *Scenedesmus subspicatus* (276/20)*, Aphanizomenon flos-aquae* (1401/3)*, Anabaena flos-Aquae* (1403/13B) and *Microcystis aeruginosa* (1450/3) *Asterionella Formosa* (1005/9) (CCAP, Scotland) and *Melosira sp.* (JA386) (Sciento, UK) were cultured according to recommended conditions (Table 3). Lighting was supplied by a *Sun-glo* and an *Aqua-glo* 30W lamp. Neutral density filters were used with the lights for all species except *Scenedesmus subspicatus*. Each species grew at a different rate and reached the maximum phase of growth with different cell concentrations (Table 3). AOM was extracted from each algal species once exponential growth conditions had been established and at the onset of the stationary phase. Checks were undertaken on a daily basis to ensure contamination had not occurred and to determine cell concentrations: as with previous studies, with cultivation of algae on a similar scale, cultures were only invaded by other organisms in the late stationary/decline phase (Lüsse et al., 1985). Cell numbers were measured in triplicate using a light microscope and haemocytometer.0

177

178 **Table 3:** Algae cell concentrations and time of growth

Algal species	Max. cell concentration (cells/ml)	Days taken	Cultivation temperature (°C)	Light/dark cycle (h)	Shaking regime	Growth media
Scenedesmus subspicatus	1.8×10^6	14	20	16/8	120 rpm	Jaworski
Aphanizomenon flos-aquae	1.8×10^6	28	20	16/8	120 rpm	Jaworski
Anabaena flos-aquae	8.8×10^5	30	20	16/8	120 rpm	Blue/green (no N_2)
Microcystis aeruginosa	1.5×10^7	32	20	16/8	120 rpm	Jaworski
Asterionella Formosa	2.9×10^5	24	15	14/10	By hand	Diatom
Melosira sp.	1.9×10^4	8	15	14/10	By hand	Diatom

179
180

181 ### *2.2 AOM extraction and characterisation*

182 AOM was extracted by centrifuging 1 L of algal cell suspension at 4,000 rcf (relative
183 centrifugal force) for 15-30 minutes. The supernatant was filtered with a 0.7 μm glass
184 microfiber filter paper (Fisher Scientific, UK).

185

186 Specific ultraviolet absorbance (SUVA) in L m^{-1} mg C^{-1} was determined from the ratio of the
187 254 nm UV absorbance (m^{-1}) to the DOC concentration (mg C L^{-1}). UV absorbance was
188 measured using a Jenway 6505 UV/Vis spectrophotometer (Patterson Scientific, UK). The
189 isoelectric point was determined by measuring the zeta potential (mV) over a pH range from
190 0-10. Zeta potential was measured using a Malvern ZetaSizer 2000 (Malvern, UK).
191 Measurements were carried out in triplicate.

192

193 Carbohydrate content was determined using the phenol–sulphuric acid method (Zhang et al.,
194 1999; Dubois et al., 1956). Protein analysis was carried out using the modified Lowry method
195 (Frølund et al., 1995). Glucose and bovine serum albumin were used for calibration with
196 absorbance at 480 nm and 750 nm respectively using the Jenway spectrophotometer. Protein
197 and carbohydrate measurements were triplicated.

198

199 The hydrophilicity and hydrophobicity of the AOM samples was determined by fractionation
200 using XAD resins (XAD-7HP and XAD-4) in tandem according to Malcolm and MacCarthy
201 (1992) and reported by Sharp et al. (2006). Charge density (meq g^{-1}) was measured using a
202 back titration adapted from Kam and Gregory (2001) and described in Sharp et al. (2006).

203

204 DOC was measured using a Shimadzu TOC-5000A analyser (Shimadzu, UK) on filtered
205 samples. DOC was calculated by subtraction of the measured inorganic carbon (IC) from the
206 total carbon (TC). The machine was calibrated daily. Up to five replicates were measured and
207 an average of three reported to reduce the coefficient of variance to <2%.

208

209 ***2.3 DBP formation and quantification***

210 Chlorination employed a method adapted from standard methods (APHA, 1992). This involved
211 buffering samples at pH 7, adding an excess of free chlorine at 5 mg Cl_2 mg^{-1} C and storing for
212 seven days at 20°C. Chlorine residuals (measured in the range 0.5-1.2 mg/L) were quenched
213 using 100 mg L^{-1} ammonium chloride for HAA_9 and HAN_4 and TCNM analysis and 100 mg
214 L^{-1} sodium sulphite for THM_4 analysis. Additionally THM_4, HAN_4 and TCNM samples were
215 buffered at pH 4.5-5.5.

216

217 THM_4 (trichloromethane, dichlorobromomethane, dibromochloromethane, tribromomethane)
218 HAN_4 (bromochloroacetonitrile, dibromoacetonitrile, dichloroacetonitrile, trichloroaceto-
219 nitrile) and TCNM were extracted using a modified form of USEPA Method 551.1. This
220 method involved salted liquid/liquid extraction with solvent extracts analysed by gas
221 chromatography (GC) with microelectron capture detection (μECD) (Agilent 6890). HAA_9
222 (monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid
223 (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid

(DBAA), bromodichloroacetic acid (DBCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA)) were analysed using a modified form of USEPA Method 552.3 (Tung et al., 2006). The derivatised HAAs (methyl esters) were measured using GC-μECD. All samples were chlorinated and analysed in duplicate. The limit of quantification for all DBPs was 1 μg L^{-1}, except for MCAA where the quantification limit was 2 μg L^{-1}. DBP yields were calculated by dividing the concentration of DBP (in μg L^{-1}) by the DOC concentration (in mg L^{-1}) to give values in μg mg C^{-1}.

3 Results

3.1 AOM characteristics

AOM from all algae characterised was predominantly hydrophilic, as suggested by low SUVA values (0.34-1.7 m^{-1} L mg C^{-1}) and verified by the high percentage (from 54% for *Scenedesmus subspicatus* to 81% for the cyanobacteria *Anabaena flos-aquae*) of hydrophilic material (Table 4). This is in accordance with other researchers, for which HPI fractions of 52-73% have been reported (Qu et al., 2012, Henderson et al., 2009). The charge density of all extracted AOM was negligible except for that from the cyanobacteria *Microcystis aeruginosa*, measured at 0.2 meq g^{-1} and indicating the excreted organics to be predominantly uncharged. The isoelectric point of the AOM samples ranged from 0.9 to 3.2 with the lowest value observed for the AOM from the diatom *Asterionella Formosa*. The protein:carbohydrate mass ratio was similar for the AOM from *Aphanizomenon flos-aquae, Anabaena flos-aquae* and *Scenedesmus subspicatus* ranging from 1.1-1.5. In contrast the AOM from *Microcystis aeruginosa* has been reported as having a much lower ratio of 0.4-0.62 (Qu et al, 2012; Henderson et al, 2008).

Table 4: Algal organic matter characteristics from this study

Algal species	*SUVA*	*HPO %*	*HPI %*	*Pr/AOM*	*Ca/AOM*	*Pr/Ca*
Aphanizomenon flos-aquae	0.79	18	63	0.99	0.9	1.1
Anabaena flos-aquae	0.34	8	81	0.52	0.34	1.5
Scenedesmus subspicatus	1.18	26	54	1.5	1.2	1.2

Pr Protein concentration, Ca carbohydrate concentration, nm not measured

The low charge density values indicate diminished quantities of the charged hydrophilic polysaccharides, and the presence of uncharged polysaccharides such as acetylamino sugars, sulphated sugars and carboxylated sugars (Leppard, 1995). These charged hydrophilic polysaccharides have been detected in AOM extracted from the stationary but not the exponential phase (Henderson et al., 2008). The organics excreted from AOM thus comprise low-SUVA organics such as hydrophobic proteins and uncharged hydrophilic polysaccharides (Edzwald, 1993), as well as proteins, peptides, carbohydrates and possibly amino acids (Bond et al., 2009, Pivokonsky et al., 2014).

3.2 DBP formation

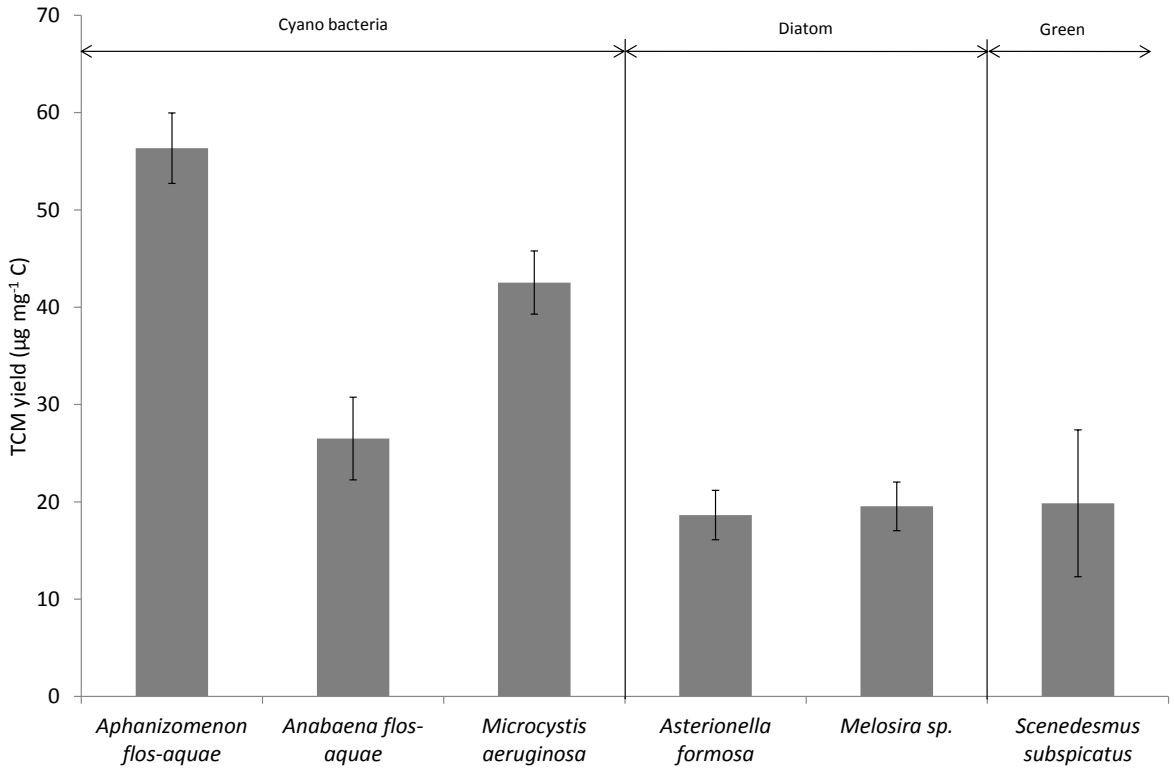
3.2.1 Trihalomethanes

Under the chlorination conditions adopted, and specifically the absence of bromide, TCM accounted for more than 99% by mass of the THMs formed from the AOM for all six algal species studied (Figure 1). *Aphanizomenon flos-aquae*-AOM followed by *Microcystis aeruginosa*-AOM formed the most TCM of all the species measured at 56.6±3.6 μg mg^{-1} C and 42.6±3.3 μg mg^{-1} C respectively. The remaining four AOM samples formed similar levels of THMs between 18.7±2.5 μg mg^{-1} C and 26.6±4.3 μg mg^{-1} C. The data complements that from previous studies (Table 1), with similar levels for *Microcystis aeruginosa*-AOM (Huang et al., 2009, Fang et al., 2010) and *Anabaena flos-aquae*-AOM (Huang et al., 2009; Wachter and Andelman, 1984). In contrast, THM formation reported for *Scenedesmus quadricauda*-AOM by Nguyen et al. (2005), referring to AOM extracted during stationary phase, varied depending on the algal growth tank size from 48±12 to 64±14 μg mg^{-1} C, significantly higher than the 19.9±7.5 μg mg^{-1} C measured in the current study. Algae grown under the same conditions and from the same tank have been shown to exhibit different behaviour depending on the algal type. The THM yield can vary with growth phase (*Anabaena flos-aquae*-AOM,

Huang et al., 2008) but has also been shown not to vary significantly with growth phase when normalised with respect to DOC (*Scenedesmus quadricauda*-AOM, Nguyen et al., 2005; Microcystis aeruginosa-AOM, Huang et al, 2009).

Comparison with alternative OM sources reveals that AOM exerts a moderate to low reactivity with chlorine. For instance THM yield concentrations generated from NOM formation potential tests have been reported to range from 20-281 μg mg^{-1} C with a median of 63 μg mg^{-1} C for a range of 35 water sources (Allgeier and Summers 1995, Afcharian et al., 1997, Collins et al., 1986, Nokes et al., 1999, Singer et al., 1995, Teksoy et al., 2008, Yang et al., 2015, Pifer and Fairey 2014). This indicates that although AOM may not be the biggest contributor to the formation of THMs compared to NOM, it could still make a significant contribution to the THMs formed.

Further to this, microbially derived OM has been shown to exhibit a yield of 23-43 μg THMs mg^{-1} C (Sirivedhin and Gray, 2005), with the yield reported to vary little across the three chemical fractions (Zhou et al, 2014). AOM is known to most resemble hydrophilic NOM and microbially derived OM and consists of hydrophilic polysaccharides and hydrophobic proteins (Henderson et al., 2008), so a comparison can therefore be made with the yield of proteins and carbohydrates. The THM yield has been reported to range from 41 to 51 μg THM mg^{-1} C for four proteins (Scully et al., 1988), and carbohydrates have been observed to form similar levels of THMs (42 to 65 μg THM mg^{-1} C) for 10 carbohydrates (Navalon et al., 2008), broadly consistent with the trends shown in Figure 1.



296
297 **Figure 1:** TCM concentrations produced by the AOM from each algal species
298
299

300 ### 3.2.2 Haloacetic acids

301 As with the THM data, brominated species did not feature amongst the HAAs assayed. DCAA
302 and TCAA comprised more than 99% of the total HAAs formed on a mass basis for the AOM
303 of all 6 species of algae (Figure 2), consistent with Nguyen et al. (2005). *Scenedesmus*
304 *subspicatus*-AOM formed the most HAAs of all the species at a yield of 35.8±2.3 µg mg^{-1} C
305 followed by *Microcystis aeruginosa*-AOM with yield of 28.7±7.5 µg mg^{-1} C. AOM from
306 *Aphanizomenon flos-aquae* and *Asterionella formosa* was comparable in HAA yield with
307 values of 24-25 µg mg^{-1} C ± ~20%. The second-lowest HAA yield was observed for *Anabaena*
308 *flos-aquae*-AOM at 18.7±1.3 µg mg^{-1} C with the lowest value of 13.2±2.3 µg mg^{-1} C recorded
309 for *Melosira sp.*-AOM. As with the THM yield values, those for HAAs measured by Nguyen
310 et al. (2005) from AOM from the stationary phase were higher than those observed in the
311 current study for *Scendesmus*-AOM (60±7.7 compared to 35.8±3.4 µg mg^{-1} C) when the AOM
312 was taken at the onset of the stationary phase. This was also the case with values reported from

the stationary phase by Huang et al. (2009) compared to those observed in the current study (66 compared to 29 µg mg^{-1} C for *Microcystis aeruginosa*-AOM, and 48 compared to 19 µg mg^{-1} C for *Anabaena flos-aquae*-AOM). The higher yield from *Microcystis aeruginosa*-AOM compared to *Anabaena flos-aquae*-AOM (Figure 2) corroborates the findings of Huang et al (2009), attributable to the difference in HPO content (Table 4).

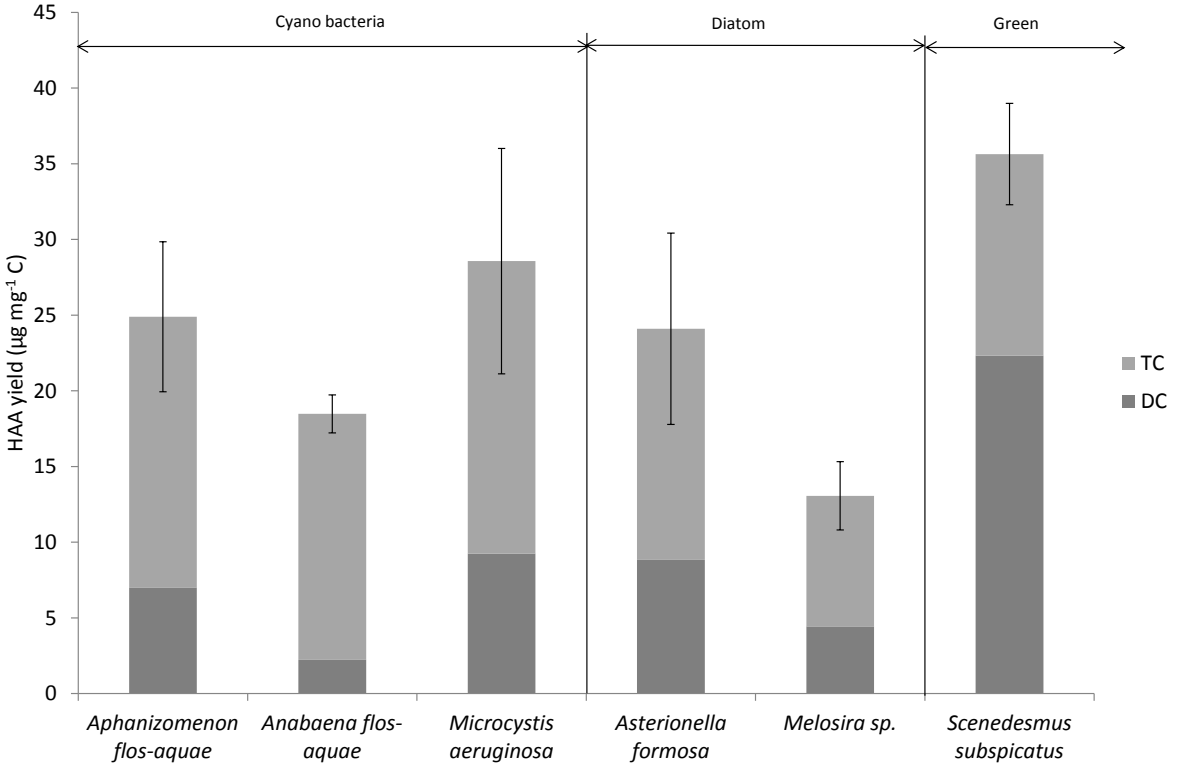


Figure 2: HAA concentrations produced by the AOM from each algal species

The TCAA:DCAA ratios observed in the current were comparable to those reported in the literature for *Scenedesmus*-AOM: 0.60 compared to 0.33-0.69 reported by Nguyen et al. (2005) over a number of days of stationary growth. However the same ratios reported by Huang et al. (2009) for AOM from *Microcystis aeruginosa* and *Anabaena flos-aqua* (0.57 and 0.85 respectively) extracted during the stationary phase were significantly lower than those from the current study (2.1 and 7.3 respectively) for samples taken at the onset of the stationary phase. The difference may be attributable to the varying amino acid content, which can have wide

328 ranging HAA yield values - insignificant to 106 μg mg^{-1} C according to Hong et al., 2009 - and
329 may consist largely of aromatic/cyclic amino acids (Bond et al., 2009).
330
331 HAA formation was positively correlated HPO (R^2 = 0.94) which was attributed mainly to
332 DCAA formation. Conversely the hydrophilic content was negatively correlated to HAA
333 formation (R^2 = 0.87), again closely linked to DCAA formation.
334
335 **3.2.3 Haloacetonitriles**
336 Dichloroacetonitrile (DCAN) comprised >99% of the total HANs formed on a mass basis for
337 the AOM for all 6 algal species (Figure 3). Trichloroacetonitrile (TCAN) was not detected in
338 any samples likely due to base-catalysed hydrolysis at pH>5.5 (Croué and Reckhow, 1989).
339 *Microcystis aeruginosa*-AOM, *Scenedesmus subspicatus*-AOM and *Melosira sp.*-AOM
340 generated the highest HAN yields of all the species measured at 1.32±0.01, 1.10±0.07 and
341 0.87±0.05 μg mg^{-1} C respectively. *Aphanizomenon flos-aquae*-AOM produced the lowest
342 yields (0.12±0.003 μg mg^{-1} C), with *Asterionella formosa*-AOM and *Anabaena flos-aquae*-
343 AOM exhibiting similar values of 0.53±0.07 and 0.39±0.10 μg mg^{-1} C respectively. The
344 formation potential for HANs from AOM has been studied by Fang et al. (2010) and for
345 fractionated AOM (Zhou et al., 2014). These authors reported slightly higher values of ~1.5 μg
346 mg^{-1} C DCAN from chlorination of *Microcystis aeruginosa*-AOM compared to the current
347 study, perhaps because the AOM was extracted during the stationary phase. For fractionated
348 samples, values of total HANs from chlorination of *Microcystis aeruginosa*-AOM over 3 days
349 ranged from 1.5–2.6 μg mg^{-1} C, with the HPO fraction having the greatest formation potential
350 (Zhou et al., 2014). This equates to a value of 1.8 μg mg^{-1} C, based on the relative amount of
351 each fraction, which is slightly higher than the values found in the current study for *Microcystis*
352 *aeruginosa*-AOM but does not take into account the synergistic effects encountered when
353 chlorinating non-fractionated samples (Kent et al., 2011). HAN yields from algal cells have

been reported under similar chlorination conditions, albeit with a 3-day exposure, of 0.76 µg mg^{-1} C DCAN and 0.05 µg mg^{-1} C TCAN from algal cell suspensions of *Microcystis aeruginosa* (Fang et al., 2010). Under the same chlorination conditions as reported here, at double the chlorine dose, Oliver (1983) reported DCAN formation of 2.3 µg mg^{-1} C and 0.5 µg mg^{-1} C for cyanobacterial (*Anabaena* Texas 1447) and green (*Scenedesmus* basiliensis) algal suspensions respectively.

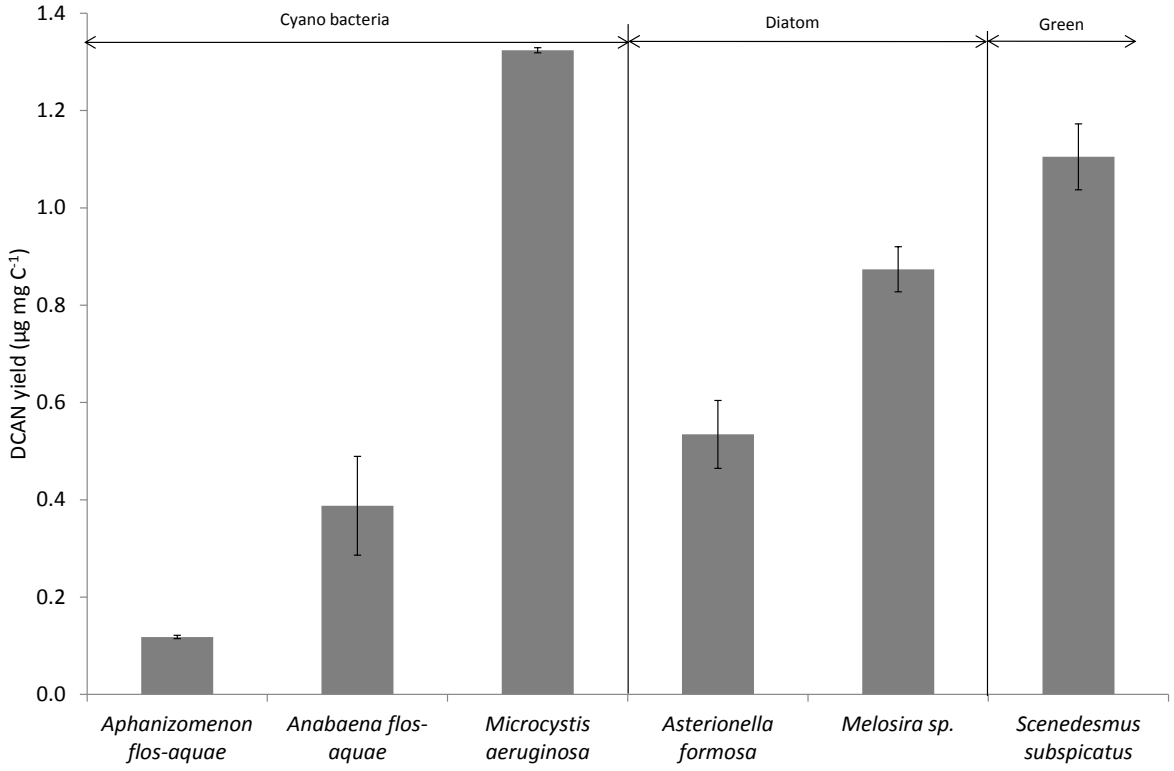


Figure 3: DCAN concentrations produced by the AOM from each algal species

In terms of THM and HAA formation, algal cells have been observed to produce similar or greater amounts than the corresponding AOM (Huang et al., 2009). Differences in algal species, organic fractions (dissolved matter vs. whole cells), and chlorination conditions make comparison with published challenging. However, the values for AOM reported in the current study are of the same magnitude as those reported in the literature for algal cell suspensions and less than the yield of DCAN from isolated fulvic acid (4.3 µg mg^{-1} C) (Oliver, 1983).

Under identical chlorination conditions, Lee et al. (2007) reported the chlorination of isolated NOM fractions to produce DCAN levels ranging from 1.65 to 2.31 μg mg^{-1} C from TPI neutral and colloidal fractions largely consisting of amino sugars, polysaccharides and proteins. Contrary to Oliver (1983), HPO fractions (including fulvic acid) produced DCAN levels of 0.33-0.77 μg mg^{-1} C (Lee et al., 2007) which could be related to the differing chlorine doses.

3.2.4 Halonitromethane

TCNM was the only HNM measured in the current study (Figure 4). *Melosira sp.*-AOM formed the most TCNM (0.36±0.02 μg mg^{-1} C) of all the species measured at followed by *Asterionella formosa*-AOM (0.24±0.03 μg mg^{-1} C). Similar values were observed for *Anabaena flos-aquae*-AOM, *Microcystis aeruginosa*-AOM and *Aphanizomenon flos-aquae*-AOM forming 0.16±0.01 μg mg^{-1} C and 0.13±0.01 μg mg^{-1} C and 0.11±0.01 μg mg^{-1} C TCNM respectively. TCNM formation by *Scenedesmus subspicatus*-AOM was below the limit of detection.

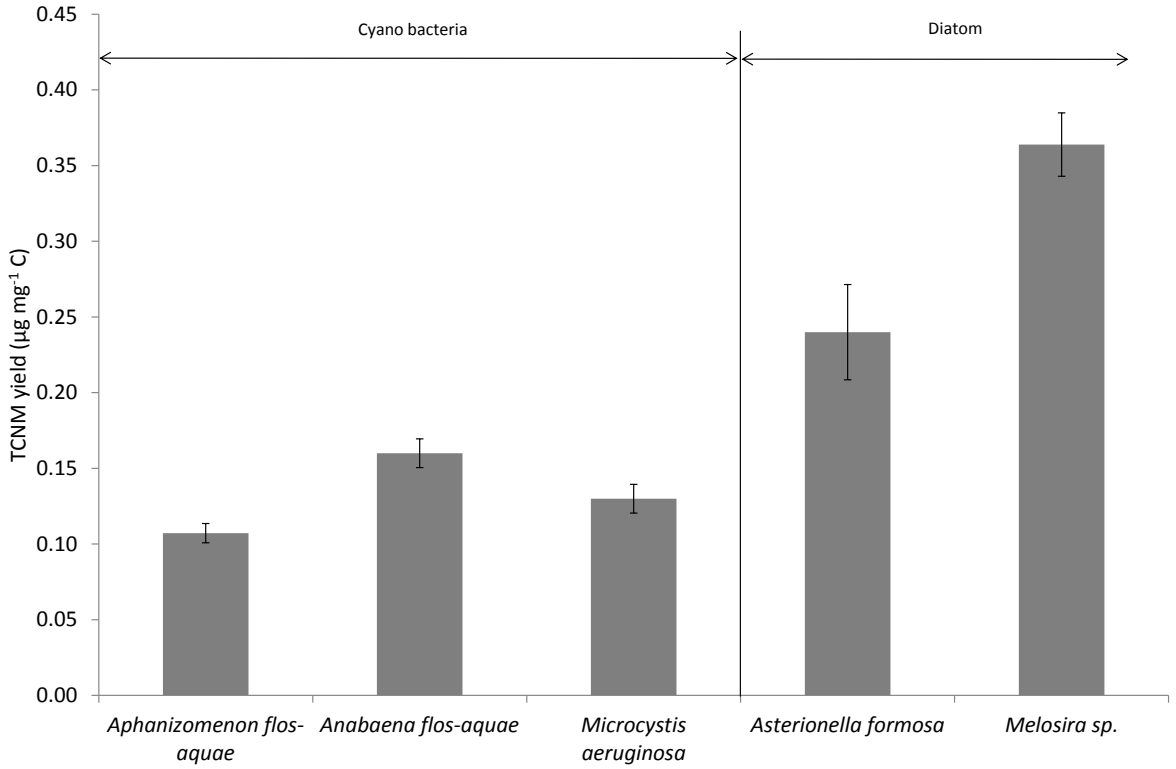


Figure 4: TCNM concentrations produced by the AOM from each algal species compared to literature values

To the authors' knowledge the formation potential for HNMs from AOM or algal cells has only been studied for *Microcystis aeruginosa*-AOM (Fang et al., 2010) with slightly higher values than observed here perhaps expected due to the difference in growth phase as described for the other DBPs measured. Values of TCNM reported from chlorination of isolated NOM fractions average at 0.33 μg mg^{-1} C (Lee et al., 2007) similar to the values reported here.

4 Discussion

AOM is mainly hydrophilic in character and on chlorination has the potential to form significant amounts of C- and N-DBPs. An unsuccessful attempt was made to link the characteristics to the DBPs formed as this has been shown to be applicable for NOM and DBPs (e.g. with NOM, THM formation can correlate positively with SUVA for a range of water samples for high SUVA (>3) waters (Ates et al., 2007, Reckhow et al., 1990). No relationship was observed between SUVA and the DBPs measured in the current study and, apart from the close correlation of HAA with the HPO fraction (Section 3.2.2), there was no correlation evident between DBPFP and any chemical fraction.

No pattern in DBP formation with algal taxonomic group was evident. For instance, AOM could form significant amounts of C-DBPs (illustrated by the specific cyanobacterial species AOM and green algal AOM) or less significant amounts of C-DBPs (illustrated by the AOM from diatomaceous species). Cyanobacterial AOM may be expected to produce significant amounts of nitrogenous DBPs compared to green and diatomaceous AOM since cyanobacterial algae are nitrogen fixers and liberate up to 45% of their fixed nitrogen as organic-N (Huang et al., 2009, Westerhoff and Mash, 2002). Indeed, when looking at formation of HANs, one particular cyanobacteria is more reactive (*Microcystis aeruginosa*-AOM) but significant

412 amounts of HAN are also formed by green and diatomaceous AOM. The AOM from the
413 diatoms (*Melosira sp.* and *Asterionella formosa*) forms the most TCNM followed by the
414 cyanobacterial AOM, with no formation of TCNM by the green AOM (*Scenedesmus*
415 *subspicatus*). Therefore when considering the risk of DBPs formed by a particular algal species,
416 it is important that the AOM produced from diatomaceous algae is considered as it can be a
417 significant precursor to HAN and HNM formation.
418
419 The chlorination of AOM involves the reaction between chlorine and molecules including
420 uncharged hydrophilic polysaccharides, proteins, peptides and carbohydrates. The amino acids
421 present in freshwater algae (as free amino acids and proteins or peptides) comprise at least 17
422 of the 20 standard amino acids (Fowden, 1951, Lewis and Gonzalves, 1962) with different
423 species containing different amino acids. For example, some cyanobacterial algal species
424 contain no cysteine whereas some green algal species contain cysteine but no lysine. All the
425 amino acids present in algae can potentially be present in AOM. It is known that acid
426 polysaccharides such as uronic acids can be excreted by algae in response to low nutrient stress
427 (Costerton, 1984). The polysaccharides present in algae and extracellularly comprise the
428 carbohydrates rhamnose, galactose, arabinose, fucose, mannose, glucuronic acid, uronic acid,
429 glucose (Rezanka and Sigler, 2007).
430
431 Amino acids, carbohydrates and carboxylic acids have been studied with respect to their DBP
432 formation (Chu et al., 2012, Shan et al., 2011, Bond et al., 2009, Navalon et al., 2008, Trehy et
433 al., 1986). The study of carbohydrates (Navalon et al., 2008) showed that they were reactive
434 with respect to THM (40-65 $\mu g\ mg^{-1}$ C). In studies of amino acids, the key finding was that the
435 compounds can have similar physicochemical properties but divergent DBP formation. For
436 example, glutamic and aspartic acid have very similar log K_{OW}, pKa, and molecular weight.

437 However, on chlorination aspartic acid forms DCAA, trichloroacetaldehyde, and DCAN at
438 0.26, 0.02, and 0.06 mol THM/mol compound (mol/mol) respectively, whereas none of these
439 species are formed from glutamic acid chlorination (Bond et al., 2009). On the other hand, little
440 difference was observed between formation of HNM (Shan et al., 2011) and DCAN (Wang et
441 al., 2013) from glutamic and aspartic acids, emphasising the different pathways of formation
442 for each group of DBPs. Mechanisms of formation have been proposed for these pathways
443 (Table 5). A study on carboxylic acids (Bond et al., 2009) showed that β-dicarbonyl 3-
444 oxopentanedioic is reactive with respect to THM and trichloropropane formation but not HAA
445 formation. This corroborated a previous report stating that the reactivity of carbohydrates and
446 carboxylic acids towards chlorine to be low (WHO, 2000) with reference to the chlorine
447 demand of the carbohydrates, though this report did not consider that significant amounts of
448 some DBPs could still be formed.
449
450 **Table 5:** Proposed pathways for DBP formation from amino acid precursors

DBP	Precursors	Intermediate	Substitution location	Reference
HNMs	Chemical structure of precursors not considered to be important			Wang et al., 2013, Shan et al., 2011
HANs	Aspartic acid, asparagine	dichlorocyanoacetic acid	nr	Wang et al., 2013
	Tyrosine	benzyl cyanide	α-carbon	
	Histidine	2-(1-chloro-1H-imidazol-4-yl)-acetonitrile	α-carbon	Li and Blatchley, 2007
THMs	Tyrosine	4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol	nr	Chu et al., 2012
HAAs	Aspartic acid and glutamic acid	β-keto acid such as 3-oxopentanedioic acid or cyanoacetic acid	Variable	Bond et al., 2009

451 nr – not reported
452
453
454 While AOM is present at lower concentrations than other DBP precursors such as NOM, its
455 nature means that it is recalcitrant to treatment by methods such as coagulation. Whilst
456 optimised coagulation has been shown to remove the algae *C. Vulgaris, M. aeruginosa and A.*

457 *Formosa* by 71, 55 and 46 % respectively (Henderson et al., 2010), the removal of dissolved
458 AOM is more challenging due to its uncharged hydrophilic nature; enhanced techniques such
459 as pre-ozonation demonstrating only partial success (Widrig et al., 1996). Given the escalation
460 of eutrophication of water sources in recent years due to anthropogenic effects, increasing the
461 levels of phosphorus and nitrogen entering water sources (Ward and Wetzel, 1980, Burrini et
462 al., 2000) AOM is likely to be a significant contributor to DBP formation in treated drinking
463 waters.
464 Another important consideration is the toxicity of the DBPs formed, particularly the
465 nitrogenous DBPs. A recent study (Zeng et al., 2016) on potable water reuse investigated a
466 range of DBPs throughout the treatment train and looked at the contribution of each DBP to
467 the toxicity of the water. The toxicity was determined as a function of concentration and toxic
468 potencies of each DBP. The toxicity in this case for unregulated halogenated DBPs was based
469 on in vitro chromic cell cytotoxicity which has some limitations and the authors stressed that
470 they were determining relative rather than absolute risk. Nonetheless they found that HANs,
471 haloacetamides and to a lesser degree haloacetaldehydes dominated the additive toxicity in
472 membrane filtrate. Thus it is important, when considering whether to use an algal impacted
473 source, that the concentration of nitrogenous DBPs (particularly HANs and haloacetamides) in
474 the treated water may be elevated compared to a source that is not algal impacted.
475

476 # 5 Conclusions

477 A study of the characteristics of formation of chlorinated disinfection by products from algal
478 organic matter (AOM) has revealed the following:
479

- AOM is mainly hydrophilic in character, with between 52 and 81% being made up of HPI fraction, and on chlorination has the potential to form up to 92.4 μg carbonaceous and 1.7 μg nitrogenous DBPs per mg organic carbon;
- No pattern in DBP formation with algal taxonomic group was evident;
- Few consistent trends between DBP formation propensity and either the specific ultraviolet absorbance (SUVA) or the AOM chemical characteristics were evident, such that characterisation of the AOM may be of limited use in determining DBP formation;
- Although little studied, the AOM from diatomaceous algae forms significant amounts of nitrogenous DBPs (up to 1.7 μg mg^{-1} C).

The hydrophilic nature of AOM, which is autochthonous in nature, makes it more difficult to remove effectively using conventional water treatment processes than allochthonous natural organic matter (NOM), which is also more hydrophobic in nature. This offers an explanation for the generally observed trend of seasonally high chlorinated DBP levels associated with higher temperatures and thus commensurately greater microbial production rates with accompanying AOM generation.

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

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