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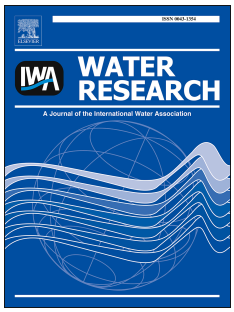

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The role of phytoplankton as pre-cursors for disinfection by-product formation upon chlorination

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Water quality remains one of the greatest concerns with regards to human health. Advances in science and technology have resulted in highly efficient water treatment plants, significantly reducing diseases related to waterborne pathogenic microorganisms. While disinfection is critical to mitigate pathogen risk to humans, the reactions between the disinfectant and dissolved organic compounds can lead to the formation of chemical contaminants called disinfection by-products (DBPs).

DBPs have been related to numerous health issues including birth defects and cancer. The formation of disinfection by-products occurs due to the reaction of oxidants and natural organic matter. DBP precursors are derived from anthropogenic sources including pharmaceuticals and chemical waste, the breakdown of vegetation from external catchment sources (allochthonous) and internally derived sources including phytoplankton (autochthonous). Current literature focuses on the contribution of allochthonous sources towards the formation of DBPs, however, the recalcitrant nature of hydrophilic phytoplankton derived organic matter indicates that autochthonous derived organic carbon can significantly contribute to total DBP concentrations. The contribution of phytoplankton to the formation of DBPs is also influenced by cellular exudation rates, chemical composition, environmental conditions and the physical and chemical conditions of the solution upon disinfection. Formation of DBPs is further influenced by the presence of cyanobacteria phyla due to their notoriety for forming dense blooms. Management of DBP formation can potentially be improved by reducing cyanobacteria as well as DBP precursors derived from other phytoplankton.

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Key words: disinfection by-products, chlorination, phytoplankton, algae, autochthonous, algal organic matter.

Abbreviations:

AOM – Algal organic matter

C-DBP – Carbonaceous disinfection by-product

CP – Chloropicrin

DBP – Disinfection by-products

DBPFP – Disinfection by-product formation potential

DHAA – Dihaloacetic acid

DCAA – Dichloroacetic acid

DHAN – Dihaloacetonitrile

DOC – Dissolved organic carbon

DON – Dissolved organic nitrogen

EOM – Extracellular organic matter

HAA – Haloacetic acid

HAN – Haloacetonitrile

HK – Haloketone

IOM – Intracellular organic matter

LRV – Log_{10} reduction value

N-DBP – Nitrogenous disinfection by-product

NDMA – *N*-nitrosodimethylamine

NLA – National lake assessment

NOM – Natural organic matter

TCAA – Trichloroacetic acid

THAA – Trihaloacetic acid

THM – Trihalomethane

THMFP – Trihalomethane formation potential

TOC – Total organic carbon

TOX – Total organic halide

US EPA – United States Environmental Protection Agency

UTOX – Unknown total organic halide

1.1 Introduction

Chemical disinfection is vital for the continued protection from bacterial, viral and some protozoan pathogens, and the common disinfectant chlorine is effective against a range of these pathogens (Table 1). While disinfection is critical to mitigate pathogen risk to humans, the reactions between the disinfectant and dissolved organic compounds can lead to the formation of chemical contaminants called disinfection by-products (DBPs). The formation of DBPs results in a residual, unintended health hazard (Richardson 2003).

1.1.1 Disinfection By-product Formation

Understanding how DBPs are produced is essential for determining the mechanisms by which phytoplankton may contribute to their formation. In addition to effectively killing pathogens, disinfectants are strong oxidising agents, able to oxidise complex natural organic matter (NOM) molecules into simpler moieties (Richardson and Postigo 2011). This is often exploited to improve the treatability of the organic carbon pool prior to coagulation/flocculation, termed ‘pre-oxidation’. However, the disinfectant can react with readily available NOM and/or inorganic constituents to yield DBPs during the disinfection process and throughout the distribution network. Therefore, it is intuitive that the formation and yield of DBPs is dependent on the availability of NOM, choice of disinfectant,

the presence of inorganic compounds and the physical conditions of the reaction.

Although there are a range of disinfectants (chloramine, ozone, chlorine dioxide) chlorine is commonly utilised for its low cost and capability to retain a disinfection residual. The chemical structure of the DBP formed is also influenced by the presence of inorganic constituents, such as bromide, iodide, nitrites and nitrates and the physical conditions of the reaction (Figure 1). Disinfection by-products were discovered with the identification of trihalomethanes (THMs) in 1974 by Bellar *et al.* (1974) and Rook (1974); since then there have been over 600 DBPs identified in drinking water or simulated in laboratory experiments (Deborde and von Gunten 2008; Hebert *et al.* 2010). Given the imperative to disinfect, mechanisms are required to minimise formation of these chemical contaminants. Considering the range of possible chemical interactions and DBPs that may be formed, the removal of DBP precursors prior to chlorination is the preferred approach and has received the most attention in recent literature (Bond *et al.* 2011). This can be achieved either by preventing DBP precursors entering the water body or removing them from the source water prior to disinfection.

Disinfection by-product precursors are derived from anthropogenic compounds, the breakdown of vegetation from

external catchment sources (allochthonous) and from internal sources including the phytoplankton (autochthonous). Anthropogenic sources of DBP precursors include pharmaceuticals and chemical wastes, which can accumulate in waterways due to their difficulty to remove during treatment. The transformation of pharmaceuticals to DBPs during the disinfection process has been detailed by Postigo and Richardson (2014). The contribution of catchment derived-allochthonous NOM towards DBP formation varies between catchments depending on local climate, soil type, vegetation and the morphology of the watershed. The relative contribution of autochthonous carbon will be a function of nutrient load and phytoplankton growth. Allochthonous organic matter often exceeds autochthonous carbon as the dominant energy source in humic and oligotrophic lakes, whereas autochthonous organic carbon is often the dominant energy source in productive, eutrophic lakes (Jonsson *et al.* 2001). It is expected that autochthonous NOM will also be the dominant source of DBP precursors in environments exposed to low or intermittent rainfall events (Soh *et al.* 2008). The organic matter is removed during the coagulation process; however, autochthonous organic matter can be harder to treat due to higher concentrations of hydrophilic compounds (Bond *et al.* 2011; Lui *et al.* 2011). Therefore, phytoplankton dominated systems

may cause problematic DBP formation within the water treatment plant and distribution network.

The majority of the literature pools various sources of NOM or focuses only on allochthonous contributions to DBP formation, with minimal studies considering the contribution from phytoplankton (Hong *et al.* 2008; Fang *et al.* 2010b; Li *et al.* 2012). This review is necessary given the limited availability of comprehensive DBP literature reviews, highlighting the significance of phytoplankton derived organic matter as a viable DBP precursor. As algal-derived organic carbon is generally more recalcitrant to conventional treatment it is imperative that the total contribution of phytoplankton to the formation of DBPs is thoroughly understood for improved management. This review aims to assess the potential for phytoplankton-derived DOC to form DBPs by determining the phytoplankton contribution to the organic carbon load in reservoirs and identify the cellular constituents of phytoplankton that may react with the chlorine.

1.1.2 Disinfection By-product Toxicity

Currently only 15 of DBPs are regulated by the World Health Organisation (WHO) as these compounds have sufficient toxicological evidence of carcinogenity, genotoxicity or adverse reproductive incidences (Richardson *et al.* 2007;

Krasner 2009; World Health Organisation 2011). Less than 100 of the 600+ known and emerging DBPs have undergone quantitative or toxicology studies (Hebert *et al.* 2010). Although many of the studied DBP chemicals produced harmful effects, attribution of toxicology to human health outcomes is difficult (Hrudey 2009). Furthermore, there is not a consistent approach by which DBPs are regulated and the key authoritative organisations adopt/set unique lists of DBPs with significant variation in guideline values (Table 2).

Comprehensive genotoxicity experiments assessed the *in vitro* cytoxicity on Chinese hamster ovary cells when exposed to various classes of DBPs (Plewa *et al.* 2004a; Plewa *et al.* 2004b; Plewa *et al.* 2008) These experiments provide evidence that the toxicity for various substituted DBP halogenated functional groups is, I > Br > Cl, and that nitrogenous DBPs (N-DBPs) are generally more genotoxic than carbonaceous DBPs (C-DBPs). This suggests that regulated carbonaceous and chlorine substituted DBP classes have lower genotoxic activities than other emerging DBP classes (Richardson *et al.* 2007). Therefore, some classes of DBPs that have higher associated health risks are not being routinely monitored under current guideline standards. The higher genotoxicity of N-DBPs is of concern given that phytoplankton are significant contributors to dissolved organic nitrogen (DON) and are known to promote the formation of N-DBPs (Mitch et al,

2009). A potential increase in more genotoxic N-DBPs may give rise to associated health risks with DBP exposure include; the potential association with bladder cancer, as well as links to miscarriages and birth defects (Hrudey 2009, Thomson and Sarkar 2014).

N-nitrosodimethylamine (NDMA) is a N-DBP of significant concern, given nitrosamines are classified as carcinogenic, mutagenic and teratogenic (Choi and Valentine 2002). NDMA is predominantly formed from reactions between chloramine and dimethylamine, whilst also forming in chlorinated water in the presence of ammonia (Choi and Valentine 2002). A report by Mitch *et al.* (2009) found that significant NDMA precursors are only dominant in wastewater samples, whilst algal dominated and pristine water samples were less problematic in generating NDMA concentrations under typical chloramine disinfection. In contrast, NDMA formation from phytoplankton indicated that extracellular organic matter (EOM) and intracellular organic matter (IOM) are capable of producing NDMA concentrations above the local Californian public health goal of 3ng/L (Li *et al.* 2012). Further investigation is required due to contradictions on NDMA formation potential from phytoplankton precursors.

2.1 Phytoplankton Contribution to Total NOM Pool

To determine how much carbon phytoplankton can contribute to the NOM pool it is necessary to obtain an estimate of the proportion of autochthonous and allochthonous NOM within a lake or reservoir ecosystem. A large-scale assessment of a broad range of aquatic environments has to be completed. A meta-analysis of the U.S. EPA National Lake Assessment (NLA) dataset of 1326 total sample points in 1076 U.S. lakes, provided a snapshot of a range of physical, chemical and biological lake properties (EPA, 2009, Rigosi *et al.* 2014). The lakes used in the NLA were selected from the U.S. National Hydrographic dataset using a generalised random tessellation stratified survey design (Stevens and Olsen 2004). All surveyed lakes located across the lower 48 U.S. states had a minimum depth of 1 meter and a minimum surface area of 0.01 km^2. Sampling for the NLA was conducted during the summer of 2007 to minimise the influence of seasonal variation. Total organic carbon (TOC) and chlorophyll *a* concentrations were recorded, allowing for a snapshot estimate of the phytoplankton derived organic matter relative to the total organic carbon pool. To achieve this we used comparative ratio between total chlorophyll *a* and TOC concentrations. The carbon to chlorophyll *a* ratio varies due to species composition and light exposure, with numerous studies reporting carbon to chlorophyll ratios between 27:1 and 83:1 (C:Chla) (Reynolds

1984; Riemann *et al.* 1989; Yacobi and Zohary 2010). The Reynolds estimation (C:Chla 50:1) is used as an general prediction of carbon based on values of chlorophyll *a* of a general phytoplankton pool, whereas other estimations are species specific. The chlorophyll a concentrations from the EPA database were multiplied by the carbon to chlorophyll ratio (C:Chla 50:1) to estimate how much carbon was found within the phytoplankton (Figure 2). Autochthonous carbon estimations from the US EPA National Lake Assessment indicated that in 520 of the sampling locations, or 39.2% of samples, phytoplankton biomass contributed >10% to the total carbon pool (Figure 2). This analysis provides an estimate of the standing pool of TOC within each lake, however, the TOC in phytoplankton is continually turning over as cells fix atmospheric CO_2 converting it to organic carbon. As the phytoplankton cells lyse the organic carbon enters the dissolved fraction of the carbon pool. It is evident from this analysis that phytoplankton can contribute a significant amount of carbon to the total dissolved carbon in a lake or reservoir.

An analysis of carbon sources in Myponga Reservoir, South Australia, identified that phytoplankton contributed 25-50 % of the total dissolved organic carbon (DOC) to the NOM pool during a period of low annual rainfall when allochthonous inputs were reduced (Linden 2008). The contribution of phytoplankton to the total DOC pool is dependent on the

trophic status of the lake and the catchment characteristics. For example, Bade *et al*. (2007) measured phytoplankton production of two oligotrophic lakes at ~20 % whereas Carpenter *et al*. (2005) made reference to a eutrophic lake where phytoplankton production was accountable for as much as 40% of the total DOC pool. Therefore, phytoplankton could be a significant DBP precursor in in similar euphotic systems, and during periods of low rainfall. Several species of phytoplankton form blooms in eutrophic water bodies resulting in water quality degradation and an increased risk to DBP formation (O'Neil *et al.* 2012). To gain more insight into how much autochthonous carbon phytoplankton contribute to the total NOM load it is necessary to consider phytoplankton chemical composition, growth and mortality rates, cellular exudation, cell lysis and loss of settling of cells. This would require sophisticated modelling beyond the scope of this review, however, both the Myponga Reservoir example and the US EPA Lake analysis suggest that phytoplankton can contribute a significant amount of organic carbon to lakes.

2.1.1 Influence of Natural Organic Matter on DBP Formation

The chemical composition of allochthonous NOM is defined by local climate and catchment characteristics, including the soil

and vegetation type (Frimmel 1998; Aitkenhead-Peterson *et al.* 2003). The characterisation of NOM into operationally defined fractions described by Leenheer and Croué (2003) can aid in the prediction of DBP formation potential (DBPFP) post chlorination (Figure 3). Humic and fulvic acids, hydrocarbons, tannins and aromatic amines are contained within the hydrophobic fraction. Terrestrial NOM is commonly derived from lignin and contains a high aromatic content; hence allochthonous NOM tends to be hydrophobic in character (Hwang *et al*. 2001; Bond *et al.* 2011). Alternatively, carboxylic acids, polyuronic acids, amino acids, peptides, proteins and carbohydrates are commonly contained within the hydrophilic fraction. Autochthonous NOM is derived from phytoplankton, macrophyte and bacterial sources, consisting of low aromatic and high nitrogen content; indicating that autochthonous NOM tends to be predominantly hydrophilic in character (Bond *et al.* 2011).

The hydrophilic organic carbon fraction is less prone to coagulation and as a result is partially recalcitrant to conventional treatment methods (Singer and Harrington 1993; Kim and Yu 2005; Matilainen *et al.* 2010; Lui *et al.* 2011). Eutrophic systems dominated by phytoplankton species can provide NOM with high hydrophilic content. Li *et al.* (2012) analysed the relative hydrophobicity of *Microcystis aeruginosa* using XAD and IRA resin fractionation technique. They

326 demonstrated that hydrophilic organic matter accounts for 86 %
327 of IOM and 63 % of EOM from *Microcystis aeruginosa*. This
328 has implications for the water treatment process as NOM from
329 phytoplankton will be partially recalcitrant to conventional
330 treatment methods. Furthermore, Lui *et al.* (2011) reported that
331 hydrophilic NOM derived from algal protein can increase the
332 DBPFP, in comparison to hydrophobic proteins. The research
333 suggested that hydrophilic proteins were 35 times more
334 effective as precursors of chloroform. Due to a high prevalence
335 of hydrophilic content, the DOC from autochthonous
336 phytoplankton production can significantly increase the
337 DBPFP, even after conventional treatment.

338 ***2.1.2 Growth and Mortality Rates***

339 The contribution of phytoplankton to the NOM pool, and
340 resulting DBPFP can be further quantified with an
341 understanding of population dynamics. Comprehension of
342 species composition and distribution involves knowledge of
343 phytoplankton growth and mortality rates. Population dynamics
344 provide insight into how rapidly autochthonous organic matter
345 derived from phytoplankton can enter the system.
346 Phytoplankton are capable of rapid growth, with individual
347 organisms expressing doubling rates between 6 hours to 10
348 days (Harris 1986). Smaller cells generally replicate faster than
349 larger algal cells. The fast growth rate of phytoplankton results
350 in the rapid turnover of autochthonous NOM within the lake

and results in a large pool of carbon that could react to form DBPs. During the life cycle of phytoplankton, the release of DOC can be substantial, ranging from 9-67 % of total primary production (Hwang 1993).

Phytoplankton mortality rates also greatly impact total contribution to the autochthonous organic matter pool. Losses within the phytoplankton community occur as a result of sedimentation, natural cell lysis, flushing, parasitism and predation (Crumpton and Wetzel 1982; South and Whittick 1987). In the event of phytoplankton mortality, intracellular content is released into the water column raising the available NOM content for DBP formation. In a study of phytoplankton mortality rates by Crumpton and Wetzel (1982), grazing was considered the dominant cause of phytoplankton mortality. During ingestion by zooplankton, 16-37 % of algal carbon content can still be released as available NOM, susceptible to DBP formation upon chlorination (Lampert 1978; Strom *et al.* 1997). Alterations in phytoplankton species dominance, growth and mortality rates provide evidence of a boom and bust lifecycle, resulting in NOM accumulation that is susceptible to DBP formation upon chlorination.

2.1.3 Cellular Exudation

Phytoplankton contribution to the NOM pool is also increased by natural exudation of dissolved organic matter. Phytoplankton excretion of NOM is theorised to occur

continuously, or as a result of environmental stressors (Malinsky-Rushansky and Legrand 1996). The rate of cellular exudation is enhanced by an increase in UV radiation closer to the surface of the water (Köhler *et al.* 2001). The increased extracellular release has been linked to the accumulation of excess photosynthates or products of photosynthesis (Fogg 1983). Experiments have closely related the rate of exudation to the rate of primary production (Mague *et al.* 1980; Descy *et al.* 2002). To estimate percentage of extracellular release, Baines and Pace (1991) assessed published results based on 225 observations of phytoplankton extracellular release, particulate primary production and biomass values. The meta-analysis determined that approximately 13 % of total carbon fixed by phytoplankton is exuded by cells and found extracellularly (Baines and Pace 1991). This indicates that the phytoplankton continuously contribute a significant NOM load to their surrounding environment, further increasing the risk of DBP formation.

There is significant variation in extracellular release between individual species and phyla. A study compared NOM production per unit of chlorophyll *a*, per hour for a species of cyanobacteria (*Oscillatoria prolifera*), green algae (*Scenedesmus quadricauda*) and diatom (*Chaetoceros muelleri*) (Nguyen *et al.* 2005). The study indicated that cyanobacteria had the highest rate of DOC exudation (9.0 µg C (µgChl *a*)$^{-1}$h^{-}

401 ^{1}), followed by green algae (3.6 µg C (µg Chl *a*)$^{-1}$h^{-1}) and
402 diatom species (1.1 µg C (µg Chl *a*)$^{-1}$h^{-1}). The continuous rate
403 of cellular exudation equates to a large autochthonous carbon
404 input, particularly in eutrophic systems where a large biomass
405 of phytoplankton is usually present. Increased autochthonous
406 DOC input from continuous cellular exudation can potentially
407 further increase the DBP formation upon chlorination. The
408 natural cellular exudation of organic matter is of even greater
409 concern to water treatment in the event of an algal bloom.

410 ***2.1.4 Phytoplankton Blooms***

411 Excess nutrient supply and adequate exposure within the
412 euphotic zone can result in a phytoplankton bloom event.
413 Eutrophication of freshwater environments from urban,
414 agricultural and industrial development has resulted in an
415 increased frequency of phytoplankton blooms (Paerl and
416 Huisman 2008). Numerous phytoplankton genera are known to
417 form blooms; however, cyanobacteria are most notorious (Paerl
418 *et al.* 2001). Measurements of *Microcystis aeruginosa* blooms
419 by Oudra *et al.* (2001) have indicated cell densities exceeding
420 10^{6} cells/mL. Cyanobacteria blooms often occur as surface
421 blooms, due to the presence of gas vesicles that provide
422 cyanobacterial cells with buoyancy and promote the formation
423 of a thick scum across the surface of the water (Oliver *et al.*
424 2012). Phytoplankton blooms significantly increase the
425 concentration of autochthonous NOM due to increased cell

biomass resulting in accelerated rates of cell lysis, parasitism, predation and cellular exudation. During a bloom event, rapid carbon turnover significantly increases autochthonous organic matter content. As the hydrophilic fraction is more recalcitrant to removal by coagulation, organic matter will carry through the distribution system resulting in the increased chlorine demand and DBP formation (Lui *et al.* 2011).

Phytoplankton are important DBP precursors, indicated by a boom and bust lifecycle, rapid cellular exudation, hydrophilic dominant cellular composition and the formation of highly concentrated blooms. Research conducted by Graham *et al.* (1998) indicated that cellular exudation and DBP formation increased with the age of the culture. There was a spike in yield of DBPs during the late stationary death phase of the cell lifecycle. The correlation between DBP yield and age of the phytoplankton culture occurs due to the breakdown of storage products into more chemically reactive compounds and the consequential release of these compounds (Graham *et al.* 1998).

2.1.5 Chemical Composition of Phytoplankton

Differences in the chemical composition of phytoplankton between individual species results in the alteration of cellular production rates, structural characteristics, chlorine reactivity and the biological lability of NOM synthesised (Nguyen *et al.*

2005). Phytoplankton have three major classed biomolecules; proteins, lipids and carbohydrates. The concentration of these major biomolecules can be measured to determine the cellular composition of phytoplankton. Surrogate compounds bovine serum albumin (BSA), fish oil and starch can be used to investigate how variations in phytoplankton composition can influence the formation of DBPs (Hong *et al.* 2008; Wei *et al.* 2011). The model compounds are considered to be statistically reliable surrogates due to chemical similarities between BSA, fish oil and starch and the respective algal derived proteins, lipids and carbohydrates. Hong *et al.* (2008) determined the DBPFP upon chlorination of the three model compounds (chlorine dose = 10 mg Cl_2/ mg^{-1} C, contact time = 96 hour, temperature = 20 °C, pH = 7). This work identified that lipids and proteins were more effective precursors of the THM chloroform and that proteins are also a dominant precursor for two haloacetic acids (HAAs); dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA). Starch was not identified as a major contributor to the formation of DBPs (Hong *et al.* 2008) (Table 3). The use of model compounds to predict total DBPFP of phytoplankton is based on two assumptions; (1) that algal cellular content is 100 % comprised of proteins, lipids and carbohydrates, and (2) that carbon percentages of proteins, lipids and carbohydrates are 53 %, 76 % and 40 % respectively (Hong *et al.* 2008). Results obtained from the chlorination of

model compounds were then used to predict the DBPFP of 49 species across three phyla based on their known chemical compositions; cyanobacteria (8 species), green algae (15 species) and diatom (26 species) (Table 4). Estimations of chloroform formation closely matched experimental data; however, DCAA and TCAA concentrations were significantly underestimated. It is likely that the presence of RNA, DNA and aromatic compounds resulted in higher than anticipated haloacetic acid concentrations (Kitis *et al.* 2002; Hong *et al.* 2008). The results identify that phytoplankton chemical composition changes the formation potential of DBPs during chlorination.

Although chemical variation exists between individual species, general trends in cellular constituents are evident across cyanobacteria, green algae and diatom phylum. A meta-analysis of the chemical composition of phytoplankton species indicates that cyanobacteria are generally comprised of more protein (41-69 %) than diatoms (12-50 %); however diatoms generally accumulate more lipids (5-43 %) in comparison to cyanobacteria and green algae (2-30 %) (Hong *et al.* 2008). Higher concentrations of proteins within cyanobacteria species may cause problematic DBP formation within the water treatment plant due to higher efficiency of protein to form THM and HAA species. Growth experiments have also indicated that diatom and cyanobacteria cell cultures produced

in excess of 20 mg/L of DOC which was significantly more in comparison to the green algae cell culture which produced between 10-12 mg/L of DOC (Nguyen *et al.* 2005). Phytoplankton are also a major source of DON in natural waters, with some species of cyanobacteria capable of excreting up to 45 % of their total fixed nitrogen as organic nitrogen (Nguyen *et al.* 2005; Zhang *et al.* 2014). The chlorination of phytoplankton enriched with organic nitrogen resulted in an increased formation of N-DBPs (Fang *et al.* 2010b). This has major implications for water quality within the water treatment plant due to the higher genotoxicity associated with N-DBPs (Richardson *et al.* 2007). Therefore, cyanobacteria species are of significant concern with regards to DBP formation due to higher protein concentrations, increased DOC formation, high DON contribution and notoriety of forming blooms.

2.1.6 Intracellular vs Extracellular Organic Matter

Phytoplankton derived organic matter arises from two sources, the metabolic excretion forming extracellular organic matter (EOM) or via cell lysis, where intracellular organic matter (IOM) is released from a break in the cell wall (Henderson *et al.* 2008). The extracellular release of organic matter from phytoplankton is dominated by proteins and carbohydrates (38 % < 1kDa) as waste and excess photosynthetic derivatives (Reynolds 2007; Li *et al.* 2012). A high concentration of

525 proteins would result in substantial formation of DBPs (Hong
526 *et al.* 2008). A comparison of EOM and IOM allows for
527 increased precision when estimating the total DBPFP within the
528 water treatment plant. A study by Li *et al.* (2012) assessed
529 cyanobacteria *Microcystis aeruginosa,* to compare total
530 contribution of EOM and IOM to organic matter yield and DBP
531 concentrations. EOM contributed significantly less organic
532 matter than IOM, 29.7 and 100.5 mg/L respectively. However,
533 assessment of DBP formation indicates that EOM contributed
534 more to the formation of both THMs and NDMA per mg of
535 carbon when water samples were subjected to chlorination and
536 chloramination (Figure 4) (Li *et al.* 2012). In comparison to
537 IOM, EOM is represented as a significant contributor to the
538 formation of DBPs, inferring that species with a large
539 surrounding mucilage component and high cellular exudation
540 rate will have a greater contribution to the formation of DBPs
541 (Nguyen *et al.* 2005; Li *et al.* 2012). A corresponding study by
542 Huang *et al.* (2009), identified that specific yield from EOM
543 resulted in a slightly higher total THM and HAA yield
544 compared with the IOM for *Anabaena flos-aquae*. However,
545 the opposite trend was observed for *Microcystis aeruginosa*,
546 contradictory to results by Li *et al.* (2012). Variability in
547 species strain, light and nutrient availability are known to alter
548 the production of EOM and are a likely explanation for
549 variations between the two studies (Mague *et al.* 1980;

Reynolds 1984). Both studies identified, using a mass specific comparison, that IOM was the main contributor to the formation of DBPs due to the significantly larger contribution of NOM (Huang *et al.* 2009; Li *et al.* 2012). This mass specific comparison of EOM and IOM indicated that intracellular content contributed 77.2, 80.9, 63.3 and 77.2 % of the total organic matter, THMFP, HAAFP and NDMAFP respectively (Li *et al.* 2012). The auto-lysis of phytoplankton cells will release excess DOC that is comprised of up to 86 % hydrophilic matter remaining recalcitrant during conventional water treatment. Therefore both IOM and EOM contribute significantly to the formation of DBPs.

3.1 Other Contributing Factors to DBP Formation

Disinfection by-product formation is influenced by environmental conditions, the choice of disinfectant, concentration of inorganic moieties such as bromide and iodide, and the physical conditions of the chemical reaction including; temperature, pH, dosage of disinfectant and contact time of the reaction.

3.1.1 Environmental Conditions

To enable adequate growth and proliferation of phytoplankton the physical, chemical and biological conditions of the lake have to be suitable. The impact of climate dramatically alters

574 community composition with variation of species dominance
575 depending upon the mixing/stratification regime and nutrient
576 availability (Lund 1965). Typically green algae and diatoms
577 rely on vertical mixing of the water column to remain entrained
578 and ensure adequate exposure within the euphotic zone to
579 satisfy their light requirements (Brookes *et al.* 2003; Oliver *et*
580 *al.* 2012). Warm conditions that enable stratification to develop
581 can favour the gas vacuolated cyanobacteria. Climate change
582 scenarios indicate that freshwater systems will be exposed to
583 increased temperatures, more intense and longer periods of
584 thermal stratification and altered nutrient loads potentially
585 favouring cyanobacteria over other phytoplankton groups
586 (Carey *et al.* 2012). Increase in cyanobacteria production due to
587 the effects of climate change is of concern given their chemical
588 composition, contribution to DOC and notoriety of forming
589 blooms.

590 Nutrient availability is fundamental for phytoplankton growth,
591 with limiting nutrients reducing the growth. Carbon, nitrogen
592 and phosphate have often been considered to restrict
593 phytoplankton growth (Hecky and Kilham 1988). Reviews by
594 Hecky and Kilham (1988) and Guildford and Hecky (2000) on
595 nutrient limitations have identified that phosphorus
596 concentration is the critical limiting nutrient that regulates algal
597 biomass and growth rates within most freshwater systems
598 (Nagar *et al.* 1974); although nitrogen limitation can occur in

599 freshwater systems (Baker *et al.* 2000). In an evaluation of
600 historical data from Myponga Reservoir, South Australia
601 Linden *et al.* (2004) compared the maximum annual total
602 phosphorus (TP) and the maximum chlorophyll *a* found in the
603 following growth period in the years between 1985 and 2000
604 (Figure 5). They showed chlorophyll *a* concentrations as a
605 measure of phytoplankton abundance increased as total
606 phosphorus increased supporting earlier works (Sakamoto
607 1966; Vollenweider and Dillon 1974; Jones and Lee 1982).
608 This indicates the significant role that phosphorus plays in
609 determining both the rate of phytoplankton growth and the
610 carrying capacity of a lake, which would determine the yield of
611 organic matter produced.

612

613 ***3.1.2 Disinfection Agent***

614 The choice of disinfectant is important in determining what
615 DBPs can be formed in the presence of NOM and inorganic
616 matter. Chlorine is predominantly used as a disinfectant for
617 water treatment due to its low cost and stability, as it provides a
618 residual to prevent microbial regrowth throughout the
619 distribution network (Bond *et al.* 2011; Fabris *et al.* 2012;
620 Zhang *et al.* 2014). At a pH < 7.5 chlorine dissolves in water to
621 form a strong oxidising agent, hypochlorous acid, capable of
622 oxidising NOM. Due to public health concerns regarding DBP

formation, there has been an increasing interest in the substitution of chlorine by other disinfectants.

Hua and Reckhow (2007) used natural surface waters collected from Newport News Virginia to study the DBP formation potential using five oxidants; chlorine, chloramine, both with and without pre-ozonation, and chlorine dioxide. To minimise variation between experiments the temperature (20°C), pH (7) and reaction time (48 hours) were held constant. A range of DBPs were monitored, including four chlorinated/brominated THMs, nine chlorinated/brominated HAAs, three dihaloacetonitriles, two haloketones, chloropicrin and total organic halide (TOX). There were several notable outcomes from this experiment; each disinfection scenario was capable of producing a unique range of DBPs with a large percentage of unknown halogenated compounds (UTOX) formed. The use of Ozone and chloramines as disinfection agents resulted in the increased formation of nitrogenous DBP's that are known to be more genotoxic. When Ozone was used in conjunction with chloramine the concentration of UTOX increased substantially. This increase in UTOX was also achieved when chloramine or chlorine dioxide were used as the sole disinfectant. These results indicated that the issue of DBP formation cannot be resolved simply by using an alternate disinfection agent.

The investigation of DBP formation from various disinfectants by Hua and Reckhow (2007) can provide an understanding of what DBPs are likely to form when the source water contains higher concentrations of hydrophilic, phytoplankton derived organic matter. Analysis of chloramination and chlorination of phytoplankton by Fang et al. (2010a) identified significant differences in DBP yields between the two treatments. Chlorination of M.*aeruginosa* culture resulted in increased formation of N-DBPs and haloaldehydes, with reduced C-DBP formation in comparison a dominant humic NOM source. Alternatively, chloramination of phytoplankton culture resulted in a slight reduction of total DBP formation in comparison to a humic NOM source. The use of a strong oxidiser such as ozone can result in an overall increase in DBP formation due to its ability to lyse algal cells, releasing IOM and increasing DBP formation during subsequent chlorination/chloramination (Fang et al. 2010a).

When choosing a disinfection agent it is also important to consider other issues including; the inability to retain disinfection residual (ozone), inefficiency against taste and odour compounds (chloramine), higher concentration of unknown total organic halide (UTOX) with a potentially higher genotoxicity (chloramine, ozone/chloramine, chlorine dioxide), and higher chemical costs (ozone, ozone/chlorine, ozone/chloramine) (Nikolaou *et al.* 1999).

3.1.3 Dose and Contact Time

Application of chlorine for the efficient disinfection of potable water supplies is driven by the maintenance of a chlorine residual post treatment, influenced by dose concentration time and the contact time of the reaction. A chlorine concentration of 0.5 mg/L at point of delivery is recommended (World Health Organisation 2011). A reduction in chlorine dose can allow for incomplete removal of biological pathogens or insufficient chlorine to reach the end of the distribution system. Chlorine residual less than the recommended concentration can allow for microbial regrowth throughout the distribution network, exposing consumers to an increased risk of disease from waterborne pathogens. However, excess chlorine dose can result in an escalated health risk by increasing total DBP formation (Sadiq and Rodriguez 2004). For example, El-Dib and Ali (1995) observed that upon chlorination of Nile River water total THM formation increased from 70 to 85 µg/L when chlorine dose was increased from 5 to 20 mg/L respectively (contact time = 2 hours, pH = 8, temperature = 20°C). A similar relationship was observed by Dojlido *et al.* (1999), identifying peak HAA concentrations when chlorine dose was highest.

Contact time with chlorine also influences the formation rates of DBPs (Nikolaou *et al.* 1999). El-Dib and Ali (1995) determined that total THM formation ranged from 30 to 90 µg/L when contact time was adjusted from 30 to 240 minutes

696 respectively (Cl_2 dose = 5 mg/L, pH = 8, temperature = 20°C).
697 A corresponding experiment by Liang and Singer (2003)
698 supports these results, whilst suggesting that HAA
699 concentration also increases with prolonged contact time.
700 However, increased contact time can also result in the
701 decreased concentration of some halogenated DBPs including
702 haloacetonitriles (HANs) and haloketones (HKs) as a result of
703 hydrolysis and further reactions with chlorine (Singer 1994).

704 An increase in chlorine concentration and contact time during
705 the disinfection of a phytoplankton dominated system has the
706 potential to significantly increase DBP formation with a
707 probable increased production of N-DBP. Chlorine dose and
708 contact time affects phytoplankton cell integrity, releasing
709 intracellular content for further reaction (Daly *et al.* 2007).
710 Further research is required to determine how chlorine dose
711 concentration affects the rate of DBP and more specifically N-
712 DBP formation from phytoplankton derived organic precursors.

713

714 ***3.1.4 Temperature***

715 Disinfection by-product formation is also influenced by the
716 temperature and pH of the water during treatment. Research by
717 Roccaro *et al.* (2008) studied the effects of temperature on
718 chlorine consumption and formation of DBPs from Ancipa
719 Reservoir samples. It was evident that chlorine consumption

720 accelerated as temperature was manipulated from 3 to 34°C and
721 disinfection by-product formation increased as reaction
722 temperature was altered from 3 to 20°C. A further increase in
723 temperature from 20 to 34°C resulted in a shift in DBP
724 speciation to a less brominated pool. Higher temperatures result
725 in increased reaction rate kinetics causing faster and higher
726 yielding formation of DBPs (Fang *et al.* 2010b). This has
727 seasonal implications suggesting that DBPFP will be
728 maximised during summer, when ambient temperatures are
729 higher (Nikolaou and Lekkas 2001).

730 Phytoplankton population densities are strongly influenced by
731 seasonal fluctuations, typically peaking in summer when water
732 temperatures are at a maxiumum and stratification is most
733 strongy developed (Reynolds 1984). Although phytoplanklton
734 are capable of surviving subarctic and arctic climates, their
735 growth rates are substantially diminished (Rautio *et al.* 2011).
736 The optimum temperature and the degree to which growth rate
737 increases with temperature; differ greatly between
738 phytoplankton species. The Q10 temperature coefficient for
739 growth describes the rate of change of growth rate with a 10°C
740 change in temperature. The Q10 for cyanobacteria range
741 between 1.8-4.3 and for chlorophytes 1.1-3.7 (Lurling *et al.*
742 2013). Therefore warmer temperature will accelerate
743 phytoplankton growth and phytoplankton-derived DOC
744 concentrations. An increase in phytoplankton-derived DOC

745 will result in increased concentrations of hydrophilic organic
746 matter contributing to DBP formation upon chlorination.

747 ***3.1.5 pH***

748 The effects of pH on DBPFP is more complex as it chemically
749 alters the speed of the rate determining step of the reaction
750 (Bond *et al.* 2011). Therefore, the effect of pH on the formation
751 of DBPs is defined by the chemical structure of the precursor.
752 Research by Hua and Reckhow (2008) assessed the rate of
753 formation of THMs, dihaloacetic acids (DHAA), trihaloacetic
754 acids (THAA) and UTOX at pH values of 5, 7 and 10 (DOC =
755 4.7 mg/L, chlorine dose = 8.1 mg/L, contact time = 72 hours,
756 temperature = 20°C). The yield of THMs and DHAAs
757 increased as pH was elevated from 5 to 10. However, the
758 opposite effect was observed for the formation of THAAs and
759 UTOX. A decrease in TOX concentration from 930 to 878 and
760 768 µg/L was also observed as pH increased from 5 to 7 and 10
761 respectively. The reduction in concentration of some DBPs
762 may result from accelerated hydrolysis and dehalogenation at
763 higher pH values (Singer 1994; Hua and Reckhow 2008).
764 Therefore it would be critical to determine the effect of pH on
765 DBP formation from phytoplankton precursors, to enable a
766 more accurate prediction of DBPFP speciation and toxicity.
767 Phytoplankton are able to modify the pH of the water due to
768 formation of by-products from photosynthesis and respiration.
769 During the day photosynthesis increases with increasing

exposure to light, consuming free CO_2 and increasing O_2 production; resulting in an increase in alkalinity. At night the opposite is true, photosynthesis rates decrease and respiration increases, raising CO_2 concentrations; resulting in an increase in acidity (Wetzel 2001). Therefore during a bloom event the time of the day will considerably influence the pH of the water and may indirectly impact DBP formation where pre-oxidation is practised.

3.1.6 Influence of Inorganic Constituents

The chemical speciation of DBP formation upon chlorination is altered by the presence of inorganic constituents, bromide and iodide. Upon chlorination, bromide and iodide are rapidly oxidised to hypobromous acid and hypoiodous acid respectively. Hypobromous and hypoiodous acids are active oxidising agents that react with NOM to form brominated and iodated DBPs. To investigate the effect of these inorganic constituents on DBP formation Hua *et al.* (2006) analysed raw water samples from drinking water treatment plant intakes at the City of Winnipeg, Manitoba and the City of Tulsa, Oklahoma. Samples were dosed with bromide and iodide at concentrations of 0, 2, 10 and 30 µM prior to chlorination. Chlorination of the samples was conducted to produce a chlorine residual of 0.5 mg Cl_2/L after a 48 hour contact time at 20°C with a pH of 7. The experiment concluded that increased concentration of bromide and iodide halogens resulted in a

general increase in DBP speciation dominated by bromo- and iodo- moieties by outcompeting chlorine substitution. The addition of 2-30 µM of bromide to Tulsa raw water samples increased the total yield of THMs (four species) by 18-74% and HAAs (nine species) by 2-35% respectively. The addition of 2-30 µM of iodide to Tulsa raw water samples had minimal effect on total THM (10 species) yield; whilst TOX decreased by 2-35 % respectively. The rate of iodide substitution was also significantly slower than bromide substitution. The formation of bromo- and iodo- substituted DBPs results in higher values of genotoxicity, causing concern for detrimental health outcomes (Plewa *et al.* 2004a; Plewa *et al.* 2004b; Richardson *et al.* 2007). The influence of inorganic constituents on DBP formation and speciation varied depending on the conditions of the NOM precursors in the source water. For example, Cowman and Singer (1996) assessed the effect of bromide on aquatic humic substances and found no correlation between bromide concentrations and HAA formation.

The concentration of inorganic constituents also alters the DBP formation potential of phytoplankton precursors. Results obtained from studies of *Microcystic aeruginosa*, indicated that the addition of bromide shifted DBP formation from HAA to THM dominated compounds (Wei *et al.* 2011). These results are contradictory to results from Hua *et al.* (2006) where whole raw water samples were used. The effects of inorganic

820 constituents on a phytoplankton dominated system could have
821 profound effects on DBP formation, speciation and the
822 resulting associated health risk.

823

824 **4.1 Mitigation of DBP formation from Phytoplankton**
825 **Derived Precursors**

826 To mitigate DBP formation it is critical that hydrophilic,
827 autochthonous organic matter is targeted and removed prior to
828 chlorination. This could be achieved by improving catchment
829 management to reduce nutrients and phytoplankton production.
830 Improved catchment management combined with an
831 understanding of the dominant species and abundance of
832 phytoplankton within the system will allow for early detection
833 of increased DBP formation potential. More advanced water
834 treatment such as activated carbon, ultrafiltration, or resins can
835 then be utilised to prevent risk of exposure to phytoplankton
836 derived DBPs during a detected increase in phytoplankton
837 abundance, reducing the concentration of NOM precursors
838 exposed to chlorination.

839 Developing a greater understanding of the risk of DBPs to
840 human health will allow for improved monitoring of harmful
841 DBPs and tighter regulation. There is still a significant
842 percentage of UTOX compounds being produced with minimal

understanding of the short and long term impacts to human health.

5.1 Conclusion

The focus on phytoplankton within water treatment has largely been on phytoplankton cell removal and the removal of toxic compounds. However, only a few species are known to produce toxins or taste and odour compounds that can compromise water quality. In contrast all phytoplankton species fix carbon and contribute to the DOC pool and potential DBP precursors. This can pose a threat to human health when increased concentration of algal derived DOC is exposed to chlorine, increasing the risk of DBP formation. The contribution of phytoplankton towards the formation of DBPs is underestimated or largely ignored. The majority of the literature pools various sources of NOM or focuses only on allochthonous contributions to DBP formation. As algal-derived organic carbon is generally more recalcitrant to conventional treatment it is imperative that the total contribution of phytoplankton to the formation of DBPs is thoroughly understood for improved management and the minimisation of associated health risks.

Phytoplankton derived DBP formation is impacted by the rapid algal growth and turnover rates, cellular composition and

biological lability. The contribution of phytoplankton to the formation of DBPs can potentially be heightened due to the notoriety of formation of cyanobacterial blooms, chemical composition and high DON contribution. Reducing phytoplankton populations within the water body is necessary to limit disinfection contact with cells and exudates. Therefore limiting nutrient supply with improved catchment management can mitigate many of the problems associated with algae (Brookes and Carey 2011). Nutrient reduction limits phytoplankton carrying capacity and growth rates minimising the abundance of toxic cyanobacteria and DBP precursors derived from phytoplankton. Reducing the algal concentrations exposed to the disinfection process will reduce DBP formation within the water treatment plant and distribution network.

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Table 1: Examples of pathogens with evidence of health significance, indicating chlorine resistance and expected time for minimal removal during chlorination. Pathogen minimum removal data collected from (Centers for Disease Control and Prevention, 2012) and references therein. (*)Indication of CT times for each pathogen group (World Health Organisation,2011).

	Pathogen	**Health Significance**	**Resistance to Chlorine [a]**	**Minimal Removal (CT_{99})**
Bacteria	Overall*	High	Low	0.04-0.08 min.mg/L (5°C, pH 6-7)
	E. *coli*	High	Low	<0.25 min.mg/L (23°C, pH 7)
	Campylobacter jejuni	High	Low	0.5 min.mg/L (25°C, pH 8)
	Salmonella Typhi	High	Low	1 min.mg/L (20-25°C, pH 7)
Viruses	Overall *	High	Moderate	2-30 min.mg/L (0-10°C, pH 7-9)
	Poliovirus	High	Moderate	6.36 min.mg/L (5°C, pH 6)
	Hepatitis A Virus	High	Moderate	<0.41 min.mg/L (25°C, pH 8)
	Rotavirus	High	Moderate	0.05 min.mg/L (4°C pH7)
	Coxsackie A	High	Moderate	0.14-0.15 min.mg/L (5°C, pH 6)
Protozoa	Overall *	High	High	25-245 min.mg/L (0-25°C, pH 7-8)
	Cryptosporidiumhominis/ parvum	High	High	15,300 min.mg/L (25°C, pH 7.5)
	Entamoeba histolytica	High	High	20 min.mg/L (27-30°C, pH 7)
	Giardia intestinalis	High	High	15 min.mg/L (25°, pH 7)

Table 2: List of regulations on DBPs with associated guideline values from the US EPA, WHO, the European Union and, Australia and New Zealand.

*Sum of the ratio of the concentration of bromoform, dibromochloromethane, bromodichloromethane and chloroform to its respective guideline value can't exceed 1.

World Health Organisation Guideline Values		**US EPA Mandatory Standards**		**European Union Standards Mandatory Standards**		**Australian Drinking Water Guidelines**	
Regulated DBPs	(µg/L)	Regulated DBPs	(µg/L)	Regulated DBPs	(µg/L)	Regulated DBPs	(µg/L)
Total THM	*	Total THM	80	Total THM	100	Total THM	250
Bromate	10	Total HAA (5 regulated)	60	Bromate	10	Chloroacetic acid	150
Bromodichloromethane	60	Bromate	10			Dichloroacetic acid	100
Bromoform	100	Chlorite	1000			Trichloroacetic acid	100
Chlorate	700					Chloral hydrate	100
Chlorite	700					NDMA	0.1
Chloroform	300					Bromate	20
Dibromoacetonitrile	70					Chlorite	800
Dibromochloromethane	100					2-chlorophenol	300
Dichloroacetate	50					2,4-dichlorophenol	200
Dichloroacetonitrile	20					2,4,6-trichlorophenol	20
Monochloroacetate	20					Cyanogen chloride	80
***N*-nitrosodimethylamine (NDMA)**	0.1					Formaldehyde	500
Trichloroacetate	200						
2,4,6-Trichlorophenol	200						

Table 3: Disinfection by-product formation as a result of chlorination of model compounds (Hong *et al.* 2008).

Model Compounds	**$CHCl_3$ (µg mg^{-1} C)**	**DCAA (µg mg^{-1} C)**	**TCAA (µg mg^{-1} C)**
BSA	27.1	25.9	22.8
Fish oil	50.0	3.36	1.27
Starch	3.06	4.91	0.09

Table 4: Total DBPFP based on a comparison of protein, carbohydrate and lipid concentrations from cyanobacteria (8 species), green algae (15 species) and diatom (26 species) (Hong *et al.* 2008).

	Protein (%)	**Carbohydrates (%)**	**Lipids (%)**	**$CHCl_3$ (µg mg^{-1} C)**	**DCAA (µg mg^{-1} C)**	**TCAA (µg mg^{-1} C)**
Cyanobacteria	61.5	25.2	13.3	24.1	17.6	14.2
Green algae	50.5	21.7	27.8	28.3	15.1	11.9
Diatoms	42.9	17.9	39.2	31.8	13.3	10.3

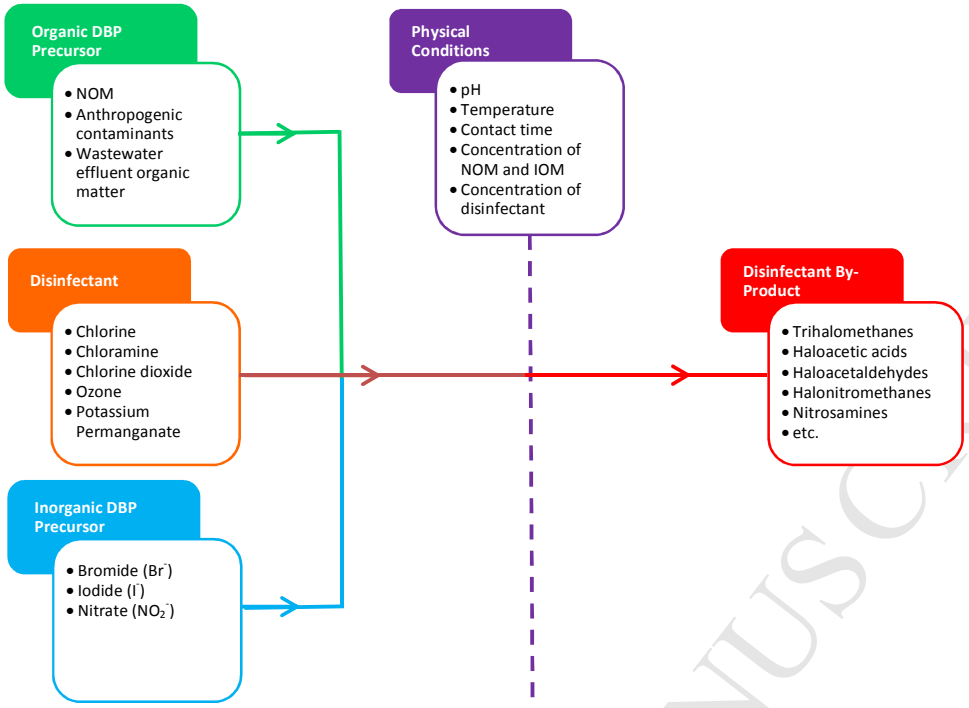

Figure 1: General schematic of DBP formation; the reaction of a disinfectant agent with an organic precursor and/or an inorganic precursor forms a suite of DBPs. The rate and yield of the reaction is governed by a range of physical conditions.

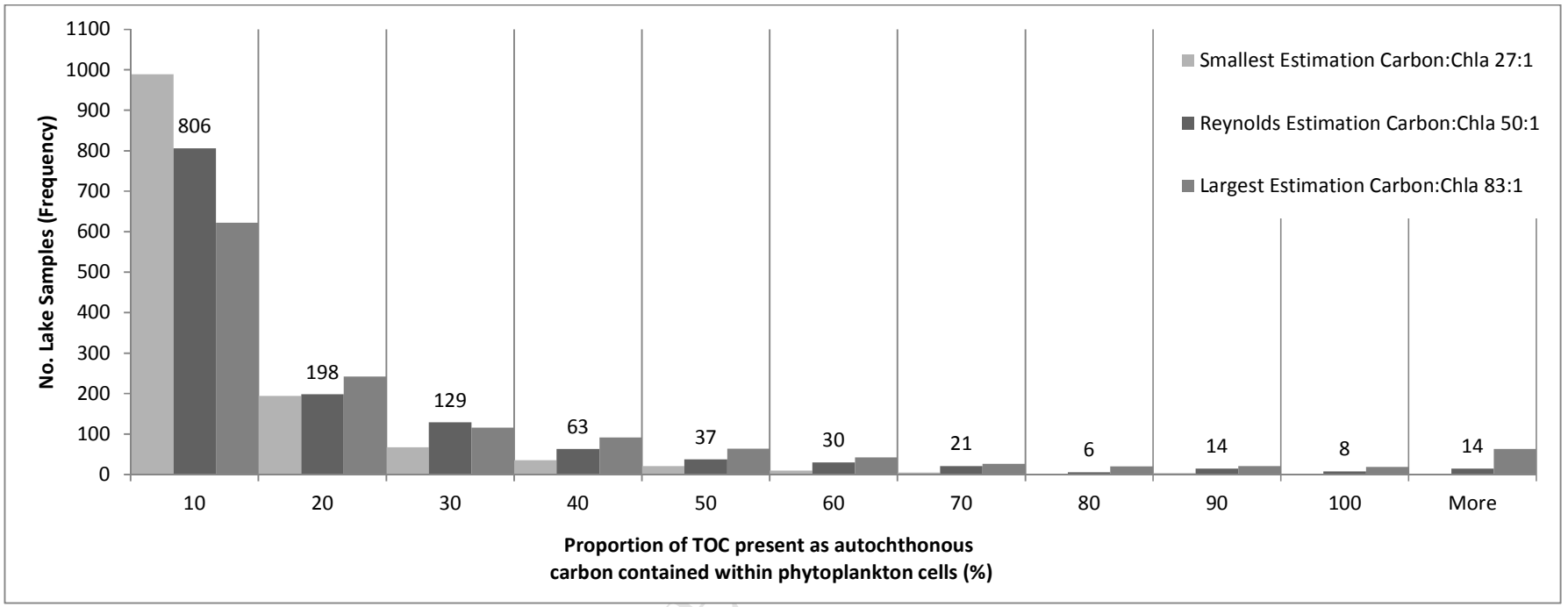

Figure 2: Analysis of the autochthonous carbon load from phytoplankton from the U.S. National Lake Assessment. Phytoplankton carbon contribution was estimated from the known chlorophyll a concentration using predictive ratios from the literature. The Reynolds Estimation (Carbon:Chla, 50:1) is an accurate average estimation of carbon based on total species composition of phytoplankton.

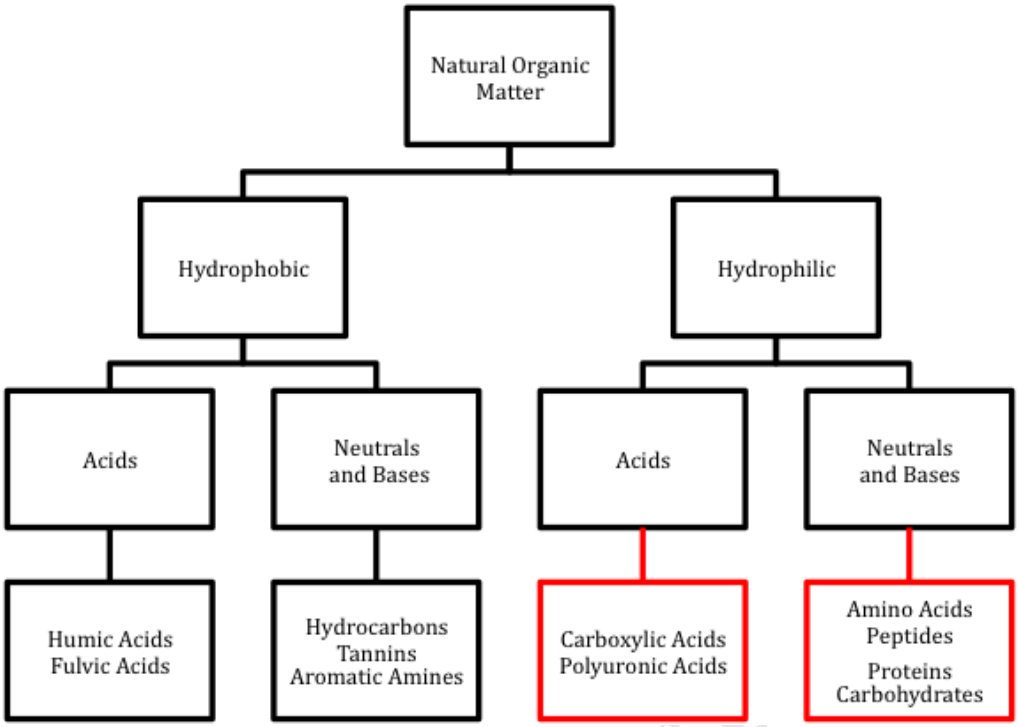

Figure 3: General classification of NOM by hydrophobicity and acidity into specific chemical groups. The red boxes highlight the major constituents of phytoplankton (Leenheer and Croué 2003).

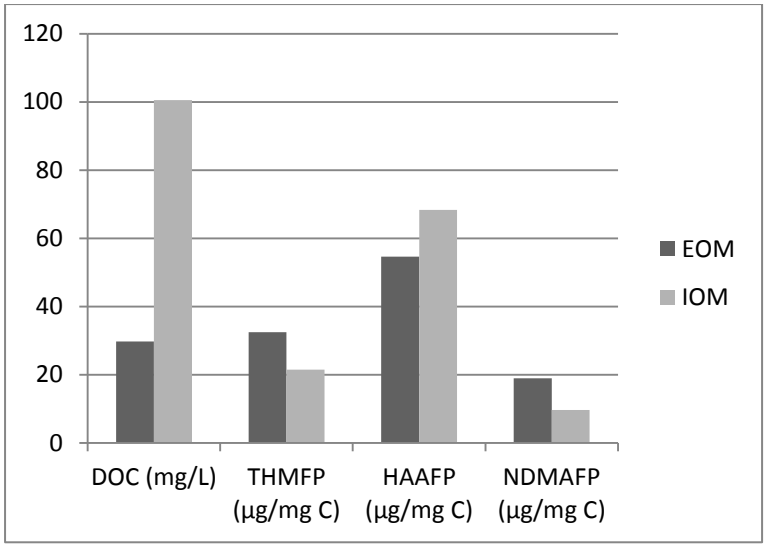

Figure 4: Comparison of IOM and EOM contribution to DOC, trihalomethane formation potential (THMFP), haloacetic acid formation potential (HAAFP) and nitrosodimethylamine formation potential (NDMAFP) (Li *et al.* 2012).

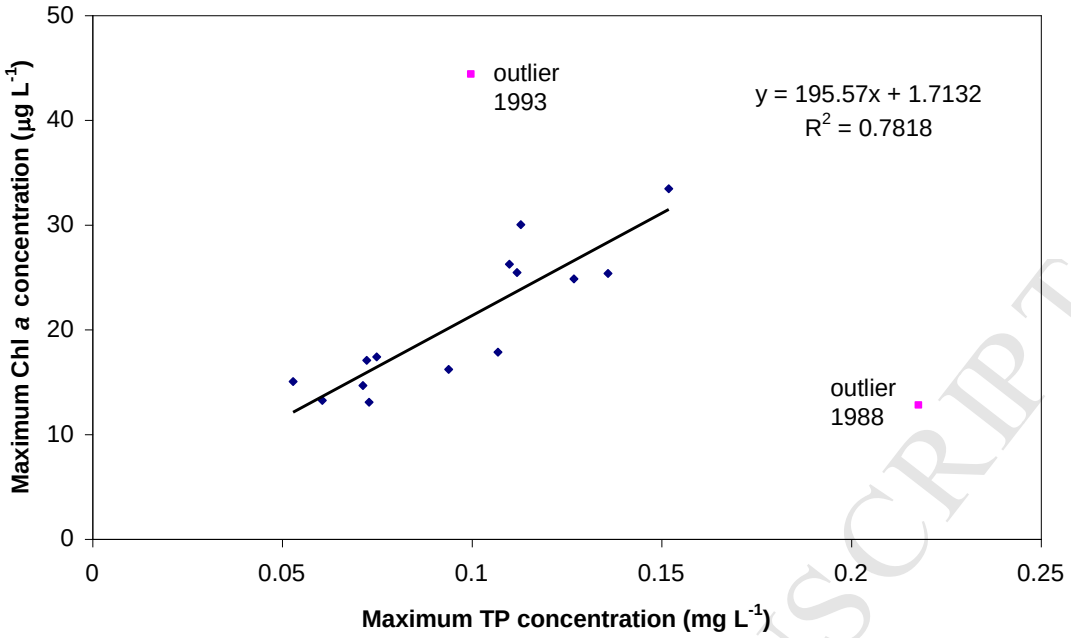

Figure 5: Positively correlated relationship between maximum total phosphorus (TP) and maximum chlorophyll a concentration (Linden *et al.* 2004)

Highlights

- Phytoplankton contains a significant proportion of hydrophilic organic matter.
- Hydrophilic NOM is more recalcitrant to conventional treatment, increasing DBP formation.
- Species population dynamics and continuous exudation contributes significantly to DOC pool.
- High protein content in some species has been linked to increased DBP formation.
- Nutrient reduction limits phytoplankton carrying capacity, aiming to reduce DBP precursors.