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Review

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

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ABSTRACT

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.

Contents

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.

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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. 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 (Fig. 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

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.

	Pathogen	Health significance	Resistance to chlorine[a]	Minimal removal (CT_{99})
Bacteria	Overall[a]	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 [a]	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 [a]	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)

[a] General indication of CT times for each pathogen group (World Health Organisation, 2011).