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Formation and speciation of disinfection byproducts during chlor(am)ination of aquarium seawater

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ABSTRACT

The chemistry associated with the disinfection of aquarium seawater is more complicated than that of freshwater, therefore limited information is available on the formation and speciation of disinfection byproducts (DBPs) in marine aquaria. In this study, the effects of organic precursors, bromide (Br^-) and pre-ozonation on the formation and speciation of several typical classes of DBPs, including trihalomethanes (THM4), haloacetic acids (HAAs), iodinated trihalomethanes (I-THMs), and haloacetamides (HAcAms), were investigated during the chlorination/chloramination of aquarium seawater. Results indicate that with an increase in dissolved organic carbon concentration from 4.5 to 9.4 mg/L, the concentrations of THM4 and HAAs increased by 3.2–7.8 times under chlorination and by 1.1–2.3 times under chloramination. An increase in Br^- concentration from 3 to 68 mg/L generally enhanced the formation of THM4, I-THMs and HAcAms and increased the bromine substitution factors of all studied DBPs as well, whereas it impacted insignificantly on the yield of HAAs. Pre-ozonation with 1 mg/L O_3 dose substantially reduced the formation of all studied DBPs in the subsequent chlorination and I-THMs in the subsequent chloramination. Because chloramination produces much lower amounts of DBPs than chlorination, it tends to be more suitable for disinfection of aquarium seawater.

Introduction

There are at least 240 large marine aquaria and life centers throughout the world (MarineBio, 2012). Chemical disinfectants are widely used in such facilities to inactivate pathogens while protecting marine animal health (Wang et al., 2014), including ozone (O_3), chlorine dioxide (ClO_2), chlorine (Cl_2), and chloramine (NH_2Cl). However, these disinfectants can react with water constituents, such as dissolved organic matter (DOM), ammonia, bromide (Br^-), and iodide (I^-), to form a variety of hazardous disinfection byproducts (DBPs), especially in a recirculating mariculture system (RMS) (Shi et al., 2013; Qiang et al., 2015). RMS enables the treatment of polluted water within a closed loop, offers improved control of effluent discharge, and allows complete environmental control, and thus has been preferentially employed to deal with the ecological problems associated with seawater in marine aquaculture (Sharrer et al., 2007).

O_3, which is primarily used to improve the physicochemical aspects of water quality rather than to provide disinfection (Tango and Gagnon, 2003), has multiple functions, such as

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decomposing DOM and controlling algae, color, odor, and taste (Gonçalves and Gagnon, 2011). Another persistent disinfectant (*e.g.*, ClO_2, Cl_2, or NH_2Cl) is necessary to maintain continuous disinfection capability because O_3 cannot provide a persistent residue in water distribution systems. ClO_2 has been recently adopted as a disinfectant in some RMSs; however, its use is typically accompanied by the continuous accumulation of ClO_3^-. For example, the ClO_3^- concentration in Beijing Aquarium from our previous research could reach as high as 55 mg/L (Qiang et al., 2015), which exceeds the United States Environmental Protection Agency (USEPA)-regulated maximum contaminant level (MCL) for drinking water by a factor of nearly 55. Cl_2 is the most frequently used disinfecting agent in drinking water treatment because of its low cost and high disinfection capacity, whereas undesirable DBPs with potentially harmful health effects, especially trihalomethanes (THMs) and haloacetic acids (HAAs), can be produced in the chlorination process (Cowman and Singer, 1996). Many utilities have been switching from Cl_2 to NH_2Cl disinfection to meet the more stringent regulations on THMs and HAAs. However, NH_2Cl may promote the formation of iodinated trihalomethanes (I-THMs) and nitrogenous DBPs (N-DBPs) (*e.g.*, haloacetamides (HAcAms)). Richardson et al. (2007) suggested that I-THMs could be more toxic than their brominated and chlorinated analogues. A toxicologic study also indicated that the HAcAms are 142 times more cytotoxic than HAAs and 12 times more genotoxic than HAAs (Plewa et al., 2008).

Br^- concentration plays an important role in the formation and speciation of DBPs because it can be readily oxidized to free bromine (FB, HOBr/OBr^-) in the disinfection process (Qiang et al., 2012). FB can further react with other inorganic or organic compounds to produce harmful DBPs (*e.g.*, THMs, HAAs, and I-THMs) (Jones et al., 2012), such that the formation of organic DBPs shifts to more brominated species that are dozens to hundreds of times more cytotoxic and genotoxic than their chlorinated analogues (Richardson et al., 2007). Bromine substitution factor (BSF) has been used to evaluate the substitution extent of DBPs by bromine, which is defined as the molar ratio of bromine incorporated into a given class of DBPs to the sum of chlorine and bromine (Hua et al., 2006).

Pre-ozonation has been commonly applied in the foam fractionation process of aquarium seawater treatment systems to enhance the removal of suspended solids and DOM (Suzuki and Maruyama, 2002). The effect of pre-ozonation on the formation of DBPs depends on water quality parameters (Hua and Reckhow, 2013).

Considerable efforts have been exerted to understand the formation mechanisms of THMs, HAAs, I-THMs, and HAcAms in drinking water. However, the chemistry associated with the disinfection of aquarium seawater is more complex than that of freshwater because of the higher concentrations of inorganic ions (*e.g.*, Cl^-, Br^-, I^-) and organic materials therein (Shi et al., 2013). Therefore, limited information is available on the formation and speciation of disinfection byproducts (DBPs) in marine aquaria. In this study, THM4, dihaloacetic acids (DHAAs), trihaloacetic acids (THAAs), I-THMs, dihaloacetamides (DHAcAms), and trihaloacetamides (THAcAms) were selected as representative DBPs. The effects of DOM, Br^- concentration, and pre-ozonation on the formation and associated BSFs of selected DBPs in the chlorination/chloramination of aquarium seawater were evaluated systematically. This study could help marine aquaria to optimize and update their seawater treatment systems for water quality improvement and animal health protection.

1. Materials and methods

1.1. Chemicals and standards

The DBP standards THM4 (chloroform, TCM; bromodichloromethane, BDCM; dibromochloromethane, DBCM; bromoform, TBM), DHAAs (dichloroacetic acid, DCAA; bromochloroacetic acid, BCAA; dibromoacetic acid, DBAA), and THAAs (trichloroacetic acid, TCAA; bromodichloroacetic acid, DCBAA; dibromochloroacetic acid, DBCAA; tribromoacetic acid, TBAA) were purchased from Accustandard (New Haven, CT, US). I-THMs (dichloroiodomethane, DCIM; bromochloroiodomethane, BCIM; dibromoiodomethane, DBIM; chlorodiiodomethane, CDIM; bromodiiodomethane, BDIM; triiodomethane, TIM), DHAcAms (dichloroacetamide, DCAcAm; bromochloroacetamide, BCAcAm; dibromoacetamide, DBAcAm), and THAcAms (trichloroacetamide, TCAcAm; bromodichloroacetamide, DCBAcAm; dibromochloroacetamide, DBCAcAm; tribromoacetamide, TBAcAm) were purchased from CanSyn (Toronto, Ontario, Canada). All of these chemicals (of analytical grade at least) were of the highest purity available. All aqueous solutions were prepared with ultrapure water produced by a Milli-Q system (Advantage A10, Millipore, Billerica, MA, US). HPLC-grade hexane and methyl-*tert*-butyl ether were purchased from Fisher Scientific (Houston, TX, US). Diethyl-*p*-phenylenediamine test kits were purchased from Hach Company (Loveland, CO, US).

1.2. Characteristics of water samples

Beijing Aquarium is a typical RMS with a total seawater volume of 18,000 m^3. Fresh artificial seawater is prepared with all major ions added externally, including Na^+ (9.50 g/L), Mg^{2+} (1.15 g/L), K^+ (0.35 g/L), Ca^{2+} (0.37 g/L), Cl^- (17.10 g/L), SO_4^{2-} (2.25 g/L), and HCO_3^- (0.14 g/L), to simulate the ion ratios of natural seawater (3.0%–3.5% salinity). The prepared artificial seawater is treated by O_3 and then supplied to non-mammal (*e.g.*, big fish, jellyfish, coral) and mammal (*e.g.*, dolphin, sea lion, white whale) tanks in sequence, to compensate the volume loss during treatment and recycling. Raw seawater samples were collected from the big fish tank (BFT) and sea lion tank (SLT). Both tanks adopt decentralized treatment, which includes sand filtration, foam fractionation, and disinfection. For the BFT, O_3 is first injected online into the foam fractionation facility, from which suspended solids are removed by air floatation, and a certain portion of DOM is decomposed by O_3 oxidation. The penetrating solid particles are further removed by sand filtration. Thereafter, a side stream of the sand-filtered seawater comes in contact with O_3 for approximately 5 min (*i.e.*, bypass treatment) and then merges with the main stream to return to the BFT. The used seawater from the BFT further flows into the mammal tanks (*i.e.*, SLT), in which O_3 is used as the primary disinfectant, followed by ClO_2 as the secondary disinfectant, to provide a persistent residue.