Chemosphere 90 (2013) 2485–2492

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Formation of haloacetic acids, halonitromethanes, bromate and iodate during chlorination and ozonation of seawater and saltwater of marine aquaria systems

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HIGHLIGHTS

- Created methods for haloacetic acids and halonitromethanes in seawater and saltwater.
- Determined HAAs and HNMs in full scale aquaria with widely varying bromide concentrations.
- Determined effect of chlorine and ozone on HAA, HNM, bromated and iodate formation.
- Provided key information on controlling DBPs in seawater and saltwater aquaria.

ARTICLE INFO

Article history:
Received 23 May 2012
Received in revised form 8 September 2012
Accepted 20 September 2012
Available online 22 November 2012

Keywords:
Water disinfection
Disinfection byproducts
Aquaria
Halonitromethane
Trihalomethane
Haloacetic acid

ABSTRACT

This manuscript addresses identification, analysis, formation and occurrence of key disinfection byproducts (DBPs) formed during chlorination and/or ozonation of both natural seawater (NSW), and synthetic high- and low-bromide saltwater (HBSW and LBSW, respectively). In this study, several groups of water disinfection byproducts were studied, including haloacetic acids (HAAs), halonitromethanes (HNMs), bromate and iodate. Three different water systems were studied including filtered natural seawater (NSW, ca. 64.9 mg L^{-1} Br^-), a high-bromide (Br^-) saltwater (HBSW, ca. 24.8 mg L^{-1} Br), and low-Br^- saltwater (LBSW, ca. 4.3 mg L^{-1} Br). Because ozone reacts with Cl^- to form free chlorine in seawater and salt water systems, similar DBP patterns were observed for both chlorine and ozone oxidants. The results revealed that some HAAs and HNMs are formed at greater than 100 μg L^{-1} concentrations and are greatly affected by water constituents and formulations when treated with chlorine and ozone. The results showed that in low-Br^- water salt water, chlorinated HAAs and HNMs predominated, while much greater concentrations of brominated HAAs and HNMs were produced in both natural and synthetic higher Br^- saltwater. Concentrations of bromate and iodate were strongly impacted by factors other than Br^- and I^- concentrations including whether the system was open or closed.

1. Introduction

Free chlorine ($HOCl/OCl^-$) and ozone (O_3) are common disinfectants used in aquaria treatment systems. In addition to serving as an effective disinfectant, ozone is particularly valuable for its ability to enhance water clarity through both microflocculation and decolorization mechanisms. Chlorine and ozone form disinfection byproducts (DBPs) through both direct reactions, and indirect reactions with secondary oxidants formed *in situ* via reactions with ammonia, chloride (Cl^-), bromide (Br^-), dissolved organic matter (DOM), and other water constituents (Beech et al., 1980; Richardson et al., 1999; Reed and Adams, 2003; Zwiener et al., 2007).

The chemistry associated with chlorination and ozonation of natural seawater and saltwater (artificial sea water formulations) in aquaria is complex due to high concentrations of inorganic ions (e.g., Cl^-, Br^-, etc.) and organic compounds. Modeling work by Reed and Adams (2003) showed that the Br^- concentration plays an important role in the chemical speciation within the aquaria with higher bromide concentrations leading to significant free bromine ($HOBr/OBr^-$) concentrations. Due to highly varied concentration differences of Br^- (and ratios to Cl^-) and DOM in the three aquaria waters, it was hypothesized that different distributions of DBPs may form at the three treated waters.

Swimming pool literature suggests that chloramines are primary disinfection byproducts (Eichelsdörfer and Slovak 1975).

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http://dx.doi.org/10.1016/j.chemosphere.2012.09.073

Chloramines are readily formed *in situ* by the reaction of free chlorine with ammonia/ammonium (NH_3/NH_4^+):

$$HOCl/OCl^- + NH_3/NH_4^+ \rightarrow NClH_2 \quad (1)$$

$$HOCl/OCl^- + NClH_2 \rightarrow NCl_2H \quad (2)$$

$$HOCl/OCl^- + NCl_2H \rightarrow NCl_3 \quad (3)$$

Ammonia is present from excrement and other sources especially in natural seawater. During water treatment, free chlorine may be added directly to the water, or may be formed *in situ* by the reaction of ozone with the high concentrations of Cl^- present in natural seawater and artificial saltwater formulations. Free bromine ($HOBr/OBr^-$) is also readily formed by the reaction of free chlorine with the Br^-. In reactions analogous to those shown above, bromamines are formed by the reactions of free bromine and ammonia/ammonium. Thus, during either chlorination or ozonation of seawater or saltwater, a suite of chloramines and bromamines may be formed in varied concentrations depending on the specific makeup of the water. It is likely that iodide (I^-) present in seawater/saltwater formations also plays an important role in DBP formation in an analogous manner to the Cl^- and Br^-.

Trihalomethanes (THMs) and five haloacetic acids (HAAs) are regulated DBPs in drinking water for chloro- and bromo-species, while iodo-THMs and other HAAs are not currently regulated. The sum of the four chloro- and bromo-THMs are regulated at a limit of 80 $\mu g\ L^{-1}$ in drinking water (USEPA, 2006). Previous work by Shi and Adams (2012) observed concentrations of THMs in seawater/saltwater aquaria at concentrations ranging up to 140 $\mu g\ L^{-1}$.

Haloacetic acids are known disinfection byproducts in drinking and swimming pool waters (Zwiener et al., 2007). The sum of five of the chloro- and bromo-HAAs (monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoactic acid (DBAA)) are regulated at a limit of 60 $\mu g\ L^{-1}$ in drinking water (USEPA, 2006). Shi and Adams (2009) observed concentrations of monobromoacetic acid (MBAA) of 192 $\mu g\ L^{-1}$ while monitoring for a wide suite of chloro-, bromo- and iodo-acetic acids.

Iodo-DBPs (including iodo-THMs and HAAs) may also be significant disinfection byproducts, though they have not been frequently measured due to lack of reliable analytical methods. Bromate is formed as a terminal oxidation byproduct for bromine in aqueous systems. While bromate in drinking water is analyzed using ion chromatography (IC) methods (USEPA Methods 300.1 and 326), high Cl^- concentrations in seawater and saltwater makes these methods unusable for marine aquaria. A new method was developed by Shi and Adams (2009) to analyze bromate concentrations in seawater/saltwater using ICPMS, and which was used in this study. While halonitromethanes (HNMs) are a group of toxic emerging DBPs in drinking water, no studies have been conducted on HNM formation in seawater and saltwater systems.

The purpose of this study was to evaluate the occurrence and formation of a suite of inorganic halogen species, HAAs and HNMs in seawater/saltwater aquaria systems disinfected with chlorine and ozone. In this study, water samples included both field samples from aquaria and laboratory prepared samples from disinfection experiments using chlorine and ozone.

2. Methods

2.1. Chemicals and instruments

Iodoacetic acids including chloroiodoacetic acid (CIAA), bromoiodoacetic acid (BIAA), diiodoacetic acid (DIAA), halonitromethane (HNM) standards including chloronitromethane (CNM), dichloronitromethane (DCNM), dibromonitromethane (DBNM), tribromonitromethane (TBNM), bromochloronitromethane (BCNM), bromodichloronitromethane (BDCNM), and dibromochloronitromethane (DBCNM), were purchased from Orchid Cellmark (New Westminster, BC, Canada). The other DBP standards monoiodoacetic acid (MIAA), monobromoacetic acid (MBAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), bromodichloroacetc acid (BDCAA), dibromochloroacetic acid (DBCAA), tribromoacetic acid (TBAA), bromonitromethane (BNM), and trichloronitromethane (TCNM), were purchased from Sigma–Aldrich (St. Louis, MO, USA). Naphthalene-d_8, sodium hypochlorite, sodium bromide, and sodium iodide were also products of Sigma–Aldrich. All of these chemicals were of the highest purity available. Deionized (DI) water (18.2 MΩ cm) was prepared by using a Milli-Q water purification system (Millipore, Bedford, MA, USA). Methanol, so-

Table 1
Formations of HAAs and other halogenated compounds by chlorination and ozonation of marine aquaria water samples.

Sample ID	Treatment	Bromoacetic acid concentrations (MSA)							BrO_3^- ($mg\ L^{-1}$)	Br^- ($mg\ L^{-1}$)	IO_3 ($mg\ L^{-1}$)	BrO_3^-/Br^- Molar ratio	BrO_3^-/IO_3^- Molar ratio
		MBAA	BCAA	DBAA	BDCAA	DBCAA	TBAA	BAAs					
NSW													
Inlet	No treatment	<2.54	<2.63	<1.36	<3.28	<2.15	54	54	<0.00165	64.0	0.090	<0.00002	<0.025
Inlet	Free chlorine	<2.54	<2.63	<1.36	<3.28	<2.15	55	55	<0.00165	No data	No data	No data	No data
Inlet	Ozone	<2.54	<2.63	<1.36	<3.28	<2.15	61	61	<0.00165	58.6	0.176	<0.00002	<0.013
Main basin	No treatment	<2.54	<2.63	<1.36	<3.28	<2.15	19	19	<0.00165	62.4	0.081	<0.00002	<0.028
Main basin	Free chlorine	<2.54	<2.63	<1.36	<3.28	<2.15	44	44	<0.00165	55.7	0.171	<0.00002	<0.013
Main basin	Ozone	<2.54	<2.63	<1.36	<3.28	<2.15	38	38	<0.00165	61.2	0.179	<0.00002	<0.013
HBSW													
Inlet	No treatment	<2.54	90	<1.36	28	<2.15	69	187	No data	21.5	0.032	No data	No data
Inlet	Free chlorine	<2.54	<2.63	59	40	17	91	207	1.10	19.5	0.135	0.04	11
Inlet	Ozone	<2.54	<2.63	50	46	13	85	194	0.90	26.9	0.117	0.02	11
Main basin	No treatment	<2.54	55	<1.36	27	7	116	205	No data	21.6	0.034	No data	No data
Main basin	Free chlorine	<2.54	<2.63	62	53	16	134	265	0.81	18.5	0.121	0.03	9
Main basin	Ozone	<2.54	<2.63	56	62	17	150	285	0.75	26.6	0.106	0.02	10
LBSW													
Inlet	No treatment	<2.54	<2.63	<1.36	122	36	<2.01	158	3.79	1.54	0.034	1.54	155
Inlet	Free chlorine	<2.54	<2.63	9	119	37	<2.01	165	4.39	1.90	0.184	1.44	33
Inlet	Ozone	<2.54	<2.63	28	139	47	<2.01	214	3.86	1.62	0.120	1.49	44
Main basin	No treatment	<2.54	<2.63	<1.36	189	34	<2.01	223	3.68	1.48	0.034	1.55	148
Main basin	Free chlorine	<2.54	<2.63	16	108	35	<2.01	159	3.65	1.37	0.173	1.66	29
Main basin	Ozone	<2.54	<2.63	9	135	40	<2.01	184	3.63	1.71	0.145	1.33	34