Chemosphere 198 (2018) 68–74

Contents lists available at ScienceDirect

Chemosphere

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

Removal of haloacetamides and their precursors at water purification plants applying ozone/biological activated carbon treatment

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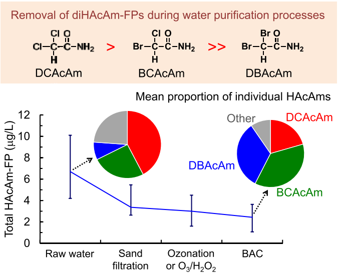
HIGHLIGHTS

- HAcAms formed by intermediate chlorination were removed via BAC treatment.
- Removal of total HAcAm-FPs during water purification processes ranged 50–75%.
- Removal of brominated AcAm-FPs was lower than chlorinated AcAm-FPs.
- DOM sites, for HAcAm precursors and high reactivity in ozonation, were different.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 October 2017
Received in revised form
16 January 2018
Accepted 21 January 2018
Available online 1 February 2018

Handling Editor: Xiangru Zhang

Keywords:
Haloacetamide
Chlorination
Bromine incorporation factor
Advanced water purification process
Dissolved organic matter fractionation

ABSTRACT

Haloacetamides (HAcAms) are nitrogenous disinfection byproducts in drinking water. The profiles of six HAcAms and their formation potentials (FPs) upon chlorination at water purification plant 1 (WPP-1) in September 2016 and at WPP-2 in September 2016 and January 2017 were investigated. HAcAms were removed effectively when they were formed via intermediate chlorination during water purification processes. Removal of total HAcAm-FPs ranged from 50% to 75%. Coagulation/flocculation/sand filtration showed the highest removal of total HAcAm-FPs. As for individual HAcAms, while chlorinated acetamide-FPs were removed, brominated acetamide-FPs, particularly 2,2-dibromoacetamide, remained. The bromine incorporation factors increased during all water purification processes except ozonation and the ozone/hydrogen peroxide process for diHAcAms (2,2-dichloroacetamide, 2-bromo-2-chloroacetamide, and 2,2-dibromoacetamide). The trends in relationships between DOM indices (fractions of dissolved organic matter, ultraviolet absorbance at 260 nm, and fluorescence intensities representing humic-like and tryptophan-like compounds) and total HAcAm-FPs during ozonation and ozone/hydrogen peroxide process were different from those during other processes.

1. Introduction

Nitrogenous disinfection byproducts (N-DBPs) are emerging compounds in drinking water and are reported to be more toxic

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https://doi.org/10.1016/j.chemosphere.2018.01.093

than regulated DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Plewa et al., 2008; Shah and Mitch, 2012). Haloacetamides (HAcAms) are one of the N-DBP groups formed after chlorination and chloramination (Shah and Mitch, 2012). When the median toxicity index values of the individual chemicals between HAcAms and HAAs were compared (Plewa et al., 2008), HAcAms were 99× more cytotoxic and 19× more genotoxic in Chinese hamster ovary (CHO) cells than those of 13 HAAs. In that study (Plewa et al., 2008), the decreasing order of tendency of the halogens for cytotoxicity and genotoxicity of HAcAms was iodine, bromine, and chlorine. In addition, oxidative stress in mice was observed after exposure to monoHAcAms, in order from highest to lowest stress of 2-iodoacetamide, 2-bromoacetamide (BAcAm), and 2-chloroacetamide (CAcAm) (Deng et al., 2014). Delay of embryos and malformation (Lin et al., 2016) and acute damage of metabolism and DNA (Lin et al., 2016; Yu et al., 2015) were observed with exposure of zebrafish to 2,2-dichloroacetamide (DCAcAm).

Occurrence of HAcAms in drinking water has not been intensively investigated like THMs, HAAs, and other N-DBPs have [e.g., *N*-nitrosamines and haloacetonitriles (HANs)]. However, it was reported that HAcAms were widely found in drinking water in several countries investigated (Bond et al., 2015; Chu et al., 2012b; Krasner et al., 2006). The HAcAms targeted were generally chlorinated and brominated acetamides (AcAms), and the number of HAcAms targeted depended on the study. In some cases, iodinated AcAms were also investigated (Chu et al., 2012b). Among the HAcAms, it was reported that diHAcAms were predominant species in drinking water (Chu et al., 2012b; Kosaka et al., 2016). In the US, the total concentrations of five HAcAms [CAcAm, BAcAm, DCAcAm, 2,2-dibromoacetamide (DBAcAm), and 2,2,2-trichloroacetamide (TCAcAm)] in finished water at 12 water purification plants (WPPs) ranged from < minimum reporting level to 7.1 μg/L (median: 1.4 μg/L) (Krasner et al., 2006). In China, total concentrations of 13 HAcAms [CAcAm, BAcAm, DCAcAm, 2-bromo-2-chloroacetamide (BCAcAm), DBAcAm, TCAcAm, 2-bromo-2,2-dichloroacetamide, 2,2-dibromo-2-chloroacetamide, 2,2,2-tribromoacetamide, 2-iodoacetamide, 2-chloro-2-iodoacetamide, 2-bromo-2-iodoacetamide, and 2,2-diiodoacetamide] in finished water at seven WPPs ranged from 0.07 to 8.20 μg/L (Chu et al., 2012b), and those of four HAcAms (DCAcAm, BCAcAm, DBAcAm, and TCAcAm) in distributed waters of six districts ranged from 0.1 to 3.1 μg/L (Huang et al., 2017). In England, total concentrations of three HAcAms (DCAcAm, DBAcAm, and TCAcAm) in finished and distributed waters were 1.3 μg/L for median and 7.0 μg/L for maximum (Bond et al., 2015). In Japan, total concentrations of six HAcAms (CAcAm, BAcAm, DCAcAm, TCAcAm, BCAcAm, and DBAcAm) in tap and distributed water at 12 WPPs ranged from 0.3 to 3.8 μg/L (Kosaka et al., 2016). The presence of HAcAms in drinking water was also reported in Western Australia (Liew et al., 2012) and Greece (Samios and Golfinopoulos, 2016). On the other hand, information on the profiles of HAcAms during water purification processes was not reported as far as we know. This was because prechlorination or intermediate chlorination was not employed at WPPs investigated and HAcAms were found in only finished water by postchlorination.

Similar to HAcAm occurrence, information on HAcAm precursors is also limited, compared to that of regulated DBPs and other N-DBPs. From studies of several countries, it has been suggested that HAcAm precursors are also widely present in environmental water and wastewater (Chu et al., 2013; Hou et al., 2012; Huang et al., 2012; Kosaka et al., 2016). It was reported that some nitrogenous compounds (e.g., aspartic acid, tyrosine, and chloramphenicol) were HAcAm precursors upon chlorination (Chen et al., 2017; Chu et al., 2010a, 2015a, 2016), and both nitrogenous (e.g., asparagine and aspartic acid) and carbonaceous (e.g., citric acid, phenol, and resorcinol) compounds were HAcAm precursors upon chloramination (Chu et al., 2016; Huang et al., 2012; Le Roux et al., 2016). Moreover, removal of HAcAm precursors during conventional and advanced water purification processes was also investigated at WPPs (Chu et al., 2011, 2012a, 2015c; Lin et al., 2016). Similarly, removal of HAcAm precursors by some unit processes, such as powdered activated carbon (PAC) treatment, potassium permanganate oxidation ($KMnO_4$), biological contact oxidation, and ultraviolet/persulfate process, was investigated (Chu et al., 2011, 2015b, 2015c). In these studies, the target was mostly chlorinated AcAms, and investigation of other types of HAcAms was very limited (Zhang et al., 2017). It was reported that the bromine incorporation factor (BIF), an index of the degree of bromine substitution (Krasner et al., 2008), of diHAcAms in drinking water was higher than that of diHAcAm formation potentials (FPs) upon chlorination in raw water (Kosaka et al., 2016). The values of the DBP-FPs are the amounts of the DBP precursors under defined experimental conditions. This suggested that the profiles of chlorinated and brominated AcAm precursors for water purification processes differed.

In this study, the profiles of chlorinated and brominated AcAms and their precursors upon chlorination during water purification processes applying ozonation were investigated. The changes in water quality parameters were also analyzed, and the relationship between changes in HAcAm precursors and water quality parameters were evaluated.

2. Materials and methods

2.1. Reagents and solutions

Ultrapure water used for preparation of aqueous solutions was made from tap water via an ultrapure water system (Gradient A10; Millipore, Bedford, MA, USA). Six HAcAms (i.e., CAcAm, BAcAm, DCAcAm, BCAcAm, DBAcAm, and TCAcAm) were selected as the target HAcAms in this study (Fig. A.1 in the Supplementary Materials). CAcAm, BAcAm, DCAcAm, and TCAcAm were purchased from Tokyo Chemical Industry (Tokyo, Japan), and BCAcAm and DBAcAm were purchased from Orchid Cellmark (Vancouver, Canada). A stock solution of chlorine (about 1000 mg Cl_2/L) was prepared from sodium hypochlorite solution (Tsurukuron TW; Tsurumi Soda, Yokohama, Japan). Quinine sulfate dihydrate was obtained from Tokyo Chemical Industry.

2.2. Sampling

Raw, process, and finished waters were collected from WPP-1 in September 2016 and from WPP-2 in September 2016 and February 2017. The samples from WPP-1 were those of actual treatment processes, and those from WPP-2 were those of pilot-scale processes. Both WPP-1 and WPP-2 employ rapid sand filtration systems followed by ozonation and biological activated carbon (BAC) treatment (Fig. A.2 in the Supplementary Materials). The speciation of granular activated carbon used for the BAC treatment is shown in Table A.1 in the Supplementary Materials. Chlorine was dosed only after BAC treatment at WPP-1 and after magnetic ion exchange resin (MIEX$^{®}$) and BAC treatment at WPP-2. For WPP-2, an ozone/hydrogen peroxide (O_3/H_2O_2) process was applied in February 2017. The O_3/H_2O_2 process is a kind of advanced oxidation processes using hydroxyl radicals ($^{\bullet}OH$) as oxidants (Glaze et al., 1987). The oxidation power of $^{\bullet}OH$ is higher than that of O_3 molecule. The doses of chlorine, O_3, and H_2O_2 at WPP-1 and WPP-2 are shown in Table A.2 in the Supplementary Materials. The raw waters of WPP-1 and WPP-2 were river and lake waters, respectively. Sodium ascorbate was added to the samples affected by chlorination to