



Effect of seawater intrusion on formation of bromine-containing trihalomethanes and haloacetic acids during chlorination



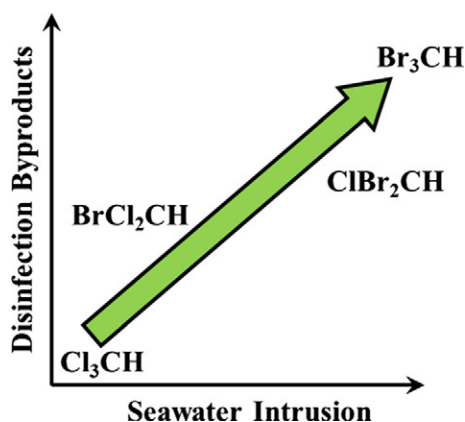
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RESEARCH HIGHLIGHTS

- Bromide increased from 38 to 974 $\mu\text{g L}^{-1}$ as seawater content increased from 0% to 2%.
- THM4 increased from 43 to 207 $\mu\text{g L}^{-1}$ as seawater content increased from 0% to 2%.
- Bromoform was the dominant THM species at 2% seawater.
- The mass concentration of HAA5 remained constant as seawater content increased.

GRAPHICAL ABSTRACT



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ABSTRACT

This study quantified the formation and speciation of halogenated organic disinfection byproducts (DBPs) during chlorination as a function of seawater intrusion by spiking fresh groundwater with 0.1% to 2% seawater by volume. The four chlorine- and bromine-containing trihalomethanes (THM4) and the nine chlorine- and bromine-containing haloacetic acids (HAA9) were the DBPs investigated. The bromide concentration increased from 38 $\mu\text{g L}^{-1}$ in fresh groundwater to 974 $\mu\text{g L}^{-1}$ in 2% seawater, and upon chlorination the concentration of THM4 increased from 43 to 206 $\mu\text{g L}^{-1}$ and the concentration of HAA9 increased from 39 to 75 $\mu\text{g L}^{-1}$. At 0.4% seawater and higher the THM4 concentration exceeded the U.S. EPA maximum contaminant level of 80 $\mu\text{g L}^{-1}$. Although the mass concentration of HAA9 increased by nearly a factor of 2 over the seawater range of 0% to 2%, the mass concentration of the five regulated HAAs (i.e., HAA5) remained approximately constant. This is because HAA5 excludes four bromine-containing species. The increase in mass concentrations of THM4 and HAA9 with increasing seawater intrusion was the result of an increased molar formation of DBP species and a shift from chlorinated species to brominated species.

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1. Introduction

Seawater intrusion has been observed in coastal aquifers and rivers around the world [1–4] with the focus of this work on coastal aquifers.

The intrusion of seawater into fresh groundwater occurs due to groundwater extraction (i.e., pumping), changes in recharge due to changes in land use and climate, and sea level rise [5]. The concern about seawater intrusion into fresh groundwater is the increase in total dissolved solids (TDS) of which chloride is the major component in seawater [6]. Elevated TDS and chloride give water a salty taste, and as such, are typically maintained below 500 mg L^{-1} and 250 mg L^{-1} , respectively, in

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drinking water [7]. The halide ions bromide and iodide are present at much lower concentrations than chloride in seawater [6] and hence do not contribute to taste, which is why they are not typically monitored or considered when studying seawater intrusion. During drinking water treatment the use of chlorine (and other oxidants/disinfectants) in the presence of bromide and iodide form brominated and iodinated disinfection byproducts (DBPs) [8], many of which are genotoxic and carcinogenic [9]. The remainder of this article focuses on the effects of elevated bromide due to seawater intrusion into fresh groundwater and the subsequent formation of DBPs during chlorination. Bromide was selected for this study because it is present at a higher concentration than iodide in seawater [6], shows conservative behavior in water [10], and there are several regulated bromine-containing DBPs whereas there are no regulated iodine-containing DBPs [9].

According to a national survey of U.S. drinking water plants, the mean concentration of bromide in drinking water sources is $60 \mu\text{g L}^{-1}$ in surface water and $103 \mu\text{g L}^{-1}$ in groundwater [11]. In comparison, bromide concentrations in drinking water sources in other parts of the world are $<5\text{--}658 \mu\text{g L}^{-1}$ in Europe (France, Germany, and Switzerland) [12], $40\text{--}300 \mu\text{g L}^{-1}$ in Sicily (median in groundwater, all provinces) [13], and $30\text{--}319 \mu\text{g L}^{-1}$ in Australia (River Murray) [14]. The formation of brominated DBPs occurs when bromide and natural organic matter (NOM) are present in water and an oxidant is added. For instance, aqueous chlorine (i.e., hypochlorous acid/hypochlorite or HOCl/OCl⁻) oxidizes bromide to aqueous bromine (hypobromous acid/hypobromite or HOBr/OBr⁻), and both chlorine and bromine react with NOM to form halogenated organic DBPs [15,16]. The most studied DBPs are the four chlorine- and bromine-containing trihalo-methanes (THM4): chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (BF), and the nine chlorine- and bromine-containing haloacetic acids (HAA9): chloroacetic acid (CA), bromoacetic acid (BA), dichloroacetic acid (DCA), bromochloroacetic acid (BCA), dibromoacetic acid (DBA), trichloroacetic acid (TCA), bromodichloroacetic acid (BDCA), chlorodibromoacetic acid (CDBA), and tribromoacetic acid (TBA). Although numerous halogenated organic DBPs have been identified [17,18], THM4 and HAA5 (i.e., the sum of CA, DCA, TCA, BA, and DBA) are the only regulated halogenated organic DBPs in the U.S. and elsewhere [9].

In this work, the bromine-containing DBPs (Br-DBPs) are defined as the subset of halogenated organic DBPs that contain at least one bromine atom. In addition to the regulated Br-DBPs there are hundreds of unregulated Br-DBPs that have been identified in recent research articles including halogenated aromatics, halobenzoquinones, halomethanes, haloacids, etc. [17–20]. Previous researchers have shown that increasing bromide concentrations can have a significant impact on the formation and speciation of Br-DBPs [19,21–23]. For example, chlorination studies have demonstrated that increasing bromide concentration increases the molar yields of THM4 and HAA9 but decreases the molar yield of HAA5 due to the shift in speciation from chlorinated species to brominated species [8]. Furthermore, regulated and unregulated Br-DBPs pose greater risk to human health than chlorinated species as demonstrated in cytotoxicity and genotoxicity assays [24], and Br-DBPs present significantly higher developmental toxicity than their chlorinated analogues [25]. Thus, the formation of Br-DBPs is expected to make compliance with DBP regulations more difficult and increase the toxicity of treated drinking water.

The gap in knowledge that this work seeks to address is the lack of data on the formation and speciation of Br-DBPs upon chlorination of drinking water sources that experience an increase in bromide due to seawater intrusion. Previous researchers have investigated the effect of bromide on DBP formation by chlorinating low bromide waters spiked with bromide salts [8,19,22,26,27], seawater-impacted drinking water [28,29], and saline waters such as synthetic seawater, saline sewage, and seawater swimming pools [30–32]. This study used fresh groundwater spiked with natural seawater to simulate different amounts of seawater intrusion in a coastal aquifer, and chlorination of

the groundwater–seawater mixtures to investigate the formation of Br-DBPs. This approach to DBP research has not been reported previously in the literature. The use of real seawater is important to mimic the process of seawater intrusion in which bromide as well as chloride is transported into the coastal aquifer. For instance, a recent study demonstrated that elevated chloride (350 mg L^{-1}) in the presence of bromide ($8000 \mu\text{g L}^{-1}$) and chlorine (30 mg L^{-1} as Cl_2) catalyzed the formation of bromine chloride (BrCl), a brominating agent that was 3.6×10^6 times more reactive than hypobromous acid in brominating dimethenamid [33]. The results from Sivey et al. [33] are significant because hypobromous acid is usually assumed to be the only species responsible for forming Br-DBPs. In addition, work by Heeb et al. [34] showed that during chlorination the concentration of reactive brominating species, such as BrCl, increased by several orders of magnitude as the concentration of bromide and chloride increased from freshwater to seawater conditions. Hence, spiking fresh groundwater with seawater provides the elevated chloride that can facilitate the formation of reactive brominating species that in turn can increase the formation of Br-DBPs relative to freshwater conditions.

The overall goal of this work was to provide new insights on the effect of seawater intrusion on the formation and speciation of Br-DBPs during chlorination. The specific objectives of the research were to (1) quantify the formation and speciation of THM4 and HAA9 for different ratios of seawater to fresh groundwater; (2) calculate the change in cancer risk posed by THM4 as a result of seawater intrusion; and (3) discuss the implications of seawater intrusion on drinking water treatment.

2. Materials and methods

2.1. Simulation of seawater intrusion

A groundwater sample was collected from well 4 at the Cedar Key Water Treatment Plant (CKWTP) in Cedar Key, FL, USA on 8 April 2013. On the same day, a seawater sample from the Gulf of Mexico was collected approximately one mile offshore at about two-thirds the depth of the water column. All samples were bottled, placed in a cooler on ice, returned to the University of Florida (approximately 1 h drive), filtered using $0.45 \mu\text{m}$ membrane filters (Millipore), and stored at 4°C in the dark until used for analysis and experiments. Simulation of seawater intrusion was achieved by mixing the Gulf of Mexico seawater with the Cedar Key groundwater at predetermined ratios in volumetric flasks. Prior to mixing the seawater with groundwater, the groundwater was diluted with three parts deionized (DI) water to one part groundwater to achieve a dissolved organic carbon (DOC) concentration that was comparable to finished drinking water (approximately 1.4 mg L^{-1}) [11]. The ratio of seawater to groundwater was adjusted to create six samples that contained 0% (i.e., diluted fresh groundwater), 0.1%, 0.2%, 0.4%, 1%, and 2% seawater by volume.

2.2. Chlorine demand and chlorination under uniform formation conditions

Chlorine demand tests and chlorination under uniform formation conditions (UFC) were conducted as described in the literature [35, 36]. The UFC are defined as $1.0 \pm 0.4 \text{ mg L}^{-1}$ free chlorine residual at pH 8 after 24 h of incubation in the dark at 25°C . The chlorine dosing solution was prepared from a 4–6% NaOCl stock solution (Fisher Scientific) by diluting to approximately 1000 mg L^{-1} . The NaOCl stock solution was standardized prior to all chlorination experiments by titrating with 0.1 N sodium thiosulfate according to Standard Method 4500-Cl B Iodometric method [37]. All glassware was made chlorine demand-free before chlorination experiments by acid washing and soaking in a 50 mg L^{-1} NaOCl solution overnight.

All samples were buffered with a pH 8.0 borate solution and adjusted to a final pH of 8.0 ± 0.05 with H_2SO_4 or NaOH prior to all chlorination experiments. Measurements were performed using an Accumet Basic AB15 pH meter and probe and the meter was calibrated with a

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