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Formation and speciation of disinfection byproducts in desalinated seawater blended with treated drinking water during chlorination

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ABSTRACT

Desalinated seawater containing bromide ion (Br^-) blended with drinking water may produce brominated disinfection byproducts (Br-DBPs) during chlorination, which would pose a potential threat to human health when incorporated into the municipal water supply system. This study investigated the formation and speciation of twenty-one DBPs during chlorination in two desalinated seawater blends, i.e., treated drinking water blended with reverse osmosis (RO) permeate and post-treatment (PT) product water. After chlorination, the number and concentrations of DBPs formed in the desalinated seawater obviously enhanced, with chlorinated DBPs (Cl-DBPs) dominating. Sixteen DBPs were found in both RO and PT blends samples during chlorination, in which haloacetic acids (HAAs) had the highest concentration, followed by trihalomethanes (THMs) and halogen acetonitriles (HANs). When the volume of desalinated seawater in the blends was increased, the transformation from Cl-DBPs to Br-DBPs was observed for THMs and HANs, indicating that Br^- was more easily incorporated into THMs and HANs than HAAs. Additionally, more Br^- participated in the DBPs formation per unit dissolved organic carbon and Br-DBPs/DBPs increased, when the blended ratio of the desalinated seawater increased. The DBP-associated toxicity in the blends was estimated based on the toxicity-weighted concentration with Br-HANs as the predominant contributor, followed by Cl-HAAs.

1. Introduction

Water resources in China are characterized by low per capita occupancy, uneven spatial-temporal distribution, serious water pollution and growing shortages in most places. Such problems seriously restrict the sustainable development of the economy and human health. Desalination is an effective approach to alleviate the water shortages. With the improvement of desalination technologies and the cost decrease of desalinated seawater, desalination plants have been built in many countries and mainly applied for the municipal water supply [1–6]. In recent years, different sized desalination plants and demonstration projects were constructed in China, which were mainly used for the industrial water supply and were rarely integrated into the municipal water supply system, because of the appearance of the “red water” and “yellow water” phenomena after using desalinated seawater [7]. Generally, desalinated seawater has weak acidity, extremely low hardness and alkalinity, and poor stability. If directly applied to the drinking water distribution system (DWDS), desalinated seawater would corrode the various types of common municipal metal pipes, causing the formation of various iron corrosion products, leaching the calcium compounds into the water and reducing the pipeline strength [8]. Additionally, desalinated seawater has low levels of total dissolved solids (TDS), calcium, magnesium and potassium elements. It cannot provide the necessary microelements for human body and may lead to the loss of the original nutrients in the body [9].

The above-mentioned problems faced during the municipal application of desalinated seawater can be mitigated by using the proper post-treatments and control technologies to meet the requirements for safe stable delivery and drinking, e.g., remineralization and blending desalinated seawater with conventional water [2,10]. Another issue that cannot be ignored during the desalination process was the formation of disinfection byproducts (DBPs), especially brominated DBPs (Br-DBPs). Sodium hypochlorite (NaOCl) is commonly used for prechlorination at seawater intakes to control biofouling. Seawater containing 50–80 mg/L bromide ions (Br^-) can produce a large number of chlorinated DBPs (Cl-DBPs) and Br-DBPs during the prechlorination process [11]. Usually, haloacetic acids (HAAs) formed from the seawater prechlorination process mainly include dichloroacetic acid (DCAA), bromodichloroacetic acid (BDCAA) and dibromochloroacetic acid (DBCAA), which can be effectively removed by the reverse osmosis (RO) process [12–14]. RO membranes exhibited higher rejection rates for the charged DBPs (e.g., HAAs) than the uncharged low-molecular-

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weight DBPs (e.g., trihalomethanes (THMs)), and the removal efficiencies of HAAs, THMs and halogen acetonitriles (HANs) were above 90%, 60% and 50%, respectively [15–19]. Therefore, although most DBPs are removed by the subsequent desalination processes after the prechlorination, there are some DBPs that enter into the produced water (permeate) through RO membranes [11].

Additionally, the disinfection of desalinated seawater was usually necessary. 100% RO permeate was found to result in higher bacterial growth than tap water or blended water containing higher initial total organic carbon (TOC) [20]. Even though the desalinated seawater produced from RO membranes has low levels of dissolved organic carbon (DOC), from < 0.1 to 0.6 mg C/L [17,21,22], it has a high concentration of Br^- (approximately 250–600 μg/L) [11]. That amount of Br^- would be enough to affect the Br-DBP formation in the subsequent disinfection process and provide access to the DWDS. During the chlorine disinfection process, desalinated seawater containing Br^- could produce hypobromous acid (HOBr), which would induce the transformation of Cl-DBPs into Br-DBPs and promote the Br-DBPs formation [23,24]. Ramavandi et al. investigated the THMs formation potential (THMFP) of the Dez River in Iran and found that with the Br^- concentration increasing, the formation of chloroform (TCM) and dichlorobromomethane (DCBM) decreased, whereas the formation of dibromochloromethane (DBCM), bromoform (TBM) and total THMs increased [25]. HOBr produced from Br^- oxidation could exhibit a stronger substitution ability to natural organic materials (NOMs) than hypochlorous acid (HOCl) in aqueous environments, which would lead to the Br-DBPs formation [25]. A study by Hong et al. also observed that both Br^- concentration and disinfectant dose significantly affected the formation of THMs, HAAs and halonitromethane (HNMs) [26]. Richardson et al. reported that a long-term exposure to DBPs was not only correlated with an increased risk of cancer but has potential adverse effects on reproductive function as well [27]. It is worth mentioning that Br-DBPs and iodinated DBPs (I-DBPs) have more cytotoxicity and genotoxicity than their chlorinated analogues [27–30]. Epidemiological and toxicology studies also stated that higher concentrations of Br-DBPs were associated with the adverse pregnancy outcomes and bladder cancer [31–35].

To date, the occurrences of DBPs in desalination plants have been reported by many researchers around the world [11,21,36–38]. Le Roux et al. investigated the incidence of DBPs in two seawater reverse osmosis (SWRO) plants using polyamide (PA) and cellulose triacetate (CTA) membranes in Saudi Arabia [38]. Low levels of THMs (0.36 μg/L) were detected in the RO permeates of one SWRO plant using PA membranes, while in another SWRO plant using CTA membranes, THMs, HAAs, DBAN and I-THMs were detected in the RO permeates, up to 66.7, 0.71, 1.98 and 2.64 μg/L, respectively [38]. After the prechlorination with 2.5–5.0 mg Cl_2/L at seawater intakes in the Tampa Bay desalination plants (USA), THMs and HAAs were detected in the RO permeates ranging from 2.3–6.4 μg/L and 1.0–2.5 μg/L, respectively [21]. THMs within the range of 2.0–39 μg/L were also observed in the RO permeates of desalination plants in Japan [11,37,39]. In addition, blending desalinated seawater with conventional water sources and the subsequent disinfection process may create circumstances favoring the formation of more toxic DBPs [11]. A survey from the east coast of Saudi Arabia reported that THMs detected in the blended desalinated seawater (with chlorinated well water) were 3.1–12.8 μg/L and TBM accounted for 61–86% of the total THMs [36].

The guidelines or directives on regulated DBPs vary by country. The Guidelines for Drinking Water Quality published by the World Health Organization (WHO) set the maximum contaminant levels (MCLs) for TCM, BDCM, DBCM, TBM, MCAA, DCAA, TCAA, DCAN and DBAN at 200, 60, 100, 100, 20, 50, 200, 20 and 70 μg/L, respectively [40]. Additionally, the total THMs (TTHMs) denoted as the sum of the ratio of the concentration of each THM to its guideline value should be no > 1 [40]. The U.S. Environmental Protection Agency (EPA) regulated the MCLs for THMs and HAA5 (MCAA, DCAA, TCAA, MBAA and DBAA) at 80 and 60 μg/L, respectively [41]. The European Union (EU) directive implemented the MCLs for THMs at 100 μg/L [42]. In China, the regulated DBPs in the Standards for drinking water quality (GB5749–2006) include TCM, BDCM, DBCM, TBM, DCAA and TCAA with MCLs at 60, 60, 100, 100, 50 and 200 μg/L, respectively, and similar to the WHO Guidelines, the TTHMs should be at no > 1 [43].

Although the mass concentration of regulated DBPs in desalinated seawater may be lower than the DBP regulations, the potential health risks of additional toxic and unregulated DBPs formed in desalinated seawater cannot be ignored. To our knowledge, little research has been undertaken to elucidate the formation of DBPs from desalinated and blended seawaters, especially during chlorine disinfection. Therefore, more attention should be given to the DBP formation in the blended desalinated seawater during chlorination before the usage of desalinated seawater in the municipal water supply. The aims of this study were to compare the water quality of desalinated seawater, treated drinking water and blends of them, to evaluate the DBPs formation from the blended desalinated seawater containing Br^- during chlorination, to illustrate the speciation variation of Cl-DBP and Br-DBP under different blended ratios, to assess the contribution of each DBP on the toxicity of disinfected blends and to reveal the potential special risks of water quality for desalinated seawater using in the municipal water supply. This study provides a fundamental understanding of the effect of blended desalinated seawater containing Br^- on DBP formation and contributes the fundamental data for desalinated seawater incorporated in the municipal water supply system.

2. Materials and methods

2.1. Chemicals and reagents

The THM mixed standard, including chloroform (TCM), dichlorobromomethane (DCBM), dibromochloromethane (DBCM) and bromoform (TBM), was purchased from Sigma-Aldrich (USA). A mixed standard of HANs, HNMs and haloketones (HKs) was obtained from Sigma-Aldrich (USA), containing trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), trichloronitromethane (TCNM, or chloropicrin), dichloroacetone (DCP) and trichloroacetone (TCP). The HAA mixture standard, including monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), dibromochloroacetic acid (DBCAA), bromodichloroacetic acid (BDCAA), tribromoacetic acid (TBAA) and dalapon acid (DA) with varied concentrations, was obtained from AccuStandard (USA) and the concentrations of each compounds are listed in the Supporting information (SI) Table S1. The internal standard (1,2,3-trichloropropane) for HAA analysis was supplied by Sigma-Aldrich (USA).

HPLC grade methyl tertiary-butyl ether (MTBE) and methanol were obtained from Fisher Scientific (USA). The NaOCl stock solution (≈5 g/L Cl_2) was prepared by diluting the NaOCl (~10% available chlorine concentration, Fisher Scientific, USA) and was standardized by the DPD (N, *N*-diethyl-*p*-phenylenediamine, Sigma-Aldrich, > 99%) colorimetric method [44]. Reagent water (18 MΩ cm) was produced from a Milli-Q water purification system (Millipore, USA). All other reagents used without further purification were analytical grade or above and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.

2.2. Sampling and blending desalinated seawater with drinking water

Desalinated seawater samples were collected following the RO and post-treatment (remineralization) processes from a SWRO plant in Oct 2016 and were denoted as RO and PT desalinated water, respectively. The SWRO plant is in Caofeidian, Hebei, China. It has a design capacity of 5×10^4 m^3/d water production and mainly consists of seawater