



Characterization of trihalomethane, haloacetic acid, and haloacetonitrile precursors in a seawater reverse osmosis system



Zhe Yang^a, Ying-Xue Sun^{a,*}, Tao Ye^b, Na Shi^a, Fang Tang^c, Hong-Ying Hu^c

^a Department of Environmental Science and Engineering, Beijing Technology and Business University, Beijing 100048, PR China

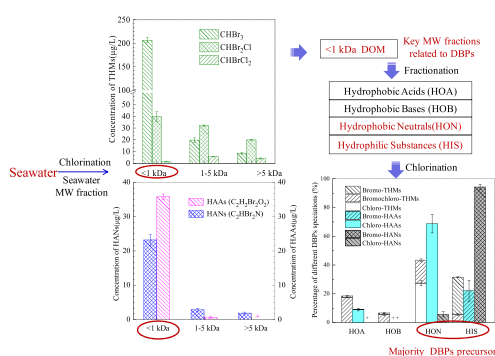
^b Department of Civil and Environmental Engineering, The George Washington University, Washington, DC 20052, USA

^c State Key Joint Laboratory of Environmental Simulation and Pollution Control, State Environmental Protection Key Laboratory of Microorganism Application and Risk Control (MARC), School of Environment, Tsinghua University, Beijing 100084, PR China

HIGHLIGHTS

- A large amount of THMs, HAAs and HANs were formed in the seawater reverse osmosis.
- The MW < 1 kDa was the dominant DOM of the seawater and contributed to DBP formation.
- The hydrophilic substances of MW < 1 kDa were the dominant precursors to form HANs.
- The hydrophobic neutrals of MW < 1 kDa were the major precursors for THMs and HAAs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 29 August 2016

Received in revised form 18 October 2016

Accepted 18 October 2016

Available online xxx

Editor: Jay Gan

Keywords:

Seawater reverse osmosis (SWRO)

Chlorination

Dissolved organic matter fractions

Disinfection by-products precursors

Brominated disinfection by-products

ABSTRACT

Seawater reverse osmosis (SWRO) has been extensively applied to replenish the limited freshwater resources. One concern of such technology is the formation of disinfection by-products (DBPs) during the pre-chlorination process. For the SWRO tested in this study, the concentrations of trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) increased by 35.1, 23.7 and 4.9 µg/L, respectively, after a seawater sample (with UV₂₅₄/DOC of 3.7 L/mg·m and Br⁻ of 50.9 mg/L) was pre-chlorinated (1–2 mg-Cl₂/L). The dissolved organic matter (DOM) with molecular weight (MW) < 1 kDa dominated the formation of total THMs, HAAs and HANs. To further investigate DBPs precursors in the seawater, the DOM with MW < 1 kDa was fractionated to hydrophobic acids (HOA), hydrophobic bases (HOB), hydrophobic neutrals (HON), and hydrophilic substances (HIS). The excitation emission matrix fluorescence spectra analysis showed that most aromatic protein and fulvic acid of the DOM with MW < 1 kDa were present in the HON and HIS fractions. The HON fraction was the dominant precursor to form THMs and HAAs, while HIS controlled the formation of HANs. Furthermore, bromo-DBPs dominated the total DBPs yields after the chlorination of HIS fraction.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

To alleviate the crisis of water shortage, seawater desalination is considered as a viable and attractive approach to replenish the limited freshwater

resources in many countries. Recently, seawater desalination technologies have been used by over 125 countries and regions all over the world (Saidur et al., 2011), of which seawater reverse osmosis (SWRO) occupies almost 80% (Morillo et al., 2014). However, disinfection by-products (DBPs) may be formed in SWRO system because pre-chlorination is usually applied to protect membranes from biofouling, and if necessary to oxidize any manganese and iron trace in seawater (Greenlee et al., 2009).

* Corresponding author.

E-mail address: sunyx@th.btbu.edu.cn (Y.-X. Sun).

Different to natural fresh water or wastewater, seawater contains higher bromide (always over 45 mg/L) (Borges et al., 2005; Heeb et al., 2014), which will form bromo-DBPs in significant amount during chlorination (Shi et al., 2013). Bromo-DBPs are generally more toxic than their chlorinated analogs (Plewa et al., 2010; Yang et al., 2014). For example, monobromoacetic acid was about 70 times more cytotoxic and 23.5 times more genotoxic than monochloroacetic acid (Plewa et al., 2010). Some species of haloacetic acids (HAAs) and haloacetonitriles (HANs) formed during the pre-chlorination could be separated from the main stream by reverse osmosis (RO) membrane (Roux et al., 2015), but still exist in the RO concentrates. Agus and Sedlak (2010) reported that the concentration of DBPs in RO concentrates could be up-to 900 µg/L. On the other hand, some DBPs such as trihalomethanes (THMs) or *N*-Nitrosodimethylamine might permeate through RO membranes and emerge in the product water of RO (Agus and Sedlak, 2010; Fujioka et al., 2013; Roux et al., 2015). Recently, with extending application of SWRO for aquifer recharge or potable reuses, the issue of DBP formation during the pre-chlorination is seriously concerned.

To control the formation of DBPs during the pre-chlorination in SWRO, it is of great importance to know the characteristics of the precursors in the source water. The effects of dissolved organic matter (DOM), bromide, aromatic compounds and humic/fulvic acid on the formation and speciation of DBPs during natural fresh water and wastewater chlorination have been extensively investigated (Hua et al., 2015; Sharma et al., 2014; Sun et al., 2009; Xue et al., 2008). However, the nature of organic DBP precursors in seawater are different from that in fresh water or wastewater due to the different biogeochemical formation pathways in terrestrial, freshwater and marine systems (Fabbriano and Korshin, 2005; Padhi et al., 2012). The influence factors for the formation of DBPs during SWRO such as chlorination conditions, Br⁻ level, and DOM component also have been investigated recently (Agus and Sedlak, 2010; Padhi et al., 2012; Roux et al., 2015). Padhi et al. (2012) found that elevated temperature could promote the yields and increase the forming rate of THMs during seawater chlorination, and increasing chlorine dosage could increase the overall DBP formation. Geographic and seasonal variability of seawater, which would influence the concentration and composition of DBPs precursor, can affect the concentration and speciation of DBPs formed in chlorinated seawater. For example, bromoform (CHBr₃) was the dominant species (>95%) of THMs formed during seawater chlorination in autumn, but only occupied 30% of THMs in winter (Agus and Sedlak, 2010). The presence of bromide in seawater could significantly influence the speciation of DBPs, which is dominated by bromo- or bromochloro-DBPs and different from chlorinated surface water that is predominated by chloro-species (Kim et al., 2015; Shi et al., 2013). Furthermore, the DOM in seawater plays an important role in DBP formation. Zhang et al. (2015) found that the concentration of THMs and HAAs formed in seawater chlorination was increased by 3.2–7.8 times with the increase of dissolved organic carbon (DOC) from 4.5 to 9.4 mg/L. Yu et al. (2015) reported that the DOM fractions (hydrophilic, transphilic, and hydrophobic) of seawater greatly impacted the formation of HAAs during chlorination, and the transphilic DOM exhibited higher contribution to HAAs formation. Nevertheless, up-to-date, limited studies have explored the characteristics (e.g., molecular weight and hydrophobicity) of the dominant DBP precursors in the DOM of seawater.

The objective of this study is to identify THMs, HAAs, and HANs precursors of DOM in the seawater during pre-chlorination in a SWRO. The DOM was isolated into different molecular weight (MW) and hydrophobic/hydrophilic fractions. Each DOM fraction was characterized by excitation emission matrix fluorescence spectroscopy to identify the organic components, which could shed further light on the dominant compounds of the different DOM fractions of seawater. Formation of THMs, HAAs, and HANs of the DOM fractions were analyzed to determine the dominant precursors.

2. Materials and methods

2.1. Water samples and water quality analysis

Water samples were collected from a SWRO plant (treatment capacity of 206.4 t/d) with a pretreatment of ultrafiltration (UF) (Fig. S1). The influent of seawater is from Bohai Bay in Tianjin, China. The UF recovery ratio was 91% and the RO recovery ratio was 30%–35%. To ensure the normal operation of SWRO, several chemical agents (as disinfectant, antiscalant, reductant and chemical cleaning) were added to the system, in which 1–2 mg-Cl₂/L disinfectant (NaClO) were continually added to the influent seawater to inhibit any bacterial proliferation.

Water samples along the SWRO plant were seawater (A), UF influent (B), UF effluent (C), RO influent (D), RO permeate (E), UF concentrates (F) and RO concentrates (G) (Fig. S1). All the water samples were filtered immediately by glass fiber filters (0.22 µm) to eliminate suspended solids, and stored at 4 °C to minimize the changes in the constituents of the water. The concentration of DOC was detected by a Sievers 5310C analyzer (GE, America). UV absorbance at 254 nm (UV₂₅₄) was measured by a UV-2401PC UV-VIS recording spectrophotometer (Shimadzu, Japan). Total dissolved solid (TDS) was measured using a SX-650 analyzer (Sanxin, China). The concentration of Br⁻ was measured by using NaClO oxidation-iodimetry method. The pH was measured with a Mettler Toledo FE20 analyzer (Mettler Toledo, Switzerland). Measurements were performed in triplicate.

2.2. Size exclusion chromatography

The MW distributions of DOM in seawater were obtained through high-performance size exclusion chromatography (SEC) using a LC-20 HPLC (Shimadzu, Japan) system with a SPD-M20A UV detector and two connected columns (a TSK-GEL G3000PWXL column followed by a TSK-GEL G2500PWXL column). The column temperature was maintained at 40 °C, and the injection volume was 100 µL. The mobile phase was composed of Mill-Q ultrapure water buffered with phosphate (0.3744 g/L NaH₂PO₄·2H₂O, 0.5728 g/L Na₂HPO₄·12H₂O) and sodium sulfate (3.55 g/L Na₂SO₄). The correlation between the MW and the chromatography retention time was determined by using MW standard materials: polyethylene glycol (330, 700, 1050, 5250, 10,225 and 30,000 Da) and acetone. The result of MW distributions of DOM in seawater was shown in Fig. S2.

2.3. Ultrafiltration of the DOM

The DOM in the seawater was fractionated using a Millipore Amicon Model-8200 membrane ultrafiltration system with Millipore 1 kDa and 5 kDa cellulose filtration membranes according to the results shown in Fig. S2. 400 mL raw seawater sample was fractionated with the membranes in series (starting with the larger pore-size membrane) to obtain three fractions as MW < 1 kDa, 1–5 kDa and >5 kDa. After fractionation, Milli-Q water was added to each fraction to increase the volume to reach the initial unfractionated seawater volume (500 mL), and then further analysis (UV₂₅₄, DOC and fluorescence spectra) and subsequent chlorination test were conducted.

2.4. Fractionation by resin adsorption

Water samples were fractionated by XAD-8 resin column (Sigma, America) to obtain hydrophobic acids (HOA), hydrophobic bases (HOB), hydrophobic neutrals (HON) and hydrophilic substances (HIS). The seawater sample (500 mL) was firstly fractionated by the Millipore membrane ultrafiltration system with 1 kDa cellulose filtration membrane to obtain the fraction of MW < 1 kDa. Then, the water sample with MW < 1 kDa was passed through XAD-8 column (the volume ratio of XAD-8 resin to water sample was 1 to 50) and the column was back-flushed with 0.1 mol/L HCl to elute HOB fraction. The previous

Download English Version:

<https://daneshyari.com/en/article/5751982>

Download Persian Version:

<https://daneshyari.com/article/5751982>

[Daneshyari.com](https://daneshyari.com)