



## Tracing disinfection byproducts in full-scale desalination plants



Julien Le Roux <sup>a</sup>, Nabil Nada <sup>b</sup>, Muhammad Tariq Khan <sup>a</sup>, Jean-Philippe Croué <sup>a,\*</sup>

<sup>a</sup> Water Desalination and Reuse Center, 4700 KAUST, Thuwal 23955-6900, Saudi Arabia

<sup>b</sup> NOMAC, P.O. Box 8337, Jeddah 21482, Saudi Arabia

### HIGHLIGHTS

- The formation and behavior of DBPs were assessed in full-scale desalination plants (MSF and RO).
- DBPs formed during prechlorination are efficiently removed along the treatment processes.
- Seawater quality and chlorination mode (continuous or intermittent) influenced DBP formation.
- Dibromoacetonitrile and iodo-THMs reached the product water in low amounts.
- Substantial amounts of DBPs are rejected to the sea.

### ARTICLE INFO

#### Article history:

Received 3 August 2014

Received in revised form 21 December 2014

Accepted 22 December 2014

Available online xxx

#### Keywords:

Chlorination

Desalination plants

Disinfection byproducts

Haloacetic acids

Haloacetonitriles

Multi-stage flash distillation

Reverse osmosis

Trihalomethanes

Iodinated DBPs

### ABSTRACT

The aim of this study was to assess the formation and the behavior of halogenated byproducts (regulated THMs and HAAs, as well as nitrogenous, brominated and iodinated DBPs including the emerging iodo-THMs) along the treatment train of full-scale desalination plants. One thermal multi-stage flash distillation (MSF) plant and two reverse osmosis (RO) plants located on the Red Sea coast of Saudi Arabia. DBPs formed during the prechlorination step were efficiently removed along the treatment processes (MSF or RO). Desalination plants fed with good seawater quality and using intermittent chlorine injection did not show high DBP formation and discharge. One RO plant with a lower raw water quality and using continuous chlorination at the intake formed more DBPs. In this plant, some non-regulated DBPs (e.g., dibromoacetonitrile and iodo-THMs) reached the product water in low concentrations (<1.5 µg/L). Regulated THMs and HAAs were far below their maximum contamination levels set by the US Environmental Protection Agency. Substantial amounts of DBPs are disposed to the sea; low concentrations of DBPs were indeed detected in the water on shore of the desalination plants.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Chlorine is widely used as an inexpensive and effective biocide for drinking water disinfection. Prechlorination is commonly used to control biofouling in seawater desalination plants (e.g., thermal multi-stage flash distillation – MSF or seawater reverse osmosis – SWRO). Large amounts of disinfectant can be required to maintain a residual during algal bloom events. As a result of the reaction with marine organic matter, a large diversity of disinfection byproducts (DBPs) is formed during seawater chlorination, including the regulated

trihalomethanes (THMs) and haloacetic acids (HAAs). Nitrogenous DBPs (N-DBPs) generally form in much smaller amounts than regulated DBPs, but have been a growing concern over the past decade because of their higher health risk [1,2]. In vitro mammalian cell tests demonstrated that haloacetonitriles (HANs), halonitromethanes (HNMs) and haloacetamides (HAcAms) are more cytotoxic and genotoxic (up to 2 orders of magnitude) than non-nitrogenous THMs and HAAs [3]. N-DBP formation has been associated with the presence of nitrogen-containing compounds (e.g., ammonia, dissolved organic nitrogen such as amino acids) in waters impacted by wastewater or algal organic matter (AOM) [4,5]. Moreover, the presence of high concentrations of bromide and iodide ions in seawater (i.e., 60 mg Br<sup>-</sup>/L and 0.05 mg I<sup>-</sup>/L in the Red Sea, respectively) promotes the formation of brominated and iodinated byproducts (Br-DBPs and I-DBPs) that are often more toxic than their chlorinated analogs [3,6,7]. Due to the toxicity and carcinogenicity of DBPs, Maximum Contaminant Levels (MCLs) have been set by the US Environmental Protection Agency (US EPA) for total THMs

\* Corresponding author at: Curtin Water Quality Research Centre, Curtin University, Perth Western Australia 6845, Australia.

E-mail addresses: [julien.leroux5@gmail.com](mailto:julien.leroux5@gmail.com) (J. Le Roux), [n.nada@nomac.com](mailto:n.nada@nomac.com) (N. Nada), [muhammed.khan@kaust.edu.sa](mailto:muhammed.khan@kaust.edu.sa) (M.T. Khan), [jp.croue@kaust.edu.sa](mailto:jp.croue@kaust.edu.sa), [jean-philippe.croue@curtin.edu.au](mailto:jean-philippe.croue@curtin.edu.au) (J.-P. Croué).

(80 µg/L), total HAAs (60 µg/L) and bromate (10 µg/L) [8], and are enforced by the Saudi Arabian Standards Organization.

Studies on the impact of brine discharges from desalination plants focused mainly on salinity, scaling control additives and the presence of heavy metals such as copper released from corrosion in multi-stage flash plants [9,10]. Limited data regarding the discharge of DBPs has been published and little is known about their potential impact on aquatic organisms. THMs have been detected near distillation plants at levels of up to 9.5 µg/L [11] and 90 µg/L [12]. Bromoform and dibromoacetonitrile (DBAN) concentrations were reported in cooling water discharges of European coastal power plants (0.72–29.2 µg/L and 0.1–3.15 µg/L, respectively) [13]. Although these concentrations are supposed to be reduced by mixing coupled with biotic (e.g., biodegradation) and abiotic mechanisms (e.g., evaporation, photolysis) within a few kilometers [14], they could have an impact in the vicinity of the point of discharge, especially towards sensitive species exposed to chronic concentrations. THMs and HAAs were found to affect bivalves and aquatic macrophytes [15,16]. A median lethal dose of 1000 µg/L was reported for bromoform exposure to oyster (*Crassostrea virginica*) larvae and significant toxicity was observed at concentrations as low as 50 µg/L [15]. Very low concentrations of monochloroacetic acid (MCAA) and monobromoacetic acid (MBAA) (7 µg/L and 20 µg/L, respectively) were found to inhibit growth in green algae *Scenedesmus subspicatus* [16]. However, no information is available about the occurrence of other DBPs (N-DBPs, I-DBPs) and their impact on marine organisms.

Very few studies reported the occurrence of DBPs in full-scale seawater desalination plants, and these studies mainly focused on THMs [17–19]. THM concentrations in the range 2.7–22.8 µg/L were found in the distillate of MSF plants in Kuwait [18]. Very low levels of HAAs were reported in the product water of a MSF plant in Saudi Arabia (1.5–2.4 µg/L) [20]. In MSF plants, more than 98% of THMs formed after chlorination are transferred to the atmosphere through the venting system. In SWRO plants, the apparent rejection of DBPs depends on the nature of the compounds (e.g., molecular weight, width, charge and hydrophobicity), as well as the membrane properties (e.g., molecular weight cut-off, surface charge and hydrophobicity) and feed water composition (e.g., pH, temperature, DOC, inorganic compounds) [21,22]. A few studies reported the rejection of DBPs by RO or nanofiltration membranes in lab-scale experiments or pilot plants [23–25]. The rejection of negatively charged HAAs (average rejections 86%–94%) by RO membranes is higher than that of neutral byproducts (average rejections ~60%–90%) [23,25]. Among neutral byproducts, the lowest rejection was observed for chloroform (TCM) (~60%), because of its low molecular weight (119.4 g/mol) [25]. While these values have been reported in lab-scale or pilot-scale studies, data on DBP occurrence and rejection in full-scale SWRO desalination plants is lacking, especially with respect to emerging species such as N-DBPs or iodo-THMs.

The goal of this study was to assess the formation and the behavior of various halogenated byproducts (THMs, HAAs, HANs) along the treatment train of different full-scale desalination plants, to evaluate the removal of DBPs by desalination processes and to monitor the quality of the water produced as well as the brine. The occurrence of DBPs was analyzed in one thermal MSF plant and two SWRO plants equipped with polyamide (PA) and cellulose triacetate (CTA) membranes, all located on the Red Sea coast of Saudi Arabia. In order to better understand the role of foulant material on the production of DBPs in the CTA RO train that is fed with chlorinated water, chlorination of the material accumulated at the surface of the membrane (i.e., recovered from harvested RO module) was performed in batch mode.

## 2. Materials and methods

### 2.1. Materials

All reagents were of commercial grade and were used without further purification. MilliQ water was produced with a Millipore system.

Sodium hypochlorite (NaOCl, 5.65–6%, Fisher Scientific) was used for DBP formation potential tests. Sodium thiosulfate (Fisher Scientific) was used to quench residual chlorine. THM calibration mix (THM4: chloroform (TCM), dichlorobromomethane (DCBM), dibromochloromethane (DBCM) and bromoform (TBM)), a mixed standard containing haloacetonitriles (HANs), trichloronitromethane (TCNM, or chloropicrin) and haloketones (HKs) (EPA 551B Halogenated Volatiles Mix), a mixed standard containing 9 HAAs (EPA 552.2 Methyl Ester Calibration Mix), iodoform and surrogate standard decafluorobiphenyl were supplied from Supelco (Sigma-Aldrich). Iodo-trihalomethanes (I-THMs) (dichloriodomethane (CHCl<sub>2</sub>I), chlorodiodomethane (CHClI<sub>2</sub>), chlorobromiodomethane (CHBrClI), dibromiodomethane (CHBr<sub>2</sub>I), bromodiodomethane (CHBrI<sub>2</sub>)) were purchased from Cansyn Chem. Corp. Synthetic seawater was prepared following the protocol of Grasshoff et al. [26] with inorganic (no organic matter added) composition similar to that of the raw seawater at SWRO plant 2 (i.e., same alkalinity, 60 mg Br/L, 0.05 mg I/L, pH 8.2).

### 2.2. Sampling

All samples from the desalination plants were collected in 500 mL amber bottles before and after each treatment step, and filled without headspace to avoid the volatilization of DBPs. Residual chlorine was quenched immediately in slight excess of sodium thiosulfate and transported in coolers with icepacks and after few hours of transportation stored at 4 °C before analyses. All bottles were washed with MilliQ water and baked at 500 °C for at least 5 h prior to use. At the MSF plant, samples were collected in July 2012 along one evaporator unit: raw seawater, chlorinated seawater, feed after heat rejection, brine recycle, brine blowdown, and distillate, as shown in Fig. S1 (Supporting Information, SI). The design capacity of the MSF unit was 74,000 m<sup>3</sup>/d, with recirculating brine consisting of 21 stages (19 heat recovery stages and 2 heat rejection stages). A chlorine residual of 0.25 mg/L as Cl<sub>2</sub> was maintained continuously to the inlet of the heat rejection section. SWRO plant 1 was located in the same area as the MSF plant, and samples were collected in July 2012 from: raw seawater, chlorinated seawater, after dual media filters (DMF), after micron cartridge filters (MCF) and sodium bisulfite (SBS), 1st pass permeate, 2nd pass permeate, 1st pass brine, and 2nd pass brine (Fig. S2, SI). SWRO plant 1 was equipped with polyamide (PA) RO membrane and its design capacity is 150,000 m<sup>3</sup>/d (10 trains). A chlorine residual of 0.50 mg/L as Cl<sub>2</sub> (measured between DMF and MCF) was maintained at the time of sampling, and was usually applied once a week for three hours in normal operating conditions. Residual chlorine is quenched using SBS immediately prior the 1st pass RO filtration. SWRO plant 2 had a design capacity of 216,000 m<sup>3</sup>/d water production with two passes of RO filtration. Continuous chlorination (0.7–1 mg/L) was applied at the intake point. The first pass of RO filtration consisted of cellulose triacetate (CTA) membranes, used for their resistance to chlorine. SBS was normally applied before this first pass of RO and was stopped for 1 h every 8 h to limit the biofouling of the membrane. Two sampling campaigns (May and July 2013) were performed at SWRO plant 2. Duplicate samples were collected at similar locations than SWRO plant 1, with additional samples at the 2nd pass RO step comprising two stages and product water after potabilization (i.e., remineralization) (Fig. S3, SI). During the first sampling campaign (May 2013), samples at the 1st pass RO (permeate and concentrate) were collected during normal dechlorination conditions (1.5–2.5 mg/L of SBS) and during the chlorination period. Raw seawater quality parameters (i.e., pH, turbidity, DOC, TDS, chloride, bromide and iodide ions) for each plant are described in Table S1 of the SI.

### 2.3. Isolation and cleaning of RO membrane deposits

Deposits from the fibers of a RO module from SWRO plant 2 were subjected to several steps of isolation and cleaning. First, fibers were

Download English Version:

<https://daneshyari.com/en/article/7008406>

Download Persian Version:

<https://daneshyari.com/article/7008406>

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