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Formation and fate of chlorination by-products in reverse osmosis desalination systems

*Eva Agus, David L. Sedlak**

Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720, United States

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ABSTRACT

Chlorination by-products may be formed during pretreatment or posttreatment disinfection in reverse osmosis (RO) desalination systems, potentially posing health, aesthetic and ecological risks. To assess the formation and fate of by-products under different conditions likely to be encountered in desalination systems, trihalomethanes, dihaloacetonitriles, haloacetic acids, and bromophenols were analyzed in water samples from a pilot-scale seawater desalination plant with a chlorine pretreatment system and in benchscale experiments designed to simulate other feed water conditions. In the pilot plant, RO rejection performance as low as 55% was observed for neutral, low-molecular-weight by-products such as chloroform or bromochloroacetonitrile. Benchscale chlorination experiments, conducted on seawater from various locations indicated significant temporal and spatial variability for all by-products, which could not be explained by measured concentrations of organic carbon or bulk parameters such as $SUVA_{254}$. When desalinated water was blended with freshwater, elevated concentrations of bromide in the blended water resulted in dihaloacetonitrile concentrations that were higher than those expected from dilution. In most situations, the concentration of chlorination by-products formed from continuous chlorination of seawater or blending of desalinated water and freshwater will not compromise water quality or pose significant risks to aquatic ecosystems.

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1. Introduction

With population growth and climate change exerting stresses on water supplies, water managers in many coastal communities are considering seawater desalination (Cooley et al., 2006). The most frequently discussed environmental impacts of seawater desalination are related to energy use and ecosystem effects of the discharge of brine (Cooley et al., 2006; Einav and Lokiec, 2003; Lattemann and Höpner, 2008). Chemical contaminants associated with desalination systems, such as residual chlorine, metals, disinfection by-products (DBPs) and anti-scalants, have generally been believed to be a minor issue in environmental assessments of desalination projects (Lattemann and Höpner, 2008; Abarnou and Miossec, 1992). However, questions have been raised about the potential environmental risks associated with chlorine use and subsequent production of chlorination by-products in desalination systems (Agus et al., 2009).

In reverse osmosis (RO) desalination plants, raw intake seawater frequently is subjected to continuous chlorination, at initial doses less than 1 mg/L and contact times up to 4 h, or intermittent chlorination at higher concentrations prior to filtration (Agus et al., 2009). Chlorine is typically used for biofouling control upstream of direct media filtration systems but not in plants equipped with microfiltration or ultrafiltration. Under these conditions, relatively high concentrations of

* *Corresponding author*. Tel.: +1 510 643 0256; fax: +1 510 642 7483.
E-mail address: sedlak@ce.berkeley.edu (D.L. Sedlak).
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brominated trihalomethanes (THMs) and haloacetic acids (HAAs) are formed (Ali and Riley, 1989; El Din et al., 1991; Magara et al., 1999; Dalvi et al., 2000). Available data on chlorination of seawater and salt-impacted freshwater suggest that other compounds of concern, such as halophenols and dihaloacetonitriles (DHANs) also are produced (Jenner et al., 1997; Allonier et al., 1999; Heller-Grossman et al., 1999). The chlorination by-products produced in desalination systems could compromise the quality of desalinated water or pose risks to aquatic ecosystems in locations where brines are discharged.

Chlorination by-products formed in pretreatment could be present in the desalinated permeate when not rejected completely by RO membranes. Incomplete rejection of uncharged organic compounds has been observed for chloroform, bromoform, halophenols, and other phenols under laboratory conditions (Bruchet and Laine, 2005; Yoon et al., 2007; Bellona et al., 2004). For example, under high-pressure membrane operating conditions of 99% salt rejection for a 5 mM NaCl solution, only approximately 25% of bromodichloromethane and 57% of bromoform were rejected during bench-top RO experiments (Agenson et al., 2003). Incomplete rejection has also been reported at full-scale plants (Agus et al., 2009; Magara et al., 1999) indicating that chlorination by-products formed in the pretreatment systems have the potential to enter water supplies.

In addition to their potential presence in the permeate, disinfection by-products rejected by RO membranes are typically discharged into the marine environment. Available aquatic ecotoxicity data on chlorine by-products indicates that some marine organisms could be affected by exposures to brines (Miri and Chouikhi, 2005; Agus et al., 2009). For example, a median lethal dose (i.e., LC_{50}) of 1000 μg/L was reported for bromoform exposure to oyster larvae while chronic effects were reported at concentrations as low as 50 μg/L (Stewart et al., 1979). Some HAAs could also pose risks to aquatic macrophytes and phytoplankton at relatively low concentrations (e.g., monochloroacetic acid and monobromoacetic acid inhibited growth in green algae *Scenedesmus subspicatus* at concentrations of 7 μg/L and 20 μg/L, respectively (Kühn and Pattard, 1990)).

Due to incomplete rejection during RO, desalinated seawater also contains between 250 and 600 μg/L bromide, which is an order of magnitude above the median concentrations observed for surface water in the US (Agus et al., 2009; Krasner et al., 2006). Disinfection of bromide-rich water can increase the formation potential of THMs in laboratory experiments (Hua et al., 2006). Therefore, the increase in bromide resulting from the blending of desalinated water with organic-matter rich water sources may lead to increased formation of chlorination by-products in potable water distribution system.

The objective of this study was to assess the formation and fate of chlorination by-products associated with chlorine pretreatment and subsequent blending at reverse osmosis desalination plants. To achieve these objectives, the formation and removal of trihalomethanes, haloacetic acids, dihaloacetonitriles and odiferous bromophenols were quantified at a pilot-scale desalination plant under various operating conditions. To complement results for the pilot plant, benchscale chlorination of seawater from different regions and blends of desalinated water and surface water were carried out. Seawater sources for benchscale chlorination included locations of proposed and existing desalination projects, specifically from the coasts of California, Florida and Singapore. Surface water samples used in the blending experiments include a source that is impacted with elevated bromide (Colorado River) and a reservoir that has low levels of bromide.

2. Experimental approach

2.1. Sampling and experimental methods

Grab water samples were collected in 4-L amber glass bottles from the locations indicated in Table 1. All samples were shipped overnight on cold packs, arrived at temperatures below 5 °C, and were stored at temperatures below 10 °C. Seawater and surface water samples were filtered with 0.45-μm disk filters prior to storage. Conductivity, pH, total dissolved solid (TDS), dissolved organic carbon (DOC), UV absorbance at 254 nm (UVA_{254}) and halogen anions (Cl^-, Br^-, and I^-) were measured within 24 h of sample receipt. Liquid–liquid or solid phase extraction was completed within 24 h of arrival of the samples. Benchscale studies were started within 3 days of sample receipt.

Seawater collected for benchscale chlorination represents the diverse coastal conditions presently used or proposed as feed water to RO desalination systems. The Carlsbad seawater was collected from a coastal lagoon in Southern California which consists of coastal seawater, once-through cooling water from a co-located power plant and storm water runoff from a suburban community. Seawater from Monterey in the Central Coast of California is collected off an open coast with rural land use and strong upwelling. The San Francisco Bay and Panama City samples represent estuaries surrounded with intense urban activities, albeit in different climactic regions. The Singapore site is a coastal region with relatively high nutrient loading and primary productivity.

For the benchscale seawater chlorination, samples were dosed in 1-L glass containers at initial chlorine concentrations of either 0.5 mg Cl_2/L (low dose) or 2 mg Cl_2/L (high dose) and stored in the dark at ambient temperature (23 ± 2 °C) for a contact time of 30 min. Each chlorination experiment was carried out in duplicate. Chlorination was stopped by adding excess (5 mL) 1 M sodium bisulfite. Control solutions without chlorine addition and chlorinated Milli-Q water were included in each experiment. Total chlorine concentrations in the chlorinated samples were monitored immediately after addition of chlorine and after 30 min contact time. For samples with initial concentration of 0.5 mg Cl_2/L, chlorine residual ranged between 0 and 0.2 mg Cl_2/L after 30 min. For the initial concentration of 2.0 mg/L, chlorine residuals were between 0.3 and 1.0 mg Cl_2/L after 30 min. The average $C \cdot t$ values were 10 ± 3 and 36 ± 6 mg Cl_2/L min for the low and high dose samples, respectively.

Pilot-scale experiments were conducted at a 0.026 million gallons per day (MGD, 0.098 million liters per day [MLD]) pilot-scale desalination plant located in Carlsbad, California (Fig. 1).

Table 1 – Water quality parameters for seawater, pilot plant and surface water samples.

Source location	Conductivity (μS/cm)	TDS (mg/L)	pH	Temp[a] (°C)	DOC (mg/L)	SUVA (m^{-1} L/mg)
Carlsbad, Southern California						
Pilot plant experiments						
Intake	51,100 ± 800	35,800 ± 2100	7.6 ± 0.3	20 ± 2	3.1 ± 2.6	1.5 ± 1.2
Feed	51,300 ± 1000	36,000 ± 1400	7.6 ± 0.2	21 ± 2	2.8 ± 2.9	2.1 ± 2.0
Concentrate	89,700 ± 1300	72,300 ± 3200	7.5 ± 0.3	21 ± 2	3.0 ± 2.4	1.6 ± 1.0
Permeate	204 ± 18	310 ± 50	8.6 ± 0.5	25 ± 2	0.62 ± 0.3	1.1 ± 0.9
Intake, *summer 2007*	48,500	36,000	7.4	23 ± 2	0.91	1.5
Intake, *winter 2008*	46,200	34,800	7.5	23 ± 2	1.5	3.6
Monterey, Central California						
	43,200	33,200	7.2	23 ± 2	1.6	1.5
San Francisco Bay, Northern California						
	42,100	31,200	7.3	23 ± 2	1.9	3.2
Panama City, Florida						
	49,300	36,700	7.2	23 ± 2	4.4	1.9
Singapore						
	44,300	33,300	7.4	23 ± 2	3.1	1.3
Raw surface water for blending studies						
Colorado River, NV	850	600	7.4	23 ± 2	7.6	1.1
San Pablo Reservoir, CA	110	100	7.6	23 ± 2	4.7	1.9

a Temperatures of pilot plant samples were measured during chlorination experiments at the Carlsbad pilot plant. Temperatures of benchscale chlorination samples were ambient laboratory temperature.

The intake was located in Agua Hedionda Lagoon, adjacent to the Encina Power Station. Chlorine (as NaOCl), ferric sulfate and polymeric flocculants were added immediately after the intake water storage tank. Prior to entering the Hydranautics SWC3 RO modules, feed water was quenched with excess sodium bisulfite and an antiscaling agent was added. The estimated hydraulic retention time between chlorine addition and quenching was 28 min. The pilot plant RO system ran at 45–50% recovery with target TDS concentration of 300 mg/L.

Samples were collected from raw intake storage tank (intake), quenched RO feed water (feed), discharged RO concentrate (concentrate), and RO permeate (permeate) of the pilot plant at approximately once-a-week for a month during two sampling seasons (Autumn 2007 and Winter 2008). During each day of sampling, the pilot plant operated with an initial chlorine concentration of 0.5 mg Cl_2/L (low dose) and 2.0 mg Cl_2/L (high dose). The pilot plant was equilibrated for at least 2 h at the desired chlorine dose before grab samples were collected. The Winter 2008 samples were collected following wet weather conditions to examine the effects of terrestrial runoff in the watershed upstream of the intake lagoon.

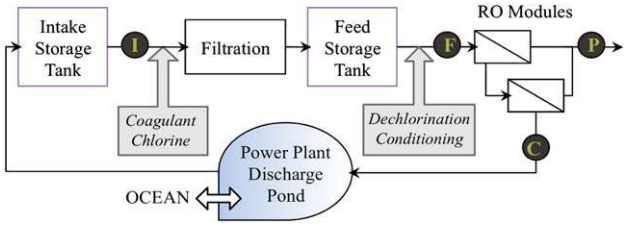

Fig. 1 – Process scheme of pilot-scale desalination plant and sampling locations. Sodium bisulfite was used for dechlorination and antiscaling and anticaking agents were used for conditioning. Raw intake seawater (I), quenched RO feed water (F), RO concentrate (C), and RO permeate (P) sampling points were collected.

To simulate the potential formation of chlorine by-products when desalinated water is blended with water from other sources, permeate from the pilot plant was blended with untreated freshwater collected from the Colorado River at Lake Mead, Nevada and the San Pablo Reservoir at Orinda, California at a 1:1 (v/v) ratio and subjected to chlorination with contact times up to 72 h. Coagulation was not performed prior to blending and, as a result, the concentrations of by-products formed during chlorination were higher than what would be expected in a potable water system. Thus, the results represent a worst-case scenario to chlorination by-product formation from blends of desalinated water and raw surface water. The removal of organic precursors by water treatment should be taken into account when considering other situations. Control solutions of 100% freshwater, 100% desalinated water and a blend with chloraminated local tap water were included in the experiments. Experiments were carried out in 1-L amber glass bottles covered with a PTFE-lined plastic cap, sealed with PTFE tape, and stored in the dark at ambient temperature. The pH of all samples was adjusted to 7.5 using NaOH or H_2SO_4 prior to chlorination. An initial chlorine concentration of 4 mg Cl_2/L was used to maintain a residual concentration higher than 0.5 mg Cl_2/L in every sample after 72 h. Samples were collected immediately after chlorine addition and after 0.5, 8, 16, 24, 48, and 72 h. The blending

experiments were conducted in triplicate. At the end of each experiment, samples were quenched with excess (5 mL) 1 M sodium bisulfite and analyzed for trihalomethanes (THMs), haloacetic acids (HAAs), dihaloacetonitriles (DHANs) and chlorine residual.

2.2. Reagents and analytical methods

All standards, chemicals and solvents used were of analytical reagent grade or higher, purchased from Sigma–Aldrich (St. Louis, Missouri) and Fisher Scientific, Inc. (Fairlawn, New Jersey). The deuterated standard d5-2,4,6-trichloroanisole (99%) was purchased from Cambridge Isotope Laboratory, Inc. (Andover, MA). Dilution water was produced with a Millipore Milli-Q system.

For benchscale chlorination experiments, fresh stock solutions of chlorine were prepared daily by diluting a concentrated NaOCl solution in dechlorinated dilution water. The total concentration of chlorine in the stock solutions was standardized daily using the N, N′-diphenyl-p-phenylenediamine (DPD) ferrous titration method (Standard Methods 4500-Cl F [APHA]).

Analysis of THMs and DHANs were carried out according to USEPA Method 551.1 with 1,2-dibromopropane as a surrogate. THMs included in the analysis are chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform. DHANs included in the analysis are dichloroacetonitriles (DCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN). HAAs were extracted in methyl tert-butyl ether (MTBE), derivatized with acidic CH_3OH and analyzed according to a modified USEPA Method 552.3 with 2,3-dibromopropionic acid as a surrogate. The designation HAA5 is used for monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA) and bromochloroacetic acid (BCAA), which are regulated by the USEPA, while the HAA9 designation includes dibromoacetic acid (DBAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA) and tribromoacetic acid (TCAA). THMs, DHANs and HAAs were analyzed by gas chromatography with electron capture detection (GC/ECD) on a Varian 3800 gas chromatograph equipped with a DB-5 fused silica column (30-m, ID 0.25 mm, 0.25 μm thickness, J&B Scientific).

Halophenols (i.e., 2,4,6-trichlorophenol, 2-bromophenol, 2,6-dibromophenol, and 2,4,6-tribromophenol) and haloanisoles (i.e., 2,4,6-trichloroanisole and 2,4,6-tribromoanisole) were subjected to solid phase extraction (SPE) and analysis by gas chromatography/tandem mass spectrometry (GC/MS/MS) using a Varian 3900 GC with a Saturn 2100T ion trap mass spectrometer and an HP5-MS fused silica column (30-m, ID 0.25 mm, 1.0 μm thickness, Agilent). No derivatization step was carried out on halophenols. Prior to SPE, 100 ng of deuterated d5-trichloroanisole was added as the surrogate standard. The pH of each 1-L water sample was adjusted to pH 4 using concentrated H_2SO_4 and ionic strength was adjusted by addition of reagent grade NaCl to match the salinity of RO concentrate from the pilot plant (~70 g/L). Extractions were carried out in silanized 6-mL glass cartridges packed with 250 mg Isolute-ENV resin at a flow rate of approximately 10 mL/min. The Isolute-ENV resin was pre-conditioned with 5 mL CH_3OH, 5 mL Milli-Q H_2O and 5 mL pH 4 Milli-Q H_2O at a flow rate of approximately 2 mL/min. Immediately after loading the resin, the cartridge was washed with 2 mL of a 30:70 acetone:Milli-Q H_2O solution and then dried for at least 10 min. The analytes were then eluted with at least 6 mL of 50:50 acetone:methylene chloride. The eluent then was spiked with 2,3,5-trichlophenol as an internal standard and dried to a volume of about 1 mL using a gentle stream of ultrapure N_2. Typical SPE recoveries were between 70 and 130%, with better yields observed for compounds with higher molecular weights.

Water quality parameters were analyzed using established methods. Conductivity was measured using a Hach SensIon 7 meter and pH was measured using a Denver Instrument UB-10 meter. Total dissolved solids were analyzed using Standard Method 2540C. Dissolved organic carbon (DOC) was analyzed using a Shimadzu 5000A TOC analyzer (MDL = 0.65 mg/L). UV absorbance at 254 nm (UV_{254}) was measured on a Perkin–Elmer Lambda 14 spectrophotometer with a 1-cm path length. Specific UV_{254} absorbance ($SUVA_{254}$) values were determined as the ratio of measured UV_{254} and DOC values, with half the DOC detection limit (i.e., 0.65 mg/L) used for non-detects. Total and free chlorine residuals were analyzed using the DPD ferrous titration method. Chloride was analyzed by ion chromatography (Dionex DX 120) while bromide and iodide anions were analyzed by high-pressure liquid chromatography (HPLC) with UV detection (Waters Alliance 2695) with quantification at 194 nm and 226 nm, respectively (Oleksy-Frenzel et al., 2000).

Statistical analysis of experimental results was conducted using JMP software from SAS Institute (Cary, NC). Half the method detection limits were used for non-detections.

3. Results and discussion

3.1. Pilot plant studies

As expected, trihalomethanes, haloacetic acids, dihaloacetonitriles and bromophenols were detected in chlorinated RO feed and concentrate at the Carlsbad pilot plant (Fig. 2). The concentration of chlorination by-products detected in feed water (Table S1 in Supporting Information) was within the range observed in other studies at seawater desalination plants and coastal power plants (Allonier et al., 1999; Jenner et al., 1997; Agus et al., 2009; El Din et al., 1991; Magara et al., 1999; Dalvi et al., 2000). In addition to formation during pretreatment, chlorination by-products were also present at low concentrations in pilot plant intake water due to chlorination at the co-located Encina Power Plant.

Upon chlorine pretreatment, the formation of chlorination by-products at the pilot plant varied with chlorine dose and seasonal conditions, especially for trihalomethanes (Fig. 2). The maximum sum concentration of THMs and HAA5 detected in pilot plant RO feed were 74 μg/L and 28 μg/L, respectively, which are below the US Maximum Contaminant Limit for drinking water (i.e., 80 μg/L for sum of THMs and 60 μg/L for sum of HAA5).

Brominated by-products dominated the disinfection by-products due to relatively high concentrations of bromide (i.e., 65 mg/L in seawater). During the rainy winter season,

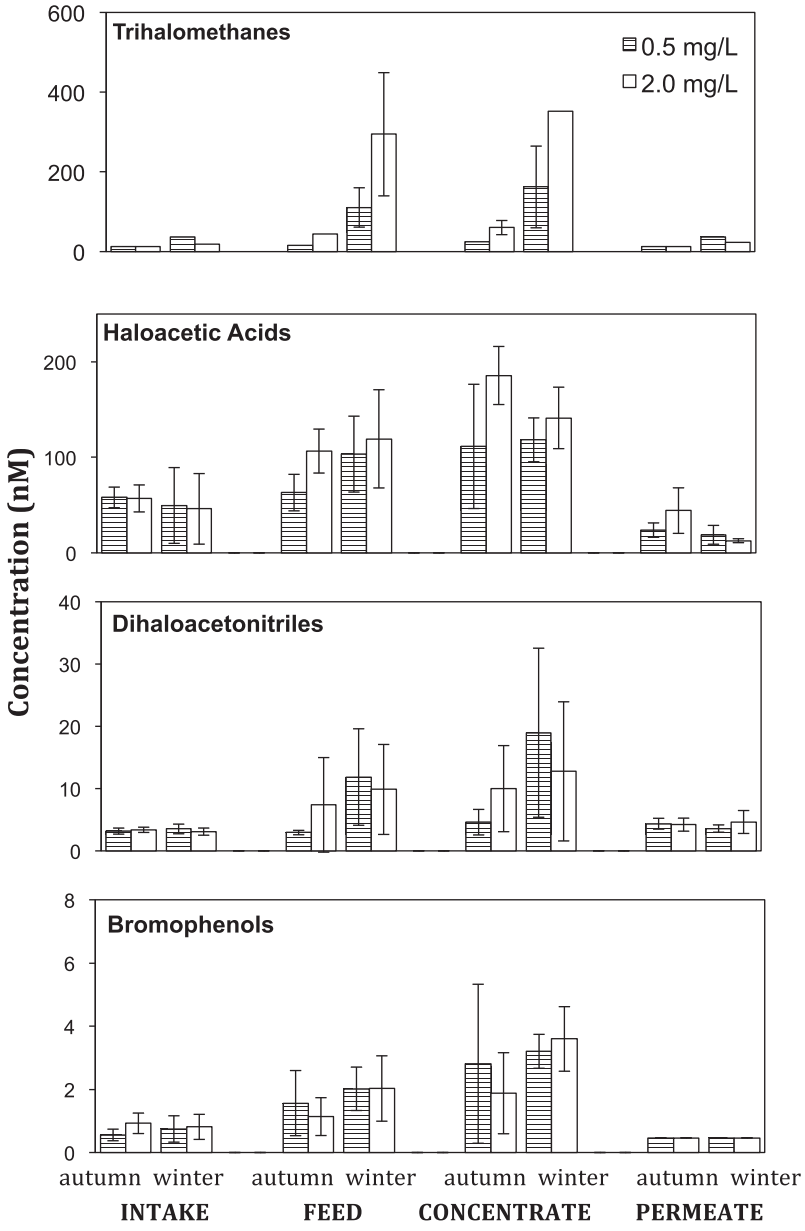

Fig. 2 – Trihalomethanes, haloacetic acids, dihaloacetonitriles and bromophenols in pilot plant samples. Fall samples collected weekly in October 2007 and winter samples collected after storm events in February–March 2008.

concentrations of THMs were generally higher and the speciation of by-products was typically more variable with a higher fraction of mixed halogenated compounds. For example, bromoform was the dominant trihalomethane (>95% of total THMs) during the dry autumn sampling period but only accounted for 30% of the total THMs during winter.

The enhanced production of by-products and increased variability observed during winter appeared to be related to variation of organic precursor concentrations and sources in the intake water. Following rain events, surface water runoff enters the lagoon where the intake is located through a small stream running through a residential area. Furthermore, higher flows into Agua Hedionda Lagoon during winter may have resuspended organic precursors from the sediments. Consistent with this hypothesis, organic precursors (as DOC) were present at significantly higher concentrations ($p < 0.05$) during winter (Fig. 3a) and THM formation was correlated with DOC during both seasons ($r^2 = 0.97$). The aromaticity of organic carbon—quantified as the $SUVA_{254}$—entering the intake lagoon did not exhibit seasonal variations (Fig. 3b).

Chlorination by-products formed during pretreatment were effectively removed by reverse osmosis at the desalination pilot plant (Fig. 2, Table S1 in Supporting Information). Overall rejection at the pilot plant exceeded published values for RO membranes from previous laboratory studies (Xu et al., 2005; Agenson et al., 2003; Yoon et al., 2007) because the pilot plant was run with a lower TDS target of approximately 300 mg/L. Results reported by Agenson et al. (2003) indicate that high desalting membranes (>99% Cl^- anion rejection)

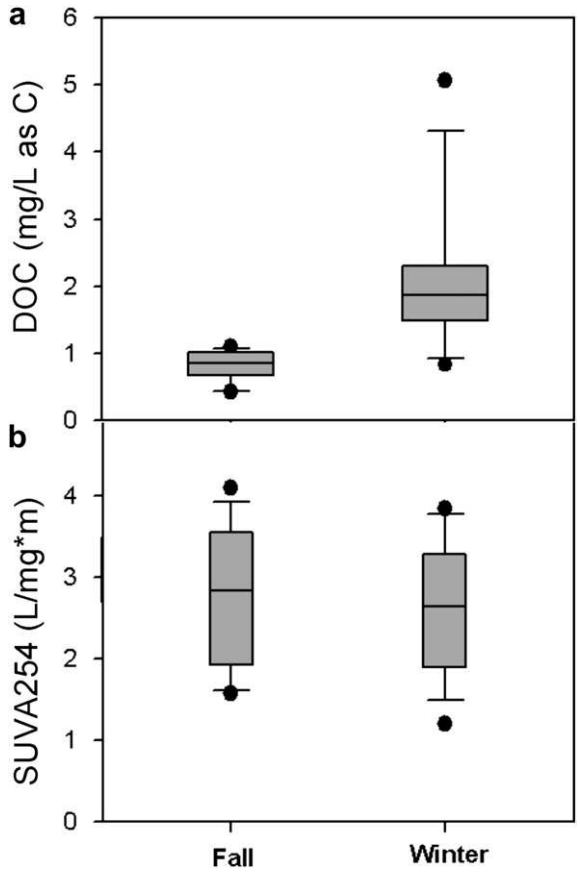

Fig. 3 – (a) Dissolved organic carbon (DOC, mg/L) and (b) specific UV absorption at 254 nm (SUVA254, m^{-1} L/mg) in pilot plant intake samples. Fall samples were in October 2007 and winter samples collected in February–March 2008.

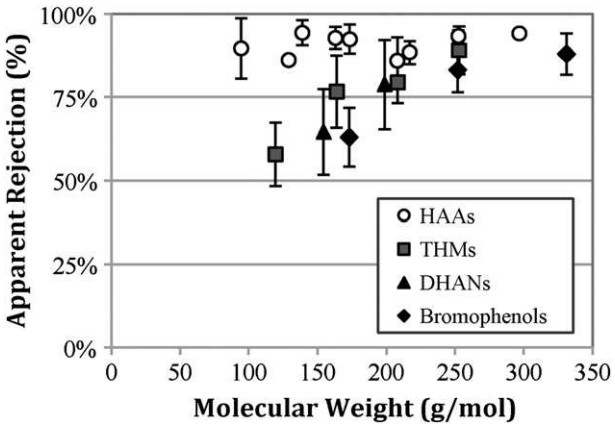

Fig. 4 – Apparent overall rejection at the pilot plant as a function of molecular weight. THMs, DHANs and bromophenols are neutral compounds (solid markers), while HAA9 is present as ionic compounds (hollow markers). Only samples in which feed concentrations were at least five times higher than the MDL were used to calculate rejection. One-half of the MDL was used in calculation whenever the permeate concentration was below the MDL.

used in seawater desalination to meet low TDS goals have higher rejection rates for organic compounds than other types of RO membranes. The rejection of neutral by-products decreased with molecular weight below the range of molecular weight cutoff of 200 Da (Fig. 4), which is consistent with previous observations (Kojima et al., 1995; Verliefde et al., 2006). Compared to neutral by-products, the negatively charged haloacetic acids ($pK_a \leq 3$) were rejected more effectively by the RO membrane (i.e., average rejections 86–94%) due to electrostatic repulsion (Bellona et al., 2004).

The chlorine pretreatment systems at those full-scale desalination plants typically have longer hydraulic retention times than the pilot plant (i.e., up to 4 h of contact time compared to 30 min at the pilot plant) (Agus et al., 2009). Therefore, the concentration of chlorine by-products in full-scale plants could be higher than those observed here, with the possible exception of the halophenols, which are transformed to smaller by-products at longer chlorine contact times (Acero et al., 2005). Although continuous application of chlorine during pretreatment can produce relatively high concentrations of by-products during wet weather conditions, the practice ultimately poses minimal risks to product water quality due to the effective RO membrane rejection for by-products of varying molecular weights.

3.2. *Chlorination by-product formation in seawater from other seawater desalination project locations*

To assess the potential of seawater from other locations to produce higher concentrations of chlorination by-products during pretreatment due to temporal and spatial variations in organic precursor concentrations, samples from other locations were chlorinated under conditions comparable to those employed at the pilot plant. Seawater from Gulf of Mexico (Panama City, Florida) produced the highest total molar yield of chlorine by-products with concentrations of THMs (mainly bromoform) that were approximately twice as high as those detected in samples from any other location (Fig. 5). This observation is consistent with the elevated concentration of DOC relative to other sites. The DOC concentration in the Gulf of Mexico sample (4.4 mg/L) is more than twice as high as the other samples. However, a clear correlation between DOC in seawater from different locations and the formation of chlorination by-products was not evident. The absence of simple correlation between DOC and chlorination by-products is consistent with the results of previous research. For example, chlorination of seawater with similar DOC concentrations at similar chlorine doses produced as little as 61 μg/L of THMs in seawater from Kuwait (Ali and Riley, 1989) and as much as 490 μg/L THMs at the Tampa Bay desalination plant (Agus et al., 2009).

In addition to the observed variability in the overall mol yield of chlorination by-products, the distribution of by-products varied among different locations. For example, haloacetic acids were the most abundant by-product group—accounting for 77% of the compounds detected on a molar basis—detected in samples collected from the California coastline during dry conditions. In contrast, the

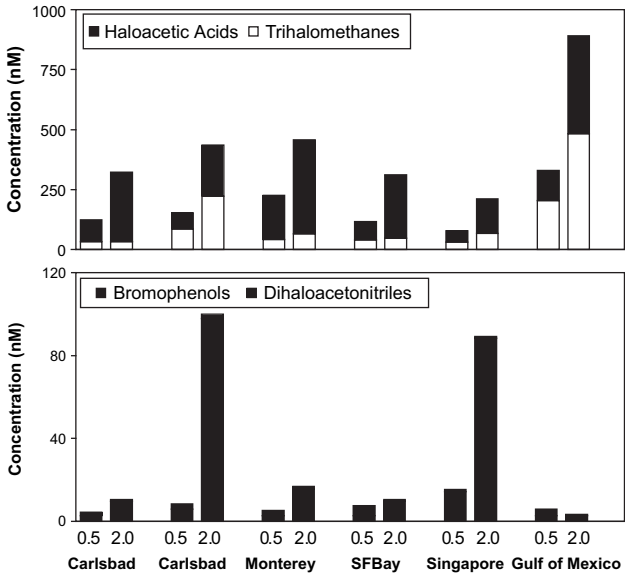

Fig. 5 – Trihalomethanes, haloacetic acids, dihaloacetonitriles and bromophenols (in nM) formed during benchscale chlorination of seawater from different locations. Locations other than Carlsbad were sampled in Spring 2008 during dry weather conditions. Chlorination conducted in the dark at ambient temperature with initial doses of 0.5 and 2.0 mg/L as Cl2 and contact time of 30 minu.

molar ratio between THMs and HAA9 was close to 1:1 in the Gulf of Mexico sample and in the winter (wet weather) Carlsbad sample. The influence of source on the ratio of THMs to HAA9 has previously been reported (Fabbricino and Korshin, 2005) and may be related the origin of the by-product precursors (i.e., coastal or deep ocean seawater).

Dihaloacetonitriles—mainly BCAN and DBAN—accounted for less than 3% of the overall by-product yield; except in water collected from Singapore and from Carlsbad during winter conditions, where they accounted for 21% and 18% of the molar yield of chlorination by-products, respectively. Benchscale chlorination of samples collected from Singapore on two different occasions at initial concentration of 2 mg/L Cl_2 resulted in formation of DHANs of 53 and 122 nM molar sum (10 and 23 μg/L mass sum). The only previous data on DHANs in chlorinated seawater known by the authors were from coastal power plants along the English Channel where an average of 18 nM (3.6 μg/L) DBAN was detected (Allonier et al., 1999). In chlorination of other bromide-rich water sources, the maximum sum of haloacetonitriles are usually lower than the maximum yields observed in this study. For example, the USEPA survey of drinking water treatment plants found a maximum of 14 μg/L for the sum of DHANs (Krasner et al., 2006) while the maximum concentration reported in chlorinated water from Lake Kinneret, Israel was 12 μg/L (Heller-Grossman et al., 1999). Additional research is needed to identify haloacetonitrile precursors and determine why some seawater sources produce higher HAN concentration upon chlorination.

Bromophenols accounted for less than 0.5% of the by-products produced upon chlorination on a molar basis—with little variability observed among geographic locations. Higher concentrations of bromophenols were detected after low-dose chlorination, because tribromophenols continue to react with chlorine, eventually undergoing ring cleavage to form low-molecular-weight by-products (Acero et al., 2005; Bruchet et al., 2008). The potent odorant 2,6-dibromophenol (odor threshold = 0.0005 μg/L) was formed at concentrations up 0.432 μg/L in chlorinated seawater from San Francisco Bay. Aesthetic issues caused by bromophenols may be avoided by their efficient removal in reverse osmosis as well as additional chlorination applied prior to distribution.

Using data on contaminant rejection in the pilot plant (Fig. 4) and measurements of by-products in chlorinated seawater (Fig. 5), predictions were made of the maximum concentrations of chlorine by-products at initial dose of 2 mg/L Cl_2 in the RO permeate and concentrate (Fig. 6). For regulated by-products, the maximum concentrations calculated based on rejection rates in the RO permeate (i.e., 14 μg/L for THMs and 3.3 μg/L for HAA5) were always well below USEPA regulatory guidelines of 80 μg/L for THMs and 60 μg/L for HAA5. These values agree with typical concentrations reported at desalination plants (Agus et al., 2009). With respect to these regulated DBPs, it appears that product water from desalination plants will normally contain much lower concentrations of regulated chlorination by-products than conventional drinking water from plants that use chlorine as a primary disinfectant (Weinberg et al., 2002). Furthermore, the efficient removal of high molecular weight organic precursors during RO will likely result in little formation of additional by-products in the distribution system.

The maximum calculated concentration of dihaloacetonitriles (i.e., 8.2 μg/L of DBAN) in the permeate is lower than the USEPA drinking water guideline of 20 μg/L for DBAN but within the range of other chlorinated surface water (i.e. 1–12 μg/L sum DHANs (Krasner et al., 2006)).

According to our calculations, bromophenols could be present in RO permeate at concentrations above their odor threshold concentrations under certain conditions. For example, the highest calculated concentration for 2,6-dibromophenol of 0.073 μg/L is approximately 150 times higher than the reported organoleptic threshold (0.0005 μg/L (Whitfield, 1988)). Concentrations of bromophenols could be reduced if RO permeate from desalination plants receives free chlorine residual in the distribution system. We are unaware consumer complaints of off-flavors associated with halophenols in desalinated seawater.

3.3. *Chlorination by-products in reverse osmosis concentrate*

By-products in the concentrate (RO retentate) are often discharged to the ocean where they have the potential to affect marine organisms (Cooley et al., 2006). Measured and calculated chlorination by-products in RO concentrate (Fig. 6) were always below the threshold for known effects in sensitive marine organisms (Kühn and Pattard, 1990; Miri and Chouikhi, 2005; Agus et al., 2009). Among the compounds monitored, the chlorine by-products that came closest to exceeding the effects threshold was MBAA, where the maximum concentration (14 μg/L) was approximately 70% of the most sensitive

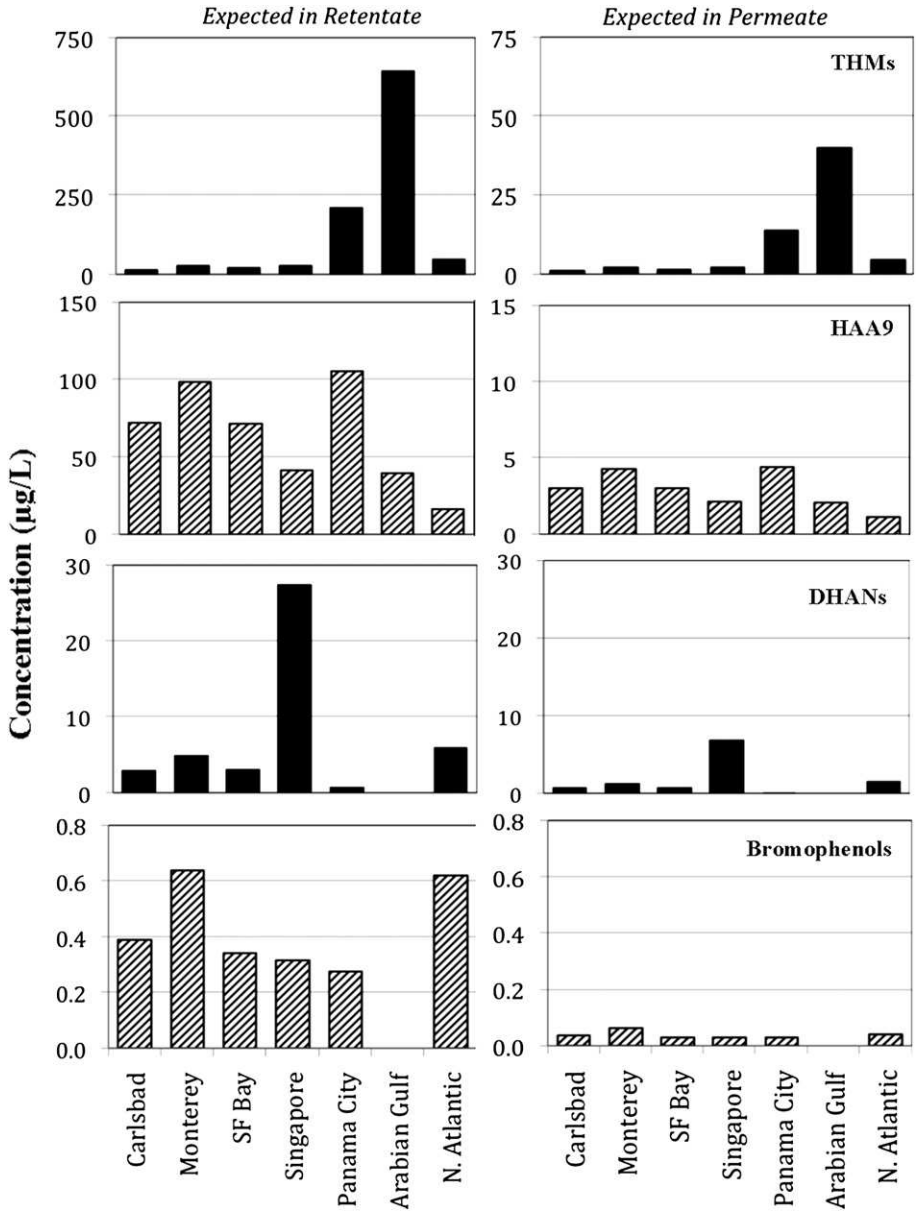

Fig. 6 – Expected retentate and permeate concentrations from benchscale chlorination results and previous studies, calculated using the average observed concentration factors and rejection rates at the Carlsbad pilot plant. Maximum THM and HAA6 concentrations for the Arabian Gulf were obtained from Ali and Riley (1989) and Dalvi et al. (2000). Mean DBP concentrations for North Atlantic were those reported in Allonier et al. (1999).

effects concentrations (i.e., EC_{10} of 20 µg/L for green algae). Concentrations of chlorine by-products in the concentrate calculated based on 50% recovery and observed rejection rates from the pilot plant samples are consistent with limited previously reported values (Fig. 6). For example, calculated THM concentrations in RO concentrate from this study ranged between 11 and 640 µg/L while concentrations between 270 and 1500 µg/L had been previously reported at other desalination plants (Ali and Riley, 1989; Agus et al., 2009). The THM concentration expected in desalination plant RO concentrate, based on feed concentration and concentration factors measured at the pilot plant, is within the same range of concentrations reported from European coastal power stations (i.e., 16 µg/L (Jenner et al., 1997) and 26 µg/L (Allonier et al., 1999)).

In most situations, RO concentrate is diluted by surrounding seawater near the discharge point (Saeed et al., 1999) and, as a result, elevated concentrations of chlorination by-products should only be present in the immediate proximity of the discharge point. In these areas, chlorination by-products may contribute to marine life stress due to oxidant residuals, hypersalinity and elevated temperatures. The most sensitive endpoints associated with desalination plants are probably those associated with exposure to hypersaline brines, especially in shallow and enclosed sites receiving high volumes of discharge (Lattemann and Höpner, 2008).

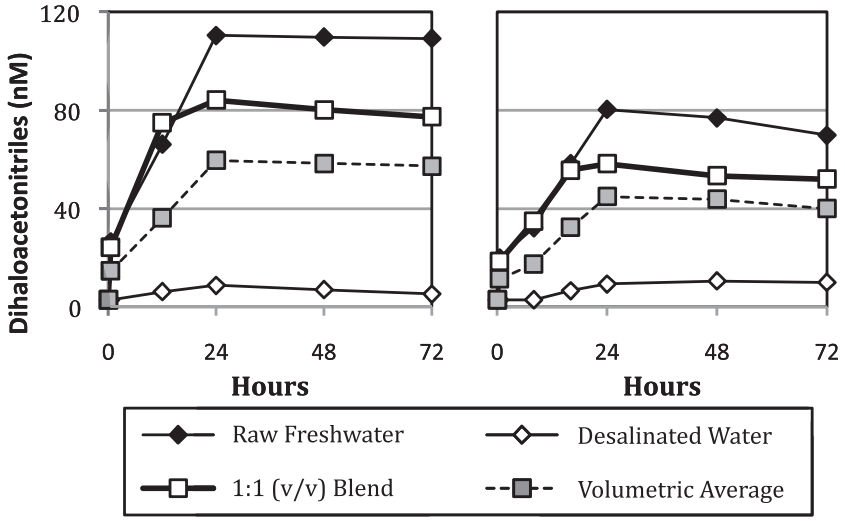

Fig. 7 – Dihaloacetonitriles formed upon 72-h chlorination of raw freshwater, Br-rich desalinated water (RO permeate) and 1:1 (v/v) blend of the two water sources. The volumetric average is calculated from the Colorado River and permeate samples. Initial dose at 4 mg/L as total Cl_2.

3.4. *Chlorine by-product formation during disinfection of blended desalinated water*

Desalinated water (RO permeate) contains relatively high concentrations of bromide and, when it is blended with surface water from other sources, there is a potential for producing elevated concentrations of chlorination by-products or shifting the distribution of by-products to brominated species. Blending Colorado River water with an equal volume of desalinated water resulted in an increase in bromide concentration from 133 μg/L (1.7 μM) to 274 μg/L (3.4 μM), while blending San Pablo Reservoir water with desalinated water increased the bromide concentration from 59 μg/L (0.74 μM) to 208 μg/L (2.6 μM).

While increasing bromide concentrations shifted the distribution of THMs and HAAs towards brominated compounds, the total concentration formed (expressed on a molar basis) was approximately equal to the weighted average from chlorination experiments conducted with unblended desalinated water and unblended surface water (Table S2 in Supportng Information). For DHANs, however, a higher-than-expected molar yield of by-products was observed (compare hollow to filled squares in Fig. 7). DHANs were formed at 30% and 20% higher-than-expected molar yield in blends with Colorado River and San Pablo Reservoir water, respectively. In chlorination of raw (unblended) surface water, DCAN and BCAN were the main DHAN species produced whereas, after blending with desalinated water, BCAN and DBAN increased almost two-fold and became the more abundant species. These findings are consistent with previous experimental results in which bromide was added directly to freshwater prior to chlorination (Hua et al., 2006, Table S2 in Supporting Information).

The experimental blending of desalinated water with surface water illustrates that the decrease of organic precursor by dilution with desalinated water can reduce the concentrations of chlorine by-products, but precise prediction of concentrations in treated blended water requires consideration of the effects of bromide on by-product formation. In practice, desalinated water is either used directly or blended with treated surface water which has undergone processes to remove organic precursors (e.g., coagulation or flocculation). In such cases, the concentration of by-products generated from chlorinating blended water will be considerably lower than those observed in these experiments with raw water.

4. Conclusions and recommendations

- Geographic and seasonal variability in seawater quality affect the concentrations of chlorination by-products produced during seawater pretreatment. In most situations, the concentration of chlorination by-products formed when continuous chlorination of seawater is employed will not pose unacceptable risks to human health or aquatic ecosystems. However, it may be prudent to monitor chlorination by-products during plant operations especially when high concentrations of organic precursors are expected (e.g., after storms).
- Neutral, low-molecular-weight chlorination by-products, such as bromoform and the dihaloacetonitriles, may be present in reverse osmosis permeate of desalination systems. Concentrations of chlorination by-products in desalinated water are likely to be below regulatory guidelines. Concentrations of bromophenols may exceed aesthetic benchmark values.
- Chlorination by-products will be concentrated in water discharged by desalination plants. With the exception of bromoacetic acids, the concentrations of most chlorine by-products in RO concentrate will be below known thresholds for aquatic toxicity. Under conditions in which the outfall is

designed to assure rapid dilution of the high salinity brine, chlorination by-products should pose minimal risks for marine ecosystems.
- Chlorination after blending of desalinated water with surface water can result in an overall decrease of by-product formation relative to the unblended surface water.

However, the addition of bromide from the desalinated water may result in higher production of DHANs than expected based on dilution of organic precursors. When desalinated water is blended with freshwater sources, experiments should be carried out to determine the effect of bromide contribution from desalinated water to by-product formation.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.watres.2009.11.015.

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