Aquifer Treatment of Sea Water to Remove Natural Organic Matter Before Desalination

by Abdullah H. A. Dehwah1, Samir Al-Mashharawi1, Kim Choon Ng1, and Thomas M. Missimer2

Abstract

An investigation of a sea water reverse osmosis desalination facility located in western Saudi Arabia has shown that aquifer treatment of the raw sea water provides a high degree of removal of natural organic matter (NOM) that causes membrane biofouling. The aquifer is a carbonate system that has a good hydraulic connection to the sea and 14 wells are used to induce sea water movement 400 to 450 m from the sea to the wells. During aquifer transport virtually all of the algae, over 90% of the bacteria, over 90% of the biopolymer fraction of NOM, and high percentages of the humic substance, building blocks, and some of the low molecular weight fractions of NOM are removed. Between 44 and over 90% of the transparent exopolymer particles (TEP) are removed with a corresponding significant reduction in concentration of the colloidal fraction of TEP. The removal rate for TEP appears to be greater in carbonate aquifers compared to siliciclastic systems. Although the production wells range in age from 4 months to 14 years, no significant difference in the degree of water treatment provided by the aquifer was found.

Introduction

Unconfined aquifer systems have been used for more than a century in the water treatment process to improve water quality in potable-water systems, such as riverbank filtration (Ray et al. 2002; Hubbs 2005), or for at the last 40 years to remove contaminants in infiltrated domestic waste water which is termed soil-aquifer treatment (Drewes et al. 2003). The groundwater system is known to produce a robust degree of water treatment caused by several processes including filtration, absorption, adsorption, dilution, and biochemical degradation. Use of shallow aquifer systems to provide feed water to sea water desalination plants is becoming another important application of aquifer treatment (Missimer 2009; Missimer et al. 2013).

Potable water deficits in many regions of the world are being met by the creation of “new” fresh water by desalting sea water. Of the various processes used for desalination, the commercially most economic one is sea water reverse osmosis (SWRO) (Ghaffour et al. 2013). While it has a higher degree of energy efficiency and lower operating cost compared to thermal distillation processes, it has had continuing difficulties with the fouling of the SWRO membranes caused by the accumulation of biological substances on the membrane face, which is termed biofouling (Flemming 1997; Flemming et al. 1997; Nguyen et al. 2012). Biofouling is caused by the complex interaction of organic substances that precondition the surface of the membrane with a relatively sticky coating, thereby allowing bacteria to attach to the membrane surface and multiply to become a biofilm. The biofilm acts to reduce the flux of sea water through the membrane which necessitates frequent cleaning, resulting in the reduction of the operating life expectancy of the membrane (Nguyen et al. 2012). Algae, bacteria, and a variety of dissolved organic compounds are ubiquitous in sea water and must be removed before entering the primary treatment process to reduce the rate of biofouling.

Most SWRO systems use a direct surface water or open-ocean intake system that necessitates the design and operation of a complex pretreatment process train before the feed water is permitted to pass into the primary process (Cho et al. 2000; Missimer 2009; Valavala et al. 2011; Sorlini et al. 2013). Elimelech and Phillip (2011) suggest that the energy demand for pretreatment in an SWRO plant accounts for the major part of ancillary energy usage. However, many of the organic compounds present in sea water are difficult to remove and still pass into the SWRO membrane resulting in biofouling (Greenlee et al. 2013).
At the macroscopic level, high concentrations of algae during blooms (HABs) can cause the pretreatment systems to fail, forcing facility shutdown (Caron et al. 2010; Berkley 2011; Villacorte et al. 2015). The specific organic substances of greatest concern are bacteria, the biopolymer (BP) fraction of natural organic matter (NOM), and transparent exopolymer particles (TEP) which are particulates and colloids that are produced as extracellular excretions of algae and bacteria (Bar-Zeev et al. 2015). TEP is a very complex and sticky substance formed by the self-assembly of various acidic polysaccharides and other organic compounds and has its highest concentrations during HABs (Passow 2000, 2002; Villacorte et al. 2009). Particulate TEP concentrations are generally highest in shallow sea water within the photic zone which is the depth from which most SWRO facilities extract raw water.

The use of well systems has been demonstrated to remove a large part of the organic substances that cause biofouling (Rachman et al. 2014; Dehwah et al. 2015a, 2015b; Dehwah and Missimer 2016). However, little documentation is available on the percentage removal of each of the various types of organic matter and the various fractions of dissolved NOM along with TEP. An unresolved issue is the impact of well age on the efficiency of organic substance removal during aquifer transport from the sea to the production wells. No SWRO treatment site has been thoroughly documented that contains wells with differing ages, so that well age can be assessed in terms of water treatment efficiency. It is the purpose of this research to determine whether well age impacts the “conditioning” of a coastal aquifer in terms of removal of particulate organic material and dissolved components of NOM.

Methodology

Description of the Investigated Site

A SWRO plant located near Jeddah, Saudi Arabia was selected for detailed analysis of the well intake system (Figure 1). The North Obhor SWRO plant has been in operation since 2001 and has undergone a number of facility expansions in capacity. It currently has a capacity to yield 15,350 m$^3$/day of treated water, which requires facility expansions in capacity. It currently has a capacity operation since 2001 and has undergone a number of facility expansions in capacity. It currently has a capacity (Figure 1). The North Obhor SWRO plant has been in operation since 2001 and has undergone a number of facility expansions in capacity. It currently has a capacity of capacity of NOM.

Site Hydrogeology

The coastal geomorphology and shallow geology of the Red Sea coastline of Saudi Arabia were investigated by Dehwah et al. (2014) as part of a subsurface desalination intake feasibility assessment. In many locations along the Red Sea coastline, a Pleistocene-age wedge of carbonate sediments was found. The unit extends from the shelf-edge offshore at the base of the modern fringing reef to the edge of the coastal plain or interfingers with alluvial outwash sediments (Figure 2). The outwash sediments are a mixture of boulders, gravel, sand, and clay which has a generally low hydraulic conductivity except where wadi channels exist.

Although no aquifer performance test data are available from the site, the estimated transmissivity of the carbonate aquifer based on well yields ranges from 2000 to 2500 m$^2$/day using the specific capacity estimation technique reported by Driscoll (1986). The transmissivity decreases from the shoreline landward based on the reduction in aquifer thickness and hydraulic conductivity. For comparison, the transmissivity of alluvial system is likely to be no greater than 100 m$^2$/day.

Higher salinity sea water with a slightly lower pH occurs in the carbonate sediments directly underlying the nearshore Red Sea bottom as documented by Dehwah and Missimer (2016). The higher salinity is likely caused by nearshore evaporative concentration which is 2–3 m of evaporation per year and low rates of nearshore circulation (Dehwah et al. 2015a, 2015b).

No fresh water occurs within the alluvial sediments landward of the carbonate aquifer and the sea water within them typically has a slightly higher total dissolved solids concentration compared to the sea water in the Red Sea. The higher salinity is likely caused by past evaporative concentration. In some nearby locations, the alluvial sediments contain hypersaline water within sabkha systems (Missimer et al. 2014). There is no fresh water/sea water interface that typically occurs within coastal aquifers. Rainfall accumulation in this region averages less than 50 mm/year. Based on the site hydrogeology, the pumping wells induce water flow solely from the sea with no significant contribution from the landward direction.

Sampling and Analysis Methodologies

Sampling

Sea water samples were collected from the sea surface along the coast near the production wells during...
each sample collection period to establish the raw water concentrations of organic material before the water entered the aquifer system. During the first sampling campaign, 13 wells were sampled along with the reference raw sea water sample and on a second sampling campaign the new well (4 months in age) and a reference raw sea water were collected (Table 1).

All water samples were collected following an established quality assurance and control protocol. The surface sea water samples were considered to be diagnostic of the local conditions and a water sample was collected from the discharge of each individual production well before the water entered and mixed in the primary intake pipeline. The facility was in continuous operation for at least a week before the samples were collected. Therefore, the measured results are believed to represent true operational conditions.

The sea water samples were placed into glass bottles and then placed into a container filled with ice to minimize biological activity. A solution containing 0.02% (w/v) of sodium azide was added to each total organic carbon (TOC) sample to further reduce the potential for biological activity. The samples were transported to the laboratory for analysis of algae, bacteria, TOC, NOM fractions, and TEP (particulate and colloidal) concentrations. Samples were stored in the laboratory at a temperature of 4°C until analyzed. The physical water quality parameters were measured in the field.

Fundamental Physical Parameters

The collected samples were analyzed to measure the fundamental physical water quality parameters including turbidity, salinity, conductivity, and pH. A portable turbidity meter (HACH 2100Q) was used to measure the
sample turbidities while a portable pH meter (WTW pH 3310) was used to measure pH values. The conductivity and salinity measurements were performed using a portable conductivity meter (WTW Con 3210).

**Microorganism Quantification**

Algae and bacteria counts in the collected water samples were determined using a flow cytometer. A BD FACSVers flow cytometer was used to analyze the algae cells, while an Accuri flow cytometer was used for bacterial counts. Light scattering properties and/or fluorescent intensity was determined by the flow cytometer to distinguish between the different organism classifications (Van der Merwe et al. 2014). Lasers were used to excite both unstained autofluorescent organisms (algae) and stained bacterial cells. The red laser wavelength was set at 640 nm and the blue laser at 488 nm. Algal cell counting was performed by combining 500 μL of each sample with a 1-μL volume of a standard containing 1-μm beads in a 10-mL tube. The tube was then vortexed and measured using the high flow rate with a 200-μL injection volume for 2 min. The counting procedure was repeated three times to assess the precision of the measurements. The different types of algae, *Cyanobacteria*, *Prochlorococcus*, and Pico/Nanoplankton, were distinguished based on their autofluorescence as well as by the cell side angle.
scatter which was used to identify them by size (Radic et al. 2009). The detection limit for algal counts was 50 cells/mL based on the instrument calibration.

The flow cytometer method is the most accurate means of doing counts and the precision is very high based on the data obtained from replicate samples. While variation occurs in the triplicate measurements, two measurements were very close and one deviates, usually due to large particle clogging within the water feed. Our data showed precision of measurement ranging from 0.41% to 1.86% and averages <1%.

For bacterial counts, a comparative protocol employing SYBR® Green stain was used. A volume of 500 μL from each sample was transferred to a 10-mL tube, incubated in a 35 °C water bath for 10 min and stained with the SYBR® Green dye (5 μL into 500-μL aliquot), vortexed, and incubated for another 10 min. The prepared samples were then analyzed at a medium flow setting with a 50-μL injection volume for 1 min. Triplicate measurements were made on each sample to assess measurement precision. The detection of the bacterial counts was about 100 cells/mL based on the instrument calibration. The precision was very good based on the replicate analysis with typical deviation at <1%. In samples with low bacterial concentrations close to the detection limits, the precision can vary between 3% and 6%.

**TOC and NOM Fractions**

The TOC concentrations in the samples were measured using a Shimadzu TOC-VCSH instrument. The detailed fractions of dissolved organic carbon were determined by using a Liquid Chromatography Organic Carbon Detector (LCOCD) from DOC-Labor. The invention of the LCOCD method and the vast improvements made in the accuracy of the measured fractions is relatively new and not commonly used in groundwater investigations in the past. The protocols and methods developed by Huber et al. (2011) were followed in order to measure different fractions of NOM using LCOCD and have been previously described in Rachman et al. (2015) and Dehwah and Missimer (2016).

The size exclusion chromatography column used for this experiment was a Toyopearl HW-50S which is produced by TOSOH. Prior to the sample measurements, a calibration curve was established for both molecular masses of humic substances and detector sensitivity. For the molecular mass calibration, humic acid and fulvic acid standards (Suwannee River Standard II) were used while potassium hydrogen phthalate and potassium nitrate (KNO₃) were used for sensitivity calibration (Huber et al. 2011).

The samples for the LCOCD were manually prefiltered using a 0.45-μm syringe filter to exclude the nondissolved organics. Before analyzing the samples, a system cleaning was performed by injection of 4000 μL of 0.1 mol/L NaOH through the column for 260 min. Following the cleaning step, 2000 μL of the sample was injected for analysis with 180 min of retention time and a flow rate of 1.5 mL/min. A mobile phase of phosphate buffer with STD 28 mmol and a pH of 6.58 was used to carry the sample through the system. The analysis result is a chromatogram showing a plot of signal response of different organic fractions to retention time. Manual integration of the data was then performed to determine the concentration of the different organic fractions including BPs, humic substances, building blocks, low molecular weight acids (LMWA), and low molecular weight neutrals (LMWN). The manual integration was performed based on the method developed by Huber et al. (2011). An analysis of precision conducted by Dr. Stefan Huber of DC-Labor showed that the BP fraction had a precision based on six replicates of 2.4% to 4.5%, the humic substances ranged between 2.4% and 2.7%, the building blocks between 3.2% and 17.5% (note that the initial concentration was very small for the sample reported), the LMWN between 9.2% and 12.4%, and the LMWA at up to 20% (http://www.doc-labor.de/Repro.html, accessed May 4, 2016). Based on the detections and accuracy, the data are reported as whole numbers (Dehwah and Missimer 2016).

**TEP Measurements**

Two types of TEP were investigated, particulate and colloidal. Particulate TEP has a size greater than 0.4 μm, while colloidal TEP size ranges between 0.1 and 0.4 μm (Villacorte et al. 2009). Analysis of TEP was conducted based on the method developed by Passow and Allredge (1995) which includes sample filtration, membrane staining with Alcian Blue, and UV spectrometer measurements. A staining solution was prepared from 0.06% (m/v) Alcian Blue 8GX (Standard Fluka) in an acetate buffer solution (pH 4) and freshly prefiltred through a 0.2-μm polycarbonate filter before usage. A 300-mL volume of sea water from each water sample was filtered through a 0.4-μm pore size polycarbonate membrane using an adjustable vacuum pump at low constant vacuum. After filtration, the
membrane was rinsed with 10 mL of Milli-Q water to avoid the coagulation of the Alcian Blue with possible salt remaining on the filter after the sea water filtration. This helps avoid overestimation of the TEP concentration. The retained TEP particles on the membrane surface were then stained with the Alcian Blue dye for 10 s. After staining, the membrane was flushed with 10 mL of Milli-Q water to remove excess dye. The flushed membrane was then placed into a small beaker, where it was soaked in 80% sulfuric acid for 6 h to extract the Alcian Blue dye that was bound to the TEP. Finally, the absorbance of the acid solution was measured using a UV spectrometer at 752-nm wavelength to determine the TEP concentration. The same methodology was applied to determine the colloidal TEP. The only difference was that a 250-mL volume of the water sample from the 0.4-μm pore size membrane to allow deposition of the colloidal TEP on the membrane surface.

In order to relate the UV absorbance values to estimated TEP concentrations, a calibration curve was established. Xanthan gum solutions with different volumes (0, 0.5, 1, 2, and 3 mL) were used to obtain the calibration curves (Figure 3). The TOC concentrations of Xanthan gum before and after 0.4-μm filtration were analyzed, and the TOC concentration difference was used to calculate the gum mass on each filter and the TEP concentration was estimated using the calibration curve. The same procedures were used for the 0.1-μm membrane to establish the calibration curve for colloidal particles. Afterward, the TEP concentration was expressed in terms of Xanthan gum equivalent in μg Xeq./L by dividing the TEP mass on the corresponding volume of TEP samples. Because particulate and colloidal TEP are determined indirectly, these values must be considered to be semiquantitative.

Table 3
Concentration of Algae by Type and Total, Total Bacteria, and TOC

<table>
<thead>
<tr>
<th>Sampling Point</th>
<th>Cyanobacteria (cells/mL)</th>
<th>Prochlorococcus (cells/mL)</th>
<th>Pico/Nano-Plankton (cells/mL)</th>
<th>Total Algae (cells/mL)</th>
<th>Bacteria (cells/mL)</th>
<th>TOC (mg/L)</th>
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<tr>
<td>SW (1)</td>
<td>99,420</td>
<td>25,455</td>
<td>4863</td>
<td>129,738</td>
<td>520,350</td>
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<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
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<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
<td>16,150</td>
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<tr>
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<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
<td>4250</td>
</tr>
<tr>
<td>Well #4</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
<td>5400</td>
</tr>
<tr>
<td>Well #5</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
<td>12,900</td>
</tr>
<tr>
<td>Well #6</td>
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<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
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<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
<td>63,350</td>
</tr>
<tr>
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<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
<td>8400</td>
</tr>
<tr>
<td>Well #9</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
<td>10,800</td>
</tr>
<tr>
<td>Well #10</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
<td>5050</td>
</tr>
<tr>
<td>Well #11</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
<td>9300</td>
</tr>
<tr>
<td>Well #12</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
<td>34,200</td>
</tr>
<tr>
<td>Well #13</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;100</td>
<td>11,150</td>
</tr>
<tr>
<td>SW (2)</td>
<td>76,780</td>
<td>7220</td>
<td>7870</td>
<td>91,870</td>
<td>1,356,600</td>
<td>1.1</td>
</tr>
<tr>
<td>Well #14</td>
<td>140</td>
<td>160</td>
<td>&lt;50</td>
<td>300</td>
<td>4300</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Results

Physical Water Parameters

The physical water quality parameters consisted of conductivity, salinity, pH, and turbidity. As shown in Table 2, the conductivity and salinity of the sea water were slightly higher in the wells compared to the surface sea water in most cases. The pH of the surface sea water was significantly higher than the well water with a comparison of about 8.2 to 7.3, respectively. The turbidity of the well discharge was normally significantly lower than surface sea water with the exception of well #7.

Algae and Bacteria Concentrations

Three different types of algae were detected in the surface sea water, including Cyanobacteria, Prochlorococcus, and Pico/Nano-plankton (Table 3). The Cyanobacteria were the major contributor to the overall algal population. Concentrations of algae between the surface sea water and the well discharges showed nearly a complete elimination during aquifer transport. The algae concentrations were below the significant detection limits of the analysis method at 100 cells/mL for the total counts and 50 cells/mL for the fractions except in a single well. The only algae counts in the wells above the detection limits occurred in well #14. While these concentrations were significant, they represented a very small fraction of those occurring in the surface sea water.

The concentration of bacteria showed a very large difference between that in the surface sea water and in the well discharges (Table 3). It appears that a large part of the bacteria concentration was removed in the aquifer during transport from the sea to the wellheads. Wells #7 and #12 showed higher concentrations compared to the other production wells.
TOC and NOM Fraction Concentrations

Some of the TOC was removed during aquifer transport from the sea to the production wells in all cases. Most commonly, the TOC concentration was reduced during transport between 64% and 73% (Table 3). However, wells #7 and #9 showed a lower removal percentage at 27.3 and 54.5%, respectively.

The NOM fractions represent the compositional breakdown of dissolved organic carbon. The fractions are shown in Figure 4 from BPs at the base with humic substances (HS), building blocks (BB), LMWN, and LMWA, which is the general order of overall molecular weight (from the highest to the lowest). The smallest fraction concentration in the background sea water samples is the low molecular weight acid fraction followed by the BP fraction. The humic substances fraction had the highest concentration followed by the LMWN during the first sampling, but this was reversed during the second sampling. The building blocks were in the middle of the concentration order.

The measured NOM fractions in the wells show that the average of all concentrations has a pattern of high to low concentration of LMWN, humic substances, building blocks, LMWA, and BPs. The average of the reference sea water samples shows the same order of concentration at the high end, but the BPs have a higher concentration compared with the LMWA. It must be noted that the LMWN concentrations were actually higher in some of the well discharges compared to the surface sea water samples (wells #1, #7, and #13). The LMWA concentrations in some of the well discharges were also significantly greater than those in the background sea water samples (wells #1, #7, and #14).

Particulate and Colloidal TEP Concentrations

In all cases, the particulate and colloidal TEP concentrations found in the well discharges were less than those in the reference sea water samples (Figure 5). In the surface sea water samples, the particulate TEP had a greater concentration compared to the colloidal TEP which is typical based on the fact that the colloidal TEP material is generally considered to be the precursor to the formation of the particulate TEP. There was a very large range of TEP concentrations in the well discharges.

Discussion

Physical Parameter Changes During Aquifer Transport

During transport from the Red Sea to the wells, the conductivity and the salinity increased slightly and the pH decreased slightly, and in general, the turbidity reduced with one exception. This same pattern of increased salinity
and decreased pH has been found beneath the seabed in this regional and is not unusual (Dehwah and Missimer 2016). The production wells are located in a zone along the shoreline at distances ranging between 400 and 450 m (Figure 2), but during pumping the wells induce water movement from both the seaward and landward sides of the site. The hydraulic conductivity to the seaward side is greater within the carbonate aquifer, so that is the predominant direction of recharge. Commonly, the alluvial aquifer system located landward can contain higher salinity water which also may cause the well discharge water to have a slightly higher salinity, but the similar occurrence of higher salinity and lower pH immediately beneath the seabed is the most likely cause of this difference.

The transport of sea water from the shallow nearshore to the production wells is clearly demonstrated by the occurrence of shallow water algae, *Cyanobacteria* and *Prochlorococcus* in one of the production wells and the presence of particulate TEP. It also should be noted that the major cation and anion ratios in the well water are identical to that in the nearshore Red Sea water.

The lower pH of well water is likely caused by calcium carbonate precipitation between the sea water entering the aquifer and during its travel to the production wells. There are modern marine hardgrounds covering the shallow seafloor at the site. These deposits are cemented with acicular aragonite and high magnesium calcite and occur in the inter-reef area of most of the Red Sea offshore.

Filtration occurs as sea water passes through the carbonate aquifer and into the wells. This filtration reduces the concentration of suspended sediments that produce turbidity by size exclusion. The higher turbidity measured in well #7 discharge may be indicative of some aquifer material than that could have been incorporated into the discharge during pumping.

**Aquifer Treatment and the Reduction of Organic Carbon During Transport**

The pumping-induced transport of sea water through the aquifer and into the production wells was found to be very effective in the removal of the most critical organic materials. The compounds, in terms of biofouling reduction, were compared to a reference surface sea water sample collected at the same time as the well water samples were collected (Table 4). There was some seasonal variability in the organic parameters measured and the reference samples may not be representative of all conditions that could occur. While there is some question concerning the use of the reference samples in terms of comparative organic matter analyses and chemistry to the well discharges, because water entering the aquifer from the sea is not uniform and can occur in a belt covering some unknown portion of the nearshore marine environment, not a single point. However, the surface water sample is representative of the water quality that would occur if a typical surface water intake system was used to supply the SWRO plant with raw water. Therefore, the aspect concerning “removal” is qualified in terms of application to the SWRO operation.

The largest particulate organic materials are the algae and bacteria which were removed during transport at percentages greater than 99.7 and 93.2% respectively. The TOC was removed at greater than 64% in all cases with the exception of groundwater from two wells.

Removal of algal and bacteria during transport is likely caused primarily by straining as the organisms pass into and through the aquifer. Also, the organisms may be adsorbed to the aquifer matrix which becomes coated with NOM, particularly with sticky polysaccharides within the BP fraction of NOM and TEP. The bacteria are removed by straining, adsorption, and perhaps by predation of other bacteria in the aquifer. It is not known if the bacteria counted are all from the sea or some are indigenous to the aquifer system containing sea water.

The substances of perhaps the greatest concern that contribute to biofouling are the BPs and both particulate and colloidal TEP (Baek et al. 2011; Filloux et al. 2012; Bar-Zeev et al. 2015). Aquifer treatment shows a reduction of between 90.9% and 100% of the BP fraction of NOM. The aquifer treatment of TEP was less effective with removal of the particulate fraction ranging from 36.2% to 100% and the colloidal fraction from 16.7% to 91.1% with the average removal percentages being 75.7% and 56.4%, respectively.

Other NOM fractions showed major reductions in concentration, particularly the humic substances and building blocks. The range in concentration reductions was 50.7% to 78.0% in the humic substances and 22.1% to 71.6% in the building blocks with corresponding average reductions of 65.6% and 51.6%, respectively.

The LMWN and LMWA concentrations differ vastly during aquifer transport with both increases and decreases in concentration. The range of concentrations of the LMWN showed a range of plus 43.6% to minus 42.3% with an average of a 12.1% reduction. The range of concentrations of the LMWA showed a range of plus 233.3% to a reduction of 61.1% with an average increase of 3.9%. These differences can be expected because during aquifer transport, the larger molecular weight fractions can be biochemically broken down into smaller molecular weight substances represented by these fraction groups.

It is well known that carbonate aquifer systems provide a high degree of TOC and DOC removal (Suess 1970; McConnell and Hacke 1993; Jin and Zimmerman, 2010). Suess (1970) reported that 14% of TOC was adsorbed and Jin and Zimmerman (2010) suggested that abiotic interactions between NOM and the carbonate aquifer matrix is a substantial controlling factor for removal of NOM. Carbonate aquifers are also particularly effective in the adsorption of fatty acids and carboxylated polymers (Thomas et al. 1993). Alginic acid, which can be detected using a polysaccharide stain (Alcian Blue), is removed at high percentages (Perry et al. 2004). This group of substances does have similarity to TEP in sea water which is produced by extracellular excretion.
Table 4
Comparison of Various Organic Particles and Substances with Percentage of Removal by Aquifer Treatment based on Reference Sample Comparison

<table>
<thead>
<tr>
<th>Wells</th>
<th>Well Age (Years)</th>
<th>Algae (cell/mL)</th>
<th>Bacteria (cells/mL)</th>
<th>TOC (mg/L)</th>
<th>BP (μg/L)</th>
<th>HS (μg/L)</th>
<th>BB (μg/L)</th>
<th>LMWN (μg/L)</th>
<th>LMWA (μg/L)</th>
<th>TEP-P (μg Xeq./L)</th>
<th>TEP-C (μg Xeq./L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>&gt;99.9</td>
<td>98</td>
<td>64</td>
<td>96</td>
<td>58</td>
<td>30</td>
<td>+371</td>
<td>+72</td>
<td>28</td>
<td>27</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>99.9</td>
<td>99</td>
<td>73</td>
<td>100</td>
<td>78</td>
<td>69</td>
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</table>

1(+): indicates that measured value at the well was higher than the corresponding value of the reference sea water sample.

Impact of Well Age on Removal of Organic Material

A comparison of the average values for the various organic constituents shows that well age does not have a significant impact on the removal percentage during aquifer transport (Table 5). The only substance that could be used to support the age having significance was the BP fraction in the groundwater collected from the most recently installed well (#14) which has only a 90% removal rate. However, it is concluded that well age does not exhibit any greater impact on the aquifer treatment process at a constant distance of transport between 400 and 450 m. This general conclusion may not be applicable to other locations where the distance of transport is shorter or the aquifer contains significant preferable transport corridors, such as in mature karst aquifers.

The aquifer investigated is a heterogeneous carbonate system which is likely to have influenced some of

Table 5
Comparison of Impact of Well Age on Organic Substances Removal Efficiencies

<table>
<thead>
<tr>
<th>Organic Types</th>
<th>14 Years</th>
<th>11 Years</th>
<th>4 Years</th>
<th>4 Months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae (cell/mL)</td>
<td>&gt;99.9</td>
<td>&gt;99.9</td>
<td>100</td>
<td>99.7</td>
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<tr>
<td>Bacteria (cells/mL)</td>
<td>98.2</td>
<td>95.6</td>
<td>97.1</td>
<td>99.7</td>
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<td>TOC (mg/L)</td>
<td>69.1</td>
<td>52.3</td>
<td>70.5</td>
<td>72.7</td>
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<tr>
<td>Biopolymers (μg/L)</td>
<td>96.1</td>
<td>95.2</td>
<td>96.5</td>
<td>90.9</td>
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<tr>
<td>Humic substances (μg/L)</td>
<td>67.6</td>
<td>54.3</td>
<td>72.6</td>
<td>72.9</td>
</tr>
<tr>
<td>Building blocks (μg/L)</td>
<td>54.9</td>
<td>38.2</td>
<td>61.8</td>
<td>44.9</td>
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<tr>
<td>Low molecular weight neutrals (μg/L)</td>
<td>17.3</td>
<td>0.8</td>
<td>11.2</td>
<td>34.9</td>
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<tr>
<td>Low molecular weight acids (μg/L)</td>
<td>22.22+23.61</td>
<td>12.5</td>
<td>+121.4</td>
<td>34.9</td>
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<tr>
<td>TEP—particulate (μg Xeq./L)</td>
<td>89.7</td>
<td>71.0</td>
<td>70.0</td>
<td>43.7</td>
</tr>
<tr>
<td>TEP—colloidal (μg Xeq./L)</td>
<td>62.2</td>
<td>58.9</td>
<td>41.9</td>
<td>75.8</td>
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1(+): indicates that measured value at the well was higher than the corresponding value of the reference sea water sample.
the variation in the removal of some of the organic compounds, such as TEP. The bacterial processes acting within the aquifer are likely randomly distributed and, thereby variation in produced water organic concentrations was observed. The variation in distance of 400 to 450 m between the wells and the sea water source does not appear to have any influence on the organic concentrations measured.

Conclusions

Aquifer treatment of sea water has been demonstrated to provide a significant degree of pretreatment for removal of particulate and dissolved organic matter. Reference samples of nearshore surface sea water were used to make assessments of the removal during aquifer transport. It is known that these reference samples may not be representative of the sea water quality entering the aquifer to replace pumped water from the wells in space and time. However, if a conventional surface intake system was used to supply the SWRO plant with raw water, the samples would be representative of the water that would enter the facility. Therefore, the “removal” percentages are valid from a facility operational perspective and that the aquifer is indeed providing a major pretreatment function.

Nearly all of the algae, over 90% of the bacteria, a significant percentage of the fractions of NOM, and a significant percentage of particulate and colloidal TEP are removed during aquifer transport. The aquifer matrix, in this case carbonate, does not seem to have a material effect on the removal of NOM fractions in general, but a higher percentage of TEP removal likely occurs in carbonate systems based on the data obtained at this site compared to the literature. Removal of these substances has a material effect on SWRO desalination of sea water in that it reduces the rate of membrane biofouling, reduces the degree of engineered pretreatment processes that have to be operated, and reduces the overall cost of desalination.

An analysis of the effect of well age on the degree of organic matter reduction achieved showed that it is not very significant. The aquifer system provides a very rapid and robust degree of treatment by straining, absorption, adsorption, and biochemical degradation of NOM. It appears that long-term “conditioning” of the aquifer is not required to provide a high degree of sea water treatment. At a distance of 400 to 450 m between the sea and the production wells, a similar degree of treatment was achieved in wells ranging from 4 months to 14 years of operation. Variations in the degree of treatment may be caused by heterogeneity with the carbonate aquifer into which the wells were constructed and by variation in biochemical activity with the aquifer.

Removal of the various fractions of NOM appears to be based on the molecular weight with the highest being removed at the greatest percentage. The order of removal from high to low is best demonstrated from the BPs to the humic substances to the building blocks. However, the LMWN and LMWA sometimes increased in concentration which may be caused by biochemical breakdown of the larger organic molecules into smaller molecular weight compounds during aquifer transport and biochemical breakdown.

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References


