# Isotope and Ion Selectivity in Reverse Osmosis Desalination: Geochemical Tracers for Man-made Freshwater

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A systematic measurement of ions and <sup>2</sup>H/<sup>1</sup>H, <sup>7</sup>Li/<sup>6</sup>Li, <sup>11</sup>B/<sup>10</sup>B, <sup>18</sup>O/ <sup>16</sup>O, and <sup>87</sup>Sr/<sup>86</sup>Sr isotopes in feed-waters, permeates, and brines from commercial reverse osmosis (RO) desalination plants in Israel (Ashkelon, Eilat, and Nitzana) and Cyprus (Larnaca) reveals distinctive geochemical and isotopic fingerprints of fresh water generated from desalination of seawater (SWRO) and brackish water (BWRO). The degree of isotope fractionation during the passage of water and solutes through the RO membranes depends on the medium (solvent-water vs. solutes), chemical speciation of the solutes, their charge, and their mass difference. O, H, and Sr isotopes are not fractionated during the RO process. <sup>7</sup>Li is preferentially rejected in low pH RO, and B isotope fractionation depends on the pH conditions. Under low pH conditions, B isotopes are not significantly fractionated, whereas at high pH, RO permeates are enriched by 20% in <sup>11</sup>B due to selective rejection of borate ion and preferential permeation of <sup>11</sup>B-enriched boric acid through the membrane. The specific geochemical and isotopic fingerprints of SWRO provide a unique tool for tracing "man-made" fresh water as an emerging recharge component of natural water resources.

## Introduction

There is general consensus about a significant rise of global water stress stemming from increasing demands associated with population growth and growing global food demands (1), and also regionally from declining resources related to climate change (2). In water-scarce areas, such as the Middle East, Northern Africa, central Asia, and western United States, water demands already far exceed natural replenishment (3), leading to aquifer depletion and water quality deterioration (4). The worldwide pressure on fresh water resources has led to intensive research for alternative water supplies, including utilization of unconventional resources such as saline waters and waste waters (5). Considerable technical progress has been achieved in desalination, which is domi-

nated by two technologies, reverse osmosis (RO) and multistage flash (MSF) distillation (6), resulting in improved membrane efficiency, optimization of the industrial processes, and consequently, significant cost reductions and a steep increase of produced volumes. The largest share of desalination capacities is concentrated in the Middle East, in particular in the Gulf region, followed by the United States and the Mediterranean countries (7). In Europe, Spain is the leading country, with 4.6% of its freshwater consumption provided by desalination plants (7). During the next decades, desalinized freshwater is expected to become a predominant water source in water-scarce areas of industrialized countries where demand exceeds natural replenishment. A worldwide doubling of desalination capacities is projected for 2015, with the largest growth rate for the Mediterranean countries (7).

Several studies have shown that the rejection of ions by RO membranes depends on the ion's valance (monovalent against divalent ions), hydrated ionic size, and charge ( $\mathcal{B}$ ). Some studies evaluated the impact of residual brines from desalination on the environment (9). This paper presents, for the first time, the isotope geochemistry (boron, lithium, strontium, oxygen, and hydrogen) of freshwaters produced from seawater and brackish groundwater through reverse osmosis. The interest of this study is 2-fold:

(1) In the global water cycle, "man-made" freshwaters will gain increasing importance. Such waters will be introduced into natural systems, soil, surface waters, and groundwaters; contribute to the overall water balances; and will induce changes in the water chemistry and, eventually, ecology. It is expected that desalinated waters will be used for various purposes, including drinking water supply and irrigation. Chemical and isotopic fingerprints should, therefore, enable backtracking their origin through diverse processes of mixing as part of integrated management of overstressed water resources.

(2) Reverse osmosis is extremely efficient (>90% removal) for most solutes in anionic or cationic form, but there are some notable exceptions. The most notorious drawback for the use of RO freshwaters is the minor element boron, due to the fact that in the low pH range used for conventional RO in the aim to limit scaling, most of dissolved B is in the form of undissociated boric acid (10, 11). The latter, as a nonpolar species, passes through conventional RO membranes to a large extent, which limits the use of the product water both for drinking water and irrigation. Boron isotopes should give a deeper insight in the mechanisms of boron removal in different types of RO plants. The other investigated environmental isotopes (Li, Sr, O, and H) allow assessing the behavior --- chemical separation and isotopic fractionation -of monovalent and divalent cations, and water itself throughout the RO desalination process.

### **Experimental Section**

**Desalination Plants.** Feed waters (seawater and brackish groundwater), product freshwaters before and after post-treatment, and residual brines were collected from three types of RO desalination plants:

(1) Low-pH seawater (SWRO) and combined seawater– brackish groundwater (SWRO-BWRO) desalination plants in Eilat, Israel (*12, 13*) and Larnaca, Cyprus (*14, 15*). In Eilat, separate plants produce freshwater from brackish groundwater (BWRO, Sabkha A and B plants) and from seawater (Sabkha C plant; Figure 1A). The latter produces 10 000 m<sup>3</sup>/ day freshwater from a blend of seawater (80%) and residual brines from Sabka A BWRO (20%) (*12*). It was, at the time of sampling, operating at low pH, but has in the meantime

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FIGURE 1. Eilat (A) and Ashkelon (B) RO plants: simplified process schemes and sampling points.

been retrofitted, including high pH steps, to meet a target boron concentration of 0.4 ppm (*13*). The SWRO site in Larnaca produces 54 000 m<sup>3</sup>/day from Mediterranean Sea water (*14*, *15*).

(2) High-pH SWRO, represented by the Ashkelon site, which is considered to be the largest seawater reverse osmosis plant in the world with a production of  $100 \text{ M m}^3$ /year (*16*, *17*). Its operation process includes four desalination stages according to the cascade concept (Figure 1B), operating both at high- and low-pH conditions (*18*), which enables, together with RO membranes specifically designed for B-retention, the reduction of the boron concentration of the end product below 0.4 ppm.

(3) Low-pH brackish groundwater RO desalination, represented by Nitzana desalination plant in the northwestern Negev, Israel.

**Analytical Methods.** Cations and boron were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) and ICP-mass spectrometry (ICP-MS), and anions were measured by ion chromatography (analytical uncertainties <10%). Boron isotopes were determined by positive thermal ionization mass spectrometry (TIMS) (analytical uncertainty  $\pm$  0.3‰). Lithium isotopic compositions were measured using multicollector ICP-mass spectrometry (MC-ICP-MS) (analytical uncertainty  $\pm$  0.5‰). Sr isotope ratios were measured by TIMS with an analytical uncertainty of  $\pm 23 \times 10^{-6}$ . O and H isotopes were determined by dual inlet

and continuous flow mass spectrometry following gas–water equilibration (analytical uncertainties  $\pm 0.8\%$  for  $\delta^{2}$ H and  $\pm 0.1\%$  for  $\delta^{18}$ O). Details on the analytical methods are provided in the Supporting Information.

#### **Results and Discussion**

1. Chemical and Isotopic Fractionation during RO Desalination. Chemical Data. The chemical data (provided in Supporting Information Table S1) show selective rejection of multivalent ions (Ca2+, Mg2+, SO42-) with removal capacities of 98-99% relative to monovalent charged ions (Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>), which were removed only by 90-94% in BWRO and 97%-98% in SWRO desalination. As a result, the molar ratios between multivalent and monovalent ions (e.g., Ca/Cl, Mg/ Cl, SO<sub>4</sub>/Cl, and Ca/Na ratios) in desalted waters are reduced by 5 times, relative to the original feed waters (Table S1, Supporting Information). Desalted water is therefore modified into a Na–Cl predominant water type (Cl+Na/TDI  $\sim$ 0.9). These results are consistent with the theory of ionexchange selectivity (8), in which ions with a smaller hydrated ionic radius have higher salt permeability through the RO membrane.

One of the most conspicuous chemical modifications of RO desalination is the relative enrichment of boron in the desalted water. In the low-pH mode (Eilat, Larnaca, Nitzana, and Ashkelon stages A and C desalination plants) most of dissolved B is in the form of undissociated boric acid (*10, 11*),

which partly penetrates through the RO membrane, whereas Cl is nearly completely rejected. As a result, the B/Cl ratios in the desalted water are higher by an order of magnitude relative to the feedwater and brine effluents (Table S1, Supporting Information). In the Ashkelon plant, the B-rich RO permeate water of stage A becomes the feedwater for the high-pH stage B. Thus, in spite of the significantly higher B rejection under high pH desalination mode, the design of RO cascade stages (Figure 1) results in progressive increase of B/Cl ratios in the desalted water. The end product of the high-pH mode of desalted water from Ashkelon (B/Cl range of 0.09 to 0.4) is similar and even higher than the B/Cl ratios measured in the low-pH desalted water from Eilat (0.1), Larnaca ( $8 \times 10^{-3}$ ), and Nitzana (0.04).

Given the low contents of  $Ca^{2+}$  and alkalinity in RO desalted water, post treatment procedures aim to increase divalent cations in the final product prior to the release of the water to the distribution system (19). Common types of post-treatment procedures are (1) dissolution of calcite with strong (e.g., sulfuric) acid and NaOH addition for final pH control (2); dissolution of calcite with carbon dioxide and NaOH addition for final pH control (3); direct adding of chemicals, such as Ca(OH)<sub>2</sub> followed by CO<sub>2g</sub>; and (4) mixing with external Ca-rich water (e.g., brackish groundwater).

The  $H_2SO_4$  application is used in the Ashkelon desalination plant. The high dissolution rate of calcite and high Ca allows limiting post-treatment to only about 25% of the total flow of the desalted water (*19*). This is reflected by the chemical compositions of the final product water with substantially higher Ca and SO<sub>4</sub> contents relative to the RO permeate water (Table 1, Supporting Information).

In contrast, where post-treatment procedures are using calcite dissolution by carbon dioxide, such as in Larnaca, the enrichment of  $Ca^{2+}$  is much more moderate without any change in the conspicuously low  $SO_4/Cl$  ratio that characterizes the RO chemical fractionation. For Eilat, the post-treatment includes both  $CO_2$ -calcite dissolution and mixing with brackish groundwater, which masks these chemical modifications. In summary, post-treatment procedures may modify the RO chemical signature for some major elements such as Ca and  $SO_4$ , but at the same time it can generate solutions with a distinctive chemical signature. Post-treatment procedures will not, however, change the high B/Cl ratios induced by RO desalination.

*Boron Isotopes (Table 1).* The mean  $\delta^{11}$ B of Ashkelon initial feed seawater (A3) is  $+39.4 \pm 0.4\%$  versus NBS951, which is the typical value of seawater (20). The first low pH desalination stage A (Figure 1) reduces boron concentrations from 5.7 ppm to  $0.6 \pm 0.1$  ppm for front-end permeate, and  $1.13 \pm 0.13$  ppm for rear-end permeate (Figure 2). The permeate is, in fact, extracted at two points of the pressure vessel; one at the front end (low TDS front-end permeate) and the other at the last elements (higher TDS rear-end permeate). This first stage is not accompanied by any significant isotopic fractionation; the  $\delta^{11}$ B of front- and rearend permeates of stage A (A4, A5) ranges from +38.3 to +39.8‰. The second desalination step (stage B) in the Ashkelon plant operates under high pH and uses NaOH alkalinized Step A rear permeate (A5) as feedwater. The resulting permeate of this stage (A7) is depleted in boron (0.11 ppm relative to feedwater from A5 with 1.13 ppm) by 89% and is extremely enriched in <sup>11</sup>B by 20‰ ( $\delta^{11}B = +58.7$  $\pm 2\%$ ) with respect to feedwater. These are among the highest  $\delta^{11}$ B values ever measured in waters, comparable only to hypersaline brines (e.g., Dead Sea brines; 21). The corresponding residual brine (A6) is enriched in boron by 5.4 ppm and is depleted in <sup>11</sup>B by 1.6‰ compared to the input water of stage B (A5). Before the third desalination stage (C), this brine (A6) is acidified back to pH 6-6.5. This low pH step is accompanied by no significant isotopic fractionation between

the permeate (A8) and feed solution (A6). In the fourth desalination stage (D), the B-rich A8 permeate undergoes a last RO stage D at high pH (9.5) that again shifts the resulting permeate A9 to high  $\delta^{11}$ B values of  $+58.4 \pm 1.36\%$  (n = 3). The end product after post treatment results from mixing of the permeates of stages A, B, and D and occupies, accordingly, an intermediate position between high  $\delta^{11}$ B values of stage B and D and seawater  $\delta^{11}$ B of stage A (Figure 2).

The key of the observed isotopic variations lies in the pH dependent concentration variations of the principal boron species in the solutions: undissociated boric acid and borate ions. We used the dissociation constants (22) generally considered as the most reliable (23) to determine the dissociation of boric acid at T = 25 °C and salinity = 35‰. Although ionic strength at the membrane surface is expected to be higher than in bulk seawater (11), the seawater pKvalue for boric acid dissociation of 8.6 was used. Figure 3A shows the relative abundance of  $B(OH)_3$  and  $B(OH)_4^-$  as a function of pH. For the low pH (<6.5) stages A and C, 99% of boron is in the form of boric acid. At high pH (stages B and D), the borate ion is predominant (90% at pH 9.5). This species is much more efficiently rejected by the RO membranes, which is the base for the high pH operational conditions in the Ashkelon RO plant.

Recently, the first experimental data on equilibrium fractionation between the dissolved  $B(OH)_3$  and  $B(OH)_4^-$  have become available (*24*). The equilibrium constant (*K*) for the reaction (eq 1)

$${}^{10}B(OH)_3 + {}^{11}B(OH)_4^{-} \leftrightarrow {}^{11}B(OH)_3 + {}^{10}B(OH)_4^{-}$$
 (1)

is >1 (the fractionation factor  $\alpha = R(B(OH)_4^-)/R(B(OH)_3)$  is <1, where  $R = {}^{11}B/{}^{10}B$ ), so that boric acid is enriched in  ${}^{11}B$ with respect to borate ion. Experimentally determined fractionation (*24*) is similar to recent theoretically predicted values (*25*) but larger than those of the reference study of ref *26*. Figure 3 shows that the permeates at high pH are strongly enriched in  ${}^{11}B$ . Their  $\delta^{11}B$  is in fact close to the predicted values of the minor B species in the high pH range, boric acid. This is consistent with the hypothesis that borate is very efficiently rejected by the membranes, contrary to the residual boric acid that represents less than 10% of total boron at pH 9.5 with a high  $\delta^{11}B$  value (+64‰ at pH 9.5).

We used the isotopic data to calculate the relative contributions of both species during the membrane passage. The  $\delta^{11}$ B values measured for the high pH stages are slightly lower than the predicted values for boric acid at pH 9.5, suggesting that a small fraction of borate passes the membrane. On the basis of the assumptions that (1) chemical exchange between B species induces isotopic fractionation and (2) that membrane processes (convection and diffusion) have no direct isotopic effects (as indicated by the lack of isotopic fractionation under low pH conditions), we established an isotopic mixing model. The model calculates the fractions of borate and boric acid passing through the membrane on the basis of the bulk  $\delta^{11}$ B value of the permeate compared to the theoretical  $\delta^{11}$ B values of boric acid and borate at pH 9.5. The model predicts that at pH 9.6  $\sim$ 80% of total B in the permeate passes through the membrane in the form of boric acid and only  $\sim 20\%$  in the form of borate ion passes through (Figure 2). Given that the overall B rejection is 89% and that borate ion is largely predominant in the feedwater ( $\sim$ 90% at pH 9.5), this implies that most of the boric acid fraction passes the membrane (i.e., 0% rejection) together with a small fraction of the borate. We estimate that only 4% of the borate ions in the feedwater penetrates through the RO membrane (96% rejection).

The slight <sup>11</sup>B-depletion of the residual brine from high pH Step B (sample A6) compared to the feed solution is also expected from mass balance considerations; most of B in the feedwater is converted to borate ion and accumulates in the

TABLE 1. Synthesis of Isotope R	esults from Asl	hkelon and Eilat R	10 Plants <sup>a</sup>						
sample type	sampling points	∂ <sup>11</sup> B (‰ vs NBS951)	δ <sup>18</sup> 0 (%。vs SMOW)	δ²H (‰ vs SMOW)	ð <sup>6</sup> Li (‰ vs LSVEC)	<sup>87</sup> Sr/ <sup>86</sup> Sr	B (mg/L)	Li (µg/L)	Sr (mg/L)
Ashkelon, seawater,	A3	39.3–39.9	2.1	10.4-13.0	31.4		5.52 - 5.85	154	
Ashkelon, permeates stage Ashkelon, permeates stage A (low nH)	A4, A5	38.3–39.8	1.7-2.6	10.8-13.2	19.9–23.9 (after NaOH adding)		0.5-1.26	0.4-1.0	
Ashkelon, permeates Stage	A7	56.4-60.1	1.8-2.0	12.6–13.6	25.5		0.11-0.14	0.03	
Ashkelon, brine stage B (hich pH)	A6	37.2	2.4	13.2	24.3		6.5	6.0	
Ashkelon, permeates stage C (low pH)	A8	35.236.4	2.0-2.1	12.7-12.9	19.2		2.95–3.08	0.06	
Ashkelon, permeates stage D (high pH)	A9	56.9–59.5	2.0-2.3	12.2-13.0	25.2		0.09-0.15	0.01	
Ashkelon, final product	A10, A11	48.7-57.5	2.0 - 2.2	12.3–13.4	22.1		0.21-0.37	0.1	
arter post-treatment Eilat, brackish groundwater, feedwater to Sabkha A	E1	33.1	-6.90	-42.3		0.706610	0.78		16.6
Eilat, permeates of Sabkha	E2, E4	32.6-34.9	-7 to -6.8	-42.1 to -41.8		0.706616-0.706618	0.53-0.69		0.24-1.6
Eilat, brines of Sabkha A	E3, E5	33.31–35.1	-6.8 to -6.8	-41.7 to -41.6		0.706574-0.706576	1.28–1.72		45.5-74.6
Eilat, feedwater to Sabkha C (80% seawater, 20% Sabkha A+R brinee)	E6	39.6	-0.1	2.3		0.707491	4.98		19.5
Eilat, permeates of Sabkha	E7	38.4	-0.1	1.4		0.707534	2.0		0.05
Eilat, brines of Sabkha C (low pH)	E8	39.3	0.0	2.5		0.707507	7.3		32.4
Eilat, final product after post-treatment	E9, E10	35.7				0.707381-0.707397	0.73		0.9
<sup>a</sup> Data can be found in the S	upporting Info	irmation.							



FIGURE 2.  $\delta^{11}B$  vs. B concentrations of feedwater, permeates, and brines from the Ashkelon RO plant.

brine, whereas the small fraction of <sup>11</sup>B enriched boric acid is removed through the membrane, leaving the brine slightly depleted in <sup>11</sup>B.

Results from the Eilat desalination plant are consistent with those from Ashkelon (Figure 1 in Supporting Information). At the time of sampling, the Eilat plant operated exclusively at low pH, except for the pH adjustment of the end products. The overall rejection of B is low both for SWRO and GWRO (32% and 60%, respectively), and the  $\delta^{11}$ B values of permeates are similar to their respective feedwater (~+33  $\pm$  1‰ for GWRO and ~+39  $\pm$  1‰ for SWRO). We do not expect a significant mass dependent difference of membrane permeability for boron because (1) boric acid is neutral, contrary to charged ions such as Li ions; and (2) the relative mass difference between <sup>11</sup>B(OH)<sub>3</sub> and <sup>10</sup>B(OH)<sub>3</sub> is only 62/61.

Lithium Isotopes (Table 1). Li isotopes were investigated in different desalination stages in the Ashkelon plant. As shown above, SWRO membranes reject monovalent cations such as Na<sup>+</sup> very efficiently (at 99.8%). The initial feedwater A3 shows a mean  $\delta^7$ Li of +31.4‰, which is consistent with the globally uniform Li isotopic ratio in seawater of +31‰ (27). Figure 4 shows that, for both low pH steps (stages A and C), the permeates are significantly depleted in <sup>7</sup>Li with respect to feed waters (by 12‰ for stage A and by 4.8‰ for stage C), indicating preferential permeation of the light 6Li. The high pH steps, stages B and D, produce an apparent inverse effect (Figure 4). However, we observed a shift in  $\delta^7$ Li values from +20.0 to +23.9‰ of sample A5 before and after chemical treatment with NaOH that could be associated with Li impurities in the NaOH solution. The isotopic fractionation that is associated with the high-pH RO process is rather small (1.6‰ enrichment of the permeate A7 compared to A5 after alkalinization), which suggests a slight preferential RO selection of the heavy 7Li isotope under high pH condition. Before the second high pH stage D, the feedwater A8 also undergoes pH adjustment through NaOH addition that can shift  $\delta^7$ Li as observed for Stage B, but we only measured the chemical and isotopic compositions before alkalinization. The permeate of high pH stage D is enriched in <sup>7</sup>Li ( $\delta^{7}L$  = +25.2‰) as compared to source water A8 (before NaOH adding;  $\delta^7 \text{Li} = +19.2\%$ ). In summary, we observed a strong selective rejection of 7Li during the low pH steps and a much smaller inverse effect during the high pH steps. The final products A10 and A11 have intermediate  $\delta^7$ Li values between A4, A7, and A9 permeates both for Li concentrations and for Li isotopic ratios, indicating conservative mixing and lack of post-treatment modifications.

The observed isotopic fractionation of Li isotopes that is associated with low pH RO process in stages A and C is consistent with previous tests of Li isotope fractionation on commercial BWRO FILMTECH<sup>™</sup> FT30 membranes (28). It was suggested that this fractionation is mass dependent, due to a slight relative retardation of 7Li during membrane passage compound to 6Li. In contrast, Li fractionation on a bentonite membrane (29) vielded an opposite effect; 7Li was preferentially partitioned into the permeate. This phenomenon was attributed to the existence of a significant concentration polarization layer (CPL) on the high pressure side of the clay membrane (contrary to commercial RO membranes) and different back diffusion rates for 6Li and 7Li (29). The seemingly inverse, yet small isotopic effect in the high pH RO stages B and D is difficult to explain by a chemical fractionation, as Li<sup>+</sup> is the largely predominant species compared to Li neutral species (e.g., LiOH<sup>0</sup>). It has also been shown that the magnitude of Li isotope fractionation depends on the flow rate (28). This means that the type of membrane and the operating conditions play an important role in the degree and the direction of Li isotope fractionation. Contrary to the other investigated isotopes systematics, impurities introduced by NaOH adding make it difficult to quantify the apparent Li isotopic fractionation under high pH conditions.

Stable Isotopes of the Water Molecule (Table 1). Ashkelon input water (A3 samples) is derived from eastern Mediterranean seawater, even though it is slightly more saline (TDS = 39670 mg/L) than the mean value of 39000 mg/L reported by (30). The isotopic composition of A3 ( $\delta^{18}O = +2.1\%$ ,  $\delta^{2}H$ =+10.4 to +13.0%) is compared with eastern Mediterranean seawater (30), which is significantly enriched in <sup>2</sup>H and <sup>18</sup>O with respect to mean ocean water (Figure 5). The A3 seawater sample is enriched (by +2.3 to +5.9‰ in  $^{2}$ H and by +0.4‰ in <sup>18</sup>O) with respect to shallow eastern Mediterranean seawater of <200 m depth. Evaporation under nonequilibrium conditions by about 2%, as inferred from the salinity data, can explain the isotopic enrichment of feedwater (31). Our data suggest that the slightly evaporated seawater undergoes several steps of SWRO without measurable diffusive O and H isotopic fractionation, so that the product freshwaters conserve the original seawater signature.

This observation is also confirmed by the results from the Eilat BWRO-SWRO plant (Figure 5). The two input waters, brackish water and Red Sea water, show extremely contrasting isotope signatures. The brackish groundwater ( $\delta^2 H = -42\%$ ,  $\delta^{18}O = -6.9\%$ ) is used as feed waters for BWRO in the Sabha A plant and is derived from the southern Arava Valley (*32*). Sabha C plant values are consistent with a mixture of 80% Red Sea water ( $\delta^2 H = +12\%$ ,  $\delta^{18}O = +1.9\%$ ; *33*) and 20% residual brine of Sabha A (samples E3 and E5;  $\delta^2 H = -41.7\%$ ,  $\delta^{18}O = -6.8\%$ ) as input water. As in Ashkelon, the RO process in the Eilat desalination plant shows no stable isotopes fractionations between feedwater, permeates, and brines.

Measurable isotope effects of a passage of water through semipermeable membranes have so far mainly been studied in laboratory experiments on clay membranes (*34–36*). Only a few studies have investigated isotopic effects during RO processes (*37*) and have found negligible oxygen isotope effects during membrane flow, which is consistent with our results.

Strontium Isotopes (Table 1). Strontium isotope ratios measured in the Eilat desalination plant (Figure 6) show a clear contrast between Sabha A fluids, comprising brackish inlet waters and the derived permeates and brines ( $^{87}$ Sr/ $^{86}$ Sr = 0.7066), and Sabha C seawater-brine mix inlet and the associated product waters and brines (mean  $^{87}$ Sr/ $^{86}$ Sr = 0.7075). The low  $^{87}$ Sr/ $^{86}$ Sr ratios in the brackish waters that



FIGURE 3. Theoretical distribution of boron species (A) and  $\delta^{11}$ B (B) versus pH. Section B shows the  $\delta^{11}$ B values as a function of operational pH conditions for Ashkelon input waters, permeates, stage B brine, and end products. Boron speciation and species isotopic fractionation values are from refs 22 and 24–26.



FIGURE 4.  $\delta^7 \text{Li}$  vs. Li concentrations of seawater, permeates, and brines from the Ashkelon SWRO plant.

feed Sabha A are similar to the ratios reported in saline waters from the vicinity of the study area (39).

In spite of the high selectivity of RO membranes with respect to bivalent cations, no significant Sr isotope effect of BWRO is observed for the Sabha A waters. This is explained by the small relative mass contrast of the two Sr isotopes. The strontium isotope ratios in the inlet water for SWRO in Sabha C ( $^{87}$ Sr/ $^{86}$ Sr = 0.7075; Sr = 19.5 ppm) result from a mixture between 80% Red Sea water (0.7088–0.7092, 8 ppm;



FIGURE 5.  $\delta^{2H}$  vs.  $\delta^{18}$ O of feed waters, permeates, and brines from the Ashkelon and Eilat BWRO and SWRO plants. For comparison: values of standard mean ocean water (SMOW), Red Sea Shallow waters (*37*), Eastern Mediterranean shallow seawaters (*30*), and groundwater from Eilat region (*38*) are presented. The mixing line represents mixing between Sabha C and A product waters and groundwater. The evaporation line was calculated after (*31*) for Sabha A product and a 40% average relative humidity for Eilat.

40, 41) and 20% BWRO brine ( $^{87}$ Sr/ $^{86}$ Sr = 0.7065; Sr range of 45 to 75 ppm; samples E3, E5). The Sr isotopic composition



FIGURE 6. Strontium isotope ratios vs. Sr concentrations of fresh waters, permeates, and brines from Eilat BWRD/SWRD plants. Mixing model of Red seawater (40, 41) and residual brine E5 from Sabha A. Input water E6 contains 20% Sr from E5, indicating conservative mixing for Sr. Regional groundwater and volcanic rock isotope ratios are reported for comparison (36, 39, 40).

of the end product waters (E10 and E9;  $^{87}$ Sr/ $^{86}$ Sr = 0.7074, Sr = 0.9 ppm) results from a mixing of Sabha A (0.2–1.6 ppm), B, and C (0.05 ppm) permeates. It is very close to Sabha C (0.7075) water but at Sr concentrations higher by a factor of 20. It is likely that Sr isotope fingerprints of the end products are controlled by the post treatment processes mainly consisting of carbonate dissolution. Marine limestone throughout Phanerozoic time would have  $^{87}$ Sr/ $^{86}$ Sr ratios within the range 0.7067–0.7091 (42). We conclude that, in spite of a lack of isotopic fractionation induced from RO processes, mixing of feed waters (e.g., Eilat) and post-treatment may alter the original Sr isotopic composition.

2. The Chemical and Isotopic Imprints of Man-made Freshwater Derived from RO Desalination. Some general features of RO desalted water can be predicted that could distinguish such man-made freshwaters from natural solutions and could potentially be used in future studies to evaluate natural and anthropogenic recharge proportions in groundwater systems. Any SWRO desalination would produce water with distinctively high  $\delta^{18}$ O,  $\delta^{2}$ H,  $\delta^{11}$ B, and B/Cl values, regardless its configuration (e.g., high pH versus low pH) and the type of post-treatment technique. The marine isotope signatures of SWRO desalted freshwater from Ashkelon  $(\delta^{18}O \sim +2\%; \delta^2H \sim +12\%)$  and Sabkha C in Eilat  $(\delta^{18}O \sim$ 0‰;  $\delta^2$ H  $\sim$  +2‰) are clearly different from meteoric waters. The latter fall on the Global Meteoric Water Line ( $\delta^2 H = 8 \times$  $\delta^{2}$ H + 10; 43) or similar local meteoric lines and are, in general, depleted in heavy isotopes compared to seawater (negative  $\delta$  values). Any massive recharge of SWRO desalted water into coastal or continental aquifers will generate mixing lines that would shift the natural water toward seawater values. Seawater intrusion into a coastal aquifer, as well as evaporation, can likewise produce water lines with a slope <8 in a  $\delta^2 H - \delta^{18} O$  system, but in these cases salinity would increase parallel to heavy isotopes enrichment, which will not be the case for RO-freshwater recharge.

The second distinctive feature of SWRO permeates with respect to most natural groundwaters (typically  $\delta^{11}B < +30\%$ ) is their <sup>11</sup>B enrichment. Low-pH and high-pH desalination product waters are characterized by  $\delta^{11}B \sim +39\%$  and  $\gg +39\%$ , respectively, in addition to high B/Cl ratios. This also

differentiates them from surface and meteoric waters; most worldwide major rivers have  $\delta^{11}$ B values in the range of  $+2\infty$ to  $+20\infty$  (44) and low B contents at the ppb level. Continental rains are systematically depleted in <sup>11</sup>B with respect to seawater (45). Coastal rains may mimic or even slightly exceed seawater  $\delta^{11}$ B (46). Nevertheless, low-saline groundwaters from coastal aquifers such as the Mediterranean coastal aquifer (Israel) typically have  $\delta^{11}$ B values in the range of +20%to +30% due to interactions with the aquifer rocks (47). Treated wastewater, another emerging anthropogenic freshwater recharge component, will show a  $\delta^{11}$ B range of 0-10%.

The second type of chemical and isotopic modifications is associated with the specific operation configuration of desalination plants, including mixing of feed waters and posttreatment procedures. Using a strong acid such as H<sub>2</sub>SO<sub>4</sub> together with solid calcite for pH adjustment and remineralisation results in high Ca and SO<sub>4</sub> contents in the final product waters. In contrast, where post-treatment procedures are using calcite dissolution by carbon dioxide, the enrichment of Ca<sup>2+</sup> is much more moderate without any affect on the SO<sub>4</sub>/Cl ratio. In such a mode, SWRO desalted water would be characterized by a moderately high Ca/Cl ratio and by a conspicuously low SO<sub>4</sub>/Cl ratio that reflects RO selective rejection of multivalent ions. Strontium isotopes are not fractionated during RO processes but would be modified upon mixing between the different water components and could also be strongly affected by post-treatment processes that include carbonate dissolution.

The <sup>6</sup>Li/<sup>7</sup>Li isotope pair has the highest relative mass difference except <sup>2</sup>H/<sup>1</sup>H, and thus a high mass dependent fractionation, resulting in the observed shifts during the RO process. Similar to boron isotopes, the large range of  $\delta^7$ Li values in nature, with more than 80‰, makes  $\delta^7$ Li a potential tracer for studying environmental and hydrological processes. So far, Li isotopes geochemistry has been mainly applied to study surface runoff in large river basins in order to assess weathering processes. The global mean  $\delta^7$ Li of runoff is +23‰, and a few groundwater measurements have shown similar isotopic range of +21.5 to +26‰ (48-51). The measured  $\delta^7$ Li values of RO permeates (+19 to +26 ‰) are in the same range, so if indeed the few available Li isotopic data for groundwater were representative, it would be difficult to use this tracer to discriminate natural groundwater from RO derived effluents. However, seawater intrusion in a coastal aquifer (+31‰) would have a conspicuous isotopic signature relative to RO derived freshwater.

Massive exploitation of groundwater resources and recycling of water (e.g., sewage effluents, desalination) introduces different water sources into aquifers in addition to the natural recharge components. The use of environmental isotopes coupled with geochemical analysis could be particularly useful for evaluating the multiple water sources in such aquifer systems. Traditional indicators such as electrical conductivity, chloride contents, and total dissolved solids would have only limited information, given the complexity and the variety of fresh and salt water sources that are replacing natural recharge. In many cases, geochemical tracers alone cannot provide a single solution. For example, high B/Cl ratios could reflect both infiltration of desalinated water but also mixing with sewage effluents (52). However, the  $\delta^{11}$ B,  $\delta^{18}$ O, and  $\delta^{2}$ H fingerprints of these water sources are different. Hence, the use of a large array of geochemical and isotopic fingerprints could provide better constraints for evaluating and modeling water sources in stressed aquifers.

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#### **Supporting Information Available**

Materials and methods, tables, and figures mentioned in this paper are additionally provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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