## Geochemical and boron, strontium, and oxygen isotopic constraints on the origin of the salinity in groundwater from the Mediterranean coast of Israel

Avner Vengosh,<sup>1</sup> Arthur J. Spivack,<sup>2</sup> Yohanan Artzi,<sup>3</sup> and Avner Ayalon<sup>4</sup>

Abstract. In order to identify the origin of the salinity and formation of saline plumes in the central part of the Mediterranean coastal aguifer of Israel, we determined the elemental and boron, strontium, and oxygen isotopic compositions of fresh and brackish groundwater (Cl up to 1500 mg/L). We distinguish between two key anthropogenic sources: (1) sewage effluents used for irrigation with high Na/Cl,  $SO_4/Cl$ , and B/Cl ratios and low Br/Cl ratios relative to seawater ratios, low  $\delta^{11}$ B values (0–10‰) and high  $\delta^{18}$ O values (>-4‰); and (2) imported water from the Sea of Galilee that is artificially recharged to the aquifer with high Br/Cl (3 × 10<sup>-3</sup>) and  $\delta^{18}$ O values (-1‰) and a low <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.70753. The brackish groundwater from the saline plumes have relatively low Na/Cl ratios (0.5–0.8) and high Ca/Mg, Mg/Cl, and Ca/(SO<sub>4</sub> +  $HCO_3$ ) (>1) ratios relative to seawater ratios; marine SO<sub>4</sub>/Cl and Br/Cl ratios;  $\delta^{11}$ B values of 24.8–49.9‰;  $\delta^{18}$ O of -2.95‰ to -4.73‰; and <sup>87</sup>Sr/<sup>86</sup>Sr ratios of 0.708275–0.708532. The composition of most of the investigated groundwater from the saline plumes differs from those of the anthropogenic sources, imported water, fresh uncontaminated groundwater (87Sr/86Sr of 0.70866,  $\delta^{11}$ B of 20-30‰), and saline water from the adjacent Eocene aquitard. Only in areas of artificial recharge does local groundwater have high Br/Cl and  $\delta^{18}$ O values that are typical to the Sea of Galilee. The linear relationships between chloride and most of the ions, including B and Sr, the relatively high  $\delta^{11}B$  (>30%) and low  $\delta^{18}O$  (<-4%) values, and the chemical signature of the saline plumes (e.g., marine Br/Cl and SO<sub>4</sub>/Cl ratios), suggest that (1) mixing processes control the chemical composition of the brackish water within the aquifer, and (2) the saline postulated end-member has a chemical composition that resembles modified seawater with a marine and higher  $\delta^{11}B$  values, and a  $\frac{87}{\text{Sr}}$  fr/ $\frac{86}{\text{Sr}}$  ratio of <0.7083. We propose that most of the salinization phenomena and the formation of saline plumes in the inner parts of the coastal aquifer are derived from upconing of underlying natural saline water bodies and enhanced by overexploitation and draw-down of the overlying fresh groundwater.

## 1. Introduction

Salinization is one the most widespread processes that degrades water quality and endangers future water exploitation. In many areas, particularly in arid and semiarid zones, groundwater salinization limits the supply of potable fresh water. This problem is intensified in coastal aquifers where human activities (e.g., water exploitation, agriculture, reuse of wastewater) result in accelerating water-quality deterioration. Monitoring and identifying the origin of the salinity are crucial for water management and remediation. Yet the variety of salinization sources, particularly in unconfined aquifers, makes this task difficult. Groundwater salinization can result from either point sources (e.g., leakage of industrial and domestic waste water,

Paper number 1999WR900024. 0043-1397/99/1999WR900024\$09.00 recharge of saline water) or nonpoint sources (e.g., agriculture return flows, irrigation with sewage effluent) derived directly from anthropogenic contamination. Salinization can also occur because of "natural processes" such as seawater intrusion and saline-water flow from adjacent or underlying aquifers [e.g., *Maslia and Prowell*, 1990].

The Mediterranean coastal aquifer (Figure 1) is one of the important water resources in Israel, supplying 20% of the national water consumption. The salinity of groundwater in this aquifer has increased during the last few decades, and saline plumes have formed in its central region. Several explanations to the rise of salinity in the aquifer include (1) recycling of salts from irrigation of local groundwater and/or evapotranspiration of meteoric water; (2) contamination by irrigation and/or leakage of wastewater; (3) recharge and irrigation with imported water from the Sea of Galilee; (4) flow of saline water from the adjacent Eocene aquifer in the east; and (5) upconing of saline water from underlying sources [Magaritz et al., 1990; Mercado, 1985; Ronen et al., 1987; Rosenthal et al., 1992; Vengosh and Rosenthal, 1994; Vengosh and Ben Zvi, 1994].

The purpose of the present study is to establish the mechanism(s) for groundwater salinization and to identify the sources of salinity by utilizing an array of geochemical and isotopic tracers (boron, strontium, and oxygen). Each of these isotopic tracers has previously been used separately to delin-

<sup>&</sup>lt;sup>1</sup>Hydrological Service, Jerusalem, Israel.

<sup>&</sup>lt;sup>2</sup>Center for Marine Sciences, University of North Carolina at Wilmington.

<sup>&</sup>lt;sup>3</sup>Jacob Blaustein, Institute for Desert Research, The Water Resource Research Center, Ben Gurion University of the Negev, Sede Boqer, Israel.

<sup>&</sup>lt;sup>4</sup>Geological Survey, Jerusalem, Israel.

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Figure 1. (a) A general map of the Mediterranean coastal aquifer in Israel and (b) the study area with the saline spots. Wells locations are marked by solid circles. Note the locations of the saline spots and chloride concentrations (in milligrams per liter) of the most saline wells in that area.

eate fluid origins and chemical modifications, for example, oxygen for tracing the source and nature of the recharged fluids [e.g., *Gat*, 1974, 1981], boron for identifying the impacts of anthropogenic sources [e.g., *Vengosh et al.*, 1994], and strontium for evaluating water-rock interactions [e.g., *Banner et al.*, 1989; *Chaudhuri et al.*, 1987; *Fritz et al.*, 1987; *Johnson and DePaolo*, 1997a, b]. Yet integration of isotopic data for a variety of elements provides a better diagnostic tool for determining the origin of the salinity.

## 2. Hydrogeological Setting

The coastal aquifer lies along the Mediterranean coast of Israel (Figure 1) and is composed of Pliocene-Pleistocene calcareous sandstone (Figure 2) and layers of clays [Gavish and Friedman, 1969]. Its thickness varies from 200 m in the west along the coastline to a few meters in the eastern margins, 20–25 km east from the seashore. In the western margins the aquifer is divided into several confined aquifer systems (subaquifers) with different piezometric levels. In its central and eastern parts there are no continuous partitioning layers and

the aquifer is not confined. In most parts of the aquifer, the unsaturated zone is made of calcareous sandstone (kurkar), loam (hamra), and heavy soils. In its western part the unsaturated zone consists of sandstone that is reflected by the high quality of the local groundwater (<50 mg Cl/L). In most areas the aquifer overlies thick and relatively impermeable units of the Saqiye Group. The Saqiye Group (Figure 2) is composed of (1) Oligocene and early Miocene marls of the Bet Guvrin Formation; (2) middle Miocene marls of the Ziqim Formation; (3) upper Miocene evaporite units (representing the Messinian event); and (4) Pliocene-aged units of alternating thick marine shales and limestone sandstone layers of the Yafo Formation. Along the eastern margin the aquifer rests upon the Eocene (Shefela Group) aquitard in the southern coast (Figure 2).

The annual volume of groundwater pumped from the aquifer, starting from the 1950s, has been  $400 \times 10^6$  to  $450 \times 10^6$ m<sup>3</sup>/yr, about one fifth of the total water consumption in Israel [*Water Commissioner*, 1995]. Overexploitation beyond the natural replenishment (~340 × 10<sup>6</sup> m<sup>3</sup>/year) caused a continuous drop in piezometric levels between the 1950s and late 1980s.



Figure 2. Schematic hydrogeological cross section of the coastal aquifer and lithohydrological units.

As a result, hydrologic depressions formed in the central areas, changing the natural east-to-west flow regime in the aquifer. Since the early 1990s, pumping has been reduced and water levels have consequently increased. Nevertheless, groundwater salinization, which began during the 1950s, has continued despite the restoration of the water levels in the last 10 years. In the Be'er Toviyya region (Figure 1) the parallel increase in water level and salinity has continued since the late 1960s [Vengosh and Ben Zvi, 1994]. As a result, saline plumes and spots have developed in the inner parts of the aquifer and in its eastern margins (Figure 1). The locations of most of the saline plumes are associated with the hydrologic depressions in the central part of the aquifer. Several saline spots have existed since the 1930s [Artzi, 1999; Vengosh et al., 1996].

## 3. Methods

## 3.1. Sample Description

The selected research area represents saline plumes from the central and eastern parts of the aquifer. From 1992 to 1995 we collected groundwater from pumping wells in areas of high salinity (Figure 1). We also collected fresh uncontaminated groundwaters (<100 mgCl/L) from the western part of the aquifer.

In order to characterize the geochemical composition of the anthropogenic sources that may affect the salinization processes, we investigated imported water from the National Water Carrier, originating from the Sea of Galilee, as well as treated sewage effluents. The treated sewage effluents, used for irrigation over the aquifer in the central coast, were sampled from open reservoirs. The imported waters of the Sea of Galilee are transported through the National Water Carrier and are used for domestic use and irrigation over the coastal plain. In addition, a large volume ( $\sim 20 \times 10^6 \text{ m}^3$ /year during the last five years) has been recharged into the the aquifer since the mid 1960s through Lake Azriqa'm (an artificial lake in an old quarry), northwest of Be'er Toviyya; Lake Merar, south of Giva't Brener; and recharge wells in the Giva't Brener area.

#### 3.2. Analytical Techniques

Elemental analyses were carried out in the analytical laboratory of the Hydrological Service in Jerusalem. Boron concentrations were determined with a modified spectrophotometric technique using the reagent Azomethine H [Kiss, 1988]. Bromide concentrations were determined by flow injection ion analyzer (QuickChem 8000) [Vengosh and Pankaratov, 1998].

Boron isotopic compositions in samples were determined by negative thermal ionization mass spectrometry (NTIMS) [Vengosh et al., 1989; Eisenhut et al., 1996]. Boron was separated from natural samples with a boron-selective resin, Amberlite IRA-743 [Kiss, 1988], eluted with 1 N HCl, mixed with a solution of MgCl<sub>2</sub> and Ba(OH)<sub>2</sub>, loaded onto Re single filaments, and analyzed with a reverse polarity, "dynamic" collector, the Finnigan MAT-261 mass spectrometer, at the University of Regensburg, Germany. Details of the analytical and mass spectrometry procedures are given by Eisenhut et al. [1996]. Some samples were analyzed with a VG-336 mass spectrometer at the University of North Carolina, Wilmington, in which a Bfree seawater matrix was added to enhance ionization. The mode of filament loading and mass spectrometry procedures were strictly repeated in samples and standards were used in order to minimize the variability of mass spectrometerinduced isotopic discrimination. A standard deviation of up to

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2% was determined by repeat analyses of National Institute of Standards and Technology (NIST) SRM-951 standard. Isotope ratios are reported as per mil deviation ( $\delta^{11}$ B) in the <sup>11</sup>B/<sup>10</sup>B ratios relative to the measured standard, NBS SRM 951:

$$\delta^{11}\mathbf{B} = \left[ ({}^{11}\mathbf{B}/{}^{10}\mathbf{B})_{\text{sample}} / ({}^{11}\mathbf{B}/{}^{10}\mathbf{B})_{\text{NBS 951}} - 1 \right] \times 1000$$

The mean of the absolute  ${}^{11}B/{}^{10}B$  ratios of NIST SRM-951 replicates analyzed with the samples was  $3.9935 \pm 0.008$  (at Regensburg) and  $4.015 \pm 0.005$  (at Wilmington). Duplicate mass spectrometry analyses were carried out for some of the samples with external precision below 2‰. Moreover, several samples were cross-checked by analyzing them at Regensburg and Wilmington. Their ratios were identical, within the 2‰ precision.

Strontium was separated by cation exchange chromatography using standard techniques. Isotope ratios were determined using a two-detector dynamic collection routine on a VG-3361 mass spectrometer at the University of North Carolina, Wilmington. We used tungsten filaments. Prior to collection of Sr ratios, <sup>85</sup>Rb was monitored by Daly detection to insure that the <sup>87</sup>Rb isobaric interference was negligible. All measured <sup>87</sup>Sr/ <sup>86</sup>Sr results were corrected to an <sup>86</sup>Sr/<sup>88</sup>Sr ratio of 0.1194 using exponential correction. Through this procedure, seawater <sup>87</sup>Sr/ <sup>86</sup>Sr yielded a ratio of 0.70923. Fractionation corrected ratios were normalized to the measured seawater ratio assuming that the modern seawater ratio is 0.709199.

Oxygen isotope ratio measurements were made on a VG SIRA-II mass spectrometer at the Geological Survey of Israel. Results are given in per mil values with respect to the standard mean ocean water (SMOW) standard ( $\delta^{18}$ O) [*Craig*, 1961]. The  $\delta^{18}$ O value of the water was determined after equilibration with CO<sub>2</sub>, by shaking with 2 mL of water for 4–6 houts at 25°C [*Epstein and Mayeda*, 1953]. Analytical reproducibility of duplicates measured on different days was better than 0.1‰.

## 4. Results

## 4.1. Anthropogenic Sources

Treated waste waters are characterized by a salinity range of 300 to 550 mg Cl/L, and a wide range of ion ratios (Table 1). High Na/Cl, SO<sub>4</sub>/Cl, B/Cl, K/Cl and low Br/Cl ratios relative to the marine ratios are typical of waste water from the Dan Region [*Vengosh and Keren*, 1996] (Figure 3). Waste water from open reservoirs has  $\delta^{18}$ O values of -3.45% to 0.92% (Table 1). Imported water from the Sea of Galilee has a salinity of 220 mg Cl/L, a high Br/Cl ratio ( $3 \times 10^{-3}$ ), a  $\delta^{18}$ O value of -1%, a  $\delta^{11}$ B of 22.8‰, and a low  ${}^{87}$ Sr/ ${}^{86}$ Sr ratio of 0.70753.

## 4.2. Brackish Groundwater

The brackish groundwater in the investigated area (Table 2) is depleted in Na<sup>+</sup> and K<sup>+</sup>, and enriched in Mg<sup>2+</sup> and Ca<sup>2+</sup> relative to diluted sea water with a similar salinity (Figure 4). In addition, we found small but consistent differences between the different saline spots: (1) in groundwater from Yavne, Hazor, and Be'er Toviyya there is a linear correlation between Cl<sup>-</sup> and Ca<sup>2+</sup>, whereas in Giva't Brener the Ca<sup>2+</sup> variation is scattered; (2) in groundwater from Yavne and Be'er Toviyya the SO<sub>4</sub><sup>2-</sup> content is depleted, whereas in Giva't Brener it is enriched relative to the seawater SO<sub>4</sub>/Cl ratios; (3) in groundwater from Yavne the Na/Cl and SO<sub>4</sub>/Cl ratios decrease, and Ca/(HCO3 + SO4) increases with salinity, while in Giva't

Table 1. Chemical	Composition	of Inve	stigat	ed Tr	eated	l Sewa	ge Efi	luents	Fron	1 Open	Rese	rvoirs	n the	Centr	al Co	ıstal I	lain of	Israel	ind the	Sea o	f Galile	Ð	
Name	Date	818O	CI, mg/I	Ca	Mg	Na	K	a	S04	HCO3	NO3	Br	В	Ъ	Na/CI	б	Mg/Cl	Ca/Mg	Ca/Cl	K/CI	SO4/CI	Br/Cl (×1000)	B/Cl (×1000
Hafetz Havim North	Aug 2 1995		473	8L C	20.6	11 00	0.50	11 03	0.76	Waste 6 30	water 135	0.01	0.047	0.03	000	0.30	0177	1 337	0.733	0.044	0.063	080	3 40
Hafetz Hayim South B	Aug. 2, 1995	-1.32	330	1.83	1.54	9.65	0.59	9.31	0.59	5.25	0.71	0.008	0.052	0.03	1.04	0.31	0.164	1.184	0.196	0.063	0.064	0.85	5.61
Hazor	Aug. 2, 1995	-0.70	379	2.18	3 1.88	10.13	0.55	10.69	0.85	5.57	0.44	0.022	0.043	0.03	0.95	0.34	0.173	1.160	0.203	0.051	0.080	2.08	4.07
Harel	Sept. 19, 1995	0.92	360	1.15	5 1.13	10.87	0.63	10.15	0.79	2.28	0.02	0.004	0.043	0.03	1.07	0.37	0.109	1.022	0.113	0.062	0.078	0.39	4.19
Tal Shahar	Sept. 19, 1995	-3.04	1 490	3.05	2.54	12.78	0.42	13.82	0.67	8.62	0.43	0.012	0.054	0.03	0.92	0.33	0.182	1.200	0.221	0.031	0.048	0.90	3.92
Na'an	Sept. 19, 1995	-1.60	347	2.10	1.54	10.22	0.93	9.79	1.04	8.70	2.43	0.006	0.074	0.02	1.04	0.22	0.156	1.362	0.215	0.095	0.106	0.61	7.56
Revadim B	Sept. 19, 1995	-3.45	311	2.58	3 1.96	9.65	0.88	8.77	0.63	10.34	3.02	0.003	0.064	0.03	1.10	0.23	0.220	1.315	0.294	0.100	0.071	0.30	7.28
Revadim A	Sept. 19, 1995	-1.94	1 553	2.20	3.17	11.78	0.17	15.60	0.79	4.84	0.14	0.019	0.046	0.04	0.76	0.39	0.200	0.695	0.141	0.011	0.051	1.23	2.92
Hafetz Hayim A	Sept. 19, 1995		481	2.25	5.13	12.52	0.60	13.57	0.79	6.85	0.94	0.011	0.063	0.02	0.92	0.29	0.155	1.059	0.166	0.044	0.058	0.77	4.63
Zorea A	Sept. 19, 1995	-2.35	356	2.13	1.71	11.00	0.74	10.04	0.77	7.89	1.27	0.005	0.053	0.03	1.10	0.25	0.168	1.244	0.212	0.074	0.077	0.47	5.26
Zorea B	Sept. 19, 1995	0.01	331	1.88	3 1.83	10.87	0.95	9.34	0.81	8.11	0.81	0.005	0.080	0.02	1.16	0.21	0.194	1.023	0.201	0.102	0.087	0.48	8.62
										Importer	d Wate												
Azriqa'am Sea of Galille	Oct. 18, 1995 Oct. 18, 1995	-0.98 1.00	223	1.20 1.11	1.17	5.04	0.19	6.29 5.90	0.67 0.95	2.00 2.55	$0.02 \\ 0.03$	0.017 0.018	$0.001 \\ 0.006$	0.01 0.02	$0.80 \\ 0.81$	$0.45 \\ 0.32$	$0.183 \\ 0.174$	1.029 0.539	$0.191 \\ 0.187$	0.030 0.027	0.106 0.060	2.73 2.97	$0.15 \\ 1.07$
Concentrations are re	ported in mmc	ol/L, rati	ios are	mola	r, and	chloric	le is al	so repo	orted i	n mg/L (	nit. Q	= Ca/	SO₄ +	HCC	3) in n	leq/L.							





Figure 3. Different ions to chloride (molar) ratios versus chloride concentration (in milligrams per liter) of sewage effluents from the Dan Region Reclamation Plant and open reservoirs in the coastal plain of Israel. Note the high Na/Cl, K/Cl, SO<sub>4</sub>/Cl, B/Cl, F/Cl and the low Br/Cl ratios of wastewater relative to the marine ratios.

Brener these ratios do not show any trends; (4) most of the brackish water has a marine Br/Cl ratio, while some samples from Giva't Brener and Hazor have high Br/Cl ratios.

The  $\delta^{11}$ B values of the brackish groundwater range from 24.8% to 49.9%, and <sup>87</sup>Sr/<sup>86</sup>Sr ratios range from 0.708275 to 0.708532 (Table 3). Fresh water from the western part of the aquifer (Cl < 100 mg/L) has lower  $\delta^{11}$ B values (21.2–32.4% [Vengosh et al., 1994]) and higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios (0.708609–0.708663; Table 3).

It should be noted that most of the isotopic results are reported for samples collected at different times. For example, several wells (Hazor A, Yavne 3, G. Brener Levinson, Gedera Moa'za, Gedera Gan Mordechai, and Revadim) were measured for boron isotopes both in 1992 and 1995 (Table 3). The  $\delta^{11}B$ results show a range of 0.3% to 10% difference, which is attributed to the natural variability of the boron isotopic ratio.

## 5. Discussion

The continued rise of salinity with time (Figure 5) reflects an increasing fraction of a saline source that is degrading the groundwater quality. Assuming that the saline source has a high salt content relative to original local groundwater, which has a chloride concentration of less than 100 mg/L, based on

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Table 2

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×100	1.25 2.08 1.48 1.11 1.05	1.60 1.61	1.19	1.36 1.52	1.56	÷	1.48	÷	 1.48	0.96	2.10	2.05	1.25 1.77	 4.12 1.75 1.35 1.67 1.67	1.16 1.31 1.357 2.17 2.57 1.94 1.07
Br/Cl ×1000	1.27 1.07 2.09 1.15 1.18	2.17 2.27	1.53	1.95	:	÷	÷	÷	::	÷	÷	:	::	::::::	$\begin{array}{c} 1.59\\ 1.60\\ 1.12\\ 1.22\\ 1.53\\ 1.53\\ 1.56\\$
SO4/CI	0.06 0.05 0.04 0.07	0.09	0.06	0.08 0.05	0.06	0.06	0.06	0.10	0.11 0.09	0.08	0.09	0.06	0.08 0.06	0.05 0.08 0.08 0.08 0.06 0.16	0.05 0.06 0.06 0.05 0.05 0.05 0.04 0.05
K/CI	0.006 0.007 0.016 0.014 0.007	0.025 0.013	0.028	0.023 0.043	0.028	0.028	0.028	0.015	0.014 0.007	0.004	0.014	0.014	0.013 0.013	0.010 0.019 0.006 0.007 0.007	0.005 0.005 0.001 0.005 0.006 0.006 0.005 0.005 0.005
Ca/CI	0.47 0.45 0.50 0.33	0.40 0.35	0.34	0.41 0.34	0.36	0.36	0.36	0.39	0.43 0.48	0.44	0.38	0.40	0.37 0.30	$\begin{array}{c} 0.27\\ 0.30\\ 0.46\\ 0.37\\ 0.25\\ 0.70\end{array}$	$\begin{array}{c} 0.48\\ 0.33\\ 0.33\\ 0.33\\ 0.33\\ 0.33\\ 0.33\\ 0.19\\ 0.19\end{array}$
Ca/Mg	2.88 2.08 1.78 2.22	2.56 1.90	1.86	2.02 1.67	1.79	1.79	1.78	1.86	2.15 2.52	3.06	1.25	1.44	1.92 1.44	1.58 1.26 1.94 3.06	$\begin{array}{c} 2.05\\ 1.61\\ 1.59\\ 0.93\\ 0.88\\ 0.83\\ 0.83\\ \end{array}$
Mg/CI	0.16 0.22 0.19 0.32 0.15	0.16 0.18	0.18	$0.20 \\ 0.20$	0.20	0.20	0.20	0.21	0.20 0.19	0.14	0.30	0.27	0.19 0.20	0.17 0.24 0.18 0.19 0.17 0.23	$\begin{array}{c} 0.23\\ 0.26\\ 0.26\\ 0.26\\ 0.22\\ 0.22\\ 0.22\\ 0.22\\ 0.23\\$
ð	0.90 0.54 0.65 0.44 0.69	0.60 0.54	0.70	0.71 0.70	0.64	0.64	0.64	0.49	0.71 0.74	1.00	0.64	0.54	0.75 0.46	$\begin{array}{c} 0.70 \\ 0.72 \\ 0.72 \\ 0.85 \\ 0.74 \\ 0.74 \end{array}$	$\begin{array}{c} 0.66\\ 0.75\\ 0.51\\ 0.51\\ 0.51\\ 0.38\\ 0.38\\ 0.38\\ 0.51\end{array}$
Na/CI	0.52 0.90 0.68 0.68 0.64	0.74 0.75	0.57	0.60 0.57	0.61	09.0	09.0	0.85	0.66 0.66	0.55	0.71	0.62	0.46 0.76	0.59 0.58 0.58 0.60 0.67	$\begin{array}{c} 0.68\\ 0.86\\ 0.88\\ 0.87\\ 0.89\\ 0.67\\ 0.64\end{array}$
Sr	:::::	0.009 0.010	0.018	0.015	÷	÷	÷	:	::	÷	÷	÷	::	::::::	0.010 0.015  0.014  0.025 0.025
н	0.007 0.011 0.013 0.013 0.009	0.012	0.009	0.011	:	÷	÷	÷	::	:	÷	÷	::	:::::	0.013 0.016 0.016 0.016 0.034 0.034 0.034
В	0.009 0.012 0.009 0.004 0.011	0.011	0.014	0.014	0.016	÷	0.015	:	 0.012	0.011	0.014	0.013	0.012 0.017	 0.012 0.012 0.012 0.012 0.007	0.006 0.015 0.014 0.018 0.018 0.022 0.022 0.022
Br	0.009 (0.	0.015	0.018	0.020	:	:	÷	i	::	:	÷	÷	::	::::::	0.009 0.018 0.011 0.011 0.011 0.011 0.023 0.023
NO3	nner 0.95 (0.66 ( 0.23 ( 0.27 ( 0.27 (	0.55 (0.19 (	1.18 (	1.35 ( 1.42	1.27	1.27	1.26	D.23	1.06 1.31	1.35	2.06	0.90	1.44 0.37	0.48 0.23 0.87 0.81 0.82 3.26	2 0.97 0.37 0.37 0.37 0.37 0.37 0.37
HCO3	iva't Bre 3.39 4.56 2.90 3.97 4.10	4.15 3.95	5.11	5.10 5.08	5.10	5.13	5.15	4.10	4.16 4.57	4.07	3.38	4.13	3.82 5.64	5.64 5.77 3.82 1.23 4.31	Yavn 3.54 3.54 4.44 5.43 5.43 5.15 5.15 5.15 4.89
S04	$G \\ 0.46 \\ 0.30 \\ 0.16 \\ 0.16 \\ 0.69 \\ 0.69 \\ 0.61 \\ 0.69 \\ 0.61 \\ 0.6$	0.65 0.60	0.65	0.83 0.57	0.60	09.0	0.57	0.57	0.89 0.77	0.92	0.58	0.36	0.70 0.63	0.92 0.58 0.58 0.88 0.88	$\begin{array}{c} 0.46\\ 0.52\\ 0.52\\ 0.52\\ 0.52\\ 0.63\\ 0.63\end{array}$
ŭ	7.39 5.73 6.23 3.58 10.04	7.11 7.05	11.68	10.21 11.62	10.13	10.18	10.21	. 5.78	8.35 8.21	11.42	6.68	6.15	9.25 9.67	16.98 5.87 7.08 7.28 5.44	5.50 5.58 5.58 5.58 6.94 9.08 9.08 13.76
K	0.05 0.04 0.05 0.05	0.18 0.09	0.32	0.24 0.50	0.28	0.28	0.28	0.09	0.12 0.05	0.05	0.09	0.08	0.12 0.13	0.04 0.04 0.05 0.04 0.04	$\begin{array}{c} 0.23\\ 0.14\\ 0.06\\ 0.14\\ 0.06\\ 0.07\\ 0.07\end{array}$
Na	3.87 5.18 4.26 2.44 6.39	5.26 5.26	6.66	6.13 6.61	6.13	6.13	6.13	4.93	5.51 5.44	6.26	4.74	3.78	4.22 7.39	10.09 6.87 3.83 3.65 3.65	3.74 7.57 4.78 6.92 6.92 6.00 9.18 9.18 9.18
Mg	$\begin{array}{c} 1.21\\ 1.25\\ 1.17\\ 1.17\\ 1.50\end{array}$	1.13 1.29	2.17	2.08 2.36	2.05	2.06	2.07	1.22	1.67 1.57	1.63	2.04	1.70	$1.77 \\ 1.99$	$\begin{array}{c} 2.90\\ 1.40\\ 1.28\\ 1.26\\ 1.25\end{array}$	$\begin{array}{c} 1.29\\ 1.67\\ 2.06\\ 3.38\\$
S	3.48 2.60 1.80 3.33	2.88 2.45	4.03	4.20 3.96	3.67	3.68	3.68	2.28	3.59 3.95	5.01	2.55	2.44	3.39 2.86	4.60 3.18 2.64 3.81 3.81 3.81	2.65 2.25 2.26 2.26 2.26 2.280 2.263
ng/L	262 203 221 127 356	252 250	414	362 412	359	361	362	205	296 291	405	237	218	328 343	208 245 251 258 258 258 193	195 193 193 246 246 232 246 220 220
8180, %0		-2.80 -2.95	-3.81	-2.93	:	÷	÷	÷	::	:	:	÷	::	::::::	
ę	, 1995 ), 1995 ), 1995 , 1995	, 1995 , 1995	, 1995	, 1995 , 1992	, 1993	, 1993	, 1993	1993	1993 3, 1992	3, 1992	3, 1992	3, 1992	3, 1992 3, 1992	, 1992 3, 1992 3, 1992 3, 1992 3, 1992 3, 1992	0, 1995 0, 1995 0, 1995 0, 1995 1, 1995 1, 1995 1, 1995 1, 1995
Da	Aug. 31 Aug. 30 Aug. 30 Oct. 18	Oct. 18 Oct. 18	Oct. 18	Oct. 19 Aug. 13	May 30	May 30	May 30	June 2,	June 2, Aug. 15	Aug. 13	Aug. 13	Aug. 13	Aug. 13 Aug. 13	Aug. 13 Aug. 13 Aug. 11 Aug. 11 Aug. 11	Aug. 3 Aug. 3 Aug. 3 Aug. 2 Aug. 3 Aug. 3 Au
	Hah ner 5 ner 6 er Hah ner	ner A ner	ner	ner A ner	пег	ner	ner	ner	ner A ner	пег	ner	ner	iet ner A ner	N n 4/1 0 3 3 4	avne B wne A om 3 om A
Name	hicler F vit Bren vit Bren vit Bren vit Bren	ayn i't Bren i't Bren	av i't Bren	evinson i't Bren i't Bren	evinson i't Bren	evinson	evinson i't Bren	evinson a't Bren	a't Bren a't Bren	Ni a't Bren	erkovit: a't Bren	ienberg	1eshute a't Bren a't Bren	iman T r Hadar r Krone Shieler 1 Shieler ( Shieler I shieler I	req 4 me 3 me 11 ron 3 utzat Y utzat Ya i Hadar
	Give S. S. Give S. S. Give S. S. Give S.	Give L	t Give	Give L	, Give L	ן פֿוָגַי	, Giv	م يز ر ا	Giv.	1 Givi	С С С Н П	+ Giv <	Giv P Giv P	S Aqii 1 Aqii 1 K. S 7 K. S 7 K. S	1 Sho 1 Yav 1 Yav 3 Gan 2 Gan 2 Gan
Ð	(421290) (411280) (411280) (411280) (4012902	13812805 13912901	14013104	4113105  4013104	14013104	14013104	14013104	13912901	1411310) 14213005	1421300	1411310	1411310-	1411310: 1401310	1401310 1401310 1421290 1421300 1411290 1411290	1401250 1381270 1371270 1371270 1351240 1351240 1341210 1341210 1341210

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1.78 0.91 0.96   1.02	1.78 2.69 3.81 5.82	1.46  1.64 	1.69 1.76  1.84 1.26	:::	$\begin{array}{c} 3.62\\ 2.53\\ 1.72\\ 1.92\\ 2.56\\ 1.91\\ 1.91\\ 1.91\end{array}$	$\begin{array}{c} 11.51\\ 11.50\\ 11.50\\ 11.20\\ 11.91\\ 11.91\\ \cdots \end{array}$
1.47 ••••	1.58 0.85 1.46 1.00 1.01	2.82	::::::	:::	2.41 1.52 1.52 1.52 1.50 2.04 2.33 2.33 2.33	1.66 1.55 1.43 1.43 1.63 1.63 1.23 1.23 1.23
0.04 0.04 0.04 0.04 0.04 0.04 0.04 0.04	0.04 0.09 0.07 0.07	 0.08 0.05 0.05	0.05 0.05 0.05 0.05 0.05	0.11 0.09 0.06	0.06 0.05 0.05 0.05 0.06 0.06 0.05	0.05 0.05 0.05 0.04 0.04 0.05 0.05
$\begin{array}{c} 0.008\\ 0.005\\ 0.005\\ 0.005\\ 0.005\\ 0.005\\ 0.005\\ 0.005\\ 0.005\\ \end{array}$	$\begin{array}{c} 0.007\\ 0.031\\ 0.014\\ 0.017\\ 0.020\end{array}$	0.004 0.013 0.012 0.008 0.007	$\begin{array}{c} 0.007\\ 0.007\\ 0.007\\ 0.008\\ 0.008\\ 0.005 \end{array}$	$\begin{array}{c} 0.013 \\ 0.022 \\ 0.011 \end{array}$	$\begin{array}{c} 0.014\\ 0.010\\ 0.006\\ 0.013\\ 0.013\\ 0.023\\ 0.023\\ 0.010\\ 0.010\\ \end{array}$	0.004 0.005 0.006 0.006 0.006 0.006 0.006
$\begin{array}{c} 0.24\\ 0.19\\ 0.19\\ 0.19\\ 0.19\\ 0.19\\ 0.19\\ 0.19\\ 0.19\\ 0.19\end{array}$	0.24 0.46 0.36 0.25 0.28	$\begin{array}{c} \\ 0.38 \\ 0.28 \\ 0.26 \\ 0.24 \end{array}$	$\begin{array}{c} 0.24\\ 0.23\\ 0.25\\ 0.25\\ 0.22\end{array}$	0.33 0.43 0.38	$\begin{array}{c} 0.23\\ 0.23\\ 0.23\\ 0.23\\ 0.23\\ 0.23\\ 0.22\\ 0.23\\ 0.22\\ 0.23\\ 0.22\\ 0.23\\ 0.22\\ 0.23\\ 0.22\\$	$\begin{array}{c} 0.11\\ 0.11\\ 0.11\\ 0.17\\ 0.15\\ 0.12\\ 0.12\\ 0.17\\ 0.17\\ 0.17\\ 0.17\\ 0.17\\ 0.17\\ 0.17\\ 0.17\\ 0.17\\ 0.17\\ 0.17\\ 0.12\\ 0.17\\ 0.12\\ 0.17\\ 0.17\\ 0.12\\ 0.12\\ 0.17\\ 0.12\\$
$\begin{array}{c} 0.86\\ 0.81\\ 0.81\\ 0.82\\ 0.82\\ 0.82\\ 0.82\\ 0.82\\ 0.82\\ 0.82\end{array}$	$\begin{array}{c} 1.22\\ 1.83\\ 1.83\\ 1.32\\ 0.89\end{array}$	1.36 1.36 1.18 1.18 1.20	$\begin{array}{c} 1.19\\ 1.18\\ 1.18\\ 1.19\\ 1.20\\ 1.23\\ 1.23\end{array}$	1.03 1.71 1.51	$\begin{array}{c} 1.15\\ 1.16\\ 1.23\\ 1.26\\$	0.49 0.48 0.49 0.49 0.94 0.94 0.71 0.94 0.71
$\begin{array}{c} 0.28\\ 0.23\\$	0.19 0.25 0.22 0.19 0.31	$\begin{array}{c} \\ 0.28 \\ 0.21 \\ 0.22 \\ 0.19 \end{array}$	$\begin{array}{c} 0.20\\ 0.20\\ 0.20\\ 0.21\\ 0.21\\ 0.18\end{array}$	0.31 0.25 0.25	0.20 0.17 0.18 0.18 0.19 0.20 0.20 0.20	$\begin{array}{c} 0.22\\ 0.21\\ 0.22\\ 0.13\\ 0.18\\ 0.18\\ 0.16\\ 0.20\\ 0.20\\ \end{array}$
$\begin{array}{c} 0.36\\ 0.71\\ 0.62\\ 0.62\\ 0.62\\ 0.63\\ 0.62\\$	0.54 0.50 0.24 0.21	$\begin{array}{c} \\ 0.45 \\ 0.50 \\ 0.53 \\ 0.53 \end{array}$	$\begin{array}{c} 0.52 \\ 0.50 \\ 0.51 \\ 0.51 \\ 0.55 \\ 0.55 \\ 0.74 \end{array}$	0.31 0.50 0.53	0.34 0.49 0.49 0.50 0.52 0.52 0.52 0.52	0.51 0.44 0.55 0.55 0.55 0.53 0.53 0.53
$\begin{array}{c} 0.82\\ 0.54\\ 0.58\\ 0.58\\ 0.58\\ 0.58\\ 0.58\\ 0.58\\ 0.58\\ 0.56\end{array}$	0.66 0.75 0.59 1.02 1.68	$\begin{array}{c} 0.63\\ 0.69\\ 0.64\\ 0.65\end{array}$	0.65 0.68 0.65 0.67 0.69 0.54	$ \begin{array}{c} 1.09\\ 0.71\\ 0.66 \end{array} $	$\begin{array}{c} 0.94\\ 0.76\\ 0.78\\ 0.79\\ 0.89\\ 0.89\\ 0.78\\$	$\begin{array}{c} 0.66\\ 0.67\\ 0.69\\ 0.69\\ 0.72\\ 0.77\\ 0.77\\ 0.77\\ 0.77\\ 0.77\end{array}$
::::::::::	0.017  0.008 0.010	0.031	::::::	:::	0.014 0.014 0.019 0.017 0.017 0.017 0.017	 0.032 0.031 
0.035	0.022 0.016 0.017 0.035	0.059  	:::::	:::	$\begin{array}{c} 0.044\\ 0.052\\ 0.033\\ 0.036\\ 0.038\\ 0.038\\ 0.038\\ 0.038\\ 0.030\\ 0.018\\ 0.018\\ 0.018\\ 0.018\\ 0.018\\ 0.018\\ 0.041\\ 0.018\\ 0.041\\ 0.$	0.032 0.046 0.046 0.046
0.015 0.018 0.017   0.017	0.024 0.018 0.015 0.026 0.026	0.042  0.016 	0.022 0.023  0.023 0.023	:::	0.033 0.019 0.015 0.015 0.013 0.013 0.013 0.0013	0.057 0.058 0.057 0.057 0.057 0.057 0.023 0.023
0.012	0.021 0.006 0.015 0.007 0.007	0.080	::::::	:::	$\begin{array}{c} 0.022\\ 0.022\\ 0.020\\ 0.021\\ 0.017\\ 0.017\\ 0.017\\ 0.017\\ 0.017\\ \end{array}$	0.063 0.065 0.055 0.055 0.033 0.023 0.023 0.023 0.025
$\begin{array}{c} 0.37\\ 0.48\\ 0.48\\ 0.48\\ 0.48\\ 0.48\\ 0.48\\ 0.48\\ 0.42\\ 0.42\end{array}$	0.35 1.19 1.05 0.13 0.19	$\begin{array}{c} \dots \\ 1.23 \\ 0.45 \\ 0.42 \\ 0.42 \end{array}$	0.40 0.37 0.40 0.40	0.85 1.13 1.10	$\begin{array}{c} 0.56\\ 0.32\\ 0.77\\ 0.77\\ 0.77\\ 0.21\\ 0.87\\ 0.02\\ 0.02\\ \end{array}$	$\begin{array}{c} 0.44\\ 0.44\\ 0.44\\ 1.61\\ 1.40\\ 0.44\\ 0.44\\ 0.44\\ 0.69\\ 0.69\\ 0.69\\ 0.69\\ 0.69\\ 0.64\\ 0.69\\$
5.15 4.31 4.31 4.43 4.41 4.41 4.39 4.39	a 5.39 5.26 6.61 6.62	5.48 5.48 5.00 5.36	5.41 5.49 5.52 5.05 5.11	5.54 5.64 5.48	7, 5.90 5.33 5.33 5.33 5.33 5.33 5.33 5.33 5.3	т 6.23 6.23 5.36 7.93 5.93 5.93 5.28 4.26 2.48 2.48 3.67
$\begin{array}{c} 0.34\\ 0.78\\ 0.70\\ 0.70\\ 0.70\\ 0.70\\ 0.68\\ 0.70\\ 0.73\\ 0.52\end{array}$	Gede 0.60 0.60 0.49 0.36	 0.56 0.70 0.68	$\begin{array}{c} 0.68\\ 0.68\\ 0.68\\ 0.65\\ 0.65\\ 1.07\end{array}$	0.64 0.63 0.54	Hazo 0.60 0.73 0.73 0.73 0.73 0.73 0.73 0.73 0.7	Kevadi 1.98 1.98 2.03 2.03 1.98 1.49 0.57 0.57 0.57 0.57
8.18 19.89 18.05 16.78 16.42 17.88 16.39 16.25 16.61	13.51 6.63 9.93 6.77 5.11	28.46 7.00 9.65 12.95 13.45	13.29 13.06 13.29 13.23 13.23 20.62	5.90 7.19 8.46	9.25 7.56 14.55 113.79 9.03 9.03 6.94 6.94 6.94 5.84	$\begin{array}{c} 38.11\\ 38.67\\ 38.13\\ 38.13\\ 38.13\\ 31.73\\ 31.73\\ 31.73\\ 31.73\\ 115.03\\ 19.69\\ 19.69\\ 13.26\end{array}$
$\begin{array}{c} 0.06\\ 0.08\\$	$\begin{array}{c} 0.09\\ 0.20\\ 0.14\\ 0.12\\ 0.12\\ 0.10\end{array}$	0.11 0.12 0.10 0.10	0.09 0.09 0.10 0.10	0.08 0.16 0.09	$\begin{array}{c} 0.13\\ 0.08\\ 0.08\\ 0.16\\ 0.16\\ 0.16\\ 0.16\\ 0.16\end{array}$	0.15 0.14 0.14 0.14 0.10 0.10 0.10 0.10
$\begin{array}{c} 6.74\\ 10.68\\ 10.28\\ 9.69\\ 9.49\\ 9.49\\ 9.49\\ 9.29\\ 9.29\end{array}$	8.96 4.96 5.87 6.87 8.57	18.01 5.79 6.61 8.70 8.70	8.70 8.92 8.70 8.70 8.70 11.09	6.44 5.09 5.55	$\begin{array}{c} 8.70\\ 7.05\\ 11.09\\ 10.87\\ 10.87\\ 10.87\\ 6.18\\ 9.44\\ 5.87\\ 5.87\\ 7.57\\ 10.87\\ 10$	25.23 25.75 26.45 26.45 16.49 14.35 10.87 15.22 10.27
2.29 4.52 3.95 3.88 3.88 3.88 3.88 3.89 3.89 3.92	2.67 1.67 2.21 1.29 1.63	1.98 2.01 2.83 2.65	2.63 2.66 3.72 3.72	1.86     1.83     2.10	$\begin{array}{c} 1.92\\ 1.92\\ 2.58\\ 1.79\\ 1.50\\ 1.17\\ 1.12\\ 1.17\\ 1.17\end{array}$	8.50 8.42 8.38 8.38 8.38 3.31 3.31 2.72 2.72 2.65
1.98 3.61 3.35 3.21 3.18 3.16 3.17 3.18 3.18 3.20	3.25 3.05 3.53 1.70 1.45	2.69 2.67 3.34 3.19	3.14 3.08 3.12 3.15 4.58	1.92 3.13 3.18	2.20 3.00 3.03 3.03 3.03 2.60 1.63 1.63 1.63	4.20 4.08 4.08 3.50 2.55 2.55 2.20 2.20
290 640 595 582 581 581 581 589 589	479 235 352 240 181	1009 248 342 477	471 463 469 444 731	209 300	207 238 246 246 234 234 234 207 203	1351 1371 1372 1352 1352 649 649 633 698 698
-4.20	4.01 4.51 4.45 4.34 0.44	:::::	::::::	:::	-4.19 -4.19 -4.28 -4.43 -4.23 -4.23 -4.29 -2.46	-4.18 -4.37 -4.37 -4.03 -4.50 -4.50 
1993 1993 1993 1993 1993 1993 1993	1995 1995 1995 1995	995 1992 1993 1993	1993 1993 1993 1993 1993	1993 1993 1993	1995 1995 1995 1995 1995 1995	995 995 992 1991 1991 1991
Aug. 31, June 6, June 6, June 6, June 6, June 6, June 6, June 7,	Aug. 31, Aug. 18, Aug. 18, Aug. 2, Aug. 2,	huly 3, 1 Aug. 8, May 23, May 23, May 23,	May 23, May 24, May 25, May 30, Une 3, 1 May 23,	May 23, May 23, May 23,	Aug. 1, 1 Aug. 1, 1 Aug. 1, 1 Aug. 2, 1 Aug. 30, 3 Aug. 30, 2 Aug. 30, 2 Aug. 30, 3 Aug. 2, 1 Aug. 2, 1 Aug. 3, 1 Aug. 2, 1 Aug. 1, 1 Aug. 1 Aug.	Aug. 1, 1 Aug. 1, 1 Aug. 1, 1 Aug. 1, 1 Vov. 3, 1 Vov. 3, 1 Uly 16, Uly 16,
<b><i><u><u></u></u></i></b> <u></u>						
darom darom darom darom darom darom darom	Moa'z Bilu Habee Jayim	Lz Chiya Moa'z Moa'z Moa'z	Moa'z Moa'z Moa'z Moa'z Gan	Kaspi Bilu Habee	Kibbu Kibbu Kibbu Soct	wiyya wiyya wiyya wiyya wiyya wiyya
an Ha an Ha an Ha an Ha an Ha an Ha an Ha an Ha an Ha	edera edera edera afetz I afetz I	eit Hil, edera edera edera edera	edera edera edera edera edera edera	edera edera	azor B agal 3 azor A azor A azor A azor A tra tra tra tra tra tra tra tra tra tra	vadim vadim vadim vadim vadim čer To čer To čer To čer To čer To
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134122 134121 134121 134121 134121 134121 134121 134121 134121	135129 135128 135128 133128 133128	133132 134128 134128 135129 135129 135129	135129 135129 135129 135129 135129 135129 135129	134128 136128 135128(	131123( 1311253) 1321233( 1321233) 1321233 1311256( 1311226( 131126( 13	131132 131132 131132 131132 126124 126124 126124 126124 126124 126124 126124 126124

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Concentrations are reported in mmol/L, ratios are molar, and chloride is also reported in mg/L unit.  $Q = Ca/(SO_4 + HCO_3)$  in meq/L.



Figure 4. Chloride versus dissolved ions concentrations (mmole/L) in groundwater in the study area as compared to seawater ratio (solid line). Note the differences among the saline spots. The dashed line Y represent chemical variations observed during sampling for several hours of well Gan Darom (see in Table 2). Note also the linear relationships between Ca and Cl in groundwater from Be'er Toviyya (BT) and Hazor (H).

historical data, a small fraction of saline water would dominate the chemical and isotopic compositions of the contaminated groundwater in the saline plumes. The following sections characterize the different types of the potential saline sources and compare them to the composition of the brackish groundwater.

## 5.1. The Chemical and Isotopic Characteristics of the Potential Saline Sources

Known potential saline sources in the Mediterranean coastal aquifers of Israel include lateral saline water flows from the

Source	ID	Date	δ <sup>11</sup> B	<sup>87</sup> Sr/ <sup>86</sup> Sr	SE	Sr	Cl	Sr/Cl	Sr/Ca	в	B/Cl (×1000)
Mediterranean sea water	•••	•••	39.0	0.709200	•••	9.59	22000	0.18	0.00038	5.3	0.8
			Be'er	Toviyya Salir	ie Plume						
Be'er Toviyya 5	12612402	July 9, 1995	•••	0.708338	3.91E-05	1.70	763	0.90	0.0031	•••	•••
Be'er Toviyya 5	12612402	July 13, 1992	46.2	•••	•••	•••	404	•••	•••	0.18	1.48
Be'er Toviyya 7	12612302	June 13, 1995	•••	0.708275	3.80E-05	1.40	587	1.92	0.0028	•••	•••
Be'er Toviyya 7	12612302	July 1, 1993	40.3	•••	•••	•••	544	•••	•••	0.24	1.45
Kefar Varburg D	12512302	July 6, 1995	•••	0.708384	1.70E-05	1.50	644	1.88	0.0029	•••	•••
Kefar Varburg D	12512302	July 1, 1993	41.4	•••	•••	•••	257	•••	•••	0.14	1.8
Kefar Varburg A	12512401	July 12, 1992	45.6	•••	•••	•••	457	•••	• • •	0.26	1.88
Be'er Toviyya 3	12612403	July 13, 1992	47.6	•••	•••	•••	715	•••	•••	0.26	1.17
Be'er Toviyya 6	•••	July 1, 1993	49.9	•••	•••	•••	711	•••	•••	0.32	1.48
TT 4 TF11 .				Hazor							
Hazor A Kibutz	13212302	Aug. 1, 1995	35.3	0.708495	9.00E-05	1.70	489	2.80	0.0032	0.29	1.94*
Hazor A Kibutz	13212302	July 19, 1992	31.7	•••	•••	•••	508	•••	•••	0.16	1.03
Hazor kibutz B	13112301	July 20, 1992	32.6	•••	•••	•••	303	•••	•••	0.20	2.13
Hazav 1	13312602	Aug. 16, 1992	34.9	•••	•••	•••	333	•••	•••	0.20	2.01
Ashdod 5	12711701	July 16, 1992	31.9	•••	• • •	•••	410	•••	•••	0.10	0.76
Ashdod 6	12811902	July 16, 1992	33.7	• • •	•••	•••	325	•••	•••	0.33	3.33
Ashdod 2	12911801	July 16, 1992	37.5	•••	•••	•••	345	•••	•••	0.39	3.71
Ashdod 10	13012001	July 16, 1992	36.6	•••	•••	•••	333	•••	•••	0.42	4.14
Gan Hadarom 1	13412102	Aug. 31, 1995	•••	0.708473	1.40E-05	2.20	520	3.41	0.0045	•••	•••
Gan Hadarom 1	13412102	June 6, 1993	38.0	•••	•••	•••	705	•••	•••	0.19	0.88
Gan Hadarom 1	13412102	June 6, 1993	30.6	•••	•••	•••	576	•••	•••	0.18	1.02
Gan Hadarom 1	13412102	June 6, 1993	32.1	•••	•••	•••	640	•••	•••	0.19	0.97
				Giva't Bren	er						
G. Brenner Levinson	14013104	Oct. 18, 1995	37.2	0.708532	3.41E-05	1.60	414	3.11	0.0023	0.18	1.43*
G. Brenner Levinson	14013104	July 17, 1995	28.8	•••	•••	•••	412	•••	•••	0.19	1.52
G. Brenner Siman Tov	14013102	July 17, 1995	38.3	•••		•••	343	•••		0.19	1.77
G. Brenner Berkovitz	14213001	July 17, 1995	48.4	•••	•••		405			0.12	0.96
Giva't Brenner A	14113103	July 17, 1995	29.6	•••	•••	•••	328	•••		0.13	1.25
G. Brenner Meshtefet	14113104	July 17, 1995	24.8		•••		218			0.14	2.05
Kevuzat Shiler C	14213002	July 17, 1995	48.5	•••	•••	•••	251	•••		0.10	1 35
Kevuzat Shiler B	14112902	July 17, 1995	44.9	•••	•••	•••	258	•••	•••	0.13	1.67
				Gedera							
Gedera Moa'za	13512901	Aug. 31, 1995	39.9	0.708425	2.90E-05	1.50	479	2.52	0.0026	0.20	1.37*
Gedera Moa'za	13512901	May 24, 1993	35.1	•••	•••	•••	463	•••	•••	0.25	1.77
Gedera Moa'za	13512901	May 23, 1993	35.1	•••	•••	•••	471	•••	•••	0.24	1.67
Gedera Gan Mordechai	13512902	July 6, 1994	34.4	0.708393	3.40E-05	2.50	772	2.61	0.0031	0.32	1.36*
Gedera Gan Mordechai	13512902	May 23, 1993	43.2	•••	•••	•••	731	•••	•••	0.28	1.26
				Yavne							
Yavne 3	13812701	Aug. 30, 1995	•••	0.708345	1.60E-05	1.30	407	2.57	0.002	•••	•••
Yavne 3	13812701	July 1, 1992	34.6	•••	•••	•••	363	•••	•••	0.17	1.54
Yavne 3	13812701	Aug. 1, 1995	43.6	•••	•••	•••	407	•••	•••	0.16	1.29*
Yavne 2	13812401	July 1, 1992	32.9	•••	•••	•••	405	•••	•••	0.11	0.89
Yavne C	13512203	July 1, 1992	35.6	•••	•••	•••	221	•••	•••	0.18	2.64
Yavne A	13512301	July 1, 1992	32.9	• • •	•••	• • •	227	•••	•••	0.21	2.96
Yavne 13	13712401	July 1, 1992	30.2	•••	•••	•••	135	•••	• • •	0.12	2.94
Yavne 10	13712601	July 1, 1992	34.4	•••	•••	•••	221	•••	•••	0.20	2.94
				Revadim							
Revadim kibuutz	13113201	Aug. 1, 1995	38.5	0.708473	6.70E-05	2.80	1352	1.67	0.0039	0.62	1.50*
Revadim kibuutz	13113201	July 15, 1994	38.2	•••	•••	•••	1409	•••	•••	0.67	1.56
				Frankwater							
Ashdod 10	13211504	Juby 2 1005		0 708662	2 400 05	<u>0</u> 40	20	11 11	0.0025		
Ashdod 18	13211304	June 2 1005		0.700000	2 20E 05	0.40	29 17	11.11 0 57	0.0033		•••
Ashdod 18	12211202	June 5, 1995 July 16, 1000	20.0	0.700009	3.00E-03	0.50	4/	0.37	0.0027	0.12	0.10
Ashdod 14	1211500	July 10, 1992	29.0	0.709660	1 605 05	0.40	40	10.07	0.0021	0.13	9.18
Ashdad 17	1511502	June 15, 1995	20 5	0.708000	1.00E-05	0.40	32	10.07	0.0031		
Ashaoa 17	15211502	July 10, 1992	30.5	•••	•••	0.01	48	•••	•••	0.10	6.83
		I	mported	Water (Sea	of Galilee)						
Azriqam reservoir*		Oct. 18, 1995	22.8	0.707528	1.40E-05	0.60	223	2.17	0.0028	0.10	1.47
Azriqa'm well	12812201	Oct. 18, 1995	•••	0.708350	1.95E-05	0.85	207	3.31	0.0033	•••	•••
Giv'at Brenner 6	14012701	Aug. 30, 1995	•••	0.708149	3.19E-05	0.80	221	2.92	0.0021	•••	•••

Table 3. Boron and Strontium Isotopic Compositions of Investigated Groundwater From the Central Coastal Aquifer of Israel

Isotopic results are reported in  $\delta^{11}$ B values as normalized to the standard NBS SRM-951. \*Analyses by MS VG-336 at Wilmington, North Carolina.



Figure 5. Variation of chloride concentrations with time of selected wells from the saline plumes in the center of the aquifer. Note the comparisons to drinking-water limit regulations of chloride concentrations.

adjacent eastern Eocence aquitard, anthropogenic salt flux from the surface via irrigation with wastewater over the aquifer, and artificial recharge and irrigation of imported water from the Sea of Galilee. In addition, recycling of fresh water through pumping and irrigation may also result in long-term accumulation of salts in a phreatic aquifer. The chemical and isotopic compositions of these sources are summarized in Table 4 and Figure 6.

Saline water from the Eocence aquitard has a wide range of salinity, up to 5000 mg Cl/L [Rosenthal et al., 1992; Nissim, 1991; Vengosh and Rosenthal, 1994; Y. Livshitz, The influence of natural and artificial factors on the chemical composition of groundwater in the north-western Negev and southern part of the coastal plain, Ph.D. thesis in preparation, 1999]. Recent studies [Artzi, 1999; Y. Livshitz, Ph.D. thesis in preparation, 1999] indicate two major types of saline groundwater: type I, shallow groundwater associated with fluvial sediments characterized by high Na/Cl (1.2), SO<sub>4</sub>/Cl, and B/Cl ratios; and type II, deep saline groundwater characterized by marine Na/Cl and

SO<sub>4</sub>/Cl ratios. Artzi [1999] shows that a saline spring near Hulda, located east of the research area, along the eastern margin of the coastal aquifer, has geochemical characteristics that are typical of type II. The only available geochemical data of saline water of type I indicate high B/Cl ratios,  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios of 0.708102–0.708132, and  $\delta^{11}$ B values of 38–48.5% (A. Vengosh and A. Starinsky, unpublished data, 1995).

Uncontaminated fresh water (Cl < 100 mg/L) from the western part of the aquifer has high Na/Cl (>1) and Br/Cl (>1.5 × 10<sup>-3</sup>) values [Vengosh and Pankaratov, 1998],  $\delta^{18}$ O values of about -5‰ [Gat, 1981], low  $\delta^{11}$ B values of 21.2-32.4‰, [Vengosh et al., 1994], and a <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.70866.

Domestic wastewaters from the Dan Region Reclamation Project and some wastewaters (i.e., with a chlorinity of ~300 mg/L) from open reservoirs in the central coast of Israel are characterized by a unique anthropogenic chemical signature. High Na/Cl (1.1), SO<sub>4</sub>/Cl, and B/Cl ( $5 \times 10^{-3}$ ) as well as low Br/Cl ratios ( $5 \times 10^{-4}$ ) are attributed to applications of NaCl salt and boron-enriched detergents [Vengosh et al., 1994; Ven-

Source	Cl, mg/L	Na/Cl	SO₄/Cl	Br/Cl, $\times 10^3$	B/Cl, $\times 10^3$	δ <sup>18</sup> O, ‰	δ <sup>11</sup> B, ‰	<sup>87</sup> Sr/ <sup>86</sup> Sr
Seawater*	440	0.86	0.05	1.5	0.8	-5	39	0.70923
Wastewater	300	1.1	0.09	0.5	2 to 5	-3 to 1	0 to 10	•••
Sea of Galilee	220	0.78	0.06	3.0	1	-1	23	0.70753
Eocene saline water					,			
Nahal Oz 2	1300	1.23	0.12	1.4	8.7	•••	43	0.70813
Hulda spring	1300	0.86	0.05	1.5	1.8	•••	•••	•••
Saline Plumes								
Revadim	1350	0.66	0.05	1.5	1.5	-4.2	38	0.708473
Gedera	772	0.54	0.05	1.6	1.8	-4.0	43	0.708393
Be'er Toviyya	763	0.78	0.05	1.4	1.8	-4.5	46	0.708338
Hazor	516	0.76	0.05	1.5	1.7	-4.0	35	0.708495

 Table 4.
 The Chemical and Isotopic Compositions of Potential Saline Sources and Major Saline Plumes From the Coastal Aquifer

\*Fifty times diluted.

gosh and Pankaratov, 1998]. The variations of the different ion ratios with chlorinity (Figure 3) suggest that the fluids in the open reservoirs are a mixture of domestic sewage effluents with a salinity of about 300 mg/L (i.e., typical of the sewage from the Dan Region Reclamation Project) and local brackish groundwaters with higher chlorinity and lower Na/Cl, SO<sub>4</sub>/Cl, and B/Cl ratios that were added to the reservoirs. Although this addition reduces these ratios, the anthropogenic geochemical signature is still distinguishable (at least for several parameters like SO<sub>4</sub>/Cl, Br/Cl, B/Cl ratios) from the marine ratios (Figure 3). The effluents are also enriched in <sup>18</sup>O (relative to local groundwater) because of the evaporation in the open reservoirs. Vengosh et al., [1994] have shown that sewage effluents are characterized by  $\delta^{11}B$  values in the range of 0-10%. Consequently, the assemblage of high Na/Cl, SO<sub>4</sub>/Cl, and B/Cl ratios; low Br/Cl ratios; low  $\delta^{11}$ B values; and high  $\delta^{18}$ O values are typical of domestic wastewater in Israel, in particular wastewater that is being used for irrigation in the central part of the coastal aquifer.

Imported waters from the Sea of Galilee are characterized by high Br/Cl ( $3 \times 10^{-3}$ ) and  $\delta^{18}$ O values (-1%), which are related to the origin of brines flowing to the Sea of Galilee [*Starinsky*, 1974], and evaporation processes over the lake [*Gat*, 1974, 1981], respectively. The high Br/Cl ratio differs from the typical low Br/Cl characteristic of domestic wastewater. The <sup>87</sup>Sr/<sup>86</sup>Sr ratio of the Sea of Galilee is 0.707520.

### 5.2. Water-Rock Interactions

There are significant chemical and isotopic differences between the potential saline sources (Table 4). Nevertheless, these geochemical characteristics may be considerably modified because of water-rock interactions. Mechanisms that can modify the original chemical and isotopic compositions are (1) base-exchange reactions with clay minerals that affect Na<sup>+</sup>, Ca<sup>2+</sup>, and Sr<sup>2+</sup> and hence the Na/Cl, Ca/(SO<sub>4</sub> + HCO<sub>3</sub>), and <sup>87</sup>Sr/<sup>86</sup>Sr ratios; (2) adsorption onto clay minerals, which affects B, K<sup>+</sup>, and  $\delta^{11}$ B; and (3) carbonate dissolutionprecipitation, which affects Ca<sup>2+</sup>, Sr<sup>2+</sup>, and HCO<sub>3</sub>- ions and <sup>87</sup>Sr/<sup>86</sup>Sr ratios. Consequently, while  $\delta^{18}$ O, Cl<sup>-</sup>, and Br/Cl are considered to be conservative tracers in the aquifer system, the other geochemical and isotopic parameters used in this study ( $\delta^{11}$ B, <sup>87</sup>Sr/<sup>86</sup>Sr ratios) may be influenced by water-rock interactions.

The effect of boron adsorption on the isotopic variations is limited to about 20% [Spivack et al., 1987], and this would increase the  $\delta^{11}B$  values of sewage-contaminated groundwater

to about 20-30‰, since the original sewage signature is 0-10‰ [Vengosh et al., 1994]. In contrast, sea water ( $\delta^{11}B = 39\%$ ) would be modified to a higher value, up to 60‰, which is significantly different from that of sewage-contaminated groundwater. The influence of the aquifer matrix on the <sup>87</sup>Sr/<sup>86</sup>Sr ratios of dissolved Sr<sup>2+</sup> is more difficult to determine since Sr<sup>2+</sup> can be derived from (1) dissolution of Pleistocene calcite matrix with a <sup>87</sup>Sr/<sup>86</sup>Sr ratio of >0.7090 and (2) ion-exchange with clay minerals [Johnson and DePaolo, 1997a, b].

The effect of water-rock interactions on the Sr isotopic systematics is recorded in two groundwater samples that represent the spreading of recharged water in the aquifer, originating in the Sea of Galilee. The Cl content, Br/Cl ratio, and  $\delta^{18}$ O values of these wells (Azriqa'm Sochnot near the recharge basin of Azriqa'm and Giva't Brener 6; Table 2) are almost identical to that of the Sea of Galilee, which reflects a longterm and direct recharge of the imported water into the aquifer (i.e., minimum dilution or mixing with local groundwater). In contrast, the <sup>87</sup>Sr/<sup>86</sup>Sr ratios of the two wells (0.708350 and 0.708149, respectively) are significantly higher than that of the recharge water (0.707528). The Sr content in these samples is also higher, suggesting a considerable addition of matrixderived Sr with a higher <sup>87</sup>Sr/86Sr ratio. Consequently, it seems that dissolution of the Pleistocene matrix with a <sup>87</sup>Sr/<sup>86</sup>Sr ratio of >0.7090 can modify the original Sr isotopic composition of external fluids in the aquifer.

## 5.3. Elemental Systematics

The chemical variations reflect two major patterns: (1) linear relationships between  $Cl^-$  and  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $SO_4^{2-}$ , and Br<sup>-</sup> in brackish groundwater from the saline areas of Be'er Toviyya, Yavne, Gedera, and Hazor and (2) nonlinear relationships which are typical of the Giva't Brener area (Figure 4). While the linear relationships between  $Cl^{-}$  and the other ions indicate mixing processes with a distinguishable saline end-member, the scatter variations suggest water-rock modifications. The chemical composition of the brackish groundwater primarily reflects the composition of the saline endmember, particularly for the ion ratios which are less sensitive to dilution with low-TDS (total dissolved solids) fresh water. The variations of Na/Cl, SO<sub>4</sub>/Cl, Br/Cl, and Ca/(HCO<sub>3</sub> + SO<sub>4</sub>) ratios suggest a saline source with a marine Br/Cl ratio, low Na/Cl (~0.5) and K/Cl, and high Ca/Mg, Mg/Cl, and Ca/  $(HCO_3 + SO_4)$  ratios relative to sea water.

In brackish water from Revadim area, on the eastern side of the aquifer, and in the Be'er Toviyya saline plume, Na/Cl ratios



Figure 6. Values of some of the geochemical and isotopic parameters of the potential saline sources as compared with those of the major saline plumes. Tenfold diluted seawater refers to mixing between seawater and freshwater with  $\delta^{18}O \sim -5\%$ .

are higher (0.66 and 0.80, respectively), but this water also has a Ca-chloride composition (i.e., Ca/(HCO<sub>3</sub> + SO<sub>4</sub>) >1). The Cl-rich water at Yavne has SO<sub>4</sub>/Cl ratios that are lower than that of sea water (<0.05), while in the other areas the Cl-rich water has a marine SO<sub>4</sub>/Cl ratio.

The chemical composition of the brackish water differs from those of uncontaminated fresh water (i.e., low chlorinity of <100 mg/L, which has high Na/Cl and Br/Cl), domestic sewage effluents used for irrigation (high Na/Cl, SO<sub>4</sub>/Cl, B/Cl, and low Br/Cl), imported water of the Sea of Galilee (high Br/Cl), and both types of saline water from the Eocence aquitard (Table 4, Figure 6). While the low Na/Cl and high Ca-chloride signals of the brackish groundwater can be changed by base-exchange reactions, the SO<sub>4</sub>/Cl and Br/Cl are not influenced by these processes, and are considered conservative tracers. Since these ratios in the brackish groundwater are different from those in fresh water (high Br/Cl), the Sea of Galilee (high Br/Cl), and wastewater (low Br/Cl, high  $SO_4/Cl$ ), we argue that the chemical data rule out (1) recycling of salts from the irrigation of local groundwater and/or evapotranspiration of meteoric water (i.e., a long-term salinization from recycling of fresh water), (2) contamination by irrigation and/or leakage of waste water, and (3) recharge and irrigation of water from the Sea of Galilee. The chemical data cannot, however, rule out the input of saline water from the Eocence aquitard of type II with marine Na/Cl,  $SO_4/Cl$ , and Br/Cl ratios (e.g., Hulda spring; Table 4). Nevertheless, the above mentioned linear correlations between Cl and other ions suggest that mixing process control the water chemistry systematics which is not consistent with base-exchange reactions.

The Ca-chloride, low-Na/Cl ratio composition of the brackish groundwater resembles the composition of modified sea water and hence suggests that the saline plumes are derived from natural saline waters that originated from sea water and became depleted in Na<sup>+</sup> and enriched in Ca<sup>2+</sup> and Mg<sup>2+</sup>. Two mechanisms are known to explain these modifications. The first is evaporation of sea water followed by halite precipitation, combined with dolomitization. Since sea water has a Na/Cl ratio less than unity, halite precipitation further reduces this ratio in the residual brine. Accordingly, the Na/Cl ratio of 0.66 suggests an  $\sim$ 20-fold evaporated sea water (data from McCaffery et al. [1987]). Conversly, the Br/Cl ratio increases during precipitation of halite from sea water, and thus one would expect corresponding high Br/Cl ratios of  $> 1.5 \times 10^{-3}$ [Carpenter, 1978; Starinsky, 1974]. The Br/Cl ratios of most of the investigated brackish water, however, are marine (Figure 6). Nevertheless, hypersaline brines with a similar chemistry (e.g., low Na/Cl, high Ca, relatively low Br/Cl ratios) were found in sabkha environments in the Bardawil lagoon of the Northern Sinai [Levy, 1977]. In addition, saline water with a chloride content of up to 30,000 mg/L and similar chemistry was discovered along the western part of the coastal aquifer [Vengosh et al., 1991].

Alternatively, the relative depletion of Na<sup>+</sup> and enrichments of Ca<sup>2+</sup> and Mg<sup>2+</sup> may be the result of base-exchange reactions of the original sea water with clay minerals. Accordingly, the water/reactive clay mineral ratio must be low in order to have a net affect on the residual brine. In either case, it is clear that the composition of most of the brackish groundwater differs completely from those of the anthropogenic sources and thus eliminates them as the major sources of salinity.

An anthropogenic contribution is apparent in several wells in the investigated area. In some wells (e.g., Hafetz Hayim C and Hafetz Hayim Kibbutz) chemical composition reflects contamination from sewage effluents, while in other wells (e.g., Giva't Brener A, 5, and 6, and Azrigam well; Table 2), which are located near the recharge sites, the impact of the Sea of Galilee is recognizable. High Na/Cl, SO<sub>4</sub>/Cl, B/Cl, and low Br/Cl ratios provide evidence for sewage contamination whereas the impact of the imported Sea of Galilee is mainly identified by high Br/Cl ratios and  $\delta^{18}$ O values.

#### 5.4. Oxygen Isotope Systematics

Regional uncontaminated groundwater has  $\delta^{18}$ O values between -5.5% and -4.0%, with a mean of -4.7% (Figure 7). The  $\delta^{18}$ O values of groundwaters sampled in the present study vary between -4.8% to -2.4% (one sample yielded a value of -0.4%; Figure 7). Most of the brackish water (22 out of 33 samples), particularly those samples with high salinity, has  $\delta^{18}$ O values of <-4%. This isotopic range generally overlaps with those of uncontaminated groundwater reported by Gat [1974, 1981]. The other wells with high  $\delta^{18}$ O values (>-4‰; Figure 7) are located specifically in Giva't Brener and the Azriqa'm area and have also high Br/Cl ratios (>1.5  $\times$  $10^{-3}$ ), reflecting local recharge from the Sea of Galilee.

The  $\delta^{18}$ O values of the brackish water differ from those of sewage effluents in open reservoirs ( $\delta^{18}O = -3.5-1\%$ ) and the Sea of Galilee (-1%). Consequently, the oxygen isotope data confirm that these anthropogenic fluids are not the saline source for the underlying groundwater. Mixing with sea water or a brine derived from sea water, as inferred from the chemical data, would not significantly modify the original low  $\delta^{18}$ O value of the fresh groundwater. For example, the total dis $\delta^{18}\!O$  of groundwater and sewage effluents from open reservoirs in the coastal plain of Israel. The  $\delta^{18}O$  values of fresh uncontaminated groundwater, sampled during early 1970s, are taken from Gat and Dansgaard [1972];  $\delta^{18}$ O values below the dash line  $(\langle -4\%\rangle)$  in the lower figure are in the range of uncontaminated groundwater and thus represent groundwater samples that are not influenced by anthropogenic (wastewater and Sea of Galilee) fluids.

solved ions would increase significantly as a result of  $\sim 10\%$ mixing sea water (i.e., Cl ~ 2000 mg/L), while  $\delta^{18}$ O would increase by only  $\sim 0.5\%$ .

#### **Boron Isotope Systematics** 5.5.

In the coastal aquifer system there are several sources of boron that can affect the isotopic composition of the investigated brackish groundwater [Vengosh et al., 1994]: (1) fresh groundwater with  $\delta^{11}$ B values of 21.2–32.4‰, (2) modern sea

o Revadim Δ Hazor õ o \$ 600 800 1000 1200 200 400 1400 0 Chloride (mg/l) Figure 7. Histograms of  $\delta^{18}$ O values and chloride versus



Brackish ground water



Figure 8. Chloride concentration versus boron and 1/boron versus  $\delta^{11}$ B values of groundwater from the study area, as compared to seawater ratios, wastewater, and fresh groundwater. The straight lines represent mixing between freshwater and saline water with  $\delta^{11}$ B values of 39‰ (line a) and 50‰ (line b) and between freshwater and wastewater (line c).

water with  $\delta^{11}$ B values of 39‰, (3) a saline source or sources with unknown  $\delta^{11}$ B values, (4) wastewater with an anthropogenic isotopic signal of 0–10‰, (5) boron derived from dissolution of marine calcite matrix with a  $\delta^{11}$ B value of 20–25‰, and (6) residual boron, derived from adsorption equilibrium between dissolved boron and exchangeable boron on clay minerals in the aquifer, relatively enriched in <sup>11</sup>B.

The boron-chloride relationship in most of the investigated groundwaters (Figure 8) suggests that boron, like most of the dissolved ions, is nearly conservative in the aquifer. The brackish groundwaters have B/Cl molar ratios  $(1.5 \times 10^{-3})$  that are approximately twice that of sea water  $(0.8 \times 10^{-3})$  and  $\delta^{11}$ B values of 25–49.9‰ (Figure 8, Table 3). On the basis of these  $\delta^{11}$ B variations, two types of brackish water are identified: (1) water with high  $\delta^{11}$ B values (>40‰), typically of the saline plumes of Be'er Toviyya and Shieller (see locations in Figure 1), and (2) water from the other saline plumes in the central aquifer and from the eastern part of the aquifer with a  $\delta^{11}$ B range of 25–40‰. The  $\delta^{11}$ B values of the latter group correspond to mixing between a saline source with a seawater-like  $\delta^{11}$ B signature and fresh groundwater. Similarly, the  $\delta^{11}$ B variations of brackish water from the Be'er Toviyya area correspond to mixing with a saline water with a high  $\delta^{11}$ B value (>50‰; Figure 8).

The boron isotope composition of the brackish water is significantly different from those of anthropogenic sources, such as sewage effluents ( $\delta^{11}B = 0-10\%$ ) or sewage-contaminated groundwater (10-25% [Vengosh et al., 1994]), and thus further rule out salinization from leakage or irrigation with sewage effluents. The high  $\delta^{11}B$  values are similar, however, to those of saline water associated with saltwater intrusion in the western part of the aquifer [Vengosh et al., 1994]. Consequently, the  $\delta^{11}B$  values suggest that the brackish water is derived from a marine source with a  $\delta^{11}B$  value of 39‰ or higher.

The relatively high B/Cl ratios and  $\delta^{11}$ B values of the brackish water are not consistent with simple mixing between fresh water and unmodified Mediterranean seawater. However, high B/Cl with a marine  $\delta^{11}$ B signature can be generated during evaporation of seawater and precipitation of halite [Vengosh et al., 1992], which is consistent with the first mechanism suggested earlier for the formation of the saline water. In contrast, simple adsorption of boron from seawater (i.e., the second mechanism of modification of seawater by base-exchange reactions) would remove isotopically light B from solution and would result in low B/Cl and high  $\delta^{11}$ B values, which contradicts our data.

## 5.6. Strontium Isotope Systematics

In the coastal aquifer system there are several sources of  $Sr^{2+}$  that can affect the Sr isotopic composition of the investigated brackish groundwater: (1) fresh water with  ${}^{87}Sr/{}^{86}Sr$  ratios >0.70860, (2) modern seawater with a  ${}^{87}Sr/{}^{86}Sr$  ratio of 0.70920, (3) saline water with unknown  ${}^{87}Sr/{}^{86}Sr$  ratios, (4) Sr derived from dissolution of Pleistocene calcite matrix with a  ${}^{87}Sr/{}^{86}Sr$  ratio >0.7090, and (5) "exchangeable Sr" derived from ion-exchange reactions with clay minerals.

Rainwaters over Israel have a  ${}^{87}$ Sr/ ${}^{86}$ Sr range of 0.7078– 0.7092, reflecting mixing of Senonian to Eocene dust and sea spray dissolved in the rainwater [*Henut et al.*, 1993]. The  ${}^{87}$ Sr/ ${}^{86}$ Sr ratio of fresh groundwater (Cl < 100 mg/l) is lower than that of the Pleistocene calcite matrix ~0.7092 [*Starinsky et al.*, 1980] and thus probably reflects the meteoric  ${}^{87}$ Sr/ ${}^{86}$ Sr ratio. The  ${}^{87}$ Sr/ ${}^{86}$ Sr ratio of the exchangeable Sr in the coastal aquifer is not known. *Johnson and DePaolo* [1997b] argued that the isotopic ratio of the exchangeable Sr reflects the composition of water with which it has interacted in the past. Since fresh groundwater in the coastal aquifer is generated within the aquifer region, the expected  ${}^{87}$ Sr/ ${}^{86}$ Sr of exchangeable Sr is between 0.70860 (the freshwater ratio) and 0.7092 (the Pleistocene calcite cement ratio).

As shown before, the Sr isotopic ratio of recharged water from the Sea of Galilee is modified as a result of water-rock interactions in the aquifer. While Cl,  $\delta^{18}$ O, and Br/Cl of two groundwater samples (Azriqa'm and Giva't Brener 6 wells) in the vicinity of recharge areas are almost identical to those of the Sea of Galilee, the <sup>87</sup>Sr/<sup>86</sup>Sr ratios are significantly higher, reflecting the addition of Sr with a higher <sup>87</sup>Sr/<sup>86</sup>Sr ratio. This implies that Sr isotopic exchange is rapid, at least in the time frame of artificial recharge of the Sea of Galilee to the coastal aquifer during the last 30 years. The Sr/Ca ratio of the brackish water (~0.003) is higher than that of typical calcite (~0.0005); thus Sr<sup>2+</sup> was not derived from simple dissolution of the calcite cement. Instead, calcite solution/recrystallization would result in relative enrichment of dissolved Sr<sup>2+</sup> over Ca<sup>2+</sup> due to the low Sr distribution coefficient (0.05) in calcite [*Katz et al.*, 1972].

Although, strontium (Figure 9), as well as calcium (Figure 4), vary linearly with chloride in the brackish waters, the Sr isotope systematics indicate that Sr is not derivded from conservative mixing of two water types. If Sr variations were determined by conservative mixing, the <sup>87</sup>Sr/<sup>86</sup>Sr ratio should vary linearly with 1/Sr. This is not the case (Figure 9). Most of the brackish water samples, particularly those with high salinity (e.g., Beer Toviyya), have <sup>87</sup>Sr/<sup>86</sup>Sr ratios scattering between 0.70825 and 0.70855. This is most likely due to the addition of Sr resulting from carbonate solution/precipitation with a <sup>87</sup>Sr/<sup>86</sup>Sr in this range or slightly higher. This is also consistent with the relatively high Sr/Cl ratios.

On the basis of these observations, several conclusions can be drawn with respect to the origin of the saline component: (1) there is salinization by an external source with a  ${}^{87}$ Sr/ ${}^{86}$ Sr ratio of <0.7083; (2) the fossil seawater (based on other geochemical criteria) interacted with carbonate rocks older than early-middle Miocene carbonates; (3) the postulated saline water did not originate from modern Pleistocene-age seawater; and (4) recycling of freshwater through pumping and irrigation is not the main cause for salinization. Consequently, the Sr isotopic data confirm an "allochthonous" saline source with an isotopic composition of older sedimentary rocks.

A  ${}^{87}$ Sr/ ${}^{86}$ Sr ratio of <0.7083 corresponds to an early-middle Miocene or older seawater isotope composition. In principle, this may indicate that the saline source is derived from earlymiddle Miocene or older seawater or that younger seawater interacted with carbonate rocks of that age and the Sr isotope composition of the water was reset by this interaction. On the basis of its relatively high Sr/Cl ratio (Figure 9a; Table 3), it is clear that the Sr isotope ratio is the result of water-rock interaction, and it thus does not constrain the time of the intrusion of the fossil seawater. The combination of high Ca/Mg ratios and the low <sup>87</sup>Sr/<sup>86</sup>Sr ratio of <0.7083 of the postulated saline end-member indicates that the original seawater was modified during dolomitization reactions with early-middle Miocene or older carbonates. According to this approach, the <sup>87</sup>Sr/<sup>86</sup>Sr constrains the minimum age of the carbonate rocks with which evaporated seawater interacted. During dolomitization, the original high <sup>87</sup>Sr/<sup>86</sup>Sr ratio of the sea water would be reduced if the carbonate rocks are older [Sass and Starinsky, 1979; Starinsky et al., 1983; Stein et al., 1997]. Thus the <sup>87</sup>Sr/<sup>86</sup>Sr ratio of the residual Ca-chloride brine is controlled by (1) the <sup>87</sup>Sr/ <sup>86</sup>Sr ratio and age of the carbonate rock, (2) the fraction of  $Ca^{2+}$  (and  $Sr^{2+}$ ) derived from the rock (i.e., degree of interaction [Sass and Starinsky, 1979]), and (3) the initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio of the evaporated seawater. The early-middle Miocene Sr isotopic signal can be a result of any combination of these processes, but indicates that the original seawater could not have interacted with younger carbonate rocks.

# 6. Conclusions: Synthesis and Mechanism of Salinization

Figure 10 summarizes the two principal processes that affect the geochemical composition of the investigated groundwater: (1) recharge of water imported from the Sea of Galilee, which is reflected by high  $\delta^{18}$ O and Br/Cl ratios in groundwater in the vicinity of the recharge areas, and (2) mixing with a Caenriched saline water that has a high  $\delta^{11}B$  (>40%) and a low <sup>87</sup>Sr/<sup>86</sup>Sr ratio (<0.7083). The correlation between  $\delta^{11}$ B and <sup>87</sup>Sr/<sup>86</sup>Sr ratios may also reflect mixing between dissolved B and Sr, derived from dissolution of the carbonate matrix, and a high- $\delta^{11}$ B, low-<sup>87</sup>Sr/<sup>86</sup>Sr saline source. On the basis of the geochemical and isotopic constraints, we suggest that fossil seawater has interacted with early-middle Miocene or older rocks and has been diluted considerably (>10 times) because of mixing with the local groundwater in the Pliocene-Pleistocene coastal aquifer. The marine sedimentary record (Figure 2) along the Mediterranean coast reflects numerous inland seawater invasions. Remnants of seawater could be entrapped on the bottom, below (the Saqiye Group) and adjacent (Avdat Group; Figure 1) to the coastal aquifer.

The entrapped seawater could enter the coastal aquifer by two mechanisms: (1) lateral flow from the adjacent Eocene aquitard in the east and (2) vertical upconing from underlying saline water sources at the bottom of the aquifer [e.g., *Maslia* and Prowell, 1990]. Table 4 shows that the chemical composition of both types of saline water from the Eocene aquitard are



Figure 9. Chloride versus strontium concentrations, and 1/strontium versus  ${}^{87}Sr/{}^{86}Sr$  ratios of groundwater in the study area. Note the enrichment of  $Sr^{2+}$  in the brackish groundwater over seawater Sr/Cl ratios. The different processes represent (1) mixing with low Sr freshwater, (2) mixing with seawater with  ${}^{87}Sr/{}^{86}Sr$  ratios of 0.7092, (3) mixing with saline water with  ${}^{87}Sr/{}^{86}Sr$  ratios of <0.7083, (4) water-rock modification in which dissolved Sr and/or exchangeable Sr with a high  ${}^{87}Sr/{}^{86}Sr$  ratios modifies the original Sr isotopic ratio, and (5) mixing with recharge of the Sea of Galilee.

different from that of the saline plumes in the aquifer. One may argue, however, that base-exchange reactions may modify the original marine-like composition of the Eocence saline water. Nevertheless, *Artzi* [1999] showed that the chemical composition of saline groundwater from the coastal aquifer, located along the Eocene-Pliestocene contact at the eastern margin of the coastal aquifer, is identical to that of the Eocene saline water. Thus the Eocene geochemical signature is clearly recognized in the adjacent groundwater within the coastal aquifer, which is different from the composition of the investigated saline plumes.

We propose the following conceptual model for the salinization mechanism in the Mediterranean coastal aquifer of Israel. Hydraulic connections between underlying units containing pressurized saline water and the surficial aquifer units enabled upward flow of the saline water and salinization of the overlying freshwater. The hydraulic connections between the overlying aquifer, the low-permeability marine shales (Yafo Formation; Figure 2), and the lower units were probably established through faults, local structures, and unconformities, as evidenced in the eastern part of the aquifer [Rosenthal et al., 1992; Weinberger and Rosenthal, 1994]. The evidence that several saline spots with high salinity existed since the 1930s [Vengosh et al., 1996] suggests that this salinization process is a natural phenomenon. It should be noted that salinization resulting from substantial quantities of saline water that flow upward because of a fault system that breaches impermeable units was also demonstrated in the upper Floridan aquifer in Georgia [Hanshaw et al., 1965; Krause and Randolph, 1989; Maslia and Prowell, 1990].

The flow of the underlying fossil brine to the aquifer was enhanced, however, because of the reduction of the hydraulic pressure and formation of deep hydrological depressions, resulting from extensive pumping of freshwater over the central parts of the aquifer. The fact that salinization has increased despite the rise in water levels during the last decade indicates that the continued upward flux of saline water is still greater than the down flow and horizontal recharge of freshwater.



**Figure 10.** Variations of Br/Cl versus  $\delta^{18}$ O and  $\delta^{11}$ B versus  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios. Note (1) the influence of the recharge water from the Sea of Galilee (high Br/Cl and  $\delta^{18}$ O) on local groundwater; (2) the wastewater signature (low Br/Cl, high  $\delta^{18}$ O, low  $\delta^{11}$ B), and (3) the correlation between  $\delta^{11}$ B and  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios, indicating mixing between fresh groundwater and a saline source with high  $\delta^{11}$ B and low  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios. Alternatively, the later reflect mixing between dissolved B and Sr, derived from dissolution of the carbonate matrix and a high- $\delta^{11}$ B and low- ${}^{87}$ Sr/ ${}^{86}$ Sr saline source.

The inferred existence of deep saline water has water resource implications. Seawater has been considered as the major raw material for desalinization in Israel. However, the large volume of saline groundwater that this work points to may be a better source for desalinization, as its use may be more economical and have a reduced environmental impact. Moreover, pumping of underlying saline water may reduce the salt flux to the aquifer and may reduce the rate of salinization process. Most of the pumping wells in the coastal aquifer penetrated to the upper and middle sections of the saturated zone. Since the inferred saline reservoir occupies the deepest part of the aquifer, its impact on the overlying freshwater aquifer has been limited. Thus a new deep drilling program is required to illuminate the extent and distribution of the saline reservoir. We suggest that this saline groundwater should also be considered as an important source for desalinization in order to solve the severe lack of potable water in the semiarid area of the Middle East.

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Y. Artzi, Jacob Blaustein for Desert Research, The Water Resource Research Center, Ben Gurion University of the Negev, Sede Boqer 84990, Israel.

A. Ayalon, Geological Survey, 30 Malchei Israel Street, Jerusalem, Israel.

A. J. Spivack, Center for Marine Sciences, University of North Carolina at Wilmington, 601 S. College Rd., Wilmington, NC 28403-3297.

A. Vengosh, Hydrological Service, P. O. Box 6381, Jerusalem 91063, Israel. (avnerv@vms.huji.ac.il)

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