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# Saline groundwater in Israel: its bearing on the water crisis in the country

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#### Abstract

One of the major causes for the deterioration of water quality bearing heavily on the water crisis in Israel is the ongoing contamination of its water resources by saline water bodies. The present paper reviews the geochemical processes forming saline water, lists and explains certain chemical and isotopic parameters which enable understanding these processes and describes the saline groundwater bodies and various salinization phenomena occurring in the country's various aquifers.

Deterioration of groundwater in Israel is caused by numerous natural processes such as encroachment of sea water, migration of connate, highly pressurized brines penetrating into fresh groundwater, by subsurface dissolution of soluble salts originating in surrounding country rocks and by water-rock interaction. In addition to sea water, two saline water bodies were identified as the main factors causing salinization of fresh groundwater: (a) Ca-chloride brines encountered in the Jordan-Dead Sea Rift Valley, in various parts of the Negev and of the Coastal Plain, and (b) Na-chloride saline water identified in the subsurface of the Negev and in the southern part of the Coastal Plain.

Intensive exploitation of groundwater in Israel has disturbed the natural equilibrium which prevailed between fresh and saline water. The newly established groundwater flow regimes have facilitated the migration of saline water bodies, their participation in the active hydrological cycle and the progressive contamination of fresh groundwater. These processes which were not anticipated by planners and water resources managers emphasize that large-scale groundwater exploitation was undertaken without giving sufficient consideration to the occurrence and subsurface migration of saline water and brines.

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### 1. Introduction

One of the factors generating the water crisis in Israel is the ongoing salinization of its water resources which is directly or indirectly intensified by water exploitation. While taking measures to meet the ever increasing demand for water, managers must attempt to minimize damage caused by such processes and prevent their getting out of control and becoming irreversible.

There is no common assent in defining the term 'saline water'. Israeli public health authorities regard a Cl content of 600 mg  $l^{-1}$  as the highest acceptable salinity level for human consumption. Water with a Cl content in the 400–4000 mg  $l^{-1}$  range is defined as brackish whereas that in the 4000–19 000 mg  $l^{-1}$  range is classified as saline. Brine is water whose Cl concentration exceeds the world average concentration of Cl in ocean water (19 000 mg  $l^{-1}$ ; Hem, 1985). In the present review, the term saline denotes any water the Cl content of which exceeds the acceptable standards for drinking water.

According to Bonne and Gruenwald (1975), the estimated potential annual renewable volume of saline water in Israel is 300 million cubic meters (MCM) (out of a total renewable volume of water of 2000 MCM). Of this volume of saline water, 180 MCM are yearly extracted by pumpage. Whereas the annually renewable volume of fresh water seems to be accurately estimated, its ongoing exploitation enhances migration and inflow of more saline water leading to the progressive salinization of additional fresh water resources.

Salinization of groundwater may result from numerous processes such as inflow of sea water, migration of saline water and its mixing with fresh groundwater and by pollution resulting from industrial, municipal and agricultural activities in areas which are in hydraulic contact with exploited aquifers. In humid areas and where water resources are abundant, the potential danger of groundwater salinization is limited because of natural flushing by abundant fluxes of fresh water. Contrarily, in semiarid areas, the absence of effective natural flushing activity enhances accumulation of salts and of saline water.

The present review describes the natural occurrence of saline groundwaters in Israel, their hydrogeochemistry and the origin of their salts. Processes of anthropogenic pollution have not been considered in the present study. An attempt has been made to establish a regional model describing the interrelationship between the various saline water bodies and their threat to the fresh aquifers. Though there are no ways to estimate the total volume of saline groundwater stored in the subsurface and potentially endangering the exploited fresh water aquifers, it may be assumed that enormous volumes are involved, exceeding by many orders of magnitude the estimated annually renewable water resources of the country.

### 2. Formation of saline water in Israel

The main groundwater basins of Israel are shown in Fig. 1. The representative hydrostratigraphic columnar section is depicted in Fig. 2.



Fig. 1. Main groundwater basins of Israel.

		AGE	GROUP	FORMATION	LITHO- LOGY	SEISMIC	HYDRO - STRATIG.
1	T	HOLOCENE	SHAHAF	MUDS, SANDS, SAND DUNES			
QUATEF	NARY	PLEISTOCENE	KURKAR GROUP	HEFER Fm.			AQUIFER
۲۲	GENE	PLIOCENE	GROUP	YAFO Fm.			AQUITARD
A	IE O		щ	MAVQIIM Fm.			AQUITARD
F	2	MIOCENE	AQI	ZIQLAG Fm.			AQUIFER
Ш			S		<u> </u>		
	ĞЩ	ULIGUCENE	5 4	MARESHA Em	÷		
	GEP	EOCENE	AVD A	ADULAM Fm.	• _ +		
	٩	PALEOCENE		TAQIYE Fm.		ļļ	
			S e	GHAREB Fm.		1.	
	S	SENONIAN	ROLE	MISHASH Fm.			
	о ш		~ ° °	MENUHA Fm.	$\frac{1}{2}$	BASE SN.	
	U V	TURONIAN		DALIYA Fm. BINA Fm.	2-2		TARD AQUI-
ACEOUS	UPP. CRET	CENOMANIAN	UDEA GROUP	NEGBA Fm.			AQUIFER
CRET	TACEOUS	ALBIAN	3 Gr. J L	TALME- YAFE Fm. YAKHINI Fm		TOPIC	AQUI- TARD AQUI- FER
	E E	APTIAN	D Z	GEVARAM Fm. TELAMIM Fm			AQUI-/
	ž	BARREMIAN HAUTERIVIAN	L R	UPPER PART HELEZ KOHAL			TARD AQUI-
	2	VALANGINIAN	¥	GEVARAM FmLOW. PART		TOP JR.	AQUITARD
	Σ	KIMMERIDGIAN		HALUZA Fm.		• •	
	IAL		1	BEER SHEVA Fm.			AGOIFER
	2	UXFORDIAN		KIDOD Fm.		TOP Z.	AQUITARD
	~	CALLOVIAN		ZOHAR Fm.	$\frac{1}{1}$		AQUIFER
C C	Ξ Θ	BATHONIAN	٩	SHERIF Fm.			AQUITARD
SS	00	BAJOCIAN	0 2	DAYA Fm.			
RA		AALENIAN	้อ	INMAR Fm.			
		TOARCIAN	RAD	QEREN Fm.	77		AQUIFER
	ST	PLIENSBACHIAN	٩	HALAL Fm.			
	Ē	SINEMURIAN		ARDON Fm.			
		HETTANGIAN		MISH'HOR Fm.			AQUITARD
					N	ot to scale	
	Η_	3 53 5	E (			8	****
1	LIMES	TONE DOLOMITE CHAL	.к	MARL SANDSTONE SHAL	E CHE	ERT S	BALT/ HYDRITE
		UNCONFORMITY	SEISM	LIC HORIZON FACIES CI	ANGE		

NORTHERN NEGEVAND SOUTHERN COASTAL PLAIN

Fig. 2. Representative schematic hydrostratigraphic column of Israel.

Five major natural processes for saline water formation were identified in Israel: direct encroachment of sea water into the coastal aquifer, evaporation of sea water, diagenetic processes related to sea water evaporation, dissolution of soluble salts, and water-rock interaction. A brief outline of these processes will be provided, followed by the description of the methodology employed for hydrogeochemical identification of saline water bodies.

#### 2.1. Direct encroachment of sea water into the coastal aquifer

As the result of sea water encroachment into the coastal aquifer, an interface zone is established between the fresh and saline water bodies. Observations carried out in the Coastal Plain aquifer of Israel (composed mainly of sands and calcareous sandstones) revealed the existence of an interface zone the width of which varies between 1 cm and several meters (Schmorak and Mercado, 1969). The chemical composition of water from the interface zone would be a mixing product between the two initial end members, i.e. sea water and fresh water deriving from the Coastal Plain aquifer. Fig. 3 depicts changes of the Na/Cl ratio upon mixing between sea water (Na/Cl = 0.86) and fresh water (Na/Cl greater than 1). Schmorak and Mercado (1969), Nadler et al. (1980) and Mercado (1985) suggested that during sea water encroachment, a chemical exchange process between sea water and aquifer rocks should have occurred. According to these authors Ca-Na ion exchange reactions with clay minerals in aquifer rocks control the chemical composition of sea water. The enrichment of Ca in the solution would further imply saturation relative to CaCO<sub>3</sub> and precipitation of calcite. It should be emphasized that such geochemical processes would initially require high clay/water ratios which would then influence the whole bulk of saline water.



Fig. 3. Changes in the Na/Cl ratio upon mixing between sea water (Na/Cl = 0.86) and fresh water (Na/Cl > 1).

### 2.2. Sea water evaporation

The geological history of Israel and of the surrounding region involves several major events during which intensive evaporation of sea water caused precipitation of salt bodies and accumulation of residual brines. These events were:

(a) Large scale evaporation of regressing sea water bodies during the Cambrian– Early Cretaceous time span; during this period, regressing seas periodically covered the margins of the Arabo–Nubian massif over which continental conditions prevailed (Said, 1962; Ilani et al., 1988).

(b) Dessication of the Mediterranean during the Messinian (Late Miocene) and deposition of halite and anhydrite of the Mavqi'im Formation in the southern parts of the coastal plain (Starinsky, 1974; Starinsky et al., 1983).

(c) Formation of Mt. Sdom, built mainly of halite. It was precipitated in an inland lake which existed in the Rift Valley and which separated during the Pliocene from the main sea water body (Zak, 1967).

(d) Formation (during the Pleistocene) of coastal sabkhas along margins of marine lagoons. The Bardawill lagoon in northern Sinai is a modern example of such environments (Levy, 1972; Vengosh et al., 1991).

During the sea water evaporation process (Fig. 4) the chemical composition of the residual evaporated sea water is modified according to the saturation stages of evaporite minerals. Starting from a degree of evaporation (times the concentration of a conservative element such as Br in ocean water) of 3, Ca and  $SO_4$  ions in the solution reach supersaturation with regard to gypsum, causing its precipitation. Because of the low Ca/SO<sub>4</sub> ratio value in sea water, the precipitation of gypsum



Fig. 4. Changes in chemical composition in evaporating sea water (data from McCaffrey et al., 1987).

has no significant bearing on the  $SO_4^-$  content, but causes the impoverishment of Ca in the evaporated sea water. From a degree of evaporation of 10, evaporated sea water reaches supersaturation with regard to halite. Its precipitation causes impoverishment of Na relative to the ongoing conservative increase in the concentrations of Mg, K, SO<sub>4</sub>, Br, B and Li in the residual solution. Following these processes, the evaporated solution has a chemical composition which is different from that of original sea water. Its ionic sequence becomes Mg > Na > Ca and Cl > SO<sub>4</sub> > HCO<sub>3</sub>. The evaporated water is also characterized by low Na/Cl and Ca/(SO<sub>4</sub> + HCO<sub>3</sub>) ratio values which are in contrast with the high values of the Br/Cl, B/Cl and Li/Cl ratios (Starinsky, 1974; McCaffrey et al., 1987; Raab and Spiro, 1991; Vengosh et al., 1991).

Magnesium sulphate (epsomite) and Mg–K–Cl (carnalite) salts precipitate above the degree of precipitation of 40–50. Hence these ions do not continue to concentrate conservatively. Conversely, Br, B and Li continue to concentrate in the residual brine. However, McCaffrey et al., (1987), Raab and Spiro (1991) and Vengosh et al. (1992) showed that a small portion of these components is coprecipitated together with the previously mentioned salts. Vengosh et al. (1992) showed that this process is accompanied by fractionization (20–30‰) of B-isotopes between the brine and the precipitated minerals.

### 2.3. Diagenetic processes accompanying sea water evaporation

Evaporation of sea water occurs in closed basins such as lagoons or sabkhas. As further indicated, under such conditions various secondary diagenetic processes take place: (a) sulphate reduction facilitated by anaerobic conditions prevailing at the bottom of lagoons  $SO_4 + 2CH_2O \rightarrow H_2S + HCO_3$ . The formation of  $HCO_3$  enhances precipitation of CaCO<sub>3</sub> and the elimination of carbonate ions from the solution. This might lead to an increase in the Mg/Ca ratio (above the marine value of 5.2) and generate (b) a process of dolomitization. Another process which might lead to an increase in the Mg/Ca ratio value would be (c) precipitation of gypsum and the resulting impoverishment in Ca ions.

During the process of dolomitization, the following reaction occurs:  $CaCO_3 + Mg \rightarrow CaMgCO_3 + Ca$ . The resulting increase in the Ca content of the residual solution would increase the  $Ca/(SO_4 + HCO_3)$  ratio to values greater than 1, thus leading to the occurrence of Ca-chloride brines. Therefore, sea water evaporated beyond the stage of halite precipitation followed by dolomitization, attains the ionic sequence of Mg > Na = Ca and  $Cl > SO_4 > HCO_3$ . Such water is also characterized by  $Ca/(SO_4 + HCO_3)$  greater than 1, Na/Cl less than 1 and  $SO_4/Cl$  less than sea water values.

According to Starinsky (1974), epigenetic dolomitization may occur as the result of interaction between evaporated sea water and calcareous rocks. Sass and Starinsky (1979) showed that high Sr/Ca ratio values may be indicative of early dolomitization of aragonite whereas relatively low ratio values may occur as the result of late epigenetic dolomitization following interaction between evaporating sea water and calcite.

In addition to dolomitization and sulfate reduction, adsorption reactions also occur during the evaporation of sea water. K and B are adsorbed on clay particles and their concentrations in the residual brine decrease. Adsorption of B is accompanied by its isotopic fractionation. <sup>10</sup>B is preferentially adsorbed on clays whereas <sup>11</sup>B is enriched in the residual solution. The Dead Sea brine is a typical example of such processes with a high  $\delta^{11}$ B value of 56‰ (Vengosh et al., 1991).

### 2.4. Solution of soluble salts

When fresh water is in contact with soluble salts such as gypsum, halite and Mg or K chlorides, dissolution processes occur. The chemical composition of resulting solutions reflects the chemistry of the initial salts and is characterized by the occurrence of Ca,  $SO_4$ , Na and Cl with molar ratios of Na/Cl and Ca/SO<sub>4</sub> close to unity. Dissolution of bitterns (such as MgCl<sub>2</sub> and Mg-K-Cl salts) will form solutions of different chemical composition. Diagenesis of soluble salts such as carnallite (KMgCl<sub>3</sub>) to sylvite (KCl) may contribute Mg, Cl, and K to the solution, changing its ionic ratios entirely (increase in Mg and SO<sub>4</sub> concentrations and reduction of the Na/Cl ratio to less than 1). The chemical composition of groundwater from the Kurnub Group aquifer (Nubian Sandstone aquifer) may serve as a typical example for such dissolution processes. Its chemistry evolved by flushing of an aquifer which previously contained saline water which precipitated evaporites such as gypsum and halite. Ratio values such as Na/Cl and Ca/SO<sub>4</sub> = 1 indicate that the main source of ions derive from the dissolution of gypsum and halite.

### 2.5. Influence of marine spray and the interaction of rain water with country rocks

Rain water and airborne dust contain salts which accumulate in groundwater by percolation through recharge areas. The chemical composition of rain water is mainly dominated by the mixture of marine spray, dissolved continental components and by products generated by anthropogenic activity such as power plants, smoke stacks, emanations from various industries, etc. Herut (1992) analyzed a large number of rain water samples from stations spread all over the country and showed that in many areas, the Na/Cl ratio values in rain water were similar to those characterizing sea water (0.86). Rain water with lower Na/Cl ratios was found in, and close to desert areas and was caused by the evaporation of sea spray and by the separation of minute halite crystals. Rain water with Na/Cl close to 1 was formed by dissolution of halite particles in the atmosphere. Rosenthal (1987) observed enrichment of Ca,  $SO_4$  and HCO<sub>3</sub> in rain water relative to sea water (these ionic relations were normalized against the Cl content assuming that its origin was exclusively from sea spray). This relative enrichment seems to be caused by dust containing calcite and gypsum and by its dissolution by atmospheric moisture. In the atmosphere, carbonate-rich dust neutralizes sulfuric acid generated by various anthropogenic sources. In areas in which dust carries insufficient amounts of carbonate particles (such as over the Golan Heights) rain water is acidic (pH < 5.6, Herut, 1992).

The chemical composition of groundwater is influenced by the chemical interaction

between rain water, soil and country rocks taking place both in the vadose and in the saturated zone. The increase in  $CO_2$  in soil because of biogenic activity enhances dissolution of  $CaCO_3$  with an increase in Ca and  $HCO_3$  content in groundwater flowing through carbonate aquifers. In dolomitic aquifers, the input of Mg increases the Mg/Ca ratio in water to values close to 1. Interaction with clay minerals will cause exchange of cations adsorbed on clays. Mercado (1980) suggested that dissolution of  $CaCO_3$  might raise the Ca content in water which is further exchanged with Na ions, thus causing an increase in Na/Cl ratios. Bar (1983) found that rain water interacting with argillaceous rocks produces groundwater with Na/Cl greater than 1. Vengosh and Starinsky (1992) suggested that Na and Mg ions could be contributed to groundwater by diagenesis of calcium carbonate. Diagenetic alteration of biogenic Na-Mg rich aragonite to low Na-Mg calcite could contribute these ions to groundwater.

# 3. Chemical parameters for identification of various types of saline water and for the estimation of salinization potentials

The geochemical processes discussed above contribute to the formation of saline water which may be identified by typical chemical composition and by characteristic ionic ratios. Piper et al. (1953) and Schoeller (1956) were the first to point out the significance of such ratios for the investigation of brine and formation water. White (1960) published a series of median ratios which he believed to be characteristic of water derived from aquifers of different lithologies or for water formed by specific hydrogeochemical processes.

Hydrogeochemical parameters commonly used for identification of groundwater bodies will be further reviewed and briefly discussed here. It should be emphasized that the identification of salinization processes should be based on several such parameters and must be confirmed by multiple hydrogeochemical indicators such as ionic ratios, stable and non-stable isotopes, etc. The professional literature suggests a significant number of chemical and isotopic parameters which can facilitate the identification of water bodies. Although the authors made use of a wide spectrum of such parameters, only those having a significant bearing on the overall interpretation of the hydrochemical model of the country are discussed in detail below.

### 3.1. Na/Cl

Groundwater flowing through the normal and active hydrological cycle is characterized by ratios in the 0.86–1.0 range (0.86 is the ratio for sea water) (Schoeller, 1956; Hem, 1985). Herut (1992) showed that Na/Cl ratios in rain water collected at various locations in Israel are identical to that of sea water. Mercado (1989) suggested that reactions with clays might lead to the exchange of Na for Ca and/or Mg ions. By such processes, groundwater may be either enriched or impoverished in Na with Na/Cl ratio changing accordingly. On the other hand Vengosh and Starinsky (1992) argued that high Na/Cl ratio values measured in fresh water flowing through the Coastal aquifer of Israel could be influenced by diagenesis of carbonate minerals. High ratio values could also be the result of fresh groundwater flowing through igneous or volcanic rocks enriched in sodic feldspars (White 1957; Schoeller, 1977). In salinization processes, the Na/Cl ratio value may indicate the chemical composition of the saline end member. As previously mentioned, evaporation of sea water and precipitation of halite cause the lowering of the Na/Cl ratio value in the residual brine. On the other hand, low Na/Cl ratio values could be caused by dissolution of bitterns such as MgCl<sub>2</sub>, MgSO<sub>4</sub> and KCl salts. Na/Cl values of = 1 may be indicative of halite dissolution.

## 3.2. Mg/Ca

For water flowing through chalk or limestone aquifers this ratio is normally in the 0.5-0.7 range (Schoeller, 1956). Ratios in the 0.7-1.1 range are commonly associated with dolomite aquifers (Hsu, 1963). In fresh water, Mg/Ca ratio values greater than 1 could be the result of water interacting with Mg-rich silicate country rock such as volcanics, with Mg being derived from olivine (Schoeller, 1956; Hem, 1985). Low Mg/Ca ratio values (less than 0.5) could be the result of CaCO<sub>3</sub> or gypsum solution.

In salinization processes the Mg/Ca ratio may reflect the chemical composition of the brine end member of the saline water dominating this process. Evaporated sea water is characterized by high Mg/Ca ratio values (caused by the elimination of Ca ions through the precipitation of gypsum). In brine involved in dolomitization, the Mg/Ca ratios are much lower.

### 3.3. K/Cl

The K/Cl ratio in fresh groundwater is usually similar to sea water values (0.018). When adsorption on clay particles is involved, lower K/Cl ratios are encountered. Sea water evaporated up to the degree of carnallite saturation is characterized by high K/Cl ratio values (conservative increase being a result of sea water evaporation). In contrast, in evaporated sea water saturated for carnallite and in brines related to diagenetic processes, the K/Cl ratio values are much lower because of elimination of K by coprecipitation and adsorption. Dissolution of bitterns such as carnallite result in high K/Cl ratios of 0.3.

## 3.4. HCO<sub>3</sub>/Cl

In recharge areas of carbonate aquifers and along their upper flow courses, the anion content of fresh groundwater is primarily dominated by  $HCO_3$ . Its concentration usually increases downflow until the solubility product of  $CaCO_3$  is attained. At this point the increase in the  $HCO_3$  concentration levels off (Schoeller, 1956). Simultaneously, as a result of dissolution of soluble salts occurring in the surrounding aquifer rocks, the concentration of Cl increases throughout the flow course of the aquifer and towards its natural outlets. This leads to a gradual decrease in  $HCO_3/Cl$  ratio values with Cl gradually becoming the dominant anion. Thus, changes in the

 $HCO_3/Cl$  ratio may be indicative of the distance of a given water sample from its initial recharge area. According to Schoeller (1977), in groundwater flowing through silicate rocks such as sandstone, the  $HCO_3$  content is about half the value encountered in carbonates. This is clearly because of lack of supply of this anion from the surrounding aquifer rocks, and has direct bearing on the  $HCO_3/Cl$  ratio value characterizing water flowing through such rocks. In salinization processes the  $HCO_3/Cl$  ratio is negatively related to the increase in the Cl content. Exceptionally high ratio values (greater than 5–6) may indicate the occurrence of  $CO_2$ , which may be related to volcanic activity (White, 1957).

### 3.5. Br/Cl

In fresh groundwater related to the active hydrological cycle, the Br/Cl ratio is usually similar to the marine value  $(1.56 \times 10^{-3} \text{ or } \text{Cl/Br} = 286)$ . In salinization processes the Br/Cl ratio usually reflects the chemical composition of the saline end member. Generally, in fresh water Br concentrations are much lower than in brine. Br is a conservative element which does not participate in secondary reactions with rocks. Therefore the Br/Cl ratio is a particularly sensitive and reliable parameter for the identification of salinization sources. Because of these conservative features, in evaporating water the Br/Cl ratio increases in positive correlation with the degree of evaporation and is not influenced by diagenetic processes. Hence, evaporated sea water or brines derived from such processes are characterized by high Br/Cl ratios such as  $2 \times 10^{-3} - 1.2 \times 10^{-2}$  (or Cl/Br less than 150-50) such as the Dead Sea brine (Behne, 1953; Valyashko, 1958; Starinsky, 1974; Hardie, 1984; McCaffrey et al., 1987). In sabkhas which are seasonally flooded by fresh water from intermittent wadis, previously precipitated salt is dissolved and carried into the main water body (Levy, 1972). The evaporation of this water body will produce a brine with low Na/Cl ratio but with a Br/Cl ratio which is lower than that of normal evaporated sea water. On the other hand, water dissolving halite (having a relatively low Br content) will have particularly low Br/Cl ratio  $(2 \times 10^{-4} \text{ or } Cr/Br = 500-3000)$ . Such ratio values were found in brines which were in direct contact with evaporites (Behne, 1953; Valyashko, 1958; Schoeller, 1977; Hardie, 1984)

3.6.  $\mathbf{Q} = Ca/(SO_4 + HCO_3)$ 

In groundwater flowing in calcareous aquifers these ratios are usually in the range of 0.6-0.8, slightly higher than the ratio value for sea water (0.34) (Starinsky, 1974; Rosenthal, 1980). During the evaporation of sea water the low values (less than 1.0) of this ratio are preserved. However, during diagenetic processes involving brines, SO<sub>4</sub> reduction and dolomitization may occur. The residual brine will therefore be enriched in Ca and impoverished in SO<sub>4</sub>, resulting in high *Q*-ratio values. Brines characterized by *Q* greater than 1 are defined as Ca-chloride brines (Starinsky, 1974). Increase in the *Q*-ratio values during salinization processes may therefore be indicative of the occurrrence of Ca-chloride brines. In such cases, increase in the salinity level will usually be accompanied by a drop in Na/Cl and Mg/Ca and by an increase in the Br/Cl ratio values. Such cases are characterized by a significant positive correlation between the Q-ratio, the Cl content and the Br/Cl ratio values, and by negative correlation between Q and Na/Cl and Mg/Ca ratios. Upward trends in the course of periodic monitoring of these Q-ratios indicate salinization processes and are warning signals of the presence of Ca-chloride brines (Rosenthal, 1988c).

### 3.7. O and H stable isotopes

Stable isotopes of oxygen and hydrogen in groundwater of an active hydrological cycle derive from and reflect the initial isotopic composition of the recharging rainwater. Within the coordinate system of  $\delta^{18}$ O vs.  $\delta$ D it is possible to discern a meteoric line, the slope of which is characteristic of a certain hydrological system. Gat et al. (1969) found that in various groundwater bodies in Israel  $\delta^{18}$ O vs.  $\delta$ D relationships fit the trace of the recent meteoric line for the Eastern Mediterranean area. On the other hand there are several water sources in which  $\delta^{18}$ O vs. $\delta$ D ratios plot below that meteoric line. Such observations were made for saline water in the Timna area, the Kurnub Group aquifer and elsewhere (Rosenthal et al., 1990). The drop in  $\delta^{18}$ O values was interpreted by various authors (Gat et al., 1969; Issar et al., 1972) as supporting evidence for old meteoric precipitation which occurred during glacial times (18 000 BP). Gat (1975) argued that the abundance of <sup>18</sup>O and deuterium in saline water may be indicative of the origin of their salinity. Because <sup>18</sup>O is enriched during evaporation of sea water, the distinctive isotope composition of sea water or of evaporated sea water can be traced to its mixture with meteoric water.

### 3.8. Boron isotope geochemistry

Boron has two stable isotopes, <sup>11</sup>B (80%) and <sup>10</sup>B (20%). The mass difference between the two isotopes and the high reactivity of boron enhance its isotopic fractionation and contribute to a wide range of  $\delta^{11}$ B (90‰ relative to the international standard). <sup>11</sup>B is enriched in sea water ( $\delta^{11}$ B = 39‰) as against  $\delta^{11}$ B almost 0‰ in rocks. Following adsorption on clay minerals, precipitation of CaCO<sub>3</sub> and of evaporite minerals during sea water evaporation, the liquid phase is enriched in <sup>11</sup>B while <sup>10</sup>B is selectively removed to the solid precipitate (Spivak et al., 1987; Vengosh, 1992a; Vengosh et al., 1991, 1992).

Because of the great variability of  $\delta^{11}$ B values in nature, the composition of boron isotopes could be used as an identifying parameter for salts dissolved in groundwater enabling identification of the salinization processes involved. It enables differentiation between salinization process resulting from sea water encroachment ( $\delta^{11}$ B = 39‰), penetration of Ca-chloride brines such as the Dead Sea ( $\delta^{11}$ B greater than 39‰), or the dissolution of salts ( $\delta$ B less than 39‰). High concentrations of B in sewage fluids may suggest that B anomalies in groundwater can be indicative of anthropogenic sources.

### 3.9. Definition of salinization potential

The term 'salinization potential' is defined here as the maximal possible level of salinization which could be attained by a certain groundwater body. Hydrogeochemical analysis of water in the process of salinization and overall consideration of all previously mentioned parameters enable identification of the dominant salinization factor locally or regionally determining the quality of a given groundwater body. This enables a quantitative estimation of the salinization potential. By introducing the representative chemical composition and the ionic ratios of the saline component into mixing equations, it is possible to calculate the final concentration of the saline end member which may have generated the salinization process in question. Thus, by assuming that the Na/Cl ratio of a water body undergoing salinization is known, the Na and Cl concentrations of the saline end member can be derived. Assuming Na and Cl concentrations of a water body in course of salinization (Na<sub>mix</sub>; Cl<sub>mix</sub>) are the mixing products of fresh water (Na<sub>f</sub>; Cl<sub>f</sub>) with an unknown saline component, the mixing equation will be

$$Cl_{f}F + Cl_{salt}(1 - F) = Cl_{mix}$$

in which

 $Cl_{salt} = Cl$  concentration (in mmol) of the saline end member, and F = fraction of fresh water component. Similarly

$$Na_{f}F + Na_{salt}(1 - F) = Na_{mix}$$

The two mixing equations are solved by assuming that  $x = Na/Cl_{salt}$ . x is given by the assumed range of Na/Cl ratio values observed in saline water, derived by the synthesis of other geochemical parameters (as mentioned above).

### 4. The occurrence and characteristic geochemical features of saline water in Israel

#### 4.1. Saline water in the Kurnub Group in southern Israel (Table 1; Fig. 5)

The Kurnub Group aquifer (Nubian Sandstone) spreads fanwise from the Gulf of Suez around the northern and eastern margins of the igneous massif of Sinai and reaches to the Northern Negev, the Dead Sea and the Gulf of Elat within the Rift Valley. This regional aquifer stands out as being an almost non-rechargeable reservoir of ancient water (up to 30 000 years BP) (Issar et al., 1972; Galai, 1983; Rosenthal et al., 1992). The estimated volume of paleowater stored in the aquifer is of the order of several billion cubic meters. (Issar et al., 1972; Rosenthal et al., 1992). The water flows from the Sinai highlands in four main directions: to the central and northern Negev, to the Dead Sea, the Gulf of Elat and westward to the Gulf of Suez.

Hydrochemical investigations were carried out in various portions of this regional aquifer (Issar et al., 1972; Kroitoru, 1980; Issar, 1981; Mercado and Ben Zvi, 1982;

Chemical composition of represents	ative salir	ie groun	dwater i	n Israel	(concentr	ations i	n mg l <sup>-1</sup>	ionic ra	tios in m	eq l <sup>-1</sup> ).				
	Ca	Mg	Na	¥	cı	SO4	нсо,	Br	TDS	Na/Cl	6	Br/Cl	Ca/Mg	618O
Mediterranean sea water	472	1 487	12 772	479	22 900	3110	165	76	41 461	0.86	0.35	$1.5  imes 10^{-3}$	0.19	1.6
I. Nubian Sandstone in Sinai and Negev		ě		2				( (		0	5	• • 	Ċ	
Nakhel I	116	92	222	21	355	485	220	0.8	1512	0.96	0.42	$1.0 \times 10^{-5}$	0.//0	
Hilal	2/2	8	956	ć	404 404	585 201	567		59/4	10.1	0.60		1.69 2 2 2	
Bir lamade	317	63	4/0	62	861	90/	204		2 644	0.84	0.88		3.06	
Yorqe'am 2	250	69	429		663	354	299		2 064	1.00	1.02		2.20	-5.46
Tamar 3	961	30	401	21	600	414	305	1.4	1 968	1.03	0.72	$1.0 \times 10^{-3}$	3.91	
Admon 2	233	103	1341	<i>LT</i>	2 0 6 9	895	182	6.5	4 907	1.00	0.54	$1.4 \times 10^{-3}$	1.37	
2. Arava Valley														
Arava 1	52 160	9 744	54319		208 660	122	60		325 065	0.40	740.24		3.25	2.36
Neogene-Quaternary aquifers														
Hazeva 1	192	101	335	18	535	674	223		2 078	0.97	0.54		1.15	-4.77
Hazeva 4	437	222	616	34	1 552	1018	156		4035	0.61	0.92		1.20	-4.85
Zofar T/18	1 000	668	1480	10	4650	1950	161		6166	0.49	1.16		0.91	
Deep-seated (Kurnub) aquifer														
En Ofarim 5 (Hazeva)	209	73	365	23	687	445	264		2066	0.82	0.77		1.74	-6.61
Paran 20	234	16	306	35	601	620	219		2 106	0.79	0.71		1.56	-7.79
Timna														
Timna (D-680)	3 130	30	2 580	18	9 270	641	12	92	15773	0.43	11.55	$4.4 \times 10^{-3}$	63.38	-8.4
Timna (D-682)	2 770	24	2350	18	8 180	717	12	86	14 157	0.44	9.15	$4.7 \times 10^{-3}$	70.12	-8.2
Timna (D-683)	1 530	24	1 525	14	4370	1 140	12	34	8 649	0.54	3.19	$3.5 \times 10^{-3}$	38.73	-7.85
3. Central and Northern Negev														
Nitzana 1	264	III	1172	27	1880	600	262	7	4 323	0.96	0.79	$1.7 \times 10^{-3}$	1.44	-5.8
Mashabei Sade I	167	83	568	16	1/6	409	292	4	2510	0.90	0.63	$1.6 \times 10^{-3}$	1.22	-5.6
Mishmar Hanegev 1	125	94	1470	9	2 251	391	405	7.8	4750	1.01	0.42	$1.5 \times 10^{-3}$	0.81	
4. Dead Sea														
Numuo Oroup (Nuotan Sandstone) Nahal Ze'elim 1	641	203	0561		1858	2 296	284	-	6512	1 02	0.61	$3.3 \times 10^{-3}$	1 97	
Mezada 1	845	106	1356		1914	2436	317		6974	1.09	0.76		4.83	
Quaternary aquifer														
Nahal Ze'elim 12	56 0 56	8 141	19 800		66 125	1 971	152		152 245	0.46	64.35		4.18	
Kane-Samar (T/1)	330	565	724	108	3 190	76	296		5 289	0.35	2.56		0.35	
Kane-Samar (T/3)	225	4 480	5750	842	25985	216	207		37 705	0.34	1.43		0.03	

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Table 1

Thermal springs En Feshcha (Zukim springs) Zohar springs Yesha springs Dead Sea	140 11400 10300 17180	155 22 500 18 700 42 430	335 20 500 27 800 39 700	23 2 575 3 500 7 590	1 080 119 900 117 530 219 250	50 1551 1060 420	275 130 142 220	20 2950 2206 5270	2 078 1 80 806 1 81 238 332 060	0.48 0.26 0.36 0.28	1.26 16.11 21.10 69.52	$\begin{array}{c} 8.2 \times 10^{-3} \\ 1.1 \times 10^{-3} \\ 8.3 \times 10^{-3} \\ 1.1 \times 10^{-3} \end{array}$	0.55 0.31 0.33 0.25	-5.18 -2.05 -1.95 4.5
<ol> <li>Eastern margin of Coastal Aquifer Na'an-Marqeret Batya area Na'an-Givton spring Na'an-Ganne Hadar 7 Naan 5 Petah-Tiqva-Magdiel-Kfar Sava area Magdiel Kefar Saba-Ramat Hadar</li> </ol>	240 220 201 201	156 60 53 53	641 137 366 135 200	<u>ه م</u> م <u>ت</u> ا	1 290 440 1 073 395 339	321 130 206 58 156	598 311 281 366 425	NU4 -0	3251 1311 2286 1214 1374	0.77 0.48 0.53 0.53 0.53	0.73 1.41 1.24 1.39 0.98	1.6 × 10 <sup>-3</sup> 1.5 × 10 <sup>-3</sup> 1.4 × 10 <sup>-3</sup> 1.1 × 10 <sup>-3</sup> 2.0 × 10 <sup>-3</sup>	0.93 2.23 1.01 2.30 2.30	
<ol> <li>Western margin of Coastal Aquifer (the Tel Aviv-Hilton North Ashqelon 6/C Giva't Olga 51/B Gaza-Khan Yunis 5/A</li> </ol>	: interface 463 3 292 1 088 2 302	<i>zone)</i> 1239 34 540 3378	10 600 8 915 5 354 33 188	392 135 174	19 812 18 257 32 960 60 262	2 600 1 049 3 160 11 165	232 32 152	62 111 210	35338 31776 43387 110657	0.83 0.75 0.25 0.85	0.40 7.36 0.49	$\begin{array}{c} 1.5 \times 10^{-3} \\ 1.5 \times 10^{-3} \\ 1.5 \times 10^{-3} \end{array}$	0.23 58.82 1.22 0.41	
8. Salt plume in Coastal Aquifer Be'er Tuvia region Be'er Tuvia 5 Be'er Tuvia 6 Be'er Tuvia 7	107 92 102	79 78 65	330 350 250	44 K 8.	649 698 533	78 105 55	260 151 260	1.8 2 1.6	1 508 1 480 1 270	0.78 0.77 0.72	0.91 0.99 0.94	$\begin{array}{c} 1.2 \times 10^{-3} \\ 1.3 \times 10^{-3} \\ 1.3 \times 10^{-3} \end{array}$	0.82 0.72 0.95	
<ol> <li>Mehola, Bet Shean and Harod Valleys Bet Shean valley-Haim spring Mehola 5 Devora 2A end member Neve Ur T/I end member</li> </ol>	194 480 34 820 1 598	81 92 1950 2018	489 1 228 40 200 9 057	11.7 42.4 400	1 062 2 698 129 393 22 054	115 219 178 864	384 220 171 168	7.2 24 1740	2 344 5 003 208 852 35 881	0.71 0.70 0.48 0.63	1.12 2.94 267.37 3.85	$\begin{array}{c} 3.0 \times 10^{-3} \\ 3.9 \times 10^{-3} \\ 6.0 \times 10^{-3} \end{array}$	1.46 3.17 10.85 0.48	
10. Cenomanian (Yargon-Taninim) Aquifer-Northern part Menashe T/3 Taninim Deep Nethania	800 1 280 1 042	1 230 1 030 1 091	12 000 9 400 10 800	390 232 360	21 200 18 300 20 496	2 980 1 800 2 560	165 189 193	75	38 840 32 231 36 542	0.87 0.79 0.81	0.62 1.58 0.92	$1.6 \times 10^{-3}$	0.40 0.75 0.58	
11. Sea of Galilee thermal springs Tiberias Hot Spring 'En Gofra Hammat Gader	3 460 210 161	651 235 42	6 990 1 330 228	350 75 19	18 400 2 980 497	750 225 167	170 320 316	250 36	31 021 5 411 1 430	0.59 0.69 0.71	9.40 1/06 0.93	$6.0 \times 10^{-3}$ $5.4 \times 10^{-3}$	3.23 0.54 2.33	-3.1 4.49 -6.5



Fig. 5. Saline water and inferred flow directions in the Kurnub Group aquifer in Israel.

Rosenthal et al., 1990; Yechieli et al., 1992). Several common hydrochemical features should be pointed out (Table 1):

1. Cl content is in the 500–1000 mg  $l^{-1}$  range with the exception of the central Negev (1450–2000 mg  $l^{-1}$  range).

2. The water is thermal with temperatures in the 38-43°C range.

3. The concentration of Na equals that of Cl and the Na/Cl ratio approaches 1.

4. The concentration of SO<sub>4</sub> is relatively high with SO<sub>4</sub>/Cl ratios of 0.5-1.0.

5. Br/Cl ratios are lower than that of modern sea water  $(1.0 \times 10^{-3} \text{ as against } 1.5 \times 10^{-3})$ .

6. The <sup>18</sup>O/<sup>16</sup>O ratio ( $\delta^{18}O = -7\%$ ) is lower than that of modern meteoric water (Issar et al., 1972).

7. In most parts of the aquifer relatively high concentrations of  $H_2S$  (1-4 mg l<sup>-1</sup>) were encountered.

8. The water is characterized by high concentrations of iron (1.7–16 mg l<sup>-1</sup>, Eckstein, 1975) and manganese ( $70 \pm 9.5 \ \mu g l^{-1}$ ) which exceed by a whole order of magnitude normal concentrations in groundwater (Arad et al., 1984).

9. In most parts of the aquifer the sequence of ions is Na > Ca > Mg;  $Cl > SO_4 > HCO_3$ .

Close to natural replenishment areas in Sinai and near the natural outlets of this aquifer in the Dead Sea–Arava Rift Valley, the chemical composition of this water changes (Table 1). In replenishment areas in Central Sinai (in boreholes Bir Tamade and Nakhel 1 Deep), the Cl content is low (340–800 mg l<sup>-1</sup>) and Na/Cl ratio values resemble those recorded in rain water (close to 0.87; Mercado and Ben Zvi, 1982). At aquifer outlets to the Rift Valley, groundwater salinity increases as a result of mixing between Kurnub Group water with Ca-chloride brine known to occur in the Rift (Starinsky, 1974; Ilani et al., 1988; Rosenthal, 1988b; Yechieli et al., 1992). In these areas the Cl content reaches 4500 mg l<sup>-1</sup> and Ca becomes the leading cation with Ca > Mg > Na and Cl > SO<sub>4</sub> > HCO<sub>3</sub>. The Na/Cl ratio drops to 0.57, Mg/Ca to 0.33, Br/Cl increases to  $0.15 \times 10^{-2}$  and Q increases to values as high as 40.

# 4.2. Saline water in the Arava Rift Valley (Table 1; Fig. 6)

According to Rosenthal (1985) and Yechieli et al. (1992), groundwater in the northern Arava Valley, south of the Dead Sea is characterized by Cl concentrations of up to  $4700 \text{ mg l}^{-1}$ . This groundwater originates in two major aquifers. One of them occurs at relatively shallow depths and is composed of clastics and carbonates of the Neogene–Recent Hazeva and Arava Fill formations. It is recharged by rain water and flash floods. The other aguifer occurs dominantly within a depth range of 700-1500 m and is composed of Kurnub Group (Nubian Sandstone) sand and sandstone. This water is ancient and non-renewable. Both water bodies are similar in their chemical composition which is characterized by Ca > Mg > Na and  $Cl > SO_4 > HCO_3$ . The chemical evolution of these two groundwater bodies is the result of two processes (Yechieli et al., 1992): (a) dissolution of MgSO<sub>4</sub> evaporites as reflected by excess Mg and SO<sub>4</sub>. The residual salts precipitated as the result of recent or semirecent fractional evaporation of rain or floodwater under arid conditions; (b) mixing to various degrees of previously mentioned aquifer water with Ca-chloride brines which occur throughout the sedimentary succession in the Arava Rift Valley area (Starinsky, 1974; Rosenthal, 1985). Such Ca-chloride brines with a Cl content of  $50-270 \text{ gl}^{-1}$  were encountered in various boreholes in the study area (Arava 1, Hemar 1, Lot 1 and Sdom 2: Bentor, 1960; Starinsky, 1974). These brines are characterized by very low Na/Cl (0.1) and by high  $(5.9 \times 10^{-3})$  Br/Cl ratios. The typical ionic sequence of these brines is Ca > Mg > Na and  $Cl > SO_4 > HCO_3$ . It is assumed that these are residual brines which were formed by evaporation of a lacustrine water body precipitating halite, in a manner similar to the evolution of the Neogene Sdom Formation (Zak, 1967).



Fig. 6. Saline water in the Arava Rift Valley.

Saline waters were encountered as seepages in the Timna copper mine and in adjacent shallow boreholes drilled into the Cambrian Shlomo and Shehoret formations (Starinsky, 1974; Beyth et al., 1981). They are characterized by Cl concentrations in the 2000–9000 mg l<sup>-1</sup> range and by Na/Cl ratio of 0.4-0.6 and a Br/Cl ratio of  $4 \times 10^{-3}$ . Their ionic content is Ca > Na > Mg and Cl > SO<sub>4</sub> > HCO<sub>3</sub>. These parameters resemble those determined for Ca-chloride water found elsewhere in the Rift though the following differences were observed: (a) high Ca/Mg ratio values (50–70) indicating high temperature reaction with basalts; (b) high SO<sub>4</sub>/Cl values (0.02–0.96) indicating dissolution of gypsum; (c) low <sup>87</sup>Sr/<sup>86</sup>Sr values (0.706) indicating interaction of brines with basalts of low <sup>87</sup>Sr/<sup>86</sup>Sr values (Starinsky and Bielsky, 1981; Beyth et al., 1981); (d) low values of the <sup>18</sup>O/<sup>16</sup>O ratio ( $\delta^{18}O = (-8)$ -

(-6)‰) indicating dilution of the Ca-chloride brines by old meteoric water (Gat and Galai, 1982); (e) low <sup>11</sup>B/<sup>10</sup>B ratio ( $\delta^{11}B = 14 - 26$ ‰) resulting from the interaction of water with rocks characterized by low <sup>11</sup>B/<sup>10</sup>B values (Vengosh, 1990).

# 4.3. Saline water in the central and northern Negev and in the Beer Sheva area (Table 1; Fig. 7)

The ever increasing salinity of groundwater in the well field of Beer Sheva (8 mg  $1^{-1}$  Cl per year<sup>-1</sup>) and the high salinities observed in wells drilled in other parts of the Judea Group aquifer south of this city (Ashalim 1 and 2, Mashabei Sade 2, Shezaf 1) became intriguing phenomena monitored over a long period of time (Rosenthal et al.,



Fig. 7. Saline water in the central and northern Negev and in the Beer Sheva area.

1991; Weinberger et al., 1992). Two sources of groundwater salinization were identified: (a) saline water flowing in the overlying Hashepela Group with Cl content of 3450 mg  $1^{-1}$  (well Mishmar Hanegev) and chemical composition similar to that of diluted sea water. This water percolates downwards along poorly cemented well casings, contaminating fresh water flowing into the underlying Judea Group aquifer; (b) saline water of the underlying Kurnub Group (Kronfeld et al., 1979; Weinberger et al., 1992). While surveying U-concentrations and U-activity ratios in groundwater of the Negev, Kronfeld et al. (1979) observed that the saline water sampled in the study area (659–1129 mg  $1^{-1}$  Cl) stands out in its low U-concentrations (0.24–0.64  $\mu$ g l<sup>-1</sup>). These concentrations are 1 order of magnitude lower than all other groundwater flowing in the Judea Group of the study area. Moreover, this groundwater is characterized by low thermal activities  $(32-39^{\circ}C)$  and relatively high  $(1-3 \text{ mg } 1^{-1})$  concentrations of Fe. Such an assembly of phenomena is usually typical of paleowater flowing in the Kurnub Group aquifer (Nubian Sandstoine) (Kronfeld and Rosenthal, 1987). This was also supported by hydrochemical evidence as the chemical composition of groundwater from the saline source plots on a perfect mixing line joining fresh water (such as that naturally recharged to the Judea Group aquifer) and typical Kurnub Group paleowater (Rosenthal and Flexer, 1988).

# 4.4. Saline water along the western shores of the Dead Sea (Table 1; Fig. 8)

Along the western shore of the Dead Sea, saline water was detected in wells springs and seepages. It is derived from three main aquifers:

(a) The 400 m thick Kurnub Group aquifer which is buried several hundreds meters beneath the limestone–dolomite aquifer of the Judea Group (Rosenthal et al., 1978; Movshovitz et al., 1984). Salinity increases from the Tamar well field in the south (750 mg  $1^{-1}$  Cl) to about 5000 mg  $1^{-1}$  Cl in the Amiaz wells located 20 km northward. The chemical composition of water with ionic content of Na > Ca > Mg and Cl > SO<sub>4</sub> > HCO<sub>3</sub>, resembles that found in the Negev and in Sinai. Further northward (in the Yeelim area) the Cl content increases to 18 600 mg  $1^{-1}$  and the chemical composition changes radically. The value of the Na/Cl ratio drops to 0.37 whereas Q is greater than 1. These chemical changes indicate mixing with Ca-chloride brines which are typical of the Rift Valley and of the Dead Sea area.

(b) The limestone and dolomite Judea Group aquifer. Its total thickness is 300-500 m of which 150-200 m are aquiferous formations. Arad (1964) assumed that groundwater flowing in this aquifer is recharged by rain falling on the eastern flanks of the Judea Mountains. On the other hand, Gilead (1980) and Rosenthal and Flexer (1988) found that water flowing in the Judea Group aquifer actually originates from the Kurnub Group. Its paleowater flows laterally into downfaulted blocks made up of Judea Group beds. The Cl content of groundwater flowing in the Judea Group aquifer is usually higher than in the Kurnub Group (1600–1800 mg l<sup>-1</sup> (for Tamar wells in the south and up to 7500 mg l<sup>-1</sup> in the Amiaz well field). Further northward in the Yeelim wells chlorinity values rise as high as 60 000 mg l<sup>-1</sup>. In the latter case, the water is characterized by low (0.33) Na/Cl and SO<sub>4</sub>/Cl ratio values and by *Q* approaching greater than 12. It resembles chemically the previously mentioned

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Fig. 8. Saline water along the western shores of the Dead Sea.

brines commonly found in the Rift. This indicates again either penetration of Dead Sea water or of ancient connate Ca-chloride brine into the Judea Group aquifer (Y. Yechieli, personal communication, 1992).

(c) The Arava Fill aquifer made up of interbedded marl, chalk and of gravel. In areas close to the fault escarpment delineating the western margins of the Rift, this aquifer consists of coarse clastics deposited as terraces or as alluvial fans spreading out at the outlets of wadis into the Rift Valley. The aquiferous horizons total a thickness of about 100 m. This aquifer is mainly recharged by flash floods in the wadis and by springs and seepages emerging along the Dead Sea shore. The Cl content of this water varies within a wide range, i.e. between 1500 mg l<sup>-1</sup> near the southern extremity of the Dead Sea to over 26 000 mg l<sup>-1</sup> at Mitzpe Shalem (Baida

and Goldschtoff, 1972). The water is characterized by low Na/Cl (0.34) and by high Q-ratio (12) values and ionic content of Mg > Na > Ca and Cl > SO<sub>4</sub> > HCO<sub>3</sub>.

Two additional occurrences of saline water and brines characterize the study area:

(1) Water of 1700–40 100 mg.Cl1 which flows out of the Feshkha (Einot Zuqim) springs at the northwestern end of the Dead Sea. This water is of low temperature  $(26-30^{\circ}C)$  with Na/Cl of 0.33–0.45, Br/Cl in the  $7.5-9.9 \times 10^{-3}$  range and a high radon content (10 000 pcl<sup>-1</sup> (Mazor and Molcho, 1972; Steinitz et al., 1992). Its ionic content is dominated as in the Arava aquifer water by Mg and Cl, i.e. Mg > Na > Ca and Cl > SO<sub>4</sub> > HCO<sub>3</sub>. This water is related to the Tiberias–Noit water group assembling saline water occurring in the Rift Valley, between the Sea of Galilee in the north and the Noit spring emerging on the fault escarpment overlooking the Dead Sea in the south (Mazor et al., 1969b, 1980). These authors suggested that the chemical composition of this water group developed by past inflow (during earlier geological times) of Mediterranean Sea water into the Rift, its subsequent dilution by fresh water and further interaction with surrounding country rocks.

(2) Thermal, saline springs (Hammei Zohar, Hammei Mazor and Hammei Yesha). These springs emerge along the western shore of the Dead Sea. Their Cl content is in the 30 000–130 000 mg l<sup>-1</sup> range with temperatures reaching 42.5°C. The water is characterized by Na/Cl of 0.3–0.4, Br/Cl of 2–9.9 × 10<sup>-3</sup>, high H<sub>2</sub>S content (up to 48 mg l<sup>-1</sup>) and Mg > Na > Ca and Cl > SO<sub>4</sub> > HCO<sub>3</sub>. Bentor (1960), Arad (1964) and Mazor et al. (1969) suggested that this spring water is the result of mixing between Dead Sea water either with fresh or with Tiberias–Noit water deriving from adjacent aquifers. On the other hand, Starinsky (1974) proposed that the salts dissolved in Dead Sea water derived from the springs which were already flowing during geological times. Considering the variations of boron and of its isotopes, Vengosh et al. (1991) confirmed Starinsky's views and excluded the possibility that the waters of hot springs were derived from dilution of the Dead Sea. The low  $\delta$ B values (52–55‰) and high (26) B/Li ratio relative to Dead Sea water (B/Li = 20;  $\delta^{11}$ B = 57‰), indicated adsorption and isotopic fractionation in which <sup>10</sup>B is selectively adsorbed by clay minerals and <sup>11</sup>B is enriched in the residual brine.

# 4.5. Saline water along the eastern margins of the Coastal Plain aquifer: influence of the Hashepela Group aquitard in the Na'an-Mazqeret Batya area (Table 1; Fig. 9)

Rosenthal et al. (1992) found that large amounts of salt have been added yearly to the central portion of the Coastal Plain aquifer along its eastern boundary which is in direct contact with a syncline made up of Eocene chalk and marl of the Hashepela Group. In wells penetrating into the Coastal Plain aquifer and located in the Na'an– Mazqeret Batya area, Cl content of groundwater is in the 1050–1100 mg  $l^{-1}$  range. Because of the high tritium level, Rosenthal et al. (1992) suggested that this water is part of the contemporary and active hydrological cycle and is in no way related to an ancient, deep seated and connate brine. Nissim (1991) reported the occurrence of similar water in northwestern Negev where the Cl content was lower (approaching 600 mg  $l^{-1}$ ), with Na/Cl and Ca/SO<sub>4</sub> approaching 1, i.e. indicating dissolution of halite and of gypsum. The water in the Na'an–Mazqeret Batya area is characterized



Fig. 9. Saline water along the eastern margin of the Coastal Plain aquifer.

by Br/Cl ratios of  $1.5 \times 10^{-3}$  which are usually typical of water either in direct contact with sea water (Behne, 1953) or make up part of an active hydrological cycle (rain water having a marine Br/Cl ratio). Such ratios exclude the possibility that salts dissolved in this water are derived from Ca-chloride brines such as the brines commonly encountered in the Dead Sea Rift Valley (Starinsky, 1974; Rosenthal, 1988b). According to Rosenthal et al. (1992) the high salinity encountered along the eastern margins of the Coastal Plain aquifer is caused by dissolution of salts lining fissures and faults cutting through rocks of the Hashepela aquitard which are exposed to the east and upstream from the Coastal Plain aquifer and are in direct hydraulic contact with it. These authors showed that in the Hashepela aquitard groundwater may circulate only through solution channels which are usually lined by crusts of halite, which accumulated there during many cycles of percolation and subsequent evacuation by capillary action. Magaritz et al. (1988) demonstrated that these soluble salts accumulated over 9000-10 000 years. During the last half century, intensive agricultural activity enhanced flushing and migration of solutes from rock surfaces and fissures into the subsurface. The ongoing lowering of water in the Coastal Plain aquifer facilitated stronger flux of solutes from the Hashepela aquitard into the subsurface and groundwater of the Coastal Plain aquifer (Rosenthal et al., 1992).

# 4.6. Saline water along the eastern margins of the Coastal Plain aquifer: Petah Tiqva-Magdiel-Kfar Sava area (Table 1; Fig. 9)

In the Petah Tiqva–Magdiel–Kfar Sava area, Vinokurov et al. (1991) described a direct hydrogeological contact between the Zor'a aquitard (Hashepela Group) and calcareous beds of the Coastal Plain aquifer. The hydraulic connection in that area is the result of a local lacuna of the Yaffo Formation aquiclude (Saqiye Group). Moreover, in neighbouring areas where the Yaffo aquiclude is present it is deeply incised by trench-like troughs filled by sand and sandstone containing saline water. In the study area the Cl content of this water is 340–400 mg  $1^{-1}$  with an ionic content of Na > Ca > Mg and Cl > HCO<sub>3</sub> > SO<sub>4</sub>. The water is characterized by Q greater than 1, Na/Cl 0.53–0.91 and Br/Cl 2.8–4.4 × 10<sup>-3</sup>. The wide spectrum of these ratio values may be indicative of mixing between fresh water and a saline ground-water body of Ca-chloride composition (Vinokurov et al., 1991).

# 4.7. Saline water along the western margins of the Coastal Plain aquifer (Table 1; Fig. 10)

The Coastal Plain aquifer extends from the foothills of Mt. Carmel southward to the Gaza area and northern Sinai. It is made up of sand and calcareous sandstone (Kurkar). In the western part of the coastal area, the aquifer also comprises beds of silt, loam and clay interbedded with sand and calcareous sandstone reaching a total thickness of 200 m. Salinization of groundwater in wells drilled to this regional aquifer has become an acute problem as it endangers the main groundwater resource of the country. Most authors (Jacobs and Schmorak, 1960; Schmorak and Mercado, 1969; Nadler et al., 1980; Melloul, 1988; Mercado, 1985, 1989) related this salinization phenomena to encroachment of Mediterranean Sea water into the Coastal aquifer. However, the chemical composition of the saline groundwater reveals striking deviation from the chemical composition of sea water. Moreover, in several wells, the Cl content is much higher than that of modern sea water (in the Gaza area 60 000 mg  $l^{-1}$ , Fink, 1970; near Giv'at Olga 33 000 mg  $l^{-1}$ , Vengosh et al., 1991). The ionic ratios of this water indicate deficiency in Na, Mg, K and SO<sub>4</sub> and enrichment in Ca content relative to that of sea water or of sea water diluted by fresh water flowing in the Coastal aquifer. Schmorak and Mercado (1969), Nadler et al. (1980) and Mercado (1989) suggested that the increase in the Ca content and the deficiency in Na (relatively to sea water composition) may be a result of cation exchange between sea water and clays interbedded in the Coastal aquifer sequence. However, such



Fig. 10. Saline water along the western margin of the Coastal Plain aquifer.

chemical processes cannot be the cause of the high Cl content. Vengosh et al. (1991) identified four main groups of groundwater occurring in the sea water-fresh water interface zone:

(a) Low salinity (Cl less than 150 mg  $l^{-1}$ ) groundwater encountered within a 3-5 km wide zone extending east of the (sea) water line (Na/Cl and Q values greater than 1).

(b) Saline water (Cl content below that of Mediterranean Sea water) with Na/Cl ratio identical and higher than that of sea water. Their ionic content resembles that of sea water. It is assumed to be sea water diluted by fresh water.

(c) Saline water with a Cl concentration range of  $1000-33\ 000\ \text{mg}\ \text{l}^{-1}$  (i.e. 1.5 times the Cl content of sea water). This water is of a typical Ca-chloride composition with

Na/Cl less than 0.86 (the marine ratio value). This saline groundwater is one of the most important salinization factors in the western part of the Coastal Plain aquifer.

(d) Brine with Cl content of up to 60 000 mg  $l^{-1}$ . These are characterized by a marine Na/Cl ratio and occur mainly in the deepest parts of the Coastal aquifer in the Gaza area (Fink, 1970). Vengosh et al. (1991) suggested that salinization of ground-water in the Coastal aquifer developed by intrusion of the Ca-chloride saline water in the first stage and by encroachment of sea water into the aquifer in the second stage. The Ca-chloride water body always occurs east of or overlying the encroaching sea water body. These stable spatial relationships enable the use of the chemical composition of water as an operational tool to identify the source and stage of the salinization process along the western margins of the Coastal aquifer. The occurrence of water related to group b (of marine composition) is usually indicative of the occurrence of Ca-chloride water (of group c) immediately to its east.

Contrary to previous studies which attributed the chemical composition of saline groundwater in the interface area to cation exchange between modern sea water and beds of clay, Vengosh et al. (1991) demonstrated that the high salinity of this groundwater cannot result from such a process. Moreover, the authors were able to demonstrate that in certain wells penetrating the deepest levels of the Coastal aquifer (which are particularly rich in argillaceous components) the chemical composition of saline water resembles that of sea water and not that of the Ca-chloride water encountered in overlying beds. In view of the chemical resemblance between Ca-chloride water (group c) with the water encountered in the Bardawill lagoon (Levy, 1972), Vengosh et al. (1991) suggested that this Ca-chloride water was formed as the result of the sabkha-forming processes during the glacial periods in which the sea retreated and the coastal shelf became exposed. Ca-chloride water could possibly have been formed by the following sequence of events:

(a) Evaporation of sea water to the stage of precipitation of halite would have caused the drop in Na/Cl ratio values of the residual brine.

(b) Dissolution of evaporite salts by seasonal floods causing a decrease in Br/Cl, Li/Cl and B/Cl ratios which differ from the high ratios characteristic of evaporated brines commonly occurring in the Dead Sea–Arava Rift Valley.

(c) Diagenetic processes (sulfate reduction, dolomitization, adsorption) causing depletion of Mg,  $SO_4$  and K and an increase in the concentration of Ca.

(d) Surface and subsurface mixing with saline water having sea water composition, migration within the aquifer, and dilution by fresh water normally circulating in the Coastal aquifer.

The highly saline water encountered in the deeper horizons of the aquifer in the Gaza area is residual brine formed in a coastal lagoon or sabkha (Gat, 1975) which existed during the early accumulative stages of the Coastal aquifer. Though its high salinity was caused by evaporative processes, its marine Na/Cl ratio values indicate that the brine did not precipitate halite. Thus, the maximal level of its salinity was lower than that of Ca-chloride source brines.

The occurrence of different groups of saline water at various depth levels in the Coastal aquifer indicates that the deposition of the sandy sequence forming this regional aquifer was concurrent with the existence of coastal lagoons along the eastern shores of the Mediterranea sea.

### 4.8. Saline spots in the Coastal Plain aquifer: the Be'er Tuvia example (Table 1; Fig. 9)

Point sources of saline groundwater occurring as isolated spots in the Coastal aquifer were discovered in several locations such as Be'er Tuvia and Gan Yavne. There, the Cl content varies in the 200-800 mg  $l^{-1}$  range. The dimensions of these saline spots increased in time and gradually merged with similar adjacent phenomena. The saline spot of Be'er Tuvia was investigated in detail by Vengosh (1992b) who discovered that the Cl content increased, over a time span of 30 years, from 200 to 800 mg  $1^{-1}$ . In 1990 the area of this point source reached 12 km<sup>2</sup>. Because of intensive groundwater extraction during the 1950s, groundwater levels dropped 7 m and a regional hydrological depression was formed, reaching its deepest level in 1967. Since 1956, the lowering of water levels was accompanied by an increase in salinity. By the late 1980s, following restriction of pumpage, the depression filled in and ultimately disappeared. Notwithstanding the almost complete restoration of the initial piezometric pattern, salinization continued its course and the dimensions of the salt plume increased at the rate of 50 m year<sup>-1</sup>. It appears that the process of salinization became irreversible and that by the year 2000, groundwater salinity at Be'er Tuvia will reach 1000 mg  $l^{-1}$ . This salt plume came into existence as a result of several processes such as lowering of groundwater levels and inflow of saline water originating at greater depths. The chemical composition of this saline water is indicative of the presence of two Ca-chloride water bodies, both of them characterized by low Na/Cl ratio and marine Br/Cl ratios. The two water bodies differ by their  $SO_4/Cl$ and B/Cl ratios. By employing the method described earlier in this paper, Vengosh (1992b) estimated the Cl content of the two saline end members: the first 570-2700 mg  $1^{-1}$  and the second 800–3350 mg  $1^{-1}$ . The first water resembles Ca-chloride water such as was formed in the coastal sabkhas (and commonly found along the western margins of the Coastal aquifer). The second type is identical with saline water found in the deep layers of the Gaza area. Such saline water may occur in isolated pockets at the base of the Coastal aquifer or in highly conductive lumachelle beds in the underlying the Yaffo Formation aquiclude.

## 4.9. Saline groundwater in the Mehola, Bet Shean and Harod Valleys (Table 1; Fig. 11)

The Mehola, Bet Shean and Harod valleys are regional recipients and mixing zones for fresh groundwater draining from a regional, multiple aquifer system including two different carbonate aquifer (Judea and Avedat Groups) and two basalts aquifers of Neogene–Pleistocene age (Rosenthal, 1988a,b,c). Because of structural conditions specific to this area, the four groundwater bodies drain to these valleys through interconnecting outlets which are common to these aquifers. Upon reaching the interconnecting zones, fresh groundwater deriving from these different aquifers intermix, losing their original hydrochemical identities.

Ca-chloride brine originating from deep-seated and confined reservoirs leaks along



Fig. 11. Saline groundwater in the Mehola, Bet Shean and Harod Valleys.

regional faults which are characteristic features of the common outlet zones. It contaminates the relatively fresh mixing products originating from the four previously mentioned source aquifers.

Two types of dilute Ca-chloride brines were identified and related to respective end members (Rosenthal, 1988b):

(a) The Devora type is a hot and hypersaline source brine which was identified at great depths (greater than 4700 m), under high pressure (greater than 480 atm). The maximal Cl content of this brine was found to be 130 000 mg l<sup>-1</sup>. The typical ionic content of this water is Ca > Na > Mg and Cl > HCO<sub>3</sub> > SO<sub>4</sub>. The water is characterized by low pH values (4.7–4.9), high CO<sub>2</sub>, very high Ca/Mg (10) and low Na/Cl ratios (0.47). The Q value is 162 and Br/Cl ratio is  $1.75 \times 10^{-2}$ . Rosenthal (1888b)

suggested that this brine could be the residual product of sea water which evaporated during the Cambrian-Lower Cretaceous continental interval and subsequent prolonged interaction with surrounding carbonate rocks. Another possibility could be the formation of this brine following high temperature reaction between Ca-chloride brine commonly occurring in the Rift Valley and basalt bodies.

(b) The Neve Ur brine represents another type of water related to the family of Cachloride brines. This water is non-thermal, its highest known salinity not exceeding 22 050 mg  $1^{-1}$ . Its hydrostatic pressures are similar to the regional piezometric levels of fresh water. Its ionic content is Na > Mg > Ca and Cl > SO<sub>4</sub> > HCO<sub>3</sub>. This water differs from the Devora type in its low Ca/Mg ratio (0.47), by Na/Cl = 0.63 and Q = 3.8. Water of similar chemistry was encountered in boreholes drilled along the eastern and southern shores of the Sea of Galilee. Starinsky (1974) and Rosenthal (1988b) suggested that this is residual water from the Neogene inland sea which preceeded the contemporary Dead Sea.

# 4.10. Salinization processes in the Yarqon–Taninim basin: the Taninim outlet (Table 1; Fig. 12)

The quality of groundwater in the Yarqon–Taninim basin (Judea Group aquifer) has deteriorated as a result of acute salinization processes occurring particularly in the Shune–Taninim outlet areas (Weinberger, 1991). Exceptionally high Cl concentrations were also observed along the western margins of the Yarqon–Taninim basin and especially in wildcat wells Beeri (5239 mg  $1^{-1}$ ), Gerar (5877), Nir Am 9 (1617), Benyamin 1 (9701), Qomemiut (1248) and Ynon 1 (800). High Cl concentrations were also observed in the central parts of the basin as at Gimzu, Kfar Uriyah and Ayalon (approaching 450 mg  $1^{-1}$ ) (Weinberger, 1991). Bar Yosef (1975) and Gutman (1988) assumed that salinization occurred as the result of saline water (known to exist in the overlying Senonian chalk) penetrating into the underlying Judea Group aquifer. On the other hand, Shaharabany (1977) assumed that salinization of groundwater in the central parts of the basin. Mercado (1980) suggested salinization occurred also because of upflow of saline water from the lower parts of the aquifer.

At the northern outlets of this aquifer, in the Shune–Taninim area, saline water occurs in the lower and upper parts of the Judea Group aquifer. In several deep wells (Menashe T/3, Taninim Deep and Netanya Oil) high salinity groundwater has been encountered (18 300–22 350 mg l<sup>-1</sup>Cl; Gutman et al., 1988). Water emerging from the adjacent Taninim springs has Cl contents in the 350-2120 mg l<sup>-1</sup> range (Bar, 1983). Identification of saline water sources and the understanding of the regional hydrogeological model are imperative for the rational management of this regional aquifer. Local specialists are not unanimous as to the possible souces of salinization. Mandel (1961), Bar Yosef (1974, 1978), Smoler (1975) and Gutman et al. (1988) suggested that the main cause for groundwater salinization is encroachment of sea water into the Judea Group aquifer. Other authors (Gutman, 1980; Mercado, 1980; Bar, 1983) have proposed that saline water encountered in the wildcat well Taninim Deep (18 300 mg l<sup>-1</sup> Cl) is not in fact sea water, but rather is related to inflow of underlying



Fig. 12. Saline water at the northern outlets of the Yarqon-Taninim basin. Broken line outlines approximate basin boundaries.

connate Ca-chloride water. Bar (1983) has noted that water in this well (located 500 m away from a major, deep seated fault) chemically resembles saline water found in other deep boreholes in the area (Asher 1 and 2; Caesarea 1; Haifa Bay 1) which are also characterized by ionic contents such as Na > Ca > Mg and Cl > SO<sub>4</sub> > HCO<sub>3</sub> with Na/Cl = 0.78 and Q > 1. This chemical composition differs significantly from that of sea water and indicates inflow of Ca-chloride water from depth (Bar, 1983). Considering 234U/238U values measured in the saline water of wildcat well Taninim Deep, Gutman (1980) also concluded that this water is not contemporary sea water. In view of the marine Na/Cl ratio value (0.87) measured in the Taninim springs, Bar (1983) assumed that groundwater flowing there in the upper parts of the Judea Group

aquifer became saline because of Mediterranean Sea water penetration into this aquifer. This was supported by Gutman et al. (1988) who showed that groundwater in borehole Menashe T/3 located along the assumed path of sea water penetration has a Cl content of 21 200 mg l<sup>-1</sup> with Na/Cl = 0.87. It therefore seems that groundwater flowing in these parts of the Yarqon–Taninim basin became saline as a result of mixing of fresh water with two saline water sources, one of these being sea water and the other, a Ca-chloride brine rising from depth. This model is in agreement with Mercado (1980), who reached this conclusion without having the benefit of data from well Menashe T/3.



Fig. 13. Saline water around the Sea of Galilee.

### 4.11. Saline water around the Sea of Galilee (Table 1; Fig. 13)

The Sea of Galilee is the main fresh water storage body of the country. Its water quality is constantly endangered by saline springs along its shores and on the bottom of the lake. Some of these springs are thermal (up to  $60^{\circ}$ C) and have a Cl content of up to 18 000 mg l<sup>-1</sup>. As the result of capturing and diversion of springs outflowing along the western shores of the lake, the flux of solutes to the lake was significantly reduced. However, springs outflowing along the eastern shores, as well as submarine outlets, contribute significant amounts of salt to the stored water.

The source of salts in these springs has been investigated by numerous authors (Goldschmidt et al., 1967; Mazor and Mero, 1969a; Mazor and Carmi, 1973; Starinsky, 1974; Kafri and Arad, 1979; Arad and Bein, 1986). Recently, Simon and Mero (1992) reviewed the hitherto proposed salinization mechanisms. According to the latter authors the largest quantity of saline water that flows into the Lake is from the Sheva and Nur springs emerging along the the NW shore of the lake with Cl content of 400–3600 mg l<sup>-1</sup>. The saline waters emerging around the lake are characterized by the ionic content of Na > Ca > Mg and Cl > SO<sub>4</sub> > HCO<sub>3</sub>, low Na/Cl (0.6), high Br/Cl ( $5.9 \times 10^{-3}$ ) and Q (10) ratios. Along the eastern shores of the lake the Ca/Mg ratio is less than 1 (Goldschmidt et al., 1967; Starinsky, 1974).

Mazor and Mero (1969b) and Kafri and Arad (1979) suggested that the salinity is of marine origin and is derived from penetration of Mediterranean Sea water inland into the northern Rift Valley. On the other hand, Starinsky (1974) showed that the previously mentioned ionic ratios indicate the influence of Ca-chloride brines which were formed in the Dead Sea area and migrated northward within the Rift. The wide range of salinities observed in the springs seems to be a result of different degrees of dilution by fresh water. Starinsky (1974) suggested that the source brine might be similar to the water encountered in wildcat well Rosh Pina 1 (105, 230 mg  $l^{-1}$  Cl and of typical Ca-chloride composition). Simon and Mero (1992) reported the occurrence of thermal Ca-chloride brine (Cl approaching 180 000 mg  $l^{-1}$  and 130°C) in a thick sequence of Neogene evaporites in wildcat well Zemah 1 located close to the southern shores of the lake. This brine might have been related to a saline lake which existed there during the Neogene (Rosenthal, 1988b). According to Starinsky (1974), the occurrence of high Ca/Mg ratio values in the water emerging along the western shores (as compared with the low ratio encountered in the water outflowing along the eastern shores) was the result of dilution of evaporated sea water which was also involved in secondary diagenetic processes such as dolomitization. Rosenthal (1988b) suggested that the latter Mg-rich group, could be a relic of the inland sea which existed in the Rift and preceded the Dead Sea. Gat et al. (1969) argued that the oxygen isotope composition of the saline water indicates dilution of evaporated sea water by fresh water. The deviation from Ca-chloride brines was recently also confirmed by the occurrence of high  ${}^{11}B/{}^{10}B$  ratio ( $\delta^{11}B = 44\%$ ) in the water of Tiberias Hot Springs, indicating mixing with a brine component characterized by high  $\delta^{11}$ B value such as found in the Dead Sea brines (Vengosh et al., 1991).

The five springs of Hammat Gader emerge in the gorge of the Yarmuq river, 7 km east of the Sea of Galilee. The springs differ by their temperatures (25–50°C) and Cl



Fig. 14. Main saline end members causing salinization of fresh groundwater resources in Israel.

content (82–527 mg l<sup>-1</sup>). All springs flow out of Eocene chalk outcropping along the northern margins of the Ajlun syncline. As a rule, salinity increases in direct relation to temperatures (Mazor and Carmi, 1973, 1980; Starinsky et al., 1979; Mazor et al., 1980; Arad and Bein 1986). The chemical composition of the most saline water is represented by Na > Ca > Mg and Cl > SO<sub>4</sub> > HCO<sub>3</sub> with low Na/Cl (0.75) and high Br/Cl ( $4.8 \times 10^{-3}$ ) ratios, by low  $\delta^{18}$ O values (-5.5% to -6.5%, Mazor et al., 1973) and low  $\delta^{11}$ B values (20.9%). In that sense, it resembles the chemistry of saline springs emerging along the western shore of the Sea of Galilee. According to Starinsky et al. (1979) this chemical composition is indicative of mixing between meteoric water with Ca-chloride water. According to Mazor (1972) rare gases such as Xe, Ar, Kr and Ne which are dissolved in this thermal and saline water have an isotopic composition indicative of equilibrium with the atmosphere. Mazor and Molcho (1972) argued that the low  $\delta^{18}$ O values reflect ancient meteoric water. Arad and Bein (1986) suggested, however, that the saline thermal water with low  $\delta^{18}$ O values developed from recent meteoric waters which were recharged at high topographic elevations of the Golan Heights.

### 5. Synthesis

After studying most groundwater salinization phenomena in Israel, the main saline end members causing these processes were identified. To facilitate further reference and enable the delineation of a regional, holistic model, identifying names were given to the main hydrochemical end members. The principal causes of groundwater salinization are as following (Fig. 14; Table 2).

### 5.1. Inland encroachment of sea water

Because of intensive exploitation of groundwater from the Coastal Plain aquifer, groundwater levels have dropped considerably facilitating inland penetration of sea water and salinization of the fresh water flowing in this aquifer. The inflow of sea water is accompanied by the occurrence of saline, Ca-chloride water. Mercado (1985, 1989) and Nadler et al. (1980) suggested that this water was the result of diagenesis of sea water reacting with aquifer country rocks. In contrast, Vengosh et al. (1991) noted that the Ca-chloride water is a relict of old brine trapped in the aquifer and subsequently diluted by fresh water.

### 5.2. Upflow of Ca-chloride brines

# 5.2.1. Dead Sea-Arava Rift Valley (from the Sea of Galilee to the Red Sea)

Ca-chloride brine with Cl contents in the 50 000–270 000 mg  $l^{-1}$  range has been encountered in Israel in most parts of the Rift Valley (Bentor, 1960; Starinsky, 1974;

Table 2 Chemical composition of	main saliı	ne end r	nembers	causing	salinizati	on of free	sh ground	lwater in	Israel (con	centratio	ns in mg l	-1; ionic ratic	s in meg l	- <u>-</u> ]-
	Ca	Mg	Na	К	cı	$SO_4$	HCO <sub>3</sub>	Br	TDS	Na/Cl	б	Br/Cl	Ca/Mg	δ <sup>18</sup> Ο
Mediterranean sea water	472	1487	12 772	479	22 900	3110	165	76	41461	0.86	0.35	$1.5 \times 10^{-3}$	0.19	1.6
Rifi Valley Group Arava 1 Devora 2A	52 160 34 820	9744 1950	54 319 40 200	- 400	208 660 129 393	122 178	60 171	- 1740	325 065 208 852	0.40 0.48	739.80 267.37	$-6.0 \times 10^{-3}$	3.25 10.85	2.36
Coastal Plain Bardawil brine type Giva't Olga 51/B Ashqelon 6/C	1 088 3 292	540 34	5354 8915	174 135	32 960 18 257	3 160 1 049	-32	111 62	43 387 31 776	0.25 0.75	7.36	$1.5 \times 10^{-3}$ $1.5 \times 10^{-3}$	1.22 58.82	4 1
Gaza brines Gaza–Khan Yunis 5/A Gaza A/6	2 302 1 742	3378 2709	33 188 26 640	I I	60 262 50 875	11 165 1 585	152 240	210	110 657 83 791	0.85 0.81	0.49 2.36	$1.5 \times 10^{-3}$	0.41 0.39	1 1
Mavgi'im-Heletz brines Heletz 30 Kokhav 7	2113 2859	786 938	23 619 27 580	420	42 474 50 481	249 86	165 220	177 179	70 003 82 343	0.86 0.84	13.39 26.48	$1.8 \times 10^{-3}$ $1.6 \times 10^{-3}$	1.63 1.85	I I
Barnea brines Ashqelon-Barnea 1 Gerar i	22 000 16 800	485 1070	24 000 34 000	- 140	81 000 86 500	490 339	110 98	1116 804	129 341 139 611	0.46 0.61	96.96 96.90	$6.1 \times 10^{-3}$ $4.1 \times 10^{-3}$	27.56 9.54	J Í
<i>Kurnub water</i> Tamar 3 Paran 20 Admon 2	196 234 233	30 91 103	401 306 1 341	21 35 77	600 601 2 069	414 620 895	305 219 182	1.4 6.5	1 968 2 106 4 907	1.03 0.79 1.00	0.72 0.71 0.54	$1.0 \times 10^{-3}$ - $1.4 \times 10^{-3}$	3.91 1.56 1.37	-7.79
Sabot brines Sadot 1 Sadot 2	127 241	42 50	9 400 10 000	94 84	14471 15420	28 44	816 566	69	25 049 26 474	1.00	0.45 1.18	$2.2 \times 10^{-3}$ $2.0 \times 10^{-3}$	1.84 2.93	4 I

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Rosenthal.1988b). These waters will be further referred to as the Rift Group of brines. The hydrochemical fingerprint of these pressurized brine is prominent in the Elat–Aqaba area, further northward all along the Arava, along the western shores of the Dead Sea, in the Jordan Valley, in the Mehola, Bet Shean and Harod Valleys, in springs and seepages along the shores of the Sea of Galilee and further northward to Rosh Pina. Amongst the striking examples of groundwater deterioration are the springs of Mehola and Bet Shean Valleys where Cl content has increased from 200 mg  $1^{-1}$  in the early 1960s to over 800 mg  $1^{-1}$  in the 1980s (Rosenthal, 1988c) with fresh water being replaced by diluted Ca-chloride brines. A similar phenomenon has been recently observed in several wells in the Arava. The previously mentioned Devora, Neve Ur and Timna brines should be regarded as local variants of the Rift Group of brines. In all these areas, salinization occurred as the result of and following intensive exploitation of fresh groundwater which facilitated migration and upflow of deep-seated and pressurized brine.

### 5.2.2. Coastal Plain (western drainage basin)

Ca-chloride brine was encountered in both shallow and deep-seated aquiferous layers of the Coastal Plain. Such waters, hitherto named Bardawil brines, were found at relatively shallow depth along the western margin of the Coastal aquifer and along the shores of the Bardawill lagoon in northern Sinai. The hydrochemical characteristics of these Ca-chloride waters differ from the brines encountered in the Rift by lower ratios of the conservative ions to chloride (Tables 1 and 2). The Gaza brines were identified in the deepest layers of the Coastal Plain aquifer, beneath the Gaza area. These brines are characterized by salinities of up to 60 000 mg  $1^{-1}$  Cl, a marine Na/Cl ratio and high (greater than 1) Q values.

In the deeper levels of the Coastal Plain aquifer, Ca-chloride brines were identified all along the stratigraphic sequence encompassed between the Lower Cretaceous Heletz and Up.Miocene Mavqi'im formations. These waters will now be denoted as the Mavqi'im Heletz brines. Starinsky (1974) previously identified these waters as the 'C-brines'. Its Cl concentrations reach 100 000 mg  $l^{-1}$  and it is characterized by marine Na/Cl ratios.

Ca-chloride brines with low Na/Cl ratios (less than 0.86) and high Q-values were identified at lower stratigraphic levels, i.e. in the Jurassic Zohar formation. They will now be known as the Barnea brines. Their chemical composition resembles that of Ca-chloride brine found in the Rift Valley (Starinsky, 1974; Starinsky et al., 1983; Bein and Sofer, 1987). It has been understood that such deep seated, highly concentrated brine would not directly endanger the fresh water flowing in overlying and adjoining aquifers supposed to be effectively separated from the brine-bearing formations. However, recently Weinberger et al. (1992) pointed out possible structural and hydraulic contact between the deep seated brine-bearing formations and the Judea Group fresh water aquifer of the Yarqon–Taninim basin. Such hydraulic contact occurs in cases in which the Yaffo formation aquiclude is missing or when deep seated faults create suitable hydrogeological conditions facilitating hydraulic contact between these formations. The Taninim outlet could well serve as an example of such an interconnecting mechanism.

### 5.3. Salinization by Na-chloride waters

Saline water of varied Cl content and of Na-chloride composition was encountered mainly in the Kurnub Group (Nubian Sandstone) aquifer of the Negev. Hence, this thermal and artesian water shall be named accordingly, i.e. the Kurnub water. According to Rosenthal et al. (1992), this water penetrates the overlying Judea Group aquifer, resulting in the salinization of its fresh water. This process occurs mainly in the Beer Sheva region as well as in other parts of central and western Negev.

Methane bearing saline Na-chloride water ( $Cl = 18\ 000\ mg\ l^{-1}$ ) was also found in the Judea and Saqiye Group formations of northern Sinai (Sadot wildcat wells, (Starinsky et al., 1985). They will now be known as the Sadot brines.

### 5.4. Salinization phenomena caused by dissolution of soluble salts

In Israel, groundwater salinization may occur not only because of brine migration but also by dissolution of soluble salts naturally occurring in country rocks. Such a process was identified by Yechieli et al. (1992) in the Arava where they identified that this process is a result of contemporary flushing and dissolution of salts which accumulated in the upper stratigraphic layers and in soils covering natural replenishment zones. Intensive irrigation in such areas enhanced percolation of irrigation return flow, dissolving these salts in its flow path. The high concentration of Mg and SO<sub>4</sub> can reflect dissolution of Mg-sulfate salts.

Along the eastern margins of the Coastal Plain aquifer Rosenthal et al. (1992) reported the occurrence of saline water with high tritium levels. It has been suggested by these authors that the high salinity of this water was caused by dissolution of soluble salts lining fissures and faults in Hashepela Group beds which are in direct contact with the sand and calcareous sandstone beds which comprise the Coastal aquifer.

### 6. The bearing of salinization processes on the water crisis in Israel

The ongoing deterioration of groundwater quality in Israel is mainly reflected by an increase in salinity levels. Accordingly, great volumes of fresh water which were initially planned for municipal usage, are continually lost or have to be allocated to other purposes. Such developments imply changes in the exploitation and management regimes and create demands and pressures on other, hitherto unexploited sections of aquifers or, in extreme cases, require development of entirely new water resources. At a later date, these new resources may be subject of the same fate and this sequence of events will ultimately not only continue but might finally get out of control.

From the present review it appears that most salinization phenomena are caused by natural processes. The intensive groundwater exploitation from the Coastal aquifer has caused encroachment of sea water and its eastward penetration into the aquifer. Elsewhere, the disturbance of the natural hydrological balance caused by intensive or excessive groundwater exploitation provoked migration of hitherto dormant bodies of saline water or of brines thus accelerating the rate of salinization and the resultant deterioration of fresh groundwater. Hence, the disturbance of the hydrological balance naturally prevailing between fresh and saline water is the major factor deteriorating the quality of water resources in this country.

Further development of groundwater resources and possible increase in the rates of their exploitation will necessarily perpetuate and possibly even aggravate these processes of deterioration. This conclusion was reached by considering the as yet incomplete evidence as to the existence of enormous volumes of saline water and brines in the subsurface and the fact that some, if not all of these water bodies, are under high hydrostatic pressure making them potentially mobile following disturbance of natural equilibria. Moreover, new geological evidence has revealed numerous possibilities for interaquifer connection and upflow of brines into fresh water aquifers which had been hitherto regarded as hydrologically isolated and secure from salinization.

Notwithstanding these salinization processes, the current water exploitation regime of Israel is being implemented under uncertain conditions as to the volumes, hydrostatic pressures, flow directions and detailed chemistries of saline water and brine occurring in most groundwater basins. The same is true as to detailed knowledge of the geological structure of these basins and of their overall hydrogeological models.

Over the past half century, great efforts have been made to reach a high level of understanding of the fresh groundwater resources of the country and to estimate their availability. No sufficient efforts were made as regards research of saline water. The general concern for a better environment and safer water resources implies changing priorities in research and in the monitoring both of fresh and of saline water in Israel as well as in many parts of the world.

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