ORIGINAL ARTICLE

Hydrochemical variation in the springs water between Jerusalem–Ramallah Mountains and Jericho Fault, Palestine

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Abstract The spatial and temporal changes of the composition of the groundwater from the springs along the Wadi Qilt stream running from the Jerusalem–Ramallah Mountains towards the Jericho Plain is studied during the hydrological year 2006/2007. The residence time and the intensity of recharge play an important role in controlling the chemical composition of spring water which mainly depends on distance from the main recharge area. A very important factor is the oxidation of organics derived from sewage and garbage resulting in variable dissolved CO_2 and associated HCO_3^- concentration. High CO_2 yields lower pH values and thus under-saturation with respect to calcite and dolomite. Low CO_2 concentrations result in over-saturation. Only at the beginning and at the end of the rainy season calcite saturation is achieved. The degradation of dissolved organic matter is a major source for increasing water hardness. Besides dissolution of carbonates dissolved species such as nitrate, chloride, and sulfate are leached from soil and aquifer rocks together with only small amounts of Mg. Mg not only originates from carbonates but also from Mg–Cl waters are leached from aquifer rocks. Leaching of Mg–Cl brines is particularly high at the beginning of the winter season and lowest at its end. Two zones of recharge are distinguishable. Zone 1 represented by Ein Fara and Ein Qilt is fed directly through the infiltration of meteoric water and surface runoff from the mountains along the eastern mountain slopes with little groundwater residence time and high flow rate. The second zone is near the western border of Jericho at the foothills, which is mainly fed by the under-groundwater flow from the eastern slopes with low surface infiltration rate. This zone shows higher groundwater residence time and slower flow rate than zone 1. Groundwater residence time and the flow rate within the aquifer systems are controlled by the geological structure of the aquifer, the amount of active recharge to the aquifer, and the recharge mechanism. The results of this study may be useful in increasing the efficiency of freshwater exploitation in the region. Some precautions, however, should be taken in future plans of artificial recharge of the aquifers or surface-water harvesting in the Wadi. Because of evaporation and associated groundwater deterioration, the runoff water should be artificially infiltrated in zones of Wadis with high storage capacity of aquifers. Natural infiltration along the Wadis lead to evaporation losses and less quality of groundwater.

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Introduction

Groundwater from catchments characterized by uniform mineralogy might have a unique, characteristic chemical composition reflecting the soluble minerals in the saturated zone. Numerous lithology-controlled factors such as dissolution rates, cation exchange capacity, fluid mobility, and reaction kinetics at mineral surfaces determine the net solute inventory added to an evolving water parcel along a flow path (Bullen et al. 1996). If the lithology along the flow path varies or if the infiltrating water mixes with saline formation water enclosed in sedimentary rocks, the solute inventory is altered. Thus, the composition of groundwater is expected to be different from that of the infiltrating water. Variation of both meteoric precipitation and the rate of water/rock interaction yield time-dependent variable hydrochemical composition of groundwater.

All these effects are important in semi-arid to arid areas with their seasonal rainfalls, where the amount and mechanism of recharge of aquifers control the quality of groundwater. These influences have been studied in the uppermost aquifer of the Jerusalem–Ramallah sub-basin, Palestine, the lithological column of which is shown in Table 1. Because it is a karst aquifer with absence of major lithologic variability but of very discontinuous structure, we only discuss the results on Wadi Qilt and the adjacent area of the Jericho Plain (Fig. 1).

It needs extensive hydrogeological studies to identify the true potential, safe yield, and quality of groundwater of this aquifer. For this reason, the hydrochemical analyses from the winter season of 2006/2007 of springs in the Wadi Qilt and of the Jericho Plain discharging from the calcareous mountain karst aquifer of the eastern slopes of the Jerusalem–Ramallah Montains are used to precisely resolve the spatial and temporal variations of water quality and its relation to mechanisms of recharge, runoff formation, flow conditions, infiltration zones, movement, and residence time of groundwater in the mountain aquifer.

Wadi Qilt is a nature reserve which includes great natural and historical values. The Wadi tributaries collect the rain water from the upper mountains of Ramallah and Jerusalem and then finally form a large stream that enters the Jericho Plain which is a semi-arid to arid area. However, numerous spring discharge in the depression of the Wadi. The springs of the Jericho Plain discharge along the foothills near the Jericho fault. These springs are the main sources for drinking water and irrigation in the Jericho area.
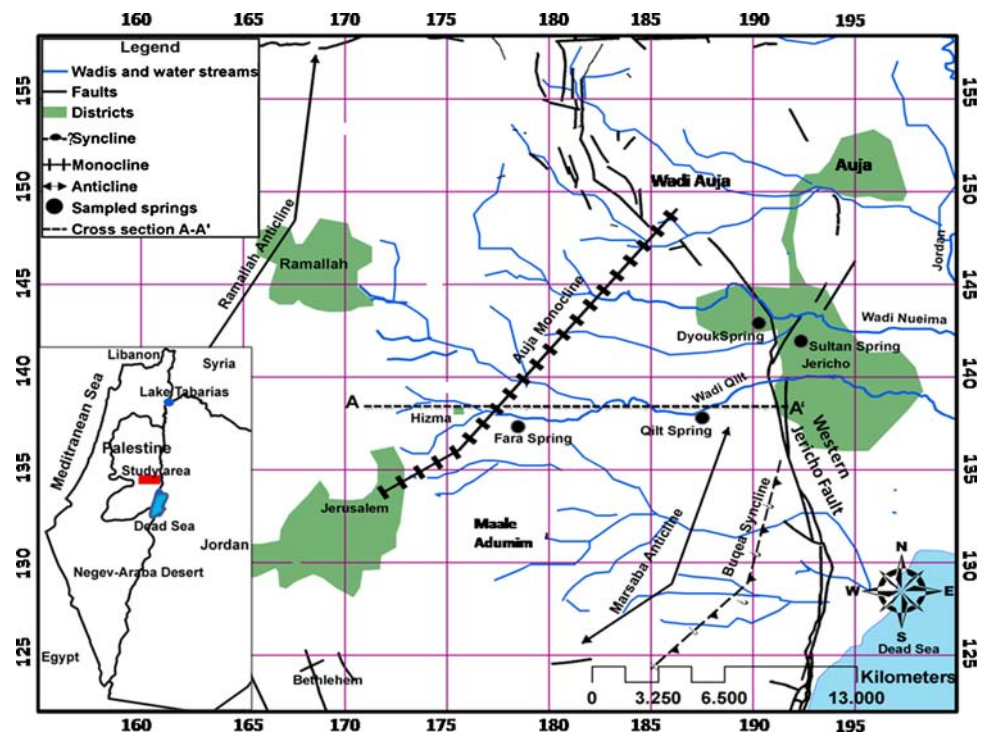
Hydrogeological setting

The Jerusalem–Ramallah sub-basin is part of the eastern basin in the West Bank, Palestine. This sub-basin extends from the Jerusalem–Ramallah Mpuntains toward the western border fault of Jericho and Auja. As part of the eastern aquifer, the Jerusalem–Ramallah sub-basin is built of karstified Upper Cretaceous limestones, which host one of the most important water resources in the region (ARIJ

Table 1 Stratigraphic table of rock units in the study area

The study area is the formation, dominated by outcrops of Upper Cenomanian (Turonian), which later on covered in the eastern part of the study area near Jericho with Campanian Abu Dis Formation (modified after Begin 1974)

1997; Wolfer 1998). The area was repeatedly mapped by Rofe & Raffety (1963), Roth (1969, 1970), Begin (1974), Arkin (1976) on a scale of 1:2,000. Wolfer (1998) and Toll (2001) concentrated on geological details of the lower Wadi Qilt area. The main hydrogeological investigations in the Wadi Qilt area were carried out by Rofe & Raffety (1963), Arad and Michaeli (1967), Kroitoru et al. (1985), and Kroitoru (1987).

The composition of groundwater in the aquifer of the eastern basin was repeatedly studied in the last few years (Wolfer 1998; Toll 2001; Guttman 2004). These studies concentrated on the spatial variation of the groundwater quality and its relation to the geology of the basin. Guttman (1997, 2004) determined the recharge quantity and delineated the groundwater flow in the area. These studies revealed only minor spatial and temporal relationships between changes in chemical composition, the geological structure of the aquifer, and its recharge mechanism in the Jerusalem–Ramallah Mountains and along the Wadis heading toward the Jericho Plain. East of Jericho, the groundwater is affected by the high-salinity groundwater of the Jordan Valley. The available potential resource of the eastern basin is estimated between 100 and 150 Mm³/year (Tahal 1990; IPCRI 1993) but it is not exploited because of its poor water quality.
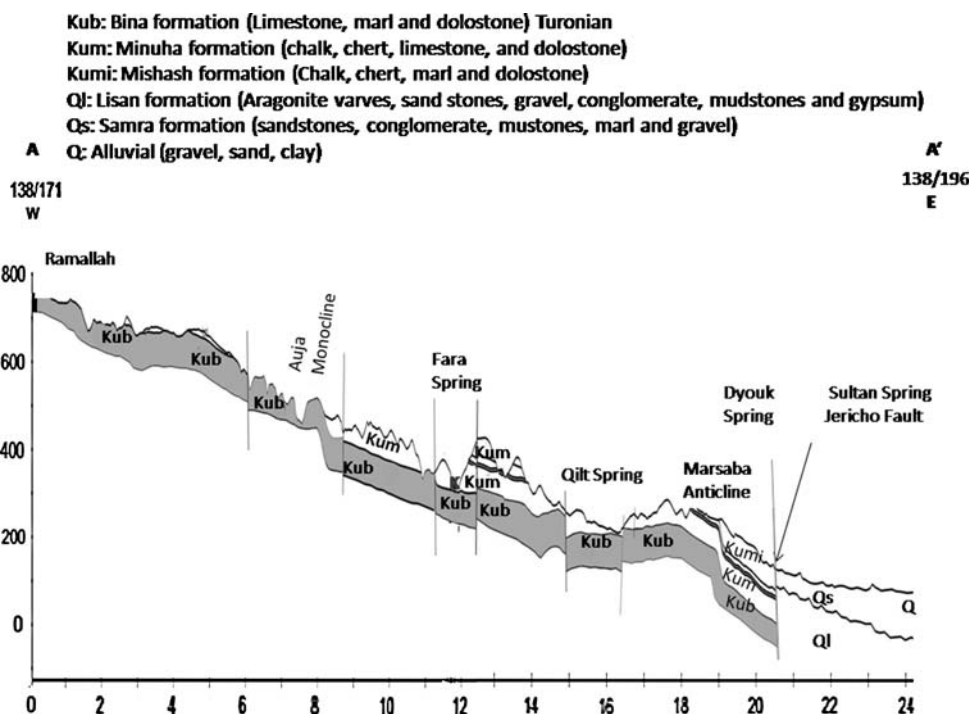
Two main sub-aquifers can be differentiated in the Upper Cretaceous limestone and dolostone layers: the lower and upper sub-aquifer the latter of which drains by the springs between Ramallah and Jericho (Fig. 1). The upper

sub-aquifer consists of the Jerusalem and Upper Bethlehem Formations (Table 1) with a thickness varying between 170 m in the Jericho area and 200 m in the Jerusalem area (Flexer et al. 1989). This upper sub-aquifer is hydrogeologically separated from the lower one by an impermeable layer of marls and chalks of the Lower Bethlehem Formation acting as an aquitard (Guttman 2000; Qannam and Merkel 2002). Indicated by springs, the upper sub-aquifer outcrops along Wadi Qilt, Wadi Nueima, and Wadi Auja of the eastern slopes draining to the Jericho–Auja area close to the Western Boundary Fault. This area mainly receives excess water from the surface runoff across the Wadis that mainly replenishes the upper sub-aquifer.

Wadi Qilt hosts several springs such as Fara, Fawwar, and Qilt. They all discharge from the upper aquifer (Fig. 1). All of them discharge water with 400–560 mg/l total dissolved solids (TDS). The sampled springs (spring = Ein) are Ein Fara and Ein Qilt in Wadi Qilt, and Ein Dyouk and Ein Sultan in the western border of Jericho Plain. The springs in Wadi Qilt immediately respond to precipitation in the mountains and due to their discharge that highly fluctuates (Guttman 2000, 2004). The locations of the springs in Wadi Qilt area are strongly controlled by the geological structure, mainly the Auja Monocline and Marsaba Anticline (Toll 2001; Wolfer 1998) (Fig. 2). Across the eastern slope, the rainfall decreases but runoff is infiltrated through soil and fractures.

The annual precipitation in the main recharge zone of the aquifer in the Jerusalem–Ramallah Mountains is about

Fig. 2 W-E Cross section A-A′ (Fig. 1) showing the aquifer and aquiclude layers (grey)

Kub: Bina formation (Limestone, marl and dolostone) Turonian
Kum: Minuha formation (chalk, chert, limestone, and dolostone)
Kumi: Mishash formation (Chalk, chert, marl and dolostone)
Ql: Lisan formation (Aragonite varves, sand stones, gravel, conglomerate, mudstones and gypsum)
Qs: Samra formation (sandstones, conglomerate, mustones, marl and gravel)
Q: Alluvial (gravel, sand, clay)

540 mm (Marie and Vengosh 2001). The climate of the study area is semi-arid, although several surface-water flows originating from the Jerusalem–Ramallah Mountain pass the basin through Wadi Nueima and Wadi Qilt (Fig. 1). Individual strong storm events control the recharge of the mountain aquifer. According to ARIJ (1997), almost 95% of the annual rainfall occurs between December and March and more than 65% in the 3 months between December and February. The dry period extends from May to end of September. During the winter months the precipitation ranges from 5 to 100 mm in each storm event. Spatial distribution of rainfall also varies strongly. In the Jerusalem and Ramallah Mountains precipitation ranges from 400 to 650 mm/year, whereas it reaches only 120–180 mm/year in the Jericho area (ARIJ 1997). Note the strong variations in monthly and even daily rainfalls in Fig. 3 shows the precipitation record during the winter 2006/2007 in the upper mountains at the station of Hizma.

This basin supports over 79 springs. These springs constitute around 90% of the total annual spring discharge in the West Bank. They mainly discharge along small Wadis that drain from west to east and feed the underlying aquifers.

Water resources in the study area are deteriorated by pollution from natural and anthropogenic sources. Runoff water mixes with waste water and leaches garbage from the Bedouins and from urban areas along its pathway. There are no sewage treatment plants and waste water is disposed in cesspits. Since the water resources in the study area are

scarce, management options and optimal water allocation policies should aim at the protection of the quality of all conventional and non-conventional water sources.

Sampling and analysis

The springs of Fara, Qilt, Dyouk, and Sultan were sampled shortly before and after rainy storms in the winter season 2006/2007. At each sampling site, temperature, electrical conductivity, redox potential, and pH were recorded. Samples were taken for cation, anion, and dissolved organic carbons (DOC) analyses. The samples for cation and anion analyses were collected in 60 ml HDPE bottles with tight caps. The cation samples were acidified by adding concentrated nitric acid. In order to prevent the bacterial activity in the anion and DOC samples, a trace amount of $HgCl_2$ was added. The chloride concentration had therefore to be determined from the cation samples. Cation and anion samples were analyzed by ion-chromatography at the Helmholtz Centre for Environmental Research in Leipzig, Germany. HCO_3^- concentrations were determined by Gran titration in the field. All results are summarized in Table 2. Dissolved CO_2, partial pressure of CO_2, and saturation indices of calcite and dolomite were estimated by the opnen domain PHREEQC program.

The sampling was scheduled mainly by limited numbers of rain events occurring in the winter 2006/2007. The samples before December were assigned as early winter

Fig. 3 Record of precipitation at Hizma Station (Ramallah)
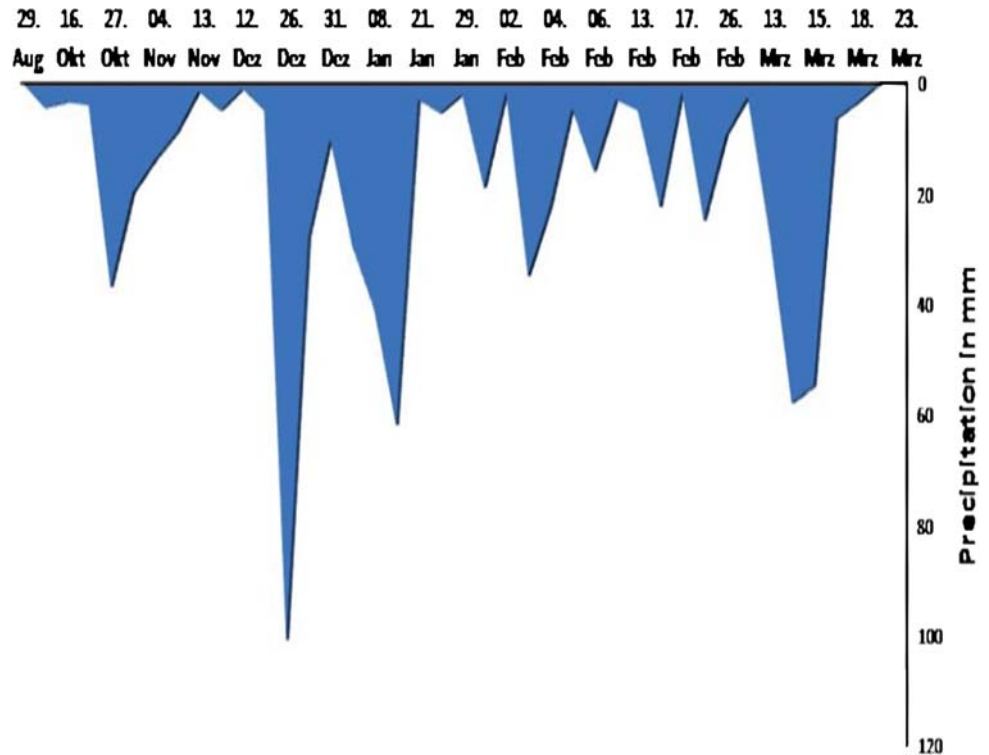
samples, while those coming after were assigned to be the late one.

Results

Total dissolved solids

All groundwater samples in the study area are of Ca-HCO$_3$ type (Table 2) because they originate from Judea Group limestone aquifer. In the Durov diagram the water analyzes clusters narrowly (Fig. 4). The scatter of total dissolved solids (TDS) is strongly related to alkalinity. There is no general tendency of TDS to increase with dissolved CO$_2$ or pCO$_2$, although the behavior of each spring is different (Fig. 5). During the winter season, some of the springs show variations in TDS at nearly constant dissolved CO$_2$, others show nearly constant TDS but variable CO$_2$.

During the wet winter season, however, the concentrations of solutes vary locally and temporally (Fig. 6a). At comparable times, the samples from Ein Fara (F) and Ein Qilt (Q) show slightly lower TDS than those from Ein Dyouk (D) and Ein Sultan (S). This indicates an increase in TDS with distance from the recharge area in the upper mountains along the flow path: Ein Fara–Ein Qilt–Ein Dyouk/Ein Sultan. Temporally, TDS increases in the first half of winter but decreases significantly in the second half due to increasing recharge in the mountain aquifer which enhances the water flow in the aquifer.

The increase in the TDS in the first half might refer to the flushing of soluble components stored during the earlier dry periods which are washed out by the first recharge events.

In general, the time-dependent trend of TDS is parallel to that of Ca and HCO$_3^-$ concentrations (with exception of Ein Qilt) but none of the other dissolved species.

Hydrochemical variations

Different from Ca, Mg shows higher and rather constant concentrations in the early period and lower ones in the later. A similar behavior shows Na in Dyouk and Sultan water. In early winter, Ca increases in Ein Fara and Ein Qilt but remains nearly constant in Ein Sultan and Dyouk. In late winter, Ca always decreases. K mostly shows a peak after the first significant rain storm and returns to initial values in the late season.

Along the water flow path in Wadi Qilt, HCO$_3^-$ concentration of groundwater increases toward the springs of Sultan and Dyouk at the Jericho western boundary fault (Fig. 6b). Dissolved CO$_2$ shows a strong maximum in Ein Qilt, Ein Dyouk, and Ein Sultan in mid-January. These peaks may refer to the same rain event, whereas the significantly lower peak in the Ein Fara water from mid-January may reflect a later strong rainfall.

Temporal changes of equivalent concentrations of Ca + Mg and HCO$_3^-$ + SO$_4^{2-}$ show little correlation Fig. 7, although their main sources are dissolution of

Table 2 The main physical and chemical results in mg/l for the groundwater samples from the springs at different times during the hydrological year 2006/2007

Spring	Sample_Date	pH	Eh(mV)	Temp	Cond	Na	K	Mg	Ca	Cl	SO_4	NO_3	HCO_3	DOC	SI calcite	SI dolomite	CO_2	pCO_2
En Dyouk	29.08.2006	7.14	275	22.3	680	23.2	2.4	27.6	68.1	45.7	19.4	28.6	257.42	5.74	−0.06	−0.2	34.276	0.020893
En Dyouk	30.10.2006	7.5	293	22.9	680	25.8	7.6	28.5	67.2	54.5	19.2	28.7	264.13	7.95	0.3	0.56	15.504	0.009333
En Dyouk	25.12.2006	7.19	292	21.4	698	27.3	2.7	28.1	72.9	47.5	19.5	28.7	298.29	3.83	0.06	0.01	34.98	0.02138
En Dyouk	14.01.2007	6.95	268	22	745	30.4	3	27.6	78.9	60.6	23.7	39.2	274.65	10.6	−0.18	−0.5	55.88	0.033884
En Dyouk	12.02.2007	7.6	284	19	650	23.5	2.7	23.1	71.6	41.2	23.6	28.3	286.7	0.39	0.41	0.6	13.64	0.007586
En Dyouk	02.03.2007	7.4	291	21.1	708	27.8	2.8	24.9	79.2	50.0	27.0	31.5	320.25	0.86	0.32	0.44	23.188	0.013804
En Dyouk	23.03.2007	7.3	334	21.2	618	19.2	1.7	18.4	62.3	36.9	23.0	25.4	201.3	1.88	−0.04	−0.32	18.656	0.01122
En Fara	29.08.2006	7.3	264	21	548	18.9	1.4	20.2	64.9	48.3	13.4	29.3	209.3	3.80	−0.01	−0.24	19.404	0.011482
En Fara	30.10.2006	7.14	251	22.2	552	19.8	3.3	21.4	54.3	46.1	12.6	21.3	211.67	5.65	−0.22	−0.53	28.028	0.017378
En Fara	25.12.2006	7.5	286	22	558	19.4	1.2	20.9	66.6	44.3	12.9	26.7	223.26	3.97	0.23	0.28	12.804	0.007943
En Fara	14.01.2007	7.3	267	21	624	21.2	1.6	22.4	70.2	50.1	13.4	22.14	244.61	8.74	0.08	−0.04	22.572	0.01349
En Fara	12.02.2007	7.05	274	21	648	26.3	2.0	17.5	69.0	52.3	19.9	28.8	236.07	1.03	−0.19	−0.68	38.94	0.023442
En Fara	09.03.2007	7.6	312	20.7	594	22.3	1.7	20.5	64.8	47.5	15.3	26.6	246.44	1.98	0.34	0.48	11.44	0.006761
En Fara	23.03.2007	7.3	32	21.3	578	20.3	1.4	18.4	56.3	33.8	12.4	18.9	232.41	2.94	−0.02	−0.22	22.44	0.012882
En Qilt	29.08.2006	7.05	229	21.7	555	18.9	1.6	19.4	64.4	47.3	14.4	20.6	240.95	3.90	−0.2	−0.61	40.04	0.023988
En Qilt	30.10.2006	7.1	248	21.7	586	19.2	1.9	21.6	71.3	44.3	12.7	23	248.27	4.57	−0.1	−0.4	36.08	0.021878
En Qilt	25.12.2006	6.89	227	21.4	625	20.5	10	21.3	65.6	41.5	10.2	25	285.48	6.17	−0.29	−0.76	67.76	0.040738
En Qilt	14.01.2007	6.8	246	21.2	657	25.9	5.86	26.3	69.9	47.4	12.8	15.5	331.84	10.7	−0.3	−0.72	96.8	0.057544
En Qilt	12.02.2007	7.35	261	21.2	620	23.4	2.5	17.5	73.2	42.7	16.2	20.9	270.84	1.37	0.19	0.07	22.44	0.01349
En Qilt	12.02.2007	7.55	283	21.1	625	20.6	2.6	18.0	74.2	39.0	14.4	18.7	256.2	1.75	0.37	0.43	13.64	0.007943
En Qilt	02.03.2007	7.55	291	20.1	650	23.8	2.5	16.7	71.3	44.6	18.1	25.0	223.26	1.32	0.29	0.23	11.88	0.006761
En Qilt	23.03.2007	7.27	308	21.3	450	17.1	2.1	13.7	61.5	28.4	14.1	15.7	213.5	2.10	−0.04	−0.43	21.56	0.012882
En Saultan	29.08.2006	7.02	256	22.1	685	24.5	2.5	28.1	77.4	49.1	16.9	28.5	313.54	3.70	−0.05	−0.23	54.12	0.033113
En Saultan	30.10.2006	7.2	263	26	690	25.6	2.5	28.4	73.5	56.9	20.0	26.6	286.09	5.51	0.12	0.19	33	0.02138
En Saultan	25.12.2006	7.15	279	21	699	26.5	2.5	28.7	75.6	49.2	19.5	23.1	310.49	16.9	0.05	−0.03	40.48	0.023988
En Saultan	14.01.2007	7.05	302	22.5	735	33	3.8	29.7	79.5	59.2	23.3	39.1	335.5	4.64	0.01	−0.09	53.24	0.033113
En Saultan	12.02.2007	7.4	286	21.6	671	25.1	3.1	23.4	72.3	44.9	24.0	30.7	253.15	0.71	0.2	0.23	18.48	0.01122
En Saultan	02.03.2007	7.5	295	21.3	705	27.7	2.7	25.2	77.2	50.2	27.2	32.2	278.16	1.93	0.36	0.53	15.928	0.00955
En Saultan	23.03.2007	7.35	331	23	525	21.1	2.3	20.2	67.4	38.8	23.1	26.2	228.78	2.46	0.11	0.03	18.48	0.0104

Fig. 4 Durov diagram shows the narrow hydrochemical cluster in the groundwater samples from the springs
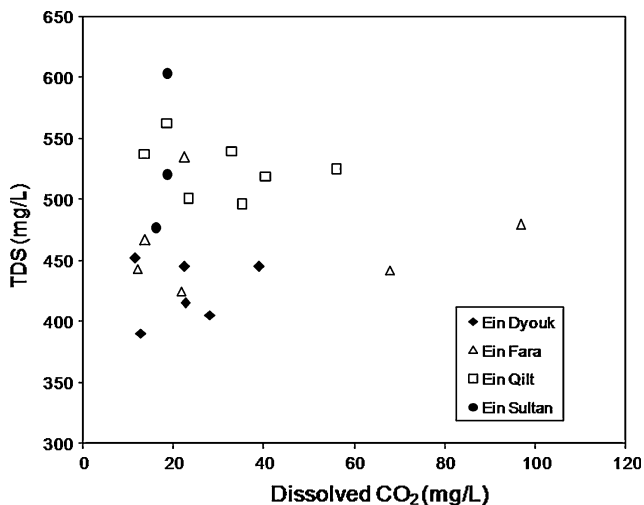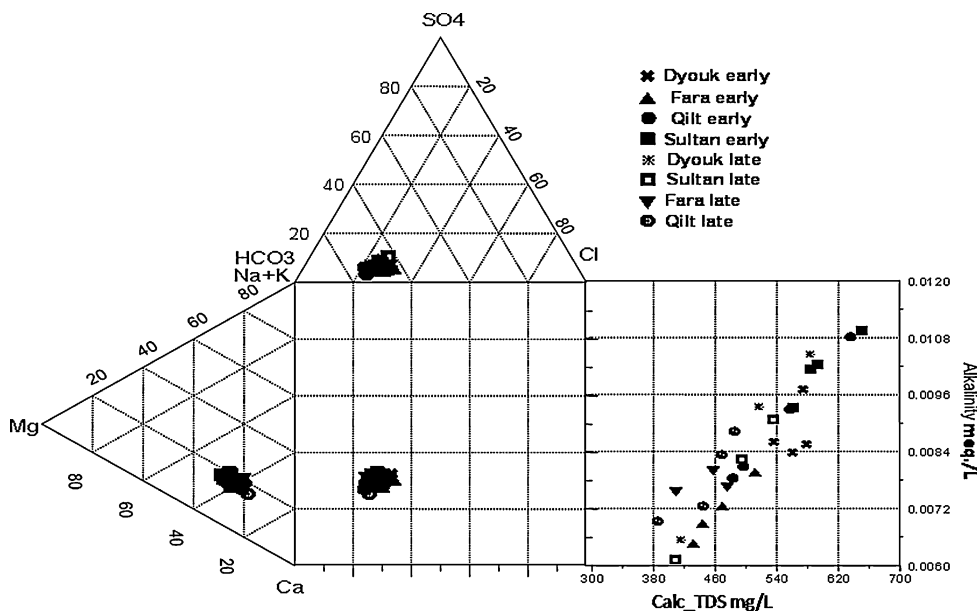

Fig. 5 Cross plots of TDS and dissolved CO₂

calcite, dolomite, and gypsum. Neither Ca nor Ca + Mg is balanced by HCO_3^- + SO_4^{2-}. Different from Ca + Mg, Ca alone shows trends corresponding with those of HCO_3^- + SO_4^{2-}. This indicates that Mg is less related to carbonate dissolution.

Defining the difference of (Ca + Mg) − (HCO_3^- + SO_4^{2-}) as "Mg" and (Cl + NO_3^-) − (Na + K) as Cl_{excess}, most of the samples reveal mixing with Mg–Cl type of water (Fig. 8). This Mg–Cl saline water can only be leached from the aquifer rocks, where it is present as inclusion in the Judea limestones.

The Mg/Ca molar ratio of 0.5 characterizes the initial conditions in Ein Fara and Ein Qilt and the final ones in Ein Dyouk and Ein Sultan which showed initial ratios between 0.6 to 0.7 (Fig. 9). The high Mg/Ca ratios of Ein Dyouk

and Ein Sultan indicate that here Mg is leached during the dry season and that this groundwater is now replaced and mixed with younger water of lower ratios.

Irrespective of fluctuations, Cl^- concentrations show a decreasing tendency with time, whereas sulfate increases; NO_3^- behaves in between. NO_3^- is related with SO_4^{2-} (Fig. 10) insofar as Ein Qilt and Ein Fara show lower contents than Ein Dyouk and Ein Sultan. The range of Cl^- concentration is nearly identical in all springs but the NO_3^- concentrations differ for Ein Qilt and Ein Fara on one hand and Ein Sultan and Ein Dyouk on the other. The correlation of NO_3^- and SO_4^{2-} with Cl^- concentration indicates that these anions have a similar source which could be the soil containing gypsum and of course evaporites from previous rainy seasons (halite, gypsum) and nitrate from sewage. These components are easily leached by percolating rain water.

Related to leachable inorganic components are organic ones comprised as dissolved organic compounds DOC (Table 2). They are the sources of changes in dissolved CO_2 which is discussed later.

Carbonate saturation

Using the analytical results on pH and HCO_3^- the pCO_2 calculated using open domain PHREEQC program. As shown in Fig. 11 pCO_2 varies between 0.01 and 0.06. The higher pCO_2 values are associated with high HCO_3^- concentrations.

In most cases, the groundwater in limestone aquifers is close to saturation (Fig. 12) with respect to calcite (and less so for dolomite). The majority of the reported waters are supersaturated with respect to calcite. Only when the

Fig. 6 Time-dependent concentrations of dissolved species in spring water from Ein Fara (F), Ein Qilt (Q), Ein Dyouk (D) and Ein Sultan (S)
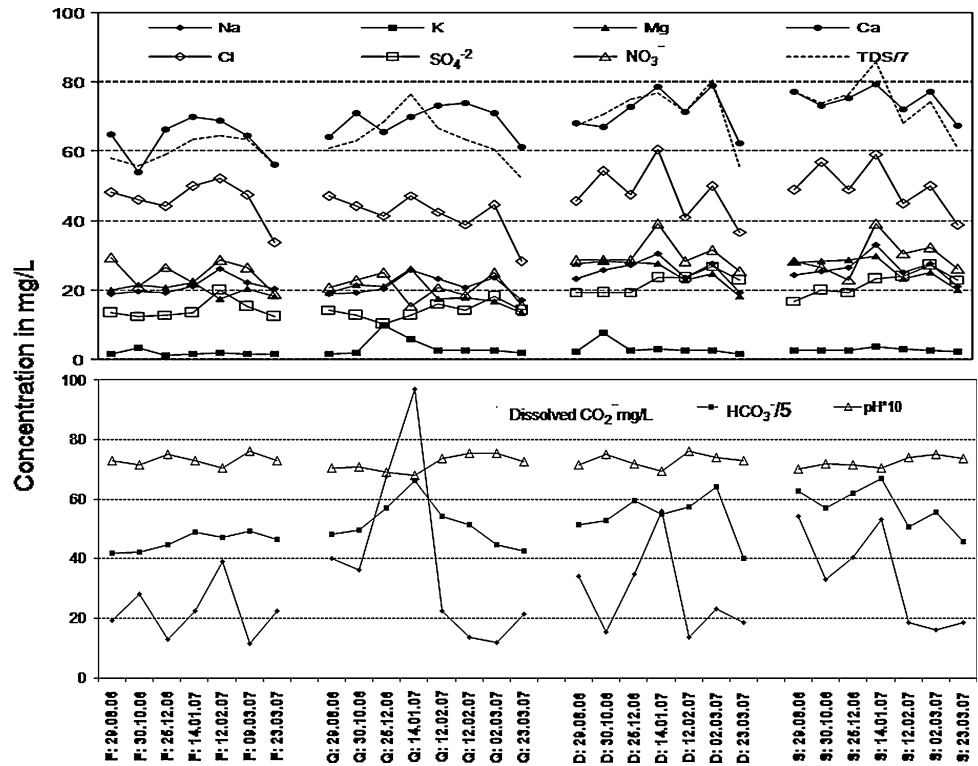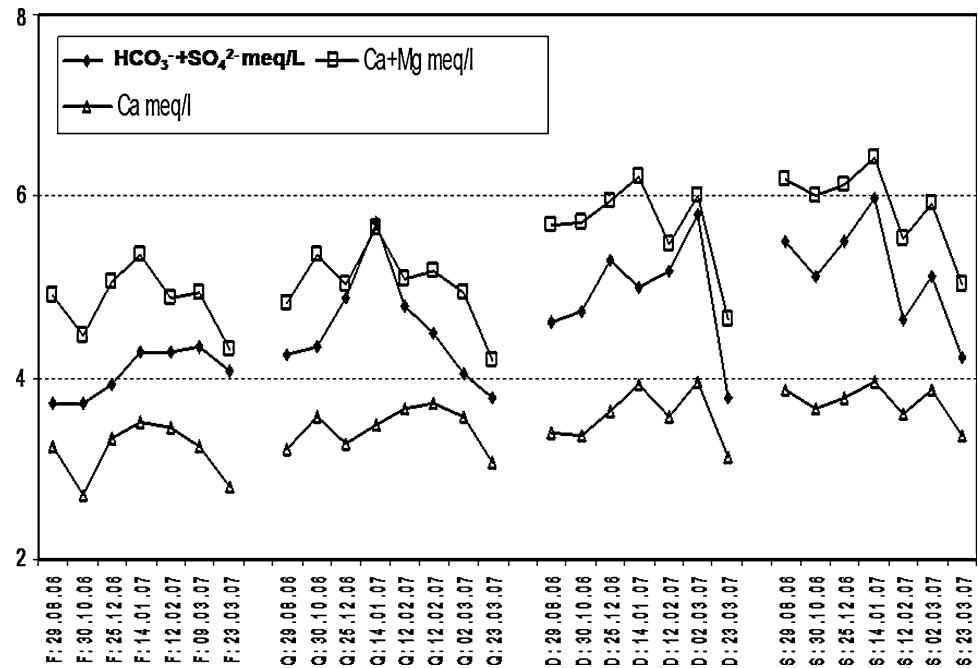

Fig. 7 Time-dependent changes of $HCO_3^- + SO_4^{2-}$, $Ca^{2+} + Mg^{2+}$, and Ca^{2+} in spring water from Ein Fara (F), Ein Qilt (Q), Ein Dyouk (D) and Ein Sultan (S)

groundwater is enriched in CO_2 (decreased in pH; Fig. 6b), the spring waters are unsaturated with respect to calcite (and dolomite). Calcite saturation during the rainy season is controlled by variations of dissolved CO_2. Excepting Ein

Qilt, saturation of calcite but not of dolomite is reached at the beginning and at the end of the rainy season. During the season excursions of +0.4 to −0.2 occur for calcite. SI dolomite varies between +0.6 and −0.8.
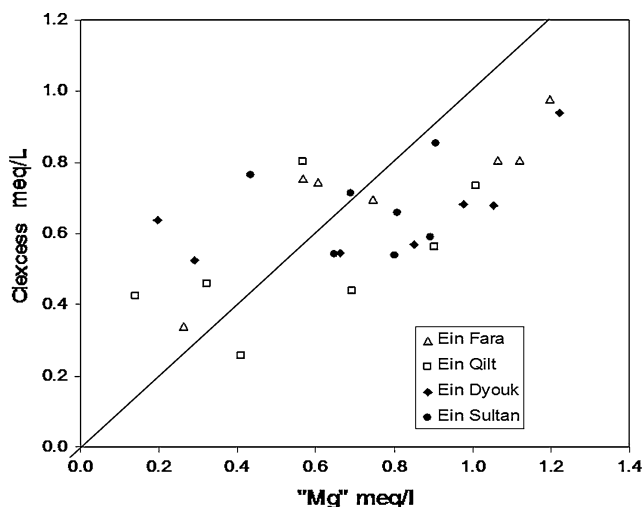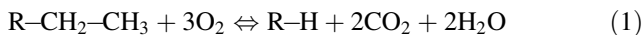
Fig. 8 Cross plots of Cl_{excess} versus "Mg"

Fig. 10 Cross plots of NO_3^- versus Cl^- (**a**) and SO_4^{2-} (**b**)

Discussion

Anthropogenic effects

Dissolved organic carbons play a significant role in groundwater chemistry. Organic substances leached from soil and garbage are oxidized according to reaction (1).

$$R–CH_2–CH_3 + 3O_2 \Leftrightarrow R–H + 2CO_2 + 2H_2O \qquad (1)$$

Because HCO_3^- is always greater than dissolved CO_2 oxidation of organics has a great impact on dissolved CO_2 in closed systems and thus pH decreases (Eq. 2). Decreasing pH finally leads to undersaturation.

$$pH = pK_1 + \log\left[HCO_3^-\right] - \log[CO_2] \qquad (2)$$

DOC is the residual of organics dissolved in the early infiltrating water. Low values indicate that decomposition by oxidation is nearly complete, whereas high ones show that oxidation has not been acting for long times. Therefore, high values are present particularly in late winter time, which indicates that the oxidation is a slow process and the initially low values are the product of low water flow and negligible infiltration during the summer season. Assuming that the high peak of dissolved CO_2 in Fig. 6b represents the water that was enriched in CO_2 during the summer season is now replaced under the influence of the first significant precipitation event (Fig. 3), the time interval of about 2.5 months characterizes the flow

Fig. 9 Time-dependent changes of Mg/Ca wt ratios in spring water from Ein Fara (F), Ein Qilt (Q), Ein Dyouk (D) and Ein Sultan (S)

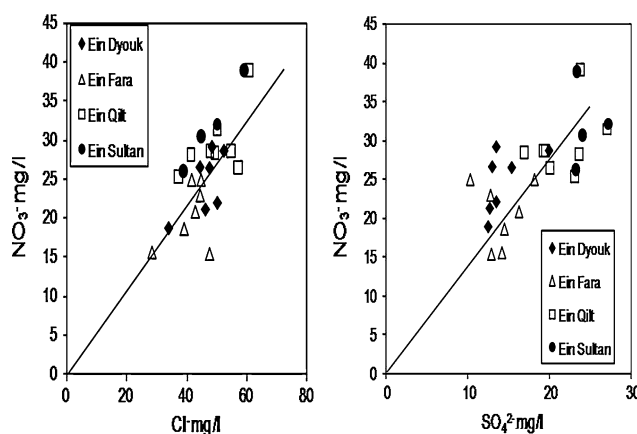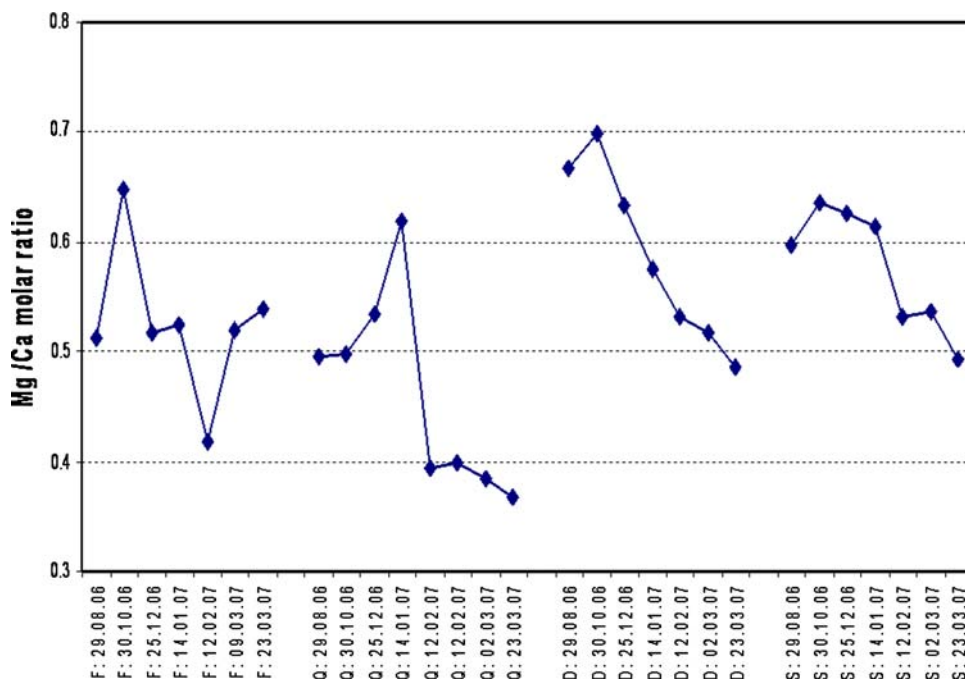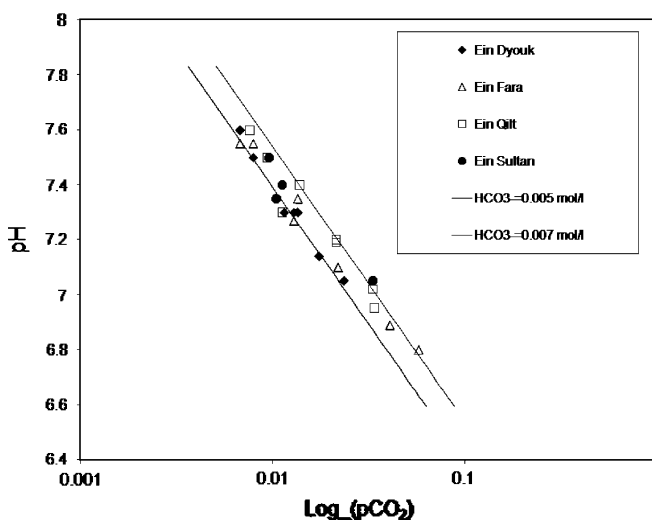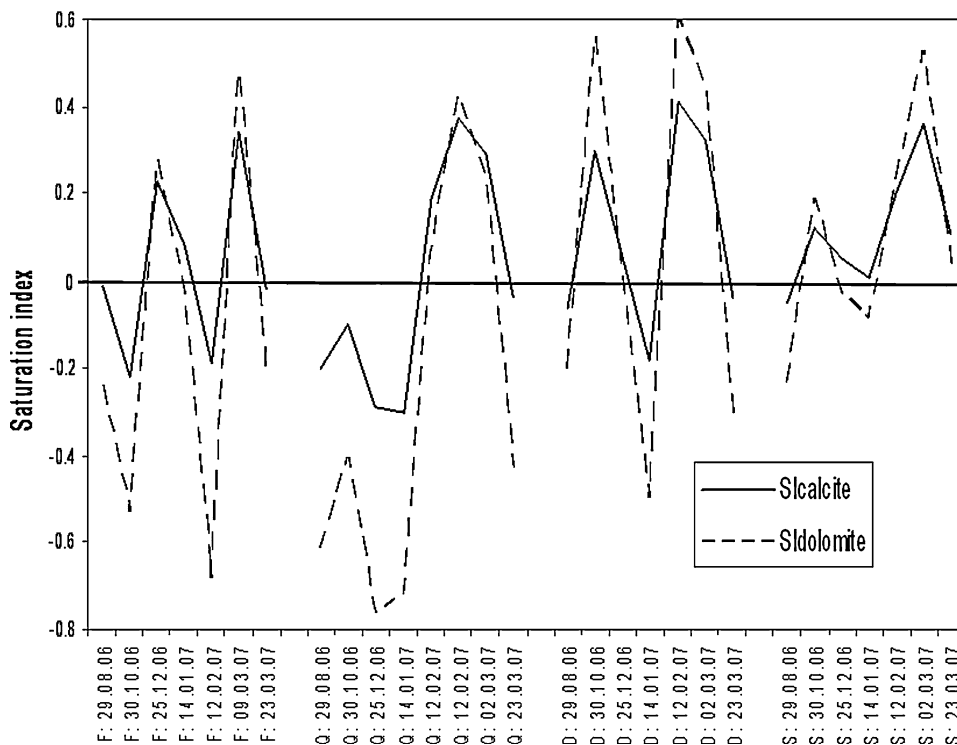**Fig. 11** Cross plots of pH versus pCO_2

Fig. 12 Time-dependent changes of saturation index of calcite and dolomite in spring water from Ein Fara (F), Ein Qilt (Q), Ein Dyouk (D) and Ein Sultan (S)

time from the recharge area of the mountain aquifer to Ein Qilt, Ein Dyouk, and Ein Sultan. This peak is not repeated as a response to later strong precipitation events which suggest that DOC is the residual of organic compounds that were immediately washed out from soil during the early rainy season. Towards the end of the winter season the CO_2 concentration is the same in all springs and similar to that at the beginning of the winter period in Ein Fara. Due to changes in dissolved CO_2, pH varies and consists of an early and late period (Fig. 6b).

The increase of dissolved CO_2 induced dissolution of calcite and thus Ca but not Mg increased. The dissolution of calcite dominantly leads to increase in TDS. The increase in the concentrations of Ca^{2+}, HCO_3^-, (and less so of Mg^{2+}), especially during the dry period, resulted from the dissolution of the host matrix, mainly calcite, under the influence of dissolved CO_2. Dissolution still plays a role in the early winter period. Thereafter, concentration of most dissolved species decrease and so does TDS due to dilution (Fig. 6). After the first replenishment of the aquifer in early winter time, the flow rate of water increases and the residence time decreases and thereby the possible interaction with CO_2 from DOC.

The behavior of Mg and Na in Ein Dyouk and Ein Sultan reflects dilution. Simultaneously, SO_4^{2-} increases continuously, probably due to leaching gypsum from Lisan sediments in the Jericho Plain. Leaching of gypsum affects the low concentrations of SO_4^{2-} much more than the high ones of Ca.

At high water level in the aquifer, gypsum is leached from the overlying Lisan Formation, which is predominant in the Jericho Plain. Because the Lisan Formation is absent in the recharge area in the upper mountains, this effect is not seen in Qilt and Fara. Without gypsum dissolution, the Ca decrease would be more than observed. This means that gypsum is an additional source for Ca and sulfate in Dyouk and Sultan springs, while in Qilt and Fara springs gypsum dissolution does not play a major role.

Anthropogenic pollutants such as nitrate are strongly related to sulfate and less so to Cl^- which indicates leaching from soil and rocks by irrigation return flow. In general, there is some correlation between NO_3^- and Cl^- concentrations which is not explicable by dilution (Fig. 10a). The rather constant NO_3^-/Cl^- ratio may be due to leaching of both components from soil or infiltration of sewage.

The correlation of sulfate, chloride, and nitrate in some springs (Fig. 10), reflects that these species are washed out from fertilized soils. In the intensive farming area, Ein Dyouk and Ein Sultan yield significant higher nitrate concentrations than Ein Qilt and Ein Fara in the nature reserve. The slope of the indicated trend line in yield NO_3^-/Cl^- wt ratios of 0.54, which is quite high indicating additional contamination by human activity such as farming, etc.

Mg/Ca ratio

The continuous decrease of Mg/Ca wt ratios in Ein Dyouk and Ein Sultan indicate mixing of water in the aquifer by the new recharge water. The mixing demands for a dual porosity flow in which the recharge water with low Mg/Ca ratio uses the larger karst conduits and mixes with the old water with high Mg/Ca ratio which is present in parts of the aquifer with less transmissivity. The less transmissivity pool decreases with time and thus the Mg/Ca ratio of the spring water decreases.

The rather constant but different Mg concentrations in spring waters during early and late seasons requires a rather large pool of Mg. In Ein Dyouk and Ein Sultan this behavior is paralleled by Na, which is much less pronounced for Ein Qilt and Ein Fara. Such a pool could be the marly layers of the overlying Lisan Formation acting as aquitard. The clay minerals may react here as ion exchanger. Leaching of Mg–Cl water from sediments or rocks is also a possibility. In any case the equilibrium is quickly established.

Carbonate dissolution dominantly controls Ca concentrations. Dissolution of calcite is slow because the waters are largely saturated with respect to calcite. High-magnesium calcite releases Mg by forming low Mg-calcite. Equilibration with dolomite at this low temperature is negligible. This explains why these waters are mostly oversaturated with respect to dolomite.

After an initial increase of Mg/Ca in Ein Dyouk and Ein Sultan the springs show a gradual decrease in Mg/Ca molar ratio resulting from higher decreases in Mg than in Ca (Fig. 9), i.e., from about 0.65 to about 0.5 in the late winter season. A similar trend is observed in water from Ein Qilt but here the ratio varies between 0.6 and 0.4. Values of 0.5 are typical ratios in calcareous aquifers of the study area (Schoeller 1977; Rosenthal, 1987).

Ein Fara shows a trend of its own. The general decrease of Mg/Ca ratios is associated with increasing precipitation and runoff (Fig. 9). These results show that with the increase of rainwater recharge the stored water in the aquifer is flushed out by the middle and the end of the winter season. In the early period the water shows the solute contents gained due to long contact with minerals of the aquifer during the dry period. This water is replaced by infiltrated runoff in the Wadi Qilt zone (zone 1) and then is going to replace the water of Sultan and Dyouk springs in the Jericho Plain zone (zone 2) by underground flow.

In general, the compositional changes in Ca and Mg concentrations mainly depend on the residence of water in the aquifer which is controlled by the volume and mechanism of recharge and the distance from the recharge area. The absolute ratios, however, do not yield a measure of the residence time. For instance, the ratio of 0.5 indicates long residence times in Fara and Qilt, but short ones in Ein Dyouk and Ein Sultan, although all these springs discharge water from the same aquifer. The mineralogical composition of the aquifer of the springs in Wadi Qilt contains less soluble Mg-bearing minerals than that the one from which the Jericho springs originate. The result in the study area indicate that the Mg/Ca ratio is not a reliable, generally applicable indicator for residence times of the water in aquifers as suggested by Edmunds and Smedley (2000), Kloppmann et al. (1998), and Langmuir (1971), being only controlled by incongruent dissolution of calcite, magnesian calcite and dolomite (Bakalowicz 1979; Musgrove and Banner 2004).

Groundwater recharge

The groundwater recharge and flow is mainly controlled by two factors: the geologic structure and geometry of the aquifer along the flow path of groundwater. These factors play an important role in controlling the aquifer flow across the eastern slope, which is reflected by the behavior of

solutes within the aquifer the different zones of Wadi Qilt and Jericho Plain.

This infiltration zone is located to the west of the Marsaba anticline (Figs. 1, 2). The section west of the anticline is uplifted. Thus, the base of the aquifer is raised and the flow gradient increases which resulted in an increase of the flow velocity and reduced residence time. Zone 1, represented by Ein Fara and Ein Qilt, is fed directly through the infiltration of meteoric water and surface run-off from the mountains.

Contrastingly zone 2, represented by Ein Sultan and Ein Dyouk, is located east to the Buqea syncline and Marsaba anticline parallel to the western fault boundary. Here, the aquifer thickness decreases from the syncline to the anticline (Fig. 2) which may act as a retardation factor to flow. The Marsaba anticline prevents the groundwater of the Upper Cretaceous aquifer from flowing further eastwards and thus the replenishment of the springs east to the anticline takes a longer period of time (Wolfer 1998; Guttman 2004) and these springs are fed by groundwater with high solute contents leached from aquifer rocks. The mentioned springs of zone 2 are located along the western boundary fault in the western part of Jericho–Auja area, where the fault acts as a flow barrier. The water normally flows laterally along the fault; the latter confines the groundwater for additional period of time resulting in increasing contact time of rocks and groundwater. The recharge mechanism for the zone 2 is different from that in zone 1 due to different geological structures. The zone of Sultan and Dyouk springs is covered by a chalky Eocene layer (Kumi; Fig. 2), which is considered an aquiclude preventing further surface runoff infiltration into the aquifer zone. Therefore, the aquifer is replenished nearly exclusively by underground flow.

Conclusion

The strongly inclined aquifers of the Wadi Quilt and the less inclined ones of the Jericho Plain result in changes with residence time of groundwater in the aquifer and with distance from the recharge area which in turn causes changes in chemical composition of spring water. Due to the monocline two zones with different recharge characteristics are distinguishable. In zone 1 on the slopes of the eastern mountains recharge of the aquifer is mainly by direct infiltration of precipitation and runoff combined with less groundwater residence time and high flow rate. The second zone is near the western border of Jericho at the foothills, which is mainly fed by the groundwater flow from the eastern slopes. This zone is characterized by higher groundwater residence time and slower flow rate than in zone 1. The main factors controlling the residence time and flow rate of groundwater are the geological structure, the amount of active recharge of the aquifer and the recharge mechanism.

A detailed analysis of dissolved species reveals that besides dissolution of carbonates, chloride, and sulfate are leached from the aquifer rocks. Mg not only originates from carbonates but also from Mg–Cl saline waters included in the rocks. Leaching of Mg is particularly high at the beginning of the winter season and lowest at its end.

A very important factor in the composition of groundwater is the oxidation of organics derived from sewage and garbage resulting in variable dissolved quantities of CO_2. High CO_2 yields lower pH values and thus undersaturation with respect to calcite and dolomite. Low CO_2 concentrations result in carbonate oversaturation. At the beginning and at the end of the rainy season calcite saturation is always achieved. Associated with dissolution of carbonates is the major source of increasing water hardness.

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