Geochemical evolution and recharge of the shallow aquifers at Tulul al Ashaqif, NE Jordan

Nizar Abu-Jaber

Abstract Shallow aquifers in the Tulul Ashqaf area in northeast Jordan represent areas where relatively high recharge is occurring in an arid environment. The significance of this phenomenon in terms of potential for water resource development in the area is related to the amount of recharge that is occurring as well as factors that may affect the water quality within the aquifers. Modeling of the geochemical evolution of these waters gives insight into these issues. Chemical data from rainwater, surficial salts, crushed basalt samples, runoff, and groundwaters were collected, and the chloride mass balance approach was used by integrating these various data into geochemical mass balance models using NETPATH. Variations between rainwater chemistry, the surficial salts and basalt, and runoff exist, suggesting various processes and sources, and allows determination of the input into the groundwater. Geochemical modeling shows that the majority of chloride added to the groundwater after runoff events was salt from surface deposits, and that the rainwater had undergone only small amounts of evaporation. Isotopic investigations of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ of the waters confirmI this result. The results indicate that most of the water that falls over the study area percolates to the shallow groundwater with little evaporation. Less than 25% of the water evaporates prior to recharge. Water stored in the aquifer is affected by water–rock interaction and little evidence suggests that evaporation is a factor in the chemical evolution of the waters of the shallow aquifers, except in areas where salt efflorescence occurs.

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Introduction

Jordan is facing a chronic shortage of water resources. An arid climate, high natural growth rates, and forced migrations have conspired to push available water resources to the limit, with little room for increasing the available amount without huge investments, which are out of reach for the country. Because demands on water resources will increase as time goes on, ways must be found to better utilize the resources available as well as resources that have been overlooked in the past.

Annual rainfall in Jordan ranges from 600 mm in the northwestern highlands to less than 100 mm in the badia region. It is estimated that 80.6% of Jordan receives less than 100 mm of rainfall per year (Salameh and Bannayan 1993). Assuming that the average rainfall in this area is 70 mm, the dry areas in Jordan receive 5 billion m^3 a year. Most of this water flows in small internal drainage basins to end up in playas (qa's), and ultimately are lost to evaporation. Little is known about the amount of groundwater recharge in these areas, particularly in the northeastern badia, although some evidence shows that it is not very high (Noble 1994; Abu-Jaber and others 1998). The problem of quantifying groundwater recharge in arid regions has received much attention in recent years (Allison and others 1994; Wood and Sanford 1995; Gaye and Edmunds 1996; Tyler and others 1996). Effective new techniques have been developed that rely on following water through the vadose zone using chloride mass balance and tritium and radiocarbon tracers. Similar arguments will be used to estimate recharge water in the shallow saturated zone.

Shallow aquifers in the Tulul Ashaqif area in northeastern Jordan have been known by the inhabitants of the area for many generations. These aquifers may provide clues for more effective water management policies in the area for a number of reasons. First, they seem to represent the areas of naturally occurring recharge. As such, it may be useful to know what factors make them most suitable for natural recharge. Second, they may help us quantify the amount of

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recharge. Third, storage of waters in these aquifers may provide a natural analog for water storage that needs to be emulated. It is clear that subsurface storage is preferable to above ground storage for a number of reasons, including safety, reduction of evaporative loss, and prevention of pollution. Thus, the aquifers at Tulul Ashaqif may fulfil the natural requirements for what may needs to be done artificially. The saturated zone is shallow (<8 m). The water is clearly of local recharge because the aquifers lie near the top of a ridge, precluding lateral flow from outside the area. It is also of recent origin, as indicated by the tritium data, which is presented later. Moreover, it is far from any source of pollution. Natural threats to the quality of the water in the area need to be understood. This will be done by assessing the sources of the various solutes that enter the groundwater. In addition, an attempt will be made herein to demonstrate a modified chloride mass balance approach that takes into account various chloride sources to estimate arid zone recharge. These, in conjunction with stable isotopic data, will be used to quantify the amount of recharge into the aquifers.

Study area

The study area lies within the basalt plateau northeast of Jordan (Fig. 1). A NNE-trending ridge known as Tulul al Ashaqif extends for a distance of about 50 km, and reaches an elevation of about 900 m a.s.l. Within the basaltic Tulul al Ashaqif, a number of wadis (ephemeral streams) drain toward the east and west. Despite low rainfall in the area (<100 mm/year), a number of perched aquifers have been discovered by the local Bedouins generations ago. Wells have been dug into these aquifers by hand, and are well known by the local population, although they have been largely neglected in recent years.

The depth to the regional water table in the area is about 200 m. The stable isotopic characteristics of the main aquifer suggest a sub-recent age (Abu-Jaber and others 1998), and may be as old as 30,000 years or more (Bajjali and Abu-Jaber 2001). The waters of the regional aquifer are of relatively low quality, with total dissolved solids (TDS) exceeding 1,100 mg/l. These waters are enriched in Na^+, Cl^- and SO_4^{2-} (Abu-Jaber and others 1998).

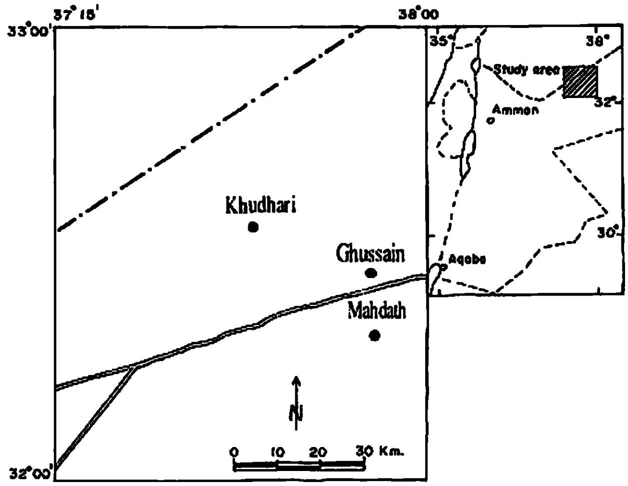

Fig. 1
Location map

Perched aquifers have been tapped at three locations (Fig. 1), these are Biyar el (i.e., wells of) Mahdath, Biyar el Khudari, and Biyar el Ghussein. At all three of these locations, hand-dug wells penetrate the saturated zones of alluvium at depths that do not exceed 10 m, and occasionally do not exceed 2 m. This study will concentrate on the recharge characteristics of the Ghussein well system, with a reference to the Khudari well field.

The Ghussein well system lies at approximately 32°26′N and 37°45′E, along the upper reaches of a small drainage basin, which flows towards the SE. Four major types of surfaces characterize the drainage area. These are playas, pavement, basalt outcrop, and alluvium. The playas are covered exclusively with fine-grained sediment consisting of various types of clays. The pavement consists of basaltic fragments, which cover fine-grained loess outside of the main channel areas. The alluvium is coarse grained in most areas, although it becomes finer along the wider areas of the wadi channels.

For 3 km along this drainage system there are shallow wells and a spring. The wells can be conveniently divided into two groups. The upper well in the NW is about 8 m deep. It is currently dry, although water was observed about 3 years ago, before the current drought lowered the water levels to below the bottom of the well. About 2 km to the southeast, the river valley narrows significantly from a wide (>3 km) plain into a small gorge less than 200 m wide (Fig. 2). At this point, shallow wells of about 3 m deep have been dug and contain water. Nearby, about 100 m away, a small escarpment of basalt, about 5 m high, defines the southwestern boundary of the wadi (Fig. 2). Along this escarpment, a small spring emanates from the basalt, suggesting that the perched water system is not confined to the alluvium, but extends into the basaltic bedrock. This also indicates that recharge may occur through the basalt and the pavement, and the fine grained eolian mantle that covers it. It also seems significant that water discharge is perennial and has continued despite the drought that has affected the region. This suggests that significant amounts of water are stored in the basalt. About 300 m downstream, the valley flattens and widens again, where a large number of shallow wells (about 2 m deep) were dug into relatively fine-grained alluvium. It is interesting to note that thin evaporitic crusts cover much of the area here during the summer, suggesting discharge by evaporation. One well in this location has been dug in the weathered northeastern basaltic outcrop and is of better quality than the other wells, and is also better maintained. The weathered basalt is remarkable because all the other basalt in the area is very fresh. This is a localized phenomenon, and suggests either an old water table or a remnant relict of an old weathering surface reflecting a more humid climatic regime. In both cases it suggests that groundwater reacts with the basalt in the area.

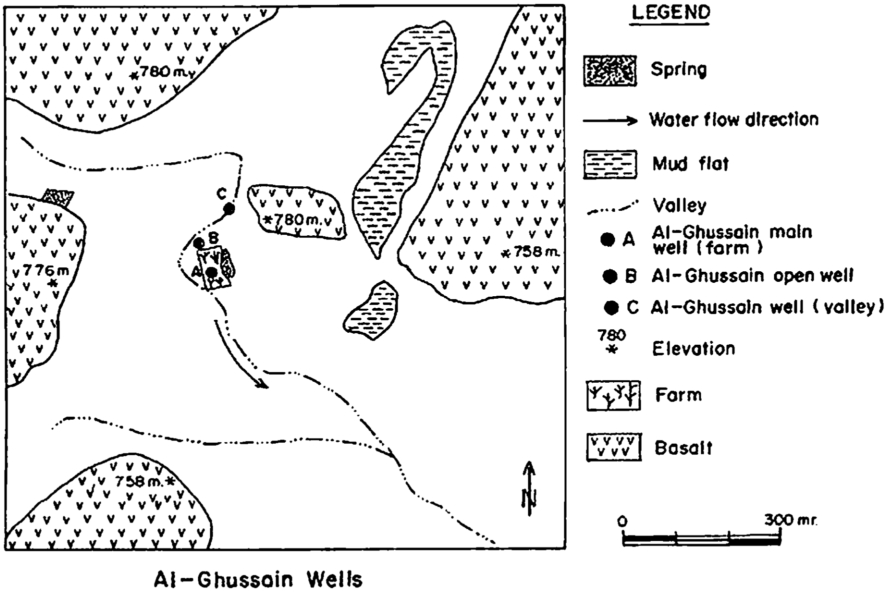

Fig. 2
Sketch of the Ghussein area

About 200 m downstream, a 5-m-deep well is used to irrigate a small farm. There is little evidence of soil salination at this location.

Review of geochemical approaches to recharge

The study of natural recharge of groundwater systems in arid environments presents some unique challenges. For example, most flow systems in arid regions are ephemeral, so it is quite rare to have any reliable information concerning flow rates in desert drainage systems. Also, with the erratic rainfall distribution, it is common to see enough rain to cause runoff generation in one location and no rain or runoff in an adjacent location. Therefore, traditional water balance techniques used in more humid regions are of little use in the desert environment.

Allison and others (1994) reviewed the major techniques used in arid zone groundwater recharge and their limitations. Because of the limitations inherent in the physical techniques used in estimating groundwater recharge, indirect measurements based on geochemical and isotopic proxies have become increasingly popular. One of the most popular techniques in recent years has been the use of chloride and isotope profiles in the vadose zones of arid regions (Allison and others 1994). Chloride has also been used to measure recharge to the saturated zone as well (Dettinger 1989; Mazor and George 1992).

The principle of chloride mass balance is that chloride acts as a conservative tracer. Because rainwater contains small amounts of Cl^-, this solute will travel through the unsaturated zone until it reaches the water table. Its concentration in the water of the vadose zone would be proportional to the amount of evaporation prior to infiltration as follows:

$$Cl^-_{gw} = Cl^-_{precip.}/f \qquad (1)$$

where f is the residual water fraction, Cl^-_{gw} is the amount of Cl^- in the groundwater (usually measured in the vadose zone), Cl^-_{precip} is the concentration of Cl^- in the precipitation (wet and dry) and residual water fraction represents the recharge into the aquifer. There is no term for runoff, as the model assumes that chloride is preserved within the drainage system. This is realistic in arid areas that have numerous small, closed drainage basins, such as this study area. In many cases (Wood and Sanford 1995), data are collected from playas that represent the termini of the drainage in the basin, which would avert this problem altogether, although it presents different problems related to recharge prior to reaching the terminus of the drainage basin.

A second assumption in this approach is that the sole source of chloride in the system is wet precipitation. It is commonly assumed that rock–water interaction is not a source of chloride except in explicit instances where the rocks contain distinct chloride-bearing minerals (Wood and Sanford 1995). This assumption will be tested in the system modeling. Although it is recognized that both wet and dry precipitation may contribute to the chloride flux into the system, there has been little work to quantify the dry precipitation. Dettinger (1989) attempted to quantify this term by direct collection of atmospheric input.

A third assumption involves the openness of the system. That is, chloride does not accumulate in the system, but is flushed out as the water moves through the system.

The use of tritium in the saturated zone is limited. In general, the guideline often used is simple: if it contains tritium, it has been recharged after 1964, if it does not, then it is older. Although this is a good rough indicator of recharge, it hardly qualifies for rigorous quantitative analysis. This problem is commonly tackled by the study of ingrown ^3He from the decay of tritium. Unfortunately, the technical facilities needed to do this are not available to the author. In any case, the point of the tritium analysis is to show that the water was recharged recently and reflects modern climatic and hydrological conditions.

Stable oxygen and hydrogen isotopes are typically used for two types of studies: First, the absolute oxygen isotope signature and the oxygen 18–deuterium relationship is used to analyze variations in climate over long periods of time. Isotopic signatures have been used both for vadose zone studies (Tyler and others 1996; Gaye and Edmunds 1996) as well as saturated zone studies (Fricke and O'Neil 1999; Bajjali and Abu-Jaber 2001). The approach is useful when discrete samples can be given unique ages with confidence, and at its optimum can indicate how recharge regimes have changed through time.

The second approach is to determine the proportion of rainwater that has undergone evaporation prior to recharge. Isotopic composition changes because fractionation occurs between the liquid and vapor phase of the water during evaporation. The fractionation phenomenon can be explained in terms of thermodynamic equilibrium or in terms of kinetic fractionations. The former is simpler to model, but is difficult to justify in real-world situations, particularly in arid regions. The general formula for kinetic isotopic fractionation can be given as follows:

$$R = R_o f^{(\alpha - 1)} \tag{2}$$

where R is the current isotopic ratio; R_o is the ratio at the initial time; f is the residual water fraction and α is the fractionation factor. This relationship is commonly referred to as Rayleigh distillation. Clark and Fritz (1997) present a concise review of the subject.

Approach and methods

The approach used in this study is to characterize solute sources in the context of other chemical changes to water as rain falls, flows in channels, infiltrates, and mixes with the groundwater and resides there. During each step, specific chemical changes are evaluated in terms of solid sources and possible evaporative concentration. The holistic use of all major chemical data will allow a more realistic evaluation of the potential sources of chloride into the system as well as understand the sources of solutes that may effect the quality of the water.

Atmospheric input consists of wet and dry precipitation. In addition, weathering and concentration of solutes in the surficial deposits can contribute to the solutes moving into the groundwater system (Weisbrod and others 2000). Analyses of rainwater in the area will be augmented by a large data set describing the regional chemistry of rainfall. This is quite straightforward. The more difficult task is to characterize other sources of solutes and their relative importance.

Dry surface deposits were sampled in the Ghussein drainage area for labile solutes. About 50 surface samples were collected from the drainage area of Ghussein to represent the various types of surfaces present. About ten samples of basalt from the study area were collected. In the laboratory they were washed with deionized water, dried, and subsequently crushed to a powder in a tungsten carbide mill. Two grams of each surface deposit and powdered basalt sample were soaked in 500 ml of deionized water for about 30 min under atmospheric CO_2 concentrations. After the samples were centrifuged, decanted and filtered, chloride and bicarbonate contents were determined using standard titration techniques. Sulfate was analyzed by measuring light absorption caused by turbidity induced from $BaSO_4$ precipitation. Sodium and potassium concentrations were measured using flame photometry and calcium and magnesium were measured using atomic absorption spectrometry.

Recognizing that the absolute concentrations of the solutes are of little to no meaning in and of themselves, the purpose was to determine the chemical ratios of the major solutes that were extracted. These would represent the labile solid phases present in the surface deposits and presumably represent the weighed average of dry eolian deposition, weathering products, and recycled solutes in the vadose zone. It is hoped that these would provide a distinct chemical signature that would be recognized in the runoff water that flows through the drainage basin.

If the chemical nature of rain is different from that of the surface deposits, then the nature of the runoff will be determined by the chemistry of the precipitation and by the chemistry of the solutes present in the surficial deposits of the drainage basin. Mass balance models can be used to predict the proportion that each has contributed to the chemical load of the runoff. After this is resolved, the question of how much evapoconcentration has occurred becomes relatively simple. The chloride mass balance law mentioned earlier can be modified to take the new factor into account:

$$\begin{aligned} &Cl^-_{runoff} * \text{proportion of } Cl^- \text{ from wet precip.} \\ &\quad = Cl^-_{precip.}/f \end{aligned} \tag{3}$$

The chemistry of the water was analyzed to determine what chemical signals were imparted onto the water over short periods of time before degradation of the silicates begins to impart its own signature. Rainwater and groundwater were sampled for chemical and isotopic analysis. Rainwater was collected at the meteorological station at Safawi, and stored in polyethylene vials prior to analysis. Water was sampled using buckets from the wells and the spring. Clean bottles were buried in the stream channel to collect runoff waters. The winter 2000 samples were collected within 24 h after rain events and the 2001 samples were collected about 1 week after the rain event. All samples were stored in clean, well-sealed polyethylene vials until analysis. Tritium contents were determined at the Water Authority Laboratories in Amman. This was done using isotopic enrichment and beta scintillation counting. The errors associated with this technique are typically ±1 tritium unit. Stable oxygen and hydrogen ratios were determined using a Finnigan–Mat Ratio mass spectrometer at the Water Authority laboratories. The errors are estimated to be $\pm 0.15‰$ for the oxygen and $\pm 1.0‰$ for the hydrogen. Evaporation was estimated using this data by applying the Rayleigh distillation relationship. The chemical nature imparted by the basalt on the runoff water can be quantified using chemical mass balance assumptions. Using the resulting models, it is relatively simple to quantify the contribution of the basalt to the chloride load in the groundwater. After this is determined, the question of chloride evapoconcentration again be addressed using a modified form of our earlier chloride mass balance equation:

$$Cl^-_{groundwater} * \text{proportion of contribution of from } Cl^- \text{ from runoff.} = Cl^-_{runoff.}/f \qquad (4)$$

NETPATH (Plummer and others 1991) models were used for this purpose because they are ideal for this sort simulation, allowing for simultaneous calculations of chemical change based on mass balance assumptions. This type of approach ignores the thermodynamic constraints of water chemistry. The chemicals used in the models were chloride, sulfate, bicarbonate, sodium, potassium, magnesium, and calcium. The phases used were empirical salt phases that define the extreme end members found in the surficial deposits. These phases are based on the leaching test and may represent mixtures of evaporitive minerals. This is difficult to determine because of their low concentrations in the bulk samples. In addition, calcite, gypsum, CO_2, and sodium and potassium silicates were considered. NETPATH allows for the dissolution and precipitation of the phases input into the model, and allows for calculations of water mixing and evaporation and dilution. Thus the models generated can explain the various chemical reactions that may lead to the change of water chemistry from one point to the next.

Results

Input functions

Although it is clear that wet deposition is the source of water to the system, the source of solutes are of wet and dry deposition as well as sediment and rock water interactions. As stated earlier, it is difficult to interpret the chloride content of the water without considering the other chemical clues dissolved into the water matrix. The signals from these input functions will be discussed.
Regional rainwater chemistry has been studied by a number of workers (Bajjali 1990; Yair and others 1991; Al-Momani and others 1998; Jaradat and others 1999; and Al-Momani and others 2000). A summary of the reported analyses is shown in Table 1 and plotted on Fig. 3. The data show that chloride concentrations in rainwater range from a little more than 3 to 19 mg/l, and that the cations in the rainwater are dominated be Ca^{2+}, although they can be marginally enriched in Mg^{2+} and Na^+. Anions are dominated by HCO_3^-, but they can be enriched in Cl^- or SO_4^{2-}. Solute sources in these waters are generally attributed to a combination of marine aerosol sources admixing with local calcareous dust (Al-Momani and others 2000).
The results of the extractions are summarized in Table 2 and plotted in Fig. 3. On average, the chemistry of the labile salts in the surface deposits are distinct from the wet deposition. The labile surface salts are poorer in SO_4^{2-} and richer in Ca^{2+}.
Labile salts within the basalt samples are similar in chemistry to the labile surface salts (Table 3; Fig. 3), although it can be argued that they are slightly enriched in K^+ and Na^+. This suggests that basalt weathering is the dominant source of solutes in the surface deposits. The similarity between the surface salts and the labile fraction

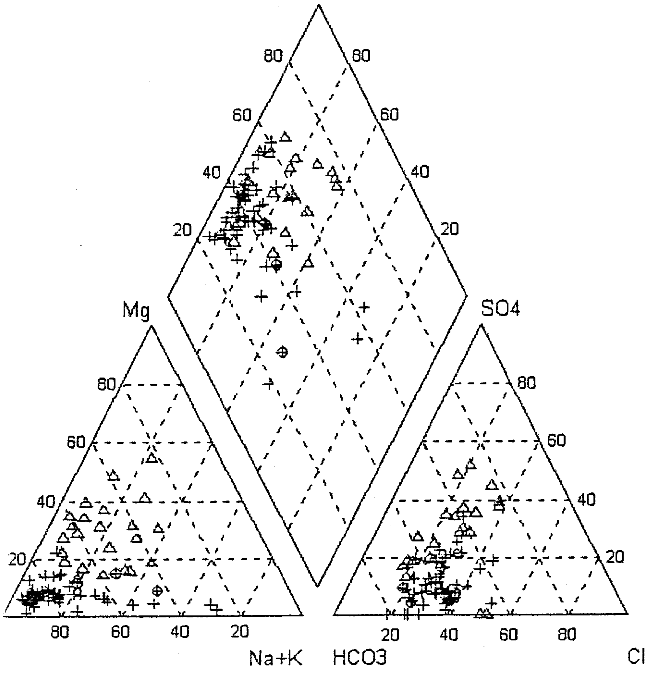

Fig. 3
Piper diagram representing input chemistries. *Open triangles* represent rainwater, *crosses* represent dry deposition, and *crossed circles* are leachates from the basalt

Table 1
Rainwater chemistry data from 25 samples. Data from Bajjali 1990; Yair and others 1991; Al-Momani and others 1998; Jaradat and others 1999; Al-Momani and others 2000

	Min.	Max.	Average	SD	Var.Coeff.	Variability (%)
Conductivity (μS/cm)	60.0	330.0	121.8	63.424	52.063	82.0
pH	6.0	7.85	6.761	6.558	97.002	24.0
Na (mg/l)	0.69	6.897	3.586	1.8	50.202	90.0
Ca (mg/l)	2.004	32.064	10.749	7.665	71.306	94.0
Mg (mg/l)	0.498	14.586	3.62	3.082	85.126	97.0
K (mg/l)	0.0	2.0	0.683	0.654	95.752	100.0
Cl (mg/l)	3.333	19.0	8.885	4.261	47.952	82.0
SO_4 (mg/l)	0.0	32.659	12.835	8.432	65.694	100.0
HCO_3 (mg/l)	3.782	131.777	32.13	30.084	93.633	97.0

Table 2
Results of leaching experiments on surface sediment samples. Results from 51 samples in the Wadi Ghussein area

	Min.	Max.	Average	SD	Var. Coeff.	Variability (%)
Na (mg/l)	0.09	18.2	1.634	3.411	208.803	100.0
Ca (mg/l)	4.23	31.29	9.288	4.265	45.924	86.0
Mg (mg/l)	0.13	1.89	0.511	0.299	58.479	93.0
K (mg/l)	0.2	6.2	1.627	1.207	74.175	97.0
Cl (mg/l)	10.0	35.0	16.98	4.835	28.475	71.0
SO_4 (mg/l)	0.0	34.42	8.864	7.034	79.363	100.0
HCO_3 (mg/l)	40.0	80.0	55.804	10.231	18.334	50.0

Table 3
Results of the leaching experiments from six basalt samples from the Wadi Ghussein area

	Min.	Max.	Average	SD	Var. Coeff.	Variation (%)
Na (mg/l)	0.3	3.8	1.15	1.322	114.9	92.0
Ca (mg/l)	2.47	10.0	5.435	2.717	50.0	75.0
Mg (mg/l)	0.3	0.45	0.372	0.063	16.97	33.0
K (mg/l)	0.2	1.2	0.717	0.431	60.12	83.0
Cl (mg/l)	15.0	22.0	17.5	2.881	16.46	32.0
SO_4 (mg/l)	2.89	11.84	6.583	3.952	60.03	76.0
HCO_3 (mg/l)	40.0	110.0	65.0	25.884	39.82	64.0

Table 4
Rainwater and runoff used to model evolution from rain to runoff. Water concentrations are in mg/l. Runoffs 1–3 are from Ghussein, number 4 is downstream from Ghussein, and 5 is from Khudari

	Safawi rain	Runoff 1	Runoff 2	Runoff 3	Runoff 4	Runoff 5
Na	4	360	19	6.8	6.8	4.5
Ca	11	35	23.6	21.5	46.5	29.8
Mg	4	37	6.2	3.4	3.6	3.7
K	4	50	25.1	3.7	3.7	4.1
Cl	12	170	5	10	9	8
SO_4	11	141	45.6	30.3	42.8	36.7
HCO_3	31	110	100	100	110	106

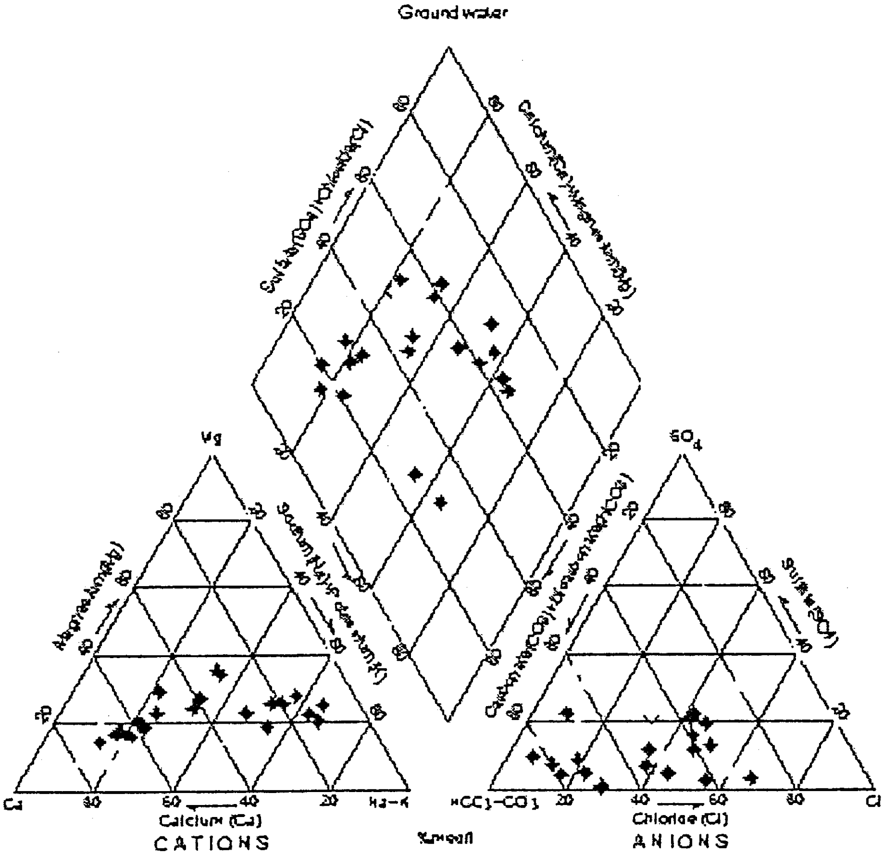

Fig. 4
Piper diagram representing runoff chemistry

of the basalt precluded any attempts to differentiate between these sources if, in fact, they are distinct in origin.

Runoff water

Only two direct samples of runoff water have been collected in 2000, and six in 2001. The results of these analyses are summarized in Table 4. Figure 4 shows the chemistry of the runoff water.

Comparing the data from the input chemistries of the wet deposition and the surficial salts as well as the characteristics of the leachates from the basalt show that there is a difference between these chemistries and those of the runoff waters. The runoff waters seem to be largely influenced by the surficial salts.

Groundwater

The chemistries of the waters of the spring and wells are summarized in Table 5 and Fig. 5. The data suggest that the groundwater and the runoff waters are similar. There seem to be seasonal trends in the chemistries of these waters as well. Summer water has higher TDS values, and also has lower sulfate values. These data suggest that one or more geochemical processes act on the water as it evolves through the system. The following section may clarify these processes using mass balance models.

Modeling of hydrochemical evolution

Rain to runoff waters

The chemistry of runoff waters is largely the result of evaporation and interaction between rainwater and salts contained in the surface sediments. To model this process, the geochemical mass balance software package NETPATH was used (Plummer and others 1991). The nature of the salts present in the surface deposits is somewhat variable, but can be restricted to three distinct end members. These end members were treated as distinct phases that were

Table 5
Chemical analyses of groundwaters from the Wadi Ghussein area. Conductivity in µS/cm and the solute concentrations in mg/l

Location	Date	Conductivity	pH	Na	Ca	Mg	K	Cl	SO_4	HCO_3
Main farm	17/1/00	810	8.0	60	74	31	20	125	84	190
	9/3/00	775	7.1	42	55.8	19.2	13.6	120	40.2	180
	15/9/00	923	8.1	30.4	88.4	18.7	10.8	100	14.3	200
	10/1/01	561	7.4	24.0	55.0	14.5	9.4	31	10.5	250
Open well at farm	17/1/00	999	7.8	50	45	31	10	150	66	380
	9/3/00	963	7.2	33	28.2	19.1	6.1	140	35	360
	5/9/00	1,391	8.3	115.1	70.4	31.8	16.9	180	11.3	240
	10/1/01	380	7.4	16.5	55.9	8.5	9.1	29	18	190
Middle valley	17/1/00	1,178	8.0	160	115	32	20	180	128	260
	9/3/00	1,139	7.0	35	39.9	30.5	15.9	160	76	240
	5/9/00	1,391	8.3	115.1	70.4	31.8	16.9	180	11.3	240
	10/1/01	380	7.4	16.5	55.9	8.5	9.1	29	18.0	190
Spring	17/1/00	1,363	8.0	230	54	61	10	225	172	280
	9/3/00	1,298	7.8	196	34.5	32.3	6.8	210	72	255
	5/9/00	1,993	7.6	382	153.5	106.6	47.7	700	42.0	550
	10/1/01	185	7.7	7.0	20.9	4.2	4.9	9	29.6	114

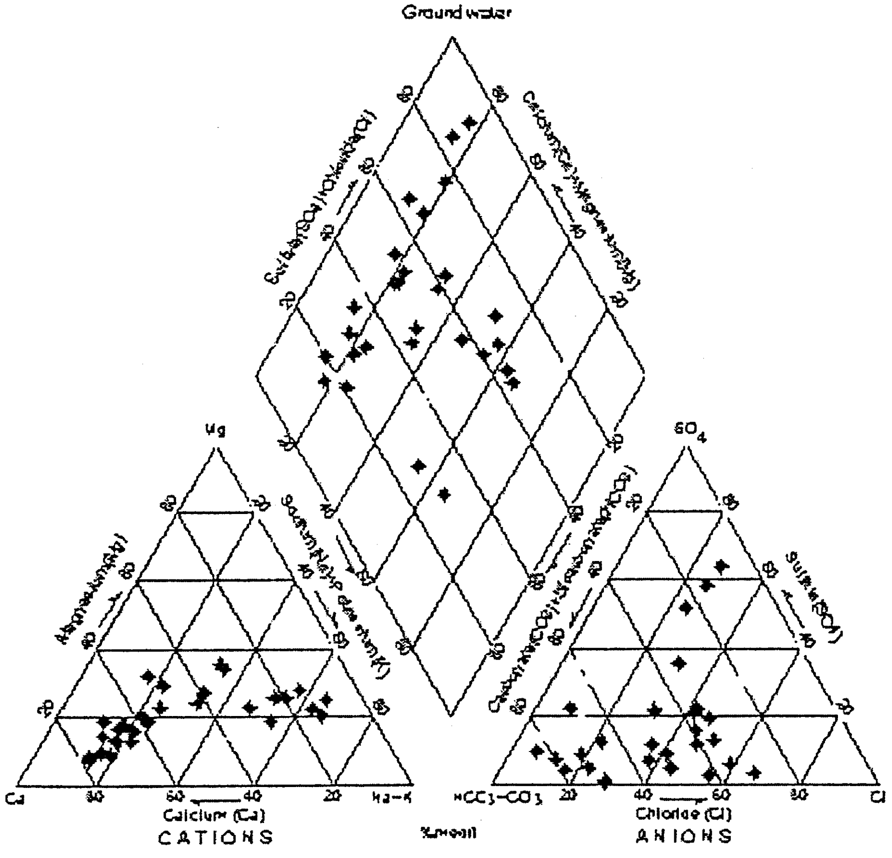

Fig. 5
Well and spring samples. *Crossed circles* are wells, *crosses* are from the spring

employed in the modeling. The chemistry of the rain and runoff waters are listed in Table 4. Details on the chemistry of the salts used are in Table 6. Other phases used were calcite, gypsum, CO_2 gas, potassium feldspar, and sodium montmorillonite.

The first runoff sample has a relatively high chloride content, and is anomalous in its chemistry compared with the other runoff samples . The first set of simulations was run without allowing for the possibility of evaporation. The models show that evolution by simply dissolving salts and mineral phases into the rainwater is theoretically possible, although it is reasonable to assume that some evaporation has taken place.

Models allowing evaporation are listed in Tables 7 and 8. The model results suggest evaporation factors ranging from 5.4 (f=0.184) to 8.4 (f=0.120). An evaporation factor of 8.4 means that 59% of the chloride in the runoff comes from the original rain, and the rest comes from the salts present in the surficial deposits. Thus, the models indicate that the source chloride has a maximum rainwater contribution of 59%, and it could go down to 0% if non-evaporation models are considered.

Table 6
Salts used in the models (in mol)

	Salt 1	Salt 2	Salt 3
Na	0.04	0.56	0.01
Ca	0.36	0.54	0.28
Mg	0.07	0.05	0.03
K	0.09	0.56	0.04
Cl	1.00	1.00	1.00
SO_4	0.03	0.00	0.64
HCO_3	1.63	4.42	1.45

Table 7
Chemical inputs for the NETPATH used to simulate the first runoff event. Initial well: rain (4/1/2000); final well: runoff (17/1/2000). Seven models were checked, four models were found

	Final	Initial
C	1.2789	0.5181
S	1.4687	0.1145
Ca	1.3232	0.2745
Mg	1.5228	0.1645
Na	1.5669	0.1305
K	1.2795	0.0512
Cl	4.7980	0.3385

Table 8
Results of the simulations for reactions producing the chemistry of the first runoff event. Positive numbers indicate dissolution and negative numbers indicate precipitation

	Model 1	Model 2	Model 3	Model 4
Albite	+0.15254	+0.06917	+0.15717	+0.03598
K-Feldspar	+0.17471	+0.04975	+0.18167	
Calcite	–0.21799	–1.30594	–0.15744	–1.73908
Gypsum	+0.05133	+0.97369		+1.34090
Salt 1	+0.44245	+1.86493	+0.36329	+2.43125
Salt 2	–0.19578		–0.20668	+0.07794
Salt 3		–1.40665	+0.07828	–1.96667
Evaporation factor	8.199	6.022	8.368	5.446
Remaining H_2O (g)	121.962	166.067	119.507	183.627

The second runoff sample is quite different from the first. It has a lower chloride concentration than the rainwater collected at the time the first rainwater sample was collected at Safawi. Unfortunately, a rainwater sample could not be obtained at the time of the later runoff events, although the variability in rainwater chemistry in the region is limited (Table 1 and Fig. 3). Subsequent modeling that required rainwater chemistry used this sample because it is quite typical of the record. The water chemistry is within the range of rainwater reported for the region (Fig. 3). Modeling the change from rainwater to the second runoff water suggests dilution (compatible with a rainwater sample with a lower solute load), and dissolution of gypsum and sodium and potassium silicates. This model suggests that none of the chloride load comes from the surface salts. Although this may be true, it may also reflect some of the variability in the input rainwater. In any case, it is difficult to speculate. It is notable that the low chloride concentration suggests that evaporation in this runoff sample can be considered negligible.

Generation of the runoff chemistries of the December 2000–January 2001 Wadi Ghussein waters was simulated the same way. The results of the simulation show that the change needed can easily be explained by salt dissolution. Tables 9 and 10 include some of the results of these simulations, with the models that suggest gypsum precipitation being ignored because of the improbability of this happening given the thermodynamic constraints. Because

Table 9
Chemical inputs for the NETPATH used to simulate the January 2001 runoff waters at Ghussein. Initial well: rain (4/1/2000); final well: Ghussein runoff (1/2001). Eight models were checked; two models were found

	Final	Initial
C	1.6575	0.5181
S	0.3155	0.1145
Ca	0.5390	0.2745
Mg	0.1399	0.1645
Na	0.2958	0.1305
K	0.0946	0.0512
Cl	0.2821	0.3385

Table 10
Simulations for the reactions needed to produce the January 2001 runoff waters at Ghussein

		Model 1	Model 2
Albite	+	–0.00208	–0.09498
K-Feldspar	+	–0.09305	
Calcite		0.25184	0.24968
Gypsum	+		0.00131
Salt 1	+	–0.74367	–0.74561
Salt 2	+	0.33842	0.34231
Salt 3	+	0.34886	0.34691
CO_2 gas		0.09805	0.08899

the runoff has lower chloride concentrations than the rainwater input, evaporation is not expected to be a major contributor to the chemical change. Allowing evaporation into the model bears this out because all models generated that allow evaporation result in dilution rather than evaporation.

Runoff to groundwater

Variability in the chemistry of the runoff samples and the uncertainty of the source of recharge to the surficial aquifer necessitates a slightly different approach. It is reasonable to assume that changes in the water chemistry of the spring and wells are a response to the first measured runoff event. Therefore, changes in water chemistry were modeled in the wells of the area following the runoff event sampled on 17 January 2000. On that day water was sampled from three wells and from the spring. The spring and wells were subsequently resampled on 9 March 2000. In the intervening time the chemistry of the wells changed notably and there was a drop in the conductivity of the waters, suggesting that fresh water had recharged the aquifer during that time. Results of the NETPATH models for chemical change in the farm well are presented in Tables 11 and 12 and those of the spring in Tables 13 and 14. The models generated are based on the premise that the change in water chemistry between the two dates is the result of mixing water of an earlier date with runoff. Phases included are the three salt end members, gypsum, calcite, CO_2, and sodium and potassium silicates. The results of the models for the farm well are similar. They both suggest that the runoff waters make up 44–70% of the mixture prior to dilution by factors of 1.8–2.1 (Tables 15 and 16). The models for the spring suggest that runoff waters make up 60–96% of the mixture prior to dilution factors of 1.3–1.5 (Tables 11 and 12). Models using the second runoff water to model the change could not be generated. Physically, dilution can only mean that the runoff water was diluted prior to mixing, or, in other words, the runoff is an evapoconcentrated version of the waters that went into recharge. In fact, the change in chemistry can be modeled by simply allowing dilution and interaction with the salt and mineral phases mentioned

Table 11
Chemical inputs for the NETPATH used to simulate the changes in the spring water after the first runoff event. Initial well 1: runoff (17/1/2000); initial well 2: spring (17/1/2000); final well: spring (9/3/2000). Seven models were checked; two models were found

	Final	Initial 1	Initial 2
C	4.2627	1.2789	4.5933
S	0.7480	1.4687	1.7924
Ca	0.8615	1.3232	1.3487
Mg	1.3296	1.5228	2.5116
Na	8.5324	1.5669	10.0148
K	0.1740	1.2795	0.2560
Cl	5.9281	4.7980	6.3530

Table 12
Results of the simulations for reactions producing the chemical changes seen in the spring after the first runoff event. Positive numbers indicate dissolution and negative numbers indicate precipitation

	Model 1	Model 2
Init 1	0.96075	0.59515
Init 2	0.03925	0.40485
Albite	9.37375	+8.59248
K-Feldspar	−1.28207	
Calcite	−0.70031	+2.97730
Gypsum	−0.57415	−3.62007
Salt 1	+3.05765	0.00000
Salt 2		−1.42860
Salt 3	0.0	4.91411
Dilution factor	1.335	1.504
Remaining H_2O (kg)	1.335	1.504

Table 13
Chemical inputs for the NETPATH used to simulate the changes seen at the farm well after the January 2001 runoff event. Initial well 1: farm (9/2000); initial well 2: Ghussein runoff (1/2001); final well: farm (1/2001). Twenty-eight models were checked; three models were found

	Final	Initial 1	Initial 2
C	4.3890	3.2559	1.6575
S	0.1094	0.1489	0.3155
Ca	1.3728	2.2066	0.5390
Mg	0.5967	0.7695	0.1399
Na	1.0443	1.3229	0.2958
K	0.2405	0.2763	0.0946
Cl	0.8747	2.8219	0.2821

Table 14
Results of the simulations for reactions producing the chemical changes seen in the farm well after the January 2001 runoff event. Positive numbers indicate dissolution and negative numbers indicate precipitation

		Model 1	Model 2	Model 3
Init 1	+F	0.69739	0.70461	0.70078
Init 2	+F	0.30261	0.29539	0.29922
Albite	+	0.00424		
K-feldspar	+		0.00442	
Calcite		−1.57825	−1.52912	−1.55748
Gypsum	+	1.47303	1.42499	1.45185
Salt 1	+	1.32573	1.22575	1.27662
Salt 2	+			0.00420
Salt 3	+	−2.50434	−2.42271	−2.46806
CO_2 gas		4.66537	4.64930	4.64806

Table 15
Chemical inputs for the NETPATH used to simulate the changes seen at the farm after the first runoff event. Initial well 1: runoff (17/1/2000); initial well 2: farm (17/1/2000); final well: farm (9/3/2000). Seven models were checked; two models were found

	Final	Initial 1	Initial 2
C	3.3922	1.2789	3.1299
S	0.4187	1.4687	0.8781
Ca	1.3929	1.3232	1.8474
Mg	0.7901	1.5228	1.2758
Na	1.8278	1.5669	2.6114
K	0.3480	1.2795	0.5118
Cl	3.3864	4.7980	3.5279

Table 16
Results of the simulations for reactions producing the chemical changes seen in the farm well after the first runoff event. Positive numbers indicate dissolution and negative numbers indicate precipitation

	Model 1	Model 2
Init 1	0.69535	0.43669
Init 2	0.30465	0.56331
Albite	+1.77591	+1.45690
K-Feldspar	−0.55966	
Calcite	+0.96645	+2.54465
Gypsum	−0.50352	−2.06384
Salt 1	+2.56165	0.0000
Salt 2		−0.57305
Salt 3	+0.00000	+2.63720
Dilution factor	2.059	1.815
Remaining water (kg)	2.059	1.815

Table 17
Chemical inputs for the NETPATH used to simulate the chemical changes seen at Khudari A well after the January 2001 runoff event. Initial well 1: Khudari A (9/2000); initial well 2: Khudari runoff (1/2001); final well: Khudari A (1/2001). Twenty-eight models were checked; three models were found

	Final	Initial 1	Initial 2
C	2.2642	4.0448	1.8001
S	0.1229	0.0187	0.4217
Ca	0.6987	1.9694	0.7437
Mg	0.1934	0.4979	0.1522
Na	0.2741	0.8660	0.1958
K	0.1151	0.1637	0.1049
Cl	0.1693	1.6931	0.2257

Table 18
Results of the simulations for reactions producing the chemical changes seen at Khudari A well after the January 2001 runoff event. Positive numbers indicate dissolution and negative numbers indicate precipitation

		Model 1	Model 2	Model 3
Init 1	+F	0.10890	0.10891	0.10890
Init 2	+F	0.89110	0.89109	0.89110
Albite	+	0.0		
Calcite		−0.17349	−0.17346	−0.17347
K-Feldspar	+		0.0	
Gypsum	+	0.03567	0.03563	0.03565
Salt 1	+	0.24957	0.24949	0.24952
Salt 2	+			0.0
Salt 3	+	−0.46579	−0.46573	−0.46576
CO_2 gas		0.66173	0.66171	0.66171

Table 19
Chemical inputs for the NETPATH used to simulate the changes seen at the farm between winter and fall 2000. Initial well: farm (9/3/2000); final well: farm (9/2000). Twenty-eight models were checked; four models were found

	Final	Initial
C	3.2559	3.3922
S	0.1489	0.4187
Ca	2.2066	1.3929
Mg	0.7695	0.7901
Na	1.3229	1.8278
K	0.2763	0.3480
Cl	2.8219	3.3864

earlier, with no input from runoff water. Physically, this means that no evapoconcentration is needed to model the chemical changes in the water.

Recalculating the mixtures to include the dilution to the recharge results in dilution factors of about 2.5 for the farm well and from 1.3–1.8 for the spring. Thus, the runoff water does not seem to be representative of the recharge water because it has been subjected to higher evaporation. As mentioned above, these could all be overestimates of the contribution of rainwater to the solute load because it is conceivable that all of the solutes could come from the salts in the soil.

If it is assumed that there was a contribution from the runoff water to the chloride of the groundwater, then the models suggest that the added chloride from the runoff water does not exceed 17%, with the balance being contributed by the salts in the surficial deposits. Again, the only exception is the water at the spring, where the runoff waters could have contributed up to 36.8% of the added chloride.

The runoff waters collected in January 2001 seem to be more representative of the waters that reach the shallow aquifers. Two examples are the changing of farm well at Ghussein and the change seen at Khudari A.

Tables 17 and 18 show the results of modeling of the farm well after the January 2001 runoff event. The data suggest that the chemistry can be explained by mixing 70% initial well water with about 30% runoff water with no evaporation. The models suggest that more chloride is removed because of salt precipitation than added from dissolution. This indicates that the runoff water has higher chloride concentrations than the water that actually caused the recharge. This supports the notion that rainwater is a very small contributor to the chloride flux to the watershed, as it has been established earlier that the runoff water itself has experienced little evaporation. Models of the Khudari A well (Tables 17 and 18) suggest that 90% of the water in the well following the runoff event came from the runoff water. Again, the models suggest that more chloride is removed into salts than is added from them.

The implications of the March 2000 models for the chloride mass balance approach are significant. Chloride added to the water in the saturated zone can be attributed entirely to dissolution of the salts present in the surface deposits. In the most optimistic scenario, 17–37% of the chloride added to the groundwater originated from rainwater. Moreover, the models imply that the rain waters enter the groundwater with small amounts of evapoconcentration. In the January 2001 models, the runoff led to significant drops in chloride concentrations and, again, it is difficult to see how evaporation of rainwater has contributed to the chloride supply to the wells.

Evolution through the summer

Changes in the chemistry though the summer of 2000 was modeled at the farm well (Tables 19 and 20). The purpose

Table 20
Results of the simulations for reactions producing the chemical changes seen in the farm between winter and fall 2000. Positive numbers indicate dissolution and negative numbers indicate precipitation

		Model 1	Model 2	Model 3	Model 4
K-feldspar	+	–0.48471	0.37284	0.19871	
Calcite		–4.61174	1.17509		–1.34089
Gypsum	+	5.62054	0.85873	1.14132	2.44368
Salt 1	+	10.79062		2.87553	5.17689
Salt 2	+		–0.88461	–0.70498	–0.50000
Salt 3	+	–9.56148	–0.45483	–2.30406	–4.41420
CO_2 gas		2.82027	1.95494	2.13066	2.33117
Dilution factor		1.636	1.030	1.153	1.293

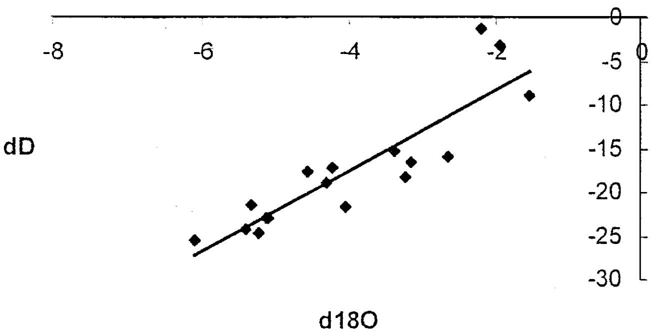

Fig. 6
δD–$\delta^{18}O$ relationships of the rain and spring waters in the area

was to determine if degradation in water quality through the summer can be attributed to evaporation or to rock–water interaction. The results clearly show that increased salinity through this period is caused by mineral dissolution and, if anything, the water was diluted during this period (an unlikely scenario).

Isotopic models

Results of the isotopic analyses of the waters of the area are presented in Table 21 and Fig. 6. They show that all of the water is clearly new, based on the tritium contents. The stable isotopes show a clear, heavy signature that can be attributed to the heavy signature of the rain in the area as well as to subsequent evaporation.

The rainwater sample is similar to those reported by Bajjali (1990) for the Azraq area, about 70 km to the south. There the reported values were –4.64‰ $\delta^{18}O$ and –20.0‰ δD for an average of 20 samples. Linear regression of the data from the rain and the wells gives us a significant relationship with a 95% confidence level. The slope of the regression line is 4.6. This suggests that the evaporation occurred with a relative humidity of about 50% (Clark and Fritz 1997). More significantly, calculation of the residual fraction of the water based on the Rayleigh fractionation equation mentioned earlier using a fractionation factor of 1.0098 (Mojabe 1971) yields evaporation of less than 25% of the original input water in most cases. This is despite the fact that the wells are open and subject to evaporation after recharge occurs. This is probably why the slope of the regression line seems to reflect summer evaporation rather than winter. The covered well and spring show very little evidence of evaporation in the stable isotopic compositions. These results are consistent with the mass balance geochemical models described earlier.

Conclusions

Careful consideration of the various chemical inputs into the groundwaters of the Ghussein area give important insights into the nature of recharge in the area and the threats to water quality in the event of using these aquifers for water storage. An initial review of the available rainwater data and labile salts in the surficial sediments and basalt of the area showed that there is a significant difference in the chemistry of both.

Mass balance models using NETPATH indicate that after one runoff event in January 2000, subsequent changes in the chemistry of the groundwaters could be attributed either to remobilization of salts and dilution of the groundwater or to infiltration of runoff in conjunction with salt mobilization and dilution. In both of the models that were generated it is clear that most chloride added to

Table 21
Tritium and stable isotope data from waters of the area. *f* is calculated based on the fractionation of the oxygen isotopes using the Rayleigh equation. Initial oxygen isotope ratio is assumed to be the average rainwater value at Azraq (Bajjali 1990). Tritium was not analyzed for the more recent samples

	Sample date	Tritium	$\delta^{18}O$ vs. SMOW	δD vs. SMOW	*f*
Rain	04/01/00	2.76	–4.04	–21.7	0.943
Main farm	17/01/00	5.47	–3.38	–15.4	0.877
Open well at farm	17/01/00	6.18	–1.53	–8.9	0.727
Spring	17/01/00	8.43	–2.66	–15.9	0.816
Well at middle valley	17/01/00	7.11	–3.16	–16.5	0.859
Ghussein 1 runoff	10/01/01	n.a.	–4.30	–18.9	0.966
Ghussein 2 runoff	10/01/01	n.a.	–5.10	–23.0	1.048
Assaf runoff	10/01/01	n.a.	–1.93	–3.2	0.758
Abiad runoff	10/01/01	n.a.	–3.23	–18.4	0.866
Mihdath runoff	10/01/01	n.a.	–2.20	–1.4	0.779
Khudari runoff	10/01/01	n.a.	–5.13	–23.1	1.052
Khudari well 1	10/01/01	n.a.	–5.39	–24.2	1.141
Khudari well 2	10/01/01	n.a.	–5.23	–24.6	1.062
Spring	10/01/01	n.a.	–4.56	–17.6	0.992
Main farm	10/01/01	n.a.	–4.23	–17.2	0.959
Well at middle valley	10/01/01	n.a.	–6.09	–25.6	1.160
Open well at farm	10/01/01	n.a.	–5.33	–21.4	1.073

the system was from remobilization of salts rather than input from rainwater. Subsequent models from more recent runoff data show that the contribution of chloride and other solutes to the waters in the aquifers is small. The result is that a significant percentage of the water at the surface percolates to the groundwater with no evaporation, or leaves the area as runoff.

Increasing salinity during storage is most likely the function of water–rock interaction rather than evaporation. This is seen from the mass balance models as well as the severe weathering seen near the water table in the basalt at Ghussein. This suggests that the aquifers may be suitable for water storage from a geochemical and water quality perspective, given the relatively low solubility of the rocks. Stable isotopic analyses of the rain and groundwaters confirm that little evaporation occurs to the water prior to recharge. The δ^{18}O–δD relationship suggests that what evaporation is seen is the result of the wells being open because the evaporation seems to have occurred in the summer at the open wells. Even in these cases, water does not seem to have lost more than 25% because of evaporation. These results are consistent with field experiments, which show that rapid recharge can occur through wadi alluvium in the area (Abu-Taleb 1999).

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