Recharge mechanism and hydrochemistry evaluation of groundwater in the Nuaimeh area, Jordan, using environmental isotope techniques

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Abstract The relationship between the stable isotopic and chemical composition of precipitation and groundwater was studied in the Nuaimeh area of the Ajloun Highlands in Jordan. The isotopic composition values of precipitation and groundwater are almost identical. The spatial variation of stable isotopes in precipitation is mainly due to the effect of seasonal temperature, altitude and amount. The groundwater reveals identical variation in isotopic composition to the precipitation due to direct recharge and the karstic nature of the outcropping Turonian aquifer. Tritium levels in wells are high and their content is similar to the weighted mean value of tritium content in precipitation, indicating local recharge and low residence time. The ^{14}C activity in the tritiated groundwater is found to be about half of the ^{14}C activity of precipitation in the region. A geochemical evolution through dissolution of carbonate by water–carbonate rock interactions reduced the atmospheric ^{14}C activity from 114 to 61 pmc in the groundwater. A ^{14}C of around 61 pmc and 7.6 TU values are considered the initial concentration for the recharge in the shallow carbonate aquifer in the Yarmouk Basin. The large fluctuation of water level in observation wells during the rainy season indicates the sensitivity and direct response of the aquifer to the recharge. The chemical composition of the groundwater (Ca^{2+}–HCO_3^-) gives emphasis to the short duration of water–rock interaction and indicates dissolution of the carbonate aquifer. The elevated concentrations of Cl^- and NO_3^- in groundwater are attributed to anthropogenic sources.

Résumé Dans la région montagneuse d'Ajloun de Jordanie on a étudié la relation entre la composition chimique et isotopique des précipitations et des eaux souterraines. La composition isotopique est presque identique dans précipitations et les eaux souterraines. La variation spatiale de la teneur en isotopes stables dans les précipitations est déterminée en principal par les variations saisonnière de la température, l'altitude ainsi que par la quantité des précipitations. A cause de la recharge directe et de la nature karstique des affleurements de l'aquifère d'age touronienne, les eaux souterraines présentent la même composition isotopique que les précipitations. La teneur en ^{3}H mesurée dans les forages présente des valeurs élevées, proches de la valeur moyenne des précipitations, ce qu'indique une recharge locale et un temps court de résidence. On a déterminé pour l'activité de ^{14}C une valeur proche de la moitié trouvée dans les précipitations. L'évolution géochimique par dissolution des carbonates pendant l'interaction entre l'eau et les roche a diminué l'activité du ^{14}C, de la valeur de 114 pcm en atmosphère à 61 pcm dans les eaux souterraines. Dans l'aquifère calcaire de surface de bassin Yarmouk, on a considéré comme de concentrations initiales, les valeurs de 61 pcm pour ^{14}C et 7.2 UT pour ^{3}H. Les grandes fluctuations des niveaux des eaux souterraines observées dans les forages pendant les saisons pluvieux montrent la sensibilité ainsi que la réponse directe de l'aquifère au recharge. La composition chimique des eaux souterraines (Ca^{2+}–HCO_3^-) montre de plus le temps court de l'interaction entre l'eau et la roche, en indiquant aussi la dissolution de l'aquifère calcaire. Les taux élevées de la concentration en Cl^- et NO_3^- dans les eaux souterraines ont été attribuées aux sources humaines.

Resumen Fue estudiada la relación entre la composición isotópica estable y la composición química, tanto de la precipitación como del agua subterránea, en el área de Nuaimeh en las montañas de Ajloun, en Jordania. Los valores de la composición isotópica de la precipitación y del agua subterránea son casi idénticos. La variación espacial de los isótopos estables en la precipitación, es debida principalmente al efecto de la temperatura estacional, a la altura y a la cantidad. El agua subterránea muestra una variación idéntica a la precipitación en cuanto a la composición isotópica, debido a la recarga directa y a la naturaleza cársica del acuífero Turoniano aflorante. Los niveles de tritio en los pozos son altos y su contenido es similar al valor medio ponderado del contenido de tritio en la precipitación, indicando una recarga local y un tiempo de residencia corto. Se ha encontrado que la actividad de

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Received: 8 August 2003 / Accepted: 17 April 2004

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Hydrogeology Journal (2006) 14:180–191
DOI 10.1007/s10040-004-0352-2

^{14}C en el agua subterránea tritiada, es alrededor de la mitad de la actividad del ^{14}C en la precipitación para la región. La evolución geoquímica ocurrida a partir de la disolución del carbonato, por las interacciones roca carbonatada–agua, redujeron la actividad atmosférica del ^{14}C desde 114 en porcentaje de carbono moderno (pcm) hasta 61 pcm en el agua subterránea. Los valores del ^{14}C cercanos a 61 pcm y de 7.6 unidades de tritio, se han considerado como las concentraciones originales para la recarga en el acuífero carbonatado somero de la Cuenca de Yarmouk. Una gran fluctuación en el nivel de agua de los pozos de observación, durante la estación lluviosa, indica la sensibilidad y la respuesta directa del acuífero frente a la recarga. La composición química del agua subterránea (Ca^{2+}–HCO_3^-), enfatiza en la corta duración de la interacción de agua–roca, e indica disolución del acuífero carbonatado. La concentración elevada de Cl^- y NO_3^- en el agua subterránea, se atribuye a fuentes antropogénicas.

Keywords Groundwater age · Hydrochemistry · Environmental isotopes · Contamination · Water-rock interaction

Introduction

Since biblical times, securing fresh-water supplies in the Ajloun region of Jordan have attracted human energy and ingenuity. The region is semiarid and surface water is both scarce and ephemeral. As a consequence, groundwater resources have played the lead role in determining social and economic growth. However, the role of sustainable development of these groundwaters require an understanding of their origin and renewability.

The study area covers the Nuaimeh area, which is part of the Ajloun Highlands. The area is an important part of the Yarmouk Basin, which is considered one of the biggest basins in Jordan, with 25% of the basin located in Jordan and the rest in the neighbouring country of Syria (Fig. 1).

The demand for water has increased tremendously in the last 20 years due to the increase in population, and the expansion of agricultural and industrial activities. To satisfy the increased need for water, new groundwater wells have been drilled at various locations in the basin, and the abstraction from all groundwater sources has increased beyond the perennial yield of the Yarmouk Basin.

The elevation of the Nuaimeh area varies from 1,000 m in the southwest to 620 m in the northeast. The long-term average annual rainfall is approximately 600 mm. The study area lies between the cities of Nu-

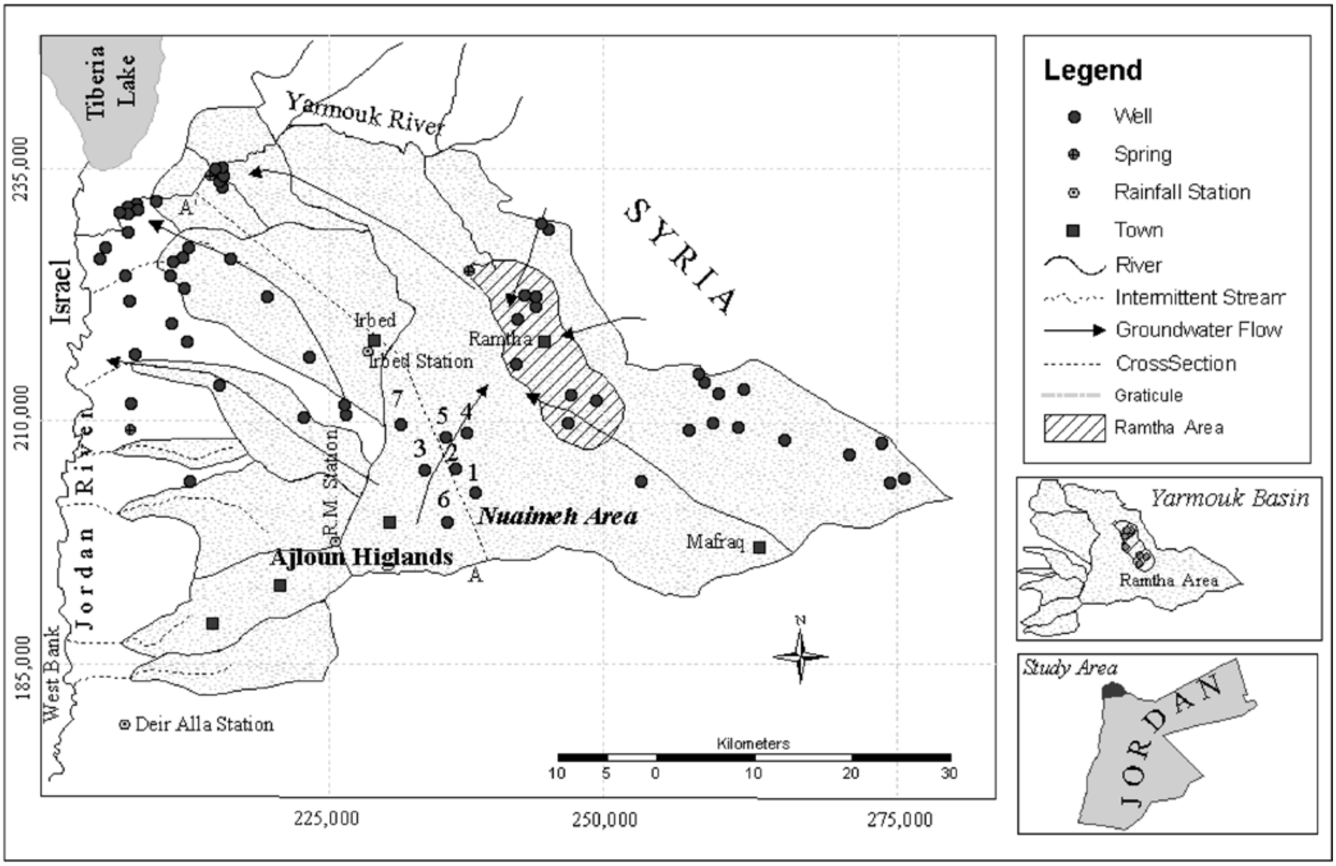


Fig. 1 Location of the Nuaimeh area in the Yarmouk Basin

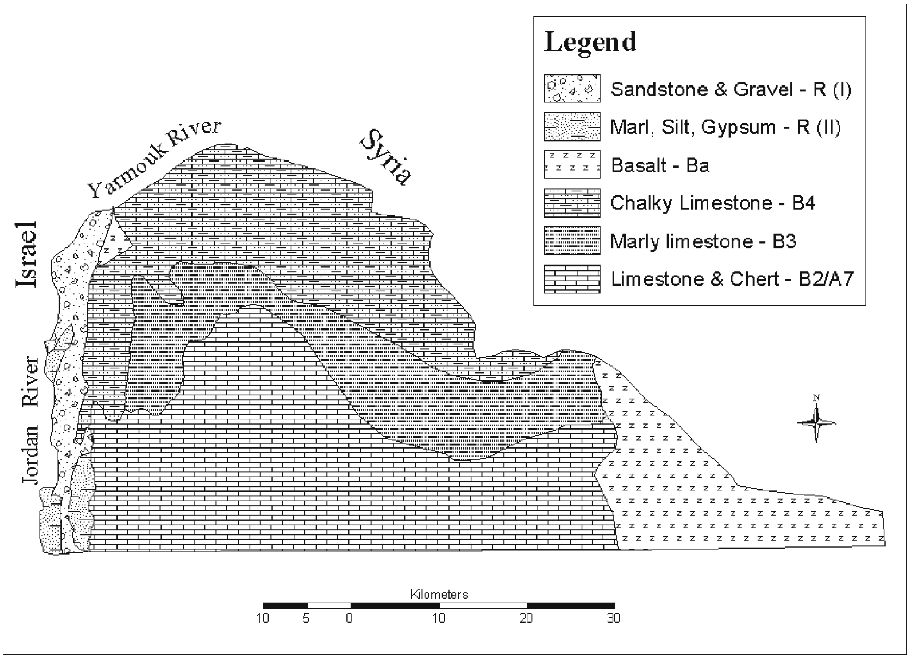
aimeh and Irbed, and covers an area of about 100 km^2 (Fig. 1).

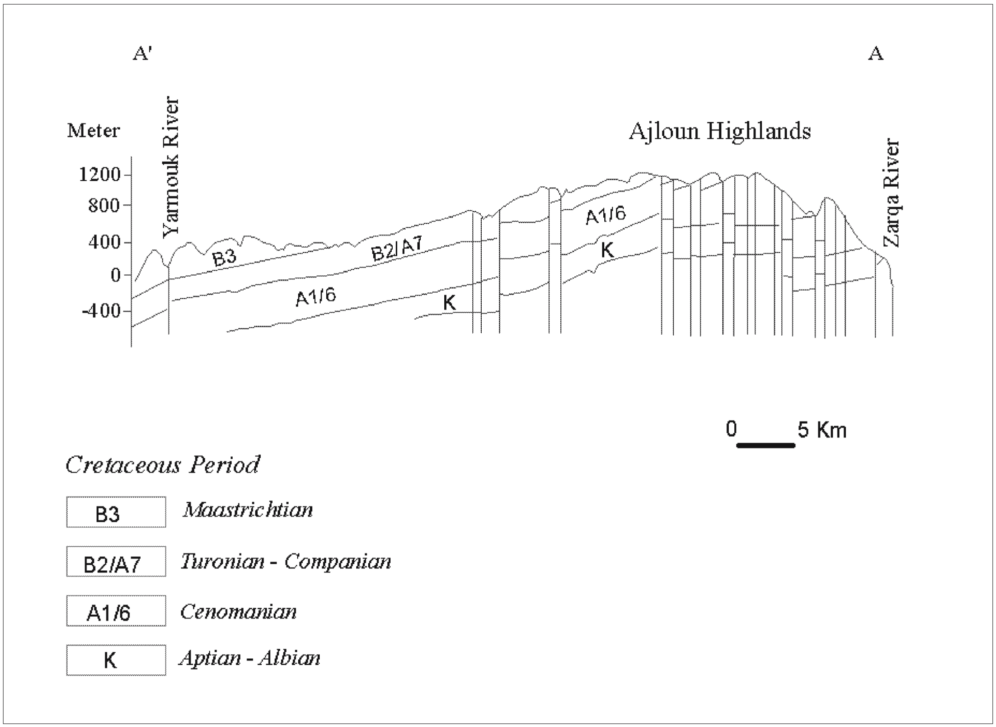
Studying the groundwater in the Ajloun Highlands will help in understanding the groundwater recharge process, amount of recharge, mechanism of infiltration, and the geochemical evolution of the percolated water. In addition, it will shed light on the general circulation pattern of the groundwater and its residence time.

Geological and Hydrogeological Setting

The general geology of the whole Yarmouk Basin is presented in Figs. 2 and 3. The bedrock surface in the area is late Cretaceous (Turonian-Campanian) in age, and consists of limestone and siliceous limestone. The Turonian Formation, locally called A7, is the main saturated aquifer and composed of karstic and permeable limestone. The carbonate bedrock terrain is covered by thin soil up

Fig. 2 Simplified geological map of the Yarmouk Basin





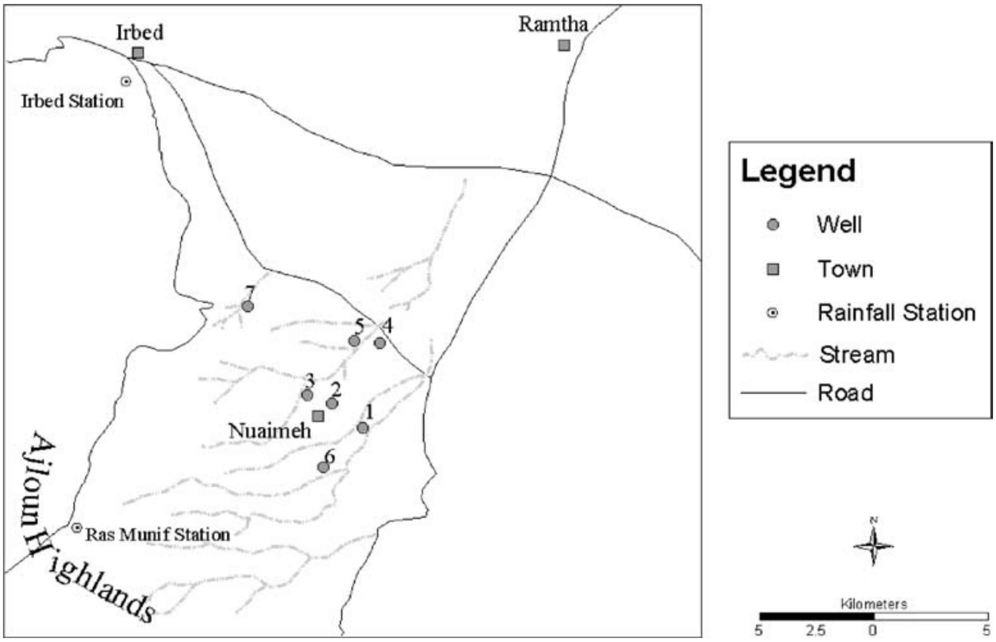


Fig. 4 Location of groundwater wells in the study area

Table 1 General hydrogeological information about the wells in the study area

Well no.	Drilling date	Coordinates		Elevation	Well depth	Aquifer	Yield
		North	East	(m)	(m)		(m^3/h)
1	-	202,850	237,200	-	302	A7	44
2	-	203,350	236,130	705	337	A7	
3	1980	203,580	235,500	717	196	A7	59
4	1976	206,180	237,880	646	334	A7	20
5	1983	206,000	237,240	668	280	A7	25
6	1974	200,680	235,880	783	267	A7	22
7	1980	207,520	233,400	695	350	A7	30

to 1 m deep. The texture of the soil is clay and silty loam over permeable subsoil, gravel and karstic limestone (Abu-Ajamieh et al. 1988). Several karstic caves are exposed in the area. Such caves can be seen in the vicinity of the productive wells in the Nuaimeh village.

The water movement is almost entirely by means of dissolution features and fractures. Several investigators (Parker 1969; Joudeh 1983; NJWRIJS 1989; EL-Naser et al. 1992) indicated that groundwater flows north and northwest from the Nuaimeh area (Fig. 1).

There are seven wells drilled in the area (Figs. 1 and 4), designated by numbers 1–7. All the wells in the area penetrate the Turonian carbonate aquifer (A7). The general hydrogeological information about these wells is listed in Table 1, and their location is shown in Figs. 1 and 4. In the period 1987–1993 five wells (nos. 1–5) were sampled several times for chemical and environmental isotopes (Table 2). Well no. 6 is the Yamoon observation well (Fig. 4), which is monitored regularly. The groundwater temperatures in the wells were recorded at 20.9–21.8 °C.

Since 1989 monthly water samples from precipitation at the three rainfall stations Ras Munif, Irbed (Ajloun Highlands) and Deir Alla in the Jordan Rift Valley (JRV; Fig. 1) were collected. Published precipitation data (Bajjali 1990) were also used in this study. Groundwater was sampled from several wells during the period 1987–1993. Stable isotope analyses of oxygen-18 and deuterium in addition to radioactive tritium were carried out for both precipitation and groundwater. Carbon-14 was analysed for two wells (nos. 3 and 4). Chemical analyses were also carried out for the majority of the groundwater wells and precipitation. The environmental isotope and chemical analyses were carried out by the Water Authority of Jordan (WAJ). Some samples, such as for oxygen-18 and deuterium, were analysed at the University of Ottawa (UO).

Geochemical data was analysed for speciation and mineral saturation indices using the geochemical program SOLMINEQ (Kharaka and Mariner 1989). Stable isotopes were analysed by gas source mass spectrometry on CO_2, equilibrated with water (^{18}O), and (^{2}H) from water-reduced zinc, with 2σ analytical precision of ±0.1 and ±1‰ respectively (WAJ and UO). Tritium was measured by β-counting on electrolytically enriched samples, with 1 tritium unit (TU) analytical precision (WAJ). Radiocarbon activity was measured by scintillation counting on C_6H_6, synthesised from $BaCO_3$ stripped in the field from 60-l water samples (WAJ). The analytical error was around 0.7 pmc.

Table 2 Chemical and isotope data for the groundwater in the area

No.	Date	$\delta^{18}O$‰ (±0.1)	δD‰ (±1.0)	TU (±1)	^{14}C (pmc)	TDS (ppm)	pH	Ca (mequiv/l)	Mg (mequiv/l)	Na (mequiv/l)	K (mequiv/l)	Cl (mequiv/l)	SO_4 (mequiv/l)	HCO_3 (mequiv/l)	NO_3 (ppm)
1	Jul. 1989	−6.4	−31.8	7.0		403	7.7	3.57	2.14	0.80	0.11	1.21	0.18	4.60	33.60
2	Aug. 1988	−5.8	−32.3	10.5		390	7.3	3.25	1.83	0.90	0.08	1.03	0.32	4.23	36.00
2	Jul. 1989	−6.4	−32.1	7.8		390	8.0	3.27	1.99	0.80	0.09	1.11	0.14	4.60	35.60
2	Feb. 1991	−6.3	−29.7	6.4		403	7.3	3.50	2.00	0.95	0.06	1.17	0.18	4.51	47.80
2	Oct. 1992	−6.2	−30.0	5.2		390	7.4	3.25	1.90	0.85	0.04	1.14	0.14	4.30	33.20
2	Dec. 1992	−6.4	−30.4	7.0		435	7.4	3.98	2.17	0.95	0.10	1.35	0.32	4.60	52.00
3	Jan. 1987	−5.5		6.2		358	7.3	3.27	1.51	0.80	0.09	0.96	0.00	4.42	20.20
3	Mar. 1987	−5.5		6.0		346	7.3	3.24	1.46			0.90	0.15	4.41	20.90
3	Feb. 1988	−7.0	−29.9	6.6	59.6±0.7	352	7.4	3.13	1.73	0.80	0.06	0.93	0.10	4.26	20.10
3	Aug. 1988	−5.4	−32.5	8.4		346	7.4	2.95	1.61	0.60	0.06	0.93	0.10	3.94	23.00
3	May 1989	−5.9	−31.5	7.0		339	7.5	3.11	2.01			0.96	0.00	4.31	20.20
3	May 1989	−5.9	−30.8	5.5		346	7.5	2.99	1.35			0.92	0.86	4.06	20.10
3	Jul. 1989	−6.1	−30.8	6.9		346	7.5	3.25	1.58	0.80	0.06	0.92	0.02	4.41	20.10
3	Oct. 1989	−5.7	−31.2	5.3		353	7.5	3.32	1.51	0.80	0.07	0.90	0.30	4.24	20.00
3	Feb. 1991	−6.0	−28.2	5.2		352	7.4	3.16	1.70	0.78	0.03	0.93	0.00	4.41	19.60
3	Dec. 1992	−6.0	−29.3	4.5		353	7.5	3.05	2.03	0.85	0.03	1.08	0.13	4.20	24.70
4	Feb. 1988	−7.2	−29.2	9.2	63.1±0.7	378	7.3	3.42	1.98	0.70	0.04	0.96	0.00	4.70	24.50
4	Aug. 1988	−5.6	−32.7	10.1		365	7.4	3.23	1.73	0.70	0.07	0.90	0.11	4.27	23.20
4	Jul. 1991	−6.3	−29.9	6.0		397	7.2	3.56	1.80	0.80	0.06	1.02	0.00	4.81	27.30
4	Oct. 1992	−6.2	−30.4	7.2		378	7.5	3.48	1.67	0.80	0.03	1.02	0.00	4.59	24.30
4	Dec. 1992	−6.2	−29.0	2.3		391	7.6	3.54	1.77	0.88	0.04	1.02	0.43	4.48	25.30
5	Feb. 1991	−5.9	−28.5	7.1		397	7.4	3.66	1.80	0.85	0.04	1.10	0.30	4.67	27.50

Result and Discussion

Chemical Compositions and Environmental Isotopes of Precipitation

Chemical and isotopic analyses of precipitation in the study area were undertaken as a basis for investigating the origin and subsurface history of groundwater in the study area. Samples were collected from three rainfall stations (Ras Munif, Irbed and Deir Alla) of differing altitudes (Figs. 1 and 5). The stations were chosen to monitor the isotopic and chemical signature of the rain, so it could be used as a guideline to evaluate the groundwater recharge processes in the study area. The locations of the rainfall stations are more or less representative of the general climate of the study area. Ras Munif and Irbed are located 1,150 and 555 m above sea level (a.s.l.) respectively in the Northern Highlands of the Yarmouk Basin, and Deir Alla is situated 224 m below sea level (b.s.l.).

Due to the worldwide variation in isotopic composition of precipitation (Dansgaard 1964; Yurtsever and Gat 1981), the long-term weighted mean value (WMV) is taken as the input function into a hydrological system. Mixing in the recharge environment enhances these variations, which permits use of mean annual values for hydrogeological applications of environmental isotopes. The isotope data from the three rainfall stations were chosen to provide averages based on monthly composite precipitation samples. In addition, the deuterium excess (d) of each month was also calculated.

Chemical Composition of Precipitation

Chemical analyses of the precipitation demonstrate a wide range of salinity (TDS; 38–211 ppm; Table 3). This range is exceedingly high for precipitation and may be attributed to the high altitude, dust and proximity to major saline-water bodies. The rainwater is classified mainly as a Ca^{2+}–HCO_3^- type of water. Some parameters show high concentrations, e.g. Ca^{2+}, Mg^{2+} and HCO_3^-. From Table 3, it can be concluded that the variability of the major cations and anions, in addition to their high load, can be attributed to the dust content and airborne salt from the sea or saline-water bodies.

Also, the regional bedrock in the study area is carbonate. The relatively high concentration of SO_4^{2-} and Mg^{2+}, and the correlation of Cl^- with Na^+ may also indicate a contribution from aerosols originating from seawater, the Mediterranean Sea (Na^+–Cl^-) and the Dead Sea (Mg^{2+}–Na^+–Cl^-). The Mediterranean is to the west of the study area, at a distance of less than 70 km from the Ajloun Highlands. Deir Alla rainfall recorded the highest concentration of Cl^- (0.72 mequiv/l) and it is located in the JRV less than 40 km north of the Dead Sea.

Isotopic Composition of Precipitation

On a global average, the general relation between $\delta^{18}O$ and δD for natural waters is found to be linear and can be expressed by the following equation (Craig 1961).

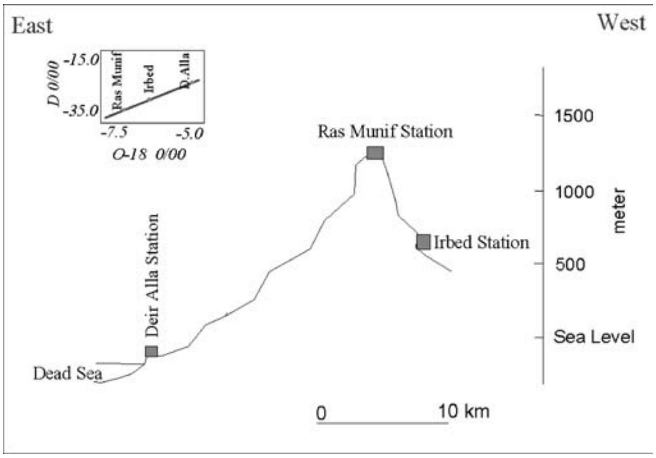


Fig. 5 Cross section between the Jordan Rift Valley and the Ajloun Highlands

$$\delta D = 8\delta^{18}O + 10(\text{ppm})$$

The deviation from this global meteoric water line (GMWL), called the local meteoric water line (LMWL), can be expressed through the deuterium excess parameter (d). The d-parameter is defined as d=$\delta D - 8 * \delta^{18}O$ (Dansgaard 1964). The location of the data on the LMWL indicates the origin of the air moisture.

Precipitation throughout the eastern Mediterranean area shows a different correlation between the $\delta^{18}O$ and δD, namely d~22‰. The eastern meteoric water line (EMWL) defined by Gat and Carmi (1970) differs from the GMWL of Craig (1961) by strong deuterium excess due to strong primary evaporation.

The relationships between the $\delta^{18}O$ and δD of the three rainfall stations' precipitation in the study area are shown in Fig. 6. The regression line for the three stations of $\delta^{18}O$ and δD of all the data plotted in Fig. 6 is:

$$\delta D = (6.46 \pm 0.26)\delta^{18}O + (12.07 \pm 5.02)$$

with a correlation coefficient of $R^2=0.90$ and number of data=72. The ± indicates 95% confidence interval on the slope and the intercept.

It can be seen from Fig. 6 that the monthly samples at all the stations fall very close to the LMWL. Notice, however, that the samples of two rainfall stations, Ras Munif and Irbed, fall on both the EMWL and LMWL. Deir Alla data show deviation from the EMWL and scatter widely along the LMWL.

The most divergent values relative to EMWL in Fig. 6, usually enriched in both oxygen-18 and deuterium, are those of months with deficient rainfall (March, April and October). Some data show the effect of enrichments, which in some months are extreme. This fact is very well demonstrated at the Deir Alla rainfall station (February–March 1988, and February 1990).

The high d-parameter persists in rain throughout Jordan (Bajjali 1990), and is regarded as a characteristic of eastern Mediterranean precipitation (Gat and Carmi 1970). The average d-parameter was calculated to be 23.9, 21.4 and 16.4 in Ras Munif, Irbed and Deir Alla respectively (Table 4). The relatively high d-parameter for the stations indicates that in winter, the cold and dry continental air masses come in contact with the warm Mediterranean Sea, resulting in rapid evaporation and large-scale convergence (Gat and Carmi 1970). The low slope indicates secondary evaporation after condensation.

Precipitation at Deir Alla shows enrichment and significant variability in isotopic composition and, consequently, in the calculated deuterium excess. An exception is the precipitation of March 1991, which is the most isotopically depleted (Fig. 6). This could be the result of a storm in this month which affected the JRV only and not the rest of the study area.

In general, it can be observed that the average of $\delta^{18}O$, δD and d is most depleted at Ras Munif, then Irbed and last Deir Alla (Table 4). These spatial variations were attributed to the seasonal temperature, altitude and amount effects (Bajjali 1994).

Table 3 Chemical analysis of precipitation

Name	Date	TDS	pH	Ca	Mg	Na	K	Cl	SO_4	HCO_3	NO_3
		(ppm)		(mequiv/l)							(mg/l)
Ras Munif	30 Jan. 1988	38.4	6.96	0.10	0.24	0.10	0.00	0.10	0.10	0.15	4.70
Ras Munif	30 Mar. 1991	121.6	7.50	1.00	0.48	0.16	0.02	0.31	0.32	1.10	1.63
Ras Munif	30 Nov. 1991	102.4	6.91	0.92	0.25	0.13	0.02	0.25	0.68	0.47	5.13
Ras Munif	30 Dec. 1991	211.2	7.50	1.60	1.20	0.25	0.00	0.49	0.54	2.16	1.59
Ras Munif	30 Jan. 1992	89.6	7.01	0.52	0.40	0.16	0.01	0.29	0.23	0.68	2.56
Ras Munif	28 Feb. 1992	160.0	7.76	1.31	0.80	0.22	0.02	0.40	0.47	1.63	2.12
Irbed	30 Jan. 1987	64.0	6.91	0.35	0.27	0.20	0.04	0.33	0.00	0.33	1.68
Irbed	30 Mar. 1989	58.0	7.48	0.49	0.17			0.20	0.24	0.51	2.87
Irbed	30 Jan. 1991	57.6	7.19	0.49	0.20	0.05	0.00	0.20	0.23	0.49	1.19
Irbed	30 Nov. 1991	44.8	7.12	0.39	0.10	0.10	0.01	0.20	0.29	0.29	2.08
Irbed	30 Dec. 1991	70.4	7.16	0.62	0.20	0.08	0.00	0.25	0.35	0.43	1.24
Irbed	30 Jan. 1992	57.6	7.17	0.39	0.20	0.05	0.00	0.17	0.15	0.43	1.46
Irbed	28 Feb. 1992	44.8	7.42	0.35	0.20	0.03	0.00	0.15	0.25	0.32	1.50
Deir Alla	30 Jan. 1987	141.0	7.30	0.92	0.33	0.60	0.06	0.72	0.27	0.33	30.30
Deir Alla	30 Jan. 1992	51.2	7.07	0.41	0.10	0.05	0.00	0.19	0.17	0.35	2.56
Deir Alla	28 Feb. 1992	76.8	7.42	0.51	0.10	0.11	0.00	0.26	0.14	0.64	4.82
Deir Alla	30 Mar. 1992	211.2	7.13	0.71	0.30	0.13	0.08	0.05	0.14	2.29	19.60

DOI 10.1007/s10040-004-0352-2

Fig. 6 Oxygen-18–deuterium diagram of the precipitation in the study area

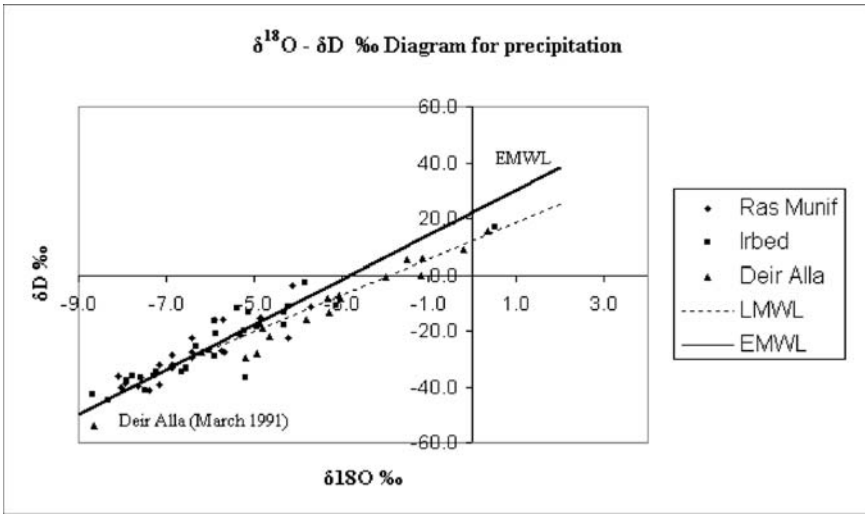


Table 4 Weighted mean value of stable and radioactive isotopes in precipitation (WMV for samples>10 mm)

Name	Period	O-18	D	TU	d
		(‰)	(‰)		(‰)
Ras Munif	Oct. 1987–Apr. 1988	−7.7	−35.8	8.4	25.4
	Nov. 1988–Jun. 1989	−6.6	−29.7	8.2	23.0
	Oct. 1989–Apr. 1990	−7.0	−33.3	6.1	22.6
	Oct. 1990–Apr. 1991	−7.2	−33.2	5.3	24.7
Average		−7.1	−33.0	7.0	23.9
Irbed	Oct. 1987–Apr. 1988	−7.1	−33.1	8.1	23.9
	Oct. 1988–Jun. 1989	−5.5	−23.1	8.5	21.3
	Oct. 1989–Apr. 1990	−6.6	−33.2	6.8	19.3
	Oct. 1990–Apr. 1991	−5.6	−23.4	5.9	21.1
Average		−6.2	−28.2	7.3	21.4
Deir Alla	Dec. 1987–Mar. 1988	−5.3	−21.7	10.3	20.3
	Oct. 1988–Feb. 1989	−2.9	−6.6	9.9	16.4
	Oct. 1989–Mar. 1990	−3.6	−13.8	7.0	15.0
	Jan. 1990–Apr. 1991	−6.0	−34.1	6.9	13.8
Average		−4.4	−19.1	8.5	16.4

Tritium Concentration in Precipitation

In all of the country, large variations in tritium occurred during the period 1987–1991, while little variation existed between the three stations (Bajjali 1990). A slight increase in the WMV is observed in the concentration of tritium with a decrease in distance from the Mediterranean.

The average of tritium concentration at the Deir Alla station is slightly higher than that of the other two stations in the mountainous region (Table 4). This, in general, is found to be the reverse process from that found in the adjacent area. Carmi and Gat (1973) found that tritium concentrations build up with increasing distance from the Mediterranean Sea, with parallel depletion in stable isotopes (Gat and Dansgaard 1972). That this was not observed in the study area could be due to various topographic features which affect the cloud paths, wind directions and interactions between air masses of different origins entering the area.

In general, the tritium level in precipitation decreases with time, which reflects the global trend following the ban on the atmospheric testing of hydrogen bombs. The good correlation between the Irbed and Ottawa (Canada) rainfall stations allowed a tentative establishment of a local record for Irbed for the pre-1965 period when no monitoring was done. The Ottawa station has the longest-term tritium record in the world. This correlation shows the highest level of tritium in Irbed was approximately 600 TU in 1963 (Bajjali 1990). The average tritium concentration in the atmosphere from the three rainfall stations for the winter season of 1988/1991 is approximately 7.6 TU.

Recharge Estimation and Perennial Yield of the Aquifer in the Ajloun Highlands

Recently, several researchers have tried to estimate the recharge in the area. El-Naser et al. (1992) estimated the direct recharge in 1991/1992 to the area from the Yamoon observation well (no. 6) to be 45.6 million cubic meter (MCM), while previous studies estimated the mean annual direct recharge in the area to be 21.5 MCM (NJWRIJS 1989).

In this study, an attempt was made to estimate the recharge by a geochemical model using the chloride mass balance (cf. equation above). This technique relies primarily on the long-term average amount of precipitation, and the chloride concentration of both the rain and groundwater (Houston 1987). The recharge area is estimated to be 100 km^2 and the long-term average of precipitation in the area was estimated to be 600 mm/year. The range of Cl$^-$ concentration found at the rainfall station closest to the wells (Ras Munif) is 0.1–0.49 mequiv/l. The average Cl$^-$ concentration in groundwater of the five wells in the area is estimated to be 1.02 mequiv/l. Except in areas of evaporite deposits, chloride is generally a conservative anion in natural water. Therefore, chloride in rainfall (derived from seawater aerosol) usually passes through the soil zone to the water table without change in concentration. The ratio of chloride concentration in rainfall to that of groundwater is a measure of recharge, thus:

$$\mathrm{Recharge(mm)} = \frac{\mathrm{Rainfall(mm)} \times \mathrm{mgCl^{-1}Rainfall}}{\mathrm{mgCl^{-1}Groundwater}}$$

The recharge is estimated to be highly variable—6–29 MCM. The high variation is due to the Cl$^-$ concentration in precipitation, intensity and amount of rain. This calculation does not account for contributions from the aquifer material by leaching in the subsurface flow, yet the concentration of evaporite containing Cl$^-$ anion in the limestone is usually negligible.

The perennial yield (safe yield) can be defined as groundwater which can be pumped from a given aquifer without producing an unpleasant condition (Todd 1976). In general, the aquifer in the Ajloun Highlands has an erratic perennial yield due to the significant seasonal variations in rainfall over the area. For example, the average amount of rain in Ras Munif was 495.1 mm in 1990/1991, and 1,151.4 mm in 1991/1992 (Bajjali 1994). The average perennial yield in the Yarmouk Basin is estimated to be 40 MCM/year). The total abstraction in 1991 was estimated to be 72 MCM, exceeding the perennial yield by 75% (Ministry of Water and Irrigation and UN Development Programme 1992). Only 22 MCM is used for municipal demand, while the remaining 50 MCM is used for irrigation. This exploitation pattern has caused a decrease in water level and deterioration of the groundwater quality.

Groundwater Fluctuation in the Study Area

Well no. 6 (Yamoon observation well) had been abandoned for several years. In 1990/1991, the well started to be used to monitor the groundwater level in the area. Monitoring data show the water-level fluctuations (Fig. 7). The sharp fluctuation shown in the graph was due to the rainy season in the winter of 1991/1992 when the area received a large amount of rain.

This amount of rain directly affects the recharge to the outcropping aquifer (A7). The water level thus rose by up to 20 m. This value is a good indication of the sensitivity of karst terrain to precipitation. The amount of rain for the period October 1991–April 1992 was 1,151.4 mm at the Ras Munif rainfall station, while the six-year average (1986–1992) and range for the same station are 633.5 and 702.1 mm respectively (Bajjali 1994). From these available values, it can be concluded that the area is a recharge

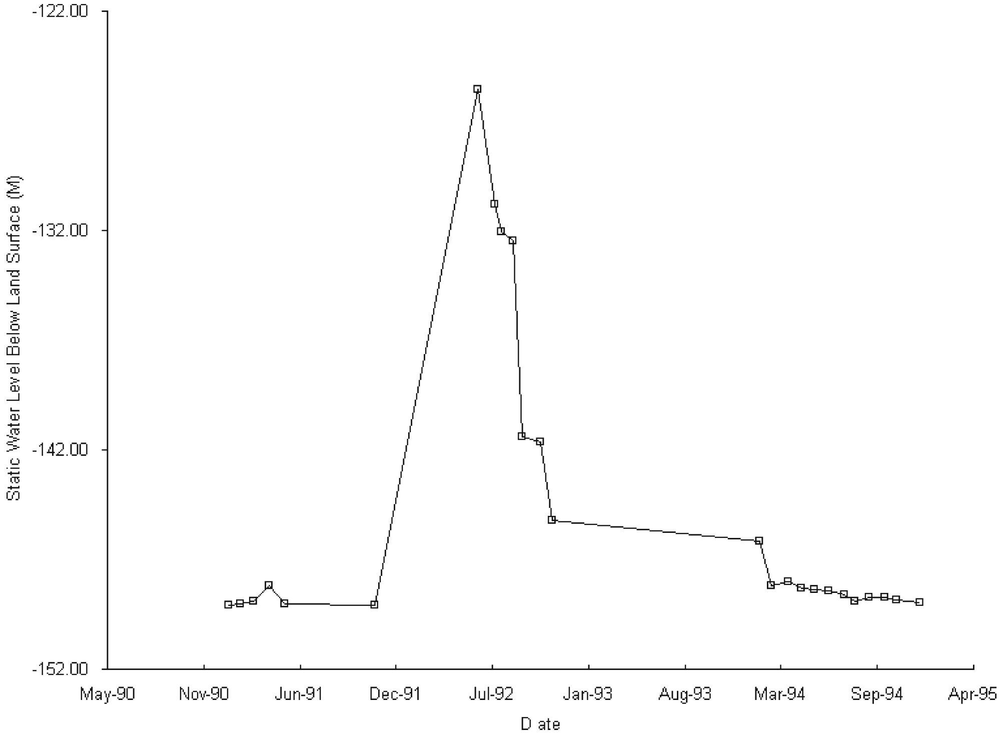


Fig. 7 Groundwater fluctuation in the Yamoon observation well

area, and the amount of recharge to the aquifer is variable in the rainy season.

Classification of Groundwater According to Chemical Content

TDS values from five observation wells vary in the range 339–435 ppm (Table 2). The composition of the water (by equivalent) is $Ca^{2+}>Mg^{2+}>Na^{+}$ and $HCO_3^{-}>Cl^{-}>SO_4^{2-}$. The average data of dissolved ions (Table 5) are plotted in a fingerprint diagram (Fig. 8), showing similarity for the ionic composition of water in wells nos. 1–5 (Fig. 4).

The results indicate that even if the groundwater apparently underwent similar patterns of geochemical evolution, the water quality varied slightly among the five wells. The Ca^{2+}–HCO_3^{-} chemical facies of this groundwater reflect dissolution of the carbonate aquifer. The homogeneity of these two parameters indicates that the lithology is mainly calcite.

The water is supersaturated with respect to calcite and dolomite (Table 6), both in winter and summer, because of the dominance of calcite in the local Upper Ajloun Group. As the water enters the saturated zone, it continues to dissolve more calcite and dolomite until saturation. The water infiltrates through the karstic formation and, at this stage, the water attains a stable chemical composition.

The log partial pressure of the CO_2 of the samples is in the range −1.96 to −2.28. These values are much higher than the log P_{CO2} of the atmosphere (−3.5), which indicates that CO_2 from the soil is incorporated during infiltration through the unsaturated zone.

Groundwater SO_4^{2-} concentrations vary with well location and depth. The SO_4^{2-} concentration was found to vary in the range 0–0.43 mequiv/l, with only one extreme value (0.86) detected in well no. 3 (Table 2). The low concentration and the strong variability of SO_4^{2-} concentration in well no. 3 (depth 196 m) can only indicate that there are variable sources of SO_4^{2-} other than the

Table 5 Average chemical composition of the groundwater

Well no.	TDS	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	NO_3^{-}
	(ppm)		(mequiv/l)							(ppm)
1	403	7.7	3.57	2.14	0.80	0.11	1.21	0.18	4.60	33.5
2	402	7.5	3.45	1.98	0.89	0.07	1.16	0.22	4.45	40.8
3	349	7.4	3.15	1.65	0.54	0.04	0.94	0.17	4.27	20.7
4	382	7.4	3.45	1.79	0.78	0.05	0.98	0.11	4.57	25.1
5	397	7.4	3.66	1.80	0.85	0.04	1.10	0.30	4.67	27.4

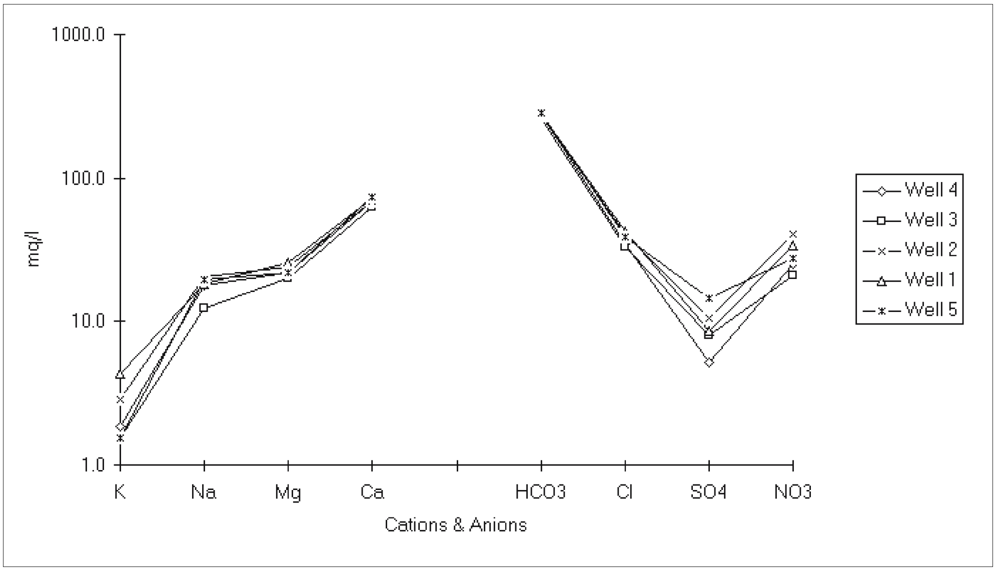


Fig. 8 Fingerprint diagram for groundwater wells in the Nuaimeh area

Table 6 Ionic strength, ratio and saturation indexes

Well no.	Ionic strength	Log P CO_2	SI calcite	SI dolomite	Na^{+}/Cl^{-} molar ratio
1	0.0091	−2.28	0.49	1.85	0.66
2	0.0089	−2.09	0.27	1.38	0.76
3	0.0077	−2.02	0.15	1.09	0.57
4	0.0119	−1.98	0.16	1.12	0.79
5	0.0089	−1.96	0.21	1.21	0.77

soluble sedimentary minerals such as gypsum ($CaSO_4.2H_2O$) and anhydride ($CaSO_4$) which are responsible for the origin of SO_4^{2-} in groundwater.

Some SO_4^{2-} may be introduced into the groundwater from rainfall. The rainfall at the Ras Munif and Irbed stations was enriched in sulphate (Table 3). In addition, seasonal fertilizing with ammonium sulphate may also affect the concentration of SO_4^{2-} in groundwater.

The pH of the groundwater varies in the range 7.19–8.03 (Table 2). Therefore, essentially all the dissolved carbonate and all the alkalinity is in the form of HCO_3^-. Chloride is the most important anion after HCO_3^-, and Na^+/Cl^- values are 0.57–0.79 (Table 6). Three sources of Cl^- likely dominate:

1. salt derived from rainwater and airborne salts;
2. the dissolution and/or leaching from marine carbonate rock, including its impurities; and
3. anthropogenic sources, since chloride is a very common pollutant from organic and inorganic sources.

In the Nuaimeh area it can occur particularly from human and animal wastes. All these possibilities exist, since the Na^+/Cl^- ratio is highly variable.

Nitrate Concentration in Groundwater

Significant variations were recorded for the NO_3^- concentration (Table 2). The concentration of nitrate in all the wells was found to be higher than the average natural nitrate level in groundwater. The elevated NO_3^- level can be attributed to anthropogenic sources, which clearly demonstrates the contamination vulnerability of the aquifer in the Nuaimeh region. Atmospheric precipitation is an important source of NO_3^-. The concentrations of NO_3^- in rainfall at the Ras Munif and Irbed stations are in the range 1.2–5.1 ppm (Table 3). Other NO_3^- sources may include sewage effluent through seepage from septic tanks, agricultural activity, and the use of manure and nitrogen fertilizers. In addition, storm-water runoff could contribute to the soil nitrate entering the streams which contribute to shallow groundwater. Well 1 is located in the middle of an animal farm (poultry). Both natural (manure) and chemical fertilisers are used for the cultivated crops in the area. As yet, none of the well samples show a nitrate concentration exceeding the permissible limits for drinking purposes (45 mg/l) over a period of 20 years.

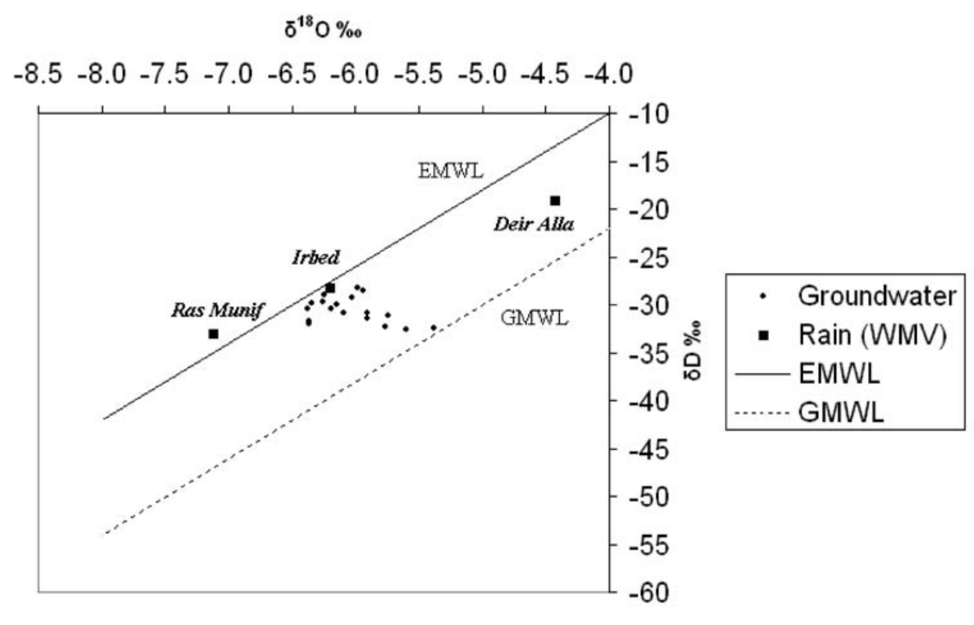
Classification of Groundwater Based on Environmental Isotopes Content

The stable isotope data of wells nos. 1–5, in conjunction with the WMV of rain of the three rainfall stations (Ras Munif, Irbed and Deir Alla), are plotted on the $\delta^{18}O$–δD diagram in Fig. 9. The groundwater samples reveal a wide variation in stable isotope content. The variations in the stable isotopic composition of the groundwater extend over a range of 1 and 4.5‰ in $\delta^{18}O$ and δD respectively. In addition, the samples are clustered widely between the EMWL and the GMWL.

The variation indicates that the groundwater is a mixture of two sources. The first source—direct recharge—involves the karstic limestone aquifer responding directly to precipitation. The direct recharge to the area is very well demonstrated by the low TDS and high concentration of tritium in the groundwater. The precipitation data given in Fig. 6 also show how this strong variation in isotopic composition, and the groundwater composition falls between the WMV of the Irbed and the Ras Munif precipitation.

From Fig. 9, it can be seen that the recharge altitude for the groundwater in the Nuaimeh area is located in the

Fig. 9 Stable isotope composition of the groundwater and WMV of precipitation



highlands between the Ras Munif and the Irbed rainfall stations. This suggests that the precipitation which fell in the southwest of the Nuaimeh area represents the main recharge altitude for the groundwater, which is 850–950 m a.s.l. The topography of the 30-km^2 area where the wells are located has a variation in altitude of approximately 400 m. This generates isotopic heterogeneities in precipitation, which will be reflected in the shallow groundwater.

The second source is the irrigation return flow. The irrigated water is exposed longer to the atmosphere during summer, which makes it more enriched in stable isotopes due to evaporation. This phenomenon can be seen from the deviation of some samples from the EMWL. The larger deviation is seen in summer. In summer, there is no rain, and the groundwater becomes the main source for irrigation, and part of the water goes back into the aquifer as an evaporated return flow.

Radioactive Isotopes of Groundwater

Radioactive Tritium

Tritium can be used to elucidate the residence time of recently recharged groundwater (Eriksson 1967). The groundwater in the Nuaimeh area has variable tritium concentrations. The tritium concentration in wells nos. 1–5 shows a significant contribution from bomb tritium, which means recent contributions to the aquifer system. The concentrations of tritium in some wells are close to those found in precipitation of Ras Munif for the same period. Thus, the transit time through the unsaturated zone is relatively short. Seasonal variations are also observed (Table 4).

At times the water sources show an irregular pattern indicating that tritium introduction may come about by an irregular event, such as flooding (cf. no. 2). Well no. 2 is located within the Al-Assara stream, which passes through the city of Nuaimeh. The high rate of infiltration from the bottom of the valley during winter time is the most probable evidence for the high concentration of tritium in this well. In addition, the rapid response of the water level in the Yamoon observation well, which rose about 20 m in the winter of 1991 due to intense rain, is another indication of the good correlation between the amount of rain and the recharge events. The replenishment area is in the formation outcrop in the Ajloun Highlands and in the area of the wells. Replenishment to the phreatic aquifer is believed to occur from local rain, flood flows and excess irrigation waters.

Radioactive Carbon-14

^{14}C was sampled from only two wells (nos. 3 and 4) to establish an input function for dating groundwater in the whole basin. The ^{14}C activity was found to vary in the range 59.6–63.1 pmc, and the tritium content was found to be 6.6 and 9.2 TU in wells nos. 3 and 4 for the same period respectively (Table 2). Based on the tritium content, the recharge events to the groundwater took place within one year, while the apparent age of water based on the ^{14}C activity is around 4,000 years. The residence time of groundwater can be calculated through the following decay equation:

$$\ln(A/A_0) * 8266.7 = \text{Age}$$

where A_0 is initial radiocarbon concentration of water.

This discrepancy between the estimated residence times causes the age estimation of groundwater using ^{14}C activity to be completely misleading. Such low ^{14}C activity has been observed in several recharge areas such as the Judean Mountains, Israel (Kroitoru et al. 1989), and the Bani Kharous catchment area, Oman (Bajjali 1999).

The average ^{14}C activity (A_0) in the atmosphere is 114±6 pmc (Bajjali 1994). This is taken to be the ^{14}C activity of modern CO_2 during recharge. The reason for the low ^{14}C activity in groundwater in the Nuaimeh wells is the interaction of the infiltrated water and the Cretaceous carbonate (limestone) formation outcropping in the area. The dissolution of carbonate by water–rock interactions lowers the ^{14}C activity of groundwater by substitution of "dead" carbon from the aquifer rock (Bajjali et al. 1997). As the water infiltrates down to the water table, it can be considered under a closed-system condition, which means it is isolated from the influence of the CO_2 reservoir. The carbon isotope geochemistry of shallow tritiated groundwaters in the study area can be directly used for the ^{14}C dilution and δC_{DIC} shift during recharge and carbonate dissolution, as they are all at saturation with respect to calcite (Table 6).

A dilution factor is thus defined as a parameter (q) which reduces the initial activity of a sample for non-decay ^{14}C. The decrease in ^{14}C activity through a geochemical reaction in the recharge water can be used to determine the dilution factor q, according to the following equation:

$$q_{\text{Recharge}} = {}^{14}C_{\text{Recharge}} / {}^{14}C_{\text{Atmosphere}}$$

where A_{Recharge} (61 pmc) and $A_{\text{Atmosphere}}$ (114 pmc) are average values of ^{14}C measured in the recharge area and the atmosphere respectively (Bajjali et al. 1997). A q value of 0.54 is obtained. Therefore, the ^{14}C activity of around 61 pmc can be used to represent the initial condition for the groundwater downgradient in the Turonian-Companion (B2/A7) aquifer (Fig. 3) in the whole Yarmouk Basin prior to further geochemical modification.

Summary

The geochemistry and isotope content of the precipitation and groundwater in the Nuaimeh area has provided useful information regarding the mechanism of recharge and residence time of groundwater. Groundwater with high tritium content was found in all the wells tapping the Turonian (A7) aquifer in the area. Therefore, the whole area of the Ajloun Highlands is considered a recharge region for the Turonian-Companion (B2/A7) aquifer. The stable isotopic content of the tritiated groundwater for all the wells falls between the WMV of Ras Munif and Irbed precipitation, which indicates local recharge corresponding to the elevation of the local terrain, which is 850–950 m a.s.l. The significant rise of the water table in the Yamoon observation well in 1991/1992 is the direct aquifer response to the precipitation. The recharge water from precipitation was estimated to be 6–29 MCM. A drop in ^{14}C activity from around 114 pmc in the atmosphere to around 61 pmc in the groundwater is due to carbonate dissolution in the recharge area. Therefore, the ^{14}C activity of around 61 pmc can be used as an input function for dating the groundwater downgradient in the B2/A7 aquifer in the Yarmouk Basin prior to further geochemical modification. The Ca^{2+}–HCO_3^- chemical facies of this groundwater reflects dissolution of the carbonate aquifer. The homogeneity of these two parameters indicates that the lithology is mainly calcite.

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DOI 10.1007/s10040-004-0352-2