

# <sup>14</sup>C AND <sup>234</sup>U-EXCESS DATING OF GROUNDWATER IN THE HAIFA BAY REGION, ISRAEL

VASILY ROGOJIN,<sup>1</sup> ISRAEL CARMI<sup>2</sup> and JOEL KRONFELD<sup>1</sup>

**ABSTRACT.** Radiocarbon activities and uranium isotopic disequilibria were measured in water samples from both the sandy Pleistocene coastal aquifer and within the upper Cretaceous Judea Group carbonate aquifer of northwestern Israel. The samples in both aquifers exhibit a decrease in <sup>14</sup>C activity that is concomitant to the growth in <sup>234</sup>U-excess. This suggests that under specific conditions, <sup>234</sup>U-excess dating of groundwater can be used to corroborate <sup>14</sup>C dates, while offering the possibility of extending the range of dating of groundwater beyond that of <sup>14</sup>C.

## INTRODUCTION

The rate of groundwater transport and recharge can be determined using radiocarbon (Vogel and Ehhalt 1963). This method has been applied in many case studies; however, the absolute age of the groundwater is debatable. The absolute age, especially in carbonate terrains, may be influenced by isotopic exchange with the aquifer wall rock over time. Moreover, the initial <sup>14</sup>C activity is often unknown and may vary from aquifer to aquifer. A variety of models (e.g., Vogel 1967; Tamers 1975; Kroitoru 1987; Ingerson and Pearson 1964; Mook 1972, 1976, 1980; Fontes and Garnier 1979; Eichinger 1983) have been put forward to gain an estimate of this initial value. These methods often necessitate additional measurement and interpretation of the stable carbon isotopes. The <sup>14</sup>C method is limited to dating water younger than *ca.* 35 ka. Older water has been dated by other means, including uranium disequilibrium isotopes. The uranium isotopic method used so far in a few special cases (e.g., Kronfeld and Adams 1974; Fröhlich, Gellerman and Herbert 1983; Ivanovich, Fröhlich and Hendry 1991) was predicated upon the existence of a reducing barrier within the aquifer. The precipitation of uranium at the barrier facilitated the generation of high <sup>234</sup>U/<sup>238</sup>U activity ratios by alpha-recoil inputs of <sup>234</sup>U. The high <sup>234</sup>U/<sup>238</sup>U activity ratios then decreased with time as the water flowed downward, away from the site of uranium accumulation. The half-life of <sup>234</sup>U is almost a quarter of a million years, which offers the potential for dating water in the range of 10<sup>5</sup> yr. However, even in the absence of a reducing barrier, alpha-recoil inputs of <sup>234</sup>U from the aquifer wall should be ongoing. If the uranium is fairly uniformly distributed within the aquifer wall rock, and there are no foreign inputs of water along the flow path, then the alpha-recoil inputs should increase the <sup>234</sup>U content of the water as a function of time (up to the point where decay of this isotope begins to be noticeable). This decay would start to be important only well beyond the lifetime of <sup>14</sup>C. The change in this added <sup>234</sup>U with flow would be most noticeable as <sup>234</sup>U-excess rather than the <sup>234</sup>U/<sup>238</sup>U activity ratio. <sup>234</sup>U-excess is defined as

$$^{234}\text{U-excess} = [\text{U concentration}] \times (^{234}\text{U}/^{238}\text{U} - 1). \quad (1)$$

To test the efficacy of delineating <sup>234</sup>U-excess increases with time, we studied uranium isotopes in groundwater within a well-delineated flow system. We measured <sup>14</sup>C and tritium in the same samples.

## The Hydrologic Setting

The chosen aquifer extends from the recharge region in the hills of the lower Galilee westward to the Haifa Bay coast (Fig. 1). A major part of this study was devoted to the Judea Group aquifer. This is a large (600–650 m thick) Upper Cretaceous marine carbonate aquifer, composed of limestone and

<sup>1</sup>Department of Geophysics, Tel-Aviv University, P.O.B. 39040, Ramat Aviv, Tel-Aviv 69978, Israel

<sup>2</sup>Department of Environmental Sciences and Energy Research, Weizmann Institute of Science, 76100 Rehovot, Israel

dolomite. Marine carbonates are usually fairly uniform in their uranium content of *ca.* 2–3 ppm U (Wedepohl 1969). Wells have been drilled along the path of flow to exploit the groundwater resource. From the phreatic recharge region in the hills, the aquifer dips seawards, becoming confined as it is overlain by the marls and chinks of the Mount Scopus Group aquiclude (Fig. 2). At its western extension, the Judea Group comes into direct hydrologic contact with and feeds the marine carbonate Kurdani Formation aquifer. This latter aquifer in turn is in direct contact with the confined lower subaquifer of the Pleistocene Coastal sands. The fresher phreatic upper Pleistocene sandy aquifer receives its replenishment directly from precipitation. It is hydrologically separated from the lower more saline sandy subaquifer by a thin, though impermeable, layer of clay (Fig. 2). The salinity of the Judea Group water continuously increases along the flow path (Fig. 3), changing from freshwater (500–600 mg L<sup>-1</sup> TDS) of Ca-HCO<sub>3</sub> type in the recharge area (+400 m elevation) to that of Ca-Mg-Na-HCO<sub>3</sub> in its confined middle section, and to brackish (2000 mg L<sup>-1</sup> TDS) water of Na-Cl type at the Na'aman springs (+5 m) discharge.

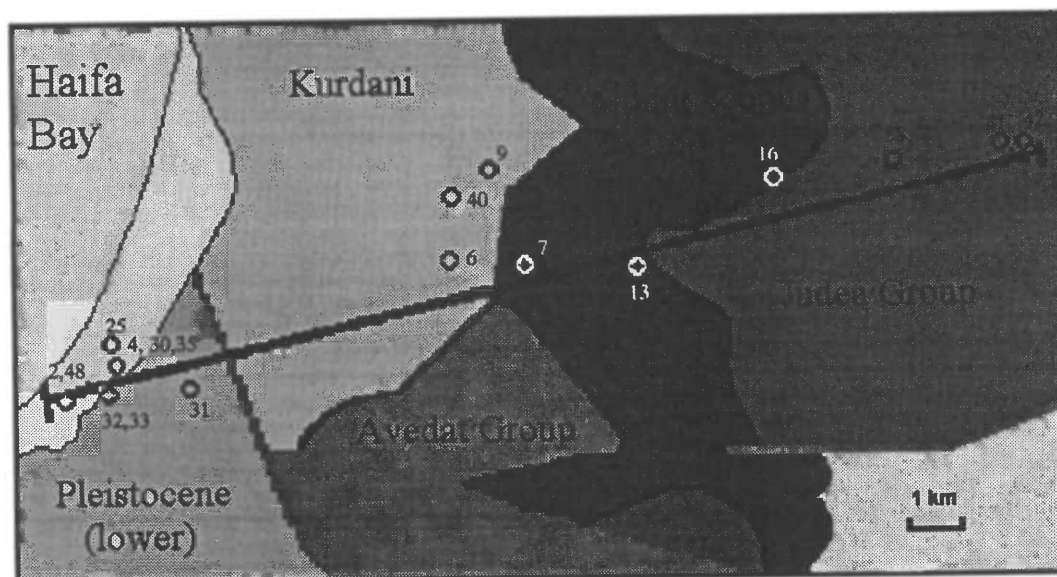


Fig. 1. Schematic geological map

#### SAMPLING AND RESULTS

Samples were collected from active producing wells, along the east-west transect in Figure 1. Samples of 40 L and 1 L were collected for <sup>14</sup>C and <sup>3</sup>H analysis, respectively, and were analyzed at the Weizmann Institute of Science. Four-liter samples were collected at the same time for uranium isotope analyses, performed at Tel-Aviv University. The latter analyses were carried out using alpha-spectrometry, following a sample preparation that employed a <sup>232</sup>U-spike along with ion exchange and solvent extraction procedures (Ivanovich and Harmon 1992). The results of the analyses are presented in Table 1. The largest <sup>3</sup>H concentrations are noted in the phreatic Pleistocene upper subaquifer, which is partially consolidated recent coastal dune sands. The other <sup>3</sup>H values are quite low, approaching our analytical limits. The <sup>3</sup>H analyses are used to denote possible additions of recent water percolating into the regional groundwater system, as appears, for example, to be the case for the Lokhame haGheta'ot and the Qiryat Khaim-Hei wells. The uranium concentration, measured

sporadically in several of these same sands to the south, was found to be uniformly low, of 1 ppm or less uranium. The absolute  $^{14}\text{C}$  ages were calculated using an initial (pre-bomb)  $^{14}\text{C}$  activity value of 64 pMC. This value was obtained for the Judea Group aquifer by using the isotopic exchange model of Ingerson and Pearson (1964). Values greater than this have been encountered and attributed to "bomb" input.

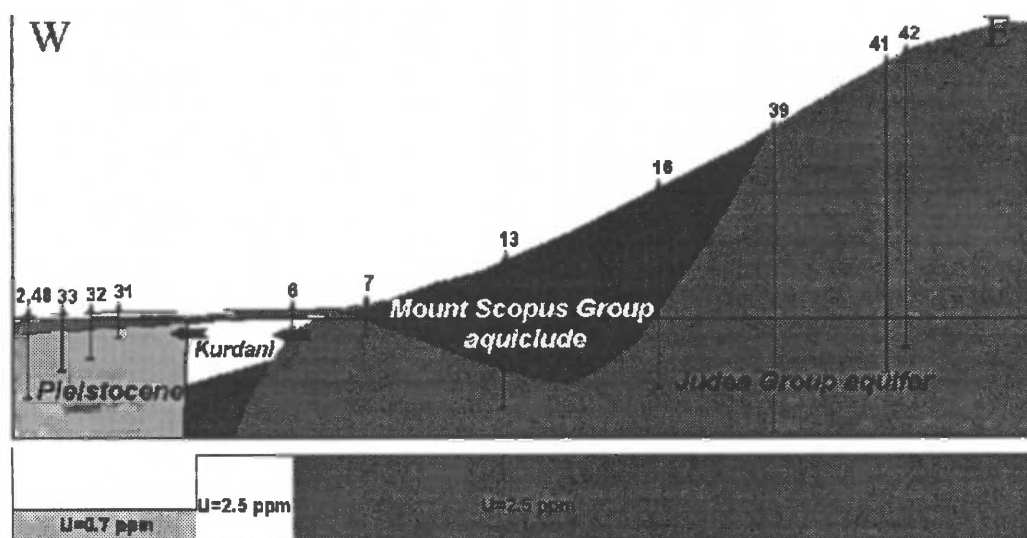


Fig. 2. Schematic geological cross-section and uranium content of host rocks

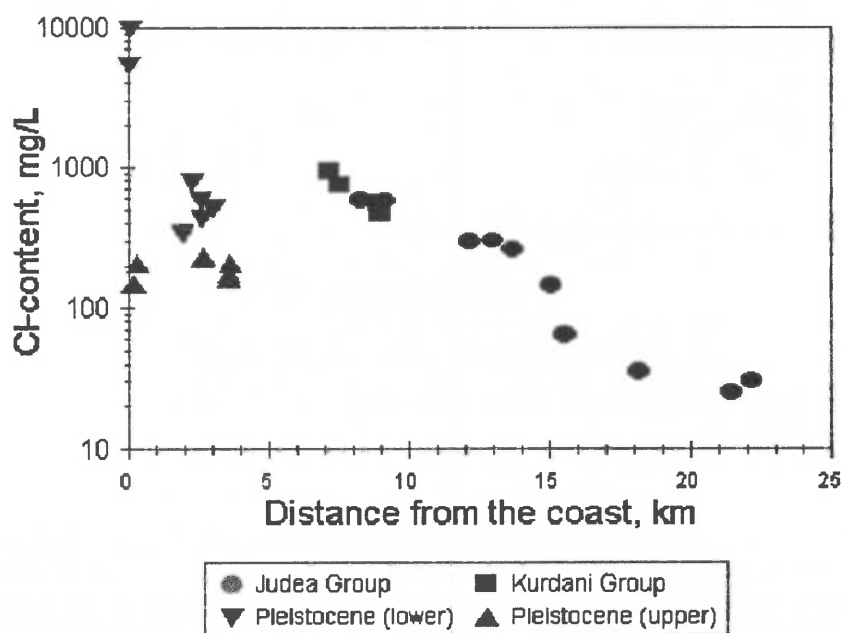
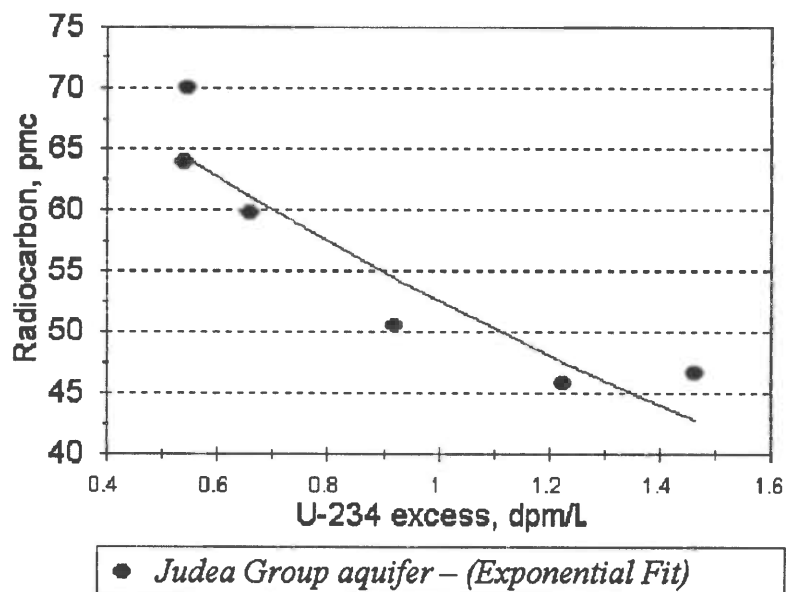


Fig. 3. Chloride content of the water from the various aquifers

TABLE 1. Results of  $^3\text{H}$ , C and U Series Isotopes Measurements in Haifa Bay Area, Israel

Sample	Well	$^3\text{T}$ (TU)	$^{14}\text{C}$ (pMC)	$\delta^{13}\text{C}$ (‰ PDB)	Age (yr)	$^{238}\text{U}$ (dpm L $^{-1}$ )	$^{234}\text{U}$		Aquifer
							$^{234}\text{U}/$ $^{238}\text{U}$	excess (dpm L $^{-1}$ )	
42	Meqed Kramim-2	2.6	70.1	-14.6	Recent	0.78	1.70	0.55	Upper Judea Group
41	Meqed Kramim-1	2.9	64.0	-15.1	Recent	0.83	1.65	0.54	Upper Judea Group
38	Miar	0.5	59.8	-15.7	561	1.13	1.61	0.69	Upper Judea Group
16	Damun-5	0.4	50.5	-14.0	1959	1.04	1.89	0.92	Upper Judea Group
13	Damun-3	1.1	48.5	-14.5	2293	1.36	2.08	1.47	Upper Judea Group
7	Afeq-Beth	0.0	45.8	-14.6	2766	1.36	1.90	1.23	Upper Judea Group
40	Lokhame haGheta'ot	2.0	55.3	-15.2	1208	1.89	1.54	1.01	Kurdani Series
9	Kefar-Masaryk-3	0.4	50.0	-12.3	2041	1.22	1.70	0.86	Kurdani Series
6	Afeq-Gimel	0.0	51.6	-14.3	1780	1.59	1.61	0.97	Kurdani Series
2	Blue Band-B	0.0	7.9	-10.3	17,316	3.37	1.35	1.19	Pleistocene sandstone
4	Q.Khaim-KafDaleth	0.2	32.6	-14.2	5577	1.80	1.55	0.98	Pleistocene sandstone
31	Q.Khaim-Hei	2.1	34.5	-8.8	5109	2.24	1.30	0.67	Pleistocene sandstone
32	Q.Khaim-KafTeth	0.2	33.5	-13.7	5352	1.49	1.75	1.11	Pleistocene sandstone
33	Q.Khaim-KafBeth	0.0	24.8	-12.7	7838	1.64	1.61	0.99	Pleistocene sandstone
34	Q.Khaim-KafGimel	0.0	21.2	-4.7	9134	1.74	1.58	1.01	Pleistocene sandstone
48	Blue Band-cooling-2	0.8	5.0	-11.3	21,077	3.43	1.71	2.45	Pleistocene sandstone
25	Q.Motskin-4a	11.2	65.5	-7.9	Recent	0.75	1.17	0.13	Recent dune
35	Q.Khaim-YudDaleth	7.1	83.5	2.5	Recent	1.43	1.19	0.27	Recent dune
30	Q.Khaim-Vav	9.2	68.2	-5.9	Recent	1.17	1.13	0.15	Recent dune

Fig. 4. Correlation between the  $^{14}\text{C}$  activity of the water and its  $^{234}\text{U}$ -excess for the Judea Group carbonate aquifer

## DISCUSSION

A sympathetic trend is clearly discerned for an increase in the  $^{234}\text{U}$ -excess to accompany an increase in the  $^{14}\text{C}$  age both in the Judea Group aquifer (Fig. 4) and in the Pleistocene sandy aquifer (Fig. 5). The rate of water flow in the Judea Group aquifer, calculated by the decrease in  $^{14}\text{C}$ , is a hydrologically reasonable 4–6  $\text{m yr}^{-1}$ . A similar flow rate is related to the rate of increase in the  $^{234}\text{U}$ -excess. In the Pleistocene aquifer, the sharp difference in age of the water between the actively recharging upper sub-aquifer and that of the much older water in the confined lower sub-aquifer is clearly shown.

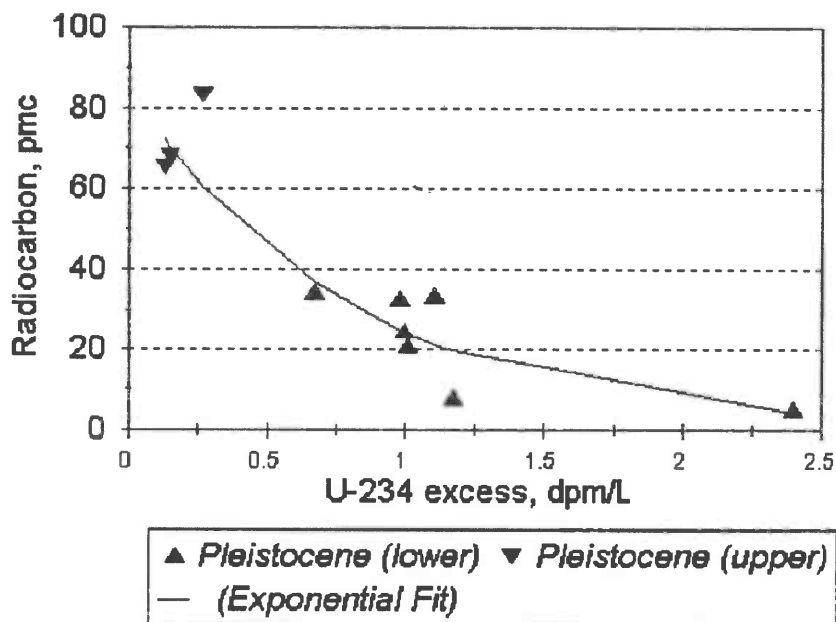


Fig. 5. Correlation between the  $^{14}\text{C}$  activity of the water and its  $^{234}\text{U}$ -excess for the Pleistocene upper and lower sandy sub-aquifers

For the carbonate aquifer water, the initial  $^{234}\text{U}$ -excess value is  $0.54 \text{ dpm L}^{-1}$ . In the sandy aquifer this is between  $0.13$  and  $0.27 \text{ dpm L}^{-1}$ . In the Judea Group aquifer the calculated rate of  $^{234}\text{U}$  transfer to the water is  $0.285 \text{ dpm L}^{-1} \times 10^{-3} \text{ yr}$ . For the sandy aquifer it is  $0.086 \text{ dpm L}^{-1} \times 10^{-3} \text{ yr}$ . The difference in the initial uranium contents and the rate of increase of  $^{234}\text{U}$ -excess between the two aquifers is consistent with each aquifer rock having a different uranium concentration. The higher uranium concentration (*ca.*  $2.5 \text{ ppm}$ ) in the carbonate aquifer generates more recoil nuclides to the water than the Pleistocene aquifer (approximate average of  $0.7 \text{ ppm U}$ ). Both aquifers exhibit trends of increasing  $^{234}\text{U}$ -excess with increasing  $^{14}\text{C}$  age (Figs. 4,5). This suggests that the  $^{234}\text{U}$ -excess is increasing at a constant rate. If we take the  $^{14}\text{C}$  activities as an absolute age ( $t$ ), the change in  $^{234}\text{U}$ -excess can be related to the  $^{14}\text{C}$  age by regression.

For the Judea Group, the  $^{14}\text{C}$  age is

$$t = [3000 \times (^{234}\text{U-excess})] - 1390 \text{ yr}, \quad (2)$$

at a regression coefficient,  $R = 0.84$ .

For the Pleistocene aquifer, the correlation between  $^{14}\text{C}$  age and the  $^{234}\text{U}$ -excess is given by

$$t = [9664 \times (^{234}\text{U-excess})] - 1510 \text{ yr}, \quad (3)$$

with an equally high degree of confidence of  $R=0.83$ .

We can thus derive a simple age equation, based upon the change in  $^{234}\text{U}$ -excess that is related to the uranium content of the aquifer wall rock, that can be generally used in either aquifer of

$$T = [7000 \times (^{234}\text{U-excess}/[\text{U}])] - 1450 \text{ yr}, \quad (4)$$

where  $T$  is the age of the groundwater, in years;  $^{234}\text{U}$ -excess in water is measured in  $\text{dpm L}^{-1}$ ; and  $[\text{U}]$  is the average uranium content of the wall rock, in  $\text{ppm}$ .

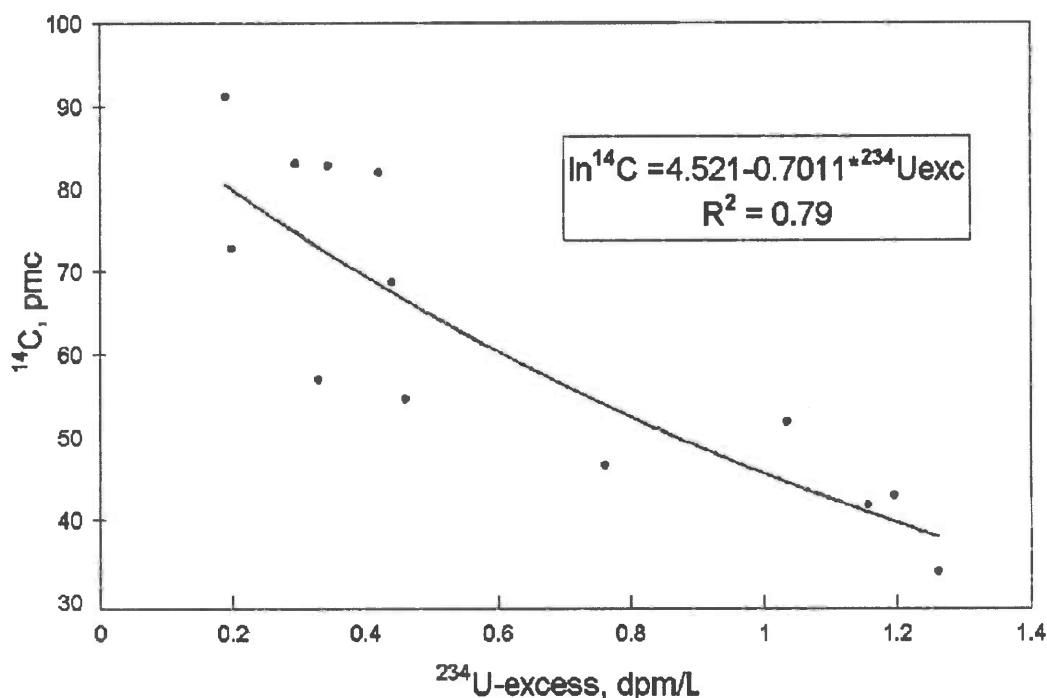


Fig. 6. Correlation between the  $^{14}\text{C}$  activity of the water and its  $^{234}\text{U}$ -excess for the eastern Judea Group carbonate aquifer in the Judea-Samaria region (from Rosenthal and Kronfeld 1982; Kronfeld, Vogel and Rosenthal 1992)

## CONCLUSION

If  $^{234}\text{U}$ -excess dating is more universally applicable and is not restricted to just these two cases, the relationship between the change in  $^{14}\text{C}$  activity and the change in  $^{234}\text{U}$ -excess should be found in other oxygenated aquifers as well. Unfortunately, very little comparative data are available in the literature. However, two isotopic studies have been carried out on the eastern part of Judea aquifer in the region extending from Jerusalem to Jericho. Although the uranium data and the  $^{14}\text{C}$  activities in these two studies were measured almost a decade apart (Rosenthal and Kronfeld 1982; Kronfeld, Vogel and Rosenthal 1992), a similar trend is noted here too (Fig. 6). Therefore, it is recommended that such correlations be looked for elsewhere, to check whether  $^{234}\text{U}$  dating of groundwater is of widespread application.

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