Natural Radium (^{226}Ra) Concentration in Groundwater in Southern Part of the West Bank/palestine

Rita Dieck and Amer Sawalha

Al Quds University, Bethany, P.O. Box 89, East Jerusalem, Palestine

Abstract: The Radium isotopes (^{226}Ra and ^{222}Rn) as well as physical and chemical characteristics were measured for groundwater samples collected from 14 different deep groundwater wells in Bethlehem–Hebron districts. Radium concentrations in all water samples do not exceed the international standards for drinking water. Several factors controlling the Radium concentrations had been studied. In both Upper and Lower Aquifer systems. The positive correlation was found between well depth and ^{222}Rn concentration. While, a negative correlation was observed between the ^{226}Ra/^{222}Rn ratio and the well depth. The low concentration of ^{226}Ra (0.0055 Bq/L–0.017 Bq/L) over the ^{222}Rn concentration (2.24 Bq/L–6.75Bq/L) had lead the possibility of studying the mechanism of ^{226}Ra in the Upper Aquifer. The results had revealed a strong negative correlation between ^{226}Ra concentration and saturation indices with (r= 0.86). And a strong negative correlation between ^{226}Ra concentration and total hardness of the water with coefficient correlation (r= 0.99). These results had led to the possibility of co- precipitation of ^{226}Ra with the Ca^{+2} salts in the studied groundwater wells of the Upper Aquifer.

Key words: Natural Radium · Groundwater · Mountain Aquifer · Palestine

INTRODUCTION

Groundwater is the only source for domestic uses in Palestine. Hebron and Bethlehem district is suffering from severe water shortage since two decades. Human water needs in both districts is less than 40 l/c.d. During the last 15 Palestinian Water Authority drilled additional wells to cover minimum water requirement. Water quality is an important requirement for drinking water, where investigation of natural radioactivity ^{226}Ra and 228 Ra concentrations are very important. Naturally occurring radioactive elements are found in water, soils and rocks. Uranium and Thorium, the common long-lived radioactive elements, decay slowly to produce other radioactive elements which in turn undergo radioactive decay. ^{238}U will decay producing ^{226}Ra and ^{222}Rn as its progeny; ^{235}U will produce ^{223}Ra and ^{219}Rn while ^{232}Th will produce ^{228}Ra, ^{224}Ra and ^{220}Rn as its progeny.

These radioactive elements can have serious effect on flora, fauna and have acute health effects on human beings when they exceed the permissible levels set by the local or international authorities.

The West Bank overlies three groundwater basins that are connected together and is known as the Mountain Aquifer: the Eastern Aquifer Basin, The Western Aquifer Basin and the Northeastern Aquifer Basin (Figure1). The structure of the Mountain Aquifer is not a simple anticline. Rather it is a complex anticlinorum with folds plunging in various directions, affecting groundwater flow systems. The apex of the main anticline structure separates groundwater flow westwards towards the Mediterranean drainage systems or eastwards to the Jordan Valley and the Dead Sea. The upper parts of the Yatta Formation separate an unconfined upper sub-aquifer from a lower confined sub-aquifer [1].

In Palestine the West Bank Aquifer system (Mountain Aquifer) extends below the area of the West Bank and it is recharged by rainfall from the mountains of the West Bank forming the phreatic portion, while the main storage areas are in the confined portions which either flows to the West towards the Israeli underground and the Mediterranean or to the East towards the Jordan Valley and the Dead Sea. So rainfall infiltrates to the water table forming the West Bank Aquifer System which is composed of dolomite and limestone rocks of the lower Cenomanian and Turonian ages. The total annual capacity of the Mountain Aquifer is estimated at 600-650 million m³/yr [2].

Corresponding Author: Amer Sawalha, Water & Enviromental Lab,Al Quds University, Palestine.

Geological Setting: The outcrops within the West Bank are predominantly carbonate sediments and rocks of Tertiary and Cretaceous age [3]. The oldest exposed rocks belong to the Albian covered by younger strata of the Cenomanian, Turonian and Eocene, exposed on both flanks of the anticlinal axis of the West Bank [4]. Almost all exposed rocks in the West Bank extended from the lower Cretaceous to Quaternary ages with limited exposures of Jurassic rocks. In the Cenomanian-Turonian era, the area was dominated by thick stratas of limestone and dolomite. The majority of the exposed rocks in the southern part of the West Bank are composed from limestone and dolomite. While in the Jordan Valley and the shorelines of the Dead Sea, the youngest formations of the Pleistocene-Holocene age are found. In Figure 2 shows the hydrogeological cross section from North West to South East of the West Bank.

The two deep carbonate Aquifer systems in the West Bank are built from Cretaceous rocks and these rocks are mainly consist of limestone, dolomite and marl of Upper Cenomanian Turonian ages (Jerusalem Bethlehem and Hebron Formations) while the Lower Cenomanian aquifer composed of Upper and Lower Beit Kahil Formations. Yatta Formation which separate the two aquifers composed of marls and clays represents the main aquiclude in the West Bank.
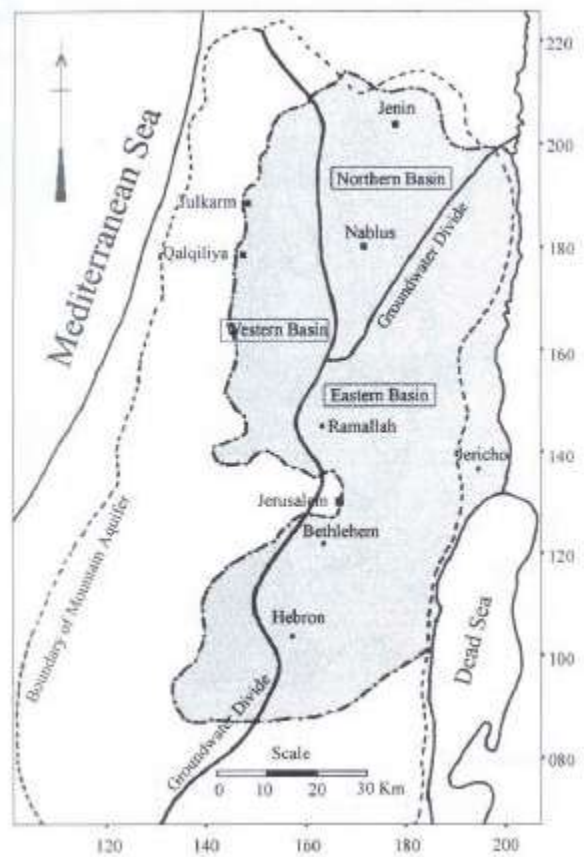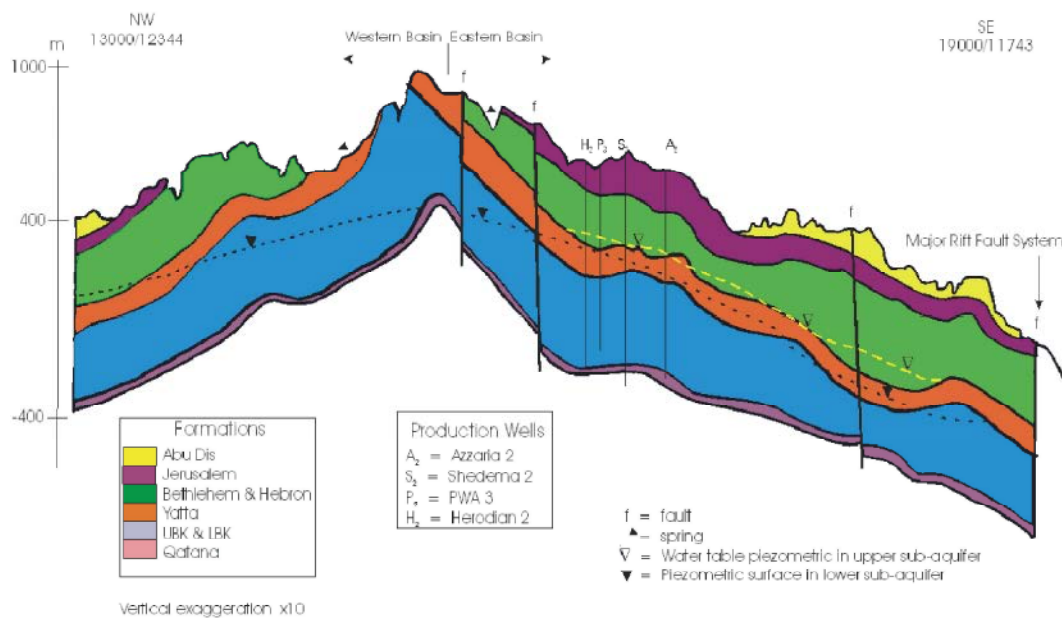

Fig. 1: Groundwater Basins [3]

Fig. 2: NW-SE hydrological cross section showing the regional aquifers and aquiclude through the Mountain Aquifer [1]

Radioactivity in Groundwater: In nature there are three radioactive decay chains. Uranium-238 (^{238}U) nucleus passes through a series of 14 transformations to become at the end stable lead-206 (^{206}Pb). Uranium-235 (^{235}U) nucleus passes through 11 transformations to become at the end stable lead-207 (^{207}Pb) while Thorium-232(^{232}Th) nucleus passes through 11 transformations to become at the end stable lead-208 (^{208}Pb). In between these transformations exist a series of nuclides with different half lives ranging from microseconds to hundreds of thousands of years. These transformations occur by emitting alpha particles, beta particles or gamma rays.

Most radionuclide's in groundwater result from interactions with rocks. The concentration of Radium in groundwater depends on the means by which it enters the water, the amount of Radium in the source, the mechanisms that remove Radium from the water and processes that move the Radium away from its source [5].

The contents of Radium and its progeny radioactive elements in groundwater depend on the combination of three factors [6]:

- Geological factor including the concentrations of these elements in the aquifer rock.
- Chemical condition of the groundwater.
- Physical processes of decay along the water-rock interface.

Thus measuring the Radium isotopes will allow determining the magnitude of radioactivity including short and long term isotopes, which enable us to show their origin, since the combination of isotopic ratios reflects the Radium sources. The Radium isotopes ratio can be used to draw their origin especially in ground water. The ratio of the Radium isotopes ^{226}Ra / ^{228}Ra depends upon their host rock origin. As ^{226}Ra is the descendent of ^{238}U and ^{228}Ra is of the ^{232}Th, so the ratio ^{226}Ra/ ^{228}Ra reflects the ratio of the rock surface as well as the rock itself [7]. For example in most cases ground water in carbonate aquifers has high ratio ^{226}Ra / ^{228}Ra > 1, while in ground water in sandstone aquifers have low ratio 226Ra / 228Ra < 1 [8].

Sampling sites: The wells that are included in this study are located in the southern part of the West Bank, Bethlehem and Hebron district, used for drinking purposes and they are taping water from the Eastern Groundwater Basin. A total of fourteen wells were sampled most of them are from Bethlehem area, three wells are from Hebron area.

Methodology: The Radium sampling procedure are collected in a container in 40-50 L then water is pumped through a plastic column (30 cm in length) placed vertically, filled with 10 grams of MnO_2 coated acrylic fiber with a piece of cotton wool that is placed on the top of the fiber in order to prevent the loss of MnO_2-fibers during the filtration [9]. The pumping rate is less than 2L/ minute, in order to ensure 100% adsorption of dissolved Radium in the water sample to the MnO_2 fibers. When the whole water sample passes through the column, the MnO_2 fibers are squeezed strongly and place it in a plastic bag. The Durridge Radon– in –air monitor (RAD7) was used for the ^{226}Ra measurement as shown in Figure 3. RAD7 uses a solid state alpha detector which is a semiconductor material usually silicon that converts alpha radiation directly to an electrical signal. ^{226}Ra is measured via ^{222}Rn (^{218}Po) after three weeks of incubation and in growth of ^{222}Rn. The most advantage of solid state devices is its ability to electronically determine the energy of each alpha particle, thus make it possible to tell exactly which isotope (polonium isotopes) produced the radiation. Because of the high quality alpha detector the RAD7 background is vanishingly small.
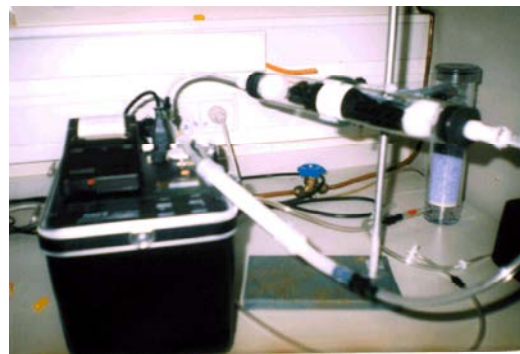

Fig. 3: Close loop during ^{226}Ra measurements

The measurement of radon was done by RAD7-H_2O which is an accessory to the RAD7 that enables to measure Radon in water with high accuracy over a range of concentrations from less than 50 pCi/L (1.85 Bq/L) to greater than 10^5 pCi/L (3700Bq/L).

The temperature, pH and EC were measured by using Multi 340 I pH-meter immediately at the sampling site. Cations (Ca^{+2}, Mg^{+2}, Na^+, K^+) were measured by Atomic Absorption, while NH_4^+ and the main anions SO_4^{-2}, PO_4^{-2}, NO_3^- were measured by Hach spectrophotometer. Chloride Cl^- and Bicarbonate HCO_3^- were measured by titration. Analysis of the water samples were conducted at the Water and Environmental Laboratory at Al- Quds University as shown in Table (1).

Calculations: The measurements process for 226Ra and 222Rn activities was conducted several times for obtaining better accuracy. Average of the cycles is taken in order to obtain one single value which is the mean in counts per minute (cpm) for 226Ra and pCi/L for 222Rn. The value taken from the Rad–7 must be corrected in order to take into consideration the amount that has been decayed in the period elapsing the date of sampling and the date of measurement. The percentage of the radionuclide remaining after a certain period of time is given by the following equation:

$$Ki = e^{-\lambda i\, t} = e^{-0.18\, t}$$

K i: Decay rate of radionuclide i
λi: Decay constant for radionuclide i and it is equal to ln2/T1/2, where the T1/2 is the half time of the radionuclide i (T1/2 for 222Rn is 3.82 days).
t: incubation time (t is the interval time between the time sampling and the time of measurement).

The measured value is simply divided by Ki to give the corrected cpm. The system efficiency must be incorporated into this value; this is obtained by using calibration samples with known activities and includes unit conversion factors to obtain a value in disintegrations per minute (dpm) and eliminates any background values that may be found in the device from previous use. This value is then divided by the volume of the sampled water to obtain units of dpm/L according to the following equation:

222Rn measurements:

$$A\ (dpm/L) = \frac{S\ (cpm) - BG}{\varepsilon\ .\ V.\ (L).\ Ki}$$

where:
S: it is the amount of signals from the sample (cpm)
BG (background value): blank measurement (cpm)
ε: it is the efficiency of measurement
V: it is volume of the sample in liters (L)
Ki:decay rate of the nuclide (222Rn)

Where (1–Ki): shows the achieved equilibrium level of radioactive accumulation of 222Rn during incubation period (% of secular equilibrium).

226Ra Measurements

$$A\ (dpm/L) = \frac{S\ (cpm) - BG\ (cpm)}{\varepsilon\ .\ V.\ (L).\ (1 - Ki)}$$

Where (1–Ki): shows the achieved equilibrium level of radioactive accumulation of 222Rn during incubation period (%of secular equilibrium).

RESULTS AND DISCUSSIONS

Results of water chemistry and radio-activity contents of groundwater are presented in Table 1 and 2. The water type in our study were identified by using Piper diagram [10] which is a trilinear plot that permits the classification of water samples into seven water types according to Langguth classification [11]. According to our results in water chemistry analysis, Piper diagram was plotted by using Aqua Chem (3.7) software as shown in Figure 4. The majority of the studied wells in Bethlehem-Hebron districts are characterized in one main group with normal earth alkaline water with prevailing bicarbonate.

Our results reveal that the main water group could be due to natural processes that had happen in the carbonate aquifer such as the dissolution of carbon dioxide (CO_2) from the atmosphere and from the soil horizons that causes the dissolution of the carbonate minerals, calcite $CaCO_3$ and dolomite Ca, $Mg(CO_3)_2$
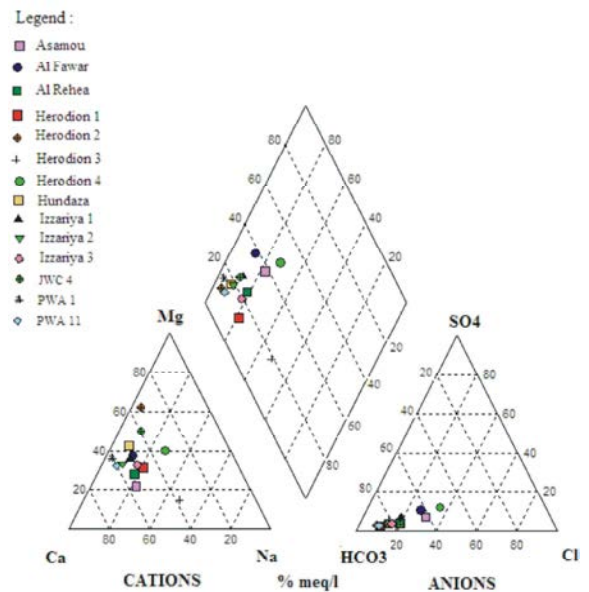

Fig. 4: Piper diagram showing the wells studied in Bethlehem-Hebron districts

Table 1: Results of chemical analysis

No	Name	Na^+	K^+	Mg^{+2}	Ca^{+2}	NH_4^+	Cl^-	HCO_3^-	NO_3^-	PO_4^{-2}	SO_4^{-2}
1	Herodion (1)	44.80	1.27	35.40	88.50	0.01	35.45	489.73	23.20	0.32	12.00
2	Herodion (2)	9.80	4.61	71.40	62.50	0	30.50	505.65	6.00	0.06	13.00
3	Herodion (3)	67.60	5.12	10.90	46.70	0.01	30.50	304.70	5.00	0.08	15.00
4	Herodion (4)	15.25	1.83	11.70	15.60	0.01	30.49	76.44	13.90	0.36	14.00
5	PWA I	5.70	0.15	31.50	87.20	0.15	33.32	368.65	16.30	0.11	10.00
6	PWA 11	16.80	2.20	39.00	120.40	0.05	35.45	529.34	9.00	0.16	13.00
7	Izzariya (1)	15.86	5.84	24.26	57.42	0.01	36.60	251.54	10.50	0.02	19.00
8	Izzariya (2)	15.00	2.39	26.80	75.40	0	33.10	327.90	10.40	0.07	15.00
9	Izzariya (3)	36.90	0.01	36.90	92.20	0.04	51.76	453.16	21.80	0.31	17.00
10	Al Fawar 1	25.44	14.12	39.68	86.26	0.02	82.95	329.36	117.5	0.02	45.00
11	Hundaza	13.18	0.67	34.84	65.92	0.01	34.24	336.36	12.80	0.13	12.00
12	JWC 4	11.68	0.84	28.24	36.36	0.02	33.32	215.92	17.70	0.11	8.00
13	Al Rehea	33.44	2.61	26.86	84.74	0.02	56.00	366.00	12.80	0.06	15.00
14	Asamoua	48.74	3.67	25.14	105.94	0	104.6	357.00	47.60	0.06	32.00

Table 2: water salinity, 222 radon, 226 radium, well depth and total hardness

Well Name	Aquifer	EC (iS/cm)	^{226}Ra (Bq/L)	^{222}Rn (Bq/L)	$^{226}Ra/^{222}Rn$	Well depth (meters)	Total Hardness (mg/L CaCO3)
Al Fawar (1)	Upper	902	0.0055	2.24	0.0055	100.5	378.4
Asamoua	Upper	852	0.0077	5.02	0.0015	191	367.7
Hundaza	Upper	546	0.0168	7.01	0.0024	330	307.8
Herodion (1)	Upper	506	0.0086	6.75	0.0013	350	366.4
Al Rehea	Lower	639	0.0332	4.87	0.0068	495	321.9
PWA 1	Lower	588	0.012	2.45	0.0041	600	347.1
Herodion (4)	Lower	598	0.0136	7.15	0.0019	691	87.1
Herodion (2)	Lower	545	0.0237	11.39	0.0021	770	449.6
Izzariya (2)	Lower	563	0.0173	6.99	0.0025	793	298.4
JWC 4	Lower	513	0.0116	8.55	0.0014	787.5	206.9
Herodion (3)	Lower	566	0.004	9.7	0.0004	800	161.4
Izzariya (3)	Lower	629	0.037	10.79	0.0034	835	381.8
PWA 11	Lower	596	0.012	7.46	0.0016	851	460.8
Izzariya (1)	Lower	519	0.0268	14.58	0.0018	996	243.1

According to our results presented in Table (2) in Table 1 and 2, there is a strong positive correlation between ^{222}Rn and well depth in both Upper and Lower Aquifer systems. In the Upper Aquifer, ^{222}Rn concentration range between 2.24Bq/L in Al Fawar well no. 1 and increase eastwards to 6.75 Bq/L in Herodion well no.1 with a strong positive correlation coefficient between ^{222}Rn concentration and well depth with r= 0.97 as shown in Figure 5.

In the Lower Aquifer ^{222}Rn concentration ranges from 2.45 Bq/L in PWA well no. 1 to 14.58 Bq/L in Izzariya well no. 1 The ^{222}Rn concentration in the Lower Aquifer is higher than in the Upper Aquifer as the Lower Aquifer is considered as a confined aquifer and ^{222}Rn remain trapped in the water. Figure 6 shows positive correlation between depth increase and ^{222}Rn concentration in the Lower Aquifer with r = 0.83.
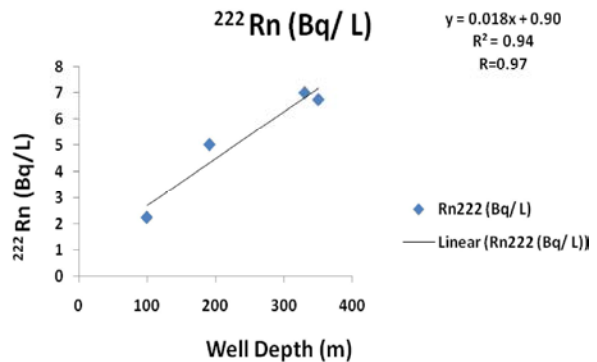

Fig. 5: Correlation between well depth and ^{222}Rn concentration in the Upper Aquifer

Figure 7 present the relationship between ^{222}Rn-concentration in Upper and in Lower Aquifer systems in relation well depth.
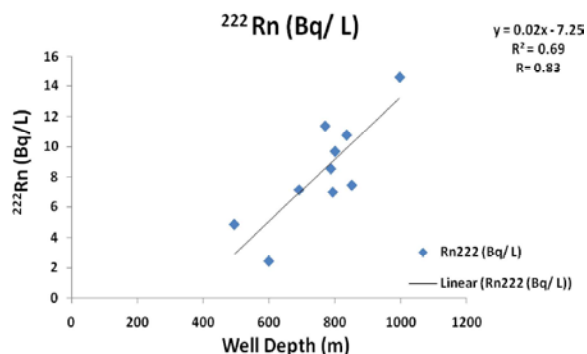
Fig. 6: Correlation between well depth and ^{222}Rn concentration in the Lower Aquifer
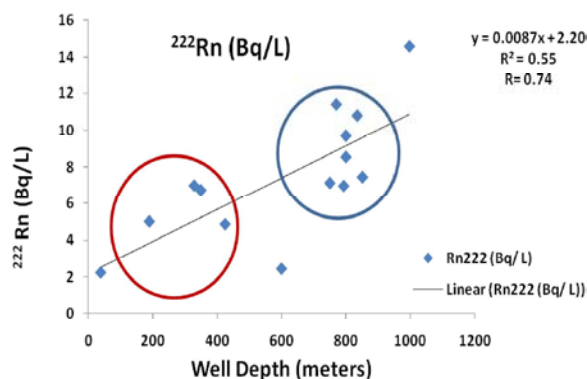

Fig. 7: Correlation between well depth and ^{222}Rn concentration of the Upper Aquifer –red circle– and the Lower Aquifer– blue circle
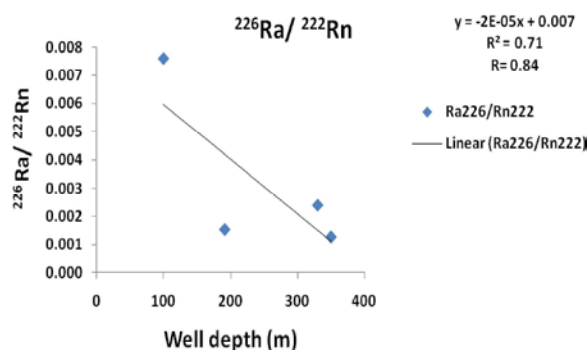

Fig. 8: Correlation between well depth and ^{226}Ra/^{222}Rn ratio in the Upper Aquifer

In studying the ratio of ^{226}Ra /^{222}Rn and the wells depth of the Upper Aquifer, a negative correlation with r= 0.84 was found (Figure 8). The low concentration of ^{226}Ra over the ^{222}Rn concentration had led the possibility of studying the mechanism of ^{226}Ra in the Upper Aquifer. A negative correlation between ^{226}Ra concentration and Saturation Indices for calcite mineral is found (Figure 9).
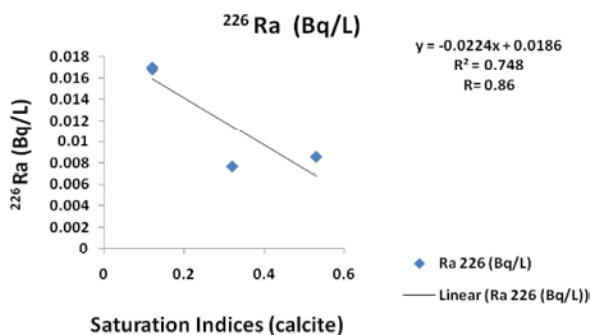

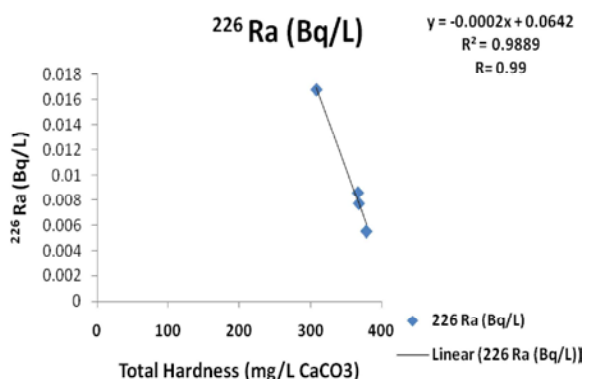Fig. 9: Correlation between Saturation Indices (calcite) and ^{226}Ra concentration in the Upper Aquifer

Fig 10: Correlation between Total Hardness (mg/L CaCO$_3$) and ^{226}Ra concentration

Saturation indices is a method for expressing the extent of chemical equilibrium between the mineral phases of the aquifer materials and water where SI $=\log K_{IAP} / K_{Sp}$

The important chemical reactions are those of adsorption of radium to active surfaces of all kinds and co–precipitation with Ca^{+2} salts in particular [12]. Calcite saturation indices is very important to present the geochemical conditions of water. If water is saturated with respect to calcite, then it will precipitate. There is a possibility that the increase in the saturation indices of calcite lead to partial removal of Ca^{+2} from the solution by precipitation and the decrease in ^{226}Ra concentration could be ascribed to the adsorption of ^{226}Ra on the active surfaces of Ca^{+2} and then co-precipitation with Ca 2. In studying more the relation between the total hardness (mg/L CaCO$_3$) of the water with the concentration of 226Ra, a negative linear correlation with r=0.99 as illustrated in figure 10. This indicates as total hardness increases the possibility of precipitation of calcite increases thus lead to decrease the 226Ra concentration as it will co-precipitate with the calcite mineral.

The observation of variations of Radium and Radon concentrations in groundwater supplies suggested that the scale length of ^{222}Rn migration in groundwater transport may be greater than that of ^{226}Ra, despite the much longer half-life of ^{226}Ra. It appears that the transport of Radium by groundwater may be extreme limited owing to continual exchange with the aquifer solid.

CONCLUSION

In both Upper and Lower Aquifers a good positive correlation was indicated between well depth and ^{222}Rn concentration due to that more water will interact with greater thickness of the aquifer. While a negative correlation was observed between the ^{226}Ra/ ^{222}Rn ratio and the well depth in the studied wells. Most of the groundwater samples of both Upper and Lower Aquifer system were oversaturated with respect to calcite thus the minerals tend towards precipitation. The relation between the 226Ra concentration and the saturation indices of calcite is highly negative in the Upper Aquifer with r= 0.86 leading to the possibility of co–precipitation of ^{226}Ra with Ca^{+2} salts, thus leading to the low concentration of ^{226}Ra (0.0055 Bq/L- 0.017 Bq/L) over the ^{222}Rn concentration (2.24 Bq/L- 6.75 Bq/L).

These results were confirmed by studying the relation between the total hardness of water and the 226Ra concentration leading to a highly negative correlation coefficient r= 0.99

ACKNOWLEDGEMENT

REFERENCES

1. Capacity Building for a program in Water Resources Management in Gaza and the West bank. Course1. Groundwater flow and Transport. Bethlehem University, pp: 10-16.

2. Ministry of Environmental Affairs, 1998. Water resources in the West Bank.

3. Roeffy and Raffety, 1963. Jerusalem District Water Supply, Geological and Hydrological Report, Hashemite Kingdom of Jordan Central Water Authority (unpublished)

4. Roeffy and Raffety, 1965. Nablus District Water Resources Survey, Geological and Hydrological Report, Hashemite Kingdom of Jordan Central Water Authority. (unpublished).

5. Oliveira, J., B. Mazzilli, M. Oliveira and B. Silva, 1998. Seasonal variations of ^{226}Ra and ^{222}Rn in mineral spring waters of Aguas da Prata, Brazil. Applied Radiation and Isotopes, 49: 423-427.

6. Vengosh, Avner, 2006. Rooting Out Radioactive Groundwater. Geotimes. http://www.geotimes.org/may06/feature_RadioactiveWater.html (21/10/2008)

7. Donald Porcelli and Peter W. Swarzenski, 2003. The behavior of U-Th-series nuclide in groundwater. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America vol.

8. Sturchio, N.C., J.L. Banner, C.M. Binz and M. Musgrove, 2001. Radium geochemistry of ground waters in Paleozoic carbonate aquifers, midcontinent, USA. Applied Geochemistry, 16: 109-122.

9. Kim, G., H. Dulaiova, W.C. Burnett, P.W. Swarzenski, W.S. Moore, 2001. Measurement of ^{224}Ra and ^{226}Ra activities in natural waters using a radon-in-air monitor.

10. Piper, A.M., 1944. Graphical procedure in geochemical interpretation of water analysis. Trans-American Geophysical Union, 25: 914-928.

11. Langguth, H.R., 1966. Die Grundwasserverhaltnisse Bereich des Velberter Sattels, Rheinisches Schiefergeberge, Der Minister fur Ernahrung. Landwirtschaft und Forsten, NRW, Dusseldorf.

12. Oliveira, J., B. Mazzilli, M. Oliveira and B. Silva, 1998. Seasonal variations of 226Ra and 222Rn in mineral spring waters of Aguas da Prata, Brazil. Applied Radiation and Isotopes, 49: 423-427.