ISSN: 0976-3031

Available Online at http://www.recentscientific.com

International Journal of Recent Scientific Research
Vol. 8, Issue, 1, pp. 15126-15141, January, 2017

International Journal of Recent Scientific Research

Research Article

EFFECT OF FLASH FLOOD ON URANIUM-SERIES DISEQUILIBRIUM AND GROUNDWATER RESIDENCE TIME USING GAMMA RAY SPECTROMETRY

Eman M. Ibrahim*

Nuclear Materials Authority, P.O. Box: 530, El-Maadi, Cairo, Egypt

ARTICLE INFO

Article History:

Received 15th October, 2016
Received in revised form 25th November, 2016
Accepted 23rd December, 2016
Published online 28th January, 2017

Key Words:

Uranium, Disequilibrium, Flash flood, Groundwater Residence Time, Sinai

ABSTRACT

Several radionuclides of the ^{238}U decay series (^{234}Th, ^{234m}Pa, ^{234}U, ^{222}Rn and ^{210}Pb), ^{235}U and ^{232}Th have been measured through gamma spectrometry in surface water and four dug wells in two successive years, in order to study the effect of flash flood event of 18th January 2010 on radionuclides distribution in Wadi Naseib, southwestern Sinai, Egypt. Variation of ^{238}U/^{235}U activity ratio by flash flood is observed in surface water sample and increased with time. This is due to that the ^{238}U activity was determined indirectly from the gamma rays emitted by its daughter products (^{234}Th and ^{234m}Pa), while ^{235}U activity was determined directly by its own gamma ray peaks. The surface water sample reached secular equilibrium between ^{238}U and its daughter products (^{234}Th and ^{234m}Pa) after about one hundred days. The water-rock interactions during the journey of flash flood (April 2010) in the studied area changed the chemistry and the specifications of the groundwater. The cations and anions results are varied with time of collecting water and place of the wells. The activity concentrations of ^{238}U, ^{210}Pb and ^{232}Th in groundwater samples collected in 2011 are found lower than that collected in 2010 while that of ^{234}U and ^{222}Rn are higher in 2011 than that in 2010. The groundwater residence time of two samples, collected from (Well-Zeid) in two successive years (2010 and 2011) were 27.93 and 42.44 ky, respectively, which show the young date just after the flash flood and gain of uranium with the new added water while after one year with the decrease of U-concentrations, the residence time increased. The last date may be coincide with the last wet period in Egypt.

INTRODUCTION

Radionuclides are naturally found throughout all environments. They are present in varying amounts in air, water, plants, animals, soil and rocks. Naturally occurring radionuclides are mainly derived from three separate decay chains (^{235}U, ^{238}U and ^{232}Th) (Vesterbacka, 2005). These chains comprise several radioisotopes presenting distinct chemical and physical properties, and are largely used in geochemical, geochronological and environmental studies. In undisturbed systems, for sufficiently long time (~1 Ma), the decay products of each chain achieve secular radioactive equilibrium, in which the activity of the parent is equal to those of all its daughters. Conversely to rock systems, in which secular radioactive equilibrium is common, surface and ground waters are characterized by significant disequilibria (Reyes and Marques, 2008). Natural radionuclides are carried to groundwater via normal recharge and as a result of water–rock interaction. Therefore, their study offers important information on the geochemical history of groundwater systems. Recent studies on rock matrix around water conducting fractures have shown U mobilizations with extreme fractionation of U isotopes (Suksi *et al.*, 2006).

The distribution of naturally occurring radionuclides in groundwater can provide important insights into water-rock interaction processes and residence time of fluids in geological systems. Processes occurring during water-rock interaction induce significant fractionation between U series nuclides that reflect their contrasting chemical behavior during their release into the fluid phase. This generally leads to pronounced radioactive disequilibria in fluid phase (Petersen *et al.*, 2013). Distributions of ^{238}U and ^{234}U have been used to constrain the source, age, and mixing of groundwater (Luo *et al.*, 2000).

Radon is noble gas and has three natural isotopes: ^{222}Rn, ^{220}Rn and ^{219}Rn. The most significant is ^{222}Rn due to its longer half-life (3.8 days). In groundwater, ^{222}Rn occurs in a dissolved form and its activity concentration may vary from a few Bq/ℓ to thousands of Bq/ℓ. The highest activity concentrations are found from bedrock water. In surface water ^{222}Rn is generally found at very low levels (Salonen, 1994; Vesterbacka, 2005).

Corresponding author:* ***Eman M. Ibrahim*
Nuclear Materials Authority, P.O. Box: 530, El-Maadi, Cairo, Egypt

In the present study, the distribution of radionuclides (^{234}Th, ^{234m}Pa, ^{234}U, ^{222}Rn, ^{210}Pb, ^{235}U and ^{232}Th) are investigated in surface and ground water samples which are collected from Wadi Naseib, southwestern Sinai, Egypt in two successive years (2010 and 2011). This study will clarify the relation between the chemistry and radioactivity of the flash flood water and the country rock type. Also, this work aims to study the effect of flash flood on radionuclides distribution and groundwater residence time in the collected samples.

U-Series Dating

Groundwater age is defined as the amount of time that has elapsed since a particular water molecule of interest was recharged into the subsurface environment system until this molecule reaches a specific location in the system where it is either sampled physically or studied theoretically for age-dating. On the other hand, **groundwater residence time** is the time it takes for particles of water to travel from the recharge area to the discharge area of the aquifer. It is the time interval between infiltrating into, and exfiltrating out of, the subsurface media. These are illustrated in Fig. 1. The groundwater residence time is the amount of time the flowing groundwater molecules resided in the groundwater reservoir (aquifer) (Kazemi *et al.*, 2006).

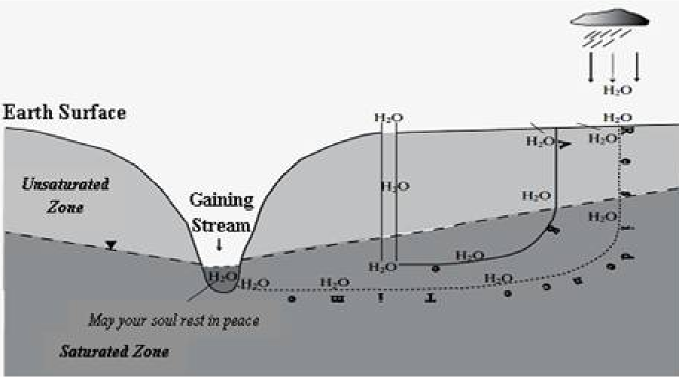

Figure 1 Groundwater age and groundwater residence time (Kazemi *et al.*, 2006).

The U-series dating methods have been used for the Quaternary period. Pluvial periods of Late Quaternary were indicated in the Eastern Desert of Egypt by dating uranyl mineralization (Osmond and Dabous, 2004). Apparently, pluvial conditions caused the mobilization and redeposition of the uranium by groundwater (Dawood *et al.*, 2014).

The U-series dating methods are based on the measurements of the activities of uranium and its daughters. The naturally occurring materials which contain uranium and did not disturbed for several million years, show a state of secular equilibrium between the parent (^{238}U) and its daughters. However, when a deposit is formed and subjected to several geochemical processes will cause isotopic and elemental fractionation and show a case of disequilibrium (Osmond and Cowart, 1976). In this case it is possible to determine the time of this event by measuring the extent to which the radionuclide system has returned to the state of secular equilibrium(Simpson and Grün, 1998). The ages are determined from the following equation which was derived by Kaufman and Broecker (1965).

$$\left(\frac{^{230}Th}{^{234}U}\right)=\left(\frac{^{238}U}{^{234}U}\right)\times(1-e^{-T\lambda_{230}})+\left\{\lambda_{230}\Big/(\lambda_{230}-\lambda_{234})\right\}\times\left\{1-\left(\frac{^{238}U}{^{234}U}\right)\right\}\times\left\{1-e^{-T(\lambda_{230}-\lambda_{234})}\right\} \qquad \ldots\ldots\ldots\ldots(1)$$

where T is the age of the sample, (^{230}Th/^{234}U) and (^{238}U/^{234}U) are the measured activity ratios, and λ_{230} and λ_{234} are the decay constants of ^{230}Th and ^{234}U, respectively.

Uranium-thorium dating relies on the propensity of uranium, a very soluble element in oxidised groundwaters, to co-precipitate with calcium during carbonate formation, in the absence of its daughter, ^{230}Th, which is almost totally immobile in the near-surface environment (Langmuir and Herman, 1980). The subsequent in-growth ^{230}Th provides a chronometer with which to measure elapsed time since carbonate deposition (Ivanovich and Harmon, 1992; Rowe and Maher, 2000). Age is calculated from the measured ^{230}Th/^{234}U and ^{234}U/^{238}U ratios in the studied sample.

The most common methods to measure the amount of uranium and its daughter thorium in a sample are by mass-spectrometry and α-particle spectrometry. The present paper deals with the method of determining the important uranium isotopes and daughters for dating by γ-ray spectrometry (Simpson and Grün, 1998). A non-destructive, gamma-spectrometric method for uranium age-dating is presented which is applicable to material of any physical form and geometrical shape. It relies on measuring the daughter/parent activity ratio ^{230}Th/^{234}U by high-resolution gamma-spectrometry using intrinsic efficiency calibration. The method does not require the use of any reference materials of known ages. It relies on evaluating the daughter/parent activity ratio ^{230}Th/^{234}U, obtained by directly measuring the count rates of the relevant γ peaks of ^{230}Th and ^{234}U.

Geologic Setting and Sampling

The hydrogeochemical characteristics of groundwater evolve with time due to water-rock interactions. The nature and distribution of rock formations, the structural setting and the hydrogeological system have an important influence in the spatial distribution and geochemistry of groundwaters (Gómez *et al.*, 2006). The four studied wells (Well-1, Well-2, Zeid and Oda) are located in Wadi (Valley) Naseib with its course from south to north in a Precambrian basement rocks non-conformably overlying by Paleozoic sedimentary cover (Fig. 2). The Precambrian basement rocks are consisted of diorite and granodiorite with extrusive acidic dykes which mainly exposed in the east and south of Wadi Naseib (Fig. 3a). The sedimentary cover exposed in both sides (east and west) of Wadi Naseib is consisted of Cambrian sandstone, siltstone and shale and lower Carboniferous dolomite, marl and black shale (Um Bogma Formation) and sandstone and grey shale of Abu Thora Formation (Weissbrod, 1969; Soliman and Abu El Fetoah, 1969). The dolomite, marl and black shale of Um Bogma Formation represent high-grade uraniferous rocks (up to 1500 ppm U) (Fig. 3b) (El Aassy *et al.*, 1986 and 2000).

Wadi Naseib was regarded by El Rakaiby and El Aassy (1989) as a graben. This Valley is drained from south (upstream), where the uraniferous rocks are exposed to north (downstream) at Wadi El Seih (outside the map).

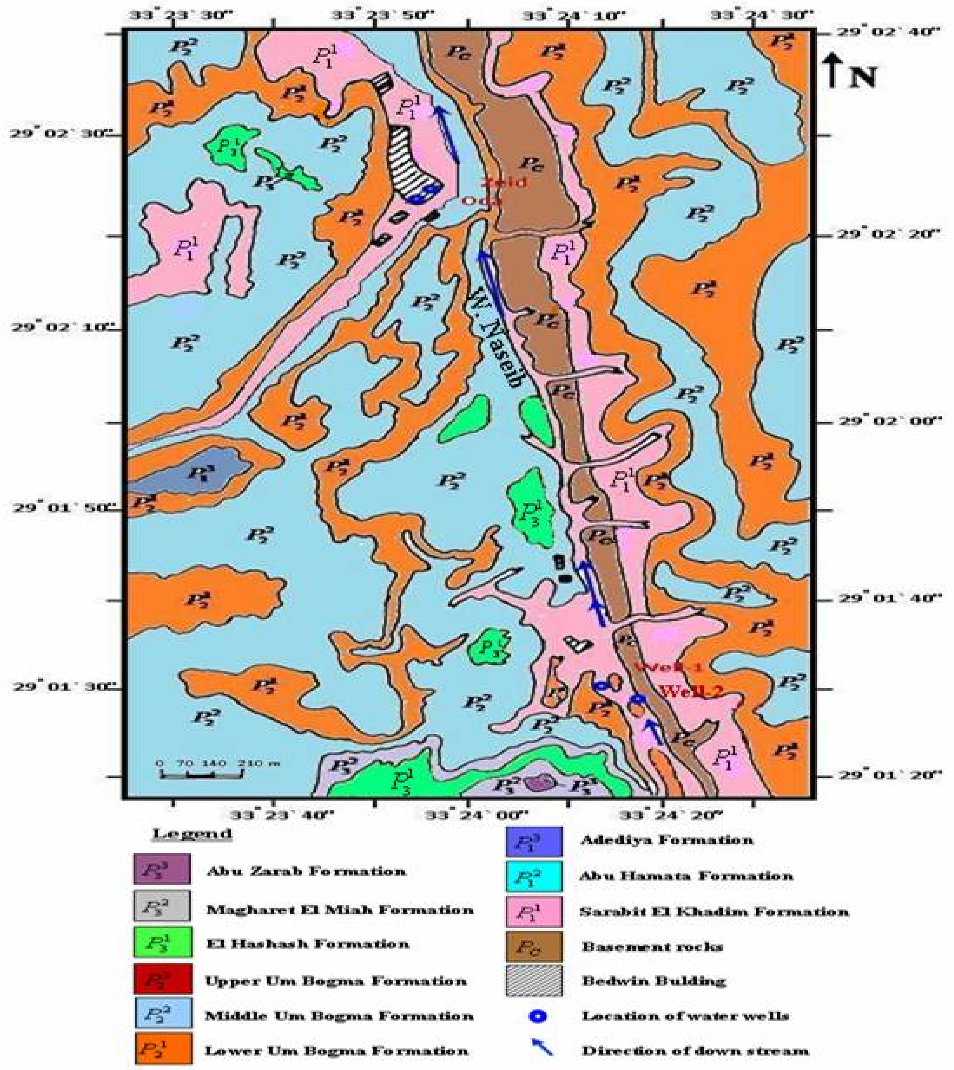

Figure 2 Geologic map of the studied area with location of studied water wells (After Nada *et al.*, 2011).

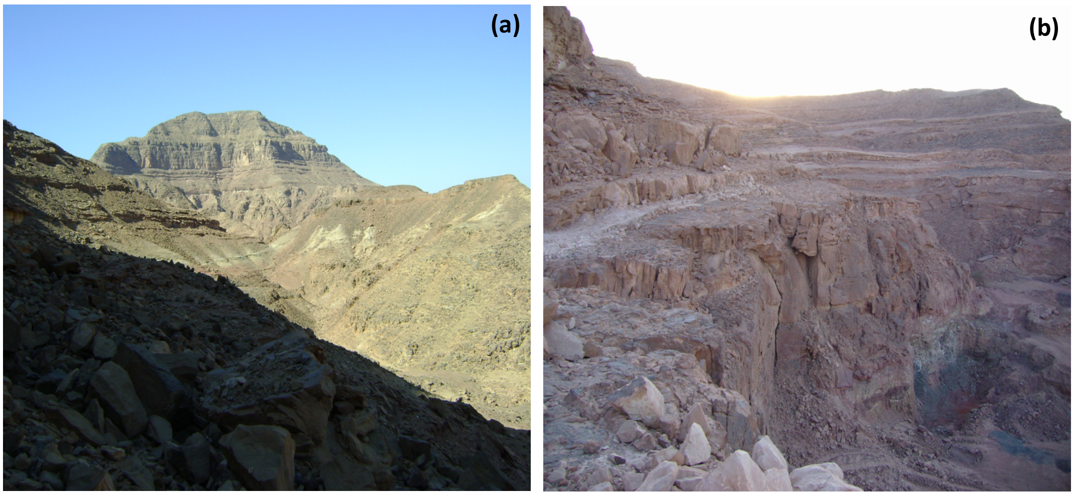

Figure 3 (a) Sandstone and shale steps with granodiorite at the base and (b) Sandstone steps underlain with shale in the flash flood course.

The flash floods in this area usually starting from Gabal (G, mountain) Alouga at the southern extreme of the map and have its course to the east and then to the north till Wadi El Seih. During this journey the water-rock interactions change the chemistry and the specifications of the groundwater.

The southern extreme of Wadi Naseib area was subjected to heavy rains on January 16 and 17, 2010 associated with heavy clouds, lightning and thunder. On January 18, 2010, a flash flood was started from the high mountains passing through irregular course and excavate a pathway through the different rocks and soils. From a hydrometeorological aspect, flash floods are best described as events involving "too much water in too little time". This means that exceptionally high amounts of rainfall, combined with very efficient and rapid runoff on relatively small catchments, are typical of flash floods (Lóczy *et al.*, 2012). The distance between the starting zone of the flash flood and the low land is more than 400 m. During the movement of the water, it is loaded with debris of the rocks and dissolves some of the uranium from the uranium carrier sediments of Um Bogma Formation.

One surface water sample of 750 ml volume was collected from the collecting pool (Fig. 4) from near the upstream of Wadi Naseib after flash flood. The surface water sample was collected at January 20, 2010 from sub-basin 500 m after a water fall which is very near from well (Well-1). Groundwater samples are collected from four dug wells of Wadi (valley) Naseib, southwestern Sinai, Egypt in the same season of two successive years (April 2010 and April 2011). Very important information is the occurring of a flash flood in January 2010 and not occurred in the same season of 2011. The studied two wells (Well-1 and Well-2) are located very near from the upstream of the valley and the other two (Oda and Zeid) are located toward the north at the midway between upstream and downstream (Fig. 2). The water wells sampling were carried out by sampler equipment from three different depths to cover the maximum depth. These three samples from each well were mixed, acidified, filtered and the clear water was divided into two parts, one for radioactive measurements and the other for chemical analyses of uranium and different cations and anions.

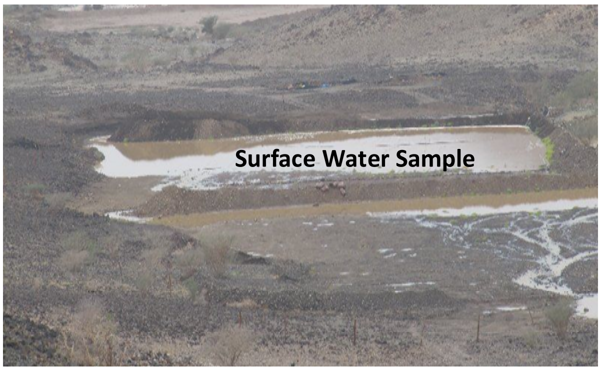

Figure 4 Collecting pool from the flash flood.

Methodology and Analytical Technique

The surface water sample and the eight groundwater samples collected from four wells in the same season of two successive years (2010 and 2011) were analysed non-destructively using two gamma-ray spectrometries with high purity germanium (HPGe) detectors. The surface water sample is measured eight times at different dates [4/2/2010, 18/2/2010, 4/3/2010, 11/3/2010, 18/3/2010, 31/3/2010, 14/4/2010 and 29/4/2010]. Part of the work was carried out using closed-end coaxial gamma-ray detector (n-type) made of high purity germanium (HPGe) in a vertical configuration (Pop Top-cryostat configuration) cooled with liquid nitrogen. The used HPGe EG&G Ortec Model GMX60P4 has a full width of half maximum (FWHM) of 1.10 keV at the 5.9 keV gamma transition of ^{55}Fe and 2.3 keV at the 1.33 MeV gamma transition of ^{60}Co. The detector has a photo-peak relative efficiency of about 60 % of the 3"×3" NaI(Tl) crystal efficiency. The detector has peak-to-Compton ratio about 56 to 1 Compton ratio at the 1.33 MeV peak transition of ^{60}Co. The minimum detectable activities of this detector for various radionuclides (^{234}Th, ^{234m}Pa, ^{214}Pb, ^{214}Bi, ^{210}Pb, ^{228}Ac and ^{208}Tl) are 0.61, 2.43, 0.08, 0.12, 0.68, 0.13 and 0.29, respectively.

The second detector has a relative efficiency of about 50% of the 3″×3″ NaI(Tl) crystal efficiency, resolution of 1.90 keV and peak/Compton ratio of 69.9:1 at the 1.33 MeV gamma transition of ^{60}Co and it is coupled to conventional electronics connected to a multichannel analyzer card (MCA) installed in a PC computer. The minimum detectable activities of this detector for various radionuclides (^{234}Th, ^{234m}Pa, ^{214}Pb, ^{214}Bi, ^{228}Ac and ^{208}Tl) are 1.43, 2.09, 0.08, 0.10, 0.13 and 0.33, respectively.

The software program MAESTRO-32 was used to accumulate and analyze the data. Energy calibration of the detector was performed using standard point sources (^{137}Cs and ^{60}Co). The two systems were calibrated for energy to display gamma photopeaks between 63 and 3000 keV. The efficiency calibration was performed by using three well-known reference materials obtained from the International Atomic Energy Agency for U, Th and K activity measurements: RGU-1, RGTh-1 and RGK-1 (IAEA 1987; Anjos *et al.*, 2005). Water samples collected in April 2010 was measured by the first detector while that collected in April 2011 was measured by the second detector.

The primordial ^{238}U is the most abundant isotope of U (99.27 %) and the initial member of the ^{238}U-decay chain with a long half-life time (4.4683 Ga). It decays to ^{234}Th with the emission of the α-particle. Through two consecutive β- transitions, ^{234}Th decays to ^{234m}Pa (half-lives of 24.10 days and 1.17 min, respectively) and to ^{234}U, with the half-life time of 245,250 years, which decays to ^{230}Th (Pękala *et al.*, 2010). Uranium-238 activity was determined indirectly from the gamma rays emitted by its daughter products (^{234}Th and ^{234m}Pa) whose activities are determined from the 63.3 and 1001 keV photopeaks, respectively (Sutherland and de Jong, 1990). The ^{234}U activity was determined directly from the gamma rays emitted from this nuclide at energies of 53.2 and 120.9 keV (Yokoyama *et al.*, 2008; Yücel *et al.*, 2010; Ramebäck *et al.*, 2010). For the measurement of the ^{230}Th activity, the γ-ray emission at 67.7 keV is used (Simpson and Grün, 1998).
The activity of ^{222}Rn was determined indirectly from the gamma rays emitted by its daughter products (^{214}Pb and ^{214}Bi). The specific activity of ^{214}Pb was measured using the 295.2 keV and 351.9 keV, while the specific activities of ^{214}Bi and ^{210}Pb were measured using 609.3 and 46.5 keV, respectively. The uranium-235 activity was determined directly by its gamma ray peaks; 143.8, 163.4, 185.7, and 205.3 keV (Yücel *et al.*, 1998; Pöllänen *et al.*, 2003; Ramebäck *et al.*, 2010). The specific activity of ^{232}Th was measured using the 338.4 keV and 911.2 keV from ^{228}Ac and 583 keV and 2614.4 keV from ^{208}Tl.

RESULTS AND DISCUSSION

Surface Water

Surface Water Specifications

In the flash flooding water, the present dissolved uranium is derived from the rock and soil that the water runs over. The location and form of uranium minerals determine the availability of uranium for leaching during the flooding; this explains the importance of geological and geographical setting for the zone in the water track.

To complete the picture of the flash flood water, cations, anions and uranium were measured chemically in surface water sample and the results are shown in table (1). The concentration of anions were in the order $SO_4^{2-} > CO_3^{2-} > Cl^-$ while the cations were present in the order $Mg^{2+} > Ca^{2+} > Na^+ > K^+$. The chemical analyses of cationic and anionic constituents of the flash flood water show that the sulphate anions are three times concentrated more than the carbonate (Table 1). This means that this water is acidified (low pH), although the main exposed rocks are carbonate (dolomite). This acidified water has the ability to dissolve the uranium from its raw materials which is very clear in the analyses of the flash flood water.

Several radionuclides of the ^{238}U decay series (^{234}Th, ^{234m}Pa, ^{234}U, ^{222}Rn and ^{210}Pb), ^{235}U and ^{232}Th have been measured eight times through gamma spectrometry in surface water sample at different dates (Table 2 and Fig. 5). After flash flood 2010, the rain waters flow through rocks and soil in the studied area which dissolve uranium from the surrounding rocks. Elemental fractionation arises due to the greater mobility of uranium in comparison with its less soluble daughters Th and Ra (Patra, 2010). Differences in solubility of oxidized U species relative to Th and of ^{234}U relative to ^{238}U cause fractionation related to water flow along a given pathway with time. Because radioactive disequilibrium requires water/rock interaction in the last million years, active pathways are distinguishable from those not related to modern water flow. Rocks exposed to water interaction subjected to addition or removal of U relative to Th, and preferential mobilization of ^{234}U relative to ^{238}U due to alpha-recoil processes during radioactive decay (Paces *et al.*, 2013).

Table 1 Chemical analyses of cations, anions and uranium (ppm) in surface water and groundwater samples (April 2010 and April 2011).

Surface Water										
Sample	**SO_4^{2-}**	**CO_3^{2-}**	**Cl^-**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**TDS**	**U**	**pH**
Surface Water	5694	1822	820	1180	1632	528	124	12425	72.7	5.7
Groundwater*										
April 2010										
Well-1	682	572	518	396	482	336	52	4230	5	6.8
Well-2	728	228	286	162	214	180	12	1860	4	7.2
Well-Oda	576	163	78	122	163	52	16	1218	4	7.3
Well-Zeid	503	133	63	92	150	44	12	1034	3	6.9
April 2011										
Well-1	512	490	480	380	420	320	48	3800	1.0	6.9
Well-2	680	200	240	145	200	170	10	1600	0.9	7.3
Well-Oda	500	150	68	109	150	46	14	1120	0.8	7.0
Well-Zeid	490	125	60	89	141	40	10	990	0.7	7.2

*After Nada *et al.* (2011).

Radionuclides Activity Concentrations

The water of rains started to collect at January 16, 2010 and form a pool in January 18, while the water sample was collected at January 20, 2010. Unfortunately, the first measurements for radionuclides was carried out at Feb. 4, 2010 by HPGe detector and repeated 8 times per two weeks except on the 4th and 5th measurements, the intervals were one week only and the results are shown in table (2).

The occurrence of thorium in natural waters has been documented as being extremely low. This is due to the low solubility of ThO_2 in water (Langmuir, 1980). However, Th^{4+} species are considered as almost chemically immobile in the near surface environment. Hence, the sorption on to particulate matter (e.g. colloids) is an important transport mechanism for thorium in aquifers or surface waters.

Table 2 Specific activity (Bq ℓ$^{-1}$) of radionuclides and different activity ratios for surface water sample at different times.

Nuclide	**Date (dd/mm/yy)**							
	4/2/2010	**18/2/2010**	**4/3/2010**	**11/3/2010**	**18/3/2010**	**31/3/2010**	**14/4/2010**	**29/4/2010**
^{238}U series								
^{234}Th	212.95± 2.54	405.24± 2.20	529.66± 2.44	590.94± 2.41	671.75± 2.39	718.74± 2.88	741.87± 2.78	770.61± 3.23
^{234m}Pa	211.70± 7.19	401.31± 10.89	531.63± 11.60	598.95± 11.38	675.58± 10.68	702.17± 17.02	726.58± 15.25	767.69± 14.74
Average	**212.32± 4.86**	**403.28± 6.55**	**530.64± 7.02**	**594.94± 6.90**	**673.67± 6.53**	**710.45± 9.95**	**734.23± 9.02**	**769.15± 8.98**
^{234}U	256.77± 37.54	431.51± 45.68	615.85± 68.07	810.21± 85.17	909.00± 60.53	930.40± 73.19	931.02± 98.90	1098.12± 97.88
^{222}Rn								
^{214}Pb	1.69± 0.04	1.24± 0.11	0.94± 0.04	0.43± 0.02	0.43± 0.06	0.39± 0.01	0.31± 0.01	0.18± 0.01
^{214}Bi	1.68± 0.03	1.24± 0.05	0.89± 0.03	0.43± 0.01	0.41± 0.02	0.36± 0.01	0.31± 0.01	0.17± 0.01
Average	1.68± 0.04	1.24± 0.08	0.91± 0.04	0.43± 0.01	0.42± 0.04	0.38± 0.01	0.31± 0.01	0.18± 0.01
^{210}Pb	29.55± 1.59	29.12± 1.71	27.32± 1.66	29.91± 1.56	29.07± 1.54	29.41± 1.03	29.35± 1.22	29.71± 2.09
^{235}**U**	35.78± 0.84	35.66± 0.78	34.82± 0.77	34.58± 0.59	34.98± 0.54	35.78± 0.81	34.97± 1.75	35.44± 0.66
^{232}**Th**	3.23± 0.40	3.41± 0.42	3.21± 0.38	3.45± 0.37	3.60 ± 0.30	3.24± 0.34	3.33± 0.39	3.55 ± 0.41
^{238}U/^{235}U	5.93 ± 0.28	11.31 ± 0.43	15.24 ± 0.54	17.20 ± 0.50	19.26 ± 0.48	19.86 ± 0.73	20.99 ± 1.31	21.70 ± 0.66
^{234}U/^{235}U	7.18 ± 1.22	12.10 ± 1.55	17.69 ± 2.35	23.43 ± 2.87	25.99 ± 2.13	26.00 ± 2.63	26.62 ± 4.16	30.99 ± 3.34
^{234}U/^{238}U	1.21 ± 0.20	1.07 ± 0.13	1.16 ± 0.14	1.36 ± 0.16	1.35 ± 0.10	1.31 ± 0.12	1.27 ± 0.15	1.43 ± 0.14
U (ppm)	17.12 ± 0.39	32.52 ± 0.53	42.79 ± 0.57	47.98 ± 0.56	54.33 ± 0.53	57.29 ± 0.80	59.21 ± 0.73	62.03 ± 0.72
Th (ppm)	0.80 ± 0.10	0.84 ± 0.10	0.79 ± 0.10	0.85 ± 0.09	0.89 ± 0.07	0.80 ± 0.08	0.82 ± 0.10	0.88 ± 0.10
Th/ U	0.047 ± 0.007	0.026 ± 0.004	0.019 ± 0.002	0.018 ± 0.002	0.016 ± 0.002	0.014 ± 0.002	0.014 ± 0.002	0.014 ± 0.002

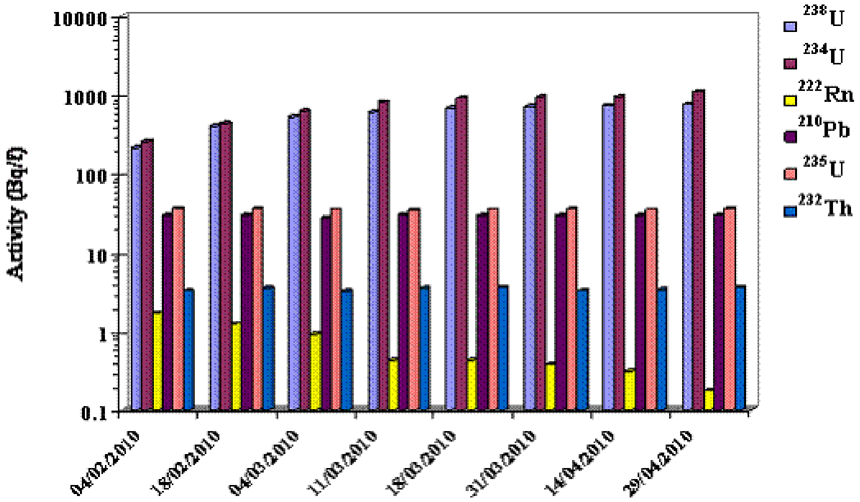

Figure 5 Distributions of ^{238}U, ^{234}U, ^{222}Rn, ^{210}Pb, ^{235}U and ^{232}Th in surface water sample at different time dates.

Under aqueous conditions, thorium generally forms colorless solutions and is particularly prone to hydrolysis (Gascoyne, 1992; Wisser, 2003). Therefore, ^{230}Th and ^{226}Ra are not found in the studied surface water sample where ^{234}Th is found which result from the decay of ^{238}U. Since the ^{238}U activity was determined indirectly from the gamma rays emitted by its daughter products (^{234}Th and ^{234m}Pa) while ^{235}U activity was determined directly by its own gamma ray peaks. The well noticed thing is that the ^{238}U activity concentrations were found to range from 212.32 to 769.15 Bq/ℓ which are increased gradually with time to reach a stable value while the ^{235}U activity concentrations ranged from 34.58 and 35.78 Bq/ℓ which are nearly constant along all the measurement dates (Fig. 5).

The regular gamma-analytical methods require a long period of at least 120 days to reach a secular equilibrium between ^{238}U and ^{234}Th in the sample for the usual ^{238}U decay series (Khorfan *et al.*, 2003). In a system in which there is an initial disequilibrium in the chain a return to secular equilibrium will occur after roughly 5-6 half lives of the daughter nuclide (Bourdon *et al.*, 2003). So, ^{234}Th and ^{234m}Pa need nearly five half lives to reach secular equilibrium with their parent ^{238}U (120.50 days and 5.85 min, respectively). The studied surface water sample take about 100 days to reach secular equilibrium between ^{238}U and its daughter products (^{234}Th and ^{234m}Pa), from the time of collection to the last measuring date (January to April, respectively).

The ^{234}U activity concentrations ranged from 256.77 to 1098.12 Bq/ℓ which are increased with time. The studied surface water sample has an excess of ^{234}U over ^{238}U as shown in figure (5). This is due to the fact that ^{234}U is produced by two ways; α-decay of ^{238}U and U-leaching from the surrounding rocks. The activity concentrations of ^{222}Rn decreased with time which are ranged from 1.68 to 0.18 Bq/ℓ while the activity concentrations of ^{210}Pb and ^{232}Th are constant through all the measurement dates (Fig. 5). Figure (6) shows comparison between partial gamma-ray spectra of the same surface water sample at different times which illustrate the gamma ray photopeaks emitted by radionuclides and their counts.

The height of these photopeaks represents the gamma ray counts which are used to calculate the activity concentration of their radionuclides. As shown in figure (6), the heights of 63.3, 1001 and 53.2 keV photopeaks (gamma rays emitted by ^{234}Th, ^{234m}Pa and ^{234}U, respectively) are increased with time while that of 143.8, 163.4, 185.7, and 205.3 keV (gamma rays emitted by ^{235}U) are constant with time.

Activity Ratios

Radioactive disequilibrium in the ^{238}U decay chain can be used to identify elemental and isotopic fractionation generated during water–rock interaction. Processes associated with alpha decay of ^{238}U can cause direct ejection of the daughter nucleus from the solid into migrating water, radiation damage of mineral lattices allowing preferential access of water, and radiation-induced oxidation of daughter ^{234}U. These processes result in U-isotope fractionation due to preferential loss of daughter ^{234}U relative to parent ^{238}U from the solid into the migrating water (Paces *et al.*, 2013). The existence of radioactive disequilibria among nuclides in the decay series is an indication of recent fractionation events, usually related to gain or loss of the more mobile nuclides (Condomines *et al.*, 2007).

In closed geological systems older than about 10^6 years, ^{234}U is in equilibrium with its parent ^{238}U (i.e., the ^{234}U/^{238}U activity ratio is 1.00). However, in open systems exposed to weathering and ground-water circulation, separation of these two isotopes can occur, causing a state of radioactive disequilibrium. The greatest deviations from equilibrium of the isotopes of the radioelements are observed in natural waters (Kaufman *et al.*, 1969). In the surface water sample, the ^{234}U/^{238}U activity ratios vary from 1.21 to 1.43 which increases with the ^{238}U activity concentrations. The isotopic variation of U results from selective leaching of ^{234}U itself and the direct α-recoil transfer of a ^{234}U precursor (^{234}Th).

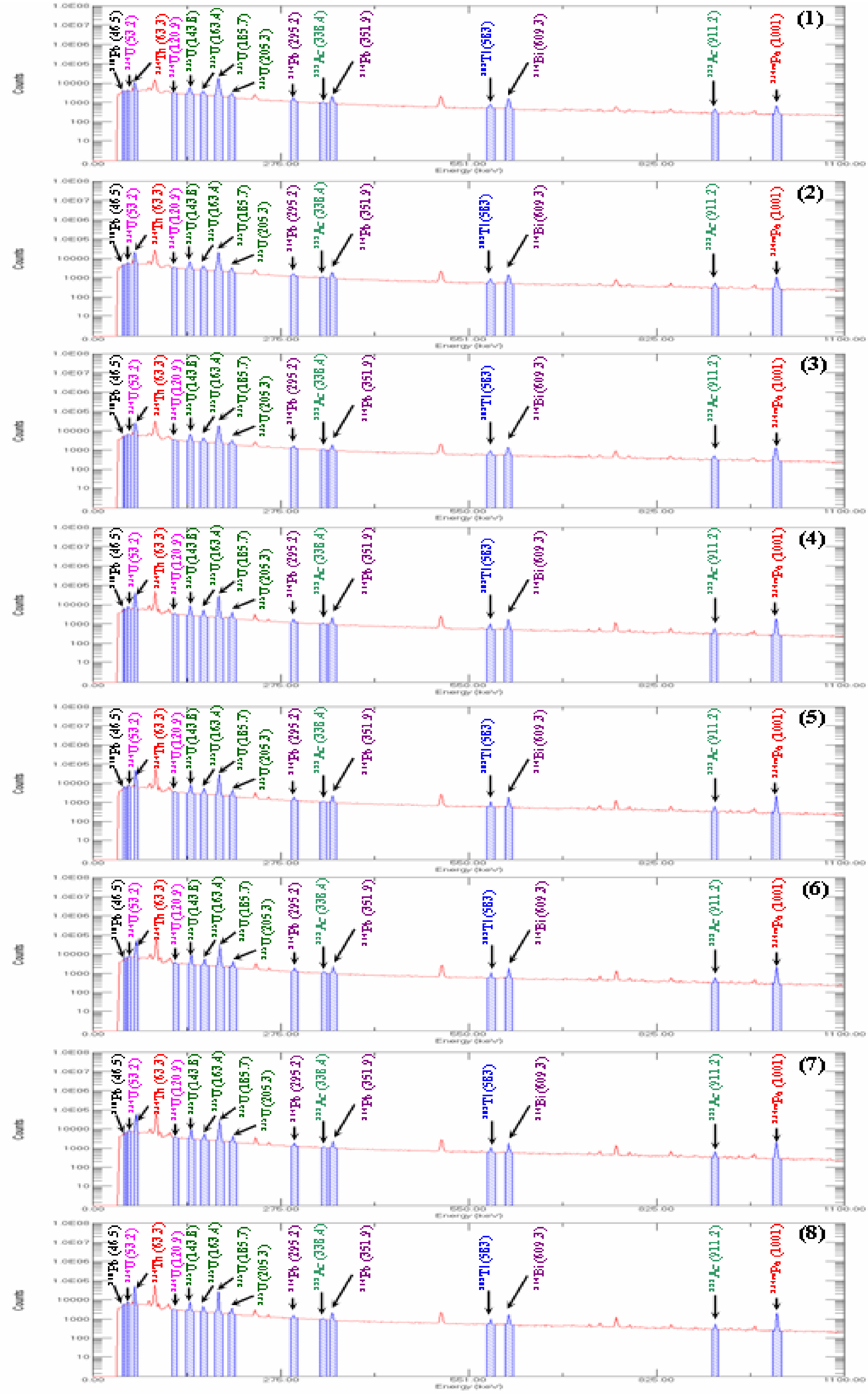

Figure 6 Comparison between partial gamma-ray spectra of the same surface water sample at different times.

The activity ratio of $^{238}U/^{235}U$ is ranging between 5.93 and 21.70 which reflect deviation from the natural ratio (21.7) and the recent dissolution of uranium from studied area affect this ratio (Fig. 7a). The $^{238}U/^{235}U$ activity ratio is increasing gradually with time until it reaches the natural value (21.7). This takes about 100 days to allow the attainment of secular equilibrium between ^{238}U and its measured progenies (^{234}Th and ^{234m}Pa). Theoretically, the in-growth of ^{234}Th to secular equilibrium with its parent ^{238}U takes 96.4-144.6 days (4-6 half lives of ^{234}Th). Much larger variations in the $^{234}U/^{235}U$ activity ratio is observed which varies form 7.18 to 30.99 (Fig. 7b) due to that the ^{234}U is more leachable than ^{238}U.

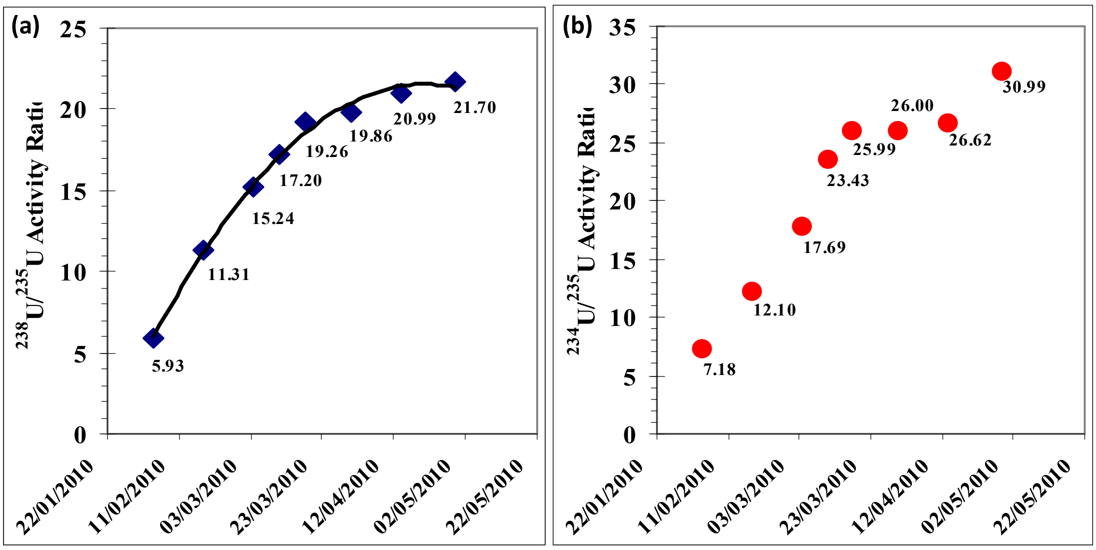

Figure 7 Activity ratio variations of (a) $^{238}U/^{235}U$ and (b) $^{234}U/^{235}U$ in surface water sample at different dates. The certified value of $^{238}U/^{235}U$ activity ratio is 21.7.

Groundwater

Groundwater is formed from seepage, which infiltrated soil and bedrock. The amount of rain and snow, evaporation, the duration of frost and the nature of soil affect the formation of groundwater. The activity concentrations of natural radionuclides in groundwater are connected to the activity concentrations of uranium (^{238}U and ^{235}U) and thorium (^{232}Th) and their decay products in soil and bedrock. This is because groundwater reacts with soil and bedrock and releases quantities of dissolved components, depending on the mineralogical and geochemical composition of the soil and rock, chemical composition of the water, degree of weathering of the rock, redox conditions and the residence time of groundwater in the soil and bedrock (Vesterbacka, 2005).

Water Specifications

Yet it is evident that the mechanisms and scales of rock weathering cannot be understood without the investigation of water geochemistry. On the other hand, the development of groundwater composition also cannot be evaluated without the geochemistry of weathering because both are related to a single process (Shvartsev, 2008).

The characterization of groundwater geochemistry, and the interpretation and understanding of hydrogeochemical evolution, form an essential part of assessing radionuclide migration in a natural environment. The chemical composition of waters is controlled by several identifiable processes (i.e. water-rock interaction, calcite dissolution and precipitation, brackish groundwaters with distinct glacial isotopic signatures…) (Négrel *et al.*, 2003).

Water from the four studied wells was collected in two seasons, the first is in April 2010 after January 2010 flash flood and the second is in April 2011 without flash floods in this year. Nada *et al.* (2011) studied the water chemistry (Table 1) and mentioned that the prevailing anions are in the order $SO_4^{2-} > CO_3^{2-} > Cl^-$ except Well-2, where $Cl^- > CO_3^{2-}$ in both times. Cations were present in the order $Mg^{2+} > Ca^{2+} > Na^+ > K^+$. From this table, it can be noticed that the cations and anions distributions are varied with time of collecting water and place of the wells which are illustrated in figures 8 (a and b). According to time, the concentrations of cations, anions and TDS are decreased in 2011 than in 2010 (year of flash flood) in the four wells. According to place the distribution of cations, anions and TDS show decrease in the order Well-1 > Well-2 > Oda > Zeid except Well-2 in the sulphate has the highest. In this concept the cations, anions and TDS concentrations decrease from the upstream wells to the downstream wells. The water of these wells can be classified as secondary alkalinity as $SO_4^{2-} + Cl^- > Na^+ + K^+$.

The chemical and biological components or quality of groundwater determine it's suitability for particular uses, such as potable drinking water, agriculture or environmental effects. As water moves through soils and rocks it can dissolve some minerals (like the case of groundwater samples which are collected after flash flood 2010). The exact concentration of different components in groundwater will depend on the type of soils and rocks the water has passed through and sometimes the microbiological action. In the same way that water can dissolve minerals, minerals can also be precipitated again as a solid (like the case of groundwater samples 2011 without flash floods). Understanding the chemical controls on groundwater can thus be a very important step in locating ore deposits, or the movement of a plume of contamination through an aquifer (Mudd 1998).

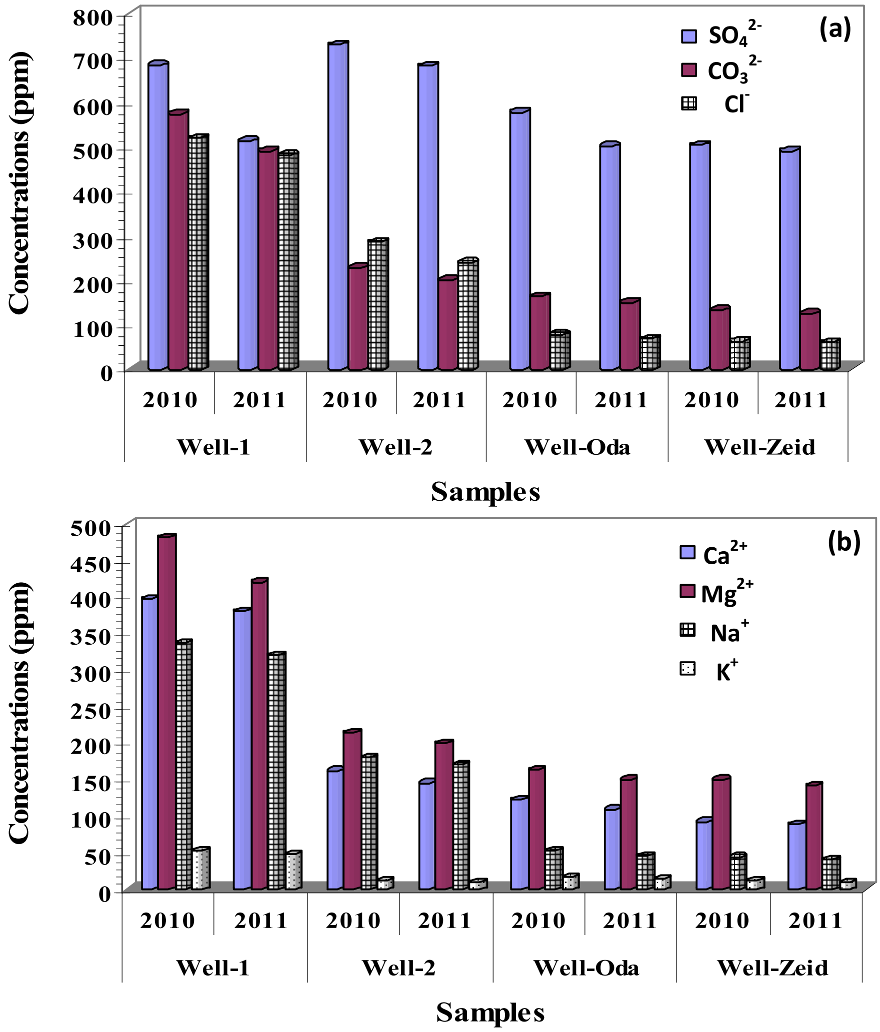

Figure 8 Concentrations of (a) anions and (b) cations of water samples in two years.

Radionuclides Distribution

Uranium-series disequilibrium can potentially provide an important tool for tracing migration of uranium series radionuclides and groundwaters from different aquifer conditions and, thus, has extensively been applied to the study of environmental, marine and earth sciences (Osmond and Ivanovich, 1992).

The measured radionuclides are ^{238}U, ^{234}U, ^{235}U, ^{222}Rn, ^{210}Pb and ^{232}Th in all the studied wells (Table 3 and Fig. 9). The results of the analyses show that in groundwaters within the study area both the $^{234}U/^{238}U$ activity ratio and the uranium content are quite variable, indicative of extensive disequilibrium within the hydrogeologic environment. Because the concentration of a radioactive nuclide in any water body decreases spontaneously with time, the spatial distribution of that concentration has often been used to determine the parameters of the process that causes that nuclide's concentration to vary from point to point (Aggarwal *et al.*, 2005). So concentration of uranium in groundwater samples collected 2011 is lower than that collected in 2010.

The maximum ^{238}U activity concentration encountered during the two seasons was found at Well-Oda sample in season 2010 (68.54 Bq/ℓ). The mean ^{238}U concentration of the investigated waters from season 2010 is about 49.55 Bq/ℓ. Waters with a higher uranium content may define zones of greater leaching of uranium by flash flood waters which move over soil and rock have high uranium content before enter the studied wells at the end of their journey.

Elemental fractionation arises due to the greater mobility of uranium in comparison with its less soluble daughters Th and Ra. Th is found at very low concentrations in most ground waters. Whereas, Ra is quite soluble in waters with high Cl^- concentration but relatively immobile in waters with high SO_4^{2-} concentrations, due to the formation of sparingly soluble radium sulphate (Patra, 2010). The studied groundwater samples have SO_4^{2-} concentrations higher than that of Cl^- in both seasons (2010 and 2011). Therefore Ra is not found in the studied groundwater samples.

Table 3 Specific activity (Bq ℓ^{-1}) of radionuclides and different activity ratios for groundwater samples (April 2010 and April 2011).

Radionuclide	**Well-1**		**Well-2**		**Well-Oda**		**Well-Zeid**	
	2010	**2011**	**2010**	**2011**	**2010**	**2011**	**2010**	**2011**
^{238}U								
^{234m}Pa	53.21 ± 8.51	11.99 ± 1.23	45.55 ± 6.65	11.51 ± 1.61	68.54 ± 7.97	9.95 ± 2.25	46.85 ± 6.23	11.51 ± 1.45
^{234}U	70.58 ± 18.85	106.06 ± 42.75	75.44 ± 34.27	119.39 ± 43.56	76.01 ± 17.72	112.94 ± 36.45	78.14 ± 26.07	108.75 ± 43.45
^{222}Rn								
^{214}Pb	0.48 ± 0.03	1.46 ± 0.05	0.76 ± 0.08	2.26 ± 0.07	0.93 ± 0.07	3.68 ± 0.08	1.26 ± 0.03	1.23 ± 0.07
^{214}Bi	0.47 ± 0.01	1.48 ± 0.05	0.75 ± 0.02	2.21 ± 0.05	0.89 ± 0.02	3.54 ± 0.08	1.26 ± 0.03	1.13 ± 0.04
Average	0.47 ± 0.02	1.47 ± 0.05	0.76 ± 0.05	2.24 ± 0.06	0.91 ± 0.04	3.61 ± 0.08	1.26 ± 0.03	1.18 ± 0.05
^{210}Pb	42.82 ± 1.30	16.46 ± 2.48	39.37 ± 1.51	16.44 ± 1.86	43.63 ± 1.28	14.20 ± 2.22	46.87 ± 1.16	11.17 ± 1.80
^{235}U	2.46 ± 0.53	0.56 ± 0.08	2.09 ± 0.46	0.53 ± 0.04	3.17 ± 0.48	0.46 ± 0.12	2.15 ± 0.17	0.53 ± 0.11
^{232}Th	3.26 ± 0.38	0.20 ± 0.01	3.04 ± 0.36	0.37 ± 0.02	3.14 ± 0.31	0.37 ± 0.02	4.34 ± 0.39	0.34 ± 0.02
^{238}U/^{235}U	21.61 ± 8.06	21.31 ± 5.32	21.76 ± 7.93	21.69 ± 4.74	21.63 ± 5.77	21.71 ± 10.52	21.75 ± 4.66	21.71 ± 7.11
^{234}U/^{235}U	28.66 ± 13.77	188.47 ± 103.67	36.03 ± 24.24	224.91 ± 99.77	23.98 ± 9.20	246.37 ± 143.14	36.28 ± 15.04	205.15 ± 123.21
^{234}U/^{238}U	1.33 ± 0.57	8.84 ± 4.47	1.66 ± 0.99	10.37 ± 5.23	1.11 ± 0.39	11.35 ± 6.23	1.67 ± 0.78	9.45 ± 4.97
^{222}Rn/^{238}U	0.009 ± 0.002	0.123 ± 0.016	0.017 ± 0.004	0.194 ± 0.032	0.013 ± 0.002	0.363 ± 0.091	0.027 ± 0.004	0.102 ± 0.018
^{222}Rn/^{234}U	0.007 ± 0.002	0.014 ± 0.006	0.010 ± 0.005	0.019 ± 0.007	0.012 ± 0.003	0.032 ± 0.011	0.016 ± 0.006	0.011 ± 0.005
^{210}Pb/^{238}U	0.80 ± 0.15	1.37 ± 0.35	0.86 ± 0.16	1.43 ± 0.36	0.64 ± 0.09	1.43 ± 0.55	1.00 ± 0.16	0.97 ± 0.28
^{210}Pb/^{234}U	0.61 ± 0.18	0.16 ± 0.09	0.52 ± 0.26	0.14 ± 0.07	0.57 ± 0.15	0.13 ± 0.06	0.60 ± 0.21	0.10 ± 0.06
^{210}Pb/^{222}Rn	90.60 ± 6.50	11.20 ± 2.03	52.07 ± 5.49	7.35 ± 1.02	47.81 ± 3.74	3.93 ± 0.70	37.30 ± 1.80	9.49 ± 1.95
U (ppm)	4.29 ± 0.69	0.97 ± 0.10	3.67 ± 0.54	0.93 ± 0.13	5.53 ± 0.64	0.80 ± 0.18	3.78 ± 0.50	0.93 ± 0.12
Th (ppm)	0.81 ± 0.09	0.05 ± 0.002	0.75 ± 0.09	0.09 ± 0.005	0.78 ± 0.08	0.09 ± 0.005	1.08 ± 0.10	0.08 ± 0.004
Th/ U	0.19 ± 0.05	0.05 ± 0.01	0.20 ± 0.05	0.10 ± 0.02	0.14 ± 0.03	0.11 ± 0.03	0.28 ± 0.06	0.09 ± 0.02

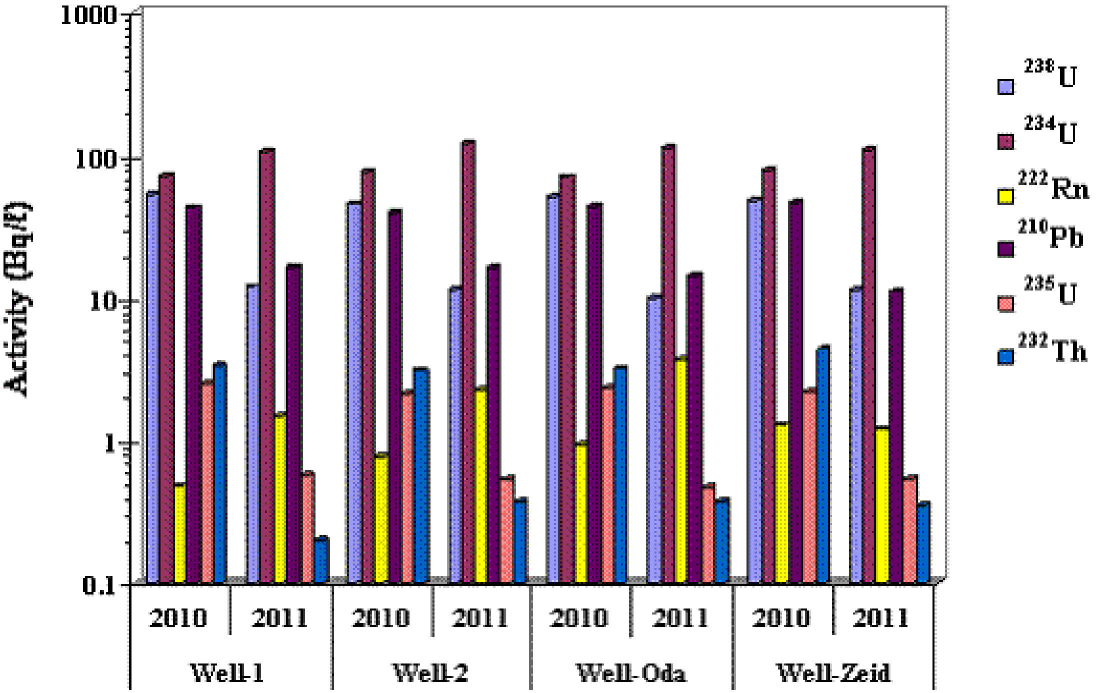

Figure 9 Distributions of ^{238}U, ^{234}U, ^{222}Rn, ^{210}Pb, ^{235}U and ^{232}Th in groundwater samples collected in two years, 2010 and 2011.

Radon is in groundwater that travels through cracks in bedrock. Water from wells normally has a much higher concentration of radon than the surface water in rivers, lakes and streams (Mazhari, 2008). ^{222}Rn is formed during the decay of radium atoms (^{226}Ra). During that process, the radon formed is propelled away from the site of decay and an alpha particle is recoiled in the opposite direction. Depending on its position and orientation in a mineral grain, ^{222}Rn may either end up in the fracture carrying water or gets buried deeper in the rock matrix (Skeppström and Olofsson, 2007).

The chemical composition of groundwater does not affect the activity concentration of ^{222}Rn.

The main parameters that affect the activity concentration of ^{222}Rn in groundwater are the activity concentration of ^{226}Ra in bedrock and soil, rock porosity and the ^{222}Rn emanation efficiency (Veeger and Ruderman, 1998). The disequilibrium between ^{222}Rn and other uranium series radionuclides is caused by the diffusive escape of ^{222}Rn (Salih *et al.*, 2004).

Furthermore, the ^{222}Rn contents of well waters were significant as well, ranging from 0.47 to 1.26 Bq/ℓ in season 2010 and from 1.18 to 3.61 Bq/ℓ in season 2011. It increases after one year from the flash flood except in Well Zeid. This may be due to the physical property decay by α-recoil.

The lead radioactive isotopes in the decay series are ^{210}Pb, ^{211}Pb, ^{212}Pb and ^{214}Pb, of which the longest lived is ^{210}Pb with a half-life of 22.3 years. Pb exists at oxidation states of +II and +IV. In aqueous solutions it is found in the +II state. In groundwater, Pb is found in an inorganic form, complexed with organic matter and adsorbed onto particles (Vesterbacka, 2005). The natural radioactive nuclides ^{210}Pb ($t_{1/2}$ = 22.3 years) has been used intensively as key tracers to study processes of chemical scavenging, particle transport and sediment deposition in marine environments due to their suitable half lives (Zuo and Eisma, 1993). The concentrations of ^{210}Pb in the water samples show a strong excess of ^{210}Pb, relative to ^{238}U and ^{222}Rn, in both seasons (2010 and 2011), indicating an additional source of ^{210}Pb from the around rocks (aquifer).

The highest activity concentrations of ^{238}U, ^{210}Pb and ^{232}Th were found in groundwater samples collected from wells in 2010 where the range activity concentrations were 4.0 – 5.2, 2.4 – 4.2 and 8.2 – 16.6 times, respectively, higher than in groundwater samples collected from the same wells in 2011. The highest activity concentrations of ^{234}U and ^{222}Rn were found in groundwater samples collected in 2011 with the range 1.4 – 1.6 and 0.9 – 4.0 times, respectively, higher than collected in 2010 (Fig. 9).

Activity Ratios

^{238}U and ^{232}Th maintain the radioactivity of their decay series in rock, soil and groundwater. The activity concentration of each radionuclide is controlled by radioactive decay and chemical and other physical processes. Due to these processes, radionuclides either leave or enter groundwater, causing disequilibrium with the nuclides in the decay series. Some daughter nuclides of uranium and thorium are too short-lived to become fractionated from their previous parents (Ivanovich and Harmon, 1982).

Disequilibrium in the uranium series can occur at several positions in the ^{238}U decay series: ^{234}U can be selectively leached relative to ^{238}U; ^{230}Th and ^{226}Ra can be selectively removed from the decay chain; and finally ^{222}Rn (radon gas) is mobile and can escape from soils and rocks into the atmosphere (Patra, 2010).

Bedrock and soil interact with the groundwater. During the interaction, radionuclides may transfer from bedrock and soil to groundwater by dissolution, desorption, erosion or atomic recoil by radioactive decay (von Gunten and Benes, 1995). In groundwater, elemental and isotopic disequilibrium exists both within and between uranium- and thorium-series nuclides. The disequilibrium is the greatest in deep groundwaters, such as in drilled well water (Salonen and Huikuri, 2002). The most significant reason for disequilibrium in groundwater is the different chemical and physical properties of each nuclide, which affect the ability of nuclides to dissolve and move in water. The chemical properties of a nuclide influence its dissolution, adsorption, desorption, precipitation and sedimentation. Examples of physical properties that differ between nuclides are the diffusion coefficient and half-life (Vesterbacka, 2005).

If the systems are exposed to weathering and groundwater circulation, the different physico-chemical conditions affecting ^{238}U and ^{234}U will result in their fractionation and, thus, the respective activity ratios will therefore be greater or less than unity. The isotopic variation of U results from selective leaching of ^{234}U itself and the direct α-recoil transfer of a ^{234}U precursor (^{234}Th). ^{234}U atoms are more susceptible to leaching than ^{238}U atoms as a result of α-recoil within the mineral lattice. The preferential leaching of ^{234}U will result in ^{234}U/^{238}U less than 1.0 in the weathering mineral. This results in the enrichment of ^{234}U in groundwater and ^{234}U depletion in the mineral. An additional mechanism is the process of daughter product emplacement from pore waters containing dissolved ^{234}U and ^{238}U, resulting in rocks that are enriched in ^{234}U and ^{230}Th relative to ^{238}U in reducing environments. Thus, using the measured daughter/parent activity ratios ^{234}U/^{238}U, ^{230}Th/^{234}U and ^{226}Ra/^{230}Th, U migration over various time-scales of 1.0 Ma, 300 ka and 6 ka, respectively, can be evaluated (Min *et al.*, 2005; Dawood, 2010).

Uranium isotope studies frequently show an inverse relationship between ^{234}U/^{238}U AR and U concentration in ground water. Other studies have reported that ^{234}U/^{238}U ARs increased with U concentrations or found no clear relationship between ^{234}U/^{238}U ARs and U concentration. ^{234}U/^{238}U ARs may be influenced by numerous factors, e.g., lithology (old, damaged clastic material may facilitate alpha recoil), mineralogy, and weathering rates (Sherman *et al.*, 2007). Dabous and Osmond (2001) reported that waters from the sandstone Nubian Aquifer in Egypt exhibit broad correlations between ^{234}U/^{238}U AR and inverse of the U concentration, consistent with mixing between recharging and aquifer waters with distinct ^{234}U/^{238}U AR as well as ^{238}U and excess ^{234}U concentrations. The data show that groundwaters collected in season 2010 have a high uranium content (68.54 Bq/ℓ) and a low ^{234}U/^{238}U activity ratio (1.11) while groundwaters collected in season 2011 have a relatively low uranium content (9.95 Bq/ℓ) and a high ^{234}U/^{238}U activity ratio (11.35). The high ^{234}U/^{238}U activity ratio values of the waters reflect preferential dissolution of ^{234}U relative to ^{238}U from rocks/ores due to the α-recoil effect during the decay of ^{238}U to ^{234}Th.

However, in groundwater ^{234}U nearly always has a higher activity concentration than ^{238}U. The mean isotopic ratio (^{234}U/^{238}U) in Finnish bedrock water has been 2 and the range is between 1 – 3 at the 95% confidence level (Salonen and Huikuri, 2002). The highest ^{234}U/^{238}U ratio measured in Finnish bedrock water has been 11. Higher activity ratios are often associated with lower activity concentrations of ^{234}U and ^{238}U. In the literature, ^{234}U/^{238}U activity ratios of up to 30 have been reported in groundwater (Ivanovich and Harmon, 1982; Vesterbacka, 2005). Innocent *et al.* (2013) found that the U activity ratios exhibit very high (^{234}U/^{238}U) ratios in some Eocene groundwaters, as high as 13.5. These very high U activity ratios indicating that the enrichment in ^{234}U due to water/rock interaction increases with time. So, high ^{234}U/^{238}U activity ratios were found in groundwater samples collected in 2011 where the recharge of water was not happened in the studied wells.

In the most analyzed samples uranium isotopes are out of secular radioactive equilibrium, exhibiting significant enrichment of ^{234}U relative to ^{238}U. However, ^{234}U/^{238}U ratios of groundwater samples from wells collected in 2011, whose average is 10.00 (range: 8.84–11.35), are in general larger and more variable than those of the same wells collected in 2010, whose average is 1.44 (range: 1.11–1.67).

The $^{238}U/^{235}U$ ratios of well water samples are consistent with naturally occurring U; i.e., there is no indication of anthropogenic enrichment or depletion of ^{238}U relative to ^{235}U (Fig. 10). Specifically, the increased mobility of ^{234}U relative to other U isotopes reflects production from ^{238}U by α-decay and subsequent emplacement in crystal sites damaged by α-recoil. Aqueous weathering of materials containing U results in preferential leaching of ^{234}U from these α-damaged crystal sites (Brennecka *et al.*, 2010). In reverse to the values of $^{238}U/^{235}U$ ratios, the $^{234}U/^{235}U$ ratios in groundwater samples range between 23.98 and 36.28 in 2010 and between 188.47and 246.37 in 2011 which mean ^{234}U is increasing with time due to chemical leaching and α-recoil (Fig. 10). Fig. (11) shows gamma-ray spectra for water sample (Well-1) in the two seasons; April 2010 and April 2011 which are analysed by the used two (HPGe) detectors.

Mainly two parameters influence strongly the $^{234}U/^{238}U$ activity ratios in groundwater were the contact time between the groundwater and the rock matrix and the extent of leaching by the groundwater. In addition to this, the groundwater chemistry also plays a role determining the activity ratio. The groundwater and host rock minerals are strongly interacted, thus both chemical and physical differentiation processes are enhanced according to rock-water ratio, surface area exposed and residence time (Tripathi *et al.*, 2013). When the widespread variations in ($^{234}U/^{238}U$) ratios that were discerned in groundwater were attributed to α-recoil, a quantifiable and fixed physical process, dating of groundwaters using U isotopes became possible (Krishnaswami and Cochran, 2008).

The existence of radioactive disequilibria among nuclides in the decay series is an indication of recent fractionation events, usually related to gain or loss of the more mobile nuclides (Condomines *et al.*, 2007).

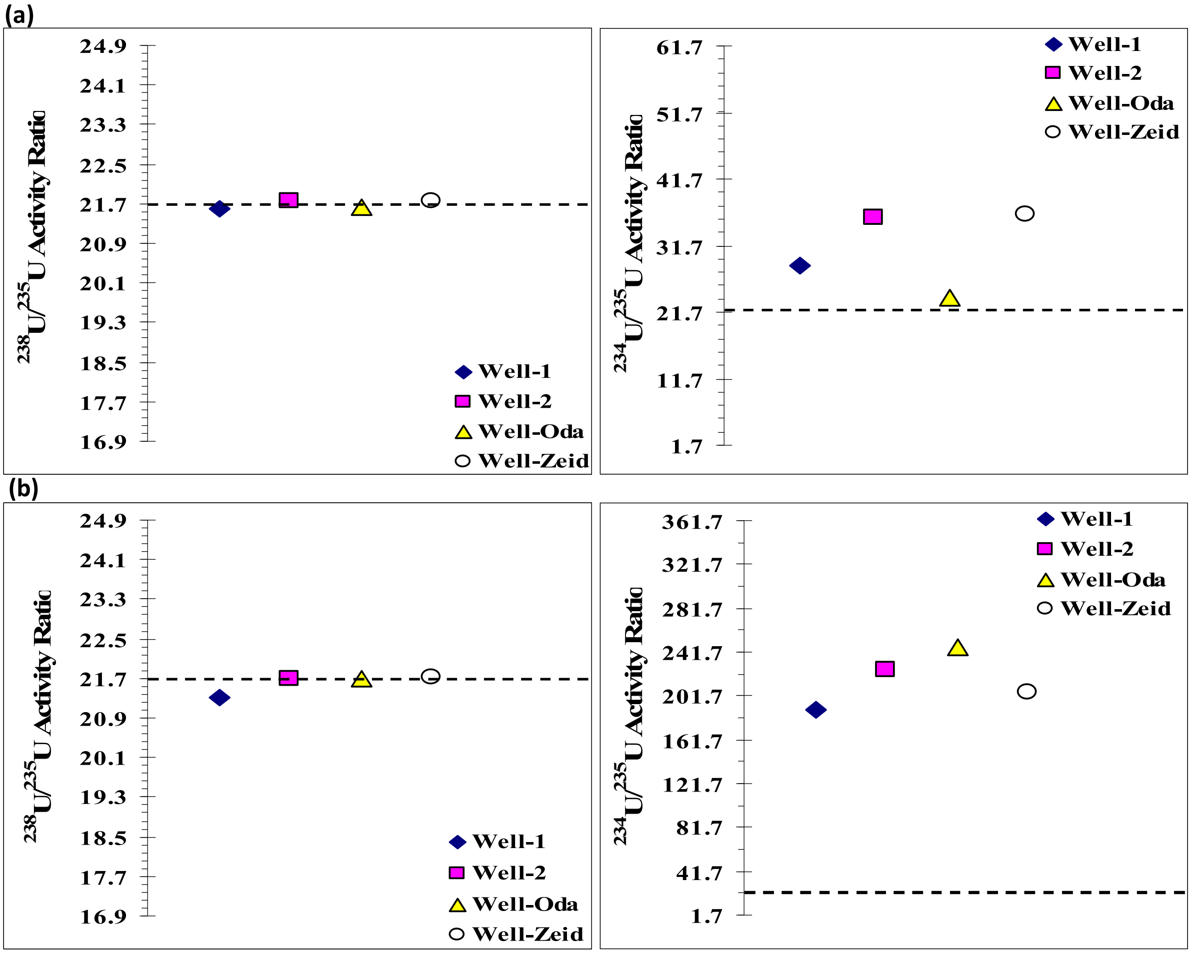

Figure 10 Variations of the $^{238}U/^{235}U$ and $^{234}U/^{235}U$ activity ratios in groundwater samples in two years; (a) 2010 and (b) 2011. The certified value of $^{238}U/^{235}U$ activity ratio is 21.7, which is shown with the dashed lines.

Groundwater Residence Time

The measured isotopic compositions and the isotopic ratios of two groundwater samples collected from (Well-Zeid) in the two years (2010 and 2011) are shown in table (3). Isochron-derived authigenic $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ activity ratios and calculated groundwater residence time are summarized in table (4). Ages and errors have been calculated using the Isoplot program of Ludwig (1994).

Uranium gain causes the calculated U-series date to be younger and U loss causes the date to be older than the true age (Szabo *et al.*, 1995). The understanding of the U-migration process is significant for the calculation of U-series dating results (Simpson and Grün, 1998).

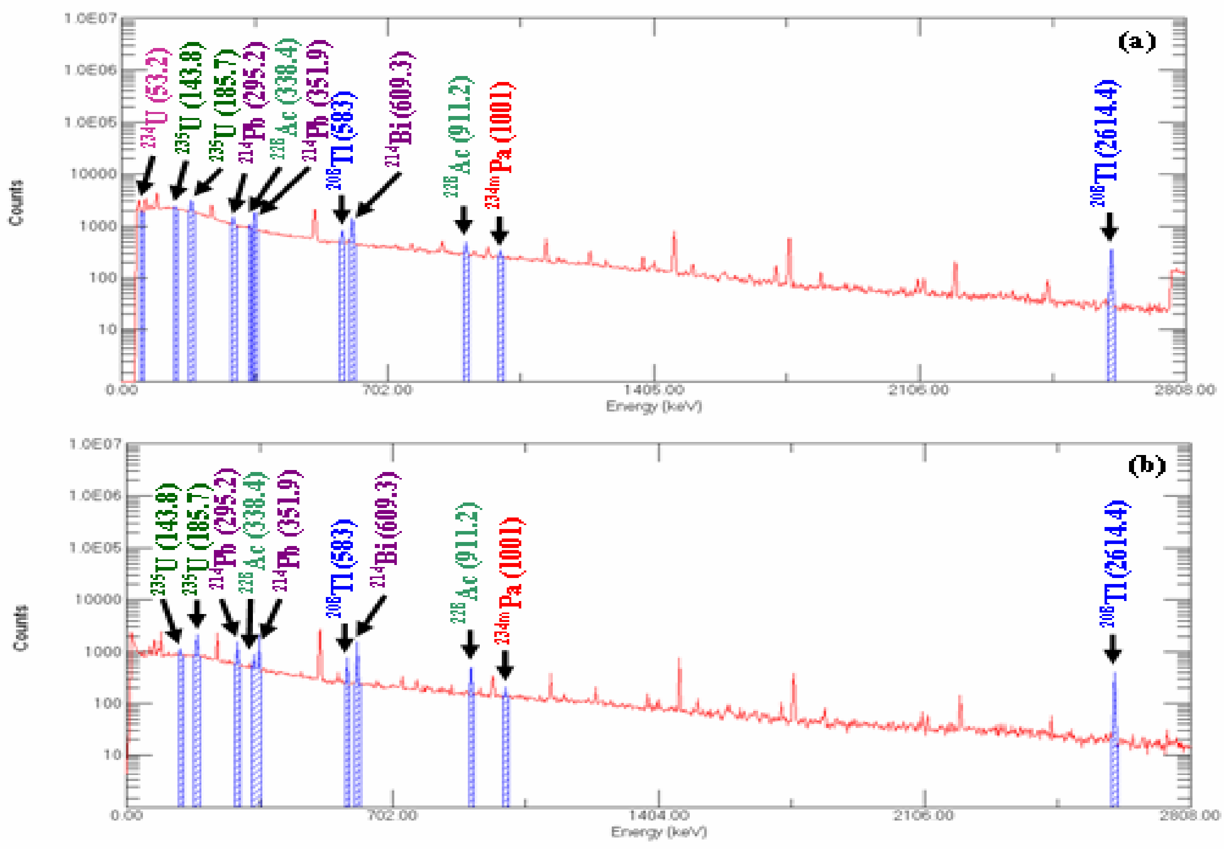

Figure 11 Comparison between gamma-ray spectra of water sample (Well-1) in two years; (a) April 2010 and (b) April 2011.

The results of groundwater residence time of two samples, collected from (Well-Zeid) in two successive years (2010 and 2011), show an important thing which is the young date (27.93 ky) just after the flash flood and gain of uranium with the new added water. While after one year with the decrease of U-concentrations, the residence time is 42.44 ky. The last date may be coincide with the last wet period in Egypt (Szabo *et al.*, 1995). These variations in residence time may be due to the fresh uranium introduced to the groundwater, after recently recharge water by flash flood in 2010, with insufficient time has lapsed for the radioactive growth of ^{230}Th and its daughter gamma-emitting isotopes and also the leached uranium during the rock-water interaction leave behind the un-supported ^{230}Th. After flash flood 2010, water infiltrated from the surface to the groundwater and mixed with the existence water, thus, the groundwater residence time became smaller than the real value. But after one year (2011) without any recharge of water and groundwater is settled, the calculated residence time of groundwater will be the corrected value of real age of the studied well.

CONCLUSION

After flash flood 2010, the rain waters flow through rocks and soil in the studied area which dissolve uranium from the surrounding rocks. Several radionuclides of the ^{238}U decay series; ^{235}U and ^{232}Th have been measured eight times through gamma spectrometry in collected surface water sample at different dates. Since the ^{238}U activity was determined indirectly from the gamma rays emitted by its daughter products (^{234}Th and ^{234m}Pa) while ^{235}U activity was determined directly by its own gamma ray peaks. The studied surface water sample take about 100 days to reach secular equilibrium between ^{238}U and its daughter products (^{234}Th and ^{234m}Pa), from the time of collection to the last measuring date (January to April, respectively). The ^{238}U and ^{234}U activity are increased with time while the ^{235}U, ^{210}Pb and ^{232}Th activity concentrations are nearly constant along all the measurement dates. The activity concentrations of ^{222}Rn decreased with time which are ranged from 1.68 to 0.18 Bq/ℓ.

The water-rock interactions during the journey of flash flood (April 2010) in the studied area change the chemistry and the specifications of the groundwater. The cations and anions results are varied with time of collecting water and place of the wells. The highest activity concentrations of ^{238}U, ^{210}Pb and ^{232}Th were found in groundwater samples collected from wells in 2010 where the range activity concentrations were 4.0 – 5.2, 2.4 – 4.2 and 8.2 – 16.6 times, respectively, higher than in groundwater samples collected from the same wells in 2011. The highest activity concentrations of ^{234}U and ^{222}Rn were found in groundwater samples collected in 2011 where the range activity concentrations were 1.4 – 1.6 and 0.9 – 4.0 times, respectively, higher than in groundwater samples collected in 2010.

In the most analyzed groundwater samples in the two successive years (2010 and 2011), uranium isotopes are out of secular radioactive equilibrium, exhibiting significant enrichment of ^{234}U relative to ^{238}U especially that collected in 2011.

After flash flood 2010 the groundwater residence time of Well-Zeid sample (27.93 ky) became smaller than the real value while after one year (2011) without any recharge of water and groundwater is settled, the calculated residence time of groundwater (42.44 ky) will be the corrected value of real age of the studied well. The last date may be coincide with the last wet period in Egypt.

Recommendation

The author recommends repeating this work in different environs with different rock types, uranium content and geochemical features.

Acknowledgments

I am grateful to Professor Ibrahim El Katany El Aassy (Nuclear Materials Authority, Egypt) for help, encouragement and a critical and helpful review of this paper.

References

Aggarwal, P.K., Gat, J.R., Froehlich, K.F.O. 2005. Isotopes in the Water Cycle: Past, Present and Future of a Developing Science. IAEA.

Anjos, R.M., Veiga, R., Soares, T., Santos, A.M.A., Aguiar, J.G., Frascá, M.H.B.O., Brage, J.A.P., Uzêda, D., Mangia, L., Facure, A., Mosquera, B., Carvalho, C., Gomes, P.R.S. 2005. Natural radionuclide distribution in Brazilian commercial granites. Radiation Measurements, 39, 245–253.

Bourdon, B., Turner, S., Henderson, G.M., Lundstrom, C.C. 2003. Introduction to U-series Geochemistry. Reviews in Mineralogy and Geochemistry, 52 (1); 1-21.

Brennecka, G.A., Borg, L.E., Hutcheon, I.D., Sharp, M.A., Anbar, A.D. 2010. Natural Variations in Uranium Isotope Ratios of Uranium Ore Concentrates: Understanding the ^{238}U/^{235}U Fractionation Mechanism. Earth and Planetary Science Letters, 291, 228–233.

Condomines, M., Loubeau, O., Patrier, P. 2007. Recent mobilization of U-series radionuclides in the Bernardan U deposit (French Massif Central). Chemical Geology, 244, 304–315.

Dabous, A.A., Osmond, J.K. 2001. Uranium isotopic study of artesian and pluvial contributions to the Nubian Aquifer, Western Desert, Egypt. J. Hydrol., 243, 242–253.

Dawood, Y.H. 2010. Factors Controlling Uranium and Thorium Isotopic Composition of the Streambed Sediments of the River Nile, Egypt. JAKU: Earth Sci., 21/2, 77–103.

Dawood, Y.H., Abd El-Naby, H.H., Ghaleb, B. 2014. U-series isotopic composition of kasolite associated with aplite-pegmatite at Jabal Sayid, Hijaz region, Kingdom of Saudi Arabia. Arab J. Geosci., DOI 10.1007/s12517-013-0963-9.

El Aassy, I.E., Ahmed, F.Y., Afifi, S.Y., Ashami, A.S. 2000. Uranium in Laterites, Southwestern Sinai, Egypt. 1st Seminar on Nuclear Raw Materials and their Technology, 1-3 Nov., 1-20.

El Aassy, I.E., Botros, N.H., Abdel Razik, A., Sherif, H., Al Moafy, A., Aita, S., El Terb, R., Al Shami, A.S. 1986. Report on the Prospection and Proving of Some Radioactive Occurrences in West Central Sinai, Egypt. Internal Report Nuclear Materials Authority Cairo.

El Rakaiby, M.L., El Aassy, I.E. 1989. Structural Interpretation of Paleozoic-Mesozoic Rocks, Southwestern Sinai, Egypt. Annals of the Geological Survey of Egypt XVI, 269-273.

Gascoyne, M. 1992. Geochemistry of the actinides and their daughters. In: Uranium series disequlibrium. Ivanovich, M. and Harmon, S. (eds.) Oxford Science Publications Second Edition, 34-61.

Gómez, P., Turrero, M.J., Garralón, A., Peña, J., Buil, B., Cruz de la, B., Sánchez, M., Sánchez, D.M., Quejido, A., Bajos, C., Sánchez, L. 2006. Hydrogeochemical characteristics of deep groundwaters of the Hesperian Massif (Spain). Journal of Iberian Geology, ISSN: 1698-6180, 32 (1), 113-131.

IAEA, International Atomic Energy Agency 1987. Preparation and Certification of IAEA Gamma Spectrometry Reference Materials, RGU-1, RGTh-1 and RGK-1. International Atomic Energy Agency. Report-IAEA/RL/148.

Innocent, C., Malcuit, E., Négrel, P., Petelet-Giraud, E. 2013. Leaching experiments on aquifer rocks of the Aquitaine Basin (France): uranium concentrations and activity ratios, preliminary results. Water Rock Interaction [WRI 14]. Procedia Earth and Planetary Science, 7, 381–384.

Ivanovich, M., Harmon, R.S. 1982. Uranium Series Disequilibrium. Applications to Environmental Problems Clarendon Press Oxford.

Ivanovich, M., Harmon, R.S. 1992. Uranium series Disequilibrium: Applications to Earth, Marine and Environmental Sciences. Oxford (Oxford University Press), pp. 911.

Kaufman, A., Broecker, W.S. 1965. Comparison of ^{230}Th and ^{14}C ages for carbonate materials from Lakes Lahontan and Bonneville. J. Geophys. Rese., 70, 4039–4054.

Kaufman, M.I., Rydell, H.S., Osmond, J.K. 1969. ^{234}U/^{238}U Disequilibrium as an Aid to Hydrologic Study of the Floridan Aquifer. J. Hydrol., 9, 374-386.

Kazemi, G.A., Lehr, J.H., Perrochet, P. 2006. Groundwater age. John Wiley & Sons, Inc. Hoboken New Jersey, pp. 325.

Khorfan, A., Wahoud, A., Rafool, W. 2003. A quick method to determine uranium concentration by gamma spectroscopy: Its application for extraction of uranium from wet phosphoric acid. Journal of Radioanalytical and Nuclear Chemistry, 257(2), 313-316.

Krishnaswami, S., Cochran, J. 2008. U–Th Series Nuclides in Aquatic Systems. Radioac. Environ., V. 13, pp. 458.

Langmuir, D. 1980. The mobility of thorium in natural waters at low temperatures. Geochim et Cosmochim Acta, 44, 1753-1766.

Langmuir, D., Herman, J.S. 1980. The mobility of thorium in natural waters at low temperatures. Geochim Cosmochim Acta, 44, 1753–1766.

Lóczy, D., Czigány, S., Pirkhoffer, E. 2012. Flash Flood Hazards. Studies on Water Management Issues, Dr. Muthukrishnavellaisamy Kumarasamy (Ed.) ISBN: 978-953-307-961-5.

Ludwig, K.R. 1994. ISOPLOT — a plotting and regression program for radiogenic-isotope data. Version 2.75. Revision of U.S.G.S. Open-File Report, 91-445.

Luo, S., Ku, T., Roback, R., Murrell, M., Mcling, T.L. 2000. In-situ radionuclide transport and preferential groundwater flows at INEEL (Idaho): Decay-series disequilibrium studies. Geochimica et Cosmochimica Acta, 64(5); 867–881, PII S0016-7037(99)00373-7.

Mazhari, J. 2008. Concentration and Removal of Radon in Well Water. Ph.D Thesis, George Mason University, Fairfax VA, 107.

Min, M., Peng, X., Wang, J., Osmond, J.K. 2005. Uranium-series disequilibria as a means to study recent migration of uranium in a sandstone-hosted uranium deposit, NW China. Appl. Radiat. Isoto., 63, 115–125.

Mudd, G. 1998. An Environmental Critique of In Situ Leach Mining: The Case Against Uranium Solution Mining. A Research Report for Friends of the Earth (Fitzroy) with the Australian Conservation Foundation, July 1998, 144.

Nada, A.A., Talaat, S.M., Abd El Maksoud, T.M., El Aassy, I.E., El Galy, M.M., El Feky, M.G., Ibrahim, E.M. 2011. Effect of Flash Flood in the Distribution of Radionuclides of Groundwater and its environmental Impacts, Wadi Naseib, Southwestern Sinai, Egypt. Isoto. Radiat. Rese., 43(4)(Suppl.2), 1575-1593.

Négrel, P., Casanova, J., Blomqvist, R., Kaija, J., Frape, S. 2003. Strontium isotopic characterization of the Palmottu hydrosystem (Finland): water-rock interaction and geochemistry of groundwaters. Blackwell Publishing Ltd Geofluids, 3, 161-175.

Osmond, J.K., Cowart, J.B. 1976. The Theory and Uses of Natural Uranium Isotopic Variations in Hydrology. Atomic Energy Rew., 14, 621-679.

Osmond, J.K., Dabous, A.A. 2004. Timing and intensity of groundwater movement during Egyptian Sahara pluvial periods by U-series analysis of secondary U in ores and carbonates. Quat. Res., 61, 85–94.

Osmond, J.K., Ivanovich, M. 1992. Uranium series mobilization and surface hydrology. In: Ivanovich, M., Harmon, R.S. (Eds.), Uranium-series Disequilibrium: Application to Earth, Marine, and Environmental Sciences, 2nd ed. Oxford Sciences Publications, Oxford, 259–289.

Paces, J.B., Nichols, P.J., Neymark, L.A., Rajaram, H. 2013. Evaluation of Pleistocene groundwater flow through fractured tuffs using a U-series disequilibrium approach, Pahute Mesa, Nevada, USA. Chemical Geology, 358, 101–118.

Patra, A.C. 2010. Disequilibrium of Naturally Occurring Radionuclides and Distribution of Trace Elements in a Highly Mineralised Zone. Ph.D. Thesis, Homi Bhabha National Institute, p. 239.

Pękala, M., Kramers, J.D., Waber, H.N. 2010. ^{234}U/^{238}U activity ratio disequilibrium technique for studying uranium mobility in the Opalinus Clay at Mont Terri, Switzerland. Appl. Radiat. Isoto., 68, 984–992.

Petersen, J.O., Deschamps, P., Hamelin, B., Goncalves, J., Michelot, J.-L., Zouari, K. 2013. Water-rock interaction and residence time of groundwater inferred by ^{234}U/^{238}U disequilibria in the Tunisian Continental Intercalaire aquifer system, Water Rock Interaction [WRI 14]. Procedia Earth and Planetary Science, 7, 685–688.

Pöllänen, R., Ikäheimonen, T.K., Klemola, S., Vartti, V.-P., Vesterbacka, K., Ristonmaa, S., Honkamaa, T., Sipilä, P., Jokelainen, I., Kosunen, A., Zilliacus, R., Kettunen, M., Hokkanen, M. 2003. Characterization of Projectiles Composed of Depleted Uranium. J. Environ. Radioa., 64, 133-142.

Ramebäck, H., Vesterlund, A., Tovedal, A., Nygren, U., Wallberg, L., Holm, E., Ekberg, C., Skarnemark, G. 2010. The Jackknife as an Approach for Uncertainty Assessment in Gamma Spectrometric Measurements of Uranium Isotope Ratios. Nuclear Instruments and Methods in Physics Research B: Beam Interactions with Materials and Atoms, 268(16), 2535–2538.

Reyes, E., Marques, L.S. 2008. Uranium series disequilibria in ground waters from a fractured bedrock aquifer (Morungaba Granitoids—Southern Brazil): Implications to the hydrochemical behavior of dissolved U and Ra. Appl. Radiat. Isoto., 66, 1531–1542.

Rowe, P.J., Maher, B.A. 2000. Cold' stage formation of calcrete nodules in the Chinese Loess Plateau: evidence from U-series dating and stable isotope analysis. Palaeogeography, Palaeoclimatology Palaeoecology, 157, 109–125.

Salih, I., Bäckström, M., Karlsson, S., Lund, E., Pettersson, H.B.L. 2004. Impact of fluoride and other aquatic parameters on radon concentration in natural waters. Appl. Radiat. Isoto., 60(1) 99–104.

Salonen, L., Huikuri, P. 2002. Elevated Levels of Uranium Series Radionuclides in Private Water Supplies in Finland, Proceedings of the 5th International Conference on High Levels of Natural Radiation and Radon Areas held in Munich, Germany on Sep 4-7, 2000. BfS Schriften. Strahlenhygine. High Levels of Natural Radiation and Radon Areas: Radiation Dose and Health Effects. Volume II: General Exposure Assessment, 24, 28-30.

Salonen, L. 1994. ^{238}U series radionuclides as a source of increased radioactivity in groundwater originating from Finnish bedrock. Future Groundwater Resources at Risk IAHS Publ. (222) 71–84.

Sherman, H.M., Gierke, J.S., Anderson, C.P. 2007. Controls on Spatial Variability of Uranium in Sandstone Aquifers. Ground Water Monitoring & Remediation 27 no. 2/ Spring, 106–118.

Shvartsev, S.L. 2008. Geochemistry of Fresh Groundwater in the Main Landscape Zones of the Earth. ISSN 0016-7029, Geochem. Internat., 46(13), 1285–1398.

Simpson, J., Grün, R. 1998. Non-Destructive Gamma Spectrometric U-Series Dating. Quaternary Geochronology, 17, 1009-1022.

Skeppström, K., Olofsson, B. 2007. Uranium and Radon in Groundwater. An overview of the problem. European Water, 17/18, 51-62.

Soliman, S.M., Abu El Fetouh, M. 1969. Lithostratigraphy of the Carboniferous Nubian Type Sandstone in West Central Sinai, Egypt. VI Arab Science Congress Damascus pt., 4, 311-377.

Suksi, J., Rasilainen, K., Pitkänen, P. 2006. Variations in ^{234}U/^{238}U activity ratios in groundwater—A key to flow system characterisation?. Phys. Chem. Earth, 31, 556–571.

Sutherland, R.A., de Jong, E. 1990. Statistical Analysis of Gamma-Emitting Radionuclide Concentrations for

Three Fields in Southern Saskatchewan, Canada. Health Physics, 58/4 (April), 4, 17-428.

Szabo, B.I., Haynes, C.V., Maxwell, T.A. 1995. Ages of Quaternary pluvial episodes determined by uranium-series and radiocarbon dating of lacustrine deposits of Eastern Sahara. Palaeogeography Palaeoclimatology Palaeoecology, 113, 227-242

Tripathi, R.M., Sahoo, S.K., Mohapatra, S., Lenka, P., Dubey, J.S., Puranik, V.D. 2013. Study of uranium isotopic composition in groundwater and deviation from secular equilibrium condition. Journal of Radioanalytical and Nuclear Chemistry, 295, 1195–1200.

Veeger, A.I., Ruderman, N.C. 1998. Hydrogeologic Controls on Radon-222 in a Buried Valley-Fractured Bedrock Aquifer System. Ground Water, 36(4), 596–604.

Vesterbacka, P. 2005. ^{238}U–Series Radionuclides in Finnish Groundwater-Based Drinking Water and Effective Doses. Radiat Nucl Safe Auth University of Helsinki Faculty of Science Department of Chemistry Laboratory of Radiohemistry Helsinki STUK-A213, 94.

von Gunten, H.R., Benes, P. 1995. Speciation of Radionuclides in the Environment. Radiochimica Acta, 69, 1–29.

Weissbrod, T. 1969. The Paleozoic of Israel and adjacent countries, Part II. The Paleozoic outcrops in southwestern Sinai and their correlation with those of southern Israel. Bull Geol. Surv., Israel, 48, 1-32.

Wisser, S. 2003. Balancing Natural Radionuclides in Drinking Water Supply, an investigation in Germany and Canada with respect to geology, radiometry & legislation. Ph.D Thesis, Johannes Gutenberg-Universität in Mainz. 156.

Yokoyama, Y., Falguères, C., Sémah, F., Jacob, T., Grün, R. 2008. Gamma-Ray Spectrometric Dating of Late Homo Erectus Skulls from Ngandong and Sambungmacan, Central Java, Indonesia. J. Human Evolution, 55, 274–277.

Yücel, H., Cetiner, M.A., Demirel, H. 1998. Use of the 1001 keV Peak of ^{234m}Pa Daughter of ^{238}U in Measurement of Uranium Concentration by HPGe Gamma-Ray Spectrometry. Nuclear Instruments and Methods in Physics Research, Section A, 413, 74-82.

Yücel, H., Solmaz, A.N., Köse, E., Bor, D. 2010. Methods for Spectral Interference Corrections for Direct Measurements of ^{234}U and ^{230}Th in Materials by Gamma-Ray Spectrometry. Radiat. Protect. Dosim., 138(3), 264–277. doi:10.1093/rpd/ncp239.

Zuo, Z., Eisma, D. 1993. ^{210}Pb and ^{210}Po distributions and disequilibrium in the coastal and shelf waters of the southern North Sea. Continental Shelf Research, 13(8/9), 999-1022.

****

How to cite this article:

Eman M. Ibrahim.2017, Effect of Flash Flood on Uranium-Series Disequilibrium and Groundwater Residence Time Using Gamma Ray Spectrometry. *Int J Recent Sci Res.* 8(1), pp. 15126-15141.