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Gamma Ray Spectrometry: Multivariate Chemometric Investigation and Source Apportionment of Kerio Valley (Kenya) High Background Radiation Area

J. O. Agora, N. O. Hashim and G. N. Mayaka
Physics Department, Kenyatta University-Kenya

Abstract: Kerio Valley is characterized by different rock types of different geological formation. The goal of this study was to analyze the natural radioactivity levels in order to assess the distribution patterns of natural radionuclides as well as the contribution of radiation from different rocks in the Kerio Valley high background radiation area (HBRA) region of Kenya. The activity concentrations of uranium, thorium and potassium in granite, sandstone, tuff, limestone, quartzite, gneiss, marble and conglomerate rocks were found to vary from 72.70±8.47 $Bqkg^{-1}$-116.15±11.46 $Bqkg^{-1}$, 40.32±14.48 $Bqkg^{-1}$-83.65± 9.91 $Bqkg^{-1}$ and 427.41±48.23 $Bqkg^{-1}$-1397.24±65.27 $Bqkg^{-1}$ respectively. PCA and HCA were used to identify the interrelationship between the activity concentration of the radionuclides and different rock types in order to assess the distribution patterns of the radionuclides on the basis of the rock types found in a given sub-region and correlate radionuclides with the rock types so as touniquely define the sources of HBRA in the region.

Key words: HCA, PCA, and HBRA.

1. INTRODUCTION

Natural radionuclides are abundant in different geological formation of any environment [12]. The contribution of radiation from rocks vary depending on the rock type and is also greatly influenced by other environmental factor such as geographical conditions such as drainage which affect the mineral and chemical transportation and composition in rocks [8]. Kerio Valley is an high background radiation area and geological samples assessed from this region have shown elevated activity concentration. This could be as a result of geology (rocks and soil). However, the source of the high background radiation has not been clearly identified. Uranium in various ore bodies of fluorite samples in this region have however, been found to have concentration ranging from 34ppm to 983ppm, while thorium ranged from 23 ppm to 166 ppm [6]. The study was carried at Soy division where mining of fluorspar is done, leaving uncertainty of whether the same trend will follow suit in the other divisions along the Kerio Valley which stretches 80 kilometres from Kimwarer to Muskut ridge. It has been found that the high background radiation is not associated with the region's geothermal field [7]. Uranium distribution is controlled by the variation of P_2O_5 and CaO and is not affectedby the variation of silica and quartz [1]. The objective of this paper was to measure the activity concentration from different rock types and find the multivariate relationship between the naturally occurring radionuclides in the rock types as well as the different regions (divisions). This could assist to assess the variation in distribution of the radionuclides in the rock types and region and hence find which rock type or region contributes much to the high background radiation in the area. Principal Component Analysis (PCA) technique was used to show the relationship between the activity concentration of the natural occurring radionuclides and the rock types while the HCA technique was used to the relationship between the activity concentration of the radionuclides and the sub regions.

Principal component analysis is a multivariate chemometric technique used in pattern recognition [4]. This method provides a way in which data matrix can be manipulated to present the variations which may be in many variables using a small number of factors. The principal components allow one analyzing data to have a clear view of the interrelationships in the many variables (multivariate) by use of small number of variables (PCs) [9]. The principal components are characterized by: the score relating to the objects or samples and the loading relating to the variables or measurements. The information of the loading and the scores relates to the interpretable parameter of direct interest to the person carrying out research.

Hierarchical cluster analysis technique is a pattern recognition method [4]. This method employs the interpoint distances (mostly Euclidian distance) to draw the relationship between samples. Often the result of hierarchical clustering is presented in graphical form called a dendrogram. In the dendrogram, the objects samples are organized in a row, according to their similarities. For this work the dendrogram are used to show the closeness of the sampling area (which correspond to rock type) in a row space that forms a two dimensional graph. The dendrogams are used to examine the similarities and differences between different rock types in terms of radionuclides measured and try to predict the relationship between sampling area and the similarities observed. Samples joined together by small distances are assumed to be similar based on the measured variables.

2. METHODOLOGY

2.1. Sample Collection

Samples were collected at thirty six different geological sites along Kerio Valley region. The rocks were chiseled out while others were handpicked from the quarries and potential quarrying sites.The sampling was randomly done and the geographical coordinates of the sampling points were determined by the Global Positioning System (GPS). The samples were kept in polythene bags to avoid contamination and were numbered for identification. The identification and geological classification of the rock samples was done at Kenyatta University by physical inspection of the rocks and assessment of features like texture, foliation, mineral composition, size of the grains, porosity and existence of layers. The samples which included granite, tuff, conglomerate, sandstone, limestone, marble, gneiss and quartzite were takenfrom Twakeu, Tambach, Kitanyi, Kabiemit and Soy divisions. The rocks were crushed, sieved and dried to remove moisture [3]. Drying was done at $100^{o}C$ in an oven for 24 hours. The dried samples were weighed, sealed in plastic containers and stored for four weeks allow the parent radionuclides in the sample to reach secular equilibrium between ^{226}Ra and its short-lived decay products [11].A NaI (Tl) gamma ray spectrometer was used to measure the activity concentration of the radionuclides in the samples. PCA and HCA techniques were applied on the measured activity concentrations and the resulting patterns used to determine the multivariate relationship between the activity concentration of the radionuclides in different rocks types and regions.

2.2 Gamma ray spectrometric analysis

The activity concentration of ^{238}U, ^{232}Th and ^{40}K was determined by gamma ray spectrometry. The interpretation of U and Th primordial radionuclides were made on the assumption that secular equilibrium was achieved.For this work IAEA certified reference material (RGK, RGTh, and RGU) were used for the calibration of the spectrometer and this was done in the energy range of 350 keV to 3000 keV. The following energy peaks were used: ^{214}Bi(609keV), ^{214}Bi(1125keV) and ^{214}Bi(1765keV) which correspond touranium activity; ^{228}Ac (911.2keV), ^{208}Tl (583keV) and ^{208}Tl (2615keV) which correspond to thorium activity; and ^{40}K(1460keV) which corresponds to activity of potassium.

The activity concentration for the natural radionuclides in the samples was computed after spectral decomposition. The decomposition was done using the stripping off method. In this method the resolution of the poorly resolved peaks are improved by decomposition. Activity concentration was calculated using the following relation;

$$\frac{A_S M_S}{I_S} = \frac{A_R M_R}{I_R} \quad (1)$$

where A_S is the activity concentration of a radionuclide in the sample, M_S is the mass of the sample, I_S is the peak intensity of the radionuclide in the sample, A_R is the activity of the reference standard sample, M_R is the mass of the reference standard sample and I_R is the peak intensity of the radionuclide in the standard sample.

Table 1.1: Average activity concentration of natural radionuclides in different rock types.

Rock type	Number of samples	^{238}U ($Bqkg^{-1}$)	^{232}Th ($Bqkg^{-1}$)	^{40}K ($Bqkg^{-1}$)
Granite	5	99.36±11.45	47.64±7.21	1397.24±65.35
Tuff	7	96.07±13.78	71.26±10.14	1192.46±21.96
Sandstone	5	72.71±8.47	64.18±6.68	677.39±29.49
Conglomerate	4	95.88±12.37	74.24±8.32	980.69±37.14
Limestone	4	104.79±8.61	40.32±7.48	427.41±41.76
Marble	3	116.15±11.46	53.58±6.61	576.46±32.35
Gneiss	4	77.58±9.61	83.65±9.91	1294.35±58.57
Quartzite	4	101.73±11.92	44.32±7.48	1224.69±64.50

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Table 1.2: average activity concentration of natural radionuclides in different rock types for different divisions in Kerio Valley.

	^{40}K (Bqkg^{-1})	^{232}Th (Bqkg^{-1})	^{238}u (Bqkg^{-1})
Twakeu	905.45±40.53	71.36±8.56	87.55±15.94
Tambachi	864.90±34.71	40.39±7.45	146.91±21.98
Kitanyi	885.378±41.87	57.04±10.59	63.99±11.76
Kabiemit	1138.14±.47.67	85.75±13.01	81.75±17.93
Soy	1239.71±70.52	76.80±8.07	96.90±9.32

2.3 Principal component analysis

The principal component of the measured data comprised of the 36 sampling sites and the measured activity concentration of various radionuclides (5 radionuclides). The principal components explained variations in the data matrix (36 x 5) which was the sum of the variations described by the two principal components. These variations were obtained after recalculation by varimax rotation to maximize the loadings of principal components. Activity concentrations for the radionuclides without regard of the area where sampling was done and rock types whose prior information we knew were analyzed. The clusters observed (Figure 1.1) were related to the location of the sampling area, the rock types collected from the areas and the activity concentration radionuclides in the rock samples.

2.4Hierarchicalcluster analysis

Hierarchical cluster analysis (HCA) was used to identify regions with similar radiometric characteristics by use of ^{238}U, ^{232}Th, ^{40}K, ^{228}Ac and ^{214}Pb variables. Using the nearest neighbor linkage and correlation coefficient for similarities, this information was presented in a dendrogram. For this work the dendrogram was used to show sampling region (which nearly correspond to rock type) which are closely related in a row space that forms a two dimensional graph (Figure 1.3 and Figure 1.4). The dendrogams were used to examine the similarities and differences between different rock types in terms of radionuclides measured and to predict the relationship between sampling region. Samples joined together by small distances are similar based on the measured variables. The dendrogram showed how regions or group of regions combine to form clusters with similar radionuclide activity concentrations and the similarity level at which the combination of radionuclides occur. However, HCA does not explain the existence of clusters and structures [5]. But it can be speculated that the grouping is based on activity concentration of the rocks with similar geological characteristics collected from different regions.

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3. RESULTS AND DISCUSSIONS

3.1 Principal component analysis of radionuclides with respect to sampling sites

From the rotated score plot (Figure 1.1), cluster A load heavily in (^{40}K) in the loading matrix (Figure 1.2). This cluster comprise of igneous rocks (granite) and metamorphic rocks of igneous origin (gneiss and quartzite). The presence of silica, quartz and gneiss mineral components in the rocks which are consistent with the compatibility of ^{40}K in rocks explains the high concentration of ^{40}K. Thorium which is not compatible with silicate has low (32.635Bqkg^{-1}- 89.962Bqkg^{-1}) activity concentration in the rocks from these sites. ^{228}Ac which is a daughter product of ^{232}Th is also not compatible with silicate and thus low activity concentration for ^{40}K.

The quantity of silica, quartz and gneiss mineral components in the igneous rocks (granite) and metamorphic rocks of igneous origin (gneiss and quartzite) vary depending on the geographical location of sampling. This is illustrated in cluster B and C in which relatively lower (467.808Bqkg^{-1} to1590.018Bqkg^{-1}) activity concentration for ^{40}K than the cluster A are observed. From the above clustering it is observed that rocks with high ^{40}K anomalies are found in Biretwo, Kiptimim, Kablok, Irong, and Kimwarer.

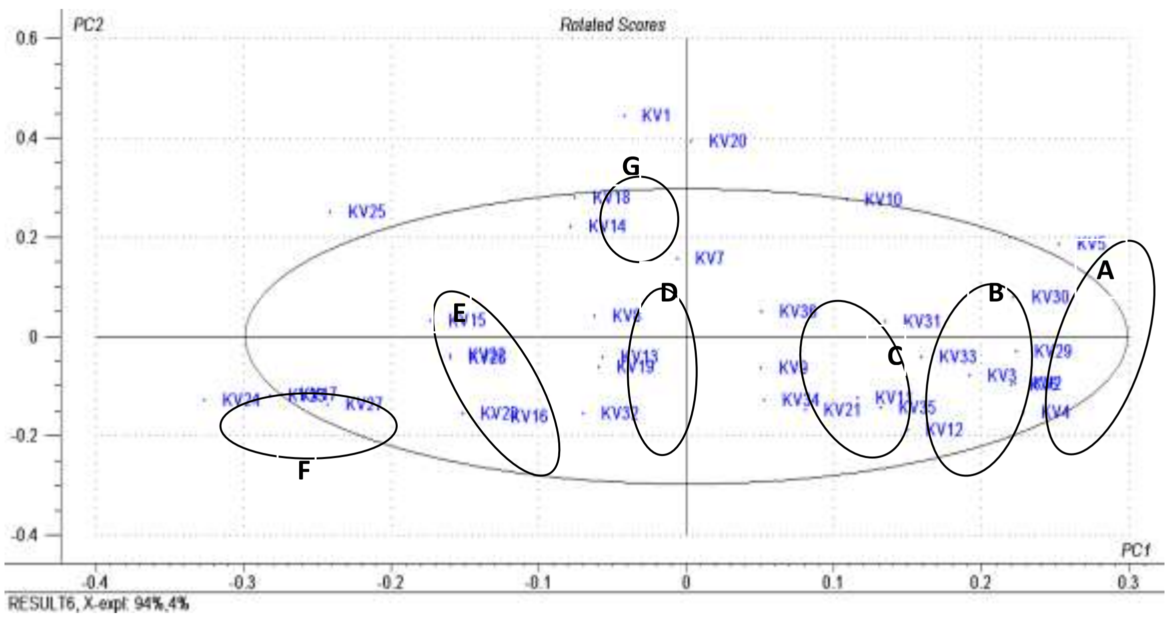

Figure 1.1: Score plot showing the clustering of sampling sites based on the activity concentration of and the sampling area.

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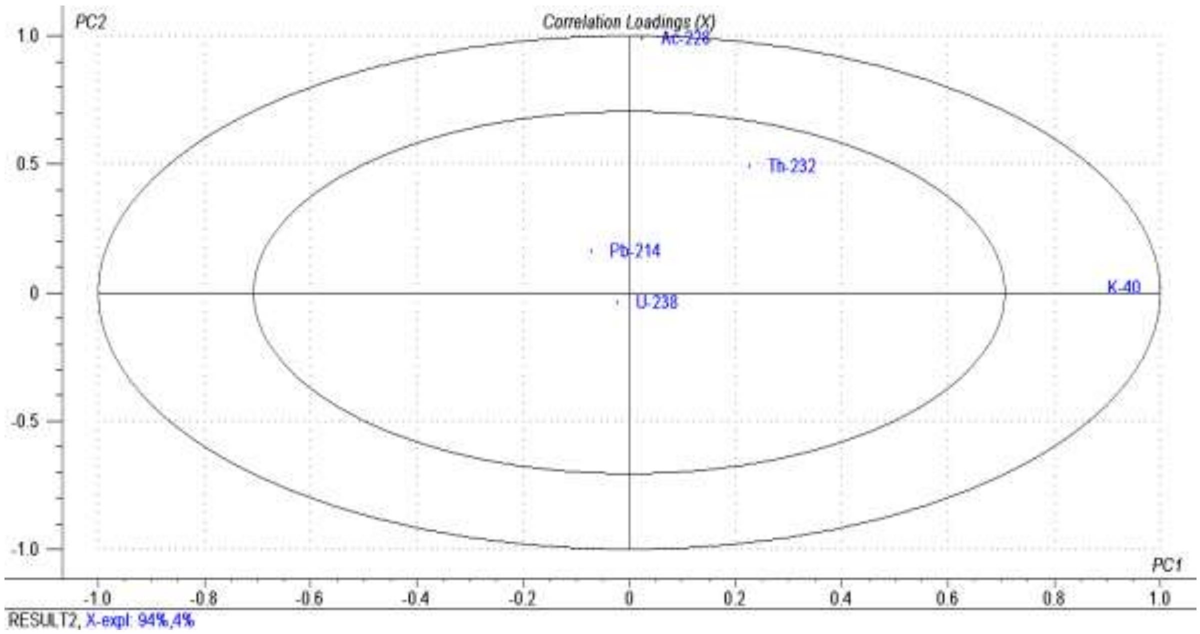

Figure 1.2: Correlation loading plot for the different radionuclides analyzed. The loading plot assists in interpreting the score plot.

Cluster F (Figure 1.1) comprises of sampling sites located near Kapturwacentre in Kerio Valley (Figure 1.1). These rocks are mainly limestone, sandstone and marble. Limestone and sandstone are sedimentary rocks while marble is a metamorphic rock from limestone. The uranium activity concentration for this cluster is high than other clusters because they are characterized by feldspar mineral components in which uranium is fixed by reducing conditions in the decaying matter where the rocks are deposited during the sedimentary forming process. Deposits of uranium are also found at the boundary of different layers of sandstone which elevates their concentration (Abd*et al*., 2010).

Cluster E comprise of limestone, sandstone and marble and thus the concentration of ^{232}Th is relatively low while that of ^{238}U is high. This cluster is distinguished from cluster F by its elevated activity concentration of ^{40}K. These rocks have quartz mineral which has low concentration of silica in which ^{40}K is fixed. Relatively high concentration of thorium and uranium are observed in cluster G. Cluster E has activity concentration for ^{232}Th below the detectable limit. The ^{238}U and ^{228}Pb radionuclides are separated from each other by a small distance (Figure 1.2) which means they are highly related (^{214}Pb is a daughter product of ^{238}U). The two radionuclides load heavily to cluster D. These sites have elevated ^{238}U activity concentration.

The PCA analysis has indicated that the amount of naturally occurring radionuclides in rocks from Kerio Valley region varies depending mostly on the rock type (rocks of the same kind or same origin cluster together). This is manifested in all clusters except cluster F which comprises of rocks sampled from the same region thus making the cluster unique. This can be attributed to rocks found in the area (limestone, sandstone and marble) which have elevated activity concentration for uranium.

3.2 Hierarchical cluster analysis

Hierarchical cluster analysis showed variation in the measured activity concentration with respect to the regions and the rock types. Cluster 1 in (Figure 1.3) comprises of two divisions; Kabiemit and Soy division. Soy division which is located in the south of the valley constitutes Kimwarer fluorspar mines and is neighbored by Kabiemit in the immediate north. The fluorspar ore body has great influence on the abundance of ^{238}U, ^{232}Th and ^{40}K radionuclides as revealed by early study (Mangala, 1987). The average activity concentration for thorium are 76.80±16.35 Bqkg^{-1} and 85.75±35.50Bqkg^{-1}for Kabiemit and Soy divisions respectively. These values are almost twice the world average for background radiation of 45 Bqkg^{-1} (UNSCEAR, 2008) indicating high background radiation (HBRA). The uranium average activity concentration is 96.9 ±10.56 Bqkg^{-1} and 81.75±36.50 Bqkg^{-1} for Kabiemit and Soy respectively. The values are also above the world average of 33Bqkg^{-1}(UNSCEAR, 2000). The average activity concentration of ^{232}Th, ^{238}U, and ^{40}K are greater than the other divisions to the north (Twakeu, Tambach, and Kitanyi). The mining activities of fluorspar have brought to the surface remnants and deposits of minerals. This has accelerated the immobilization of radionuclides to different rocks during the sedimentary and metamorphism processes thus changing their mineral and chemical composition leading rocks with different enhanced (Te-NORM) radionuclide abundance.

Marakwet region [10]. Phosphates which are used in the manufacture of fertilizers contain natural radionuclides such as ^{238}U, ^{232}Th and ^{40}K [2]. The fertilizers and other farm inputs incorporate some relative amounts of anthropogenic radionuclides which can lead to enhanced concentration in a geological environment [13]. Due to the use of artificial fertilizers and other farm inputs, the area has high potential of naturally anthropogenic occurring radionuclides which are then immobilized by runoffs and washed down by the rivers down the valley making rocks vulnerable to absorption of the radionuclides during the interaction.

Cluster 2 has two sub-clusters (Figure 1.3), one comprising Twakeu and Ketinyi while the other is Tambach division. The Tambachisubcluster is isolated from the other because of its elevated average activity concentration for ^{238}U (146.92±10.97 Bqkg^{-1}) which is almost twice the levels recorded in the other divisions. However, the concentration for ^{40}K, and ^{232}Th are low (864.90±142.43 Bqkg^{-1} and 40.39±31.74Bqkg^{-1} respectively). The level of ^{238}U is geogenic (depends on the rock type based on the chemical and mineral composition). Majority of the rocks collected from this area are marble and limestone which are known to have high activity concentration of ^{238}U.

The HCA clustering in this section indicates non uniformity on the activity concentration of different naturally occurring radionuclides in different parts of the valley. Rock to the southern part of the valley contribute much to the background radiation than the other parts of the valley in term of all the three radionuclides analyzed in this work.

Figure 1.4 shows a dendrogram constructed from a data matrix of activity concentration and different rock types. The dendrogram indicates the relationship in terms of activity concentration of naturally occurring radionuclides between different rocks. The clustering is based on the chemical and mineral composition of the rocks which define the rock type. Cluster A was found to comprise of sedimentary rocks (limestone and sandstone) and a metamorphic rock (marble) which forms from limestone. These rocks are characterized by high ^{238}U and low ^{40}K and ^{232}Th.

Cluster B was found to comprise of granite rocks (granite and tuff) and metamorphic rocks of igneous origin (quartzite and gneiss). This sub-cluster is further divided into two: Conglomerate is made up of rounded crystals which are a mixture of sedimentary rock, igneous rock and metamorphic rocks. The clustering in this section brings out the uniqueness in different rock types in terms of activity concentration of the radionuclides and the geological characteristics of the rocks. Rocks of the same origin are found to be related in terms of the content of the naturally occurring radionuclide.

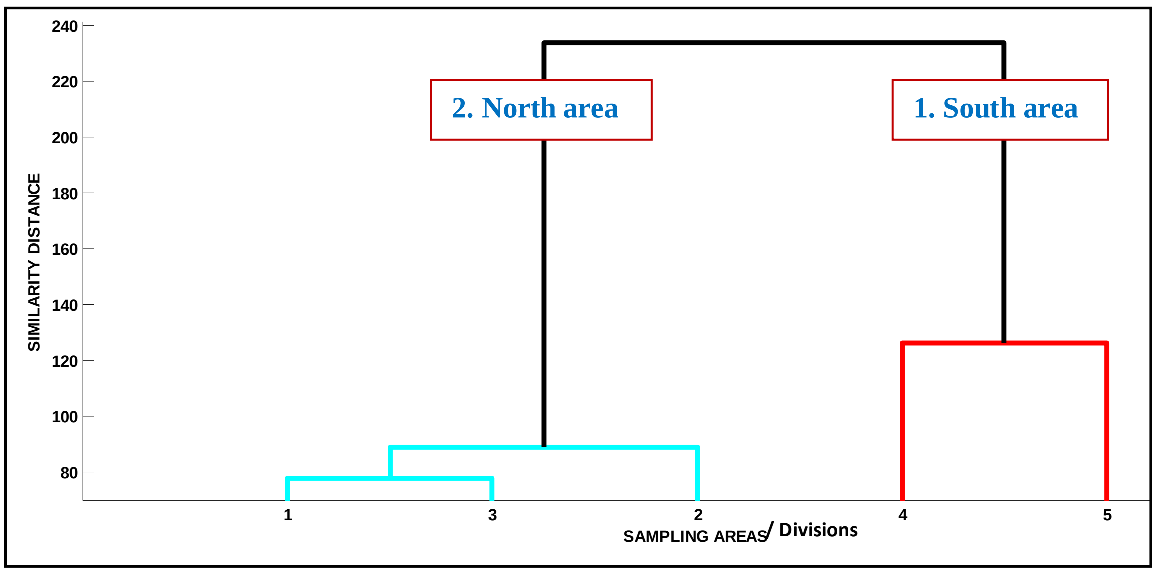

Figure 1.3: Dendrogram for the average activity concentration of radionuclides for five areas (divisions) where sampling was done: 1-Twakeu, 2-Tambach, 3-Kitanyi, 4-Kabiemit and 5-Soy.

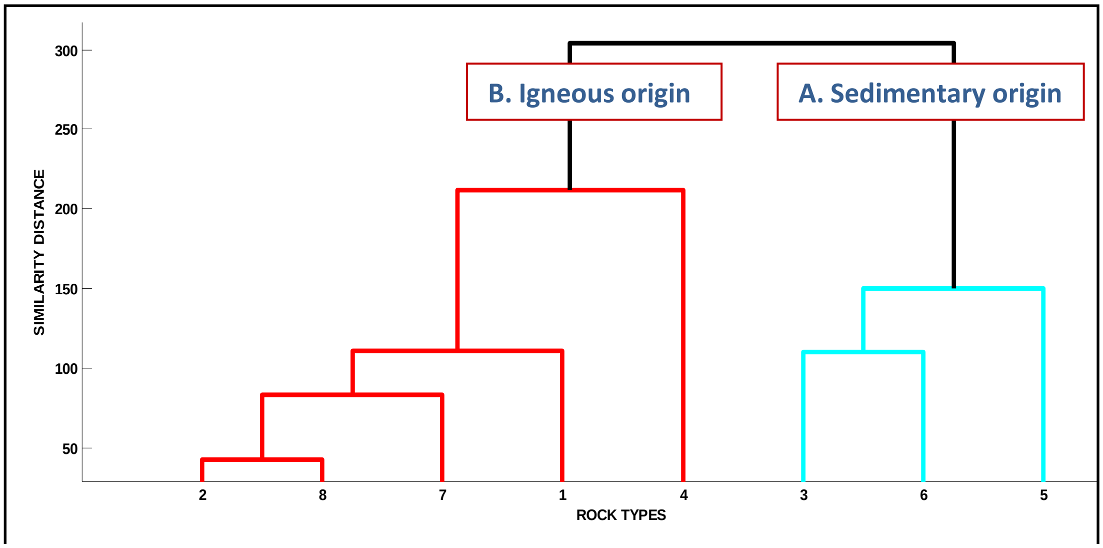

Figure 1.4: Dendrogram for the eight different rock types sampled from different areas in Kerio Valley: 1-Granite, 2-Tuff, 3-Sandstone, 4-Conglomerate, 5-Limestone, 6-Marble, 7-Gneiss, and 8-Quartzite.

The results of HCA indicate that the activity concentration of the naturally occurring radionuclides depends on the area from which a rock has been sampled and also on the rock type. Rocks with the same geochemical characteristics cluster together (Figure 1.4). Also clustering is observed in terms of the location from which the rocks have been sampled with samples from the north distinguishing themselves from those sampled in the south of Kerio valley (Figure 1.4).

4.1 Conclusion

This study has demonstrated strong multivariate statistical relationship of the measured activity concentration for different rocks from Kerio Valley. From the above analysis and discussion the following conclusion can be made:

The igneous rocks and metamorphic rocks of the igneous origin have abundant radionuclides than sedimentary rocks. This means that the former contributes muchtoenvironmental dose.

Mineral components such as quartz, silica and gneiss influence the abundance of radionucldes in different rock types. Potassium which is compatible with silica and quartz is more abundant in rock with such mineral components as opposed to those without.

Human activities have contributed to deposition of anthropogenic radionuclides. Such activities include agriculture in the areas surrounding the valley and the mining activity at Kimwarer in Soy division.

The region to the south of the Kerio Valley has elevated activity concentration and their contribution to environmental radiation exceeds the other regions. This is as result of fluorspar mineral associated with the region and also the mining activity which has affected the nature of the rocks found in the region.

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