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Natural radioactivity in virgin soils and soils from some areas with closed uranium mining facilities in Bulgaria

Abstract: The natural radionuclide (^{238}U, ^{226}Ra, ^{232}Th and ^{40}K) contents in soil were determined for three different regions of Bulgaria using high-resolution gamma-ray spectrometric analysis. A comparison of the dynamics of their behavior throughout the years was performed. Bulgaria is a country with intensive uranium mining activities. That is why radiological monitoring of closed uranium mining facilities in different regions of the country are obligatory and of great interest. This work presents results from such investigations made in regions where remediation was necessary. The results have been evaluated according to Bulgarian radionuclide environment contamination legislation.

Keywords: natural radioactivity, gamma-spectrometry, alpha-spectrometry, soil, uranium, radium

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1 Introduction

Most of the natural and man-made radionuclides in the environment remain mainly in the soil. The radionuclides in the earth's crust are one of the main natural sources of ionizing radiation to which human beings are exposed. An important part of the radiation monitoring is the natural radioactivity in soils. The significant contributions to the dose in humans come from the radionuclides in the ^{238}U and ^{232}Th series and ^{40}K.[1]. This is a type of exposure which is "neither widely variable nor relatively constant at the surface of the globe" [2]. The amount of ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K in soils depends on the type of rock from which they originate and the processes of soil formation. Analysis of radionuclide content of soil, plants, water and knowledge of the behavior of the radionuclides in soil–plant systems provides an important part of a data for dose estimation [1,2]. The assessment of activity concentration of natural radionuclides is of particular importance as the principles of long-term environmental and human protection need to take into account the natural background [3]. Human activities can cause accumulation of radioactive elements modifying natural concentrations. An example of this includes areas with former uranium mining facilities. The concentrations of natural radionuclides from uranium decay series in such areas are higher and the risk of higher human exposure is increased, which makes them the object of special interests and studies. According to the Ministry of Environment and Water in Bulgaria, there are about 1 800 ha contaminated with radionuclides grounds in the country [4]. Following the release of Resolution № 163/20.08.1992 on the cancelation of uranium mining and the related "Instruction for the termination of uranium extraction", issued November 1992, were questions about the rapid and efficient recovery of the areas damaged by the uranium mining industry. In these cases, regulatory target values should be evaluated against local background levels which varies within and between countries [5].

Obtaining such data is the aim of our study on the basis of regular radiological monitoring of virgin soils from high mountain areas, hills and plains covering most of the territory of Bulgaria. The region around Kozloduy NPP, mountain areas and former uranium mining sites are of special interest.

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2 Material and Methods

2.1 Sampling

Sampling of soils was done annually from referred sampling points as part of the radiation monitoring covering almost the whole area of the country. Sampling areas were specified considering the wind direction and differences in altitude. According to the altitude of the investigated areas, three groups have been defined: plains – mainly North Bulgaria, (40 sampling points sp); hilly – the valleys of Struma and Mesta Rivers (15 sp) and mountain area – in South Bulgaria (25 sp). Sampling was done also in the water catchment basin on the Beli Iskar River in the Rila Mountains (10 sp) but only in one survey (in 1996) and not as a part of the regular monitoring scheme.

The soil samples were taken according to the procedure described in ISO 18589-2 for collecting samples of undisturbed soil using a uniform approach, with sampling performed at depths independent of the natural variations of the soil characteristics, from the soil layer 0-5 cm [6].The sampling sites are undisturbed and flat with minimum impact of water and wind erosion. A composite sample of at least 5 increment samples is taken from each sampling area.

Besides the areas included in the national radiation monitoring scheme, sampling was done from fields with former uranium mining facilities (“Balkan”, “Buhovo”, “Sliven”, “Sborishte” etc.)

2.2 Measurement of natural radioactivity

The soil samples were homogenized, dried at 80ºC and sieved through a 2-mm mesh before measurement with a gamma-spectrometer. The samples were stored in air-tight containers for a minimum of 28 days to allow ^{226}Ra to come into equilibrium with its short-lived progeny. The measurements were done following standard procedures [5]. A Canberra high-purity germanium detector with 20% efficiency an energy resolution of 1.8 keV for ^{60}Co γ-ray energy line at 1332 keV was used. The detector was calibrated with standard reference radionuclide source, type MBSS2, containing ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr, ^{88}Y, ^{210}Pb, ^{203}Hg supplied by the Czech Metrological Institute. The measuring system included a multichannel analyzer DSA 1000 (Canberra, USA). The spectrum was analyzed by GENIE-2000 software with measurement uncertainties less than 10%. Typical counting times were 19–24 h.

The ^{238}U concentration was derived from the weighted mean of the photopeaks of ^{234}Th (63.5 and 92.6 keV), and the ^{226}Ra concentration was derived from ^{214}Bi (609.3 keV) and ^{214}Pb (295.2 and 352.0 keV) in the same way. In addition, ^{226}Ra was evaluated at its 186.1 keV line taking into account the contribution of the overlapping line at 185.72 keV of ^{235}U calculating the specific activity of ^{235}U through the specific activity of ^{238}U (ISO 18589-3,2007). For ^{232}Th, the photopeaks of ^{212}Pb (238.6 keV), ^{208}Tl (583.1 keV) and ^{228}Ac (911.1 keV) were used. Activity concentration is expressed as Bq kg^{-1} dry weight soil. Gamma-spectrometry soil analyses were done every year.

Some of the samples were analyzed by alpha spectrometry in order to determine the isotope activity ratio ^{234}U/^{238}U. The chemical separation and source preparation for alpha particle measurements was done by extraction with trioctylphosphinic oxide (TOPO) and back extraction with NH_4F, coprecipitation with LaF_3, anion exchange and electroplating from HCl/oxalate solution [7]. The scheme of the analytical procedure is shown in Fig. 1.

3 Results and Discussion

3.1 Natural radioactivity – local background values

The concentration of ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K as long-lived natural radionuclides of significance in the soil will be discussed in this paper. Summary of the data obtained for the period (1996-2010) is presented in Figs. 2, 3 and 4. Herein, averaged values are calculated for the same groups of samples described above. The registered concentration of ^{238}U, ^{232}Th in the soils of North Bulgaria (NB) are in good agreement with the value of 40 Bq kg^{-1} estimated in UNSCEAR, 1993 report as average concentration of these radionuclides in soils of Nordic countries. Activity concentrations of ^{226} Ra are also in the range of values stated in the same report. The slightly higher concentrations in soils from South Bulgaria (SB) and the River Mesta Valley (RMV) are also logical as the soils in these areas are on rocks containing shale and gneiss with higher concentration of natural radioactivity [3].

The activity concentrations of ^{40}K in the soils from the three observed areas are as follows:

- North Bulgaria (NB) – ranged between 330 and 580 Bq kg^{-1} with average value 440 ± 60 Bq kg^{-1}
- South Bulgaria (SB) – ranged between 460 and 700 Bq kg^{-1} with average value 620 ± 90 Bq kg^{-1}

– River Mesta Valley (RMV) - ranged between 500 and 810 Bq kg^{-1} with average value 640 ± 120 Bq kg^{-1}

The exposure rate to a particular individual is due mainly to the concentrations of radionuclides in the soil and the time spent outdoors. In this study, the assessment of the radiation risk for the population is done by calculating the external hazard index H_{ex}, according to the following criterion [8]:

$$H_{ex} = C_U / 370 + C_{TH} / 259 + C_K / 4810 \leq 1 \quad (1)$$

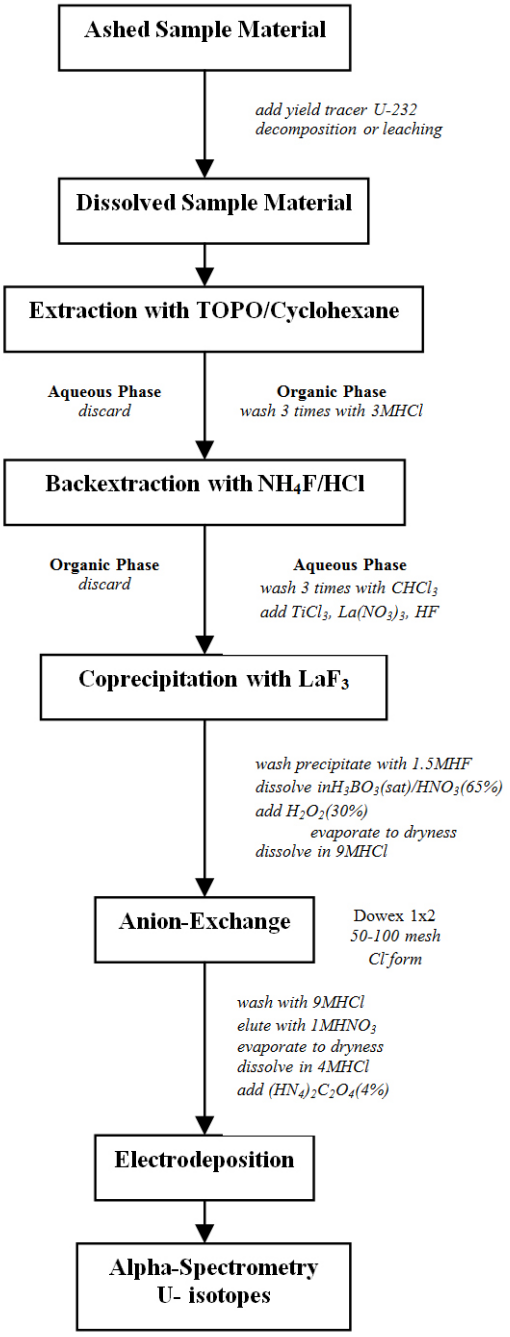

Figure 1: Principle scheme of the analytical procedure used for uranium isotopes determination.

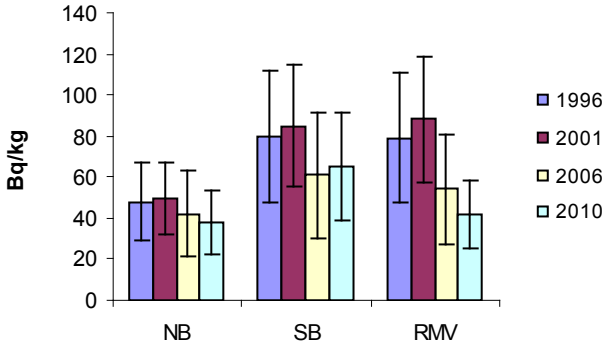

Figure 2: ^{238}U activity concentration in soil samples from different regions (1996-2010).

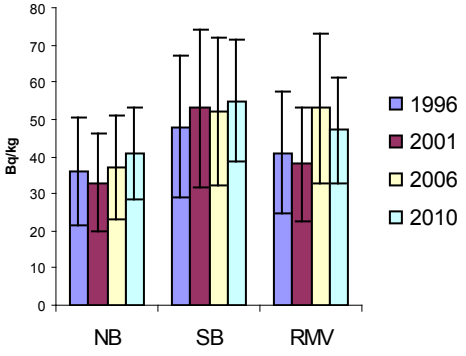

Figure 3: ^{226}Ra activity concentration in soil samples from different regions (1996-2010).

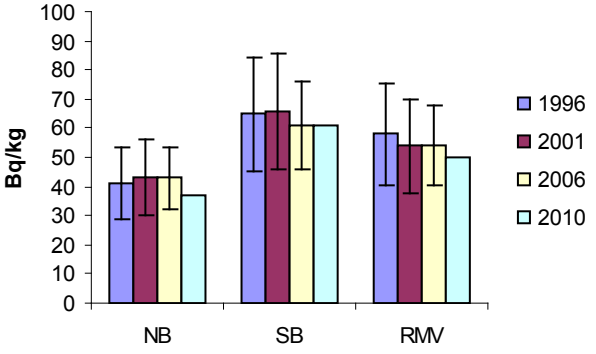

Figure 4: Content of ^{232}Th activity concentration in soil from different regions (1996-2010).

Table 1: Activity concentrations of U^{238}, Ra^{226}, Th^{232} and ^{40}K in $Bq.kg^{-1}$.

SAMPLE	Contaminated Site	U^{238}	Ra^{226}	Th^{232}	K^{40}
Virgin Soil	„Balkan"- 1	30 ± 5	37 ± 7	52 ± 5	750 ± 30
Virgin Soil	„Balkan"- 2	55 ± 10	45 ± 8	60 ± 5	830 ± 30
Virgin Soil	„Balkan"- 3	55 ± 10	60 ± 6	60 ± 5	790 ± 20
Destructed Soil ***	„Balkan"- 1	100 ± 10	180 ± 10	40 ± 4	770 ± 20
Destructed Soil ***	„Balkan"- 2	150 ± 30	240 ± 25	70 ± 7	930 ± 20
Destructed Soil ***	„Balkan"- 3	150 ± 15	270 ± 30	30 ± 4	840 ± 30
Virgin Soil	Buhovo-1	70 ± 8	60 ± 10	50 ± 7	740 ± 30
Virgin Soil	Buhovo-2	90 ± 8	70 ± 8	50 ± 7	780 ± 30
Destructed Soil ***	Buhovo-1	1060 ± 60	2900 ± 90	80 ± 7	860 ± 30
Destructed Soil ***	Buhovo-2	1360 ± 60	4600 ± 80	75 ± 7	950 ± 30
Destructed Soil ***	Buhovo-3	1380 ± 50	3200 ± 90	60 ± 7	890 ± 30
Virgin Soil	Sliven-1	110 ± 10	60 ± 10	40 ± 7	880 ± 20
Virgin Soil	Sliven-2	60 ± 7	40 ± 5	35 ± 5	810 ± 30
Destructed Soil ***	Sliven-1	2200 ± 60	3200 ± 8	50 ± 7	710 ± 20
Destructed Soil ***	Sliven-2	1000 ± 30	1200 ± 50	80 ± 7	830 ± 30
Destructed Soil ***	Sliven-3	2800 ± 30	2300 ± 50	50 ± 7	830 ± 30

***Soil mixed with geological material in soil heaps

The averaged values of H_{ex} for the soils in North Bulgaria, South Bulgaria and the River Mesta Valley were 0.23, 0.56 and 0.52 respectively. The calculated values were lower than unity which characterizes the radiation hazard as insignificant and the result means that it is safe for humans to carry out their activities in the areas studied.

3.2 Natural radioactivity – in areas with former uranium mining facilities

All the data discussed above concern areas without former uranium mining facilities. The areas where uranium mining facilities existed are an object of special interest. In general, activities related to mining and processing of uranium ore are characterized by complex negative impact on the environmental components (soil, water and air), which is directly dependent on the extraction technology. There are several fundamental methods for extraction of uranium ore:

1. Classical methods:
   a/ open-air method –via construction of quarries;
   b/ classical underground method;
2. Geo-technological method – extraction of uranium concentrate by sulfuric acid.

The classical underground method does not directly disturb the integrity of the soil layer with the exception of a small area where the shafts and stulms are. The anthropogenic impact in this case is related to a large amount of geological material, which is brought to the surface and takes up a significant amount of space. These materials are unsuitable substrate for growing plants and are dangerous due to the residues of uranium ore that they contain.

These changes and disturbances in the environmental components require precise and proper planning of the reclamation and restoration activities, combined with the recommended activities for usage of the damaged land. This is a complex and lengthy process that begins with a detailed survey of the area affected by mining works.

We have studied some of the objects with former uranium mining facilities, which were developed by the classical underground method [9]. The sampling included virgin soils and soils destroyed by the mining process activities.

We present here results for natural radionuclides concentrations in soils mixed with geological material and undisturbed soils from three areas around former uranium mining facilities – Balkan, Buhovo and Sliven where the uranium ore was extracted by the classical underground method (Table 1).

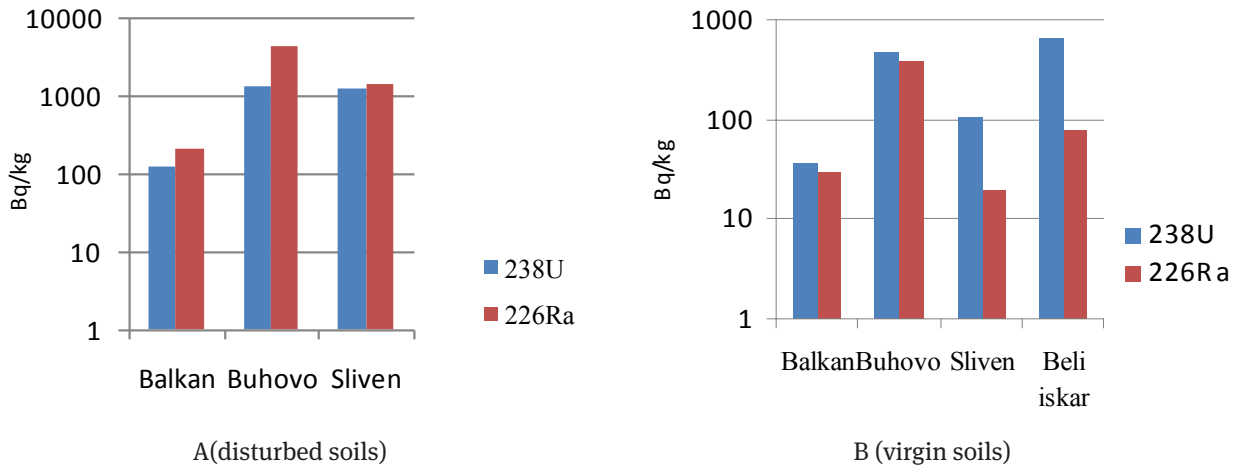

Figure 5: ^{238}U and ^{226}Ra concentrations in disturbed (a) and virgin (b) soils from areas with former uranium mining facilities [Bq kg^{-1}].

The Bulgarian legislation states 200 Bq kg^{-1} massic activity for Ra^{226} in soil as the utmost acceptable level [10]. The determined activity concentrations of Ra^{226} listed in Table 1 were higher in all samples of soil destructed by uranium mining activities. In the areas of Sliven and especially Buhovo the concentrations are about one order of magnitude higher. For U^{238}, the results are also much higher than the estimated local background values shown in Fig. 2.

In the soil samples from areas not affected by human activities, the decay products of ^{238}U and ^{232}Th in most cases are in radioactive equilibrium with their precursors. In the areas with former uranium mining activities, this equilibrium is broken in the majority of cases. Because of this, the activity ratios ^{238}U /^{226}Ra and ^{234}U /^{238}U were examined as an additional assessment of the contamination of the studied areas.

Information about the results obtained is presented in Figs. 5a and 5b.

The activity concentration is presented in logarithmic scale because the variability of the results was quite high – ^{238}U (between 30 Bq kg^{-1} and 1360 Bq kg^{-1}) and ^{226}Ra (between 37 Bq kg^{-1} and 4600 Bq kg^{-1}) . Results only for ^{238}U and ^{226}Ra are shown because they are members of one and the same decay series and the ratio between their activity concentrations may be indicative for the type of pollution recognizing the differences in their chemical behavior. In the soil hardly influenced by the uranium mining industry, the activity of ^{226}Ra is often higher than the activity of ^{238}U while in the virgin soils ^{238}U has equal or higher activity.

In Fig. 5 (B), Beli Iskar is included as an example of undisturbed soil from a mountain region (Rila Mountain) with high natural activity concentration of uranium (^{238}U – 650 Bq kg^{-1}; ^{226}Ra 80 Bq kg^{-1}) and ratio ^{238}U /$^{226}Ra \approx 8$. This disequilibrium is most probably caused by the high amount of organic matter in this soil as uranium, unlike radium, makes compounds with the huminic acids in the soil [11,12].

The activity ratio of ^{234}U /^{238}U was determined by alpha spectrometry in some samples from disturbed and virgin soils. This study was done for samples from Beli Iskar (area not influenced by uranium mining industry) and Buhovo (area with relatively higher radioactive contamination as a result of uranium mining). In the case of virgin soils, the activity ratio varied between 0.96 ± 0.08 and 1.21 ± 0.06 which is comparable to isotopic activity ratios of ^{234}U /^{238}U in soil (0.8–1.2) reported elsewhere [13,14]. In the disturbed anthropogenic soils from Buhovo, the activity ratio of ^{234}U /^{238}U was relatively higher – up to 1.45 ± 0.12. The most probable reason for such variation of ^{234}U /^{238}U activity ratio is the preferential leaching of ^{234}U from solid phase as a progeny of ^{238}U due to radiation damage of crystal lattice upon alpha decay of ^{238}U.

The calculated external hazard index (H_{ex}) for the virgin soils in the three studied areas ranged between 0.50 and 0.57. For estimation of the radiation hazard for the disturbed soils, the external hazard index is defined as [15]:

$$H_{ex} = C_{Ra}/370 + C_{TH}/259 + C_K/4810 \leq 1 \quad (2)$$

This definition is used because of the broken disequilibrium between ^{238}U and ^{226}Ra and the relatively higher activities of ^{226}Ra. In case of mine "Balkan," H_{ex} ranged between 0.8 and 1.11 with average value of 0.98 ± 0.16 which is equal to the criterion limit of 1. For Buhovo, the external hazard index ranged between 8.32 and 12.91 with average value

10.1 ± 2.46 and for Sliven – between 3.72 and 6.58 with average 6.37 ± 2.55. These results are a sign for a significant radiation hazard and show that, for eliminating the radiation hazard for the population and the danger of contamination of the environment, appropriate measures should be chosen. Such measures are obligatory especially for the areas of Buhovo and Sliven mines.

4 Conclusions

Natural radioactivity concentrations in the investigated virgin soil are in good agreement with the values presented in the UNSCEAR reports for different soil types in the Nordic countries.

The calculated external radiation hazard index for all studied territories without former uranium mining facilities is less than 1. They are safe for human activity.

The activity of natural radionuclides in the three sites studied clearly showed level of activity many times higher than the estimated local background values. Appropriate measures should be chosen for reducing activity levels in the soil together with the measures for soil fertility remediation.

References

[1] UNSCEAR, In: Sources and Effects of Ionizing Radiation, Report of the General Assembly with Scientific Annexes, vol. 1 (New York), 2000
[2] UNSCEAR, In: Sources and Effects of Ionizing Radiation, Report of the General Assembly with Scientific Annex B, (New York), 1993
[3] Montes M.L., Mercader R.C, Taylor A., Runco J., Desimoni J., Assessment of natural radioactivity levels and their relationship with soil characteristics in undisturbed soils of northeast of Buenos Aires province, Argentina; J Environ Radioactiv, 2012, 105;30-39
[4] Ministry of Environment and Water in Bulgaria (MEWB), Annual Report 1998, (in Bulgarian)
[5] ISO 18589-3, Measurement of Radioactivity in the Environment - Soil, Part 3 - Measurement of Gamma-emitting Radionuclides
[6] ISO 18589-2, Measurement of Radioactivity in the environment - Soil, Part 2: Guidance for the selection of the sampling strategy, sampling and pre-treatment of samples, 2007
[7] Pimpl M., Yoo B., Yordanova I., Optimization of Radioanalytical Procedure for the Determination of Uranium Isotopes in Environmental Samples, J Radioanal Nucl Ch, 1992, 161(2), 437-441
[8] Yu KN, Guan ZJ, Stoks MJ, Young EC, The assessment of natural radiation dose committed to the Hong Kong people, J Environ Radioactiv, 1992, 17:31-48.
[9] Yordanova I., Natural Radioactivity in Samples from Some Regions in the Rila Mountains and around Former Uranium Mining Areas, J Environ Prot Ecol, 2006, 7, No 1,151-156
[10] Regulation No1/15.11.1999 on norms for radiation protection and safety purposes during liquidating the backlash of uranium mining industry in Republic of Bulgaria
[11] Degering D., Schlenker S., Unterricker S., Radionuclide Behaviour in Natural Organic Matter (Peat, Coal and Forest Soil Surfaces), NRC 5, 5th International Conference on Nuclear and Radiochemistry, Pontresina, Switzerland ,2000, 3-8, p. 449-452
[12] IAEA, Applicability of Monitored Natural Attenuation at Radioactively Contaminated Sites. Technical Reports Series No. 445, Vienna, 2003
[13] Fisenne I.M., USDOE remediation site case study, Environ. Int., 1996, 22, S243-S249.
[14] Goldstein S.J., Rodriguez J.M., Lujan N., Measurement and Application of Uranium Isotopes for Human and Environmental Monitoring, Health Phys., 1997, 72(1), 10-18
[15] Masitah Alias, et al., An assessment of Absorbed Dose and Radiation Hazard Index from Natural Radioactivity, Malays J Anal Sci, 2008, 12, No. 1, pp 195-204