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Uranium Series Disequilibrium and Precision Measurement of Radionuclides Activity in Sediment Sample Using Low Background Gamma Spectrometry

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Abstract

Low background gamma spectrometry was used to measure the radionuclides activity of ^{238}U, ^{232}Th, and ^{235}U series as well as ^{40}K and ^{137}Cs in a sediment sample. The goal of the study was to measure the ^{238}U (63.3 keV peak of ^{234}Th; 1001 keV peak of ^{234m}Pa) and ^{235}U (143.76 keV, 163.33 keV, and 205.31 keV peaks) activity by low background gamma spectrometry in sediment sample. ^{235}U activity in environmental samples is difficult to accurately measure by gamma spectrometry due to its low abundance in nature and low gamma line intensities at 143.76 keV, 163.33 keV, and 205.31 keV. We have shown that by using low background gamma spectrometry, it is possible to accurately measure the ^{235}U activity in sediment samples. The ^{235}U activity was measured without using the major peak of 185.7 keV (I_γ = 57.2%) which requires interference correction from 186.21 keV of ^{226}Ra. ^{226}Ra activity was determined by measuring ^{222}Rn daughters (^{214}Pb and ^{214}Bi). The precision and accuracy of the gamma activity measurement in the sediment sample were verified by using the HPGe detectors with Certified Reference Material (CRM) Irish Sea Sediment (IAEA-385). The results obtained for the 63.33 keV energy line of ^{234}Th are compared with the 1001 keV energy line of ^{234m}Pa. The values of ^{238}U and ^{235}U activities, as well as ^{40}K, ^{137}Cs, and ^{226}Ra, agreed with the certificate values of CRM. The results show that the ^{238}U is in equilibrium with its daughters (^{234}Th, ^{234m}Pa, and ^{210}Pb). ^{232}Th is also in equilibrium with its daughters (^{228}Ra, ^{212}Pb, ^{212}Bi and ^{208}Tl). ^{235}U/^{238}U activity ratio of 0.046 ± 0.007 in the sediment is constant in nature but fluctuates due to geological processes. A value of 0.055 ± 0.008 was found in our sediment sample.

Keywords

Low Background Gamma Spectrometry, HPGe Detector, Sediment, ^{238}U, ^{235}U, Secular Equilibrium

1. Introduction

Natural uranium and thorium are present in all rocks, soils, and sediments. Natural uranium consists of ^{238}U, ^{235}U, and ^{234}U. It has 99.284% of ^{238}U, 0.711% ^{235}U, and a trace amount of 0.0055% ^{234}U. Thorium presents naturally in sediment as ^{232}Th and ^{234}Th (progeny of ^{238}U). ^{232}Th is less soluble and found mostly in secular equilibrium with its progeny i.e., ^{228}Ra, ^{212}Pb, ^{212}Bi, and ^{208}Tl. Gamma spectrometry is extensively used for ^{238}U, ^{232}Th, ^{226}Ra, and ^{40}K determination in environmental samples because of its simplicity in terms of sample preparation. It can simultaneously perform multi-nuclide determinations based on the detection of photon emissions and, therefore, does not require sophisticated sample treatment, however, it requires precise calibration of gamma detectors with NIST traceable standards or Monte Carlo methods (Semkow et al., 2015; Azbouche et al., 2015). Gamma spectrometry can be easily applied to determine ^{238}U, ^{226}Ra, and ^{235}U in environmental as well as in food samples simultaneously without any radiochemical separation. In secular equilibrium, ^{238}U can be determined by the gamma energy peak of ^{234}Th at 63.3 keV (I_γ = 3.7%) or at ~92.6 keV (doublet: I_γ = ~4.8%). Other low-intensity gamma energy peaks of ^{234m}Pa at 766.4 (I_γ = 0.1%) and 1001 keV (I_γ = 0.837%) were also often used (Yücel et al., 1998) for ^{238}U in materials rich in thorium. For environmental samples, the weak intensity of 766.4 keV and 1001 keV gamma lines together with the lower efficiency of HPGe detectors at higher energies often cause problems in detection. With the use of large-volume coaxial germanium detectors which provides better detection efficiency and counting statistics at 1001 keV of gamma energy for ^{234m}Pa.

For the measurement of uranium series radionuclide concentrations, radiochemical analysis followed by alpha spectrometry is mostly used (Minteer et al., 2007; Carvallo & Oliveira, 2009). However, this method is time-consuming and complicated. On the other hand, gamma-ray spectrometry is a simple, non-destructive, and fast method, and is suitable for accumulating data for many radionuclides simultaneously. So, high-resolution gamma-spectrometry has been extensively used for the quantitative analysis of uranium and thorium (Papadopoulos et al., 2013) and for the absolute determination of uranium content in rocks (Kaste et al., 2006). If one wishes to measure the ^{238}U content of a sample independent of the ^{235}U content, one is faced with the problem that the ^{238}U isotope emits directly only very weak gamma radiation which is at 49.55 keV (0.064%).

It is possible, however, to measure the emission of gamma rays from a daughter nuclide that is in equilibrium with the ^{238}U parent. In many cases, this equili-

brium state in a natural system may not have been reached, especially for a daughter that is quite far down the decay chain. Under secular equilibrium, radionuclides (Figure 1) in the ^{238}U series should have the same activity. ^{232}Th is less soluble than ^{238}U and found mostly in secular equilibrium with its progeny i.e., ^{228}Ra, ^{212}Pb, ^{212}Bi, and ^{208}Tl. Disequilibrium results from geochemical sorting, whereby a process acts to move a parent or daughter into or out of a system at a rate that is significant relative to the half-life of the daughter (Osmond & Cowart, 1982). The decay chains in deeply buried, unweathered materials are generally in equilibrium. However, weathering processes that occur at or near the earth's surface operate on a sufficiently short time scale that disequilibrium results. Other mechanisms by which disequilibria are established in the surficial environment are 1) solution and precipitation reactions (because of different chemical properties of the elements in the decay chains), 2) gaseous diffusion of the radon isotopes, and 3) alpha particle recoil.

The development of low-background gamma-ray spectrometer (LBGS) was originally for basic physics research such as neutrino oscillation, 0νββ decay, and dark matter search (Heusser, 1995; Povinec et al., 2004; Laubenstein et al., 2004; Aalseth et al., 2012; Armengaud et al., 2013; Khan et al., 2014) during the last two decades, however, LGBS has found several important applications such as monitoring natural radionuclides such as ^{226}Ra, ^{228}Ra (Semkow et al., 2019; Khan et al., 2020) as well as anthropogenic radionuclides such as fission products in the environment for contamination control and nonproliferation applications.

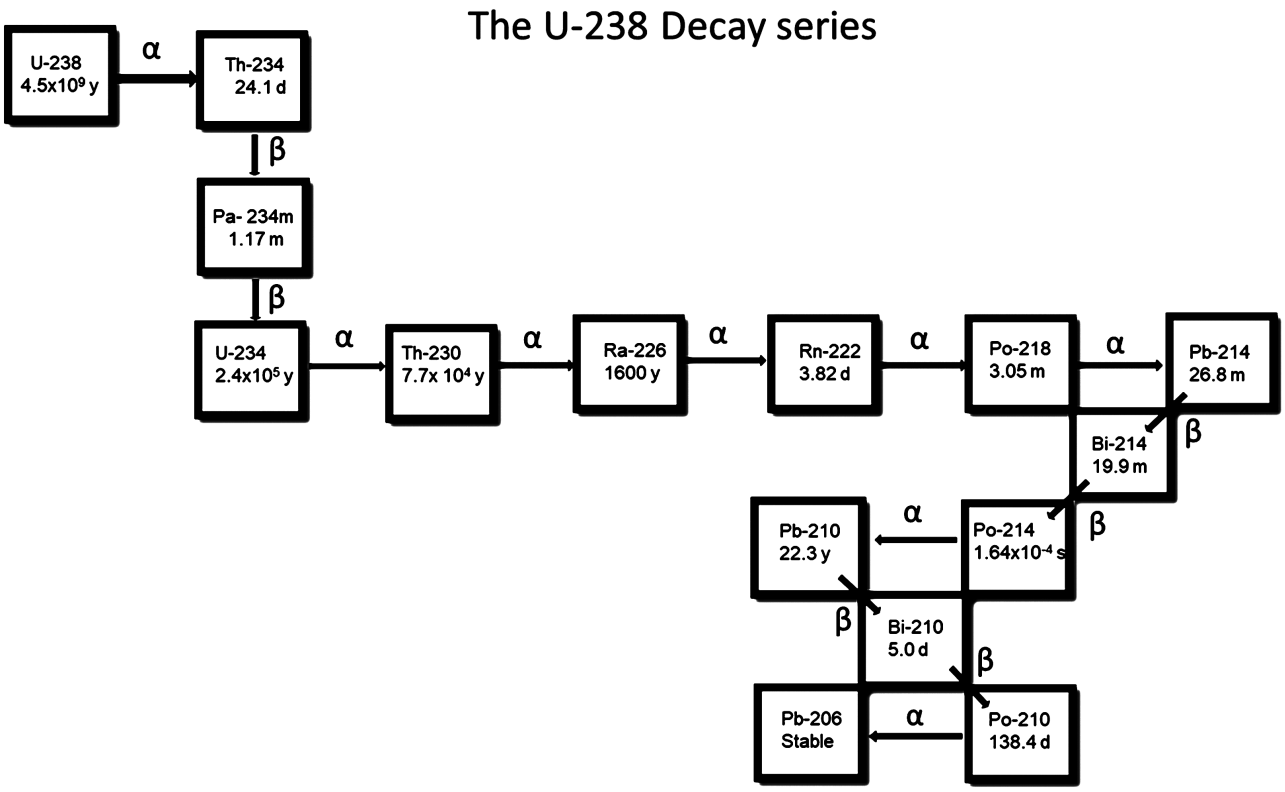

Figure 1. ^{238}U series decay chain.

The Nuclear Chemistry Laboratory (NCL) at the New York State Department of Health has been operating LBGS for over two decades (Semkow et al., 2002; Haines et al., 2011; Khan et al., 2014). NCL has one ultra-low background HPGe p-type coaxial spectrometer and three low background HPGe spectrometers. Details of the available HPGe spectrometers at NCL are given in Table 1. By lowering the gamma background, the sensitivity (hence the signal-to-noise ratio) of the gamma spectrometers is improved, which greatly enhances studies involving environmental radioactivity. Background reduction is another way to lower the decision limits of samples containing only traces of the radionuclides under investigation.

In gamma-ray spectrometry procedures, secular equilibrium in the natural radioactive decay series is assumed. However, the equilibrium between progeny particularly with ^{226}Ra and uranium can be strongly affected by several geological processes (weathering, exhalation of gases, passage to groundwater). Due to the constant ratio between ^{235}U and ^{238}U in nature, the 185.71 keV (57.2%) peak from ^{235}U may be a good choice for the ^{235}U measurement. To measure ^{235}U accurately it must be de-convoluted together with the 186.21 keV (3.64%) peak of ^{226}Ra which is not trivial. In this paper, we aim to show that ^{238}U (using 63.3 keV peak of ^{234r}Th) and ^{235}U activity can be accurately measured by using 143.76 keV (10.96%), 163.33 keV (5.08%), and 205.31 keV (5.01%) peaks by using our low background gamma spectrometry method. We also examine the equilibrium condition of both the ^{238}U and ^{232r}Th radioactive decay chains in a recently deposited fluvial sediment sample collected from the vicinity of the Nine Mile Point nuclear power plant in the town of Scriba, approximately five miles northeast of Oswego, New York, on the shore of Lake Ontario. Further, to obtain the precise and accurate results of the radioactivity of the environmental samples and the capability of the gamma spectrometry method at the NCL, we analyzed the sediment sample using our ultra-low background HPGe spectrometer (called GE12) and three low background HPGe spectrometers (GE03, GE08, and GE09) and one GC8021 (GE11) detector which has comparatively high gamma background. The gamma measurement results were validated using Certified Reference

Table 1. Characteristics of p-type co-axial HPGe detectors at NCL.

Detector	Model	Relative Eff (%)	FWHM (keV) Co-60 (1332.5 keV)	Muon Guard
GE03	GC10020	100	1.98	Top
GE08	GC10021	100	2.06	Top
GE09	GC13021	130	2.06	Top
GE12	GX13023	>130	2.43	All 4 sides plus Top
GE11*	GC8021	80	1.82	No

*Outside the steel room.

Material (CRM) Irish Sea sediment (IAEA-385).

2. Radioactivity and Secular Equilibrium in Sediment Samples

Secular equilibrium due to the radioactive disintegration in the rocks and sediment is discussed in detail (Ivanovich & Harmon, 1992). If the daughter's half-life is much shorter than that of the parent nuclide: i.e., $\lambda_0 \ll \lambda_1$, where $\lambda_i = \left(\ln 2/\zeta_{1/2}\right)_i$, is the decay constant for the "i"th radionuclide and $\zeta_{1/2}$ is the half-life of the radionuclide. Consequently, the activity of the parent does not decrease markedly over many daughters half-lives than for a parent-daughter pair, which simplifies to

$$N_1\lambda_1 = N_0\lambda_0\left(1-\mathrm{e}^{-\lambda_1 t}\right) \tag{1}$$

where N_0 and N_1 are the numbers of radioactive atoms of the parent and daughter nuclides, respectively, λ_0 and λ_1 are the respective decay constants, and t is the elapsed time. Then for values of t much greater than the daughter's half-life:

$$N_1\lambda_1 = N_0\lambda_0 \tag{2}$$

This is the condition known as secular equilibrium. For a decay chain, where the parent half-life is much longer than that of the longest-lived daughter, secular equilibrium implies

$$N_0\lambda_0 = N_1\lambda_1 = N_2\lambda_2 = \cdots = N_i\lambda_i \tag{3}$$

In secular equilibrium, the activity concentration of longer-lived radionuclides for ^{238}U decay chain (**Figure 1**) should be the same, in other words, parent and daughter activity become equal as given below:

$$A_{(^{238}\mathrm{U})} = A_{(^{234}\mathrm{U})} = A_{(^{230}\mathrm{Th})} = A_{(^{226}\mathrm{Ra})} = A_{(^{222}\mathrm{Rn})} = A_{(^{210}\mathrm{Pb})}. \tag{4}$$

Disequilibrium is the condition where the activity concentrations of the parent and daughter nuclides are not equal.

3. Materials and Methods

3.1. Sample Collection and Preparation

The sediment sample was collected from the vicinity of the Nine Mile Point Reactor located in the town of Scriba, approximately five miles northeast of Oswego, New York (**Figure 2**). This is a sediment sample collected from the shoreline of Lake Ontario boat launch collected right where the water meets land. Distance from the reactor is ~1.44 miles E of Unit 2 with a heading of 82 deg. Depth is skimmed off the top at approximately 2 cm and sifted in the field to remove large rocks. The sample was kept in a cooler and brought to the lab where the sample was kept at 105˚C overnight to dry and gain constant weight. The sample was then weighed and transferred into 800 ML Marinelli beaker up to the top and sealed with Phenoseal Vinyl Adhesive Caulk (PHENOSEAL, Baltimore, MD 21224) and black electric tape (S-17841; Uline, Pleasant Prairie, WI

Figure 2. Location of the sediment samples collection.

53158) to avoid the escape of ^{222}Rn gas from the container. The sediment sample was kept for four weeks to reach ^{226}Ra in equilibrium with ^{222}Rn Progeny (^{214}Pb and ^{214}Bi) before counting. The sample was counted for 60,000 s on all HPGe detectors. The background was counted for 240,000 s. The characteristics of HPGe detectors are given in Table 1.

3.2. Gamma Spectrometry

In this study, we have utilized five p-type high purity Germanium co-axial detectors (HPGe) having relative efficiencies varying from 80% to 140% by Mirion Technologies (Canberra) Inc. (Meriden, CT, USA). The detectors (except GE11) are situated inside a 15-cm thick wall steel room made of pre-World War II steel (Dixie Manufacturing Co., Baltimore, MD, USA), which is located under a 47-story

building providing 33 meters of water equivalent (mwe) shielding from cosmic rays in the vertical direction. GE03, GE08, and GE09 detectors have general low-background lead shields and are equipped with custom active muon shields made of plastic scintillators positioned on the top, which reduce cosmic muon background by a factor of 2. The 140% detector (GE12) has a custom 3-layer ultra-low background lead shield of a 17 cm total thickness, which is surrounded by plastic scintillators from five sides for muon rejection (Khan et al., 2014). This spectrometer has an integrated background rate of 2.4 counts per minute (cpm) in the gamma energy range between 50 - 2700 keV, corresponding to a background rate of 15 counts·ks^{-1}·kg^{-1} Ge.

To quantify radionuclides by their gamma rays, calibration of Ge gamma spectrometers is performed which involves determination of detector peak efficiency as a function of gamma energy and geometry. In addition, the density and coincidence-summing (cascade-summing) corrections to the peak efficiency are applied, the latter requiring either measured or calculated total efficiency. One can categorize the variety of the HPGe spectrometer calibration techniques into four major categories: empirical, semi-empirical, computational Monte Carlo (MC), and efficiency transfer. We used a semi-empirical method that is based on a direct measurement of the efficiency at a given geometry as a function of gamma energy for a set of radionuclides in a mild acidic solution (often called calibration in water). The measured water peak efficiencies, ε_p, are corrected for the coincidence-summing (as in Equation (5) below). Then, a smooth efficiency curve is often fitted to the water calibration using algorithms $\ln(\varepsilon_p)$ against polynomials of $(\ln E)^n$ or $(\ln(c/E))^n$, where E is gamma energy, n is the polynomial order, and c is a constant. There are also other algorithms that were not used here (Gilmore, 2011). When analyzing activity in real samples, the corrections are applied to the efficiency curve, to convert the peak efficiency for water at a particular gamma energy to the peak efficiency of the matrix and a particular radionuclide at the same energy as follows:

$$\varepsilon_p\left(\text{matrix};\text{radionuclide}\right)=\varepsilon_p\left(\text{water};\text{energy}\right)C_dC_s \tag{5}$$

where C_d is the density correction factor and C_s is the coincidence-summing correction factor.

The NIST traceable mixed-gamma radionuclide standards containing ^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{54}Mn, ^{88}Y, ^{65}Zn, ^{60}Co were provided by EZ Analytics, Atlanta, GA, USA. The radionuclides and their standardized gamma energies are listed elsewhere (Semkow et al., 2015). Gamma-ray spectra were acquired using Apex Gamma software of Mirion Technologies (Canberra) Inc. (Meriden, CT, USA) however, the spectra were analyzed using Genie 2000 software for the sediment sample as well as for efficiency calibration.

Calculations of radionuclide activities need to account for emission probabilities (**Table 2**), full energy peak efficiency, geometry-dependent true coincidence summing, density correction factor, and background characteristics of the detector. The gamma activity using the HPGe detector can be measured by the

Table 2. Key Gamma-emitting radionuclides from natural radioactive series (Values taken from NNDC, Brookhaven National Laboratory).

Radionuclide	Energy (keV)	Intensity (%)	Uncertainty (keV)
U-238 series			
^{234}Th	63.3	3.70	0.40
	92.4	4.25	0.28
^{234m}Pa	1001	0.837	0.10
^{226}Ra	186.21	3.64	0.04
^{214}Pb	295.22	18.42	0.04
	351.93	35.60	0.07
^{214}Bi	609.32	45.49	0.16
	1120.29	14.92	0.03
	1377.67	3.99	0.01
	1764.49	15.30	0.03
^{210}Pb	46.54	4.25	0.04
Th-232 series			
^{228}Ac	270.24	3.46	0.06
	338.32	11.27	0.09
	911.20	25.80	0.4
	964.77	4.99	0.09
	968.97	15.80	0.3
	1588.2	3.22	0.08
^{212}Pb	238.63	43.60	0.5
	300.09	3.30	0.04
^{212}Bi	727.33	6.67	
^{208}Tl	583.19	85.0	0.3
	860.56	12.5	0.1
	2614.51	99.75	0.004
U-235 series			
^{235}U	143.76	10.96	0.14
	163.33	5.08	0.06
	185.71	57.20	0.8
	205.31	5.01	0.07

following equation (Joel et al., 2017):

$$A\left(\mathrm{Bq}\cdot\mathrm{kg}^{-1}\right)=\frac{\frac{N_s}{t_s}-\frac{N_B}{t_B}}{M_s*\mathcal{E}*I_\gamma*C_d*C_s} \tag{6}$$

where A denotes the activity concentration of a radionuclide, N_s/t_s, and N_B/t_B are

the count rates of the radionuclide and background, M_s is the mass of the sample, $\mathcal{E}$ is full energy peak efficiency, and I_γ denotes an emission probability of the specific γ-ray, C_d is the density correction factor and C_s is the coincidence-summing correction factor. Density and coincidence summing corrections were calculated with the Gespecor program (Sima et al., 2001). **Table 2** also lists gamma energies used for the activity of the radionuclides and emission probabilities for key members of the ^{238}U, ^{232}Th, and ^{235}U series. For radionuclides with multiple energy lines, a weighted mean of each gamma line's measured activities was taken. The other main natural source, ^{40}K, emits 1461 keV photons with a probability of 10.66% ± 0.16%.

The error σ_A for a radionuclide activity is calculated using:

$$\left(\frac{\sigma_A}{A}\right)^2 = \left(\frac{\sigma_s}{S}\right)^2 \pm \left(\frac{\sigma_{\mathcal{E}}}{\mathcal{E}}\right)^2 \pm \left(\frac{\sigma_{I_\gamma}}{I_\gamma}\right)^2 \pm \left(\frac{\sigma_{C_d}}{C_d}\right)^2 \pm \left(\frac{\sigma_{C_s}}{C_s}\right)^2 \quad (7)$$

The uncertainty (σ_A) of activity calculation is a built-in function of the Genie2000 software. Our reported total uncertainty is expressed at the 95% confidence level, i.e., 1.96σ.

Minimum detectable activity (MDA) is defined by (Gilmore, 2011) as being the smallest quantity of activity that can be detected in a sample with a predefined probability of 95% (approximately $k = 2$), considering of 5% probability of making type I errors (false positive) and making type II errors (false negative). MDA of a particular radionuclide is calculated by Genie 2000 software (Mirion Tech) which used the Currie (1968) formulation as given below:

$$\text{MDA} = \frac{k^2 \pm 2k\sqrt{B + B\dfrac{N}{2m}}}{M_s * \mathcal{E} * I_\gamma * t * C_d * C_s} \quad (8)$$

where B is the background, $\mathcal{E}$ is the detection efficiency, I_γ is the emission probability of the specific γ-ray, t is the measurement time in sec, N is the number of channels of the region of interest (ROI) and m is the number of channels to the left and to the right of the ROI. k is a confidence level equal to 1.645. The sediment sample was counted for 60,000 s at each detector and the background was counted for 240,000 s. **Table 3** gives the MDA of radionuclides for specific energy in the sediment sample as well as in the distilled water sample (method blank) measured at each detector for 60,000 s. The verification of the radionuclides' activity and the capability in terms of precision and accuracy of our gamma spectrometry measurements were established by using a Certified Reference Material called Irish sea sediment (IAEA-385) under the same conditions.

4. Results and Discussions

The results of the radionuclides activity of ^{238}U and ^{232}Th series in sediment samples measured by available HPGe detectors at NCL are presented in **Table 4**. The spectra of the major gamma energy lines of the background and the sediment sample are presented in **Figure 3** and **Figure 4**. The details of the results

Table 3. MDA of radionuclides due to major gamma lines measured by HPGe detectors using Genie 2000 software.

Nuclide	Energy (keV)	MDA (Bq·kg^{-1})									
		GE03		GE08		GE09		GE11		GE12	
		Sediment	Water	Sediment	Water	Sediment	Water	Sediment	Water	Sediment	Water
K-40	1461	2.60	0.49	3.15	0.46	1.66	0.49	1.94	1.26	2.08	0.20
Cs-137	661	0.33	0.05	0.28	0.03	0.24	0.04	0.27	0.08	0.31	0.02
TL-208	583.2	0.26	0.15	0.29	0.22	0.25	0.27	0.24	0.18	0.25	0.02
Pb-210	46.5	46.2	5.37	86.8	10.1	215.9	34.3	27.3	6.8	13.8	0.00
Bi-212	727.3	2.98		2.97		2.22		2.30	2.13	2.61	0.19
Bi-214	609.3	0.50	2.29	0.55	0.81	0.43	0.10	0.50	0.15	0.46	0.05
PB-214	351.9	0.54	0.12	0.60	0.10	0.50	0.10	0.53	0.18	0.55	0.03
AC-228	911.2	0.92	0.08	0.95	0.16	0.78	0.15	0.82	0.69	0.86	0.05
Th-234	63.3	12.95						11.49		11.3	0.34
Pa-234m	1001	16.94		18.64		14.23		17.38	9.40	20.94	1.54
U-235	185.7	0.32	0.05	0.32	0.08	0.32	0.07	0.33	0.13	0.37	0.02
Am-241	59.5	1.83	0.26	2.45	0.33	3.86	0.69	1.18	0.30	1.19	0.10

Table 4. Radionuclides activity (Bq·kg^{-1}) in sediment sample measured by various HPGe detectors.

Radionuclide	Detector				
	GE03	GE08	GE09	GE11	GE12
Th-234 (63.3 keV)	20.1 ± 4.9	20.4 ± 6.9	19.4 ± 7.5	21.6 ± 4.4	23.2 ± 3.7
U-238 (Pa-234m, 1001 keV)	26.2 ± 5.1	22.5 ± 5.8	19.7 ± 4.4	25.6 ± 5.6	25.4 ± 6.6
Pb-210 (46.54 keV)	ND*	ND*	ND*	24.2 ± 7.5	24.2 ± 3.8
Pb-214	23.3 ± 0.3	22.8 ± 0.3	23.1 ± 0.2	22.5 ± 0.3	23.3 ± 0.3
Bi-214	22.2 ± 0.3	21.8 ± 0.3	20.9 ± 0.2	21.8 ± 0.3	22.4 ± 0.2
Ra-228	23.0 ± 0.3	22.7 ± 0.3	22.9 ± 0.3	22.4 ± 0.3	23.2 ± 0.3
Pb-212	22.3 ± 0.4	22.9 ± 0.4	23.0 ± 0.4	22.1 ± 0.4	22.9 ± 0.5
Bi-212 (727.33 keV)	23.0 ± 1.1	23.0 ± 1.0	22.0 ± 0.8	21.1 ± 0.9	21.8 ± 0.9
Tl-208	22.3 ± 0.4	21.5 ± 0.4	22.1 ± 0.3	21.0 ± 0.4	22.1 ± 0.3
U-235 (143.76 keV; 163.33 keV; 205.31 keV)	1.18 ± 0.4	1.18 ± 0.4	1.12 ± 0.4	1.26 ± 0.4	1.39 ± 0.4
K-40 (1461 keV)	555 ± 11	557 ± 11	549 ± 11	556 ± 11	555 ± 11
Cs-137 (661.7 keV)	0.95 ± 0.05	0.89 ± 0.06	0.95 ± 0.05	0.92 ± 0.06	0.84 ± 0.06
U-series disequilibrium	0.99 ± 0.15	1.04 ± 0.21	1.10 ± 0.18	0.96 ± 0.14	0.94 ± 0.13
$^{235}U/^{238}U$ activity ratio	0.052 ± 0.02	0.053 ± 0.02	0.052 ± 0.02	0.057 ± 0.02	0.062 ± 0.01

*Not detected.

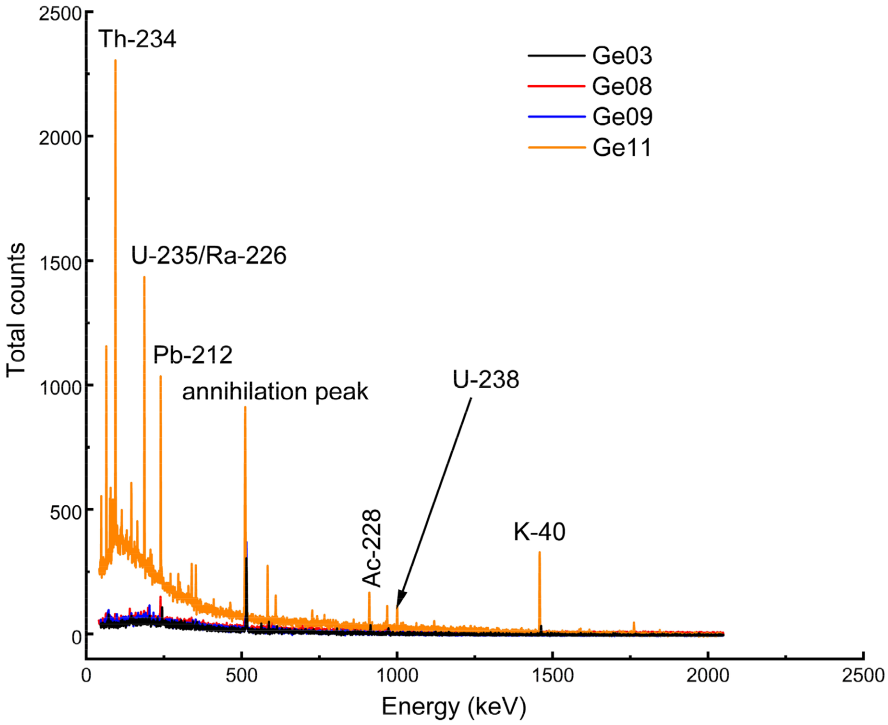

Figure 3. Background spectra for 240,000 s in GE03, GE08, GE09 and GE11 HPGe detectors.

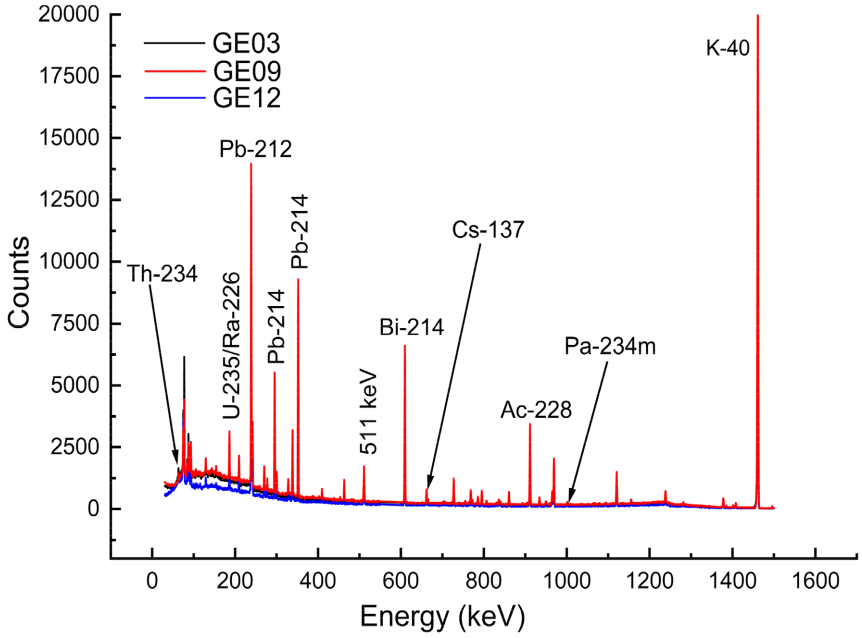

Figure 4. Major gamma lines from natural and man-made sources in the sediment sample.

are discussed below. The results are density and coincidence summing corrected.

4.1. ^{238}U Series Measurement

4.1.1. ^{238}U Activity Measurement

Usually, the activity of ^{238}U in a sediment sample cannot be directly determined

by gamma spectrometry since the ^{238}U emits a weak gamma-ray at 49.55 keV (0.064%). However, its activity can be measured by means of its progeny ^{234}Th (63.3 and 92.5 keV) and ^{234m}Pa (1001 keV) as both are reached in secular equilibrium with ^{238}U in ~120 days in a closed system due to their short half-life. ^{234}Th at 63.3 keV (4.5%) peak is a cleaner peak and suitable for ^{238}U analysis. However, the 92.5 keV peak is a doublet consisting of 92.37 (2.61%) and 92.79 keV peaks (2.58%) and is affected by several other peaks i.e., ^{231}Th X-ray (0.42%), ^{214}Bi X-ray (0.083%), ^{228}Ac X-ray (3.19%) and ^{235}U X-ray (5.56%). Due to these interferences, the use of the 92.5 keV peak for directly quantifying ^{234}Th is not possible and we use the 63.3 keV peak for ^{234}Th determination. Another possibility is the use of ^{234m}Pa at the 1001 keV gamma line. The weak intensity of the ^{234m}Pa gamma line (1001 keV; 0.837%) in conjunction with the low efficiency of HPGe detectors at higher energies, often leads to a non-detectable peak in sediments. However, the 1001 keV peak does not have any interference with any other peaks and is not affected by self-absorption (Yücel et al., 1998), hence this peak is useful to determine the ^{238}U concentrations in the sediment samples. However, analysis of ^{238}U by 1001 keV gamma peak requires a long-integrated counting time. By using our low background gamma spectrometers (GE03, GE08, and GE09) and ultralow background spectrometer (GE12), we can easily determine the ^{238}U by using ^{234m}Pa, 1001 keV peak accurately. The ^{238}U activity in the sediment sample by using ^{234}Th (63.3 keV) and ^{234m}Pa (1001 keV) peak is presented in **Table 4** and plotted in **Figure 5**. The ^{234}Th and ^{234m}Pa activities in the sediment sample give very similar results within the measurement uncertainty among all five HPGe detectors. The ^{234}Th activity varies from 19.4 ± 7.5 Bq·kg^{-1} to 23.2 ± 3.7 Bq·kg^{-1} and ^{234m}Pa activity varies from 19.7 ± 4.4 Bq·kg^{-1} to 26.2 ± 5.1 Bq·kg^{-1} among the detectors. The large uncertainties and the variation in radionuclide activities are due to the low emission probability of 3.70% ± 0.04%

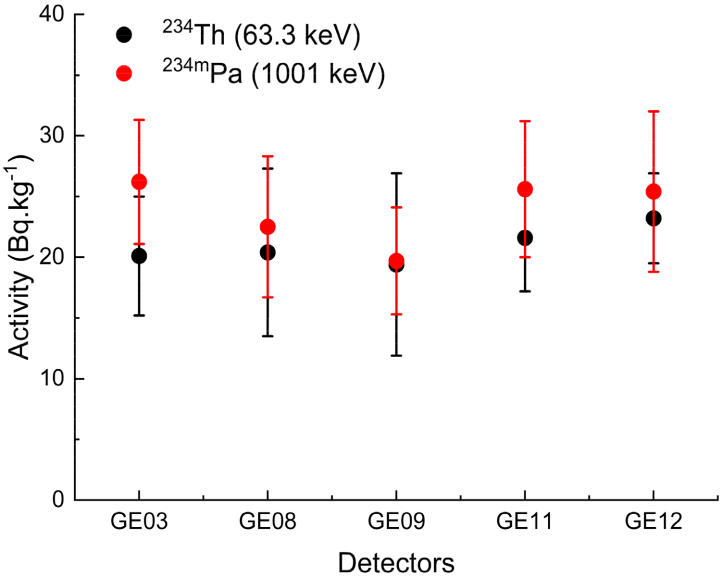

Figure 5. ^{234}Th and ^{234m}Pa activities in sediment sample.

for the 63.3 keV gamma line and 0.0837% for the 1001 keV gamma line. The low efficiency of the HPGe detectors at low energies is another factor for the variation in ^{234}Th activity as well as in ^{234m}Pa activity (Figure 6). GE12 (XtRa HPGe) detector has higher efficiencies as compared to GE03 shown in Figure 7 for both the radionuclides due to its unique thin-window contact on the front surface which extends the useful energy range down to 3 keV. Conventional p-type coaxial detectors e.g., GE03, GE08, GE09, and GE11 have a lithium-diffused contact typically between 0.5 and 1.5 mm thick. This dead layer stops most photons below

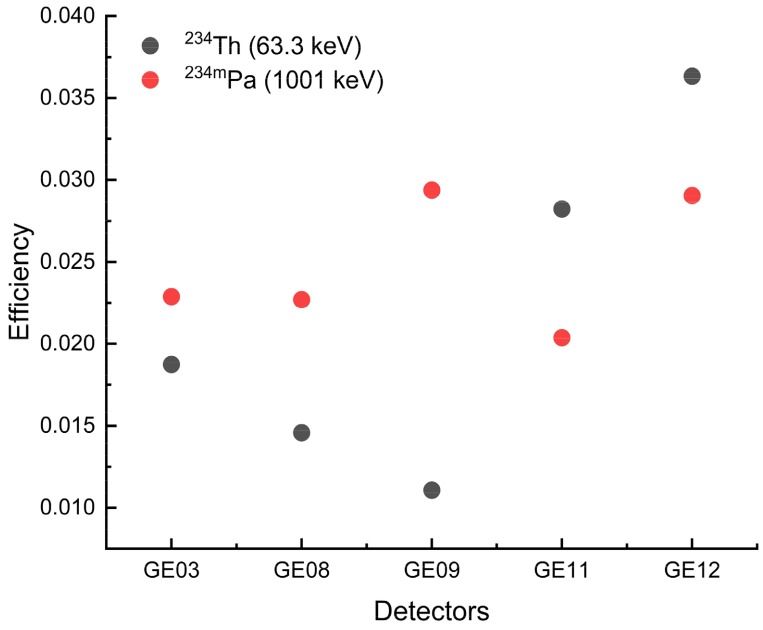

Figure 6. Measured efficiency of the HPGe detectors for ^{234}Th and ^{234m}Pa.

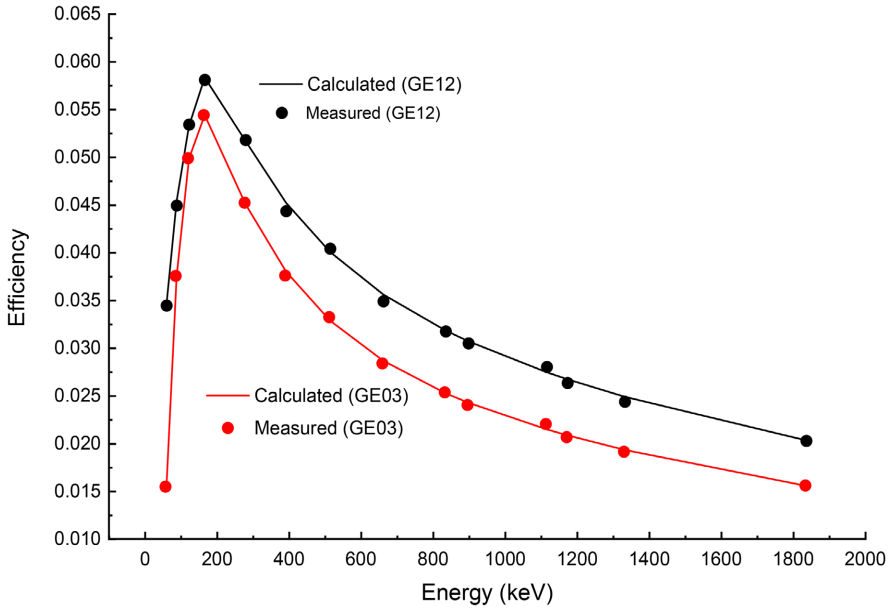

Figure 7. Comparison of the efficiency with conventional p type HPGe detector (GE03) vs HPGe p-type (XtRa) low energy detector (GE12).

40 keV which is not a good choice for low-energy gamma detection. The precision of the ^{234}Th activity measurement is good in all five detectors, however, the GE12 HPGe ultralow background detector is the better choice for ^{238}U measurements due to its low uncertainty. The mean gamma activities of ^{234}Th and ^{234m}Pa are 20.9 ± 2.5 Bq·kg^{-1} and 23.9 ± 2.5 Bq·kg^{-1} respectively and the ratio of ^{234}Th/^{234m}Pa is 0.87 ± 0.16 which shows that ^{234}Th and ^{234m}Pa are in secular equilibrium with ^{238}U.

4.1.2. ^{210}Pb Activity Measurement

^{210}Pb (E = 46.54 keV; I_γ = 4.25%) occurs naturally as one of the decay products of the ^{238}U series. Disequilibrium between ^{210}Pb and its parent nuclide ^{226}Ra ($T_{1/2}$ = 1600 y), arises through the diffusion of the intermediate gaseous isotope, ^{222}Rn ($T_{1/2}$ = 3.8 d). Direct gamma counting of the 46.54 keV gammas produced in 4.25% of the ^{210}Pb decays. There are two challenges related to this measurement: the low intensity of this gamma decay; and the very low energy of the photon, for which the detection efficiency of HPGe detectors is low (**Figure 7**). The results presented in **Table 4** show that ^{210}Pb is not detected by GE03, GE08, and GE09) detectors. The reason is that they are very old p-type HPGe coaxial detectors (more than 25 years old). The thickness of the dead layer in p-type HPGe coaxial detectors increases with time which attenuates the low-energy photons and these photons do not reach the detectors' active volume (Huy, 2011; Kaya et al., 2022). This also affects the efficiency of the detector in low-energy regions. The ^{210}Pb activity in the sediment sample measured by GE11 and GE12 was 24.2 ± 7.5 and 24.2 ± 3.8 Bq·kg^{-1}, respectively, however, the uncertainty in GE12 is much lower as compared to GE11 because of its low background and higher efficiency at 46.5 keV (**Figure 7**). The result presented in **Figure 8** shows that

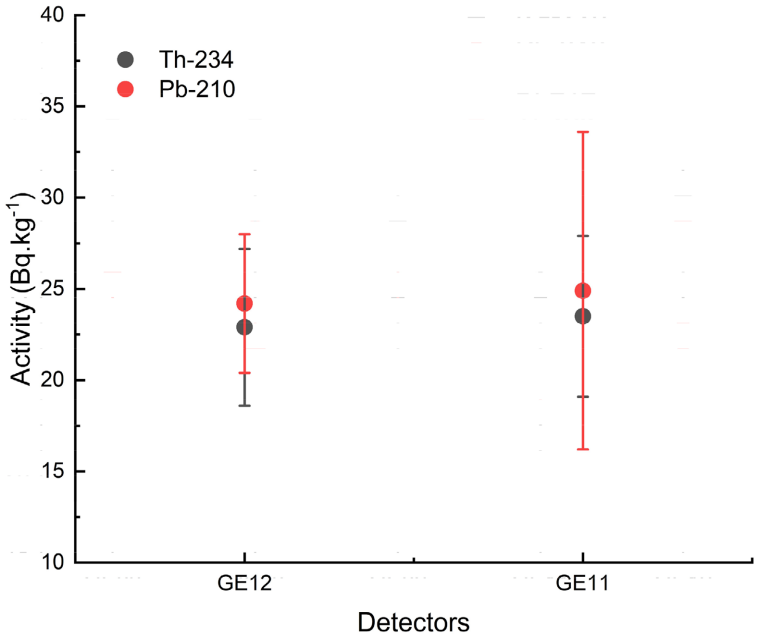

Figure 8. ^{234}Th and ^{210}Pb activity in sediment sample showing secular equilibrium.

^{234}Th (^{238}U) and ^{210}Pb are in good agreement which clearly shows that both the radionuclides are in secular equilibrium with ^{238}U. This also shows that if secular equilibrium breaks due to the emanation of ^{222}Rn it is recovered afterward.

4.1.3. ^{226}Ra Activity Measurement

^{226}Ra is determined either directly by measuring the 186.21 keV γ-peak or indirectly by measuring the γ-peaks of ^{222}Rn progeny i.e., ^{214}Pb and ^{214}Bi after secular equilibrium established with ^{226}Ra (~4 weeks). Direct measurement of ^{226}Ra with 186.21 keV by gamma spectrometry is difficult due to the interference of 185.7 keV γ-peak from ^{235}U and requires interference correction from ^{235}U (185.71 keV) peak (Suárez-Navarro et al., 2018). We measured ^{226}Ra activity in the sediment sample by sealing the Marinelli beaker against ^{222}Rn escape via the emissions from its short-lived daughters ^{214}Pb and ^{214}Bi. ^{226}Ra activity was calculated based on the assumption that it is a weighted mean of the activities of the gamma rays of ^{214}Pb (295.22 keV, 351.93 keV) and ^{214}Bi (609.32 keV, 1120.29 keV, 1377.67 keV, 1764.49 keV). The ^{226}Ra results of the ^{214}Pb and ^{214}Bi activities measured by each detector are presented in **Table 4**. The results from each detector for both the radionuclides are in good agreement and show the high precision of our gamma spectrometry method. The results also suggest that the ^{226}Ra is in secular equilibrium with ^{234}Th.

To conclude, we would like to add that the measured activity of ^{238}U series radionuclides (i.e., ^{234}Th, ^{234m}Pa, ^{226}Ra, and ^{210}Pb) is found to be in good agreement as given by equation 4 suggesting that the ^{238}U progeny are in secular equilibrium with ^{234}Th. The ratio of ^{234}Th activity to the weighted mean activities of ^{234m}Pa, ^{226}Ra, and ^{210}Pb presented in **Table 4** varies from 0.94 ± 13 to 1.10 ± 0.18 with a mean value of 1.01 ± 0.07 among HPGe detectors in the sediment sample which shows good agreement and precision of the measurements.

4.2. ^{232}Th Series Measurement

^{232}Th decays to stable ^{208}Pb by a series of alpha and beta decay modes. The decay of the daughters is always accompanied by the emission of gamma radiation and this mode of decay provides an opportunity to apply low-level gamma spectrometry for the determination of ^{228}Ra and its progeny. ^{232}Th is less soluble than ^{238}U and found mostly in secular equilibrium with its progeny i.e., ^{228}Ra, ^{212}Pb, ^{212}Bi, and ^{208}Tl in rocks, soil, and sediments. However, it should be noted that in the case of ^{208}Tl, only 35.94% of ^{212}Bi decay leads to this nuclide while 100% of ^{228}Ac or ^{212}Pb activity is in secular equilibrium with ^{232}Th. The results of the ^{228}Ra, ^{212}Pb, ^{212}Bi, and ^{208}Tl are presented in **Table 4**. ^{228}Ra activity in the sediment sample is measured by the weighted mean of the activities of the ^{228}Ac peaks of 270.24 keV, 338.32 keV, 911.20 keV, 964.77 keV, 968.97 keV, and 1588.2 keV. ^{228}Ac ($T_{1/2}$ = 6.15 h) is the immediate daughter of ^{228}Ra ($T_{1/2}$ = 5.75 ± 0.03 y) and expected in secular equilibrium with ^{228}Ra in the sediment sample. ^{212}Pb activity was measured by the gamma peaks of 238.63 keV and 300.09 keV; ^{212}Bi activity was determined by using gamma energy of 727.33 keV and ^{208}Tl activity was

calculated using the weighted mean activities of gamma peaks 583.19 keV, 860.56 keV and 2614.51 keV. The gamma activity of the radionuclides in the sediment sample measured by available HPGe detectors is agreed very well within uncertainty. The average activities of the radionuclides ^{228}Ra, ^{212}Pb, ^{212}Bi and ^{208}Tl in the sediment sample are found to be 22.7 ± 0.27 Bq·kg^{-1}, 22.5 ± 0.23 Bq·kg^{-1}, 21.8 ± 0.32 Bq·kg^{-1}and 21.7 ± 0.33 Bq·kg^{-1}, respectively. The ^{232}Th series radionuclides activity agrees with each other which shows that the ^{232}Th is in secular equilibrium with its radioactive progeny.

4.3. ^{235}U Measurement

^{235}U emits several gamma lines between 70 and 300 keV however the main gamma line at 185.71 keV (emission probability 57.2%) is interfered with the ^{226}Ra gamma line at 186.21 keV. The best gamma line is at 205.31 keV which is sufficiently well separated from other likely peaks (e.g., 204 keV peak from ^{228}Ac) to use for determination although its low intensity (4.7%) precludes its use in many samples. Two other lines of interest are those at 143.76 keV and 163.33 keV with intensities of 10.5% and 4.7%, respectively, however, the former is interfered with ^{230}Th peak at (143.87 keV; 0.048%), and by the 144.2 keV emission of the daughter ^{223}Ra. The interference at 163.1 keV (0.154%) of the short-lived ^{231}Th is assumed to be in equilibrium with ^{235}U. We used the weighted mean of the activities of gamma lines at 143.76 keV, 163.33 keV, and 205.31 keV and the results are presented in Table 4.

The measured ^{235}U activity in the sediment sample shows (Figure 9) good precision in all HPGe detectors. The ^{235}U activity varied from 1.12 ± 0.4 Bq·kg^{-1} to 1.39 ± 0.4 Bq·kg^{-1} with a mean value of 1.22 ± 0.18. ^{235}U activity measured by GE11 and GE12 detectors show 1.26 ± 0.4 Bq·kg^{-1} and 1.39 ± 0.4 Bq·kg^{-1}, respectively. Our results suggest that ^{235}U activity in the environmental sample can be

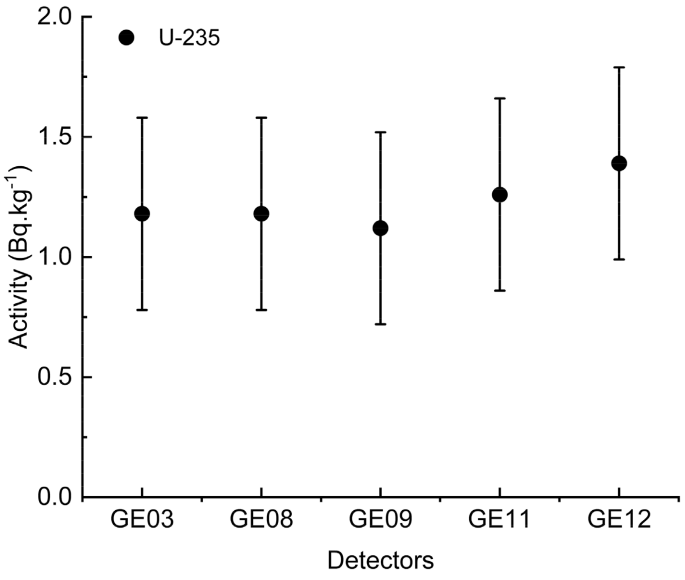

Figure 9. ^{235}U activity in sediment sample by low background gamma spectrometry.

measured precisely and accurately by low background gamma spectrometry. The activity ratio of the radionuclides ^{235}U to ^{238}U is constant in all environmental samples, except where contaminated by processed uranium or taken from certain specific, well-known locations. The $^{235}U/^{238}U$ activity ratio is 0.046 ± 0.007 (Dowdall et al., 2004). The mean activity ratio of the ^{235}U to ^{238}U in the sediment sample is found to be 0.055 ± 0.007. The high $^{235}U/^{238}U$ ratio either may be uncertainty in ^{235}U measurements or washed-out of ^{238}U from the surficial sediment.

4.4. ^{40}K and ^{137}Cs Measurement

^{40}K is a primordial natural radionuclide and is present in all rocks, sediment, and soil however ^{137}Cs is a manmade radioactive isotope released in the atmosphere by nuclear testing during the 1950s and 1960s and nuclear accidents like Chernobyl in 1986 and Fukushima in 2011. The activity of ^{137}Cs was calculated from the 661.6 keV peak and ^{40}K from the 1461.0 keV peak by HPGe detectors. The ^{40}K activity in the sediment sample is presented in **Table 4**. The ^{40}K activity varies from 549 ± 11 $Bq{\cdot}kg^{-1}$ to 557 ± 11 $Bq{\cdot}kg^{-1}$ with a mean of 554 ± 5 $Bq{\cdot}kg^{-1}$. ^{40}K activity in the sediment sample was measured very precisely with our gamma spectrometers. ^{137}Cs activity in the sediment sample varies from 0.84 ± 0.06 to 0.95 ± 0.05 $Bq{\cdot}kg^{-1}$ among the five HPGe detectors. ^{137}Cs value in the sediment sample is very low and measured very precisely by all detectors presented in **Table 4**. The ^{137}Cs values are in good agreement with uncertainty.

4.5. Certified Reference Material

Certified reference materials (CRMs) and Standard Reference Materials (SRMs) are important for method development and validation. They can indicate the need to improve or change existing methods and/or the need for further training. It is well known that the use of Proficiency Tests (PTs) and CRMs is among the most important quality control tools to produce reliable and valid measurement results and to fulfill international standards requirements regarding method validation, quality control, and metrological traceability. IAEA-385 Irish Sea sediment (Pham et al., 2008) was used for verification of our gamma spectrometry results for radionuclides in the sediment sample. 55 g of IAEA-385 sample was measured on GE08, GE09 and GE12 detector. The sample was counted for 60,000 s on each detector. The results of the radionuclide activities are presented in **Table 5**. The same gamma energy lines were chosen to calculate the activities of individual radionuclides as discussed in section 3.4. Good agreement was found with the certificate values and the measured values by our low background gamma spectrometry measurement of radionuclides with some exceptions. Th-234 (63.3 keV) activity by GE08 shows 16.8 ± 13.4 $Bq{\cdot}kg^{-1}$ which is lower than the certificate value with large uncertainty may be due to the low intensity (I_γ = 3.7% ± 0.4%) of gamma-ray (**Figure 10**), however, the activity of ^{238}U measured by GE09 and GE12 show good agreement with the certificate value. The precision of the measured activity of ^{235}U in GE08, GE09, and GE12 show

Table 5. Radionuclides activity in Certified Reference material (IAEA-385 Irish Sea Sediment).

Radionuclides	IAEA-385 Sediment (Bq·kg^{-1})			
	Cert value	GE08	GE09	GE12
Th-234 (63.3 keV)	33.0 ± 2.4	16.8 ± 13.4	33.3 ± 16.2	31.5 ± 7.6
U-238 (Pa-234m (1001 keV)	29.4 ± 1.2	Not Detected	36.3 ± 24.3	28.0 ± 11.3
Pb-214	22.8 ± 0.6	23.0 ± 0.7	23.4 ± 0.8	23.5 ± 0.8
Bi-214	22.8 ± 0.6	21.6 ± 0.9	22.4 ± 0.8	22.6 ± 0.8
Pb-210 (46.54 keV)	28.5 ± 1.9	ND*	ND*	29.6 ± 3.5
Th-232	33.8 ± 0.9	33.7 ± 2.0	33.6 ± 2.1	33.5 ± 1.8
Ra-228	33.6 ± 2.0	33.2 ± 1.2	33.8 ± 1.9	33.5 ± 1.0
U-235 (143.76 keV; 163.33 keV; 205.31 keV)	1.36 ± 0.11	2.0 ± 1.8	1.85 ± 1.3	2.03 ± 0.6
K-40 (1461 keV)	611 ± 27	585 ± 23	604 ± 24	586 ± 29
Cs-137 (661.7 keV)	19.8 ± 0.6	15.3 ± 0.5	15.1 ± 0.5	15.8 ± 0.9
Am-241 (59.5 keV)	3.81 ± 0.17	3.43 ± 0.6	3.44 ± 1.0	3.42 ± 0.34

*Not detected.

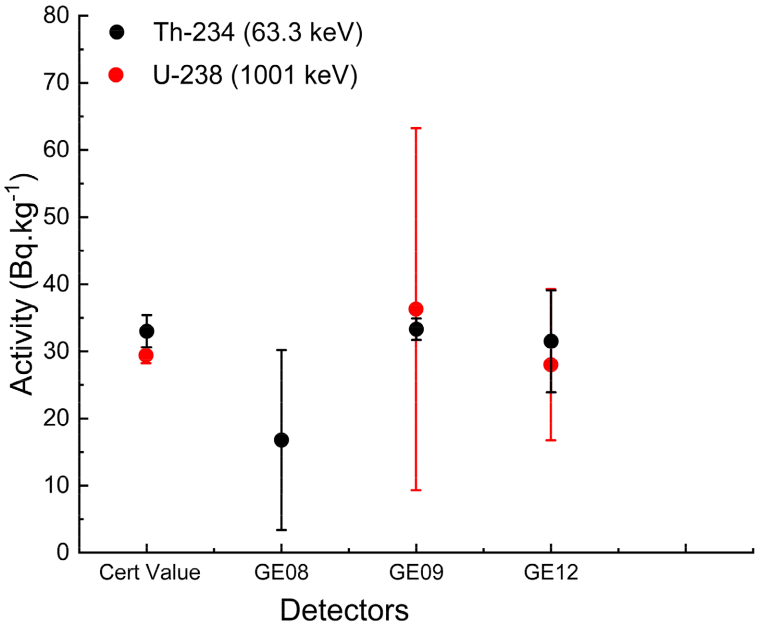

Figure 10. ^{234}Th and ^{238}U (^{234m}Pa) activity in CRM IAEA-385 sediment.

2.0 ± 1.8 Bq·kg^{-1}, 1.85 ± 1.3 Bq·kg^{-1}, and 2.03 ± 0.6 Bq·kg^{-1} which agrees with the certificate value of 1.36 ± 0.11 Bq·kg^{-1} (95%) confidence interval is (1.24 – 1.51 Bq·kg^{-1}) as shown in Figure 11. The certificate value of ^{235}U activity is based on the 16 measurements either by Alpha Spectrometry or ICPMS. Our measured activity values of 15.3 ± 0.5 Bq·kg^{-1}, 15.1 ± 0.5 Bq·kg^{-1}, and 15.8 Bq·kg^{-1} on GE08, GE09, and GE12 HPGe detectors for ^{137}Cs do not agree with the certificate value of 19.8 ± 0.6 Bq·kg^{-1} presented in Table 5, however, our ^{137}Cs activity results

show good agreement and precision among three detectors. To validate our ^{137}Cs results further, we used a PT soil sample from IAEA-CU-2006-03 World-Wide Open Proficiency Test on the Determination of Gamma Emitting Radionuclides (Shakhashiro et al., 2007). Our laboratory participated in this PT exercise in 2006. Soil sample from the 2006 PT batch was analyzed for this study on GE08 and GE12 for 60000 s and the results agree with the PT value (**Figure 12**). The results of the Certified Reference Material IAEA-385 sediment and 2006 IAEA PT soil sample show the accuracy and precision of NCL's low background gamma measurement capability for measuring radionuclides in environmental samples, particularly for ^{238}U and ^{235}U.

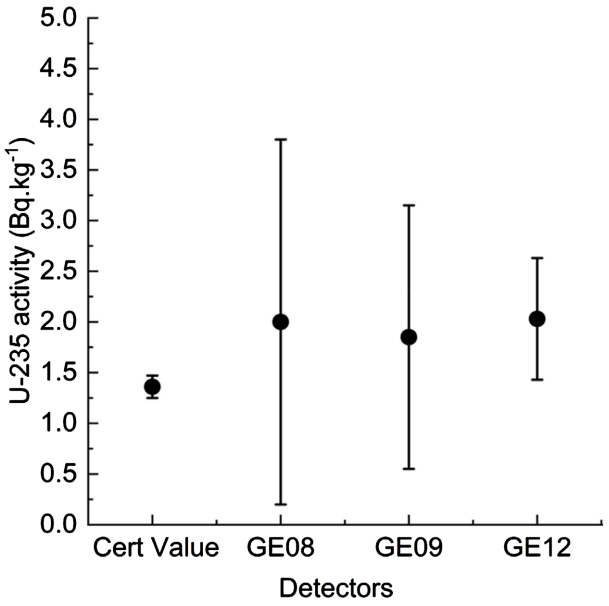

Figure 11. ^{235}U activity in CRM IAEA-385 sediment.

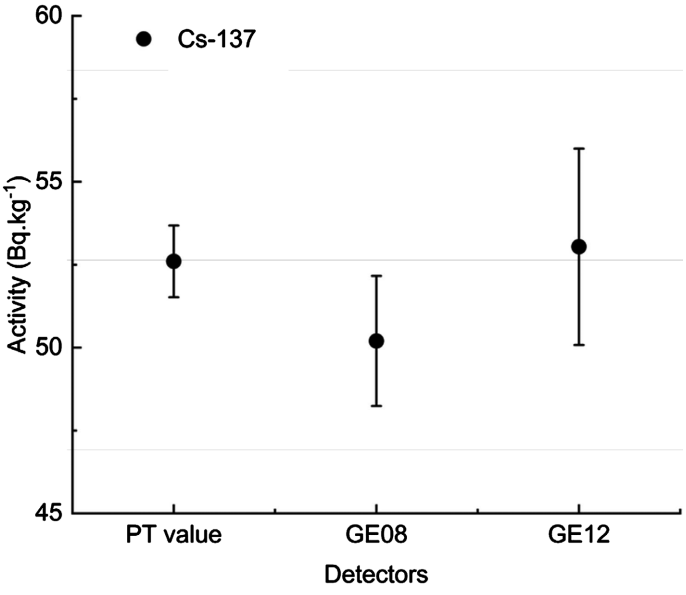

Figure 12. ^{137}Cs activity in PT sample of IAEA 2006 radionuclide testing exercise.

5. Conclusion

Artificial radionuclides produced in nuclear fission and activation processes have been released into the environment during nuclear explosions and nuclear accidents. In addition, naturally occurring radionuclides also contribute to the environmental radiological hazard. Low background gamma spectrometry was applied to determine activity concentration due to naturally occurring radionuclides of ^{238}U, ^{232}Th, ^{235}U decay series, and ^{40}K, ^{137}Cs in a sediment sample. This study shows that low background gamma spectrometry can be successfully applied to accurately measure ^{238}U and ^{235}U activity in sediment or similar matrix without any interference correction from nearby peaks. The sediment results show that the ^{238}U is in equilibrium with its daughters i.e., with ^{234}Th, ^{234m}Pa as well as with ^{210}Pb. ^{232}Th is also in equilibrium with its daughters (^{228}Ra, ^{212}Pb, ^{212}Bi and ^{208}Tl. ^{226}Ra activity in sediment is best determined by using the activities of ^{222}Rn short-lived daughter radionuclides ^{214}Pb and ^{214}Bi rather than the direct peak of 186.21 keV which is influenced by 185.71 keV peak of ^{235}U. Care must be taken to avoid any escape of radon gas from the container. Certified Reference Material (IAEA-385 Sediment) was used to verify the radionuclide activities in the sediment by gamma spectrometry. The results are in good agreement with the certificate values. Multi-detector analysis of radionuclides in sediment samples as well as in CRM shows that the NCL gamma spectrometry program is robust, precise, and accurate. ^{210}Pb (E = 46.5 keV; I_γ = 4.25%) is not detected by GE03, GE08 and GE09) detectors. The reason is that they are old p-type HPGe coaxial detectors (more than 25 years old). The thickness of the dead layer in p-type HPGe coaxial detectors increases with time which attenuates the low-energy photons and these photons do not reach the detectors' active volume. This also affects the efficiency of the detector in low-energy regions.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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