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Determination of ^{224}Ra and ^{226}Ra Activities in Soil and Sediment Using Interference Correction Method by Ultra Low-Level Gamma Spectrometry

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Abstract

Radium isotopes, particularly ^{226}Ra and ^{228}Ra, pose environmental concerns due to their long half-lives (1600 years and 6 years, respectively) and their persistence in soils and sediments, especially in regions affected by coal combustion and uranium mining. This study introduces a novel deconvolution method using ultra-low-background gamma spectrometry to directly quantify ^{224}Ra (240.99 keV) and ^{226}Ra (186.21 keV) in soil and sediment samples, effectively correcting for spectral interferences from ^{214}Pb (241.99 keV) and ^{235}U (185.71 keV). By measuring multiple gamma lines of ^{235}U (143.76, 163.33, 205.31 keV), the method enables precise interference correction. Samples collected from Lake Ontario sediments (2018-2023) and certified reference materials (IAEA-312, IAEA-385, IAEA-412, IAEA-447, and an IAEA 2006 proficiency testing (PT) soil sample) underwent gamma counting for up to 240,000 s. Results showed ^{224}Ra activities in sediments ranging from 23.1 - 23.8 Bq·kg^{-1} (mean 23.5 ± 0.2), closely matching ^{228}Ra levels, indicating secular equilibrium. Corrected ^{226}Ra activities (22.6 - 24.6 Bq·kg^{-1}; mean 24.2 ± 0.9) aligned well with radon progeny ^{214}Pb and ^{214}Bi measurements. CRM analyses confirmed method accuracy: ^{226}Ra in IAEA-312 was 296 ± 28 Bq·kg^{-1} (certified 250 - 287 Bq·kg^{-1}), while other radionuclides (^{40}K, ^{137}Cs, ^{241}Am, ^{234}Th, ^{234m}Pa, ^{235}U, and ^{210}Pb) measured in samples and CRMs showed strong agreement with certified values. This validated deconvolution approach provides a reliable and time-efficient alternative for direct radium isotope quantification in environmental matrices, thereby enhancing the capability for monitoring both natural and anthropogenic radionuclide distributions.

Keywords

^{224}Ra, ^{226}Ra, Soil, Sediment, CRMs, IAEA-312, Low Background Gamma Spectrometry

1. Introduction

Radium is a naturally occurring silvery-white radioactive metal (atomic number 88) that forms from the radioactive decay of uranium and thorium. It exists in several isotopes: ^{226}Ra, ^{228}Ra, ^{224}Ra, and ^{223}Ra. ^{226}Ra and ^{228}Ra are the isotopes of primary environmental concern due to their long half-lives, which promote significant environmental accumulation. The half-life of ^{226}Ra is about 1600 years, while that of ^{228}Ra is approximately 6 years. ^{226}Ra is part of the ^{238}U decay series and decays to ^{222}Rn through alpha particle emission (**Figure 1**). Both ^{226}Ra and ^{228}Ra can be found in soil and rocks within the Earth's crust. The reported mean concentration of ^{226}Ra in 356 surface soil samples collected from 33 states was 41 Bq·kg^{-1} (Myrick et al., 1981), which is quite like the 48 Bq·kg^{-1} of ^{226}Ra found in typical igneous rock (Eisenbud & Gessell, 1997). ^{226}Ra concentrations vary by rock type: Sandstone averages 26 Bq·kg^{-1}, Limestone averages 16 Bq·kg^{-1}, and Shale averages 41 Bq·kg^{-1}. Coal burning, uranium mining, and milling operations have led to elevated levels of radium in the soil. Kalin (1988), Landa (1984), and Tracy et al. (1983) reported that the concentration of ^{226}Ra in soils contaminated by mining and milling activities ranged from 37 Bq·kg^{-1} to 137 Bq·kg^{-1}. Uranium present in the Earth's crust serves as an indicator of radium levels. National radioactivity surveys indicate that elevated radium levels in soil are expected in the western third of the continental United States, including large areas of California and Idaho (ATSDR, 1990). Furthermore, these surveys predict increased radium levels in several states across the USA, including Wisconsin, Minnesota, the Appalachian Mountains, and Florida. Under the Safe Drinking Water Act, the U.S. Environmental Protection Agency (EPA) has established maximum contaminant level goals (MCLGs) of zero for radioactivity in drinking water. However, the maximum contaminant level (MCL) for combined ^{226}Ra and ^{228}Ra in drinking water is set at 185 mBq·L^{-1} (5 pCi·L^{-1}), requiring both radium isotopes to be measured separately (EPA, 2000). Currently, no regulations exist for radium isotopes in soil and sediment.

Two short-lived isotopes of radium also occur naturally, ^{223}Ra and ^{224}Ra, which are alpha-gamma emitters from the ^{235}U and ^{232}Th radioactive decay series (**Figure 2**) with half-lives of 11.4 days and 3.6 days, respectively. ^{223}Ra and ^{224}Ra are appropriate tracers for studying water circulation and mixing in nearshore lakes. Due to the low abundance of ^{235}U (0.72%) in the Earth's crust, ^{223}Ra is difficult to determine by gamma spectrometry; however, ^{223}Ra in water is measured by a delayed coincidence counter system (Moore & Arnold, 1996). In sediment, ^{224}Ra is primarily found in secular equilibrium with ^{232}Th and so with ^{228}Ra and continuously

produced by the alpha decay of ^{228}Th ($T_{1/2}$ = 1.9 y); however, in freshwater and seawater, ^{224}Ra shows different geochemical characteristics. In freshwater, ^{224}Ra is firmly bound onto particle surfaces; however, as the ionic strength increases during mixing with seawater, some ^{224}Ra may be released due to desorption. This process leads to some disequilibrium that may occur between ^{224}Ra and ^{228}Th in near-surface sediment. Measurements of ^{224}Ra in water (Sun & Torgersen, 1998; Kim et al., 2001; Parsa et al., 2005; Zhao et al., 2018) are reported quite often however, the measurements of ^{224}Ra in soil and sediment are scanty and time-consuming due to the chemistry of sample processing and counting procedure using a delayed coincidence counter (Cai et al., 2012; 2015). High-resolution gamma spectrometry has been successfully applied to measure the radium isotopes in drinking water (Khan et al., 2020), sediment (Khan et al., 2023; Dowdall et al., 2004; Herranz et al., 2006), and building materials (Suárez-Navarro et al., 2018). However, energy discrimination of ^{224}Ra and ^{226}Ra isotopes by gamma spectrometry is not always straightforward due to interfering energy peaks emitted by radium isotopes and their progeny (Lake et al., 2025).

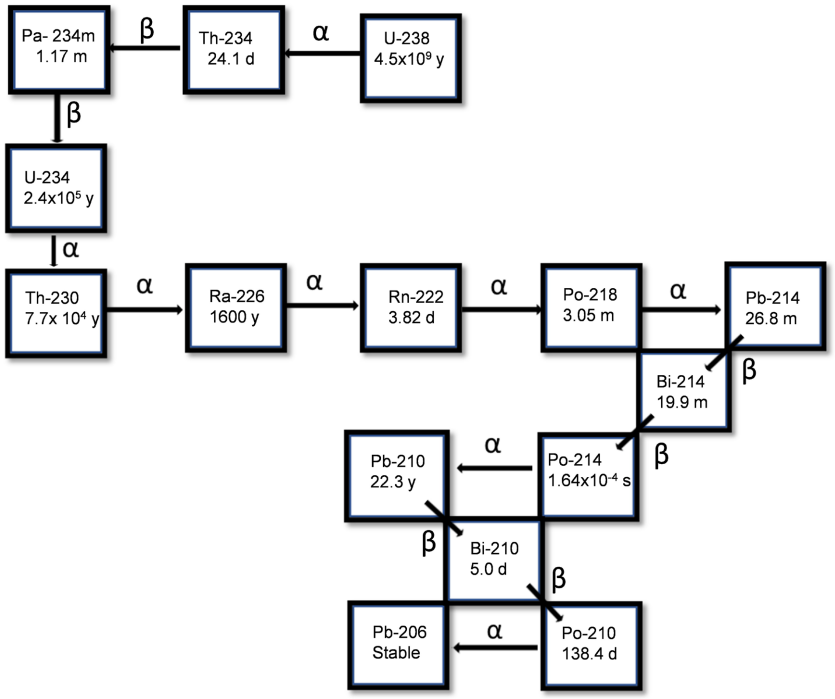

Figure 1. Decay scheme of ^{238}U natural radioactive series.

In addition to ^{224}Ra and ^{226}Ra, several other natural (^{40}K, ^{210}Pb, ^{228}Ra, ^{234}Th, ^{234m}Pa, ^{235}U) and anthropogenic (^{137}Cs and ^{241}Am) radionuclides were measured in soil, sediment, and CRM samples. The details of the gamma measurements of natural radionuclides are available in an earlier paper (Khan et al., 2023). This study is crucial for maintaining a reference data record (baseline) to document potential changes in natural and artificial radionuclides in the future, resulting from either contamination due to nuclear energy production or nuclear accidents. ^{137}Cs ($T_{1/2}$

= 30.05 ± 0.08 y) is the most common anthropogenic radionuclide in the environment, arising from fallout from nuclear weapon tests in the 1950s and early 1960s and the Chernobyl nuclear accident in 1986. The deposition density of ^{137}Cs from global fallout in the eastern US ranged from 2500 to 8000 Bq·m^{-2}, with some localized regions receiving even greater amounts (Simon et al., 2004). ^{137}Cs decays through ^{137m}Ba into stable ^{137}Ba via beta particles with E_{max} = 512 keV, Ba Kα X-rays at 32 keV, and a gamma energy line of 661.7 keV (I_γ = 85.1%). ^{241}Am is the most significant radioisotope of americium concerning its occurrence in the environment. The other long-lived isotope, ^{243}Am, is produced in nuclear reactors but has a smaller activity than ^{241}Am. The activity of ^{242m}Am ($T_{1/2}$ = 160 y), which originated from atomic weapons tests, was nearly six orders of magnitude lower than ^{241}Pu activity, from which ^{241}Am is derived. ^{241}Am is produced in nuclear power plants during the activation of ^{239}Pu and ^{240}Pu by neutrons, followed by beta decay of ^{241}Pu ($T_{1/2}$ = 14.35 y). ^{241}Am is detectable at minimal levels across the entire Northern Hemisphere due to atmospheric nuclear weapons tests in the 1950s and early 1960s.

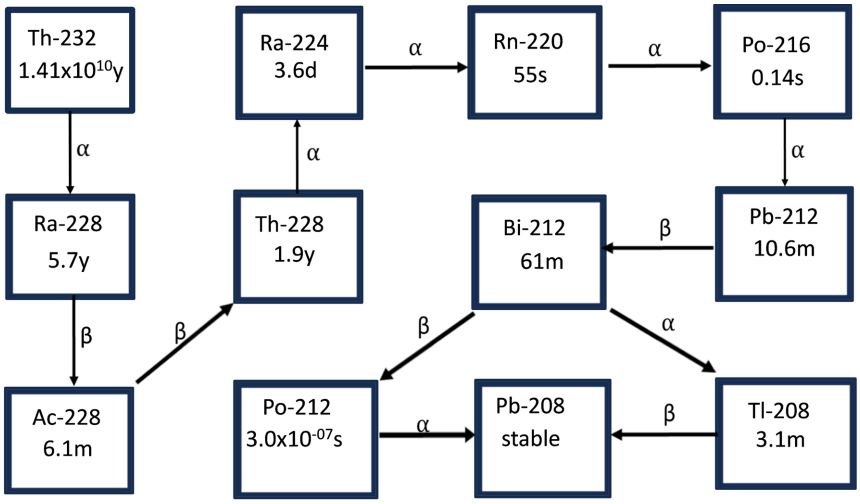

Figure 2. Decay scheme of ^{232}Th natural radioactive series.

In this paper, we applied the deconvolution method for the first time to directly measure the ^{224}Ra (E_γ = 240.99 keV; I_γ = 4.4.1%) and ^{226}Ra (E_γ = 186.21 keV; I_γ = 3.64%) activity in soil and sediment samples, correcting for spectral interference from ^{214}Pb (E_γ = 241.9 keV, I_γ = 7.26%) and ^{235}U (E_γ = 185.71 keV; I_γ = 57.2%) present in the matrices using ultra-low background gamma spectrometry (Haines et al., 2011; Khan et al., 2014). This method will save time for the ^{226}Ra measurement needed to establish secular equilibrium between ^{222}Rn progeny (^{214}Pb and ^{214}Bi). In this study, we used 143.76 keV (10.96%), 163.33 keV (5.08%), and 205.31 keV (5.01%) gamma energy lines to accurately measure the ^{235}U activity in soil and sediment samples using ultra-low background spectrometry, a capability that conventional gamma spectrometry lacks due to the low intensity of gamma energy lines and high background in the detector (Khan et al., 2023). We compared the

^{224}Ra activity in soil and sediment with that of ^{228}Ra, as ^{224}Ra is expected to be in secular equilibrium with ^{228}Ra. The ratio of ^{224}Ra/^{228}Ra provides insights into the disequilibrium of radionuclides in the matrices. The results for ^{226}Ra activity were also compared with those of the ^{222}Rn progeny (^{214}Pb and ^{214}Bi) after secular equilibrium was established with ^{226}Ra. Certified reference materials (CRMs) for soil and sediments were used to verify the activity results for ^{224}Ra and ^{226}Ra. Activities of several other radionuclides in CRMs, such as ^{40}K, ^{137}Cs, ^{238}U (via ^{234}Th and ^{234m}Pa), ^{235}U, and ^{241}Am, were also reported to validate our gamma measurement findings. For CRMs IAEA-312 (soil), no information is available in the literature or the report (Strachnov et al., 1991) concerning radionuclide activities, except for ^{226}Ra. In this paper, we present a detailed analysis of natural and anthropogenic radionuclide activity in IAEA-312 (soil) for the scientific community interested in utilizing this CRM for gamma soil analysis and quality control to verify their results for comparison.

2. Materials and Methods

2.1. Sample Collection and CRMs

The sediment samples (S1 to S4) were collected at various time intervals between 2018 and 2023 from the shoreline of the Lake Ontario boat launch (**Figure 3**, marked by a red star), precisely where the water meets the land. Depth was skimmed off the top at approximately 2 cm and sifted in the field to remove large rocks. One topsoil sample (500 g) was collected from a backyard, as shown in **Figure 3** (marked by a black cross) at a depth of 6 inches, and sieved for gravel and stones, along with one soil sample from the IAEA-2006 PT exercise that was used. The PT soil sample was milled and sieved to obtain the appropriate fraction at a mesh size of less than 0.1 mm before being homogenized. The soil matrix was characterized, and several samples were pre-screened for radionuclides before spiking. The results indicated that the material was free from radionuclides, except for ^{137}Cs, which was detected at 2.6 ± 0.2 Bq·kg^{-1} based on dry mass (Ref. date: 2006-01-01). Additionally, ^{210}Pb was found at 48 ± 1.5 Bq·kg^{-1} dry mass. The moisture content measured 2.3% ± 0.2% (Shakhashiro et al., 2007). The topsoil sample was kept in a cooler and transported to the laboratory, where it was dried overnight at 105˚C to achieve a constant weight. An aliquot of the soil sample (65.6 g) was then weighed and transferred into a 50 ML jar, filled to the top, and sealed with Phenoseal Vinyl Adhesive Caulk (PHENOSEAL, Baltimore, MD 21224) and black electrical tape (S-17841; Uline, Pleasant Prairie, WI 53158) to prevent the escape of ^{222}Rn gas from the container. CRM samples were also counted in a 50 ML geometry. Before gamma counting, the sediment sample was allowed to sit for four weeks to ensure ^{226}Ra was in equilibrium with ^{222}Rn progeny (^{214}Pb and ^{214}Bi). The samples were counted for 60,000 s to 240,000 s on an Ultra-Low Background HPGe detector, depending upon the sample's size, activity, and geometry. The background was counted for 240,000 s. Radiological testing laboratories must validate their analytical methods using PTs and certified reference materials (CRMs)

as quality control tools to provide reliable and valid measurement results for method validation, quality control, and metrological traceability. For this purpose, four CRMs obtained from the IAEA were also analyzed: IAEA-447 (Moss Soil, MS), IAEA-312 (Soil), IAEA-412 (Pacific Ocean Sediment, PO), and IAEA-385 (Irish Sea Sediment, IS).

Figure 3. Location of sample collection (red star: sediment sample, black cross: topsoil sample; Source: Nations Online Project. New York State Map. http://www.nationsonline.org/).

2.2. Gamma Spectrometry

In this study, measurements were performed using a p-type coaxial high-purity germanium (HPGe) detector (Model GX13023, XtRa, Mirion Technologies, CT, USA) with a relative efficiency of approximately 140%. The detector is housed in a copper cryostat with a carbon-composite top-entry window of 0.62 mm thickness, providing sensitivity to photon energies as low as ~10 keV. The spectrometer is installed inside a room constructed of 15-cm-thick pre-World War II steel (Dixie Manufacturing Co., Baltimore, MD, USA), located beneath a 47-story building that provides approximately 33 m of water-equivalent (mwe) overburden for vertical cosmic-ray attenuation. To further suppress ambient radiation, the detector is enclosed in a custom-designed, three-layer ultra-low-background lead shield with a total thickness of 17 cm and is surrounded on five sides by plastic scintillation panels for active muon rejection (Khan et al., 2014). Under this configuration, the system exhibits an integrated background rate of 2.4 counts per

minute (cpm) over the gamma-energy range from 50 to 2700 keV, corresponding to approximately 15 counts·s^{-1}·kg^{-1} of germanium. Energy and efficiency calibrations of the detector were performed as described elsewhere (Khan et al., 2023). Nuclear decay data, including half-lives and gamma-ray emission probabilities, were obtained from the Brookhaven National Laboratory database (https://www.nndc.bnl.gov/nudat3/).

While radiochemical separation techniques are typically required to detect low-level ^{241}Am in soils and sediments, where surface activities are often on the order of 20 - 40 Bq·m^{-2}. Its presence can also be resolved by ultra-low-background gamma spectrometry via the 59.5 keV gamma emission. The sensitivity of the present system enables direct detection of ^{241}Am at environmental levels without the need for extensive chemical preconcentration.

2.3. ^{224}Ra Measurements

^{224}Ra decays with gamma emission at 240.99 keV (I_γ = 4.10%). However, this gamma line must be deconvoluted from another gamma-ray energy of 241.99 keV (I_γ = 7.26%) emitted by ^{214}Pb. ^{214}Pb also emits distinct gamma energy lines at 295.22 keV (I_γ = 18.47%) and 351.93 keV (I_γ = 35.72%). These two gamma energy lines were used for interference correction. In soil and sediment, ^{224}Ra is in secular equilibrium with the radionuclides of the ^{232}Th decay series. In this paper, we measured the ^{224}Ra activity using the gamma energy line of 240.99 keV in soil and sediment samples, correcting for interference from the ^{214}Pb. The weighted mean activity of ^{214}Pb from the gamma energy lines of 295.22 keV (I_γ = 18.47%) and 351.93 keV (I_γ = 35.72%) was measured through ultra-low background spectrometry and subtracted from the ^{224}Ra activity measured by the 240.99 keV energy line. The ^{224}Ra activity is also measured in CRMs, with results compared to those of ^{228}Ra and ^{212}Pb in the samples. The interference correction was applied using the following equations. The count rate under the 241 keV peak was treated as a sum:

$$C_T\left(^{224}\mathrm{Ra};241\ \mathrm{keV}\right)=C_A\left(^{224}\mathrm{Ra};240.99\ \mathrm{keV}\right)+C_B\left(^{214}\mathrm{Pb};241.99\ \mathrm{keV}\right) \quad (1).$$

C_T is the total count rate under the peak area of 241 keV. This includes the contribution from ^{224}Ra and ^{214}Pb. C_A and C_B are the count rates of the peak area of 240.99 keV of ^{224}Ra and 241.99 keV of ^{214}Pb, respectively. C_B is calculated by using the equation below (Justo et al., 2006):

$$C_B\left(^{214}\mathrm{Pb},241.99\ \mathrm{keV}\right)=\frac{\left(^{214}\mathrm{Pb},295.22\ \mathrm{keV}\right)*\mathcal{E}_{241.99\ \mathrm{keV}}*I_{241.99}}{\mathcal{E}_{295.22\ \mathrm{keV}}*I_{295.22\ \mathrm{keV}}} \quad (2)$$

If the 351.93 keV peak of ^{214}Pb is also present, then the average of the count rates for both peaks is needed. In the above equation, $\mathcal{E}_\gamma$ is the efficiency of the gamma line of the radionuclide. I_γ is the emission probability of the gamma line. I_γ for 241.99 keV is 7.26%, for 295 keV is 18.47%, and for 351.93 keV is 35.72%. The activities of ^{224}Ra and ^{214}Pb are density and coincidence summing corrected. The gamma activities and uncertainties are calculated using the formula given

elsewhere (Khan et al., 2023).

2.4. ^{226}Ra Measurements

^{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, specifically ^{214}Pb and ^{214}Bi, after secular equilibrium is established with ^{226}Ra (approximately 4 weeks). Direct measurement of ^{226}Ra at 186.21 keV using gamma spectrometry is challenging due to interference from the 185.71 keV γ-peak of ^{235}U, necessitating correction for the interference from the ^{235}U (185.71 keV) peak. In this paper, we describe the measurement of ^{226}Ra activity in soil and sediment using E_γ = 186.21 keV; I_γ = 3.64% gamma energy peak after correcting for interference from ^{235}U (E_γ = 185.71 keV; I_γ = 57.2%) as detailed below:

The total count rate (C_T) at 186 keV peak is given as:

$$C_T\left(186\,\text{keV}\right) = C_{\text{U-235}}\left(^{235}\text{U},185.71\,\text{keV}\right) + C_{\text{Ra-226}}\left(^{226}\text{Ra},186.21\,\text{keV}\right) \tag{3}$$

$C_{\text{U-235}}$ is the count rate of ^{235}U under the peak of 185.71 keV, and $C_{\text{Ra-226}}$ is the count rate of ^{226}Ra under the peak of 186.21 keV. The count rate of ^{235}U in the 186 keV peak can be determined using the 143.76 keV peak below.

$$C_{\text{U-235}}\left(^{235}\text{U},185.71\,\text{keV}\right) = \frac{C_{\text{U-235}}\left(^{235}\text{U},143.76\,\text{keV}\right) * \mathcal{E}_{185.71\,\text{keV}} * I_{185.71}}{\mathcal{E}_{143.76\,\text{keV}} * I_{143.76\,\text{keV}}} \tag{4}$$

where $\mathcal{E}_\gamma$ is the efficiency of the individual gamma line depending upon the geometry of the container, and I_γ is the emission probabilities (57.2 % for E_γ = 185.71 keV; 10.94 % for E_γ = 143.76 keV). The activity for ^{235}U is calculated from the weighted mean activities of gamma energy lines of 143.76 keV, 163.33 keV, and 205.31 keV if all appear in the spectrum. The interference-corrected direct ^{226}Ra activity in soil, sediment, and CRM samples was compared with the activities of ^{222}Rn progeny, i.e., ^{214}Pb and ^{214}Bi.

3. Results and Discussion

3.1. Interference-Corrected ^{224}Ra and Secular Equilibrium in the ^{232}Th Decay Series

The ^{214}Pb interference-corrected ^{224}Ra activities measured in soils, sediments, and certified reference materials (CRMs) are summarized in **Table 1**. A representative gamma spectrum for sediment sample S1, highlighting the principal gamma lines relevant to ^{224}Ra determination, is shown in **Figure 4**. Certified values for CRMs are indicated in parentheses in the tables.

In the Lake Ontario sediment samples (S1 - S4), the corrected ^{224}Ra activities are 23.8 ± 0.7, 23.7 ± 1.5, 23.1 ± 1.6, and 23.4 ± 2.7 Bq·kg^{-1}, respectively, yielding a mean activity of 23.5 ± 0.2 Bq·kg^{-1}. These values are in close agreement with the corresponding ^{228}Ra activities of 24.3 ± 0.2, 20.6 ± 0.2, 22.3 ± 0.2, and 23.8 ± 0.2 Bq·kg^{-1} (mean: 22.8 ± 0.8 Bq·kg^{-1}). The agreement between ^{224}Ra and ^{228}Ra, as well as with other ^{232}Th decay products (^{212}Pb, ^{212}Bi, and ^{208}Tl), is illustrated in **Figure**

5 and indicates that secular equilibrium is maintained in these sediments.

The near-unity $^{224}Ra/^{228}Ra$ ratios observed across all sediment samples suggest that ^{224}Ra remains in near-secular equilibrium with its parent ^{228}Th. This behavior reflects stable geochemical conditions within the Lake Ontario surface sediments, with no evidence for recent disturbance, resuspension, or pore-water exchange processes that would preferentially mobilize short-lived ^{224}Ra. The consistency of this ratio across samples collected at different times further supports the validity of equilibrium-based gamma-spectrometric assumptions for these sediments.

Table 1. Radionuclide activities in soil and sediment samples in $Bq{\cdot}kg^{-1}$.

Sample Type	^{224}Ra	^{228}Ra	^{212}Pb	^{212}Bi	^{208}Tl	^{226}Ra	^{214}Pb	^{214}Bi
IAEA-447 (MS)	43.8 ± 3.5	35.3 ± 0.7 (37.3 ± 2.0)*	35.8 ± 1.0 (37.3 ± 1.5)*	36.6 ± 2.1	35.5 ± 0.8	26.8 ± 5.6 (25.1 ± 2.0)	21.6 ± 0.6 (26.0 ± 2.0)*	20.3 ± 0.5 (24.8 ± 2.0)*
IAEA-312 (Soil)	289 ± 32	347 ± 4 (371 ± 41)**	314 ± 6	345 ± 10	325 ± 4	296 ± 28 (250 - 287)	245 ± 4	234 ± 3
IAEA-2006 Soil (PT)	80 ± 19	58.6 ± 0.9	60.6 ± 1.6	56.3 ± 3.2	59.5 ± 1.1	42.5 ± 7.2	47.3 ± 0.8	46.6 ± 0.8
Soil (BS)	21.8 ± 3.4	23.3 ± 0.5	23.2 ± 0.7	21.1 ± 1.6	23.3 ± 0.5	32.4 ± 7.7	33.1 ± 0.6	33.1 ± 0.6
Sediment (S1)	23.8 ± 0.7	24.3 ± 0.2	23.6 ± 0.4	23.4 ± 0.5	24.0 ± 0.5	24.6 ± 1.4	24.3 ± 1.4	23.3 ± 0.2
Sediment (S2)	23.7 ± 1.5	20.6 ± 0.2	19.1 ± 0.6	20.9 ± 0.2	20.1 ± 0.2	23.2 ± 1.9	20.7 ± 0.2	19.9 ± 0.2
Sediment (S3)	23.1 ± 1.6	22.3 ± 0.2	21.1 ± 0.4	22.8 ± 0.5	21.8 ± 0.2	22.6 ± 1.3	21.7 ± 0.3	22.2 ± 0.2
Sediment (S4)	23.4 ± 2.7	23.8 ± 0.2	22.5 ± 0.3	22.7 ± 0.4	22.1 ± 0.2	24.4 ± 1.1 20.7 ± 3.8	23.3 ± 0.2	22.2 ± 0.2
IAEA-385 Sediment (IS)	33.7 ± 3.0	33.6 ± 0.5	33.4 ± 0.9	33.6 ± 1.5	33.6 ± 0.8	(22.8 ± 0.6)	23.5 ± 0.4	22.6 ± 0.4
IAEA-412 Sediment (PO)	38.7 ± 3.2	36.4 ± 0.5 (36.2 ± 2.3)	35.5 ± 0.9	36.7 ± 1.4	35.9 ± 0.6	26.9 ± 3.3 (27.4 ± 1.0)	25.5 ± 0.4	25.0 ± 0.4

*Values taken from the reference: IAEA/AQ/22; ** Value taken from the reference: Farias et al. (2011).

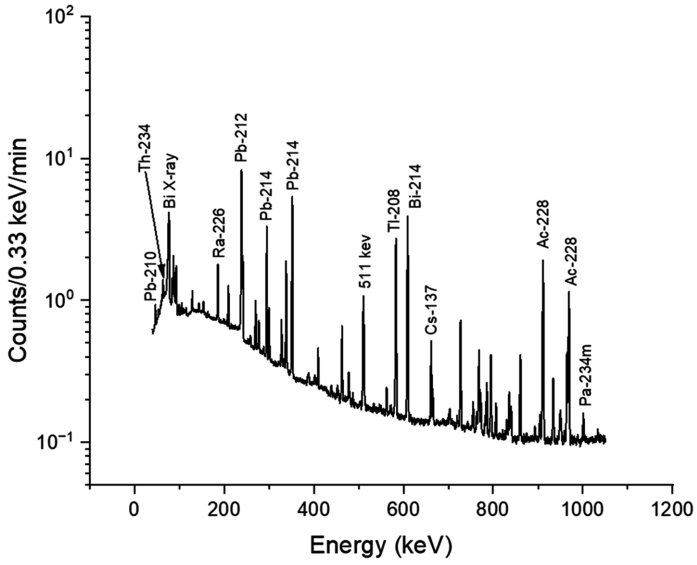

Figure 4. Gamma spectra of the sediment sample (S3) showing major gamma lines.

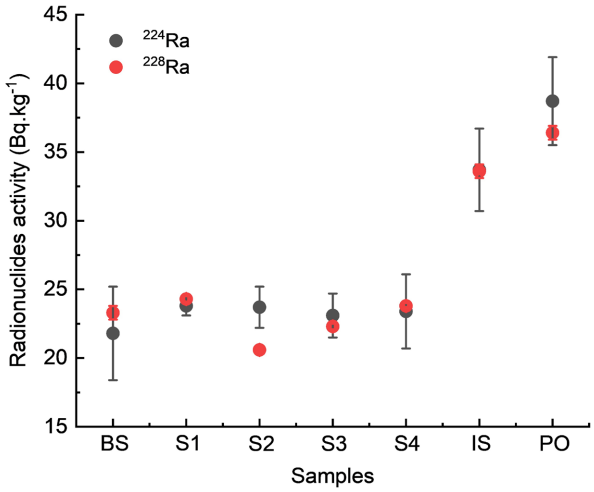

Figure 5. ^{224}Ra and ^{228}Ra in soil and sediment samples.

Independent confirmation of the interference correction is provided by CRMs. For IAEA-412 (PO), the certified ^{228}Ra activity is 36.2 ± 2.3 Bq·kg^{-1}, while the measured value in this study is 36.4 ± 0.5 Bq·kg^{-1}. The corresponding corrected ^{224}Ra activity is 38.7 ± 3.2 Bq·kg^{-1}, in agreement within uncertainty. Similar consistency between ^{224}Ra and ^{228}Ra is observed in IAEA-385, IAEA-447, IAEA-312, and IAEA-2006 PT soil samples, demonstrating that the ^{214}Pb interference correction yields accurate ^{224}Ra activities across diverse matrices.

3.2. Verification of ^{226}Ra Correction for ^{235}U interference

Direct ^{226}Ra measurements obtained from the 186.21 keV gamma line were corrected for interference from the closely spaced ^{235}U gamma line at 185.71 keV. The corrected ^{226}Ra activities are listed in Table 1 and compared with indirectly derived ^{226}Ra activities based on the short-lived ^{222}Rn progeny, ^{214}Pb, and ^{214}Bi. Figure 6 illustrates the strong agreement between these independent determinations.

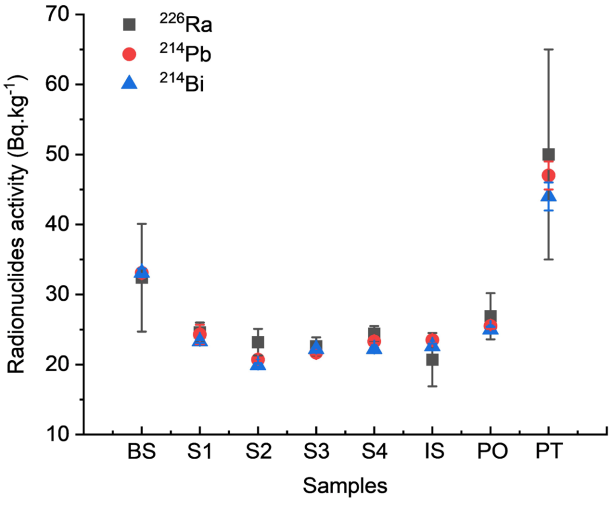

Figure 6. ^{226}Ra, ^{214}Pb, ^{214}Bi activities in soil and sediment samples.

In the Lake Ontario sediments (S1 - S4), the corrected ^{226}Ra activities range from 22.6 ± 1.3 to 24.6 ± 1.4 Bq·kg^{-1}, with a mean value of 24.2 ± 0.9 Bq·kg^{-1}. These values are consistent with the corresponding ^{214}Pb activities (mean: 22.5 ± 0.8 Bq·kg^{-1}) and ^{214}Bi activities (mean: 22.0 ± 0.1 Bq·kg^{-1}), confirming that secular equilibrium between ^{226}Ra and its progeny is preserved in these sediments.

In soil samples, the BS soil shows a corrected ^{226}Ra activity of 32.4 ± 7.7 Bq·kg^{-1}, in excellent agreement with the ^{214}Pb and ^{214}Bi activities of 33.1 ± 0.2 Bq·kg^{-1}. Similarly, in the IAEA-2006 PT soil, the corrected ^{226}Ra activity of 50.0 ± 15 Bq·kg^{-1} aligns with the ^{214}Pb and ^{214}Bi activities of 47 ± 2 and 44 ± 2 Bq·kg^{-1}, respectively.

CRM measurements further validate the correction approach. For IAEA-447 (MS), the measured ^{226}Ra activity of 26.8 ± 5.6 Bq·kg^{-1} agrees with the certified value of 25.1 ± 2.0 Bq·kg^{-1}. In IAEA-312 (soil), the measured activity of 296 ± 28 Bq·kg^{-1} falls within the certified range of 250–287 Bq·kg^{-1} (95% confidence interval). For sediment CRMs IAEA-385 (IS) and IAEA-412 (PO), the measured ^{226}Ra activities (22.8 ± 0.6 and 26.9 ± 3.3 Bq·kg^{-1}, respectively) closely match the certified values, confirming that the combined ^{235}U interference correction and ultra-low-background counting approach yields accurate ^{226}Ra determinations.

3.3. Natural and Anthropogenic Radionuclides in Soils, Sediments, and CRMs

Activities of additional natural and anthropogenic radionuclides are summarized in Table 2. The ^{40}K activity in the BS soil sample is 598 ± 15 Bq·kg^{-1}, while sediment samples S1 - S4 range from 531 ± 11 to 632 ± 12 Bq·kg^{-1}, with a mean value of 566 ± 8 Bq·kg^{-1}. These values fall within the global range of 140 - 850 Bq·kg^{-1} reported by UNSCEAR (2000), indicating typical lithogenic contributions.

Table 2. Anthropogenic and natural radionuclide activities in soil and sediment in Bq·kg^{-1}.

Sample type	^{40}K	^{137}Cs	^{210}Pb	^{234}Th	^{234m}Pa	^{235}U	^{241}Am
IAEA-447 (MS)	520 ± 13 (550 ± 18)	313 ± 9 (328 ± 8)	333 ± 9 (306 ± 15)	22.4 ± 3.6 (22.2 ± 0.8)	29.0 ± 8.9 (22.2 ± 0.8)	1.7 ± 2.9 (NA)	1.9 ± 0.3 (2.3 ± 0.2)
IAEA-312 (Soil)	433 ± 11	88 ± 2	826 ± 24	214 ± 25	176 ± 19 (194 ± 9)	9.1 ± 1.2	
IAEA-2006 Soil (PT)	710 ± 18	52.4 ± 1.5 (52.6 ± 1.1)	293 ± 10 (260 ± 13)	28.1 ± 8.1	28.1 ± 12.0	1.96 ± 0.6	101.7 ± 2.0 (96.6 ± 2.8)
Soil (BS)	598 ± 15	1.4 ± 0.1	66.5 ± 3.1	28.2 ± 3.9	31.4 ± 8.7	1.7 ± 0.7	
Sediment (S1)	542 ± 11	0.79 ± 0.02	24.4 ± 1.7	24.4 ± 2.9	22.3 ± 1.9	1.2 ± 0.1	
Sediment (S2)	632 ± 12	0.96 ± 0.03	BDL*	19.4 ± 7.5	19.7 ± 4.4	0.88 ± 0.2	
Sediment (S3)	531 ± 11	1.1 ± 0.02	BDL*	21.2 ± 2.5	20.0 ± 1.3	1.0 ± 0.1	
Sediment (S4)	563 ± 11	0.87 ± 0.02	BDL*	22.2 ± 2.3	21.0 ± 1.4	0.97 ± 0.09	
IAEA-412 Sediment (PO)	539 ± 13 (561 ± 26)	5.0 ± 0.2 (5.7 ± 0.2)	104 ± 2.9 (88.2 ± 3.2)	34.4 ± 4.0 (31.2 ± 1.7)	35.3 ± 6.1 (31.2 ± 1.7)	1.7 ± 0.3 (1.4 ± 0.05)	

*Below detection limit as explained in Khan et al., (2023).

The measured ^{137}Cs activity in the soil sample is 1.4 ± 0.1 Bq·kg^{-1}, while sediment samples show lower activities ranging from 0.79 ± 0.02 to 1.1 ± 0.02 Bq·kg^{-1} (mean: 0.93 ± 0.03 Bq·kg^{-1}). These values are consistent with reported ranges for surface soils and sediments in the United States, where ^{137}Cs activities vary widely depending on fallout history and sedimentation processes (McHenry et al., 1973; Hamilton, 1997). The relatively low ^{137}Cs activities in the Lake Ontario sediments suggest limited recent anthropogenic input and post-depositional redistribution.

The ^{210}Pb activity in the BS soil is 66.5 ± 3.1 Bq·kg^{-1}, while sediment sample S1 shows an activity of 24.4 ± 1.17 Bq·kg^{-1}; samples S2 - S4 are below the detection limit. This pattern is consistent with atmospheric deposition of excess ^{210}Pb and variable sediment mixing. The activities of ^{234}Th and ^{234m}Pa are in close agreement in both soils and sediments, confirming near-secular equilibrium with parent ^{238}U. The measured ^{235}U activities in BS soil (1.7 ± 0.7 Bq·kg^{-1}) and sediments (mean: 1.01 ± 0.12 Bq·kg^{-1}) are consistent with global background levels reported by UNSCEAR (2000).

CRM results further demonstrate the accuracy of the measurements. For example, in IAEA-2006 (PT) soil, the measured ^{60}Co activity of 58.3 ± 2.5 Bq·kg^{-1} agrees with the certified value of 56.1 ± 1.4 Bq·kg^{-1}. Similarly, measured ^{137}Cs and ^{210}Pb activities in IAEA-447 (MS), IAEA-412 (PO), and IAEA-312 (soil) closely match certified values, confirming the reliability of the ultra-low-background gamma spectrometry system.

3.4. Methodological Implications and Limitations

The combined results demonstrate that interference-corrected ultra-low-background gamma spectrometry enables accurate determination of ^{224}Ra and ^{226}Ra in soils, sediments, and CRMs. The agreement between corrected activities, decay-chain progeny, and certified values supports the robustness of the methodology for routine environmental monitoring, regulatory assessments, and characterization of both Naturally Occurring Radioactive Material (NORM) and Technologically Enhanced Naturally Occurring Radioactive Material (TENORM) materials.

However, the approach relies on assumptions of secular equilibrium and accurate deconvolution of closely spaced gamma peaks. Deviations from equilibrium, matrix heterogeneity, or uranium-series disequilibrium could introduce additional uncertainty and should be assessed on a case-by-case basis. Complementary analytical techniques, such as alpha spectrometry or radon emanation measurements, may further strengthen interpretations in complex or disturbed systems.

4. Conclusion

This study demonstrates the effectiveness and reliability of ultra-low-background gamma spectrometry for determining natural and anthropogenic radionuclide activities in environmental matrices, including soils, sediments, and certified reference materials (CRMs). The corrected activities of ^{224}Ra in sediments and soils, following interference adjustment for ^{214}Pb, were found to be in close agreement

with the activities of ^{228}Ra and other daughter products of the ^{232}Th decay series (^{212}Pb, ^{212}Bi, and ^{208}Tl), indicating that secular equilibrium prevails in these samples. Similarly, the consistency between directly measured ^{226}Ra activities and those derived indirectly from ^{214}Pb and ^{214}Bi confirms the validity of the energy interference correction between ^{226}Ra and ^{235}U gamma peaks.

The measured ^{226}Ra activities in soils, sediments, and CRMs such as IAEA-447, IAEA-312, IAEA-385, and IAEA-412 were in strong agreement with certified values, affirming the accuracy of the analytical method. The detection of ^{40}K, ^{137}Cs, ^{210}Pb, ^{234}Th, ^{234}mPa, ^{235}U, ^{241}Am, and ^{60}Co in various environmental samples also aligned closely with global average values and CRM certificates.

The interference-corrected gamma-spectrometric approach provides a reliable and time-efficient means for the direct quantification of radium isotopes while simultaneously validating equilibrium conditions within natural decay chains. The demonstrated method is well-suited for routine environmental radioactivity monitoring, regulatory and compliance-driven assessments, and the characterization of NORM and TENORM impacted sites, offering a practical alternative to more labor-intensive radiochemical techniques while maintaining high analytical confidence.

Authorship Contribution Statement

Abdul J Khan: Project Design, Conceptualization, Methodology, Data Analysis, Data curation, Writing-Original Draft, Literature Survey, Supervision; Umme-Farzana Syed: Sample Preparation, Review and Editing; Cynthia A. Costello: Sample Collection and Distribution, Review and Editing.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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