

Article

Determination of Heavy Metal Concentration in Borehole Water and Mineral Composition, and Radionuclides in Sediments from Ha-Masia Tshikwarani Village

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Abstract: Groundwater in rural regions of South Africa is recognised as the primary source of drinking water. The quality of this water is affected by the presence of heavy metals and minerals from rocks. Soil samples were collected in May (dry season) and November (wet season) to support assessments of groundwater quality and subsurface lithology, and no dynamic water levels were measured during these samplings. The quantities of heavy metals in the borehole water and soil sediments were measured using an ICP-OES. As, Cd, and Ni were not detected, while Cr was detected at an average concentration of 0.003 mg/L in May and 0.006 mg/L in November. The elemental composition of the sediment was determined by XRD, which identified 13 minerals, including Quartz (1.7–22.4 wt.%), Albite (11.5–47.9 wt.%), and Mica (6.3–24.6 wt.%). The AT6101DR detector was used to analyse radionuclide levels in soil sediment, including ^{40}K , ^{212}Pb , ^{228}Ac , ^{208}Ti , and ^{214}Bi , at depths of 19 m, 57 m, 63 m, 83 m, and 120 m. At depths of 3 m and 46 m, ^{40}K , ^{228}Ac , and ^{208}Ti were present. The overall dose rate for radionuclides ranged from 0.067 to 0.078 $\mu\text{Sv/h}$, equivalent to 586.92 to 683.28 $\mu\text{Sv/yr}$, which is below the permissible limit of 1000 $\mu\text{Sv/yr}$. The findings offer crucial information for consumers, and ongoing monitoring is advised to maintain water safety.

Keywords: Heavy Metals; X-Ray Diffraction; Mineral Compositions; Water Quality; Inductively Coupled Plasma Optical Emission Spectrometer; Radionuclides; Borehole

1. Introduction

Water is an inorganic, transparent, tasteless, odourless, and nearly colourless chemical compound that is essential for supporting global socioeconomic progress and all known forms of life [1]. Access to clean and safe water is linked to improved global health outcomes. However, despite advances in making potable water more accessible, millions still face preventable health problems caused by drinking contaminated water [2]. Water primarily comes from two natural sources: surface water, including lakes, rivers, and streams, and groundwater, which includes borehole and healthy water [3]. Groundwater is a key water resource and plays a vital role in human social development, local livelihoods, and the maintenance of ecological balance and biodiversity, especially in arid and semi-arid areas [4]. Research conducted in rural and semi-arid areas indicates that groundwater quality is shaped by both natural processes and human activities. To evaluate water quality, detect patterns, and promote sustainable groundwater management, scientists analyze major ions and trace metals and apply statistical methods such as correlation analysis and principal component analysis (PCA) [4,5].

Groundwater is often favoured over surface water due to its natural protection from pollution and effective

filtration as it percolates through soil. As a vital resource, it is essential for human life due to its perceived high microbiological quality. This makes groundwater a common choice for drinking water, with treatment generally limited to disinfection. It is typically clean, odourless, and can have a pleasant taste, making it appealing to many people. Nonetheless, although groundwater is often perceived as safe, numerous studies have shown that it can also be vulnerable to contamination [6]. According to Buba and Maina [3], it is noted that groundwater contamination can arise from both natural processes and human activities, which may be linked to geological formations, as well as sources such as domestic, agricultural, or industrial activities. The residents of Ha-Masia Tshikwarani depend on groundwater extracted from a borehole as their primary water supply throughout the year. This borehole water is crucial for meeting the daily needs of most of the local population, given the unreliability of other water sources.

Heavy metals like lead, arsenic, chromium, cadmium, and mercury can be hazardous to human health when ingested in large amounts because of their toxic nature and potential to cause cancer [7]. Heavy metals are metallic elements characterised by their high density (mass per unit volume) and toxicity, even at minimal concentrations. These metals and metalloids have an atomic density greater than 4 g/cm^3 , which is five times that of water [3]. Heavy metals are naturally occurring elements that can infiltrate groundwater due to geological processes, human activities, or leaching from adjacent soil and rocks [8]. For instance, heavy metals such as nickel can enter the environment from mafic and ultramafic rocks, as well as the soils derived from them, due to weathering and pedogenesis [9].

The contamination of groundwater by heavy metals is a growing concern in developing nations, driven by rapid urban growth, inadequate waste disposal, human-related activities, and industrial operations [1,8]. A study conducted by Mabe, Gololo, and Molefe [10] assessed the presence of heavy metals in borehole water and identified substandard water quality in Ga-Matlala, Limpopo Province, South Africa, with lead (Pb) levels surpassing the World Health Organization (WHO) recommended limits. In several Nigerian cities, well and borehole water have been found to contain heightened concentrations of Cd and Cr, exceeding the guidelines set by the WHO and the Nigerian Standard for Drinking Water Quality (NSDWQ) [3].

A radionuclide, also known as a radioisotope, is an unstable variant of a chemical element that undergoes radioactive decay, emitting radiation as it gradually stabilizes. These radionuclides can occur naturally or be manufactured artificially. Soil plays a crucial role in radioactivity, serving as the primary source of radiation exposure to humans and accounting for approximately 67.7% of this exposure [11]. Radiation emissions can result in health problems like cancer and skin burns, varying with exposure levels, and pose a significant risk to human health [12]. Radionuclides can infiltrate the food chain via plants, accumulating in both humans and animals, which may have health implications. They also influence water and air quality through the ecological cycle [11].

Naturally occurring radioactive materials (NORM) comprise radionuclides that originate from natural processes, such as volcanic eruptions and erosion. The primary isotopes include uranium (U), thorium (Th), radium (Ra), radon (Rn), lead (Pb), and polonium (Po) [13]. Furthermore, the levels of naturally occurring radionuclides in soil vary due to geographic and geological influences, resulting in their uneven distribution across the Earth's surface [14]. While roughly 85% of the general population's annual exposure to ionizing radiation comes from natural sources such as uranium, thorium, radium, and radon gas, various human activities, including nuclear accidents, weapons testing, mineral extraction, and the application of certain fertilizers, can also elevate radiation levels in the surrounding environment [14,15]. Studies indicate that soil in regions with granitic rock exhibits higher levels of radionuclides compared to areas with sedimentary rock [12]. Monitoring and assessing the distribution of radionuclides in soil sediments from boreholes is essential due to the non-uniform distribution and radionuclide levels exceeding recommended thresholds in certain regions, which can lead to related health effects [14].

While groundwater is crucial for rural populations, the study area depends on a single communal borehole of 126 m below ground surface as its primary water supply. The setting is largely rural and lacks major industrial activities. While no prior groundwater quality assessments have been carried out specifically at this site, studies from comparable hard-rock aquifer systems suggest that geological characteristics and water-rock interactions can play a major role in shaping groundwater quality [16]. Determining the metal content in sediments is important because of their potential effect on groundwater quality and their ability to point to possible contamination sources based on the types of rocks and soils involved. Access to clean and safe water is crucial for human health, environmental sustainability, and economic development. In many rural South African communities, untreated groundwater drawn from communal boreholes serves as the primary source of water. This study targets the region because of its

heavy reliance on groundwater and the absence of comprehensive water quality information. Earlier studies have shown that interactions between water and surrounding rock, as well as underlying geological conditions, can affect groundwater quality [17]. This study aims to measure the concentration of heavy metals in the borehole, analyse the mineral composition of the borehole sediments, and assess the presence of radionuclides in soil sediments. The goal is to ensure that the water quality is safe and suitable for human use. The study's findings will raise awareness among Ha-Masia Tshikwarani residents and support the development of sustainable water systems in the region.

2. Materials and Methods

2.1. Study Area

The study area is situated in the northern part of South Africa, specifically within the Limpopo Province. It is part of the Vhembe District Municipality, which comprises four local municipalities: Thulamela, Makhado, Musina, and Collins Chabane, as illustrated in **Figure 1**. Ha-Masia Tshikwarani is located at the geographic coordinates of $23^{\circ}11'4.1''$ S and $30^{\circ}18'35.2''$ E, as depicted in **Figure 1**. The geographic coordinates specify the exact position of the community borehole that was sampled, which served as the sole sampling site in this study, according to the Vhembe District Municipality [18]. The climate of the area is typically subtropical, characterised by mild, moist winters and wet, warm summers, particularly in the Lowveld region, which can be arid and semi-arid. In Vhembe District Municipality [18]. It was further revealed that the area receives an annual rainfall of approximately 500 mm, with about 87.1% of this rainfall occurring between October and March. The rainfall pattern is significantly influenced by the orographic effect of the Drakensberg Mountains, which intersect with the Soutpansberg Mountains, leading to a decrease in rainfall from east to west across the district. Annual temperatures range from a minimum of 10°C in winter to a maximum of around 40°C , especially in the Musina Local Municipality [18]. The regions consist of intrusive igneous, sedimentary, and metamorphic rocks, indicating a fractured hard-rock aquifer system. They are underlain by the Goudplaats River Gneiss geological formation, which is part of the Limpopo Belt. The dominant composition of the Goudplaats-Hout River suite includes light to dark grey gneisses, along with some minor leucocratic gneisses, hornblende amphibolite, and hornblende-biotite tonalitic gneisses [18,19].

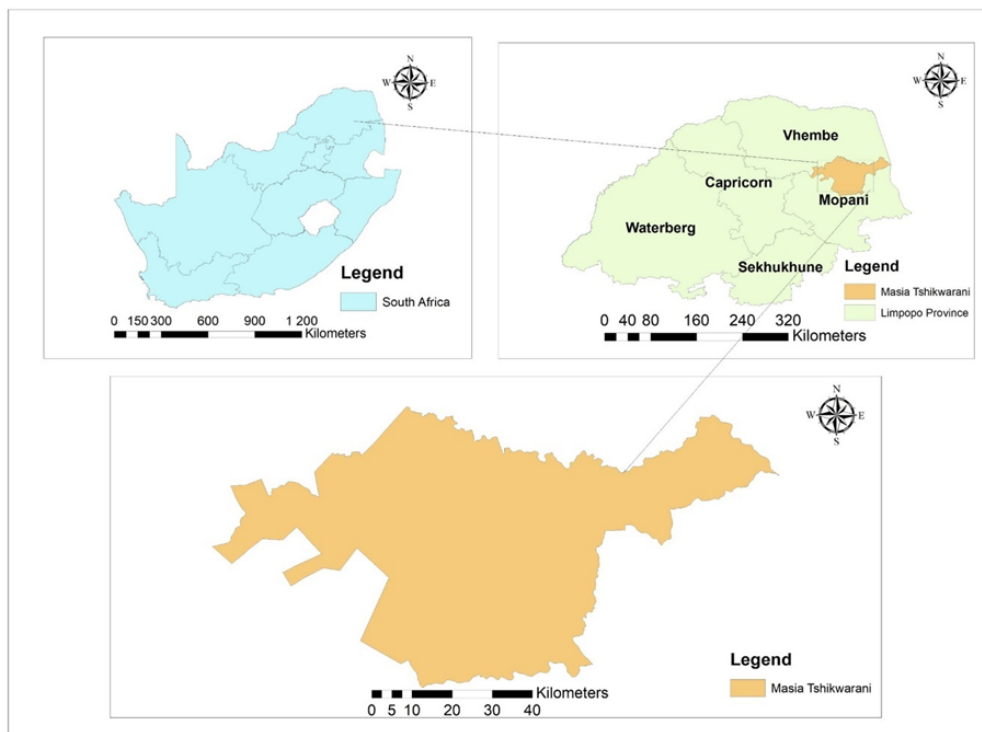


Figure 1. Map of the study area and sampling site (Community Borehole): $23^{\circ}11'4.1''$ S, $30^{\circ}18'35.2''$ E [20].

2.2. Sample Collection and Preparation

In this study, water and sediment were obtained from a single community borehole, the main water source for the area situated at 23°11'4.1" S, 30°18'35.2" E. A random sampling approach was used to collect samples from the borehole, which is 126 m deep.

2.2.1. Collection of Water Samples

Groundwater samples from the Ha-Masia Tshikwarani borehole were collected during two seasonal periods, in May (dry season) and November (wet season), using sterilised glass jars labelled BH (May) and BH (Nov). To prevent contamination, a new pair of disposable gloves was worn for each sample. Before collection, the jars and their lids were thoroughly rinsed, following a recommended procedure by Okorie, Okechukwu, and Omokpariola [7]. Static and dynamic water levels were not recorded during the sampling campaign; however, samples were taken from the borehole tap only after the tap had been running continuously for at least five min. However, no data were recorded regarding the duration of prior groundwater use.

2.2.2. Soil Sediment Samples (Borehole Cuttings)

A total of 126 sediment samples were obtained through coring from a borehole with a depth of 126 m, yielding one sample for each metre interval. Throughout the drilling operation to a depth of 126 m, the borehole penetrated a combination of worn, fractured, igneous, sedimentary, and metamorphic rocks. Sediment samples were obtained at intervals throughout the borehole to facilitate the evaluation of lithological composition and groundwater quality. Cutting samples were collected and allowed to dry naturally on-site. These samples were subsequently stored in labelled, sealed plastic bags and organised in a box for preservation. While sediment samples were obtained from the whole drilling depth (0–126 m), comprehensive heavy metal studies were performed on representative samples chosen from depths of 119 m to 125 m below ground surface. These depths were selected because these levels coincide with groundwater-bearing and fractured zones, where water-rock interaction is more significant, and due to equipment, time, and resource constraints.

2.3. Heavy Metal Analysis

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was employed to detect metallic elements in sediment and water samples. For the analysis of heavy metals in water, a preservation method was utilised in which 45 mL of groundwater was combined with 5 mL of nitric acid in a microwave digestion vessel, following the procedure specified by Mabe et al. [10]. The mixture was digested for 20 to 30 min. Aqua regia was prepared by mixing concentrated HNO_3 and HCl acids at a ratio of 1:3, respectively. This solution was subsequently combined with 0.5 g of powdered soil sediment in each vessel [21] to digest sediment samples at the Hydrology and Water Resources Laboratory, University of Venda, using a Microwave Digestion System before ICP-OES analysis. After digestion, all samples were cooled at room temperature. Once cooled, the solutions were filtered using standard filtration techniques and transferred into a 50 mL Falcon conical centrifuge tube. They were then stored in a refrigerator and analysed. Metal concentrations were measured using a PerkinElmer Optima 8000 ICP-OES, which has a detection limit of 0.0001 ppm. The relative standard deviation, calculated from triplicate analyses, was under 3%. **Table 1** below summarises the experimental conditions for the Optima™ 8000 ICP-OES.

2.4. Sediment Samples Analysis (Borehole Cuttings)

The mineral content of the sediment sample was ascertained through X-ray diffraction (XRD). The sediment samples were microwave-dried and then ground into fine powders using a Restch-RS 200 milling machine for about five (5) min before XRD analysis [22]. To avoid contaminating the new samples with residue from previous samples, it was essential to clean the milling pot with silica sand. Pellet-making equipment and a compressor were used to turn the samples into pellets after they had been fully ground into a fine powder. A representative and pulverised portion of the sample was measured using a Bruker D2 Phaser diffractometer, with a step size of 0.02°, a two (2)-theta (θ) angle, and a counting time of 1 s per step, applied over a range of 3° to 60° 2 θ . The method uses the net intensity of the prominent peaks of the mineral, and identification is based on the mineral's crystal structure. Only crystalline minerals/phases in amounts sufficient to diffract, usually not less than three mass percent, are detectable.

Table 1. The experimental conditions of Optima™ 8000 ICP-OES.

Parameters	Values
Plasma gas flow	8 L/min
Auxiliary gas flow	0.4 L/min
Nebuliser gas flow	0.6 L/min
Peristaltic pump flow rate	1.5 mL/min
RF power	1500 W
Viewing height	15 mm
Purge Flow	High
Read parameters	Auto
Processing Peak	Area
Calibration	Linear Calculated Intercept
Plasma view	Axial
Spray Chamber	Cyclonic Glass
Nebulizer	Concentric Glass, MEINHAR
Injector	Alumina 2.0 mm I.D
Quartz torch	1-slot

2.5. Radioactive Sample Analysis

A total of five (5) different soil sediments from various depths in the borehole were selected for radionuclide analysis. The activity of the radionuclides was measured using the AT6101DR detector at the University of Venda's physics lab, where the measurements were taken. The detector was mounted and calibrated at a height of 15 cm. Background checks, sample spectral analyses, and the use of potassium chloride as a halogen source were performed to calibrate the detector, and the peaks in the spectra were examined to determine the presence of specific radionuclides. In particular, the peak appearing at energies above 1.022 MeV, associated with pair production, was employed as a characteristic indicator for certain radionuclides. To display radioisotope composition data, including the effective activity of naturally occurring radionuclides and the specific activity or concentrations of individual radionuclides, the ALGIZ 10X computer software was used for processing instrumental spectra, as described by Nemangwele et al. [12]. The ambient dose equivalent rate for gamma radiation was also measured. The inspection site was identified using spectrum analysis with a spectrum-dose operating function.

2.6. Data Analysis

Groundwater quality was assessed using the Department of Water Affairs and Forestry (DWAF, 1996) guidelines, which are frequently referenced in South African research and facilitate comparison with past studies. Although newer standards such as SANS 241:2015 and the WHO guidelines are available, the DWAF limits remain suitable for evaluating borehole water in the rural setting, like Tshikwarani village. The data analysis presented in this study was conducted in triplicate using MS Excel. All results presented in the tables and figures were obtained from a single sampling site with the geographic coordinates of 23°11'4.1" S and 30°18'35.2" E.

3. Results and Discussion

3.1. Heavy Metal Concentration in Borehole Water

The concentrations of four selected metals, chromium (Cr), cadmium (Cd), arsenic (As), and nickel (Ni), in borehole water samples from Ha-Masia Tshikwarani were determined as described in the Methods (Section 2.3), ensuring accurate and reliable measurements for comparison with guideline values and were analysed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and compared to the Department of Water Affairs and Forestry (DWAF, 1996) [23] standards for drinking water quality. According to DWAF [23], ingesting water containing chromium concentrations above 0.05 mg/L may pose a potential risk of gastrointestinal cancer due to prolonged exposure, in addition to causing an unpleasant taste and mild nausea in humans. Results from this study showed that only chromium (Cr) was detected at 0.003 mg/L in May and 0.006 mg/L in November, which is well below the DWAF threshold of 0.05 mg/L (**Figure 2**). Arsenic, cadmium, and nickel were not detected in the water samples for either of the two seasonal periods. This indicates that the water meets DWAF (1996) criteria and it's suitable for consumption. While groundwater quality was mainly assessed using the Department of Water Affairs and Forestry (DWAF, 1996) guidelines, the detected chromium levels (0.003 and 0.006 mg/L) were also lower

than the World Health Organization (WHO) [24] drinking water guideline of 0.05 mg/L, demonstrating that the water meets both national and international standards. Although chromium (Cr) concentrations remained below the DWAF guideline threshold, a clear seasonal pattern was observed. Cr levels increased from 0.003 mg/L in May (dry season) to 0.006 mg/L in November (wet season). This increase is most likely linked to higher rainfall and surface runoff during the wet season, which transports metals from soils and sediments into the groundwater, and in the dry season, these contributions are comparatively minor [25]. Additionally, studies conducted in Ghana and other regions demonstrate that heavy metal concentrations, particularly chromium, frequently increase during the rainy season, when precipitation and runoff transport metals from the soil into adjacent water bodies [26,27]. The concentrations of chromium (Cr) in this study were considerably lower compared to those reported in the Limpopo region [6,28]. The average concentrations of chromium (Cr) in the borehole water during dry and wet seasonal periods of this study were lower than those reported by Varol and Tokatlı [29] in their research on seasonal variations of toxic metal(loid)s in groundwater from an intensive agricultural area in northwestern Turkey.

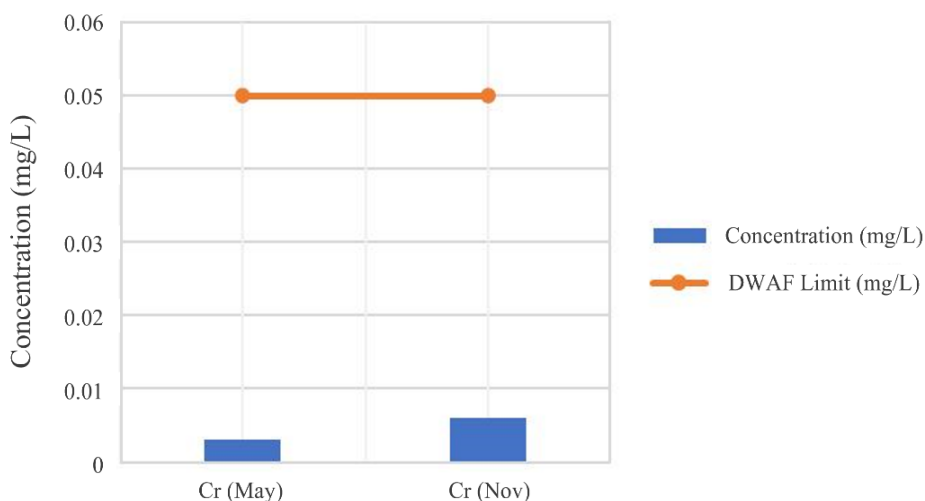


Figure 2. Cr Concentration of Borehole Water Samples.

Note: The horizontal dashed line represents the Cr guideline for drinking water (0.05 mg/L) [23].

A related investigation by Mutileni et al. [30] in the Vyeboom area of the Vhembe District, higher chromium (Cr) concentrations were reported, resulting in estimated carcinogenic risk indices that exceeded recommended thresholds. In contrast, a direct comparison of mean values shows that the Cr concentrations in the present study are considerably lower. This difference may be attributed to the geological characteristics of the study area and to local land use practices, such as agriculture, residential development, and natural forest cover [31]. A comparable investigation by Buba and Maina [3] examined the levels of specific heavy metals in borehole water and hand-dug well water in Jiwa village, located on the outskirts of Abuja, Nigeria. Their results revealed higher concentrations of chromium (Cr) than those observed in the current study. In a comparable investigation on the Assessment of Groundwater Quality, Heavy Metal Contamination, and Human Health Risks at the Roundhill Municipal Landfill in the Eastern Cape, South Africa, Silwani et al. [32] reported chromium (Cr) levels exceeding those observed in the present study. This indicates that leachate from the nearby landfill is markedly elevating heavy metal concentrations in groundwater. Statistical analyses confirmed landfill leachate as the primary source of pollution, underscoring the detrimental effects of waste disposal on groundwater quality.

Similar investigations by Okeke et al. [1] showed Cr concentrations higher than those found in this study. The differences in metal concentrations in the boreholes of this study, compared to previous studies, may result from factors such as distance from the contamination source, infiltration of contaminants into groundwater, soil contamination levels, and soil solubility [33]. Discrepancies may also result from variations in geographical location, study duration, study period, and contamination from industrial runoff [1]. In aquatic environments, chromium primarily exists as trivalent (Cr^{3+}) and hexavalent chromium (Cr^{6+}), with the latter known for its high toxicity and

carcinogenic potential. Elevated chromium levels in borehole water may indicate leaching from chromium-rich rocks or contamination from activities like metal plating, tanning, or inadequate industrial waste management [1]. Moreover, prolonged exposure to even small amounts of Cr^{6+} can be harmful, potentially causing kidney and liver damage or increasing the risk of cancer [34]. Therefore, it is advisable to continue monitoring and implement appropriate water treatment methods to prevent potential health hazards.

3.2. Heavy Metals Analysis in Sediment Samples

Heavy metals occur naturally in soils due to the weathering of underlying rocks. Their presence is influenced by environmental factors, including pH levels and the content of organic matter. Soil contamination poses risks to humans and ecosystems through direct contact, ingestion, the food chain, and contaminated drinking water, among other pathways [35]. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to examine soil sediments from borehole cuttings at specific depths to detect heavy metals. Four metals, arsenic (As), nickel (Ni), cadmium (Cd), and chromium (Cr), were analysed three times each. Only nickel and chromium were identified in the examined sediment depths (**Figures 3 and 4**), whereas arsenic and cadmium were absent. The measured concentrations were compared to the Canadian Council of Ministers of the Environment (CCME) sediment quality guidelines (SQGs) [36], where Threshold Effect Level (TEL) and Probable Effect Level (PEL) are the threshold effect level and the probable effect level, respectively.

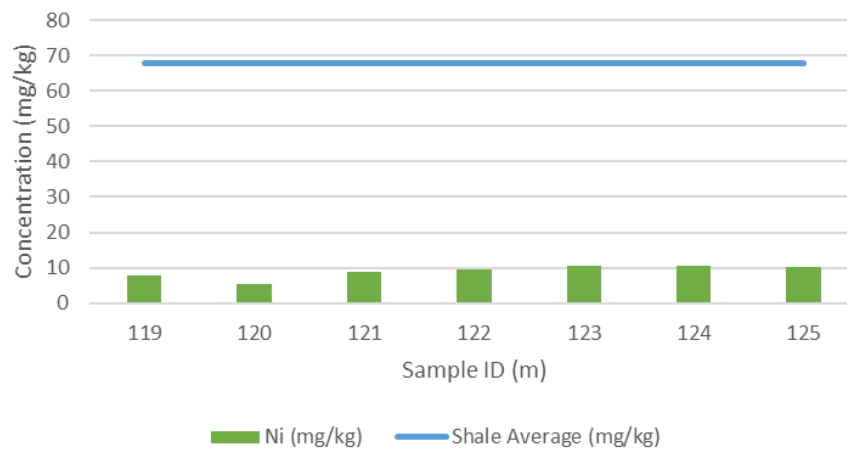


Figure 3. Concentration of Nickel from Soil Sediments (Borehole Cuttings).

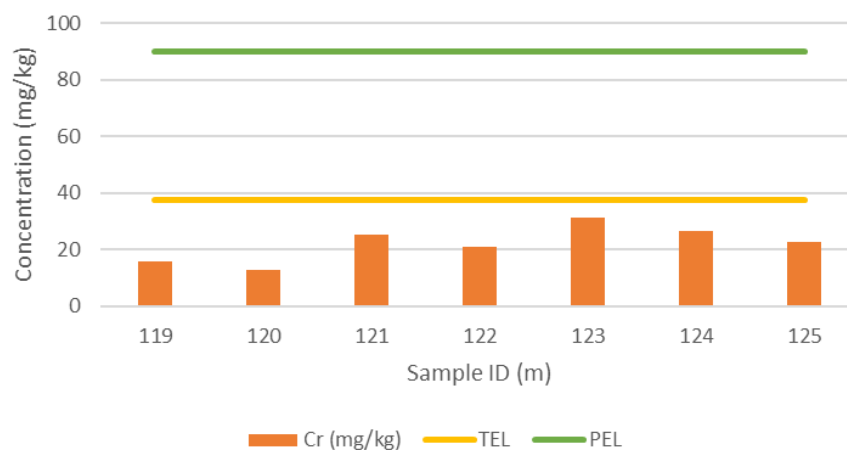


Figure 4. Concentration of Chromium from Soil Sediments (Borehole Cuttings).

3.2.1. Nickel (Ni)

Nickel is a major pollutant originating from metal processing industries and the burning of coal and oil. Prolonged exposure to elevated concentrations of Ni can result in respiratory issues, as well as damage to the liver, heart, and cells, accompanied by weight loss [21]. In this research, the nickel concentration averaged across selected sediment depths was recorded as 7.78, 5.33, 8.93, 9.66, 10.40, 10.51, and 10.28 mg/kg, with the lowest concentration at 120 m and the highest at 124 m. While there are currently no SQGS values for nickel [37], the shale average for nickel in sediments is set at 68 mg/kg. All the recorded measurements in this study were within safe thresholds. According to El-Naggar et al. [9], nickel contamination can arise from soil runoff and deposition, potentially polluting surface water bodies either directly or indirectly by leaching into groundwater. The findings of this research are similar to those from the study on heavy metal and metalloid contamination in the sediments of the Spekboom River, South Africa, conducted by Addo-Bediako et al. [38], who recorded a higher concentration of Ni compared to the present study. According to Addo-Bediako et al. [38], nickel is present at very low levels in the environment and is essential in small doses, but it can be toxic when the maximum tolerable level is exceeded. However, related studies [39,40] showed Ni concentrations exceeding those found in the present results.

3.2.2. Chromium (Cr)

The average chromium (Cr) concentrations measured for the selected soil sediment depths (m) were: 15.58, 12.99, 25.19, 21.07, 31.43, 26.57, and 22.81 mg/kg, with the lowest concentration recorded at 120 m and the highest concentration at 123 m. The concentrations recorded at all the soil sediment depths (m) were below the TEL and PEL limits [36]. Although all the measured soil sediments were within the permissible limit, the high concentration (31.43 mg/kg) recorded, which is closer to the TEL limit, might be attributed to anthropogenic origins or geological formations [8,41]. Chromium is associated with allergic dermatitis in humans. It can also damage the liver, lungs, and cause organ haemorrhages [40]. Chromium sources in the soil may stem from waste containing lead-chromium batteries, coloured polyethylene bags, discarded diesel engines that use anti-corrosive agents, and discarded plastic materials [7]. The average concentration is very close to that reported for the evaluation of heavy metals in water and sediments, pollution in Naltar Lakes, Pakistan (15.0–35.6 mg/kg) [42], lower than the concentration in wastewater and soil samples from open drainage channels in Nairobi (21.37 to 81.17 ppm), as reported by Kinuthia et al. [35]. The results of the current study are comparable to those of a study on the physicochemical properties and health risk assessment of selected heavy metals from soil and borehole water in Ifite-Awka, Anambra State, Nigeria, conducted by Das and Chatterjee [5], which reported lower concentrations than those found in the current study.

3.3. Mineralogical Composition of Borehole Sediments

The mineral composition of the selected borehole sediment samples collected at depths of 3 m, 11 m, 15 m, 19 m, 27 m, 36 m, 45 m, 54 m, 60 m, 69 m, 79 m, 86 m, 98 m, 100 m, 105 m, 113 m, 115 m, 120 m, and 123 m below ground surface was analyzed using X-ray Diffraction (XRD), and the results are shown in **Table 2** below.

Table 2. Mineral Composition Detected from Borehole Cuttings.

Minerals	Albite	Microcline	Orthoclase	Mica (Muscovite/Biotite)	Pargasite	Clinocllore	Hornblende	Actinolite	Quartz	Vermiculate	Illite	Magnetite	Hematite
Ideal Chemical formula	NaAlSi ₃ O ₈	KAlSi ₃ O ₈	KAlSi ₃ O ₈	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	NaCa ₂ (Mg ₄ Al)(Si ₆ Al ₂)O ₂₂ (OH) ₂	(Mg,Fe) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ ·(Mg,Fe) ₃ (OH) ₆	Ca ₂ (Mg,Fe,Al) ₅ (Al,Si) ₈ O ₂₂ (OH) ₂	Ca ₂ (Mg,Fe) ₅ Si ₈ O ₂₂ (OH) ₂	SiO ₂	(Mg,Fe ²⁺ ,Fe ³⁺) ₃ [(Al,Si) ₄ O ₁₀](OH) ₂ ·4H ₂ O	(K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ ·(H ₂ O)]	Fe ₃ O ₄	Fe ₂ O ₃
3 m	33.7	NP	12.7	6.3	NP	NP	NP	NP	14.7	NP	29.9	1.4	1.4
11 m	22.6	24	8	NP	NP	NP	NP	38.2	3.6	3.6	NP	NP	NP
15 m	38.1	24.8	NP	17.4	NP	NP	NP	10	9.2	<1	NP	NP	NP
19 m	28.1	16.8	16.8	NP	NP	NP	NP	32.2	5	1.0	NP	NP	NP
27 m	34.1	23	NP	15.1	14	6.1	NP	NP	7	<1	NP	NP	NP
36 m	32.9	20.1	NP	19.4	12.1	3.8	NP	NP	11.5	<1	NP	NP	NP
45 m	36	20.3	NP	18.1	15.6	5.1	NP	NP	4.8	<1	NP	NP	NP
54 m	31.2	21.6	NP	19.5	NP	4.8	NP	18.9	3.8	<1	NP	NP	NP
60 m	11.5	NP	17.1	29.5	NP	5.5	30.9	NP	5.5	NP	NP	NP	NP
63 m	29.8	NP	16.8	18.4	NP	6.3	26.2	NP	2.4	NP	NP	NP	NP
69 m	28.5	20.1	NP	15.1	NP	4.8	20.5	NP	10.9	NP	NP	NP	NP
79 m	36	28.6	NP	8.4	NP	3.3	NP	2.9	20.8	NP	NP	NP	NP
86 m	36.1	NP	17	6.3	NP	4.4	13.8	NP	22.4	NP	NP	NP	NP
98 m	33.1	NP	14.9	8.6	NP	10	30.4	NP	3	NP	NP	NP	NP
100 m	29.6	NP	16.4	6.7	NP	11.1	32.8	NP	3.5	NP	NP	NP	NP

Table 2. Cont.

Minerals	Albite	Microcline	Orthoclase	Mica (Muscovite/Biotite)	Pargasite	Clinocllore	Hornblende	Actinolite	Quartz	Vermiculite	Illite	Magnetite	Hematite
Ideal Chemical formula	NaAlSi ₃ O ₈	KAlSi ₃ O ₈	KAlSi ₃ O ₈	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	NaCa ₂ (Mg ₄ Al)(Si ₆ Al ₂)O ₂₂ (OH) ₂	(Mg,Fe) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ ·(Mg,Fe) ₃ (OH) ₆	Ca ₂ (Mg,Fe,Al) ₅ (Al,Si) ₈ O ₂₂ (OH) ₂	Ca ₂ (Mg,Fe) ₅ Si ₈ O ₂₂ (OH) ₂	SiO ₂	(Mg,Fe ²⁺ ,Fe ³⁺) ₃ [(Al,Si) ₄ O ₁₀](OH) ₂ ·4H ₂ O	(K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ ·(H ₂ O)]	Fe ₃ O ₄	Fe ₂ O ₃
105 m	29.7	NP	13.4	17.3	NP	5.8	28.6	NP	5.1	NP	NP	NP	NP
113 m	33.9	NP	14.4	16.1	NP	5.9	26	NP	3.6	NP	NP	NP	NP
115 m	29.1	NP	9.9	24.6	NP	4.7	25	NP	6.7	NP	NP	NP	NP
120 m	47.9	NP	14.8	7.9	NP	6.4	11.8	NP	11.3	NP	NP	NP	NP
123 m	32.1	NP	18.9	NP	NP	NP	42.4	NP	1.7	4.9	NP	NP	NP

Note: NP = Mineral not present at the sampled depth. Bulk Mineral Composition in mass%.

The analysis of borehole cuttings from Ha-Masia Tshikwarani reveals a composition primarily consisting of silicate and oxide minerals. The identified minerals include Albite, Microcline, Orthoclase, Mica (Muscovite and Biotite), Pargasite, Clinocllore, Hornblende, Actinolite, Quartz, Vermiculite, Illite, Magnetite, and Hematite (**Table 2**). Among these minerals, Quartz, Feldspars, and Mica were the dominant minerals. In contrast, Amphibole minerals were present as minor phases in the upper depths, except for hornblende, which was recorded from 60 m to 123 m deep in the borehole. Clay minerals (Vermiculite, Illite) and oxide minerals were present as minor phases in the upper depths.

Similarly, Keskinen et al. [43] reported that Quartz and K-feldspar were identified as the main mineral components of agricultural topsoil in Finland in their study. The abundance of Feldspar minerals, including Albite, is particularly evident in borehole cuttings at depths ranging from 3 m to 123 m of the selected sediment depth, where Albite constitutes as much as 47.9 wt.% of the total mineral composition at specific depths (**Table 2**). Amphiboles are common minerals found in both igneous and metamorphic rocks. They crystallise over a wide range of temperatures and pressures, but are particularly abundant in intermediate to high-grade metamorphic rocks and in intermediate to mafic igneous rocks [44]. Amphibole minerals were found in the soil sediments, primarily as hornblende, pargasite, and actinolite. Micas, particularly biotite and phlogopite, are prevalent ferromagnesian minerals in various volcanic, plutonic, and metamorphic rocks across different tectonic environments [45].

The concentration of mica (muscovite/biotite) in wt.% increases from topsoil to 60 m below the surface (**Table 2**). Clay minerals, although less abundant, such as Illite, were discovered 3 m below the surface, while Vermiculite was recorded between 11 m and 123 m below the surface (**Table 2**). These clay minerals are excellent adsorbents due to their unique structural and chemical properties. They are not only naturally abundant and low-cost but also possess a large surface area and high cation exchange capacity (CEC). This makes them highly effective in capturing and immobilising heavy metals, such as chromium (Cr) and nickel (Ni), across environments with varying pH levels and ionic strengths [46]. Investigation by Onipe et al. [22] revealed that clay in the soil can act as a natural barrier, protecting groundwater from fluoride contamination due to its strong adsorption capabilities. The analysis of borehole cuttings revealed the presence of oxide minerals in small amounts, occurring 3 m below the surface (**Table 2**).

3.4. Gamma Spectrometry

To investigate the unknown radionuclide from the Masia borehole, 3 m, 19 m, 46 m, 57 m, 63 m, 81 m, 86 m, 120 m, 124 m, and 125 m borehole soil samples were analysed by AT6101DR detectors. The AT6101DR detector operates in an energy range of 50 keV–3 MeV and monitors ambient dose equivalent rates of 0.03–130 µSv/h. Specific activity measurements of ²²⁶Ra, ²³²Th, ⁴⁰K, ¹³⁴Cs, and ¹³⁷Cs were performed as described by Nemangwele, Nemakonde, and Mudau [12]. Naturally occurring radionuclides such as ²²⁶Ra, ²³²Th, and ⁴⁰K are prevalent in the Earth's crust. These radionuclides are found in the environment in sediment, soil, and water [47]. Soil radioactivity originates from naturally occurring radionuclides found in the environment [44]. This results from the weathering of bedrock, which releases uranium (U), thorium (Th), and potassium (K) into the soil. These elements can migrate into the environment and groundwater through processes like erosion and weathering [14]. The **Figures 5–14** below illustrate the correlation between energy and counts for the radionuclides discovered and retrieved from the various depths of the soil sediments in the drilled borehole. The analysed soil samples revealed the presence of several radionuclides, including ²²⁶Ra, which was identified through its daughters ²¹²Pb at depths of 3, 19, 57, 63, 86, 120, 124, and 125 m, and ²¹⁴Bi at depths of 19, 57, 63, 81, 124, and 125 m. The presence of the ²³²Th radionuclide

was confirmed by its daughters ^{228}Ac and ^{208}Ti at all sampled depths (**Figures 5–14**). The natural radionuclide ^{40}K is a significant source of environmental radioactivity [48]. ^{40}K was measured directly by its 1460 keV gamma-ray emission at all sampled depths, as shown in **Figures 5–14**, respectively. The overall dose rate range for all the detected soil samples was 0.067–0.078 $\mu\text{Sv/h}$, equivalent to 586.92–683.28 $\mu\text{Sv/yr}$, and the total dose rate is less than the allowable limit of 1000 $\mu\text{Sv/yr}$.

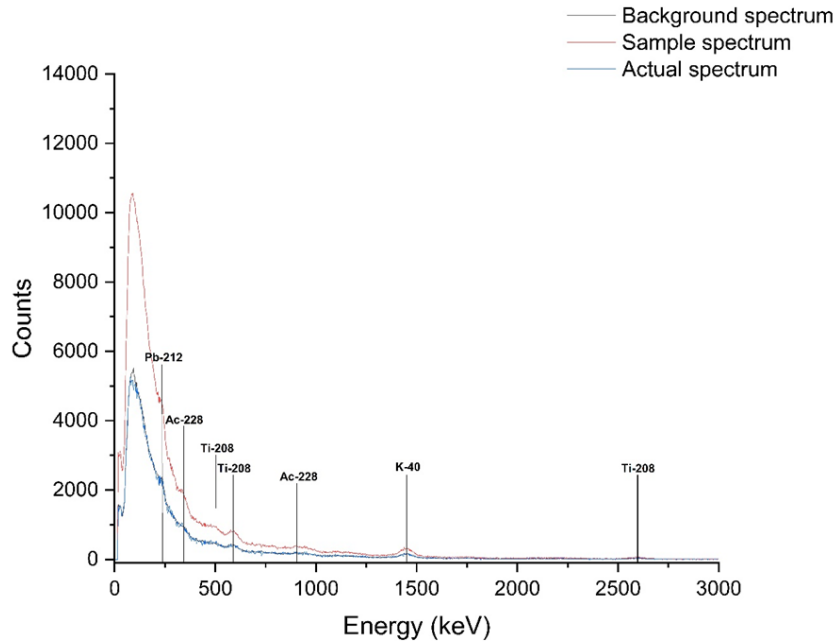


Figure 5. Gamma Spectrometry of soil sample at 3 m depth.

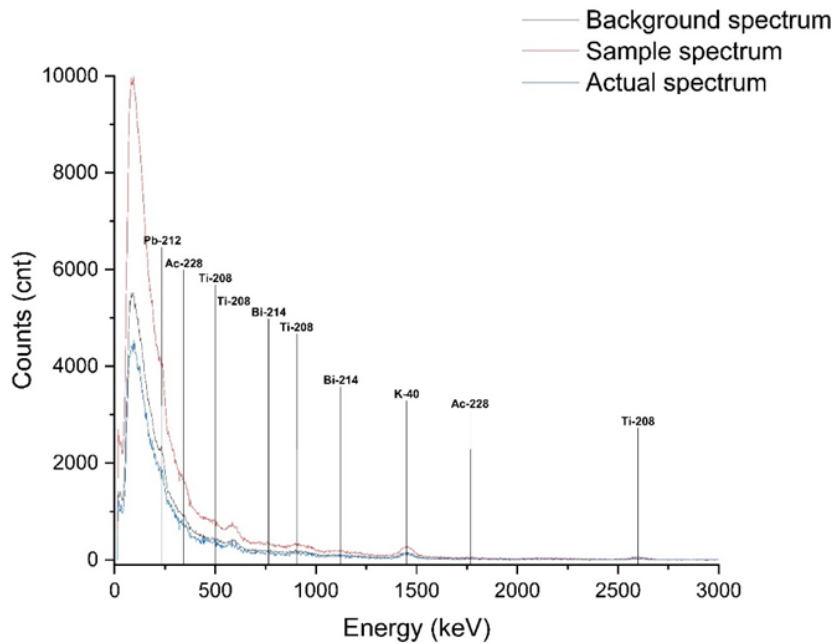


Figure 6. Gamma Spectrometry of soil sample at 19 m depth.

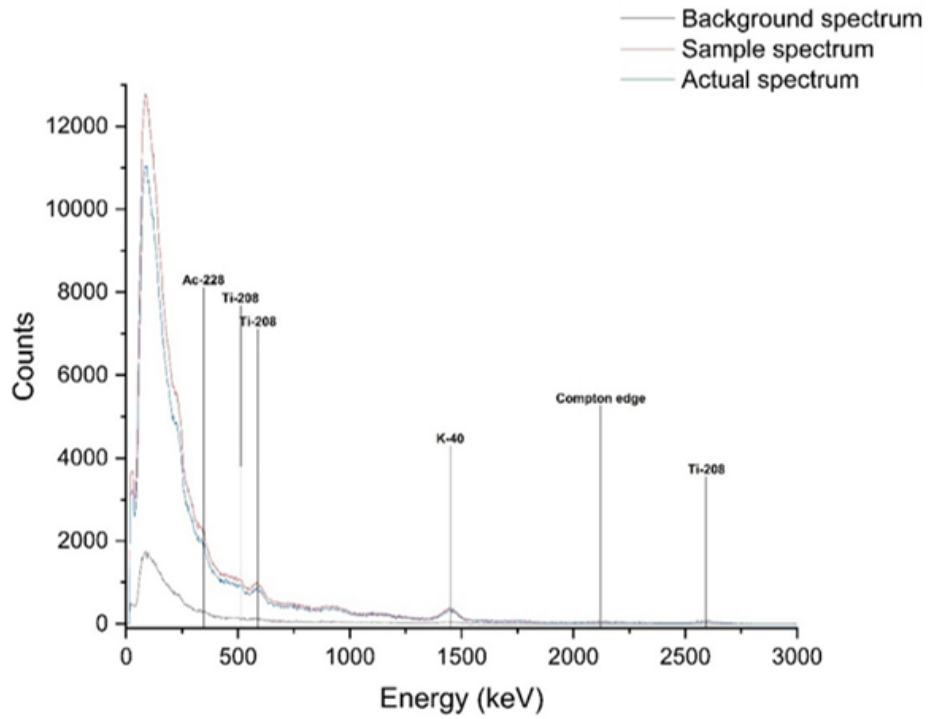


Figure 7. Gamma Spectrometry of soil sample at 46 m depth.

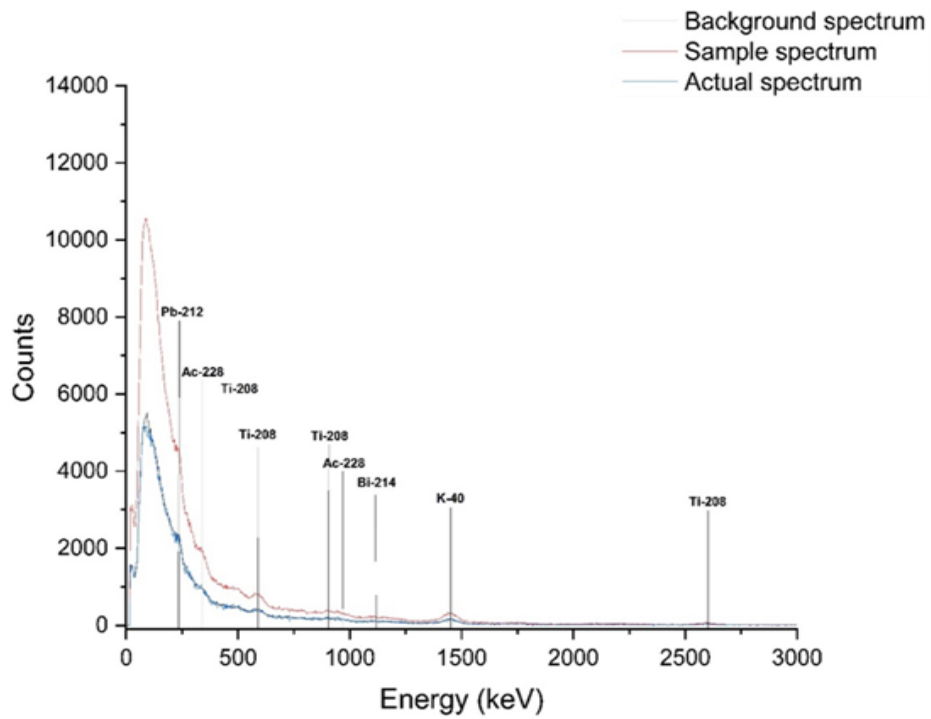


Figure 8. Gamma Spectrometry of soil sample at 57 m depth.

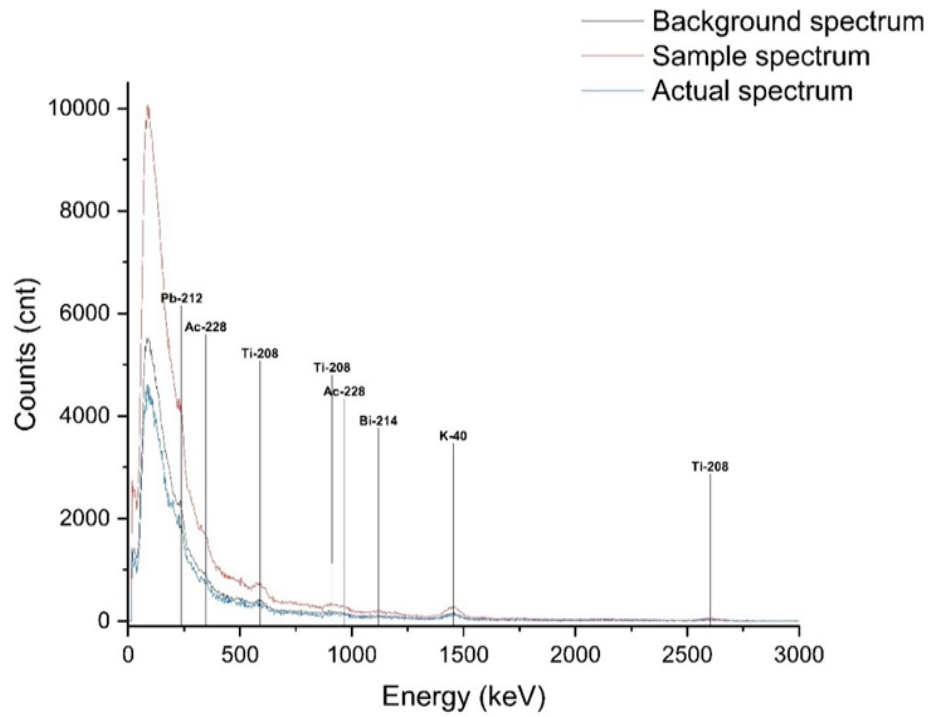


Figure 9. Gamma Spectrometry of soil sample at 63 m depth.

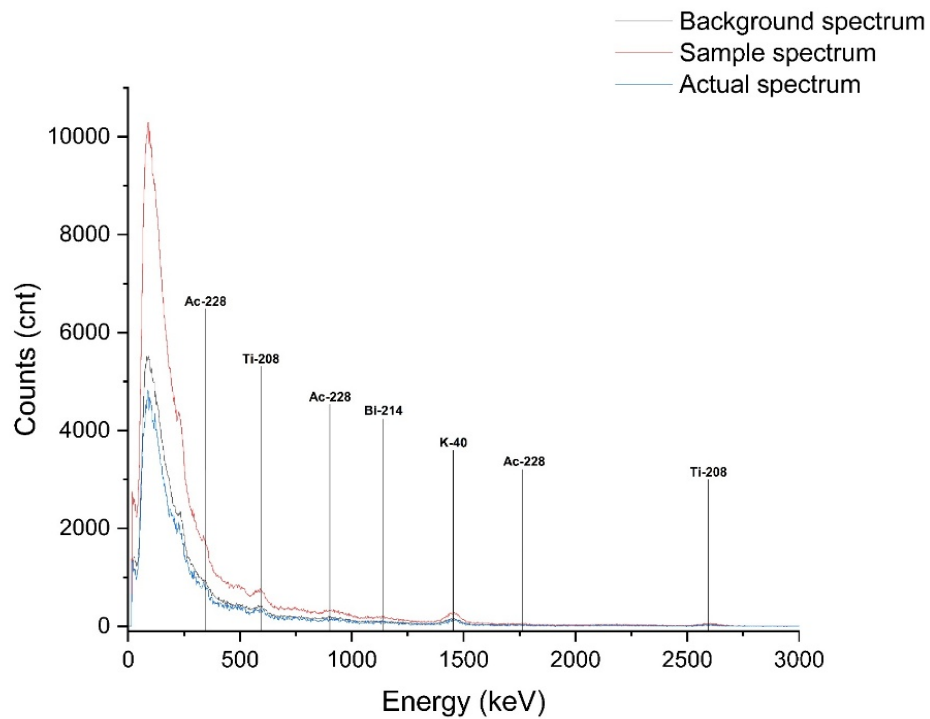


Figure 10. Gamma Spectrometry of soil sample at 81 m depth.

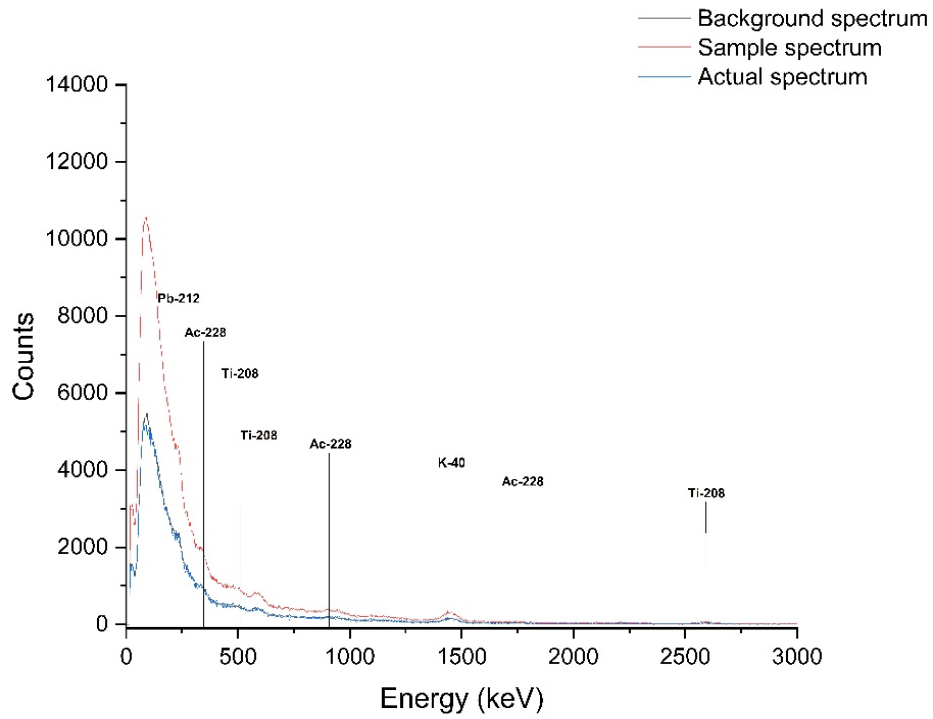


Figure 11. Gamma Spectrometry of soil sample at 86 m depth.

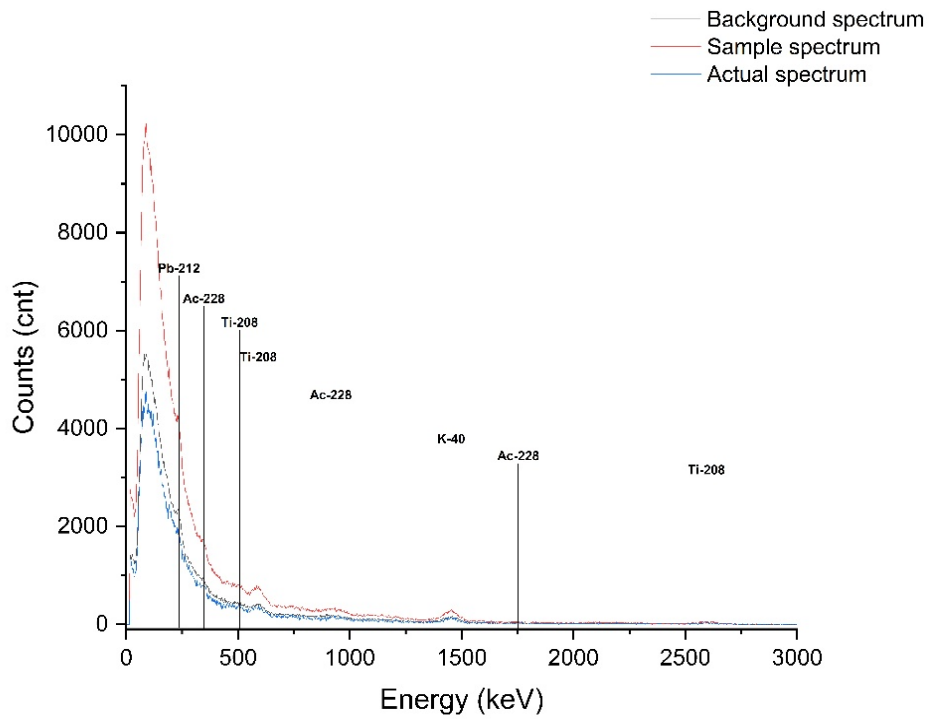


Figure 12. Gamma Spectrometry of soil sample at 120 m depth.

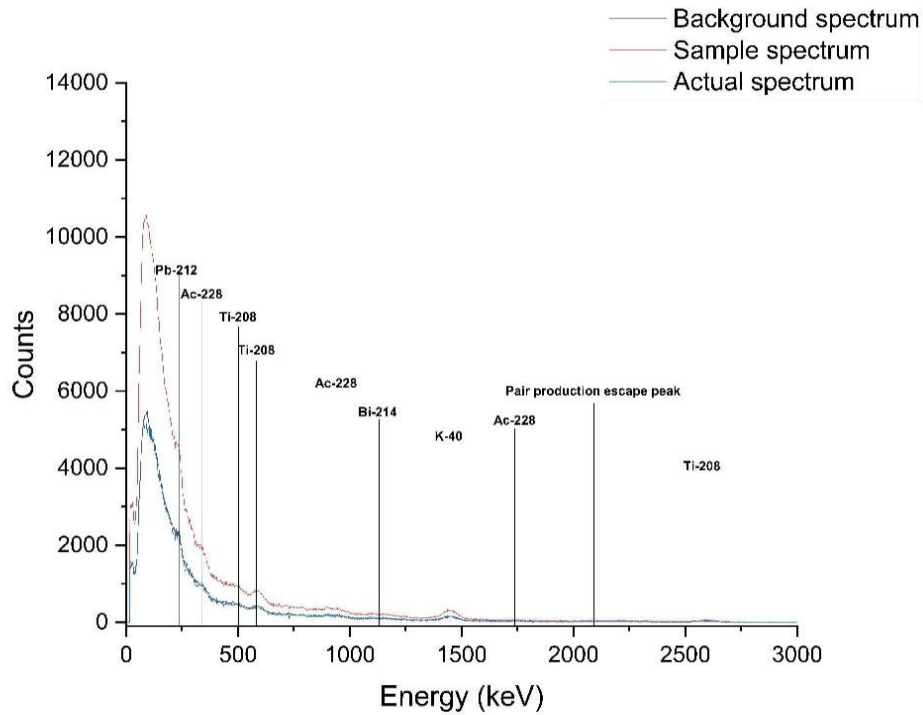


Figure 13. Gamma Spectrometry of soil sample at 124 m depth.

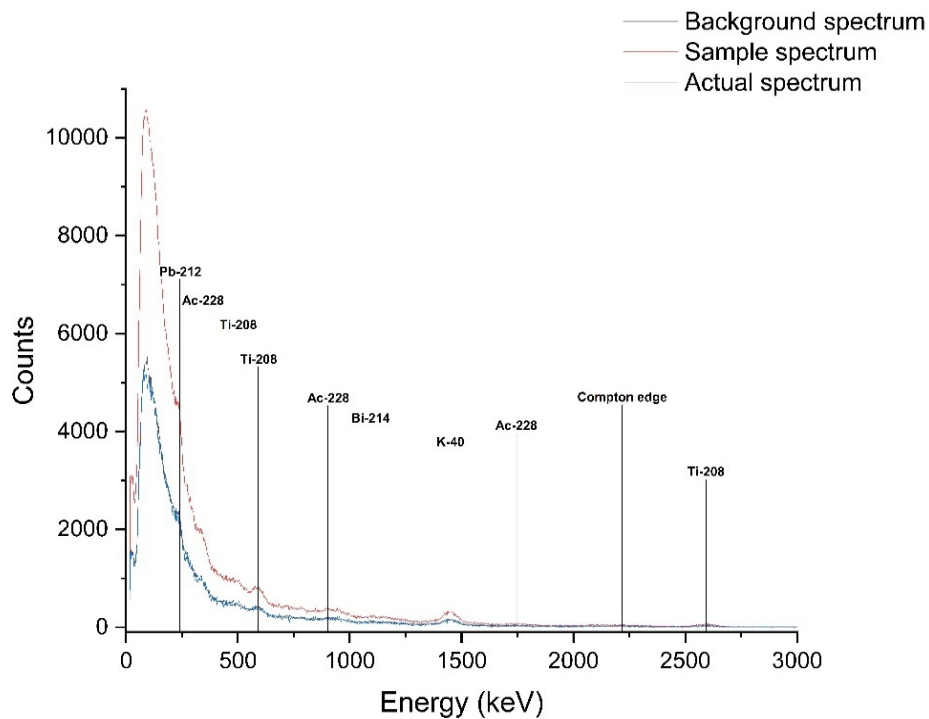


Figure 14. Gamma Spectrometry of soil sample at 125 m depth.

In the gamma-ray spectra, both Compton scattering and pair production escape peak processes affected the shape of the recorded peaks. A distinct Compton edge was observed in the 46 m and 125 m samples, positioned

below the main photopeaks. This feature arises from Compton scattering in the scintillator or detector, specifically due to photons that scatter at an angle of 180° and subsequently escape the detector [49]. Additionally, a pair production escape peak was observed in sample 124 m, a crucial feature in gamma-ray spectroscopy, particularly for detecting high-energy gamma rays. This peak occurs when a gamma ray with sufficient energy (greater than 1.022 MeV) interacts with a material, resulting in the production of an electron-positron pair, which is used to identify specific radionuclides in the soil samples [50].

The obtained results were also comparable to the data from France on Radionuclides in waters and suspended sediments in the Rhone River [51]. A study on the distribution and depth profiles of natural radionuclides, including caesium-137, and risk assessment for soil samples in the western regions of China reported comparable results [9]. The study also detected the presence of radionuclides through their decay products and recorded 40K at an energy of 1460 keV. As stated by several studies [12,14,52], regions with granitic rock have higher concentrations of radionuclides in soil compared to areas with sedimentary rock. Granitic rocks contain different amounts of naturally occurring radionuclides of terrestrial origin, ^{238}U and ^{232}Th series, and ^{40}K [53], therefore, the radionuclides detected in this study might be attributed to the minerals that were detected in this study area from soil sediments, such as Quartz, K-feldspar, plagioclase, and biotite, which are the primary components of granitic rock [52].

4. Conclusions

This research examined the levels of heavy metals and the mineral composition in borehole water and soil sediments at Ha-Masia Tshikwarani village. The average chromium concentration in the drinking water samples was 0.003 mg/L in May (dry season) and 0.006 mg/L in November (wet season), which did not exceed the Department of Water Affairs and Forestry (DWAF) standards from 1996 and the WHO, 2017. This indicates that the borehole water in Masia Tshikwarani is safe for consumption. ICP-OES analysis of borehole cuttings identified chromium and nickel at specific depths that were within the TEL and PEL guidelines. XRD analysis of borehole soil sediments revealed that Albite, Quartz, Microcline, and mica are the predominant minerals, indicating that they represent the most abundant and higher-quality components of the sediments. Smaller amounts of amphibole minerals, specifically hornblende and actinolite, were also detected, along with trace levels of orthoclase, pargasite, and clinocllore. Oxide minerals were identified only at a depth of 3 m, implying that their overall abundance is limited. Clay minerals are known for their ability to capture and immobilise heavy metals, and they were also identified in the borehole cuttings. The low levels of chromium (Cr) and nickel (Ni) observed suggest that there is minimal release of these elements from the parent minerals. Furthermore, the presence of clay minerals and iron oxides indicates that these trace amounts are effectively adsorbed and immobilised within the sediments. The study also assesses the radionuclide levels using the AT6101DR Detector and revealed the presence of several radionuclides, including ^{226}Ra , which was identified through its daughters ^{212}Pb at depths of 3, 19, 57, 63, 86, 120, 124, and 125 m and ^{214}Bi at depths of 19, 57, 63, 81, 124, and 125 m. The presence of the ^{232}Th radionuclide was confirmed by its daughters ^{228}Ac and ^{208}Tl at all sampled depths, and ^{40}K was measured directly by its 1460 keV gamma-ray emission at all sampled depths. For all reported soil samples, the overall dosage rate range was between 0.067 and 0.078 $\mu\text{Sv/h}$, or 586.92 and 683.28 $\mu\text{Sv/yr}$. The total dosage rate is less than the 1000 $\mu\text{Sv/yr}$ allowable limit. The study revealed that the presence of Radionuclides in the soil sample is attributed to the minerals such as quartz and feldspar that make up the granitic rock. In summary, the study indicates that borehole water is safe for drinking; however, continuous monitoring is essential to ensure long-term safety, particularly due to seasonal variations and the measurement of radionuclide levels in water samples. Additional research is recommended to understand how seasonal changes impact heavy metal levels, which will help better protect rural groundwater resources.

Author Contributions

All authors contributed equally to the conception, design, data collection, analysis, and writing of this study. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

AI Use Statement

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