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Research article

Radiological health risk assessment of drinking water and soil dust from Gauteng and North West Provinces, in South Africa

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ABSTRACT

Long-lived natural radionuclides such as (^{238}U) uranium-238, (^{232}Th) thorium-232, (^{226}Ra) radium-226 and (^{40}K) potassium-40 and heavy metals are normally exposed to the surface during mining activities. They enter the human body when inhaled (as dust) or ingested (by drinking contaminated water). An intake of large concentrations of these radionuclides and heavy metals can lead to health effects such as development of cancers. The aim of this work was to assess the radiological health risk due to intake of radionuclides in dust and drinking water from the West Rand gold mining area and Modiri Molema Municipality (MMM) water treatment plant. The dust samples were analyzed for radionuclides of interest using the well-type high purity Germanium detector. Water samples were collected before and after purification from the Modiri Molema Municipality water treatment plant and analyzed using the ultra-low level Liquid Scintillation Counter (LSC), to evaluate the gross alpha and beta radioactivity dose levels of the radionuclides in water. An Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to evaluate the heavy metal concentrations in the drinking water after purification at the treatment plant. The total inhalation effective dose obtained in this study was (2.71×10^{-1} and 1.31×10^{-1}) $\mu Sv.y^{-1}$ for adults and infants respectively, which is below the prescribed dose range of 5–10 $\mu Sv.y^{-1}$. The mean activity concentrations of the radionuclides in air dust were found to be; ^{226}Ra, (2.14 ± 0.82) $\times 10^{-6}$ ($Bq.m^{-3}$), ^{238}U (6.08 ± 2.17) $\times 10^{-7}$ ($Bq.m^{-3}$) and ^{232}Th (2.65 ± 1.1) $\times 10^{-7}$ ($Bq.m^{-3}$). The activity concentration of ^{226}Ra obtained exceeded the world average by 2 times. The Ra_{eq}, the external hazard (H_{ex}) and internal hazard (H_{in}) indices were calculated and the values obtained from soil were lower than the world average. However, the absorbed dose rate in air was higher than the world averages of 60 $nGyh^{-1}$. The minimum and maximum gross alpha activity obtained was 0.0041 ($Bq.L^{-1}$) and 0.0053 ($Bq.L^{-1}$) respectively, while the minimum and maximum gross beta activity obtained for water samples was 0.0083 ($Bq.L^{-1}$) and 0.0105 ($Bq.L^{-1}$) respectively. More heavy metals were detected in the first two stages of the water treatment than on the last two stages, nevertheless, their concentrations did not exceed recommended limits. The results for soil dust indicates that the windward areas might pose health risks for human population staying in the area and the activity concentration for drinking water indicate that the specific activity in the water supply after purification is below the WHO guideline limit of 0.5 ($Bq.L^{-1}$) for gross alpha and 1 ($Bq.L^{-1}$) for gross beta. The results obtained were also within the range of the South Africa Department of Water Affairs and Forestry target water quality limit of (0–1.38) ($Bq.L^{-1}$) for gross beta activity. Heavy metals concentrations in drinking water did not exceed the stipulated limits by USEPA and DWAF. Therefore, this water after treatment is radiologically and toxicologically safe for the members of the public.

1. Introduction

Naturally occurring radionuclide materials such as ^{40}K (Potassium), ^{238}U (Uranium), ^{232}Th (Thorium), ^{226}Ra (Radium) and heavy metals such as Cr), manganese (Mn), arsenic (As), selenium (Se), silver (Ag), are prevalent in the environment, resulting in human exposure throughout human history. Anthropogenic activities such as mining, has led in high environmental concentrations of these contaminants (Kamunda et al., 2016). These activities are liable for a series of environmental and human health problems and by producing huge quantities (Lee at el., 2004) of waste into the environment and by emitting sizable quantities of dust particles into the air, this includes dust particles of 10 μm in diameter or

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less (Bensen, 2016). Even with comparatively effective mining activities, high levels of natural radionuclides and heavy metals are released into the atmosphere and water leaving a repercussion of environmental contamination in neighboring communities.

These levels of natural radionuclides, enters the human body when inhaled or ingested. If large concentrations of these radionuclides build up in the human body, this can lead to health effects such as development of cancers (Kamunda et al., 2016), cardiovascular and respiratory diseases, especially because it is difficult to expel dust particles which penetrated deeper into the lungs. The risk of cardiovascular and respiratory mobility, asthma, lung cancer, inflammation and increased mortality may increase when these radioactive dust particles o are inhaled. However, when considering internal exposure, larger dust particles are less of a concern because they are unable to penetrate deep into the lungs and can be easily expelled by coughing (Bensen, 2016), therefore, it is important to monitor radionuclides in dust in areas around mines.

On the other hand, heavy metals also tend to build-up as they cannot be broken down and they can be transferred from one place to another. Humans through food, water, air or soil can ingest them daily. The toxicity levels of these metals depends on the type of metal, the dose taken and whether or not the exposure was acute or chronic (CSIR, 2008). Several heavy metals are carcinogenic while others are harmful to the organs of the body (USEPA, 1995).

Some of the radionuclides contaminant such as radium and uranium transferred to water are long alpha emitters These Alpha emitters are the most hazardous radionuclides when they are ingested (Winde, 2013). Radium, because of its chemical similarity to calcium is commonly fixed in bones and uranium poses a chemo toxicity due to its high solubility in water (Bitrus et al., 2015). Uranium and radium, when ingested in large doses, through drinking water, can cause biological effects such as changing the genetic material and changes to bone structures which will then result to cancer (Canu et al., 2011).

Nevertheless, USEPA (2006) observed that radionuclides concentration in drinking water are very low and thus the chance of radiological harm is very small. However, human activities such as mining and processing of minerals can contribute to higher levels of concentrations, which increase the chance of human exposure to radiation. Therefore, it is important to monitor concentration levels of these radionuclides in water to protect human health. For example, SA-DWAF (South Africa-Department of Water Affairs and Forestry) target water quality is (0–1.38) ($Bq.L^{-1}$) for gross beta activity (London et al., 2005) and if this target is exceeded, the Water Supplier of Sedibeng Water in Modiri Molema should make sure that the water is purified.

The World Health Organization WHO (2011) describes safe water as a basic human right and it suggested guideline limits for gross alpha activities at 0.5 ($Bq.L^{-1}$) and for gross beta activities at 1 ($Bq.L^{-1}$) for drinking water. Similarly, the yearly dose limit for an individual is 1mSv (WHO, 2011).

(Pirsaheb et al., 2015) studied radon concentrations in drinking water of Kermanshah city in Iran and the annual effective dose to the stomach and lungs per person was calculated according to parameter introduced by UNSCEAR. The results obtained showed that the concentration of radon in drinking water used by the community was lower than the recommended values, therefore, there was no significant radiological risk.

(Pirsaheb et al., 2018) evaluated the relationship between indoor radon and thoron concentrations, geological and meteorological parameters in three hospitals in Kermanshah Iran using the RTM-1688-2 radon meter and analyzed the type and porosity of soil and meteorological parameter using a STATA-Ver.8.statistical package. It was discovered that soil porosity had an extreme effect on the indoor radon amount.

(Pirsaheb et al., 2013) wrote a systematic review of recent studies associated with evaluation of radon gas levels to the public in Iran. Measurements of radon in water resources, tap water, indoor places and exhalation of radon from building material and major sources of indoor gas were considered. High levels of radon gas were found mostly in water and residential building. This study concluded that building materials such as granite stone and adobe coverings should not be recommended for construction purpose.

(Mathuthu and Olobatoke, 2016) carried out an investigation to assess the heavy metals and radionuclides concentrations of water from the wastewater treatment plant in Mafikeng local municipality. Gross alpha and beta activities were evaluated using a liquid scintillation counter and the activity concentrations of individual concentrations were done using gamma spectroscopy. They evaluated the concentration of heavy metals in water using an inductively coupled plasma mass spectrometry. The results obtained showed that the heavy metal concentrations were higher than the limits of the South Africa Target Water Quality (SATWQ) range and the WHO limits.

(Keramati et al., 2018) performed a study to review conducted studies regarding the concentration of radon 222 in the tap drinking water by estimation of ingestion and inhalation effective dose and the health risk assessment in the adults and children was determined using Monte Carlo simulation. This study shows the effective ingestion dose of radon 222 in adults age groups was 1.35 times higher than in children. The overall concentration of radon 222 in drinking water in Iran was obtained to be lower than the WHO and EPA standard limit.

(Miri et al., 2017) investigated the heavy metals content of fish species consumed by the population and its associated health risk factors. The authors found that the mean concentrations of Pb, Cd and Cr were slightly higher than the standard levels and the cancer risk factor for Pb was below the accepted lifetime carcinogenic risks.

The main aim of this study was to evaluate the radiological health risk due to heavy metals and natural occurring radionuclides in drinking water and dust from Gauteng and North West Provinces, in South Africa.

2. Materials and method

The study entailed investigation of dust and water contamination by naturally occurring radionuclides. The geological area, sampling and sample preparation is described separately below.

2.1. Geographical area

The study area of the West Rand gold mine in Carletonville lies west of Johannesburg and is one of the richest gold mining areas in South Africa. The map on Figure 1 shows the West Rand gold mine where dust samples were collected. Another study area was Modiri Molema Municipality, one of the four-district municipality of North West province in South Africa. It is located at the center of the province with an area of 28114 km^2. This is where water samples were collected.

2.2. Sampling and sample preparation

2.2.1. Dust sampling

A polycarbonate nucleopore filter of sizes 47 mm in diameter and pore size10μm were used to collect windblown dust samples. Dust sample were also collected from a background site, where a sequential air sampler unit (RP Partisol-plus, Model, 2025; supplied by Thermo scientific) was mounted and dust particulate were collected on this unit, at a height of 1 m above the ground. This sampler operates at a flow rate of 16 L per minute. The mass of each filters were recorded before accumulating dust. The filters were left for a period of 30 days, after which they were removed and replaced with new filters the following month. To prevent cross-contamination, the dust filters were placed separately each in a Millipore Petri slide dish and sealed. The filters were then taken to the Analytical laboratory for analysis. Clean stainless steel tweezers were used to place the filters into cassettes and to remove them for weighing. The weight of the filters plus dust was measured using a sensitive analytical balance (Mettler AE200) from Microsep (PTY) LTD, in order to get the mass of the dust collected. Dust samples were collected at the

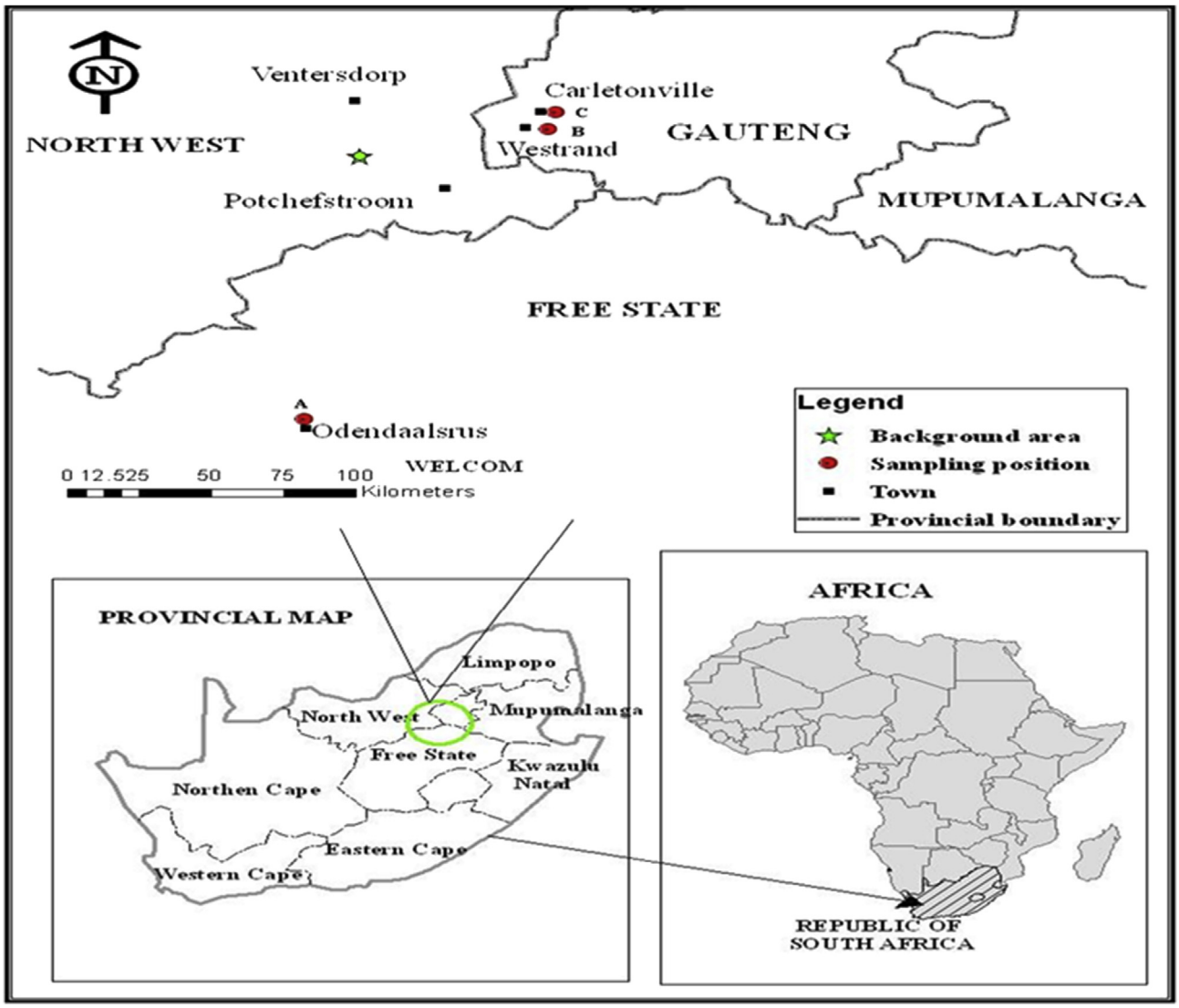

Figure 1. Map of the study area for dust sampling (Dudu et al., 2018).

location shown in Figure 1. Samples were collected throughout the year to cater for seasonal variations from January 2016 to December 2016. During the monitoring period, the exposure time complied with the standard operating procedure of 30 ± 2 days from the South African National Standards (SANS, 1929:2011).

2.2.2. Dust sample preparation and analysis by gamma spectrometry

For gamma spectroscopy, the dust samples were left sealed for four weeks in labelled airtight vials to prevent the escape of radiogenic gases radon (^{222}Rn), and thoron (^{220}Rn), and to achieve secular equilibrium of the ^{238}U and ^{232}Th and their respective progenies (Mahur et al., 2008; Frostick et al., 2011).

Measurements were done in the Analytical Laboratory at the Centre for Applied Radiation, Science and Technology (CARST) of the North-West University (Mafikeng Campus), using a High Purity Germanium (HPGe) well detector and the counting time was 12 h per sample. The radionuclides of interest were identified at the following energies: ^{238}U (351.9 keV for ^{214}Pb, 609.2 keV^{214}Bi), 186 keV for ^{226}Ra, ^{232}Th (238.6 keV for ^{212}Pb, 583.1 keV for ^{208}Tl, 911 keV for ^{228}Ac) and 1460 keV for ^{40}K. For quality assurance, standard procedures for energy and efficiency calibration were done by following procedures stated by the American National Standards Institute. In addition, a reference standard for U, Th & Ra were measured in the HPGe detector. The GENIE 2000, Gamma Acquisition V.3.3 and Gamma Analysis Software Vs.3.3 were used for data acquisition and analysis respectively.

2.3. Irradiation from inhaled radionuclides

The annual effective dose from inhalation E_{inh} (Sv.y^{-1}) is calculated using the equation (Corrigall, 2004; Han and Park, 2018);

$$E_{inh} = CA.R_{inh}.DF_{inh} \quad (1)$$

where, C_A is the concentration of the radionuclide in air (Bq.m^{-3}), R_{inh} is the inhalation rate (m^3.a^{-1}), (Default inhalation rates for adults and for 1-2 year-old infants are 8400 and 1400 m^3.a^{-1} respectively) and DF_{inh} is the inhalation dose coefficient (Sv.Bq^{-1}).

For the effective dose coefficient, the activity median aerodynamic diameter (AMAD) was assumed to be 1 μm as recommended by ICRP (2012) when considering environmental exposures in the absence of specific information of physical characteristics of the aerosol. Committed effective dose coefficients for inhalation (Sv.Bq^{-1}), used in this work were obtained from the ICRP, guidelines (ICRP, 2012).

2.4. Sampling and sample preparation for drinking water

2.4.1. Sampling

Water samples from four stages of water treatment were collected at Modiri Molema Municipality water treatment plant. The stages of water treatment are; water-in, reactor water, sedimentation and water-out. One liter of water from each stage was collected into polypropylene bottles and then acidified with nitric acid (1 ml of sample to 10 ml of HNO_3) to keep the radionuclides in the water from sticking on the sides of the bottle (Gorur and Camgoz, 2014).

2.4.2. Sample preparation for inductively coupled plasma mass spectrometry

Water samples (10 ml) were filtered utilizing a Whatman filter paper 541 (CAT No. 1541-150) into plastic vials and then diluted with 1 ml of HNO_3 and deionized water was added to fill up to the 10 m mark. The instrument runs each sample three times for 60 s for each total run. Samples were analyzed using Total Quant method of the NexION 2000 Inductively Coupled plasma mass spectrometry (ICP-MS). Standards and blank solutions were utilized in order to correct for the analytical and instrumental drifts. The calibration was achieved using the multi-element calibration standard (Perkin Elmer pure plus) with a concentration of 10 mg/L and the present elements were; Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V and Zn. All chemicals and reagents used were of certified analytical grade and acquired from Merck (South Africa).

2.4.3. Sample preparation and analysis using the liquid scintillation counting

Water samples were filtered into labeled glass beakers. 10 ml of each water sample was pipetted into polyethylene vials. This procedure was repeated twice to make duplicates of each sample resulting in eight samples. The background was also prepared in the same way using deionized water. 10 ml of a scintillation cocktail (Ultima Gold uLLT cocktail) was added to each polyethylene vial and mixed vigorously. Each sample was counted in a Perkin Elmer, Quantulus 1220 Ultra Low Level Liquid Scintillation Counter (LSC) for 5 h in order to measure their gross alpha-beta activities.

2.5. Optimum PSA procedure

The optimum Pulse Shape Analysis (PSA) was set in order to avoid alpha and beta spillover to each other's channel during counting. In order to set the optimum PSA value 5 samples of ^{241}Am standard (a pure alpha emitter) and 5 samples ^{90}Sr standard (a pure beta emitter) were quenched so that different values could be counted for 5 min at different PSA levels. After counting the samples, the count rates of α′sand β′s were used to calculate the spillover obtained at different PSA level. This procedure is called PSA calibration and it is done to minimize spillover.

$$y = 0.2768x - 103.51 \text{ With } r^2 = 0.91 \quad (2)$$

where, y is the optimum PSA setting, x is the measured external spectral quench parameter (SQP(E)). Increase in quenching affects the alpha spillover more than the beta spillover. Therefore, spillover can be calculated using the total count rates of both alpha and beta channel.

The spillover of alpha's and beta's can be calculated by the following equation

$$X_\alpha = \frac{MCA11}{MCA12 + MCA11} \quad (3)$$

$$X_\beta = \frac{MCA12}{MCA11 + MCA12} \quad (4)$$

where, X_α is the fraction of counts observed in the beta channel (MCA11) with respect to the counts observed in α and β channel (MCA12 + MCA11) when a pure α is measured. X_β is the fraction of counts observed in the alpha channel (MCA11) with respect to the counts observed in α and β channel (MCA12 + MCA11) when a pure β is measured. The MCA11 contains pure sample β measurements while MCA12 contains pure sample of α measurements (Dias et al., 2009; Hoang, 2016). The spillover values for each sample were used to construct a linear graph with a linear Eq. (2), which relates the quenching parameter SQP(E) with PSA setting (Mashaba, 2011).

2.6. Gross alpha-beta determination

The gross $\alpha\beta$ activities were calculated using the following equation (Abdellah, 2013)

$$A_\alpha = \frac{(MCA12_{G\alpha} - MCA12_{B\alpha})}{V \times T} \quad (5)$$

$$A_\beta = \frac{(MCA11_{G\beta} - MCA11_{B\beta})}{V \times T} \quad (6)$$

where, $MCA12_{G\alpha}$ and $MCA11_{G\beta}$ are the number of gross counts per minute recorded in the α and β window, respectively for the water sample vial. $MCA12_{B\alpha}$ and $MCA11_{B\beta}$ are the number of backgrounds counts per minute recorded in the α and β window, respectively for the blank vial. A_α and A_β are the gross alpha and beta ($Bq.L^{-1}$) of the sample respectively. V is the volume of sample analyzed in liters. T is the measuring time (seconds).

3. Results

The following are the results obtained after analyzing dust and drinking water samples using HPGe detector, Inductively Coupled Plasma Mass Spectrometry and Liquid Scintillator Counter.

3.1. Activity concentrations of radionuclides in dust

Activity concentrations of radionuclides are shown in Table 1. The activity concentrations for ^{226}Ra varied from (0.94–2.04) $\times 10^{-6}$($Bq.m^{-3}$) with a mean activity concentration of (2.14 ± 0.82) $\times 10^{-6}$ ($Bq.m^{-3}$). ^{40}K had the highest activity concentration with a range of (2.98 $\times$ 10^{-6} -6.00) $\times$ 10^{-6} followed by ^{226}Ra, then ^{238}U and the least activity concentrations were from ^{232}Th with a range of (1.47–2.48) $\times$ 10^{-7} ($Bq.m^{-3}$).

As shown in Table 2, the total inhalation dose varies considerably between infant sand adults. The total inhalation dose for adults (2.71 $\times$ 10^{-1} $\mu Sv.y^{-1}$) is 2 times the values for infants (1.31 $\times$ 10^{-1} $\mu Sv.y^{-1}$). In both adults and infants, the ^{226}Ra is responsible for the main contribution to inhalation dose. The world averages for the mean atmospheric activity concentrations of ^{232}Th, ^{226}Ra and ^{238}U associated with dust are 0.5, 1.0 and 1.0 $\mu Bq.m^{-3}$, respectively (Han and Park, 2018). Table 3 shows the activity concentrations of soil samples in $Bq.kg^{-1}$.

Contributions of the different radionuclides to total annual effective dose from inhalation in adults was 63% (^{226}Ra), 14.7% (^{238}U), 22.1% (^{232}Th) and 0.2% (^{40}K) whereas in infants aged 1–2 years the contributions were 68.7%, 15.3%, 15.3% and 0.7% for the radionuclides ^{226}Ra, ^{238}U, ^{232}Th and ^{40}K respectively. This is in agreement with (Jia and Torri, 2007) who found that radionuclides from the uranium series especially ^{226}Ra contributes mainly to inhalation dose.

Table 1. Activity concentrations of radionuclides in dust.

Radionuclide	Mean ± sd ($Bq.m^{-3}$)	Median	Range
226_{Ra}	(2.14 ± 0.82) × 10^{-6}	2.04 × 10^{-6}	(0.94–2.04) × 10^{-6}
238_{U}	(6.08 ± 2.7) × 10^{-7}	5.96 × 10^{-7}	(1.01–5.96) × 10^{-7}
232_{Th}	(2.65 ± 1.1) × 10^{-7}	2.48 × 10^{-7}	(1.47–2.48) × 10^{-7}
40_{K}	(36.40 ± 9.21) × 10^{-6}	3.39 × 10^{-5}	(2.98–6.00) × 10^{-6}

Table 2. Inhalation effective dose E_{inh} ($\mu Sv.y^{-1}$) from the radionuclides in dust.

Radionuclide	Adult	Infant
226_{Ra}	1.70×10^{-1}	9.00×10^{-2}
238_{U}	4.00×10^{-2}	2.00×10^{-2}
232_{Th}	6.00×10^{-2}	2.00×10^{-2}
40_{K}	6.00×10^{-4}	9.00×10^{-4}
Total effective inhalation dose	2.71×10^{-1}	1.31×10^{-1}

Table 3. Radionuclide activity concentrations of soil samples ($Bq.kg^{-1}$).

Radionuclide	Mean ± sd	Median	Min-Max
^{226}Ra	113 ± 45	96	75–199
^{232}Th	27 ± 13	24	12–47
^{40}K	208 ± 29	201	174–274

3.2. Activity concentrations and estimated exposure risk in soil

3.2.1. Activity concentration of radionuclides in soil

^{232}Th activity concentrations had the lowest value with a mean of 27 ± 13 $Bq.kg^{-1}$, range of 12–47 $Bq.kg^{-1}$and a median value of 24 $Bq.kg^{-1}$. For ^{40}K, the value of activity concentrations was the highest and the range was 174–274 $Bq.kg^{-1}$, mean of 208 ± 29 $Bq.kg^{-1}$ and median value of 201 $Bq.kg^{-1}$ (Table 3). According to the UNSCEAR report of 2000 (UNSCEAR, 2000), the average worldwide measurements for activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K (in $Bq.kg^{-1}$) are 32, 45 and 420 respectively. Therefore, the activity concentrations of ^{226}Ra in this mine has exceeded the world averages. The ^{40}K world average recorded by UNSCEAR (2000) was more than double that observed in this mine. The elevated levels of ^{226}Ra are due to the gold and uranium mining activities in the area, different activities, the type of soil and geology influence the concentrations of the radionuclides.

3.2.2. Estimation of exposure risk using radium equivalent and hazard indices in soil

Radium equivalent activity (Ra_{eq}) was calculated using the equation:

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_K \quad (7)$$

whereA_{Ra}, A_{Th} and A_K are the radiological concentrations or specific activities of ^{226}Ra, ^{232}Th and ^{40}K respectively. The formula is derived based on the estimation that 1 $Bq.kg^{-1}$ of ^{238}U, 0.7 $Bq.kg^{-1}$ of ^{232}Th and 13 $Bq.kg^{-1}$ of ^{40}K produce the same gamma ray dose rates. Table 4 shows that the average Ra_{eq} activity in the soil samples were found to be 168 ± 66 $Bq.kg^{-1}$

The Ra_{eq} results obtained in this study were lower than the maximum recommended limit or internationally accepted value of 370 $Bq.kg^{-1}$, and therefore do not pose a significant radiological hazard but caution should be taken against cumulative long term effects.

The external hazard index (H_{ex}) was used to evaluate the hazard of the natural γ-radiation. It was calculated using the equation:

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \quad (8)$$

Table 4. Radiation hazard indices.

Study area	Mean± std	Ra_{eq} ($Bq.kg^{-1}$) Median	Mean H_{ex}	Mean H_{in}
West Rand gold mine	168 ± 66	145	0.45	0.76
Recommended limit (UNSCEAR, 2000)	370	-	1	1

where A_{Ra}, A_{Th} and A_K are the radiological concentrations or specific activities in $Bq.kg^{-1}$ of ^{226}Ra, ^{232}Th and ^{40}K respectively. The formula is derived from the Ra_{eq} expression by assuming that the maximum value allowed corresponds to the upper limit of Ra_{eq} (370 $Bq.kg^{-1}$). H_{ex} and H_{in} values must be less than unity so that the radiation hazard is considered insignificant. The external hazard index value obtained were 0.45 as shown in Table 4. This value is less than unity meaning that the soils in the areas are considered safe for humans living there. That is, there is no threat of exposure to the population. Internal hazard index (H_{in}) was used to quantify the internal exposure and is defined by as:

$$H_{in} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \quad (9)$$

The H_{in} is less than unity meaning the radiation hazard is considered negligible or insignificant.

3.2.3. Absorbed dose rate in air (ADRA)

$$ADRA = 0.461A_{Ra} + 0.623A_{Th} + 0.0417A_K \quad (10)$$

The absorbed dose rate in air due to terrestrial gamma rays from the nuclides ^{226}Ra, ^{232}Th and ^{40}K at 1m above ground level was calculated as (UNSCEAR, 2000). Where, A_K, A_{Th}, A_{Ra} are the average activity concentrations of ^{40}K, ^{232}Th, ^{226}Ra. The calculated absorbed dose in air was 77.59 $nGyh^{-1}$, which is higher than the world average value of 60 $nGyh^{-1}$. This could pose a health risk on the population staying in the area, as they will receive high doses of these harmful radionuclides.

3.3. Activity concentrations of radionuclides in drinking water

3.3.1. Liquid scintillation counting results

Water samples labeled A and B are water from the same sample and there are duplicate samples of each water sample. The minimum and maximum gross alpha activity obtained was 0.0041 ($Bq.L^{-1}$) and 0.0053 ($Bq.L^{-1}$) respectively, while the minimum and maximum gross beta activity obtained for water samples was 0.0083 ($Bq.L^{-1}$) and 0.0105 ($Bq.L^{-1}$) respectively. There is a small difference of gross alpha activity in all the samples and the same true on gross beta activity. The gross alpha activities are less than the gross beta activities; this could be due to some alpha particles spilling over to the beta channel. Sample 3 has highest gross alpha activity whereas the common difference for the rest of the samples is 0.0003 ($Bq.L^{-1}$), this could be due to chemical quenching during the purification process. After purification (sample 4A and B), the activity was less. Therefore, the Municipal purification process reduced radionuclides. Table 5 shows the Liquid Scintillation Counter (LSC) results.

3.3.2. Inductively coupled plasma mass spectrometry (ICP-MS) results on heavy metals in drinking water

Heavy metals concentrations in drinking water that were detected using the ICP-MS technique was; aluminum (Al), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), silver (Ag), antimony (Sb), mercury (Hg), thallium (Tl), uranium (U) and lead (Pb). More heavy metals concentrations were detected in the first (water-in) and the second stage (Reactor water), than detected in the third (sedimentation) and fourth stage (water out). Only manganese, iron and selenium were detected on the fourth stage and their concentrations did not exceed the limits prescribed by the World Health Organization (WHO), the Department of Water Affairs and Forestry of South Africa (SA-DWAF) and the United States Environmental Protection Agency (USEPA). In the first stage Ag, Sb, Hg and Tl were not detected but in the following stage they were detected, this could imply that these metals are from the chemicals introduced during the water treatment procedures. Table 6 shows a profile of the heavy metals detected.

Table 5. Liquid Scintillation Counting results.

Sample name	Sample Code	Gross alpha activities (Bq.L^{-1})	Error	Gross beta activities (Bq.L^{-1})	Error
Water-in	1A	0.0045	0.0005	0.0105	0.0018
Water-in	1B	0.0048	0.0002	0.0104	0.0012
Reactor water	2A	0.0048	0.0003	0.0083	0.0008
Reactor water	2B	0.0045	0.0009	0.0095	0.0007
Sedimentation	3A	0.0053	0.0010	0.0101	0.0009
Sedimentation	3B	0.0053	0.0010	0.0105	0.0018
Water-out	4A	0.0041	0.0012	0.0083	0.0008
Water-out	4B	0.0044	0.0006	0.0090	0.0011

Table 6. Heavy metals concentrations in drinking water (μg.L^{-1}).

Sample ID	Al	V	Cr	Mn	Fe	Co	Cu	Zn	As	Se	Ag	Sb	Hg	Tl	Pb	U
1A	102.58	0.81	0.5	3.99	133.55	0.03	5.93	6.55	0.02	0.02	0	0	0	0	0.36	0.03
2A	0	64.62	2.32	2.1	55.6	0.39	0	0	0.08	0.13	2.46	4.56	0.13	0.04	0	0.77
3A	0	0	0	0.67	23.7	9.74	0	0	0	0.06	0	0	0	0	0	1.15
4A	0	0	0	0.02	0.05	0	0	0	0	0.04	0	0	0	0	0	0
WHO (2004)	n/a	n/a	50	100	300	n/a	2000	500	10	40	n/a	n/a	6		10	15
SA- DWAF (1996)	n/a	0–320	0–50	0–50	1–1000	n/a	0–10	0–3000	0–10000	0–20	n/a	n/a	n/a	n/a	n/a	0–70
USEPA (2011b)	200	n/a	100	50	300	100	1300	500	10	50	100	6	2	2	15	30
ME STD (Perkin Elmer)	0	8.00	8.00	0	0	8.00	0	0	8.00	8.00	8.00	0	0	8.00	8.00	8.00

n/a = not applicable.

4. Discussion

Gamma spectroscopy was applied in this research to analyse individual radionuclides (^{238}U, ^{232}Th and ^{226}Ra) found in dust. The liquid scintillation counter was used to evaluate the total gross alpha and beta activity of the radionuclides present in the water. These results from these two techniques show that both dust and water activities did not exceed the prescribed limit and thus cannot pose a risk on human health. According to (Poschl and Nollet, 2006), the average annual effective dose from inhalation of uranium and thorium series (with exception of radon and thoron) is between 5 and 10 μSv.y^{-1}. In this study, the values obtained were below the prescribed range for both adults and infants. This means that there is minimum exposure risk for individuals in the study area, due to low activity concentrations of the radionuclides in dust.

The world average activity concentrations for ^{232}Th and ^{238}U in dust is 30 Bq.kg^{-1} and 35 Bq.kg^{-1} respectively (Han and Park, 2018). However, the calculated values in this study area were 4.5 times less for ^{232}Th and 2.3 times less for^{238}U. On the other hand, the world mean atmospheric activity concentrations of ^{232}Th, ^{226}Ra and ^{238}U associated with dust are 0.5, 1.0 and 1.0 μBq.m^{-3}, respectively (Han and Park, 2018). From Table 1, the results of this study area show that the mean activity concentrations were about a factor of two, below the world averages for ^{232}Th and ^{238}U. However, the activity concentration of ^{226}Ra exceeded the world average by 2 times, and if the concentration level of this radionuclide builds-up, the community near the area might suffer from cancer in the future. The Ra_{eq} results obtained in this study were lower than the maximum recommended limit or internationally accepted value of 370 Bq.kg^{-1}. The external hazard index (H_{ex}) value obtained were 0.45 and the internal hazard (H_{in}) obtained was 0.76. These values were less than unity 1 and are considered insignificant and safe for humans living there. That is, there is no threat of exposure to the population. But caution should be taken against cumulative long term effects The calculated absorbed dose in air was 77.59 nGyh^{-1}, which is higher than the world average value of 60 nGyh^{-1}.the absorbed dose could pose health risks such as cancer or respiratory diseases.

The LSC results obtained indicated that there is a small difference between the gross alpha and gross beta activities of each water sample. For instance, sample 1A and 1B are the same sample but there is a difference in the gross alpha and beta activities obtained, this might be a result of alpha particles spilling over to the beta channel and beta particles spilling over to the alpha channel (Hoang, 2016). Sample 3A and 3B has the same gross alpha activity and they are the same sample. After purification radionuclides concentration in the water samples were reduced, this explains why the activities were less in sample 4. Although the gross beta activities are high, they do not exceed the target water quality limit of 0–1.38 (Bq.L^{-1}) stipulated by the DWAF. The gross alpha-beta activity limit stipulated by the WHO was not exceeded either.

The outcomes acquired from the ICP-MS demonstrates all the concentration of metals detected in Modiri Molema Municipality water treatment were within the stipulated limits by the USEPA, SA- DWAF and WHO in spite of the fact that there were staggering varieties in concentrations at various processing stages. This could be because of the impacts of the treatment. However, the majority of the metals were not identified in the water-out stage (sample 4A) with the exception of Mn, Fe and Se. These perceptions area recommendation that the water treatment carried out at the MMM water treatment plant might be exceptionally proficient in evacuating the heavy metals of the wastewater conveyed to it.

For quality assurance and quality control, a standard daily performance check was performed to check the performance of the instrument using a setup solution. Replicate samples were run together with a multi element standard and blank solution (NexION STD/DRC mode detection limit blank solution, Perkin Elmer). The calibration procedure updates the internal response data that correlates measured ion intensities to the concentrations of the elements in the solution. Results of the Standard sample are presented in Table 6.

5. Conclusion

Contributions of different radionuclides to total annual effective dose from inhalations in adults and infants show that uranium series especially ^{226}Ra contributes mainly to the dose and it had the highest activity concentration followed by ^{238}U and ^{232}Th. The total annual effective inhalation dose obtained was 2.71 × 10^{-1} μSv.y^{-1} for adults and 1.31 × 10^{-1} μSv.y^{-1} for infants. The annual effective dose obtained in this study was below the prescribed dose range of 5–10 μSv.y^{-1} for both adults and infants, which means that the individuals are at minimum exposure risk.

The specific activity concentration for ^{226}Ra was twice the world mean atmosphere value, which is 1.0 μBq.m^{-3}. The Ra_{eq}, the external hazard (H_{ex}) and internal hazard (H_{in}) indices was calculated and the values obtained were lower than the world average, this shows that the radionuclides do not pose a significant radiological hazard but caution should be taken against cumulative long-term effects. However, the absorbed dose rate in air was higher than the world averages of 60 nGyh^{-1}, this could mean that the population is at risk and in the future the people might suffer from respiratory diseases or cancers. Dust and soil activities in gold mines should be monitored to ensure safety to the community located close to the mines and the community should be warned about the consequences of staying close to a mine.

Results of gross alpha and beta levels from this study do not exceed the WHO guidelines limits. The SA-DWAF target water quality limit was not exceeded. This indicates that the drinking water from MMM is safe for consumption and does not pose radiological health problems to the community. The results obtained from ICP-MS supports the results obtained from LSC because the heavy metals concentrations in drinking water did not exceed the stipulated limits.

Declarations

Author contribution statement

Dakalo Madzunya, Violet P Dudu: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Manny Mathuthu, Munyaradzi Manjoro: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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