INFLUENCE OF MINING ACTIVITY ON THE RADIOLOGICAL AND TOXICOLOGICAL HEALTH RISK IN THE ENVIRONMENT. A CASE STUDY OF SOME MINERAL MINING SITES IN NIGERIA.

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Abstract

Heavy metal and natural radionuclides characterisation of soil around some mineral ore mining industries have been carried out using Energy Dispersive X-Ray Fluorescence (EDXRF) analyses. The results show that heavy metals such as Cd, Pb, As, Cu, Cr, Zn, Ni, etc were present in varying concentrations. Nickel was found in nearly all the samples with concentration ranging from $260 - 450 \text{ mg kg}^{-1}$, Cadmium was detected ($2.31 \pm 0.32 \%$) in the samples from tin mining site and $9200 \pm 860 \text{ mg kg}^{-1}$ in the sample from tantalite mining site. As (> 200 mg kg⁻¹) was found in both iron and tantalite mining locations and Pb ($2200 - 5270 \text{ mg kg}^{-1}$) was found in large quantity in tantalite mining site. Cd, Zn and Fe were found in the same sample in some locations and the potential risk to the living organism as a result of Cd and Zn inhibiting the metabolism of Fe has been discussed. Uranium and Thorium also occurred in varying concentrations in the soil and mineral ore from tin mining sites. The external hazard index was much higher than unity for the samples and the mean outdoor effective dose due to the radionuclides from both the soil and the tin ore is ~ $0.70 \pm 0.04 \text{ mSv}$ h⁻¹ and the value of $2.0 \text{ Sv} \text{ y}^{-1}$ could be reached occupationally in the tin mining industries.

Keywords: Heavy metal, soil, mineral ore, radionuclide, health

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Introduction

The basic concept in environmental protection is to identify, measure and evaluate the potential risk to man posed by certain environmental factors. Unfortunately, this health risk is enhanced by human induced factors like mining activities, which have been known to contribute significantly to the health risk posed to human health all over the world.

Mining activities are well known for their deleterious effect on the environment and the negative impact of such activities on the environment is mainly due to deposition of large volume of tailings [1 - 6], which significantly affect the natural composition of the ecosystem and increased soil toxic metal concentrations [7 - 9].

Indiscriminate and improper deposition of tailings, especially on steep slopes, increases their mobility and hence, could be transported to large area [10]. These tailings usually contain high concentrations of heavy metals and the irreclaimable reagents and chemicals used in the extraction processes, which tend to increase the natural metal content of the soil. Moreover, they could attach to dust and aerosol during atmospheric deposition from smelting processes [11]. Heavy metals do not degenerate; hence, unregulated dumping of tailings from mining sites will lead to their bioavailability and bioaccumulation in the soil, surface water and natural vegetation. All these factors make mine tailings sources of pollution to the ground-and surface-waters, and soil in their vicinities.

The effect to man is of particular importance when these tailings prone lands are used for crops production thereby increasing the risk of heavy metal exposure to humans, either directly by inhaling suspended dust in air and dermal contact, or indirectly, by consumption of crops grown on the affected lands. Heavy metal overload is detrimental to the body and their accumulation on the wall of coronary arteries may impede normal blood flow and hence increase the probability of cardiovascular blockages. Heavy metal inhalation may result in serious health effect, normal functioning of the immune system may be compromised considerably [12]. The elements of toxicological health concern, which will be discussed here are Cd, Pb and As.

Cadmium

Cadmium stays in the body a very long time and can build up from many years of exposure to low levels. Exposure to cadmium can occur in the workplace or from contaminated foodstuffs and can result in emphysema, renal failure, cardiovascular disease, and perhaps cancer. According to Hellström et al [13], consumption of locally grown vegetables and root crops was an important exposure pathway for individuals living near cadmium waste generated plant.

Lead

Inorganic lead is not significantly absorbed through the skin, but is absorbed in small amounts from the gastrointestinal tract and more readily from respiratory tract in form of dust, fumes or vapours. In the blood compartment, it readily goes to the liver and kidneys, and is then stored in the bones. It also affects the red blood cells (anaemia and other blood related effects can occur), causes damage to organs including the liver, kidneys, heart, and male gonads, as well as causes effects to the immune system. However, the severity of these effects depend largely on several factors such as the form at which it is present in the soil, soil chemistry, oral bioavailability, and oral accessibility, which indicates the fraction that is soluble in the gastrointestinal environment and is available for absorption [14].

Arsenic

Arsenic is found in the soil inform of inorganic arsenic compounds with oxygen, chlorine, and sulphur and organic arsenic compounds with carbon and hydrogen in plants and animals.

Organic arsenic is usually less harmful than inorganic arsenic. Inorganic arsenic compounds are mainly used to preserve wood. They are also used to make insecticides, weed killers, fungicides and antifouling paints and its compounds in the environment can dissolve in water. Breathing workplace air, ingesting contaminated water, soil, or air at waste sites, are some of the possible ways in which the element get to humans. The element can damage many tissues including nerves, stomach and intestines, kidney, and skin [15] and can react with haemoglobin to form a very strong haemolytic poison. The element has been linked with cancer of the bladder, lungs, and skin, and kidney, nasal passages, liver and prostate.

In most mining sites in Nigeria, unregulated mining activities have been operational leading to indiscriminate dumping of industrial waste. Agricultural practices have been the main occupation of inhabitants around the mining area. The main staple foodstuff grown in the area are root tubers, cereal and vegetables and are being irrigated from streams and dams which also serve as repository for waste generated from proximate mining industries. Surface well water is often used as domestic and drinking water by the inhabitant of such area. In some other studies, heavy metals have been found in foodstuff and hence, have a potential health hazards to man through the dietary pathway in Nigeria [16]. Enhanced toxicity level posed by mining practices remains a source of concern in both occupational and public toxic protection programs.

The subject of safeguarding human health is very important since all activities of human endeavour depend on it. The identification and evaluation of the potential risk associated with mining industries remains the most powerful tool needed to protect man and the environment. Thus, there is the need to have a holistic approach to the investigation of all human induced factors and environmental phenomena in terms of exposure to pollutants and most significantly, radioactive materials. The radiation burden of an environment has been noted to increase significantly as a result of tin mining activities in Jos plateau [17]. The most critical aspect of this burden as noted earlier is the high probability of getting into the ingestion pathway due to improper and indiscriminate waste disposal mechanism. In response to the basic principle of protecting human health, this work is aim at identifying and characterising heavy metal composition in pollution source target, investigate the present activity level of radionuclides in the soil around some mineral ores mining industries and as well discussed the radiological and toxicological health implications to the populace in such areas.

Materials and Methods

Sample collection and preparation

Ten soil samples were collected from each of the three mining sites in Ekiti and the two mining sites in Kogi states in the South-western and central part of Nigeria (fig 1), respectively. In order to have representative samples from each location, soil samples were collected at a depth of 5 cm from ten locations within 1 km radius of the mining sites. Tin and tantalite ores were collected from several miners and the quantities were pooled together as the representative samples from Kabba and iron ore sample from Itakpe in Kogi state. Tin, tantalite and iron ores were collected from Ijero, Ilukun and Ipoti in Ekiti state, respectively. The samples were collected in clean polyethylene bags for transportation to the laboratory. Prior to analysis, all samples were sun-dried, pulverised and homogenised by grounding into fine powder in an agate mortar. The samples and the standard were pressed into thick pellets of about 13 mm diameter in Spec-Caps [18] without the aid of a binder ready for DEXRF analysis.

EDXRF Analysis

A Siemens FKO-04 tube type EDXRF spectrometer with Mo anode of a Kristalloflex 710H X-ray generator was employed in this work. The spectrometer made use of a Canberra series 7300 Si (Li) detector with a resolution of 165 eV at 5.9 keV, a Canberra series S 100 MCA card interfaced to a PC with a Canberra model 1510 integrated signal processor. The equipment operates under quantitative X-ray analysis system (QXAS) with data acquisition, spectrum and quantitative analysis and interpretation software. The samples and standards pellets were irradiated separately for 20 min at fixed tube operating conditions of 30 kV and 5 mA. The unfiltered Mo - $K_{\alpha,\beta}$ excitation allows determination of elements with characteristic K- and L- lines in the energy region of 3.3 – 16 keV [19]. A parameter-less smooth-filter model in the AXIL program of QXAS package was used to filter the spectra over the energy region of interest. The accuracy and precision of the analytical technique was performed using geological standards LINK Analytical Profile Reference standards by analysing the Bureau of Analysed sample LTD Standard Reference Material: BCS-CRM No. 355 (Tin Ore).

Results and discussion

The results of the elemental and natural radionuclides characterisation of some mineral ores and farm soil around the mining sites in Nigeria using EDXRF have been presented. The concentrations of the various elements found in farm soil from tin mining sites (Kabba and Ijero) are presented in Table 1. Seven elements (K, Ca, Cr, Mn, Fe, Cu and Cd,) were found in the soil from Kabba mining site while thirteen elements (K, Ti, Cr, Mn, Fe, Ni, Rb, Sr, Nb, Ta, Re, Th, and U) were found in the sample from Ijero mining site. The reason for the low number of elements found in the soil from Kabba as compared to that of Ijero is not clear. However, this might be due to geological factors since both locations are are situated in different geological belt of the Nigerian basement complex. Kabba is within the undifferentiated schist belt of Igara and Kabba-Jakura formation while Ijero fall within the politic schist of the South-western Nigeria. Furthermore, this could also be an indication of the difference in the level of pollution as a result of tin mining activity in the areas.

The concentrations of elements in farm soil from Iron mining sites are given in Table 2. Fourteen elements (K, Ca, Ti, V, Mn, Fe, Zn, Rb, Sr, Zr, Nb, Ta, Bi and Pb) were found in the sample collected from Itakpe while fifteen elements (K, Ca, Sc, Ti, V, Mn, Fe, Ni, Zn, As, Rb, Nb, Ta, Bi and Pb) were present in the sample from Ipoti. Itakpe is within the Okene migmatite complex in the South-central Nigeria and Ipoti falls within the politic schist of the South-western Nigeria. The elements found were quite similar although the soil samples from the two locations fall within different geological belt. This might suggest some level of pollution probably due to improper waste disposal mechanism.

The elements found in the farm soil around tantalite mining site from Kabba are presented in Table 3, eighteen elements (K, Ca, Ti, Fe, Cr, Mn, Ni, Zn, As, Br, Rb, Zr, Nb, Cd, Ta, Pb, Bi and Ra) were found in the sample. The presence of Pb, As, Cd, U, and Th, which are of serious public health concern in the soil samples, calls for comprehensive monitoring and documentation of the potential risk available from the various contamination pathways in the area. In response to this, the toxicological risk in relation to the metabolic roles of these heavy metals will be discussed and in addition to the radiological health hazards posed by radionuclides in the samples.

TOXICOLOGICAL HEALTH IMPLICATIONS

The primary elements of interest in this work are the heavy or toxic metals of Cd, Pb, and As, which are of toxicological importance to human health since there is no biological need for any of these heavy metals. Cadmium was detected in major quantity $(2.31 \pm 0.32 \%)$ in the samples from tin mining site, $9200 \pm 860 \text{ mg kg}^{-1}$ in the sample from tantalite mining site, Arsenic (> 200 mg kg⁻¹) was found in both iron and tantalite mining locations and Lead (2200

- 5270 mg kg⁻¹) was found in tantalite mining site. Lead concentrations in natural occurring surficial soils have been reported to range from less than 10 to 700 mg kg⁻¹ with an arithmetic mean of 19 mg kg⁻¹ for soils in the conterminous United States [20]. The high lead concentration reported in this study ($2200 - 5270 \text{ mg kg}^{-1}$), call for concern in view of the potential risk and the various contamination channels available in the area. The natural background concentrations of arsenic in the soil range from 0.1 to 40 mg kg⁻¹ [15]. However, it has been found in high concentrations ranging from 10000 to 20000 mg kg⁻¹ in American barrel and Midvale slag superfund sites [15]. In this study, although arsenic was found ranging from 200 to 280 mg kg⁻¹ in soils from iron and tantalite mining sites, its availability in the soil from both sites may also have been due to other anthropogenic sources such as agricultural uses (e.g. pesticides, insecticides, defoliants, feed additives and livestock dips), tanning operations, wood treatment/preservation operations, and releases as a by-product of burning coal. The potential risk posed by these elements call for more concerted effort in the management of industrial tailings.

The detection of Cd and Fe in the same soil samples from the tin and tantalite mining sites in Kabba could be very interesting in view of the interaction between the metabolisms of both elements in living organism. Furthermore, the presence of Zn and Fe in the soil samples from the iron mining Itakpe, and Ipoti (table 2), and the tantalite mining Kabba (table 3) could also be a source of concern. Siewicki et al [21] found that the dietary intake of Zn and Cd reduces the biological availability of dietary iron. According to them, foodstuffs containing high concentrations of these elements might reduce the dietary availability of iron and consequently escalate anaemia in persons or animals with marginal iron status. Studies from other authors have also shown that anaemia is caused by the reduction in iron absorption as a result of the competition between iron and cadmium ions in mucosal cells [22]. In view of the above, iron status in foodstuffs grown in such soil could be compromised. Consequently, the

already impoverished (apparently due to the few iron intake available from other sources) consumers of such foodstuffs might be prone to anaemia. The results presented in this study (tables 1-3) did not indicated directly, lead and Arsenic pollution of the farm soil except for Pb in Itakpe iron mining site (table 2). The contamination observed could be due to the chemical reagents used during mineral ore smelting and processing operations and other sources. However, direct cadmium contamination of the farm soil by the waste generated in the tantalite mining sites in Kabba and Ilukun could be suggested in view of the result in Table 3. Other anthropogenic sources earlier mentioned could also not be ruled out.

RADIOLOGICAL HEALTH IMPLICATIONS

Considering the values obtained using the EDXRF technique in the tin mining sites (table 1), and assuming secular equilibrium among uranium and thorium and their progenies for the purpose of calculating dose. Thus, the concentrations (%) given in Table 1 were converted to activity concentrations (Bq kg⁻¹) and ²³⁸U activity concentrations in Kabba tin ore and soil are 1.93 MBq kg⁻¹ and 1.01 MBq kg⁻¹, respectively. The Ijero ore and soil will be 1.61 MBq kg⁻¹ and 1.43 MBq kg⁻¹, respectively. The ²³²Th activity concentration in Kabba tin ore and soil are 0.37 MBq kg⁻¹ and 0.29 MBq kg⁻¹, respectively. The Ijero ore and soil will be 0.18 MBq kg⁻¹ and 0.34 MBq kg⁻¹, respectively. The ⁴⁰K activity concentration in Kabba tin ore and soil are 4.25 MBq kg⁻¹ and 3.11 MBq kg⁻¹, respectively. The Ijero ore and soil will be 5.08 MBq kg⁻¹ and 3.91 MBq kg⁻¹, respectively. The results show elevated activities of ²³⁸U and ²³²Th in the tin ores and soil samples from both locations and are in agreement with similar studies conducted in the tin mining areas of Jos plateau. Tin mining sites in the Jos plateau have been noted to be an area of elevated radionuclides activities [23 - 27].

Apart from the internal contamination pathway (via food, accidental unwashed hand to mouth, direct ingestion of soil and the respiratory passage) discussed earlier in this work, external radiation exposure from the gamma emitting radionuclides must not be neglected. Soils and tailings from mining industries have been reported to form a major component of building materials used by dwellers in the vicinity of the mining sites in Jos [27 - 28]. In view of the health hazards posed by the usage of these materials, the absorbed dose rate (D), the radium equivalent activity (Ra_{eq}) and the external hazards index (H_{ex}) due to the radionuclides from both the mineral ores and soil were estimated. The radionuclides activities concentrations presented earlier were converted to the absorbed dose rate using the equation:

$$D = C_{Ra} \times A_{Ra} + C_{Th} \times A_{Th} + C_K \times A_K, \qquad 2$$

where A_{Ra} , A_{Th} and A_{K} are the activities in Bq kg⁻¹ of ²²⁶Ra, ²³²Th and ⁴⁰K, respectively, and C_{Ra} , C_{Th} and C_{K} are the dose conversion factors in nGy h⁻¹ per Bq kg⁻¹ for ²²⁶Ra, ²³²Th and ⁴⁰K, respectively. The radium equivalent activities for the samples were obtained with the assumption that 10 Bq kg⁻¹ of ²²⁶Ra, 7 Bq kg⁻¹ of ²³²Th and 130 Bq kg⁻¹ of ⁴⁰K will produce the same gamma-ray dose rates defined as [29]:

$$Ra_{eq} = A_{Rq} + 1.43A_{Th} + 0.077A_K,$$
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where A_{Ra} , A_{Th} and A_{K} are the activities in Bq kg⁻¹ of ²²⁶Ra, ²³²Th and ⁴⁰K, respectively. It has been noted that in order to keep the external dose < 1.5 mGy y⁻¹, the maximum value of Ra_{eq} must be < 370 Bq kg⁻¹. Hence, equation 4 gives the external hazards index H_{ex} (Huy and Luyen, 2006):

$$H_{eq} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_{K}}{4810}$$

The absorbed dose rate due to these radionuclides in the tin ores and soil from Kabba are 1.30 \pm 0.50 mGy h⁻¹ and 0.76 \pm 0.18 mGy h⁻¹, respectively. The absorbed dose rate in the tin ore and soil from Ijero are 1.02 \pm 0.25 mGy h⁻¹ and 1.00 \pm 0.12 mGy h⁻¹, respectively. Radium

equivalent activity values are obviously higher than the recommended value of 370 Bq kg⁻¹. This suggested that there seems to be a serious radiological health risk to the area and the utilization of these materials for building construction purposes poses a lot of radiological threat to the populace. Thus, the calculated external hazard index H_x value is much higher than the limit recommended. External hazard index has been found to be higher than this limit by about 90% [27] in a tin mining site with elevated activity. The activity concentration values were converted to absorbed dose rate and subsequently into mean effective dose using 0.7 Sv Gy⁻¹ [30] and the occupancy factor of 0.33 representing 8 hrs of working hour for mine workers in the area. The effective dose values due the tin ore and soil around Kabba are 0.88 mSv h⁻¹ and 0.53 mSv h⁻¹, respectively, while that of Ijero tin ore and soil are 0.71 mSv h⁻¹ and 0.70 mSv h⁻¹, respectively. The results presented here suggested that the mean annual effective dose of 2 Sv y⁻¹ could be reached occupationally in both locations.

Conclusion

The elemental and radionuclide compositions of farm soil around some mineral ores mining sites in Nigeria have been presented in this work using the EDXRF technique. Heavy metals of environmental and public concern were found in the farm soil sampled and the implications to the natural ecosystem and human health have been enumerated. The presence of toxic metals like As, Cu and Pb in farm soil around these mining sites leaves much to be desired and made occupational and public toxic protection programme inevitable. Cd, Zn and Fe were found in the same sample in some locations and the potential risk to the living organism as result Cd and Zn inhibiting the metabolism of Fe has been discussed. Elevated activity concentrations of 238U and 232Th were found in the tin ore samples from the tin mining locations and in agreement with similar studies in the tin mining locations in the Jos plateau. External hazard index is much higher than unity in all the samples. The mean outdoor effective dose due to the radionuclides from both the soil and the mineral ores is $\sim 0.70 \pm 0.04$

mSv h⁻¹ representing 2.0 Sv y⁻¹ in tin mining industries. This result and the deleterious health hazards posed by the incorporation of toxic metals into the natural ecosystem call for caution, and indiscriminate dumping of mine tailings by mining industries in the area could undermine public health. As at present, little or no data is available as to the tolerance levels of heavy metal and the baseline background level of radionuclide in the studied area. Hence, a more comprehensive study in the area that will involve gamma spectroscopic analysis for nuclide specific determination and bioassay measurements (blood, urine and faeces) is necessary in order to be able to determine the level of internal contamination.

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