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Heavy Metal Composition of Some Solid Minerals in Nigeria and Their Health Implications to the Environment

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Abstract: Heavy metals overload taken via ingestion, inhalation and dermal have been found to be detrimental to both the occupationally exposed group and member of the public. The body burden of these metals has been a source of concern in environmental safety regulatory programs. The risk factor becomes potentially high in an environment where regulatory safety criteria are either neglected or not available. The implication of indiscriminate or unregulated mining activities has been pointed out as a major risk to public health. In order to assess the potential toxicological and radiological health hazard posed to the environment due to mining activities in Nigeria, solid mineral ores (iron, tin and tantalite) from south-western and north-central (Kogi and Ekiti States) part of the country were analysed for their trace-metal contents. The analysis was performed using Energy Dispersive X-Ray Fluorescence (EDXRF) analyses spanning several months between 2005 and 2006. The samples were found to contain some major, minor and trace elements of varying concentrations. The elements reported here are K, Ca, Ti, V, Cr, Mn, Fe, Ni, Sr, Y, Zr, Nb, Sn, Ta, Re, Th, U, Sc, Cd, Bi, Ra and Zn. Toxic metal of serious environmental and public concern like Cadmium was detected. The possibility of altering heavy metal constituents of the natural ecosystem as a result of mining activities and the implications of such alterations has been enumerated. Possible pathway into the food chain as a result of mining activity has also been presented.

Key words: Heavy metals, natural radionuclide, contamination, mineral ore, public health

INTRODUCTION

Heavy metals are natural constituents of the Earth's crust, but human activities have drastically altered their geochemical cycles and biochemical balance (Giachetti and Sebastiani, 2006). Mining activities all over the world have contributed immensely to this observed disequilibrium and therefore affect the terrestrial ecosystem due to the excavation of large amount of sand and the eventual accumulation of large volume of tailings. Serious environmental impact like the destruction of natural soil, extraction of important volumes of materials and elevated levels of trace elements are frequently common characteristics of most mining tailings (Vega *et al.*, 2004). Although heavy metals are released in varying quantities into the soil from parent materials, increasing environmental contamination has been caused by human activities, such as mining, smelting, fossil fuel combustion, agricultural practices and waste disposal and extraction of metal ore causes generally a multi-elemental contamination of the environment (Remon *et al.*, 2005; Perry *et al.*, 2005; Adamo *et al.*, 2003; Banat *et al.*, 2005; Akinlua *et al.*, 2006; Birkefeld *et al.*, 2006). 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. Heavy or toxic metals are trace elements that are non bio-degenerate and indiscriminate dumping of tailings from mining sites will lead to bioavailability and bioaccumulation in the soil, surface water and natural vegetation. The most critical effects of this pollution occur when toxic waste accumulates in farmlands. High concentration of these metals in soil may cause long-term risk to ecosystems and humans (Querol *et al.*, 2006). Food crops grown on such land accumulate toxic metals, which find their way into the food chain. The health risk to human become very high from heavy or toxic metal exposure either by direct inhalation of suspended dust particles in air and dermal contact or indirect ingestion through consumption of food crops grown in tailing enriched land. Although the body need some trace elements for proper functioning, there are however, some toxic metals that interfere with enzyme systems and metabolism of the body (Calabrese, 1981). Heavy metal overload is detrimental to the body, accumulation on the wall of coronary arteries impede

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normal blood flow and hence increase the probability of cardiovascular blockages (www.tuberose.com/heavymetaltoxicity.html). Heavy metal inhalation may result in serious health effect, normal functioning of the immune system may be compromised considerably (www.tuberose.com/heavymetaltoxicity.html). 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 like root tubers, cereal and vegetables are being irrigated from streams and dams in the mining sites. The dams and streams also serve as domestic drinking water for the inhabitant of such area. Heavy metals have been found in food crops and have a potential health hazards to man through the dietary pathway in Nigeria (Obiajunwa *et al.*, 2001). In view of the serious hazards posed to man, especially through the ingested and inhalation pathway, their concentration and disposition pattern cannot be neglected in order to properly access the overall body burden. This study is aim at identifying and characterising heavy metal composition in some solid minerals with the view to identifying their implications to both the occupational and public health groups as a result of mining and smelting activities in the area.

MATERIALS AND METHODS

Geology of the sampling sites: The study area lies within the Nigerian basement complex with three broad litho logical groups. The poly-metamorphic migmatitegnesis of various compositions, the low-grade sediment dominated schist and the sync-tectonic to late tectonic granitic rock of varying compositions. Two distinct provinces can be distinguished in this basement complex, the Western which is characterised by narrow low grade schist belt and the Eastern which comprises mostly migmatites, granites and Mesozoic young granites. The South-western Nigeria is a part mostly recognised by five major groups of rocks: the migmatite-gneisis complex which comprises quartzite, quartz schist and small lenses of calc-silicate rocks; the slightly migmatised to unmigmatised paraschists and meta-igneous rocks which consist of politic schist, quartzite amphibolites, talcose rocks, met conglomerates, marbles and calc-silicate rocks; charmockitic rock; older granites, unmetamorphosed dolerite dykes believed to be the youngest. The migmatite-gneisis complex is thought to have resulted from a complex association of deformative shearing and folding and granitisation and migmitisation processes. The slightly migmatised to unmigmatised Para schist represent a sedimentary cover on the gneisis-migmatite complex. Iktape where iron ore was collected is within the Okene migmatite complex in the South-central Nigeria and the deposit is described as a hematite-magnetite quartz body in a ferruginous quartzite type. The Kabba area where tin and tantalite is found is within the undifferentiated schist belt of Igara and Kabba-Jakura formation. This is part of the most Easterly schist belts in the South-western Nigeria distributed around the Okene Migmatic nucleus. There is no geochronological evidence available for the age of this belt, but there are diverse structural trends and association with Pan African granites which suggested a Kiboran age. The Ijero tin, Ilukun tantalite and Ipoti iron ores fall within the politic schist of South-western Nigeria. The schist belt in this area is extremely poorly exposed because of tropical climate conditions and rainforest vegetation.

Sample collection and preparation: Mineral ore samples were collected from mining sites in Ekiti and Kogi states in the South-western and central part of Nigeria, respectively. Tin and tantalite ores were collected 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 (Obenauf, 1991) without the aid of a binder ready for analysis.

Analysis: A Siemens FKO-04 tube type EDXRF spectrometer with Mo anode of a Kristalloflex 710H X-ray generator was employed in this study. 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) (Annonymous, 1993) with data acquisition, spectrum and quantitative analysis and interpretation software. The procedure by Obiajunwa *et al.* (2002) was employed in which 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. The 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 characterisation of some mineral ores mined in Nigeria using EDXRF have been presented. Trace and major elements were found in tin ore from two mining sites (Kabba and Ijero) are presented in Table 1. The following elements (K, Ca, V, Mn, Fe, Ni, Sr, Y, Sn, Ta, Re, Th and U) were found in tin ore from Kabba mining site while the elements (K, Ca, V, Mn, Fe, Ni, Sr, Y, Zr, Nb, Sn, Ta, Re, Th and U) were found in the sample from Ijero mining site. The concentrations of the various elements in trace and major quantities; in Iron ore from two mining sites are shown in Table 2. The elements (Ti, Cr, Mn, Fe, Ta and Ca) were found in the sample collected from Itakpe while the following elements (Sc, Ti, Cr, Mn, Fe, Cd, Ta, Re, Ca and Bi) were present in the sample from Ipoti. The elements found in tantalite ore from Kabba mining site were shown in Table 3, the elements (Ca, Ti, V, Cr, Mn, Fe, Zr, Nb, Cd, Ta and Ra) were found in the samples. It should be noted that Ti and Cr were not found in tin ore samples from both mining sites presented in Table 1 while Zr and Nb found in the same sample from Kabba were not present in the sample from Ijero and Ca found in major quantity in the sample from Kabba was found in trace quantity in the sample from Ijero. The differences in the elemental composition of tin samples from the two locations could be attributed to different chemical formations of tin compounds with other metals and geological factors since the two locations fall under different lithological groups of the Nigerian basement complex. Geological factors have also been adduced for the presence of Sc, Cd and Bi in the sample from Ipoti and not in the sample from Itakpe. Calcium was found in the sample from Itakpe and not present in the sample from Ipoti and Ti found in significant proportion in the sample from Ipoti was found in trace proportion in the sample from Itakpe. It is also worthy of note that iron ore presented in Table 1 has the greatest elemental composition when compared ith other mineral ore samples analysed. Iron is the most abundant metal on Earth and is believed to be the tenth most abundant element in the universe. It is also the second most abundant (by mass, 34.6%) element making up the Earth and readily form compounds with other inorganic elements; the concentration of iron in the various layers of the Earth ranges from high at the inner core to about 5% in the outer crust. Tantalite-columbite or tantalite-niobium ores are oxides of tantalum, niobium oxide, iron and manganese $(Fe,Mn)(Ta,Nb)_2O_6$.

Table 1: Concentration (mg kg^{-1} except otherwise stated in %) of elements in Tin Ore from two mining sites

Elements	Kabba (Kogi)	Ijero (Ekiti)
K	1.64±0.64 (%)	1.96±0.63 (%)
Ca	1.34±0.31 (%)	9760.00±220
Ti	ND	ND
V	720±120	600±110
Cr	ND	ND
Mn	960±170	1190±200
Fe	103±180	4740±730
Ni	680±120	410±70
Sr	1200±210	500±100
Y	1440±250	770±160
Zr	ND	860±200
Nb	ND	1.47±0.23 (%)
Sn	77.45±4.78 (%)	64.05±4.00 (%)
Ta	5.87±0.32 (%)	7.16±0.35 (%)
Re	2840±630	2000±470
Th	9.03±1.63 (%)	4.25±1.09 (%)
U	15.50±2.95 (%)	13.00±2.27 (%)

ND: Not Detected

Table 2: Concentration (mg kg^{-1} except otherwise stated in %) of elements in Iron Ore from two mining sites

Elements	Itakpe (Kogi)	Ipoti (Ekiti)
Sc	ND	9260±187
Ti	2790±730	33.33±5.00 (%)
Cr	2300±470	800±160
Mn	7670±144	8160±133
Fe	45.54±6.82 (%)	28.17±4.22 (%)
Cd	ND	6.14±1.05 (%)
Ta	2480±230	2320±490
Re	ND	1380±250
Ca	980±220	ND
Bi	ND	4900±170

ND: Not detected

Table 3: Concentration (mg kg^{-1} except otherwise stated in (%)) of elements in Tantalite Ore from a mining site

Elements	Kabba (Kogi)
Ca	680.00±140
Ti	2150.00±335
V	1030.00±180
Cr	340.00±70
Mn	4.10±0.61 (%)
Fe	9.50±1.42 (%)
Zr	5930.00±950
Nb	31.00±4.66 (%)
Cd	5170.00±120
Ta	31.46±1.49 (%)
Ra	1.96±0.32 (%)

In this study, although most toxic metals of public concern (Pb, As and Hg) were not found in any of the mineral ore sampled, the presence of toxic metal like Cd, which is also of toxicological importance to human health should be noted. According to Hellström *et al*. (2007), Cadmium is known to be a toxic metal, which is widely spread in the biosphere in spite of restrictions for its use and it is important to consider all routes of exposure. Cadmium was detected as one of the major element (6.14±1.05%) in iron ore from Ipoti and in trace quantity (5170±126 mg kg^{-1}) in tantalite ore from Kabba and this call for concern. There is no biological need for this heavy metals and it has many commercial applications, including electroplating and the manufacture of batteries. Although Cd occur naturally on bedrock and soil, anthropogenic sources of Cd such as industrial emissions and the application of soil amendments like lime, phosphate-fertilisers and sewage sludge to farm land, may lead to contamination of soil by Cd and increase uptake by cereal crops, vegetables and root crops (Hellström *et al*., 2007). Cadmium enters air from mining industry, burning coal and household wastes. Cadmium particles in air can travel long distances before falling to the ground or water. WHO (2000) reported an annual mean air Cd concentration between 0.1 and 0.5 ng m^{-3} for rural areas in Europe. Additionally, levels up to 100 ng m^{-3} were found in the proximate vicinity of an emission source. Cadmium enters water and soil from waste disposal and spills or leaks at hazardous waste sites. It binds strongly to soil particles; some dissolves in water and doesn't break down in the environment, but can change forms. Fish, plants and animals take up cadmium from the environment. 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 (www.tuberose.com).

Chromium value ranged 800-2300 mg kg^{-1} in iron ore samples from Ipoti and Itakpe mining sites and has value of 340 mg kg^{-1} in tantalite ore from Kabba. The metabolic role of Chromium is such that trace quantity of the element is useful in the body; however, increased body load of the element may result in allergic reactions. Nickel was found in tin ore with concentration ranging from 410-680 mg kg^{-1} and it is needed in the body. According to Nielsen (1985), Nickel acts as a facilitator for the intestinal absorption of ferric iron and it is therefore an essential metal. Titanium was found in high concentrations raging between 2150 mg kg^{-1} and 33.33 % in iron ore and tantalite ore. In spite of the abundance of titanium in lithosphere and soil, the element was not found in tin ore. The high concentration of titanium in the mineral ores may not pose serious health hazards because it is being poorly absorbed and retained by plants (Olabanji *et al*., 2006). Vanadium has been found in tin and tantalite ores with concentrations ranging between 600 and 1030 mg kg^{-1}. Vanadium is a relatively toxic element and few micrograms per gram of dietary vanadium could easily exert a pharmacological effect in vivo, especially if the nutritional status of the organism were suboptimal and high body burden can influence the metabolism of a number of nutrients (Nielsen, 1985). Manganese and iron were found in all the mineral ores analysed, Mn concentrations ranged between 960 mg kg^{-1} and 4.10% and Fe ranged between 1030 mg kg^{-1} and 45.54%. Although these elements are considered to be among the least toxic elements, increased body load can be harmful. Calabrese (1981) noted that some essential elements like Fe, Mn, Zn and Ca are beneficial to human body, but overload of such elements could influence the metabolism of toxic elements like Cd and Pb. Thorium and uranium, which are of both occupational and public radiological concern were present in major quantities in tin ore with concentration ranging between 4.25 and 15.50%. Trace quantity (4900 mg kg^{-1} at Ipoti) of their daughter product Bi was also found in iron ore and Ra in major quantity (1.96%) in Tantalite ore. Tin mining activity has been known to contribute to increased radionuclide burden of the environment. Oresegun and Babalola (1988) noted the presence of elevated activity of thorium and uranium in tin tailings in Jos plateau. Over the years, more attention has been given to environmental research around the Jos plateau and no information exists on the levels of radionuclides in the present study area.

In view of the deleterious health hazards posed by the incorporation of these heavy metals into the natural ecosystem, it is worthy of note that the indiscriminate dumping of mine tailings by these mining industries will undermine public health. As at present, little data available indicate the presence of these elements in food in Nigeria (Olabanji *et al*., 2006; Obiajunwa *et al*., 2005). Majority of the inhabitants of the mining communities are peasant farmers and large scale agricultural practices like food crops cultivation is on the increase. The same farmland used for crop production also serves as repository for waste generated from the proximate mining industries. Although various contamination channels are possible, anthropogenic contamination pathway like mining and smelting activity is also plausible due to the generation of industrial tailing. In this study, most heavy metals of public concern were not found in the mineral ores sampled. However, this is not an indication that the environment is risk free in spite of active mining activities of these mineral ores. The presence of toxic metals like Cd; whose overload may result in nephrotoxicity and Cr which may result in allergic reactions calls for caution. The possibilities of altering the natural constituents of the essential metals with limited body load in the environment remain one of the major reasons to be cautious. In order to evaluate and assess various channels of mineral overload in the environment, possible heavy metal incorporation pattern into the food chain and hence member of the public was developed as presented in Fig. 1. The Fig. 1 presents the various possible pathways by which the member of the public could have contact

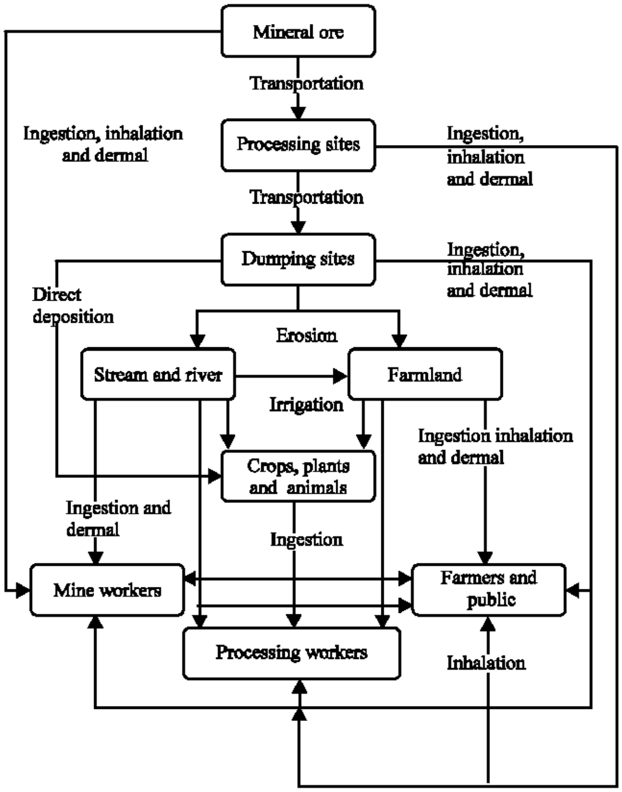

Fig. 1: Heavy metal incorporation pattern into the natural ecosystem and inhabitants around mining site in Nigeria

with these metals as a result of mineral ore mining activities in an unguided tailing deposition environment. During mining and processing activities, mine and processing workers directly inhale dust and fumes containing airborne particulates of these minerals. Other means of direct internal contamination include ingestion of food during routine work and dermal from dust that are likely to settle on sweat prone skin surfaces due to high temperature environment and heavy exercise. The indirect means of contamination include internal contact through ingestion pathways from crops and animals grown in contaminated areas. Inhabitants with close proximity to the processing sites are also prone to direct contact through inhalation of airborne particulates, which can travel long distances. Hellström *et al.* (2007) also noted that almost half of indoor dust is considered to be derived from outdoor. Apart from the direct channel, industrial tailings dumped indiscriminately could influence the natural concentrations of heavy metal in the soil (Giachetti and Sebastiani, 2006; Norland, 1995; Wong *et al.*, 1998). Increased bioavailability of these metals in crops grown in such land indirectly lead to increased body burden in humans.

CONCLUSIONS

The elemental compositions of some mineral ores mined in Nigeria have been presented in this work using the EDXRF analytical technique. Heavy metals of varying concentrations were found in the mineral ores (Iron, Tin and Tantalite) sampled. Although no heavy metals of serious environmental and public concern except Cadmium were detected, the possibility of altering metal constituents of the natural ecosystem as a result of mining activities and the implications of such alterations have been enumerated in this study. The possibilities of enhancing Cd uptake by cereal crops, vegetables and root crops therefore call for caution and make occupational and public toxic protection programme inevitable in the area. Thorium and uranium have been found in major quantities in tin ore from Kabba and Ijero were such information had never existed. Possible heavy metal pathways into the food chain and humans have been developed for easy assessment of contamination in the environment. The possibility of both public and occupational exposure to toxic metals by inhalation, ingestion and dermal also make proper management of waste products from mining industries in Nigeria very important.

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