Environmental and health impact of potentially harmful elements distribution in the Panyam (Sura) volcanic province, Jos Plateau, Central Nigeria

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Abstract The Panyam volcanic province is a plateau covering a superficial area of about 1200 km², dotted by a number of dormant volcanoes forming prominent landmarks above the host continental gneiss–migmatite–granite rocks and stretching for about 12 km. The volcanism is basaltic, characterized by alkaline–calc–alkaline compositions. Large population of people live and depend on the volcanic environment for potable water and agriculture, most of whom display various forms of health problems ranging from dental caries, goitre, podoconiosis, etc. This study therefore seeks to evaluate the concentration levels of potentially harmful elements (PHEs) in the various components of the volcanic environment and their relationship with the inherent human health problems in the area. Volcanic soils and underground waters (springs/boreholes waters) were collected from within the volcanic province for the analysis of major cations and anions. Samples of the volcanic soils were analyzed for the following heavy elements; Be, Co, Cr, Cu, As, Cd, Pb, Sb, Se, V, and Zn. Water samples were analyzed for the major cations (Mg²⁺, Ca²⁺, Na⁺ and K⁺) and major anions (NO₃²⁻, SO₄²⁻, Cl⁻, HCO₃⁻ and F⁻) to determine their hydrogeochemical characteristics so as to identify the major sources of the cations and anions and factors controlling their distribution. The volcanic soils display mean values in Be, Co, Cr, Ni, Pb, Sb and Se above the baseline regional values with enrichment factors (EF) ($2 \leq EF \leq 5$) indicating moderate

to strong enrichment in the volcanic soils. Contrarily, there is clear impoverishment of As, Cd, Cu, V and Zn in the volcanic soils relative to the baseline values ($0 \leq EF \leq 2$). Except for Ni and Se which seem to have contaminated the volcanic soils [pollution load index (PLI) > 1], these other elements As, Be, Cd, Cr, Cu, Pb, Sb, V and Zn with PLI < 1 did not, possibly suggesting little or no anthropogenic input. The rare earth elements (REEs) are equally enriched in the volcanic soils and like most of the other PHEs, they must have been scavenged and co-precipitated with Fe during the weathering of the parent basaltic rock. The significantly lower La/Ce ratios (0.30–0.57) in the volcanic soils attest to the moderate to slightly severe intensity of weathering the parent basaltic rock was subjected to. The waters are predominantly (80 %) of Ca–Mg–HCO₃ type with the remaining 20 % of Na–K–HCO₃ type suggesting a control by water–rock alteration process from the host granitic basement and the overlying basaltic rocks. The fluoride content in all the water sources is positively correlated with the contents of Mg²⁺, Na⁺, and K⁺ suggesting a similar source and geochemical process. Tooth decay, a common tooth disease conditions in the volcanic province, could be linked to the low F content in the waters.

Keywords Volcanoes · Basaltic rocks · PHEs · Human health · Jos Plateau · Panyam volcanic line

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Introduction

The Panyam volcanic province, situated on the Jos Plateau Central Nigeria, consists of seven major dormant volcanoes namely: Ndai Volcano (referred to as Wushik volcano), Amshal Volcano (referred to as Kogul Volcano), Dutsin

Volcano, Kerang Volcano, Timgya'ras Volcano, Ampang Volcano (referred to as Mufil Volcano), and Pidong Volcano or Pidong Volcanic Crater Lake; all aligned along NNW–SSE trend (Lar et al. 2007) and stretching for a distance of about 10 km (Figs. 1, 2). It is the second largest volcanic province in Nigeria with a superficial area of 1200 km² after Biu volcanic province with an area of about 2500 km² (Lar et al. 2007; Lar and Usman 2012). None of these volcanoes has erupted in time immemorial. There is sufficient evidence to suggest that the lava that gave rise to these edifices extruded through a series of linear megastructures in the host Basement migmatite–gneisses complex (Tsalha et al. 2014). The volcanoes occur either as large single cones or as composite cones usually with very large craters (up to 1 km). The volcanic edifices are built of mainly basaltic scoria and pyroclastics riddled with voids filled with phenocrysts of olivine, clinopyroxene or garnet. Mineralogically, the fresh basaltic rocks consist of olivine, pyroxene (augite), plagioclase (labradorite) and accessory minerals such as ilmenite/magnetite and garnet displaying the same characteristics as those of the Benue trough and that of the Cameroon volcanic line (Lar and Tsalha 2005).

Recent Ar–Ar dating of similar volcanic edifices on the Jos Plateau has recorded ages of spanning from 1.95 to 1.34 Ma (MacLeod et al. 1971; Lar et al. 2007) ascribing their emplacement to the Pleistocene epoch. The high proportion of fragments of the host basement rocks in the pyroclastic pile in addition to the highly vesicular nature of

Fig. 1 Satellite image of Panyam volcanic province

Fig. 2 Geological map of Panyam volcanic province (modified from the satellite image)

the basaltic materials in the volcanic edifice suggest violent eruptions in most cases (Lar et al. 2007). The basalts have been affected by various degrees of weathering where they have been decomposed to lateritic soils. However, fresh unweathered basaltic lava flows can be traced along river channels, for example at Ajing, Bwonpe, Kerang, Pang and Kogul (Panyam) (Gusikit 2010).

Volcanic eruption process is known to bring along with it chemical elements from depth (mantle) which ordinarily are not abundant on the earth's surface. Thus, soils developed from these basalt piles contain concentrations of heavy metals which could be released and redistributed into the soils, surface and ground water through the weathering processes.

In most soils developed on basalts, high baseline values of heavy metals such as Pb, Zn, Sb, Hg, Cd, Cr and Cu have been recorded (Cicchella et al. 2005), however, this has been attributed partly to anthropogenic contribution due to a long period of human activity in the area (Cortizas et al. 2003). Certain forms of diseases such as cancer especially in males have also been reported to be higher than the regional average on the Ischia volcanic Island attributable to high radioactivity (Fratinin et al. 2006). Human exposure of unprotected feet to high concentrations of Zr and Be in volcanic soils which have the ability to induce granuloma in the lymphoid tissue of man is a causal factor in the development of pododermatitis (Frommel et al. 1993). Goiter prevalence in the Kenyan Rift African valley, an active volcanic environment, has been linked to iodine

deficiency in drinking water (3.7–24 µg/l) from wells and surface water sources in the area (Davies 1995, 2008). Recent studies in the Biu Plateau Volcanic province, North Eastern Nigeria have revealed high values of As, Pb, Sb and Se in drinking water sources and linking over-exposure to essentially Arsenic to various forms nail of deformities and skin hyperpigmentation (Lar and Usman 2012).

This paper therefore attempts to assess the concentration levels of some potentially harmful elements and the possible human health impact on the human population who live and are engaged in subsistence agriculture in the fertile volcanic soil of the Panyam volcanic province.

Materials and methods

Field methods

Seven soils were collected from the volcanic province each from a square grid of a 20 m × 20 m dimension in accordance with IGCP 259 recommended practice (Darnley et al. 1995). Using a soil auger, four holes at the corner of the square grid (field) were dug up to 30 cm (below the A₀ horizon) and a composite soil sample collected from each hole. The four sub-samples were homogenized, and about 400 g was collected and stored in a plastic container for chemical analysis. Eleven samples of potable water were collected: four from boreholes and seven from springs each in a 200-ml capacity. The bottles were pre-soaked in de-ionized water over the night to eliminate contaminants. At each sampling point, each bottle was rinsed with the sample water to be collected three times before it was finally collected. The samples were acidified with two drops of concentrated nitric acid to prevent fungal growth and the adsorption of the analytes to the walls of the sample container. Borehole water was pumped out for several minutes to ensure that only fresh water oozing out from the aquifer is collected. For the spring's water, the samples were collected close to the emission points.

Sample preparations

The soil samples were pulverized using an agate mortar and pestle to a size below 2-mm mesh. 50 g of each sample was weighed and stored in airtight glass vials for shipment for geochemical analysis. Polyethylene sampling bottles of 30-ml capacity were rinsed with distilled water before being used for sample collection. Each of the water sample bottle was tightly sealed and stored in a refrigerator at a temperature of about 23 °C for a week before shipment for analysis. Laboratory procedures were in accordance with the standard test procedures. Geochemical analysis of both water and soil samples was done at the Activation

Laboratories, Canada. In the laboratory, the soil samples were dried at a low temperature of 30–35 °C for 6–12 h to avoid loss of Se, Hg, and As. A 0.5-g sample was digested in aqua regia at 250 °C in a microprocessor-controlled digestion box for 2 h.

Analytical technique

Both the soils and water samples were analyzed for the following trace elements: Cr, Ni, Co, As, Se, Pb, Cu, V, Be, Cd, Ni, Sb, and Zn by inductively coupled plasma–mass spectroscopy (ICP/MS) using a Perkin Elmer SCIEX ELAN 6100. The quality of the analysis was controlled through the analysis of International certified reference materials USGS GXR-1, GXR-2, GXR-4, and GXR-6 introduced at the beginning and end of each batch of samples. Internal control standards are analyzed every 10 samples and a duplicate is run for every 10 samples. The values obtained by the instrument from the reagent blank are automatically subtracted from the raw data before printout. This makes the data free from whatever impurities inherited from the reagents including distilled and de-ionized water. The results turnouts have an accuracy of ±2–5 % depending on the number of standards used and concentration levels. The instrument was calibrated prior to the introduction of sample by measuring in-house standards and blank solutions. Ion chromatography was used to analyze for Fluoride including other anions such as Cl, Br, NO₂, NO₃, PO₄ and SO₄.

Data evaluation

Determination of enrichment factor (EF)

To assess the level of depletion or enrichment of the heavy elements in the soils, an enrichment factor was used (Krzysztof et al. 2003), where;

$$EF = \frac{C_n(\text{sample}) / C_{\text{ref}}(\text{sample})}{B_n(\text{background}) / B_{\text{ref}}(\text{background})}$$

where C_n (sample) = concentration of the elements in the soil sample, C_{ref} (sample) = concentration of the element in the fresh basalt, B_n (background) = mean of the concentration of the elements in the soil sample, and B_{ref} (background) = mean of the concentration of the elements in the fresh basalt.

The EF values are classified into five (5) classes by Sutherland (2000), where $0 \geq EF \leq 2$ is classed as deficiently to minimal enrichment (Class 1); EF between 2 and 5 signifies moderate enrichment (Class 2); $5 \geq EF \leq 20$ indicates significant enrichment (Class 3); values of $20 \geq EF \leq 40$ are classified as very high enrichment

Table 1 The values of the enrichment factor of the PHEs in the volcanic soils

Locations	As	Be	Cd	Co	Cr	Cu	Ni	Pb	Sb	Se	V	Zn
Ajing1	0.01	2.99	0.30	2.40	2.18	2.77	5.46	0.78	0.41	0.18	1.97	1.30
Bwonpe	0.01	2.99	0.20	2.78	2.78	2.95	7.40	0.55	0.31	0.12	2.30	1.35
Kurgwam	0.01	2.87	0.35	2.42	2.42	2.61	6.00	0.44	0.10	0.15	2.00	1.35
Punguk	0.01	3.35	0.25	2.52	1.64	0.60	3.96	0.69	0.31	0.12	1.95	1.29
Amshal	0.01	2.99	0.30	1.76	1.37	1.53	2.47	0.82	0.31	0.15	2.33	1.00
Konji	0.01	2.40	0.40	1.67	1.29	1.65	1.61	1.02	0.26	0.06	1.86	0.86
Ugut	0.01	2.40	0.40	1.67	1.29	1.89	2.27	0.70	0.41	0.12	1.59	1.60

(Class 4) and finally $EF \geq 40$ is characterized as extremely high enrichment (Class 5). EF values equal to or less than 1 indicate no anthropogenic contribution but from predominantly crustal material (the background) and/or weathering process, whereas EF values greater than 1 suggest an anthropogenic origin of the element (Gong et al. 2008). The values of the enrichment factors for each of these elements are presented in Table 1.

Determination of pollution load index (PLI)

To assess the extent to which the volcanic soil have been contaminated by the PHEs, a pollution load index (PLI) (Tomlinson et al. 1980) was employed and is expressed by the equation:

$$PLI = \sqrt[CF1 \times CF2 \times CF3 \times \dots \times CFN]{}$$

where CF, contamination factor = $C_{\text{metal}}/C_{\text{background value}}$, N , number of heavy metals, C_{metal} , the concentration of pollutant in soils, $C_{\text{background}}$, background value of the heavy metal. The values of PLI are presented in Table 2. The PLI values are classified into 5 classes ranging from uncontaminated (PLI value of <1) to extremely contaminated (PLI value of >1). The contamination factor (CF) has been categorized ranging from low contamination to very high contamination as shown below (Hakanson 1980):

Contamination factor	Level of contamination
$CF < 1$	Low contamination
$1 \leq CF < 3$	Moderate contamination
$3 \geq CF < 6$	Considerable contamination
$CF > 6$	Very high contamination

Calculation of the percent change in the concentration of the total rare earth elements (REE)

A simple mass balance calculation is used here to determine the percentage change in the concentration of the

REEs in the basaltic rocks during alteration. The percentage increase or decrease of the REEs in a sample relative to the reference fresh parent basaltic rock is calculated using the formula $\left(\frac{(\sum REEs)_{\text{sample}}}{(\sum REEs)_{\text{parentrock}}} \right) - 1 \times 100 \%$ (Lar et al. 2000, modified from Nesbitt 1979). The values for the percentage change in the REEs in the samples are presented in Table 3. The percentage change of the REEs in a sample relative to that of the reference parent rock approaches 100 % whenever the sample is severely weathered and is equal to 0 % for unaltered rocks.

Results and discussion

The potentially harmful elements (PHEs) and rare earth elements (REEs) compositions in the volcanic soils are presented in Tables 3 and 4, respectively.

Table 2 Pollution load index of potential harmful elements (PHE) in volcanic soils of the study area

Metal	Pollution load index	Remark
As	00	Uncontaminated
Be	0.50–0.90	Uncontaminated
Cd	–2.00 to –3.00	Uncontaminated
Co	–0.20 to –0.89	Uncontaminated
Cr	–0.2 to 0.40	Uncontaminated
Cu	–1.3 to –3.70	Uncontaminated
Ni	–1.10 to 1.10	Uncontaminated to moderately contaminated
Pb	0–0.80	Uncontaminated
Sb	–2.1 to –3.90	Uncontaminated
Se	1.40–3.00	Moderately contaminated to strongly contaminated
V	–1.20 to –1.80	Uncontaminated
Zn	–0.5 to –1.3	Uncontaminated

Table 3 Rare earth elements (REEs) concentrations (in mg/kg) in the volcanic soils

Sample Number	Location	Coordinate	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Total REEs	% Change REE	La/Ce	La/Yb
Sm1	Ajing	N ⁰ 18'06" E ⁹ 13'42"	55.7	115	14.3	52	10.2	2.9	8.7	1.2	6.6	1.1	2.7	0.4	1.7	0.2	272.5	62.5	0.48	32.77
Sm2	Bwonpe	N ⁹ 18'03" E ⁹ 13'05"	55.2	115	12.9	47.5	9.3	2.7	8	1.1	5.8	1	2.4	0.3	1.3	<0.1	262.5	56.7	0.48	42.46
Sm3	Kurgwam	N ⁹ 19'53" E ⁹ 12'00"	50.5	89.1	12.4	45	9.3	2.9	8.2	1.1	6.4	1.1	2.7	0.4	1.5	0.1	230.6	37.6	0.57	33.67
Sm4	Punguk	N ⁹ 21'51" E ⁹ 10'22"	48.3	137	12.3	44.5	9.1	2.6	7.5	1	5.5	1	2.4	0.3	1.3	0.1	272.8	62.7	0.35	37.15
Sm5	Amshal	N ⁹ 22'00" E ⁹ 10'59"	52.4	141	13.7	49	10	2.8	8.7	1.1	6.1	1.1	2.7	0.3	1.8	0.2	290.7	73.6	0.37	29.11
Sm6	Konji	N ⁹ 21'24" E ⁹ 10'26"	36.5	122	8.7	30.4	5.8	1.3	4.7	0.6	3.6	0.7	1.7	0.2	1.4	0.2	217.6	29.9	0.30	26.07
Sm7	Ugut	N ⁹ 22'29" E ⁹ 10'24"	42.8	102	11.1	39.7	8	2.1	6.7	0.9	4.9	0.9	2.1	0.3	1.3	0.1	222.4	32.7	0.42	32.92
Fresh basalt (Taylor 1964)	Average Crustal Abundance		15	48	20	5.3	0.8	5.3	0.8	–	1	2.1	0.2	2.1	0.6	0.15	93.08	–	0.31	25
Fresh basalt sample (Lar et al. 2000)	From Jos Plateau, Nigeria.		38.6	67.99	7.46	29.36	6.06	1.97	5.76	–	4.81	0.78	1.81	–	1.49	0.23	167.7	–	0.57	25.91

Table 4 Potentially harmful elements (in mg/kg) in the volcanic soils

Locations/elements	As	Be	Cd	Co	Cr	Cu	Ni	Pb	Sb	Se	V	Zn
Ajing	0.09	2.50	0.06	55.20	244	46.30	303	11.40	0.08	0.60	144	87.10
Bwonepe	0.09	2.50	0.04	64	311	49.30	411	7.96	0.06	0.40	168	90.30
Kurgwam	0.09	2.40	0.07	55.50	271	43.50	333	6.43	0.02	0.50	146	90.80
Punguk	0.09	2.80	0.05	57.90	183	10	220	10	0.06	0.40	142	86.80
Amshal	0.09	2.50	0.06	40.50	153	25.60	137	11.90	0.06	0.50	170	67.10
Konji	0.09	2	0.08	38.30	144	27.50	89.30	14.90	0.05	0.20	136	57.80
Ugut	0.09	2	0.08	38.30	144	31.50	126	10.20	0.08	0.40	116	107
Background values (Taylor 1964)	2	1	0.22	48	170	87	130	6	0.02	0.05	250	105
Mean values	0.09	2.39	0.06	49.96	207.14	33.39	231.33	10.40	0.06	0.43	146	83.80

Major cations and anions in the water sources

Analysis of the major dissolved cations and anions in the underground water sources (springs/boreholes) is presented in Table 5.

Magnesium concentration in the waters vary between 2.2 and 26.4 mg/l (mean of 18 mg/l) and calcium varies between 4.7 and 27.6 mg/l (mean = 15 mg/l). Both Mg and Ca display values below the maximum permissible limits of 50 and 75 mg/l, respectively. Sodium and potassium display concentrations varying from 8–61.3 (mean 14 mg/l) to 2.1–18.8 mg/l (mean 8 mg/l), respectively. The cation levels decrease in the order $Mg > Ca > Na > K$ (Table 5). The bicarbonate concentration varies between 78.66 and 461.61 mg/l (mean = 310 mg/l). The chloride concentration remains relatively constant in all the waters with a mean of 6 mg/l. HCO_3^- is the dominant anion (mean values 309.75 mg/l) followed in decreasing order by $SO_4^{2-} > Cl^- > NO_3^-$. None of these cations exhibits values that exceed the WHO (2004) permissible limits in drinking water (Table 5), suggesting a low level of anthropogenic input, which is further corroborating the minimal pollution loadings into the entire volcanic province as revealed in the calculated PLI values below.

In an attempt to classify these underground waters and to better understand the hydrogeochemical processes controlling water chemistry, the major ions are plotted in a piper diagram as cation and anion percentages in milliequivalent (meq) (Fig. 17). In the Piper diagram, most of the water samples fall in the top central portion of the cation triangle indicating the dominance of the alkali earth metals ($Mg^{2+} + Ca^{2+}$) over the alkali metals ($Na^+ + K^+$), suggesting a mixing of $Mg-Ca-HCO_3$ and $Na-K-HCO_3$ water types. The presence of these two water types is a reflection of the interaction between the predominant granitic basement rocks and the basaltic cover in the study area. The water samples that plot close to the Na^+ and K^+ field seem to have originated from a volcanic aquifer derived from the dissolution of plagioclase in the basaltic rocks.

A correlation between fluoride content in water and other ions are also presented to best understand the behavior of F in the classified water chemical types. The concentration of Fluoride is positively correlated with Mg^{2+} , Ca^{2+} , Na^+ (Figs. 12, 13, 14) as well as with K^+ (Fig. 15) and Ba^{2+} (Fig. 16), indicating that these cations are of similar source and or controlled by the same geochemical process. The NO_3^{2-} content does not seem to affect the F^- content (Fig. 11), indicating an external source for the NO_3^{2-} .

The significantly low F content below the WHO admissible limit of 1.5 mg/l for drinking water (World Health Organization 2004) in both the spring and borehole waters

Table 5 Major cations and anions in the waters (mg/l) of the Panyam Volcanic province

Element	Water source	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	NO ₃ ²⁻	F ⁻	Ba ²⁺
Ajing1	Borehole	4.3	9.9	19.7	14.5	250.47	1.33	7.63	4.32	0.12	<0.02
Bwonpe	Spring	5.5	11.9	17.5	14.2	264.96	5.33	5.1	1.13	0.19	<0.02
Kurgwam	Borehole	2.5	9	2.2	4.7	78.66	<0.03	2.28	1.17	0.12	0.02
Panyam	Borehole	6.1	61.3	16.2	16.3	459.54	55.1	7.27	<0.02	0.59	0.04
T/Kerang	Spring	9.1	19.7	22.6	27.6	418.14	4.36	9.24	2.79	0.14	0.04
Punguk	Spring	5.9	13.4	18.3	22	333.27	3.38	4.88	2.52	0.20	0.03
Kerang	Spring	2.1	8	13.7	14.3	311.14	2.09	6.84	0.86	0.15	0.05
Amshal 1	Spring	8.1	12.9	18.2	14.9	279.45	3.05	3.88	3.19	0.21	<0.02
Amshal 2	Spring	7.1	11.5	16.2	14.5	225.63	3.35	4.79	4	0.18	<0.02
Konji	Spring	7.6	10.9	15.4	17.9	262.89	3.58	4.27	2.23	0.20	0.06
Jwakmang	Borehole	18.8	28.2	26.4	24.6	461.61	1.86	8.58	2.12	0.18	<0.02
Ugut	Spring	8.6	23.2	20.5	21.5	382.95	7	6.18	1.44	Nil	<0.02
Pang	Spring	9	15.2	21.5	15.8	298	2.95	5.52	4.5	Nil	<0.02
WHO (2004)		200	200	50–150	75–200	NS	250	250	50	1.50	0.70

of the volcanic province is in support of its origin from shallow aquifers often recharged by precipitation with little resident time for ion exchange and accumulation. The spring water in the volcanic province is the main source of potable drinking water for the inhabitants. The observed tooth decay (Plate 2) and dental caries which are a common dental disease conditions among the elderly people (30 years and above) in the province is a reflection of this low fluoride level in the waters. These disease conditions are however absent in the younger children in the volcanic province, who have resorted to the use of fluoride tooth-paste in recent times.

Potentially harmful elements (PHEs) (As, Be, Cd, Co, Cr Cu, Ni, Pb, Sb, Se, V and Zn) in the volcanic soil

The concentration levels of PHEs in the volcanic soils are presented in Table 4. The values for the EF of each of these elements are also presented in Table 2.

Except for Ni and Se, most of these elements display values that below the regional baseline values and are concentrated in lateritic soils. As, Be, Cd, Co, Cr, Cu, Ni, Pb, Sb, V and Zn display average concentrations of 0.09, 2.39, 0.06, 49.96, 207.14, 33.39, 231.33, 10.40, 0.06, 146 and 83.84 mg/kg, respectively.

Beryllium presents moderate enrichment ($2 \leq EF \leq 5$) in about $\frac{3}{4}$ of the volcanic province (Fig. 3) and minimal enrichment ($EF \leq 2$) outside this zone. Also, Co, Cr and Cu display moderate enrichment ($2 \leq EF \leq 5$) in the southeast portion of the volcanic province especially in areas around Ajing, Bwonpe, Kurgwam (Figs. 4, 5, 6). Vanadium on the

Fig. 3 Enrichment factor map for Beryllium

other hand exhibits a rather “swell and pinch” enrichment pattern running diagonally from NW to SE covering the villages of Pungul, Amshal in the NW to Kurgum and to Bwonpe and Ajing in the SE. Nickel, however, displays strong to severe enrichment ($5 \leq EF \leq 20$) (Fig. 7) in the SE portion of the volcanic province, with values decreasing outwards to moderate enrichment ($2 \leq EF \leq 5$) towards Punguk, Amshal and Konji followed by a minimal enrichment outside these areas (Fig. 8). Other elements such as As, Cd, Pb, Sb, Se and Zn display minimal enrichment in some other areas in the volcanic soils ($0 \leq EF \leq 2$). These PHEs (Co, Cr, Cu, Ni, V and Zn) are often associated with Fe and therefore are preferentially scavenged or co-precipitated along with Fe-rich mineral phases in the lateritized volcanic soils (Zhang et al. 2007).

Except for Ni and Se which present pollution indices (PLI) of 1.10 and 1.40–3.0, respectively, suggesting a moderate contamination for Ni and from moderate to

Fig. 4 Enrichment factor map for Cobalt

Fig. 5 Enrichment factor map for chromium

Fig. 6 Enrichment factor map for Copper

strong contamination for Se, all the other elements As, Be, Pb, Cd, Cr, Cu, Sb, V and Zn present $PLI < 1$, and therefore did not contaminate the soil (Table 2). Pre-

Fig. 7 Enrichment factor map for Nickel

Fig. 8 Enrichment factor map for Vanadium

sumably, the endemic non-filarial elephantiasis observed affecting some inhabitants of the volcanic province might have been caused by the exposure of the unprotected feet to Be and Zr, in volcanic soils, known to induce the development of podoconiosis (Frommel et al. 1993; Davey et al. 2007; Price 1974), (Plate 1).

Rare earth elements (REEs)

The values of the sum total of REEs ($\sum REEs$) for each sample are presented in Table 3 and range from 217.6–290.7 relative to 167.7 mg/kg for the parent basaltic rock material.

The REEs composition of the volcanic soils and the reference parent basaltic rock normalized to chondrites plotted in a spidergraph (Figs. 9, 10) display clear light rare earth elements (LREE) ($100\text{--}200 \times \text{Chondrite}$) enrichment relative to heavy rare earth elements (HREE) ($2\text{--}5 \times \text{Chondrite}$) typical of the continental basalts (Fig. 9). There

Fig. 9 Spidergraph of rare earth elements in the volcanic soils compared with parent basalt rock material from the Jos Plateau (in Lar et al. 2000)

Fig. 10 Spidergraph of rare earth elements in the volcanic soils compared with the chondrite

is a similarity in the spectra of the volcanic soils with that of the reference parent basaltic rock indicating a derivation from the same parent material and/or have been affected by the same process with the same intensity (Lar and Tsalha 2005).

The volcanic soils normalized to the reference parent rock, however, also display LREEs enrichment up to 70–80× relative to HREE of 1–4×.

The percentage change in the concentrations of the total REEs in the soils, which could possibly be explained by alteration processes show that the accumulation of REEs ranges from 32.7 to 73.6 % (Table 3). Only Sample SM5 shows significant REE enrichment of up to 73.6 % relative to that of the parent rock. For example, in the case of

Fig. 11 Correlation diagram of NO_3^{2-} versus F^- in waters from the Volcanic province

Fig. 12 Correlation diagram of Mg^{2+} versus F^- in waters from the Volcanic province

Fig. 13 Correlation diagram of Ca^{2+} versus F^- in waters from the Volcanic province

Fig. 14 Correlation diagram of Na^+ versus F^- in waters from the Volcanic province

Fig. 15 Correlation diagram of K^+ versus F^- in waters from the Volcanic province

Fig. 16 Correlation diagram of Ba^{2+} versus F^- in waters from the Volcanic province

samples SM1, 2 and 4, about 56–62 % of the REEs was accumulated, while for samples 3, 6 and 7, they display moderate enrichment in the range 30–38 %. These values are well corroborated with the La/Ce ratios ranging from 0.30–0.37 to 0.42–0.57 relative to 0.57 in the reference parent rock suggesting that the degree of weathering on the parent basaltic rocks was mainly moderate but severe in some cases. Indeed, the visible positive Ce anomalies in all the soil samples go further to support the high degree of weathering the parent basaltic rocks of the volcanic province must have undergone (Figs. 11, 12, 13, 14, 15, 16, 17)

The calculated 73.6 % accumulation in sample SM5 (Table 3), implies the severity of weathering in places. However, its low La/Ce ratio (0.35) with a very high percentage of total REEs, instead of a lower total REEs, can best be explained by significant enrichment of total HREE relative to total LREE values in this case, and this can be supported by the decreasing La/Yb ratios from $42.46 > 37.15 > 33.67 > 32.77 > 29.11$ and > 26.7 (Table 3).

Conclusion

This study has established that the dominant underground water types in the volcanic province is the Mg–Ca– HCO_3 water type forming 80 % and Na–K– HCO_3 water type making the remaining 20 %. The composition of these major ions in the waters seems to have been controlled by the water–rock alteration process(es) by mixing of water from the dominant underlying host crustal and the overlying basaltic rocks in the volcanic province.

It has also revealed that the soils in the Panyam volcanic province are minimally to moderately enriched in most potentially harmful elements (Be, Co, Cr, Ni, Pb, Sb, Se, V and Zn), with Ni and Se displaying strong enrichments. The higher baseline values of these transition metals are due to their relative immobility as they substitute and co-precipitate along with Fe during the weathering of the basalt host rocks. Except for Ni and Se which seem to have contaminated the volcanic soils, these other elements As, Be, Cd, Cr, Cu, Pb, Sb, V and Zn did not, suggesting little or no anthropogenic input. The rare earth elements are equally significantly enriched in the volcanic soils as a result of moderate to slightly severe intensity of weathering the parent basaltic rocks were subjected to.

Fig. 17 Piper Trilinear diagram of waters from the volcanic province

The common human disease conditions observed in the volcanic province, podoconiosis and tooth decay/dental caries are a reflection of the higher contents of the heavy metals and the deficiency of fluoride in waters, respectively. We advocate for a more comprehensive research to establish the links between the distribution of these potentially harmful elements in the volcanic soils and the many observed common human disease conditions.

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