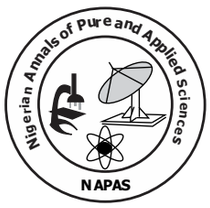

Geochemical Appraisals of Elemental Compositions of Stream Sediments and Some Vegetables from Village Hostel, University of Jos, Nigeria

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Abstract
This study focuses on geochemical appraisals of elemental compositions of stream sediments and some vegetables at Village Hostel, University of Jos. Stream sediments were collected from River Delimi and some vegetables were collected along the bank of river Delimi at Village Hostel, University of Jos. Two (2) stream sediments and four (4) vegetable samples (Spinach, lettuce, carrot and tomato) were selected for geochemical analysis and subjected to X-Ray fluorescence (XRF) analysis. The elemental compositions of stream sediments include: Mo (11.29 - 20.32 ppm), Zr (262.3 - 817.4 ppm), Sr (14.04 - 53.14 ppm), Rb (101.6 - 126.3 ppm), Th (13.30 - 21.96 ppm), Pb (20.43 - 30.43 ppm), As (6.98 - 21.01 ppm), Zn (101.3 - 272.5 ppm), Fe (9.54 - 40.86 wt.%) and Mn (119.5 - 199.4 ppm). The elemental values of Sr, Rb, Pb, Th, Zn, Fe, Mn and Cu from stream sediments and some vegetables exceeded World Health Organizations (WHO) permissible limits and the vegetables can be harmful to the consumers. The values of Fe and Mn in the stream sediments suggest the occurrence of ferromagnesian minerals in the area. Higher values of Mo, Zr, Rb, Th, As, Zn, Co, Fe and Mn in the stream sediments than the vegetables suggests that the stream sediments have been enriched in hematite, zircon and manganite through weathering, dissolution and leaching of underlying mineralization and transported by erosion and runoffs along river Delimi. Higher values of Sr, Pb, Cu and Nb in the vegetables than the stream sediments are indicative of soil contaminations from geogenic and/or anthropogenic sources which were subsequently being absorbed by vegetables

Keywords: Stream, Sediments, geogenic, anthropogenic and elemental

Introduction

Stream sediment materials occur naturally and are derived through the process of weathering and dispersed by agents of transportation. Sediments represent the geochemical compositions of materials from the upstream drainage basin (Rompaey *et al*., 2001) and mineralogical compositions of bedrock (Fernandez *et al*., 2003; Calmano *et al*., 1993).

The accumulation of heavy metals in the sediments had been reported in Hong Kong (Liang *et al*., 2003), Brazil (Machado *et al*., 2002) and Malaysia (Yap *et al*., 2002). The levels of metal values in sediments had been adopted in the description of metal contaminations in a lot of environment (Li *et al*., 2007). Vegetables absorbed heavy metals from the soils and accumulate them in their edible and inedible parts with various concentrations (Rajesh *et al*., 2007; Cui *et al*., 2004; Na *et al*., 2007).

The consumptions of contaminated vegetables contribute to buildup of heavy metals in the liver and kidney of humans which can results to disruption of many biochemical processes and as well lead to nervous, kidney, cardiovascular, and bone diseases (Ogwuegbu & Mahanga, 2005). Exposure to high levels of heavy metals can lead to acute and chronic health effects, such as damage to central and peripheral nervous systems, blood, lungs, kidneys, liver and even death. (Adaramodu *et al*., 2012).

The contaminations of soils and sediments with As, Pb and Fe have been reported by Ashano *et al*. (2006) from Rop Complex, Jos-Plateau and were associated with cassiterite, sulphide mineralization, mining and other activities. Most of the cassiterite has been derived from greisens veins in the biotite granite as well as quartz veins (Black, 1971). There are limited reports on the elemental compositions of stream sediments and vegetables grown along the bank of the river Delimi at village hostel, University of Jos. The present study focuses on geochemical appraisals of elemental compositions of stream sediments and some vegetables (spinach, lettuce, carrot and tomato) at village hostel using XRF analysis.

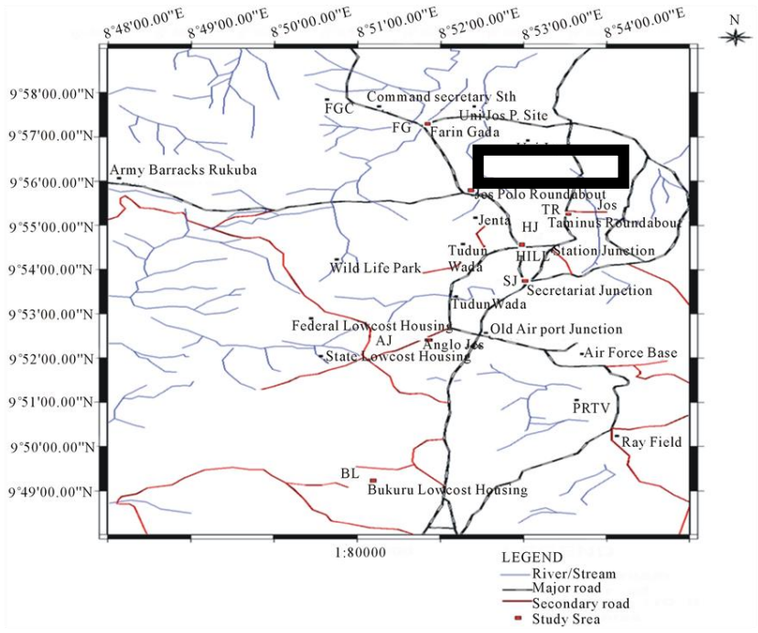

Fig. 1: Location map of the study area showing drainage patterns

Materials and Methods

i. Sample Collection

The study area is located in the village hostel at University of Jos Permanent Site, Plateau State, Nigeria on latitudes 09° 57^{l} 00.4^{ll} to 09° 57^{l} 56.3^{ll} N and longitudes 08° 52.1^{l} 10.1^{ll} to 08° 52^{l} 32.3^{ll} E (Fig. 1). Stream sediments were collected along river Delimi close to village hostel at University of Jos, Permanent Site, off Faringada - Bauchi Junction road, Jos, Plateau State. The sediments were collected along river Delimi at depth of about 20cm using a shovel and labeled with appropriate sample number

Vegetables such as tomato (Solanum lycopersicum); lettuce (Lactuca sativa); carrot (Daucus carota) and spinach (Amaranthus spp) were collected from nearby farmland about 50metres to river Delimi. The vegetable samples were obtained by uprooting fresh plants of spinach, lettuce, carrot and tomato from the farmland and labeled with sample number. Stream sediments and vegetable samples were shipped from village hostel to the Laboratory for sample preparation and analysis. Two (2) representative stream sediments samples were selected from the stream sediments at village hostel while four (4) vegetable samples (Spinach, lettuce, carrot and tomato**)** were selected from nearby farms to river Delimi at village hostel for geochemical analysis.

ii. Sample Preparations

The sediments and vegetable samples were air-dried at room temperature for about two weeks in the Laboratory to remove moisture and the dried samples were ground to powdered form using agate mortar and pestle. The pH analysis was also carried out on dried stream sediments and vegetable samples using a pH meter. 10 grams of each sample was weighed and transferred into separate 50cm^3 beaker, 30cm^3 of distilled water was added to each beaker and stirred with glass rod. The suspension of each sample of stream sediments and vegetable was allowed to stand for 30 minutes with intermitted stirring. Measuring Electrode was immersed into the suspension of each sample in the beaker and the pH value was determined from digital display of the pH meter.

iii. Determination of the elements by XRF

Two (2) stream sediments and four (4) vegetable samples were subjected to X-ray fluorescence (XRF) analysis to determine their elemental compositions at Department of Science Laboratory Technology, University of Jos. XRF-Analyzer (XL3-98293) was used for the analysis and is relatively non-destructive chemical analyses of the samples. It works on wavelength-dispersive spectroscopic principles and was typically used for bulk analyses of the stream sediments and vegetable samples. The analysis was carried out through the behavior of atoms when materials are excited with high-energy, short wavelength X-rays radiation and the atoms then become ionized.

Once the energy of the radiation is sufficient to dislodge a tightly-held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron. The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays were used to detect the abundances of elements that were present in the stream sediments and vegetable samples.

Stream sediments and vegetable samples were analyzed for elemental compositions which include: zirconium (Zr), strontium (Sr), uranium (U), rubidium (Rb), thorium (Th), lead (Pb), arsenic (As), zinc (Zn), cobalt (Co), copper (Cu), iron (Fe) and manganese (Mn) using XRF spectroscopy. The obtained values of the elements from stream sediments and some vegetables were compared with FAO/WHO (2001) permissible limits.

Results

The Mo content of stream sediments ranges from 11.29 to 20.32 ppm, Zr content of the stream sediments ranges from 262.3 to 817.4 ppm, Sr composition ranges from 14.04 to 53.14 ppm, Rb ranges from 101. 6 to 126.3 ppm, Th content ranges from 13. 30 to 21.96

ppm, and Pb ranges from 20.43 to 30.43 ppm respectively. The Arsenic composition of stream sediment ranges from 6.984 to 21.01 ppm, Zn content ranges from 101.3 to 272.5 ppm, Cu ranges from 0 to 36.54 ppm, Co ranges from 0 to 238.4 ppm, Fe content ranges from 9544.16 to 40856.6 ppm and Mn content ranges from 119.5 to 199.4 ppm (Table 1).

The Mo content of vegetables ranges from 8.796 to 11.62 ppm, Zr content ranges from 20.01 to 60.99 ppm, Sr composition ranges from 60.03 to 186.2 ppm, Rb ranges from 36.58 to 100.9ppm, Pb ranges from 5.282 to 48.06 ppm, Zn content varies from 42.94 to 185.9 ppm, Cu varies from 0 to 40.47 ppm, Fe content ranges from 598.13 to 4130.85.6 ppm, and Nb ranges from 10.25 to 15.32 respectively (Table 2). The histograms of distribution of the elemental compositions of stream sediments are presented in Figure 2 while Figure 3 shows the distribution of elemental compositions of carrot, spinach, lettuce and tomato. This indicates that Fe is the major element while Mo, Zr, Sr, Pb, Rb, Th, As, Zn, Co, Cu and Mn occur as trace elements.

Discussion

The value of Mo in the stream sediments (11.29 - 20.32 ppm) and vegetables (8.796 - 11.62 ppm) exceeded Occupational safety and Health Administration (OSHA) permissible limit of 1.5 ppm. Zr content in stream sediments ranged from 262.3 to 817.4 ppm while Zr in the vegetables ranged from 20.01 to 60.99 ppm and exceeded OSHA permissible unit of 1.3 ppm. Sr content in the stream sediments ranged from 14.04 to 53.14 ppm while Sr content in the vegetables ranged from 60.03 to 186.2 ppm and exceeded Environmental Protection Agency, EPA (2004) tolerance limit of 4.0 ppm.

Rb content in the stream sediments ranged from 101.6 to 126.3 ppm while Rb content in the vegetables (except lettuce) ranged from 36.58 to 100.9 ppm and exceeded OSHA (2013) tolerance limit of 7.0 ppm. Pb value in the stream sediments ranged from 20.43 to 30.43 ppm and exceeded WHO permissible limit of 5 ppm for soils while Pb value in the vegetables (except lettuce) ranged from 5.282 to 48.06 ppm and exceeded WHO permissible limit of 0.43 ppm. Th content in the stream sediments ranged from 13.30 to 21.96 ppm and exceeded WHO permissible limit of 1.6 ppm but Th was not detected in all the vegetable samples (carrot, spinach, lettuce and tomato).

Arsenic content in stream sediments ranged from 6.984 to 21.01 ppm and exceeded WHO tolerance limit of 0.39 ppm for soils. Zinc content in the stream sediments ranged from 101.3 to 272.5 ppm and exceeded WHO tolerance limits of 50 ppm while Zn content in the vegetables except lettuce ranged from 42.94 to 185.9 ppm and exceeded WHO tolerance limit of 0.6 ppm for vegetable. The iron content in the stream sediments ranged from 598.1 to 40856.6 ppm and exceeded WHO permissible limit of 50 ppm for soils and Fe content in the vegetables ranged from 598.1 to 4130.9 ppm and exceeded WHO permissible limit of 20 ppm for vegetables.

Table 1: Elemental Compositions (ppm) of Stream Sediment from River Delimi

Elements	Sample 1	Sample 2	WHO (2001) limits for soils
Mo	11.29	20.32	-
Zr	262.3	817.4	-
Sr	14.04	53.14	-
Rb	101.6	126.3	-
Th	13.30	21.96	1.6
Pb	20.43	30.43	5
As	21.01	6.984	0.39
Zn	272.5	101.3	50
Cu	ND	36.54	36
Co	ND	238.4	-
Fe	9544.2	40856.6	50
Mn	119.5	199.367	50

ND: Not Detected

Table 2: Elemental Compositions (ppm) of Some Vegetables from village hostel

Elements	Sample 3 (carrots)	Sample 4 (Spinach)	Sample 5 (Lettuce)	Sample 6 (Tomato)	Permissible limits for vegetables
Mo	8.796	10.27	11.62	9.254	1.5 (OSHA, 2013)
Zr	20.01	30.46	54.27	60.99	1.3 (OSHA, 2013)
Sr	60.03	113.98	74.41	186.2	4.0 (EPA, 2004)
Rb	100.9	36.58	ND	95.64	7.0 (OSHA, 2013)
Pb	12.41	48.06	ND	5.282	0.43 (WHO, 2001)
Zn	42.94	185.9	ND	103.4	0.6 (WHO, 2001)
Fe	598.1	1481.9	4130.9	1357.8	20 (WHO, 2001)
Nb	10.25	12.73	15.32	10.25	-
Cu	ND	ND	ND	40.47	10 (WHO, 2001)

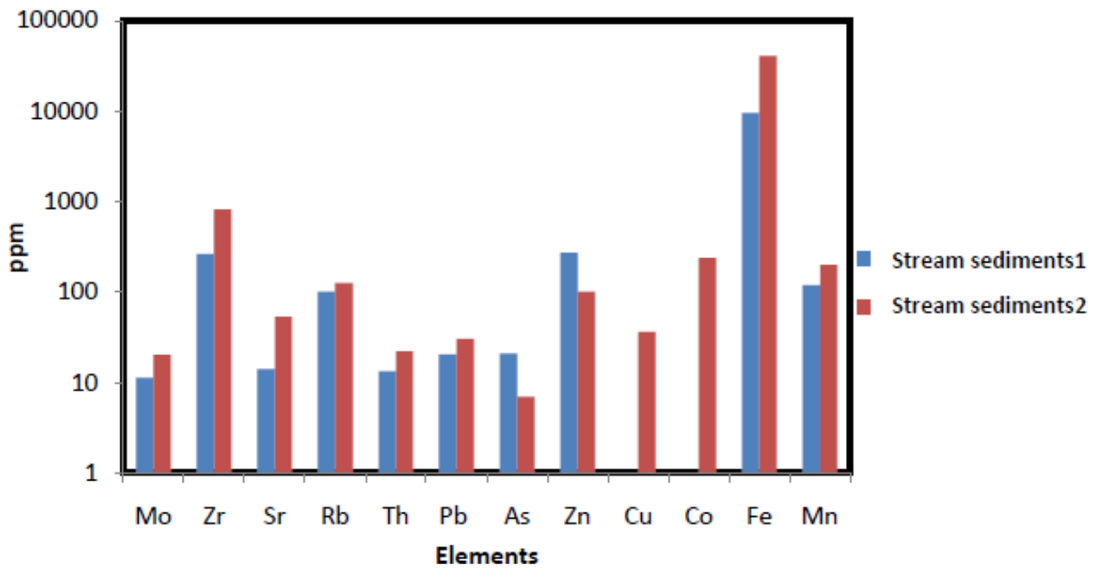

Fig. 2: Distribution of elemental compositions of stream sediments from River Delimi

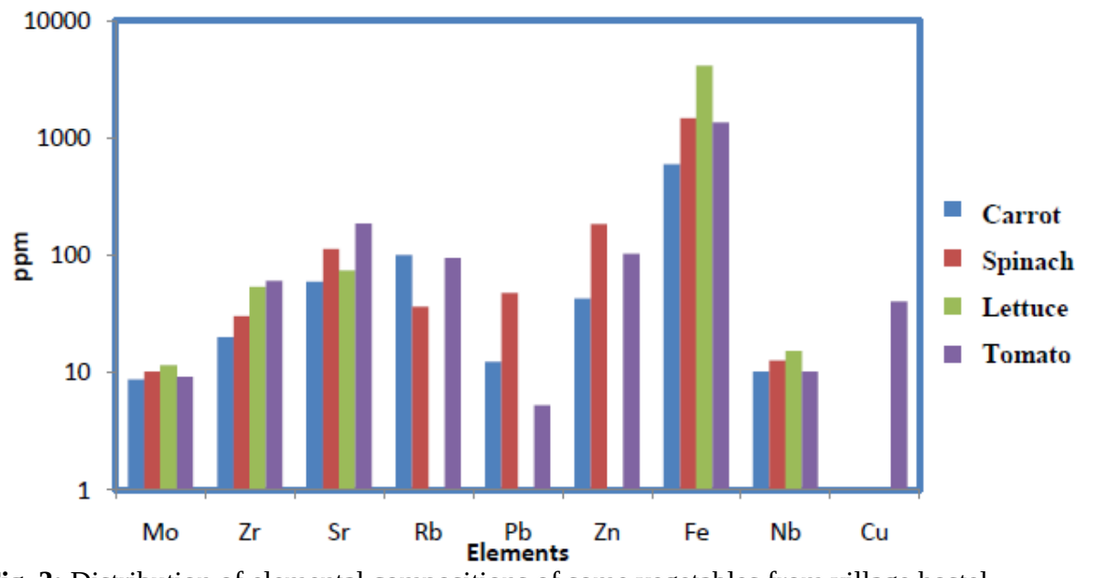

Fig. 3: Distribution of elemental compositions of some vegetables from village hostel

Manganese content in the stream sediments ranged from 119.5 to 199.367 ppm and exceeded WHO tolerance limit of 50 ppm but Mn was not detected in the vegetable samples. Cu content of 36.54 ppm in stream sediments at site 2 exceeded WHO permissible limit of 36 ppm while Cu content of tomato (40.47 ppm) exceeded WHO tolerance limit of 10 ppm. Copper values of stream sediment 2 (36.54 ppm) and tomato (40.47 ppm) were higher than Cu values of tomato (6.24±2.22 ppm) from Kano (Abdullahi *et al*., 2007). Lead value in stream sediments (20.43-30.43 ppm) and vegetables (5.282-48.06 ppm) were higher than Pb content of tomato (3-10.7ppm) reported from Kayseri, Turkey (Demirezen & Aksoy, 2006). This indicates that the soils and sediments in the study area have been contaminated by lead which could be from geogenic and/or anthropogenic sources.

Arsenic content ranged from 6.984 to 21.01 ppm in stream sediments and was higher than As values of soils (0.23- 0.66 ppm) and plants (0.01-0.37 ppm) from Lafiya metropolis which indicates that the plants were polluted by the soils (Opaluwa *et al*. 2012). Cobalt content of 238.4 ppm in the stream sediments at site 2 was higher than Co content in soil (0.33 - 0.63 ppm) and plants (0.01-0.36 ppm) from Lafiya metropolis (Opaluwa *et al.,* 2012). The values of Fe (9544.16 - 40856.6 ppm), Zn (101.3 - 272.5 ppm), Cu (0 - 36.54 ppm) and Mn (119.5-199.4 ppm) from this study were higher than the values reported by Ayodele (2019) on beach sediments from Lagos.

Li *et al*. (2007) reported on heavy metals in coastal wetland sediments (China) that were significantly contaminated by Cd, Zn, Ni, Pb, Cu and Cr. This is similar with the present study where stream sediments and vegetables from Village Hostel have been contaminated by Mo, Zr, Rb, Th, Zn, Fe, Sr, Pb and Mn. The pH values of the stream sediment sample 1 (5.25), stream sediment sample 2 (5.15), Carrot (5.35), spinach (5.50), lettuce (5.61) and tomato (5.18) suggest that the stream sediments and vegetables are mildly acidic

Higher values of Sr, Pb, Cu and Nb in the vegetables than the stream sediments are indicative of the contamination of soils by these metals through leaching, dispersion of minerals and weathering of underlying rocks. This suggests that geogenic and/or anthropogenic sources are the main agents of contamination which are subsequently being absorbed by these vegetables

The presence of Fe indicates the possible occurrence of ferromagnetism minerals while Al indicates that the stream sediments are enriched in aluminosilicate minerals such as feldspar and micas (Colman & Dethier, 1986). The values of Fe (9544.16 - 40856.6 ppm) and Mn (119.5 - 199.4 ppm) in the study area attested to the occurrence of ferromagnesian minerals in the stream sediments along River Delimi.

Zirconium value (262.3 - 817.4 ppm) of the stream sediments indicates possibility of zircon minerals in the area because zircon is the major source of Zr or Hf (Levinson, 1980). The value of Fe (9544.16 - 40856.6 ppm) from the stream sediments suggests the possibility of hematite according to Levinson (1980) that hematite mineralization can be associated with circulating hydrothermal fluids during late stages of cooling of molten magma. This was confirmed by the report of Funtua (2001) on the tailings from Jos that consists of heavy accessory minerals such as zircon and hematite

Stream sediment geochemical survey of Ara, Epe and Ijero Area, southwestern Nigeria was reported by Ayodele (2011) and revealed that the area was mineralized in phosphate minerals (probably monazite, turquoise, or apatite) and ferruginous minerals which could be hematite and manganese-bearing minerals such as manganite or mica rich manganese from pegmatites that intruded the country rocks. This is in contrast with the present study where the mineralization in the area have been dispersed to the stream sediments and associated with hematite, manganite and ferromagnesian minerals based on the values of Fe and Mn which were suggested to have originated from the greisen veins in the younger granites

Iron (Fe) has the highest concentration in the stream sediments ranging from 9544.2 to 40856.6 ppm and vegetables (598.1 - 4130.9 ppm) indicating that a significant amount of the element might have originated from the

weathering of silicate-bearing rocks rich in feldspar and mica.

The Fe values obtained in the stream sediments from the study area was significantly higher than Fe value (220 - 1860 ppm) reported by Ayodele (2011) on stream sediment geochemical survey of Ara, Epe and Ijero Area, SW Nigeria which suggested to have originated from weathering of silicate-bearing rocks.

According to Ayodele (2011), manganese value of 22 to 292 ppm was reported in Stream Sediment of Ara-Ijero area and suggested the possibility of manganite enrichment in the underlying lithologies that originated from the pegmatites. The Mn value of 119.5 to 199.4 ppm in the stream sediments from River Delimi also indicates the possibility of manganese enrichment from greisen veins in the Younger granitic rocks.

The values of elements such as Mo, Zr, Rb, Th, As, Zn, Co, Fe and Mn in the stream sediments were higher than the vegetables this suggests that the stream sediments have been enriched in hematite, zircon, manganite and ferromagnesian minerals through weathering, dissolution and leaching of underlying mineralization and transported by erosion and runoffs along river Delimi. This was confirmed by report of Black (1971) where finely disseminated sphalerite (source of Zn), galena (source of Pb), pyrite and chalcopyrite (source of Cu and Fe) and molybdenite (source of Mo) were present in greisen and quartz veins in the Rop Complex, Jos Plateau.

Conclusion

The values of Sr, Rb, Pb, Th, Zn, Fe, Mn and Cu in stream sediments and vegetables (carrot, spinach, lettuce and tomato) exceeded the WHO tolerance limit and thus the vegetables when consume can be harmful to the consumer.

The values of Fe and Mn in the stream sediments indicate the occurrence of ferromagnesian minerals in the area. The values of Mo, Zr, Rb, Th, As, Zn, Co, Fe and Mn in stream sediments suggest that the stream sediments have been enriched in hematite, zircon, manganite and ferromagnesian minerals

Higher values of Sr, Pb, Cu and Nb in the vegetables than the stream sediments are indicative of bioaccumulation of these elements in the vegetables as a result of leaching, dispersion of minerals and weathering of underlying rocks from geogenic and/or anthropogenic sources which were subsequently being absorbed by vegetables

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