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RESEARCH ARTICLE

CADMIUM, LEAD, ARSENIC AND MERCURY LEVELS IN EARTHENWARE CLAY DEPOSITS ATVUME, IN THE SOUTH TONGU DISTRICT OF GHANA, USING ATOMIC ABSORPTION SPECTROPHOTOMETRIC TECHNIQUE

*,[1]Samlafo, B. V., [1]Bobobee, L. H., [2]Quarshie, E. and [3]Sarsah, L. A.

[1]Department of Chemistry Education, University of Education, Winneba Box 25, Winneba, Ghana
[2]Non-Ionizing Department, Health Physics and Instrumentation Centre, Radiation Protection Institute, Ghana Atomic Energy Commission, Box LG80, Legon-Accra
[3]Radiopharmacy and Nuclear Medicine Centre, Radiological and Medical Sciences Research Institute, Ghana Atomic Energy Commission, Box LG80, Legon-Accra

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ABSTRACT

This paper screened for potentially harmful heavy metals such as As, Pb, Cd and Hg in earthenware clay deposits at Vume in the Volta region of Ghana using Atomic Absorption Spectrophotometric (AAS) technique. The concentrations of As in the clay samples ranged from 0.90µg/g to 2.04 µg/g with a mean of 1.49 µg/g, and standard deviation of 0.47. Lead levels ranged from 2.85 µg/g to 4.08 µg/g with a mean of 3.67µg/g, and a standard deviation of 0.38. Cadmium was below the detection limit of 0.002 µg/g in some samples: however, the levels measured ranged from 0.15 µg/g to 0.51 µg/g with a mean of 0.29 µg/g, and a standard deviation of 0.13. The concentrations of mercury ranged from 0.18 µg/g to 0.69 µg/g with a mean of 0.53 µg/g, and a standard deviation of 0.15. The levels of Hg,Cd and Pb fell below their respective US EPA(1990) safe levels of 18.0 µg/g, 1.7 µg/g and 80.0 µg/g, except that of As which was above its US EPA(1990) safe level of 0.07 µg/g.The levels of Arsenic in the study area, though higher than the US EPA safe level, were comparable to the worldwide background level of 5 µg/g in soil. The precision and the accuracy of the AAS method were assessed via the use of reference material IAEA Soil-7. The values obtained for the various elements in the standard reference material (by analysing it with the AAS method) compared favourably well with the recommended values as Spearman's correlation coefficient was + 0.96. The experimental values were within ±5% of the recommended value. The measurement precision determined by the relative standard deviation was within ±4%. With the exception of As levels which need some remediation, the quality of the clay at Vume was found to be generally good for the production of earthenware products.

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INTRODUCTION

Earthenware clay deposits occur in the ground, usually, in areas where streams or rivers once flowed. Hence, it is usually mined around streams, river banks, and designated clay deposits (Akintunde *et al.*, 2014). It is a secondary clay that has been transported by moving water from some distance, picking up minerals and other materials before settling in a river bed.The clay is made from minerals, remains of plants and animals' life, and has all the ingredients of soil. It (earthenware clay) naturally contains many minerals, such as iron oxide (rust), and in its raw state may contain some sand or small bits of rock. Over time, water pressure breaks up the remains of flora, fauna, and minerals, pulverizing them into fine particles. Larger particles are filtered out through rocks and sand, leaving silt to settle into beds of clay. How far silt travels from its source and how pure the silt is, determines the type of clay it becomes (Akintunde *et al*, 2014). Pottery in Vume is both an art and a profession among the indigenous people. Aside its products of aesthetic values, Vume produces both traditional and contemporary utilitarian pottery.While the contemporary pottery is almost exclusively done by men, the traditional pottery is done by women (Hulluska, 1999). The women in Vume use very coarse, strong clay. The raw clay is sundried and then combined with water to make it moist and workable. If the clay is not completely dried before it is mixed with water, it does not fully absorb water and will not be good

Corresponding author: Samlafo, B. V.
Department of Chemistry Education, University of Education, Winneba Box 25, Winneba, Ghana.

to work with. Grog is added to the clay with some water dripped on it. It is then kneaded to produce a uniform mixture. The freshly made pot is then preheated and fired for 6 hours. Ordinarily, clay is inert when not subjected to physical, mechanical or chemicalpressures. At the dry state, it is hard but brittle and often composed of disc-like particles.When moist with required amount of water, it becomes plastic and can be transformed into various forms when it is subjected to kneading. It becomes active chemically when adjusted with other ceramic and fibre materials. Processing of clay, both physically and chemically, continues during drying, and when subjected to heat of certain temperatures (Akintunde *et al.*, 2014)The pepper-grinding bowls popularly called *ayiwa* by the Akans and *wegba* by the Ewes is made by traditional potters. These bowls and pots are functional products in most Ghanaian homes for grinding of pepper, cooking and water storage (Samlafo *et al.*, 2011). These products are low fired, therefore fragile, but inexpensive to replace and environmentally friendly compared to its modern plastic types which are not biodegradable, and therefore environmentally unfriendly.

According to Matschullat (2000), low levels of As are naturally present in soil. The background level of As is around 5 µg/g worldwide with substantial variation depending on the origin of the soil (Mandal & Suzuki, 2002) (WHO, 2001). However, the worldwide background level of As is over seventy times higher than its US EPA (1990) safe level of 0.07 µg/g;indicating that the levels of Asin soils worldwide are on the average not safe. Long-term exposure to As in drinking water is related to increased risk of skin, lung, bladder and kidney cancer, as well as other skin changes such as hyperkeratosis and pigmentation changes (WHO, 2001). Adults exposed to high levels of lead can experience anaemia, nervous system dysfunction, weakness, hypertension, kidney problems, decreased fertility, increased level of miscarriages, low birth weight, hormonal changes or menstrual irregularities and premature deliveries (WHO, 2010). The US EPA, 1990 standard for cadmium in soil is reported as 1.7 µg/g. Soil cadmium values higher than the recommended values are likely to affect calcium metabolism. Long-term exposure to cadmium caused severe chronic effects predominately in the lungs and Kidney (WHO, 1990). Mercury in the human diet is almost completely absorbed into the blood-stream and distributed to all tissues within four days. In vitro studies in experimental animals showed that, the nervous system is a target of methyl-mercury, with foetuses appearing to be at a higher risk than adults. (WHO, 1990). Children born of women exposed to methylmercury during pregnancy have exhibited a variety of developmental neurological abnormalities, including delayed onset of walking and talking, cerebral palsy, altered muscle tone and deep tendon reflexes, as well as reduced neurological test scores (Steven*et al.*, 2005)

Unfortunately, traditional potters do not perform any chemical test on the clay to screen for toxic heavy metals. What the potters look for is its suitability in terms of plasticity. If the geochemistry of the clay has high level of toxic heavy metals, above the recommended levels, then the quality of the products become a health hazard as these heavy metals pass through the food chain. It is against this background that this study assesses the levels of harmful heavy metal such as Hg, Cd,Pb and As in earthenware clay deposits at Vume in the Volta region of Ghana.

MATERIALS AND METHODS

Study Area

Vume, the study area, is located in the South Tongu District in the Volta region of Ghana. The South Tongu District, with Sogakope as its capital, lies between latitudes 6°10’ and 5°45’ North and longitudes 30°30’ and 0°45’ East. The District is generally low lying by virtue of its location within the coastal savannah plain, with characteristic coastal savannah vegetation but rises gradually to a height of 75 metres above sea level (Ghana Statistical service, 2014). The savannah vegetation supports the production of livestock, and the swampy areas favour the cultivation of rice, okra, pepper and sugar cane. Numerous creeks and lagoons run parallel to the Volta River through the District, which serves as good breeding grounds for tilapia, shrimps and mud fish. The District lies within the wet semi-Equatorial and dry Equatorial climate zones. The District experiences a double maxima rainfall regimes in May-June for the major season, and September-November for the minor season with an average of 195 mm and 73mm of rainfall respectively. Temperatures range between 22.6°C and 29.3°C (Ghana Statistical Service, 2014). The underlying rocks in the District are metamorphic in origin. The major soils formed over these geological formations include Ziwai-Zebe complex, Tondo-Motawme complex and Agawtaw-Pejeglo complex soils which are formed over the Dahomeyan Acidic gneiss rocks. The District has both alluvial, gneiss and schists deposits as their parent rocks. The District is endowed with large clay deposits at Lolito, Vume and Sokpoe communities which are predicted by geologists to last for over 100 years if it is mined commercially and in a sustainable way. Most females are found to be engaged in earthenware craft and related trades than their male counterparts. On the other hand, a higher percentage of males undertakes skilled agriculture, forestry and fishery than their female counterparts in the District (Ghana Statistical service, 2014).

Sampling

Ten clay samples were taken on three different occasions from earthenware clay deposits at Vume in the Volta region of Ghana in October, 2015. At each sampling sitean aggregate sample, made up of five (5) subsamples taken from different locations, was taken using anauger from a depth of 30cm beneath the surface of the clay deposit. The samples were put into clean plastic containers, sealed, and labelled V_x where $_x$ = 1-10. The clay samples were dried at room temperature to a constant weight. The dried samples were ground and homogenized in a porcelain mortar, sieved to 0.5mm mesh size and packed into their respective well labelled containers.About 2 g of each aggregateclay sample were transferred into 100 mL polytetrafluoroethylene (PTFE) Teflon bombs. Ten millilitres (10 mL) of concentrated nitric acid was added to the soil samples and allow to stand for 10 minutes. About 30% H_2O_2 was also added to the mixture until the mixture no longer effervesced on addition of H_2O_2. To each mixture in the Teflon bombs, 2 mL of concentrated H_2SO_4, and then 5 mL of concentrated $HClO_4$ were added successively. The resulting mixtures were digested for 25 minutes in a Milestone microwave oven (Ethos 900) using the following operation parameters; 250W for 2 min, 0W for 2 min, 250W for 6min, 400W for 5 min, 650W for 5 min and 5 min for venting (Milestone Technical paper, 2001). The rotor was put in a bowl of water to cool the content of the tube and also to reduce the associated pressure. The digested soil samples were filtered using Whatman No 1 filter paper into a 50mL volumetric flask and made up to the mark using de-ionized distilled water.The chemicals used were analytical grade chemicals obtained from Sigma Aldrich.

The calibration standards for Cd, Pb, As, and Hg were prepared, and together with the reagent blanks, subjected to same digestion procedure as the samples. Subsequently, the digested standards, reagent blanks, and samples were read at the wavelengths of228.8 nm, 217 nm, and 193.7nm using Varian Fast Sequential Atomic Absorption Spectrometer, model AA240FS for the determination of Cd, Pb, and As respectively in the clay samples. Acetylene gas was used as the carrier gas, for Cd, Pb, and As while inert argon was pass through the system to remove interfering gases between each reaction time. Cold vapor was used for Hg determination using 3% HCl in 1.1% $SnCl_2$ and 3% HCl as the reductant at a wavelength of 253.7 nm

RESULTS AND DISCUSSION

The precision and accuracy of the AAS method was evaluated by analysis of standard reference material IAEA soil-7. Table 1 shows the recommended values for As, Cd, Pb, Hg, Cu, Al, Co, and Ba in the standard as against the experimental values obtained using AAS. The values obtained compared favourably well with the recommended values as Spearman's correlation coefficient was +0.96. The experimental values were within ± 5% of the recommended values. The measurement precision specified by the relative standard deviation was within ± 4%. The error margins are standard deviations. The mean concentrations of As, Pb, Cd and Hg in earthenware clay samples are presented in Table 2 whilst Figure 1 is a bar chart showing the mean concentrations of the various elements measured in the clay samples.

The concentrations of arsenic observed in the clay samples ranged from 0.90 µg/gto 2.04 µg/g with a mean of 1.49 µg/g and a standard deviation of 0.47 (Table 2). The levels of As were all very high considering a safe level of 0.07 µg/g by the US EPA, 1990 standard.The minimum level of 0.09 µg/g As recorded in this study is about 13 times higher than the (US EPA, 1990) safe level for As. However, the levels of As measured in the study area were comparable to the worldwide background level of 5 µg/g reported by Mandal & Suzuki (2002). The fact that the worldwide background level of 5 µg/g is (over seventy times) higher than the safe level suggests that naturally the level of as in soil worldwide is, on the average, unsafe. However, the possibility that the levels in the study area might have been somehow elevated by the impact of agricultural practices such as fertilizer and pesticide application cannot be ruled out. Arsenic in fertilizer and pesticide residue could have been transported to the clay deposit by flood waters and run-offs as a result of seasonal flooding and recurrent run-off due to the low lying nature of the study area. Samlafo*e t al*. (2011) reported a mean As concentration of 9.48 µg/g in earthenware clay samples in Otsew in Gomoa West district of Central region of Ghana. The mean value reported by Samlafo *et al*. (2011) was six times higher than the mean As values of 1.49 µg/g observed in Vume, Volta Region of Ghana.A study conducted by (Tait *et al*., 2003) reported a geometric mean of 0.27 µg/g of As in non-urban soil and a geometric mean of 2.81 µg/g in urban soil.Woode, (2014) reported As levels of 0.6µg/g to1.8 µg/g in geophagy clay samples in Anfoega in the Volta region of Ghana. Arsenic levels in Vume clay deposit compares favourably with the Anfoega geophagy clay deposits which is eaten directly. Lead concentrations in Vume clay deposit ranged from 2.85 µg/g to 4.08 µg/g with a mean of 3.67 µg/g and standard deviation of 0.38. Lead levels were within the US EPA, 1990 limit of 80.0 µg/g. Woode (2014) however, reported 10.7 µg/g to 18.3 µg/g of Pb in geophagy clay deposit at Anfoega in the Volta region of Ghana, which when compared to the values observed at Vumeindicates that, the Vume clay deposit is of a better quality in terms of Pb levels.Cadmium levels observed in Vume ranged from 0.15 µg/g to 0.51 µg/g. Cadmium was however below the detection limit of 0.002 µg/g in samples coded $V_{1,}$ V_2, V_4 and V_6 (Table 2). Cadmium levels were within the safe limit of 1.7 µg/g, as well as lower than the range, 0.7 µg/g to 0.9 µg/g, in Anfoegageophagy clay deposit reported by Woode *et al.* (2014).

Table 1. Analytical results (µg/g dry weight) of standard reference material, IAEA SOIL-7 showing local laboratory values and the recommended values

Elements	Recommended values/µg/g	Experimental values/ µg/g
As	13.40±0.8	12.96 ± 1.5
Pb	60.0± 5.12	59.86 ± 2.5
Cd	1.3 ± 0.2	1.4 ± 0.5
Hg	0.04 ± 0.01	0.05 ± 0.02
Co	8.90 ± 1.2	8.96 ± 2.34
Cu	11.0 ± 2.0	10.90 ± 1.8
Al	47000.0± 56.56	47090 ± 56.80

Table 2. Mean concentrations (µg/g dry weight) of As, Pb, Cd and Hg in Clay soil, n=5

Sample code	As/µg/g	Pb /µg/g	Cd /µg/g	Hg/ µg/g
V_1	1.11	3.36	ND	0.54
V_2	1.59	3.39	ND	0.69
V_3	1.05	3.81	0.15	0.53
V_4	2.04	3.84	ND	0.57
V_5	0.90	2.85	0.21	0.18
V_6	0.96	3.87	ND	0.39
V_7	1.80	3.96	0.30	0.66
V_8	2.01	3.99	0.21	0.57
V_9	2.04	4.08	0.51	0.69
V_{10}	1.41	3.51	0.33	0.48
Min	0.9	2.85	0.15	0.18
Max	2.04	4.08	0.51	0.69
Mean	1.49	3.67	0.29	0.53
Median	1.5	3.83	0.26	0.56
SD	0.47	0.38	0.13	0.15
US EPA(1990) Safe levels	0.07	80.0	1.7	18.0

ND= Not detected (below detection limit of 0.002µg/g)

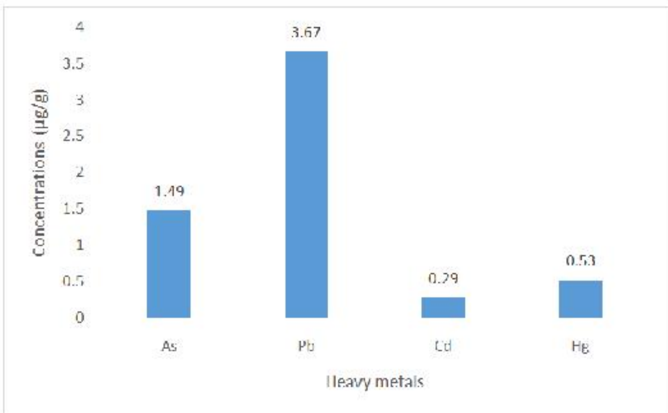

Figure 1. Mean levels of As, Pb, Cd and Hg in Vume Clay deposit

Mercury levels observed in Vume range from 0.18 µg/g to 0.69 µg/g with a mean of 0.53 µg/g and a standard deviation of 0.15. All the Hg levels were within the safe limit of 18 µg/g. Although Hg values were within the acceptable limit, there is a high tendency that, the available Hg could be lost during the firing process in the production of the earthenware products as Hg is volatile at high temperatures, hence reducing the already low levels to the barest minimum in the final product. Samlafo *et al.* (2011) reported a mean of 0.14 µg/g of Hg in clay deposit at Otsew in the Gomoa West district of the Central region. Woode *et al.* (2014) however, reported 0.3 µg/g to 4.2 µg/g in geophagy clay deposit at Anfoega in the Volta region of Ghana.

Conclusion

Arsenic is extremely high in the study area considering the safe limit of 0.07µg/g by US EPA (1990) standard. The finished products from this area is likely to enhance as consumption as As has a higher tendency to be leached into foods of low pH prepared in these products. Some remediation interventions should be put in place in order to reduce the as levels before the clay is used to produce earthenware products, since food is prepared or cooked directly in these products. However, the levels of Arsenic in the study area, though higher than the US EPA safe level, were comparable to the worldwide background level of 5 µg/g in soil. Mercury, lead and Cadmium levels observed in the Vume clay deposit were found to be within US EPA (1990) safe limit. With the exception of As, Vume clay deposit can be deem to be of high quality as far as safe levels of Hg, Pb, and Cd are concerned. Considering the volatility of Hg during the firing process in the production of earthenware products, Hg levels were expected to be very low in the final product.

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