THE CONCENTRATION OF HEAVY METALS IN SELECTED CLAY SAMPLES IN EKITI STATE, SOUTHWESTERN NIGERIA.

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ABSTRACT: The presence and possible effect of heavy metal (such as cadmium, zinc, lead, e.t.c) concentration in the clay used in pot making were investigated. Clay samples were collected at three locations where they are used mostly in making pots and other kitchen utensils. The concentrations of heavy metals were determined using the Atomic Absorption Spectrometer (AAS). Results indicate that the concentration Cu, Zn, Cr, Pb, As, and Mn falls within the range of the maximum admissible concentration of heavy metals of several countries mostly in Europe. However, the concentration Cadmium and Nickel are relatively higher than the maximum admissible concentration of toxic metals in soil for countries like Denmark and Sweden.

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INTRODUCTION

Heavy metals are natural components of the earth crust and are used in many industrial and agricultural applications (Lenntech et al, 1998). These heavy metals may adversely affect soil ecology, agricultural production or product quality, and ground water quality, and will ultimately be harmfull to mankind by food chain. These effects are closely related to the biological availability of heavy metals, which in turn are controlled by the metal ion speciation in the soil (Davis *et al*., 1992; Katbata-Pendias, 1993; Alloway,1995). Metals exist in a number of different soluble and particulate forms, which influence their mobility and bioavailability (Ge *et al*., 2005).

Theoretically, every 1000 kg of "normal soil" contains 200 g chromium, 80 g nickel, 16 g lead, 0.5 g mercury and 0.2 g cadmium (IOCC,1996). Monitoring the endangerment of soil with heavy metals is of interest due to their influence on groundwater and surface water (Wieting,1988, Clemente et al,2008, Boukhalfa,2007) and also on plants (Stimpfl, et al, 2006, Pandey, et al, 2008, Stobrawa,et al, 2008), animals and humans (Lagisz,et al, 2008, de Vries et al, 2007, Korashy et al, 2008). However, their harmful effects on the environment and human health are of great concern. Heavy metal poisoning could result, for instance, from drinking contaminated water resulting from lead pipes or clay pots (Clay pots are used in storing water), high ambient air concentration near emission source, or intake via the food chain (Lenntech et al, 1998). "Heavy metals poisoning" can include excessive amount of iron, manganese, aluminium, or beryllium (the fourth lightest element); or such a semimetal as arsenic as well as the true metals. It excludes bismuth, the heaviest of the stable element, because of its non- toxicity (kuhn et al, 2004).

The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic (Jarup, 2003). While the essential elements, iron, copper and zinc are desirable in the nutrition of man, animals and plants, and their presence could reduce the bioavailability of lead, their undue presence in the food chain could be harmful (Davidson et al,1979,Udosen et al,1990). Reports have indicated that excess amounts, as could result from industrial pollution, have varying deleterious effects on man. These range from severe mucosal irritation and corrosion, widespread capillary damage and central nervous system irritation, to possible necrotic changes in the liver and kidney in the case of copper (WHO, 1984). With excessive intake of zinc and iron, vomiting, dehydration, electrolyte imbalance and lack of muscular co-ordination have also been indicated (WHO, 1984). Cadmium exposure may cause kidney damage. The first sign of the renal lesion is usually a tubular dysfunction, evidenced by an increased excretion of low molecular weight proteins or enzymes (Jarup et al,1998, WHO, 1992). It has been suggested that the tubular damage is reversible, but there is overwhelming evidence that the cadmium induced tubular damage is indeed irreversible (Jarup et al,1998).

However, exposure does not result only from the presence of a harmful agent in the environment. The key word in the definition of exposure is contact (Berglund et al,2001). There must be contact between the agent and the outer boundary of the human body, such as the airways, the skin or the mouth. The symptoms of acute lead poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system. Lead encephalopathy is characterized by sleeplessness and restlessness. Children may be affected by behavioural disturbances, learning and concentration difficulties (Jarup,2003). In less serious cases, the most obvious sign of lead poisoning is disturbance of haemoglobin synthesis, and long-term lead exposure may lead to anaemia. Acute exposure to lead is known to cause proximal renal tubular damage (WHO, 1995). General population exposure to arsenic is mainly via intake of food and drinking water. Food is the most important source, but in some areas, arsenic in drinking water is a significant source of exposure to inorganic arsenic. Contaminated soils such as mine-tailings are also a potential source of arsenic exposure (WHO,2001). The WHO evaluation (WHO,2001) concludes that arsenic exposure via drinking water is causally related to cancer in the lungs, kidney, bladder and skin, the last of which is preceded by directly observable precancerous lesions.

Ara Ijero and Isan area of Ekiti State are predominantly known since ancient time for clay pots making while the clay deposit in Ire Ekiti are mostly used for block making. Consequently a block factory was sited at that location. Isan Ekiti sample composed of clay samples from three sources in the area namely: Turoo, Orudi, and Aradee villages . Meanwhile, Ara Ijero and Isan Ekiti are of utmost interest in this research. This is because there are very high possibilities of bioaccumulation of some heavy metals via food and water intake using the pots made from the clays. This work is focused at determining the concentration of Cd, Pb Zn, Cu, Cr, As, Mn, Al and Ni in the clay samples collected and also to evaluate if the concentration is within the admissible concentration of known limits around the world bearing in mind the possibilities of bioaccumulation.

MATERIALS AND METHOD.

Clay samples were collected from three major locations in Ekiti State: Ara Ijero where clay is used in pots making, Isan Ekiti where three different clays from three different locations are mixed at equal proportions by volume for making pots, Ire Ekiti where the clay is used in the manufacture of bricks.

The clay samples were dried, grounded in a mortal and sieved into a fine powder using 1mm mesh. Acid digestion was carried out using concentrated Hydrofluoric acid (HF), aquaregia ($HCl + HNO_3$, 3: 1) and saturated boric acid solution. 1.2 g of each sample was weighed on a analytical balance into a plastic container of 100 ml capacity. 3 ml of Conc. HF was added to each sample: Subsequently, 5 ml of the Aquaregia was added to each samples and heated for 45 minutes then 10 ml of saturated solution of boric acid was added to the solution and heated at 180^0 for 30 minutes. The samples were made up to the mark with distilled water and then taken for Atomic Absorption Spectrometry (AAS) analysis. Analyses were performed in two replications and average values are presented. The signal reading obtained for each metal from the spectrometer is calculated into concentration in part per million (ppm or $mgkg^{-1}$).

RESULTS AND DISCUSSION

The concentration in ppm of the eight heavy metals considered for each of the location is presented in the Table 1 below.

Table 1: Concentration (in ppm/mg kg^{-1}) of the heavy metals in the clay for each of the location.

S/N	Sample Name	Cu	Zn	Cr	Pb	As	Mn	Cd	Ni
1	ARA IJERO	1.228	3.566	1.459	0.731	0.000	51.450	0.000	5.250
2	IRE EKITI	0.921	2.972	2.919	2.193	0.000	115.200	0.000	2.250
3	TUROO	0.921	2.972	2.919	0.731	0.000	91.300	0.000	3.000
4	ORUDI	1.228	2.398	1.459	0.731	1.800	78.300	1.400	1.500
5	ARADEE	1.535	5.944	1.459	1.462	1.800	150.000	1.400	4.500
6	ISAN EKITI (3+4+5)	0.616	4.755	2.919	0.731	4.500	189.850	2.800	4.500

Table 2. Critical limits for heavy metals in soils in several countries[1]

COUNTRY	Critical Limits(mg/kg)[2]						
	Pb	**Cd**	**Cu**	**Zn**	**Ni**	**Cr**	**Hg**
Denmark	40.0	0.3	30.0	100.0	10.0	50.0	0.1
Sweden[3]	30.0-60.0	--	--	--	--	--	0.2-0.3
Finland	38.0	0.3	32.0	90.0	40.0	80.0	0.2
Netherlands	85.0	0.8	36.0	140.0	35.0	100.0	0.3
Germany[3]	40.0-100.0	0.4-1.5	20.0-60.0	60.0-200.0	15.0-70.0	30.0-100.0	0.1-1.0
Switzerland	50.0	0.8	50.0	200.0	50.0	75.0	0.8
Czech Republic	70.0	0.4	70.0	150.0	60.0	130.0	0.4
Eastern Europe[4]	32.0	2.0	55.0	100.0	85.0	90.0	2.1
Ireland	50.0	1.0	50.0	150.0	30.0	100.0	1.0
Canada	25.0	0.5	30.0	50.0	20.0	20.0	0.1

1 From De Vries and Bakker, 1998
2 Values are for protection of all land uses
3 The first value is for sandy soils; second value for clay soils
4 Eastern Europe includes Russia, Ukraine, Moldavia and Belarus

Table 3:Maximum Admissible concentrations of toxic metals in soil on which sewage sludge is applied.

Country	**Concentration ($mgkg^{-1}$)**						
	Cd	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
USA	20	1500	750	8	210	150	1400
SWEDEN	0.5	30	40	0.5	1.5	40	100
NORWAY	1	100	50	1	30	50	150
FINLAND	0.5	200	100	0.2	60	60	150
DENMARK	0.5	30	40	0.5	15	40	100
UK	3	400	135	1	75	300	300
FRANCE	2	150	100	1	50	100	300
GERMANY	1.5	100	60	1	50	100	200
EU	1-3	100-150	50-140	1-1.5	30-75	50-300	150-300

SOURCE: Adapted from Alloway (1995)

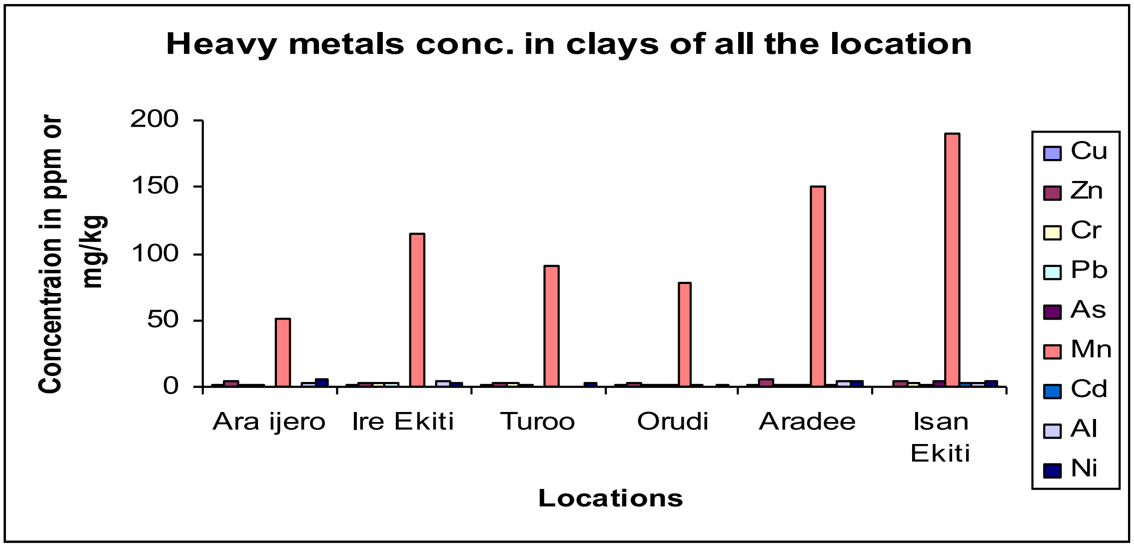

Fig.1: Chart of heavy metals concentrations in clays from all the locations

DISCUSSIONS

Copper

The results in Figures 1 and 2 shows that the concentration of copper for all the locations ranges from 0.616 – 1.535 $mgkg^{-1}$ and falls within the range of all known limits as presented in Tables 2 and 3.

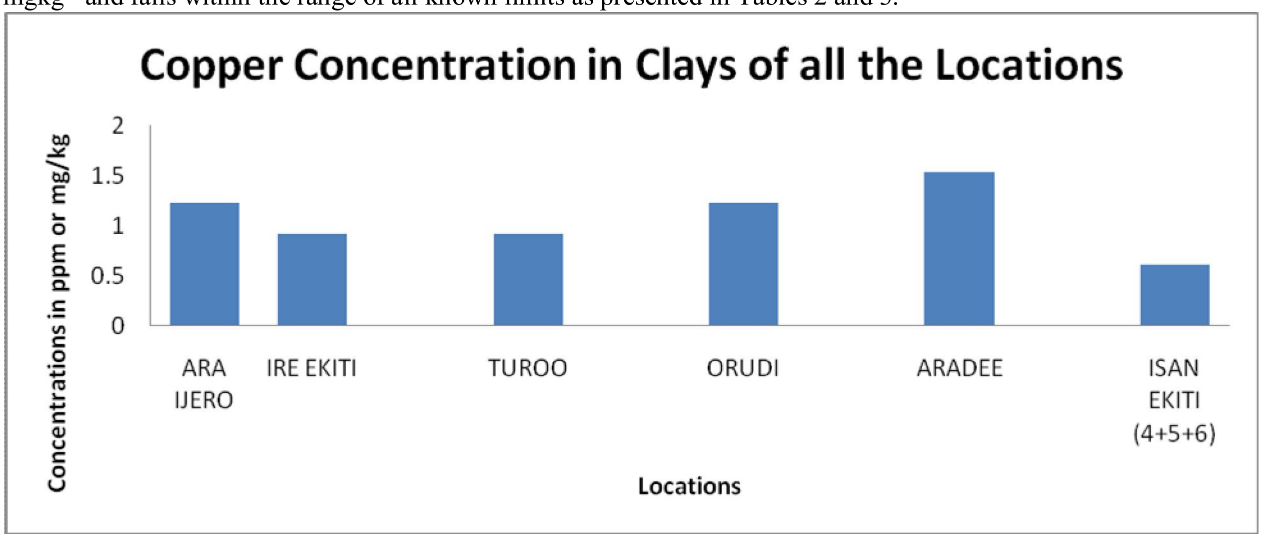

Fig 2: Copper concentrations in clays for all the locations

Zinc

Figures 1 and 3 shows zinc concentrations in clays at various locations. The concentration ranged between 2.972 – 5.944 $mgkg^{-1}$ which falls below the limits for all the countries considered.

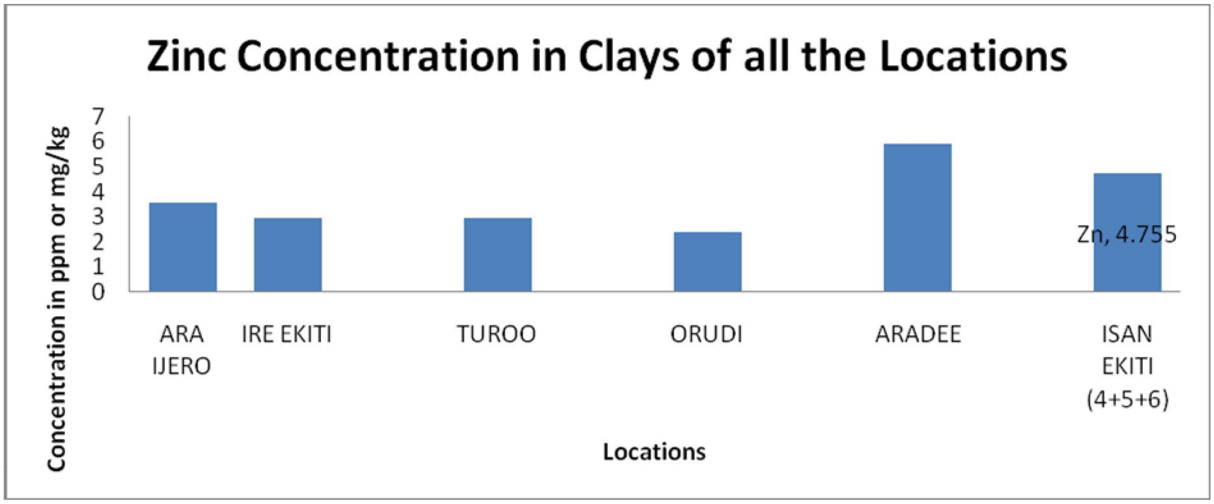

Fig 3: Zinc concentrations in clays for all the locations

Chromium

Figure 4 shows chromium concentrations in clays at various locations, ranging from 1.459 – 2.919 $mgkg^{-1}$ and are all within the stated limits.

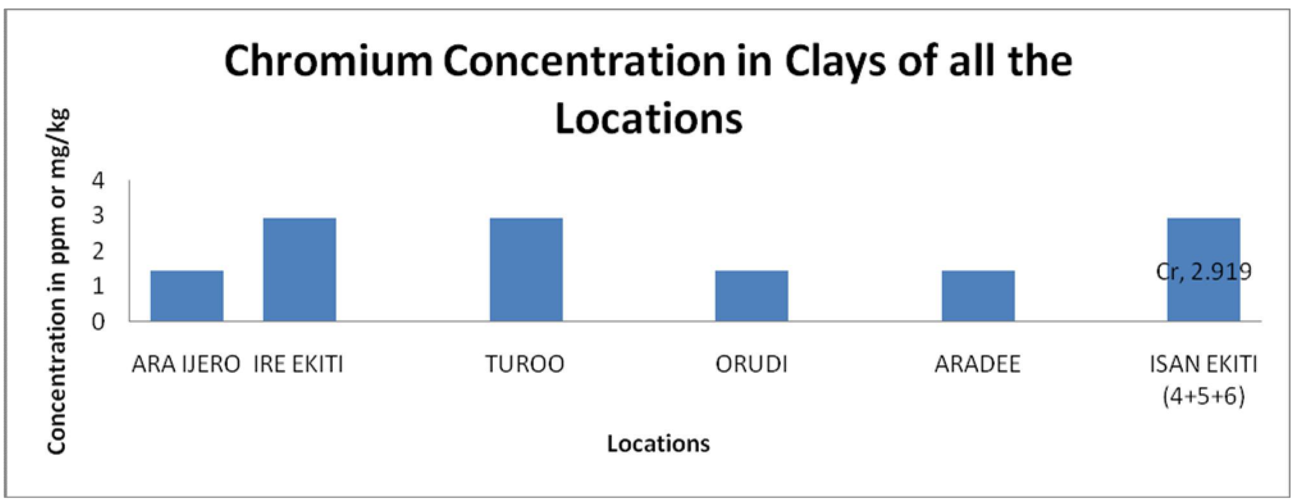

Fig 4: Chromium concentrations in clays for all the locations

Lead

In figure 5, the concentrations of lead in clays of all locations ranged from 0.731 - 2.919 $mgkg^{-1}$ and therefore falls below the known limits (De Vries etal,1998), hence posing no harm to human health.

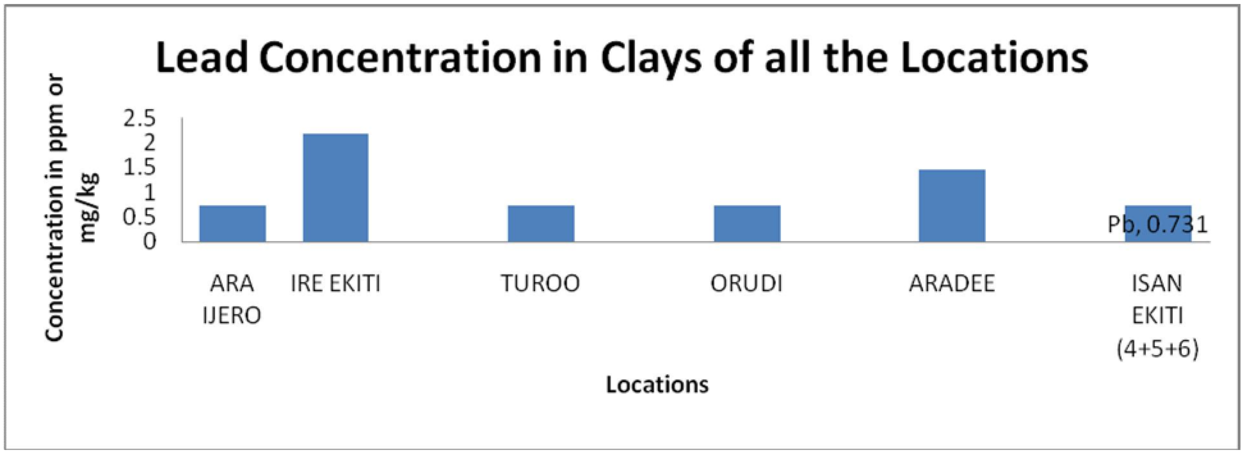

Fig 5: Lead concentrations in clays for all the locations

Arsenic

In fig 6, it is evident that Arsenic is only detected in the Isan Ekiti with a concentration of 4.5 $mgkg^{-1}$ in the mixture.

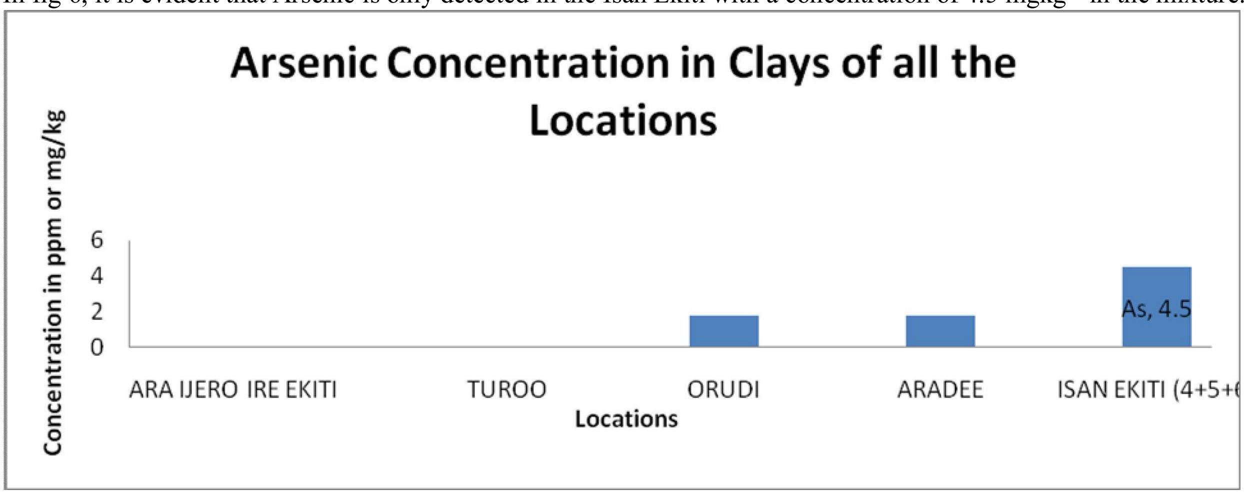

Fig 6: Arsenic concentrations in clays for all the locations

Manganese

Fig 7 shows manganese concentrations for all the locations ranging between 91.30 – 189.85 $mgkg^{-1}$.

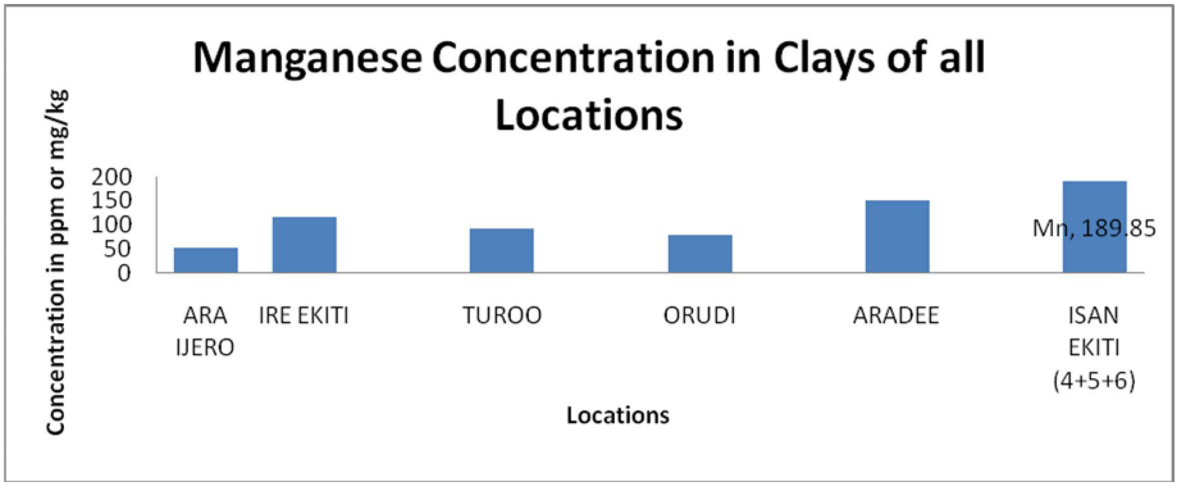

Fig 7: Manganese concentrations in clays for all the locations

Cadmium

In figure 8 the lead concentrations were detected only in three samples (Isan Ekiti's location) with values ranging from 1.4 – 2.8 mgkg^{-1}.This concentration is above the maximum admissible concentration/critical limits of heavy metal in soil for almost all the country considered as presented in Tables 2 and 3 (Alloway,1995,De Vries et al 1998). Hence, the use of Isan Ekiti's clay in pot making can lead to some of the health effect mentioned above (Jarup,2003) considering the factor of bioaccumulation.

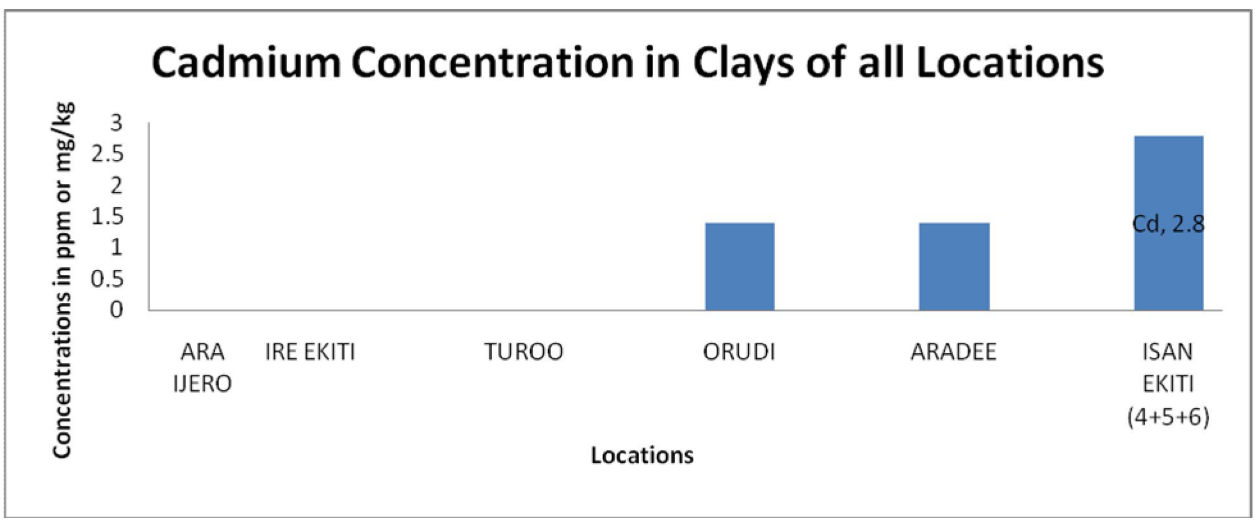

Fig 8: Cadmium concentrations in clays for all the locations

Nickel

Fig 9 shows nickel concentration in the clays of all locations with values ranging from 1.5 – 5.25 mg kg^{-1}. The concentrations of nickel in all the locations is therefore higher than the maximum admissible concentration of toxic metal in soil for Sweden (Alloway,1995), hence, exposing the people drinking water from the pot made therefrom to some health risk considering the factor of bioaccumulation.

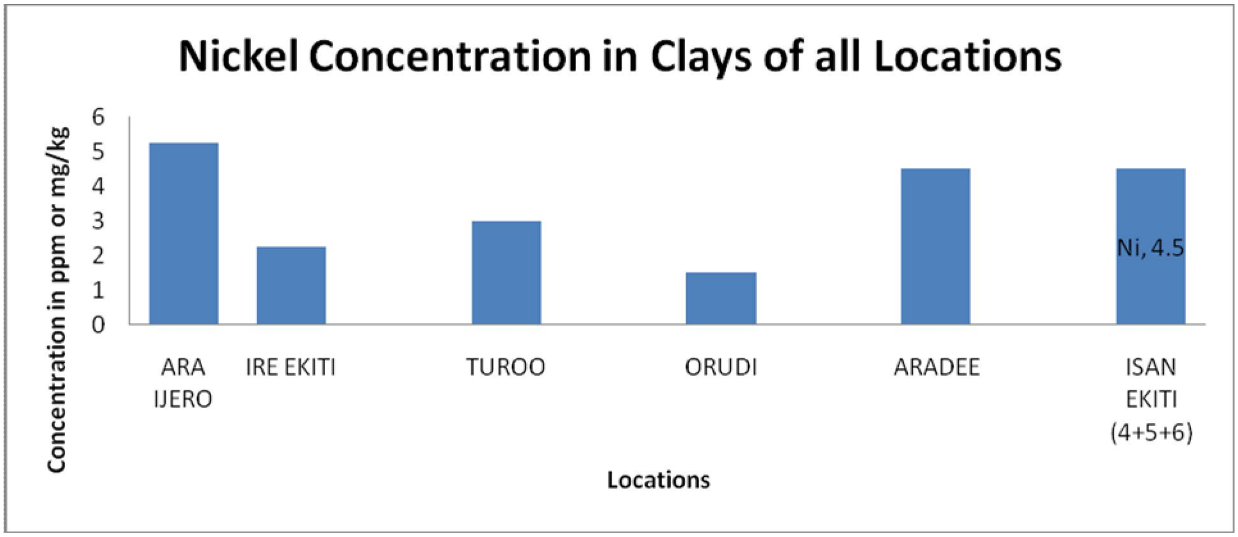

Fig 9: Nickel concentrations in clays for all the locations

CONCLUSION

The heavy metal concentration of the clay samples investigated was found to be relatively high especially in Isan Ekiti for Cadium and Nickel as compared to the standard limits thereby posing a health threat to people using earthenware made there from. Therefore, more research should be carried out in these locations to investigate mostly the heath effect of the heavy metal concentrations on the populace of these locations.

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