Locally made utensils as potential sources of heavy metals contamination of water: A case study of some pots made in Nigeria

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Abstract: This research work was carried out to determine if locally made utensils can be the sources of water contamination by heavy metals. A reference water of known metal concentration (Distilled water) was heated for 1- 2 hours in both clay and metal pots made in different locations in Nigeria. Geochemical analysis of the heated water from the different variety of pots revealed that the major cations Al (0.109-0.79mg/l), Ca (5.011-16.43mg/l), Fe (0.042-0.178mg/l), K (0.35-2.72), Mg (0.506-2.51mg/l), and Na (1.74-4.88mg/l) have preferentially been released into the heated water displaying significantly elevated concentrations compared to that of the reference water concentrations (0.49mg/l, 6.42mg/l, 0.005mg/l, <DL, 0.54mg/l, 1.88mg/l respectively). On the other hand, water from the metal pots present relatively similar concentrations in the major cations but exceptionally higher concentrations in Al (1.79-14.71mg/l), Ca (5.47-14.15mg/l) and K (4.69-5.91mg/l. With respect to heavy metal concentrations, the heated waters from the clay pots display significantly higher concentrations in As (0.043-0.440mg/l), Tl (0.326mg/l) and Zn (0.801-1.16mg/l) relative to their concentrations in the metal pots (0.072-0.23mg/l), 0.037-0.259mg/l) and 0.67-1.11mg/l). Analysis of geochemical data using a standard pollution index; Contamination Factor (CF) revealed that the water from both the clay and metal pots have been very highly contaminated by As (clay pots (CF for As = 4-44); metal pots (CF for As =7-23). Whereas the water from the metal pots are considerably contaminated by Sb (CF = 0.65-3.35), that from the clay pots are moderately contaminated (CF=0.45-1.9). Both waters from the clay and metal pots are very highly contaminated in Se (CF= up to 7.2). Thus, the continuous long-term usage of locally made utensils for cooking purposes could introduce significant amount of heavy metals into the human body system through the food chain with its attendant human health risks.

Keywords: Locally Made Utensils, Clay, Metal, Heavy Metals, Contamination, and Distilled Water

1. Introduction

Monitoring the presence of heavy metals in foods intended both for human and animal is of interest because of their toxic effects [1]. Although they can be found in high concentrations in the body, a number of heavy metals such as aluminum, beryllium, cadmium, lead and mercury have no known biological function. Others such as As, Cu, Fe, and Ni are considered essential at low concentrations but are toxic at high levels [2], [3].

In general, heavy metals disrupt basic metabolic functions in two ways. On one side, they disrupt the functioning of vital organs and gland such as the heart, brain, kidney, bone or liver and secondly they alter nutrients that are essential minerals preventing them from fulfilling their biological function. For example, Al as chelator has the ability to capture and prevent the uptake of essential elements and thereby disrupt the proper use of many of them such as Ca, Zn, Or Cu [4]. This metal is heavily involved in the onset of Alzheimer's disease [5]. It is also responsible for the alteration of neurons [6]; [7]; [8].

Two traditional utensils revealed that aluminium pots and clay pots are sources of contamination by heavy metals for people in poor countries who use them daily. Therefore, cooking utensils can be a source of contamination by toxic metals [9].The used of an atomic absorption spectrophotometric analysis of the concentration of heavy

metals present in food samples processed with different types of milling equipments, viz locally fabricated milling machine, grinding stone, blender, mortar and pestle and cooked using locally made iron pot, earthernware pot and stainless steel pot revealed that the increase in concentration of the heavy metals in the experimental sample over the control (milled using a commercially procured blender and cooked in stainless steel pot) sample showed the amount of heavy metal is added more by locally fabricated cookware and milling techniques [10].

Environmental pollution is a major cause of the presence of heavy metals into the food chain [11]. Food can be contaminated during the different stages of agricultural production, particularly in the soil where heavy metals may be naturally present [12]. The preparation of these agricultural products into palatable food is also a major source of food contamination by heavy metals [13]. Indeed, the preparation process requires the use of utensils and ingredients which are also responsible for the presence of heavy metals in food [1]. Located at the end of the chain of food preparation, packaging and cooking utensils contaminate food based on materials used in their design.

In Nigeria, as in most developing countries, much of the urban population and almost all the rural population still use traditional cooking utensils. Examples are the clay and metal pots. Unlike modern utensils, traditional ones do not have protective layer of inert material to prevent contamination of food. This study aims to determine if locally made utensils could be a potential source of heavy metal contamination of water.

1.1. Locally Made Cooking Utensils

Pottery is widely practiced in Nigeria because of the numerous uses of pots as a vehicle for cooking, storage and decoration. The art of pottery has no ethnic or regional distribution. Excavations have shown that pottery attained a high level of development in Nigeria several hundred years ago. This tradition has been maintained, as a result Nigeria pottery today is ranks among the most artistic in the world [14].

Clay pots are classified based on their shape, use, size and colour. Their shapes depend on the culture and religious believe of the manufacturers. Certain shapes are believed by some traditions to make the pots stronger and durable. The basic use of locally made clay pots are usually for fetching and storage of water, decoration and cooking depending on the size, 25cm in high and 60cm in diameter. Clay pots can also be classified based on their colour which is a characteristic of the clay type used as raw material for its production. The various clay types used as a raw material differ in colour, chemical composition and texture depending on the geologic conditions in which they were formed. Generally, there are three types of clay for pottery in Nigeria which are the earthenware clay, stoneware clay and the kaolin clay, however, two different clay types can be mixed at a certain ratio and used [14].

The earthenware clay is the most commonly used; it contains a fair amount of iron giving it a reddish coloration. Clay pots from Sokoto, Benue, Plateau and Niger States are produced with this type of clay. The stoneware clay is a mixture of various clay materials. This has a high degree of plasticity and its colour is usually grey, dark grey, brown or black. Most pots made from the stoneware clay change to a complete black colouration after firing, very good examples are the clay pots from Calabar, Kwara and Kogi States. The clay pot from Osun State is a mixture of the stoneware and kaolin clay. Kaolon clay is very pure, with white colour. As it does not have a high degree of "Plasticity," it is usually used in conjunction with other clays.

Since clay pots are made of clay, major potential contaminants include all heavy metals from the earth crust. This is so because before clay formation, the parent material undergoes so many interactions with other earth materials over a very long time. During this interaction, heavy metals dissolve to form different solutions as a result of chemical weathering resulting to contamination. Other earth elements that could not go into solution at the time of the clay formation still remain embedded as very tiny crystals in the clay and can still be of great health effect when ingested. Generally, potential contaminants from the use of locally made clay pots include heavy metals such as As, Cd, Co, Cr, Tl, Cu, Fe, Pb, Sb, Se and Zn among others.

2. Materials and Methods

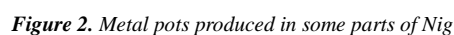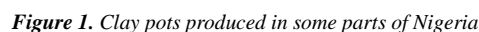**Table 1.** *Specimen of the clay pots*

S/No	Sample ID	State of Production and Clay Geology	Clay type	Description of clay raw material used
1	IFE	Osun (Dahomey Basin)	Stoneware and Kaolin	Fine grained, dark grey colour
2	MNA	Niger (Bida Basin)	Earthenware	Very fine grained, pink colour
3	MKD	Benue (Upper Benue Trough	Earthenware	Fine grained, brown colour
4	SKT	Sokoto (Illeummeden Basin)	Earthenware	Very fine grained, red colour
5	LKJ	Kogi (Middle Benue Trough)	Stoneware	Very fined grained, dark red colour
6	ILR	Kwara (Migmatite-Gneiss Complex)	Stoneware	Very fine grained, grey colour but turn black after burning
7	PLA	Plateau (Younger Granite Complex)	Earthenware and kaolin	Fine grained with micro crystalline inclusions
8	CLB	Cross – river (The Calabar Flank)	Stoneware	Very fine grained, dark grey colour but turn to black after burning

The markets where these clay and metal pots are commercialized were personally visited and sample pots were chosen and bought at random. Only the major producing states mentioned above were considered for sample collection in both locally made clay and metal pots. A total of eight (8) clay and (4) metal pot samples were collected as shown in Tables 1 and 2 below.

2.1. Procedure for Samples Preparation and Analysis

The pots were properly washed several times withnd distilled water of known concentration was used to rinse several times before starting the experiment proper. The distilled water was boiled in the pots for 1-2 hours. The water was allowed to cool and collected carefully in a polythene bottle (250ml) for geochemical analysis. Two drops of concentrated Nitric acid was added to the samples collected to prevent any absorption and precipitation of ions. Finally, the samples were sealed and properly labeled.

The twelve (12) samples were taken to the University of Jos, Department of Geology Geochemical Laboratory for chemical analysis using the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The ICP-OES is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within a given sample.

The heavy metals analyzed include the following Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Sb, Se, Tl, and Zn at a standard deviation/error of 0.001.

Table 2. Specimen of the metal pots

S/no	Sample ID	State of production
1	PLM	Plateau
2	NASM	Nassarawa
3	ONIM	Anambra
4	KDM	Kaduna

Figure 1. Clay pots produced in some parts of Nigeria

Figure 2. Metal pots produced in some parts of Nig

3. Results

The results obtained from the chemical analysis are shown in Table 3 and 4 below respectively.

Table 3. Geochemical Results of Water from Clay Pots

	IFE Stoneware and kaolin clay	MNA Earthenware clay	MKD Earthenware clay	SKT Earthenware clay	LKJ Stoneware clay	ILR Stoneware clay	PLA Earthenware and kaolin clay	CLB Stoneware clay	DW
Al (mg/l)	0.571	0.787	0.443	0.109	0.320	0.067	0.148	0.320	0.490
As (mg/l)	0.119	0.043	0.109	0.135	0.063	0.086	0.135	0.440	0.095
Ca (mg/l)	11.61	14.26	6.716	6.986	7.331	5.011	16.43	6.150	6.424
Cd (mg/l)	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Co (mg/l)	0.003	0.005	0.001	0.001	0.001	0.005	0.002	0.005	0.001
Cr (mg/l)	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL

	IFE Stoneware and kaolin clay	MNA Earthenware clay	MKD Earthenware clay	SKT Earthenware clay	LKJ Stoneware clay	ILR Stoneware clay	PLA Earthenware and kaolin clay	CLB Stoneware clay	DW
Cu (mg/l)	<DL	<DL	0.006	<DL	<DL	<DL	<DL	0.004	<DL
Fe (mg/l)	0.134	0.260	0.079	0.025	0.178	0.042	0.079	0.55	0.005
K (mg/l)	1.276	2.122	0.349	<DL	0.916	<DL	2.715	<DL	<DL
Mg (mg/l)	1.539	2.035	1.133	0.646	0.937	0.506	2.512	0.710	0.540
Na (mg/l)	4.008	5.168	2.987	1.736	2.088	1.452	2.365	4.881	1.883
Ni (mg/l)	0.004	0.005	0.002	<DL	<DL	0.006	<DL	<DL	<DL
Pb (mg/l)	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Sb (mg/l)	0.009	0.025	0.038	0.018	0.031	0.034	0.032	0.013	0.012
Se (mg/l)	<DL	0.073	0.004	0.014	<DL	0.018	<DL	<DL	0.031
Tl (mg/l)	0.263	<DL	0.326	0.079	0.143	0.139	0.150	0.138	0.104
Zn (mg/l)	1.237	2.225	1.136	0.808	0.900	0.867	1.163	0.801	0.669

<DL = below detectable limit, DW = Distilled water used
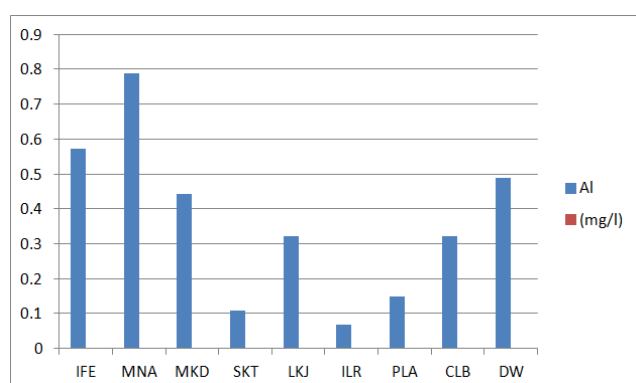
Figure 3. *Concentrations of Al in water boiled in the clay pots.*
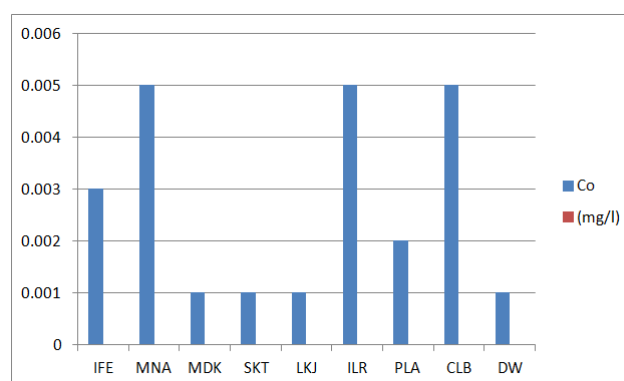
Figure 5. *Concentrations of Co in water boiled in clay pots*
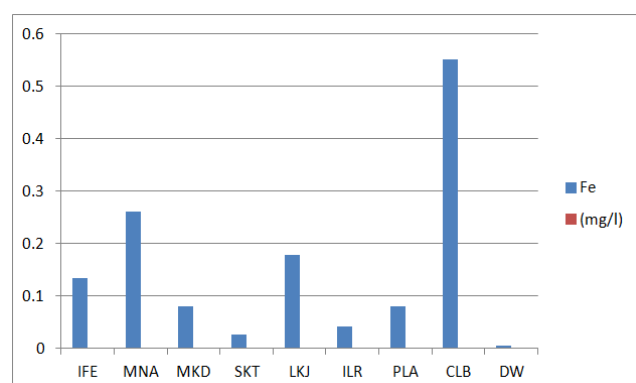

Figure 4. *Concentrations of Fe in water boiled in the clay pots*
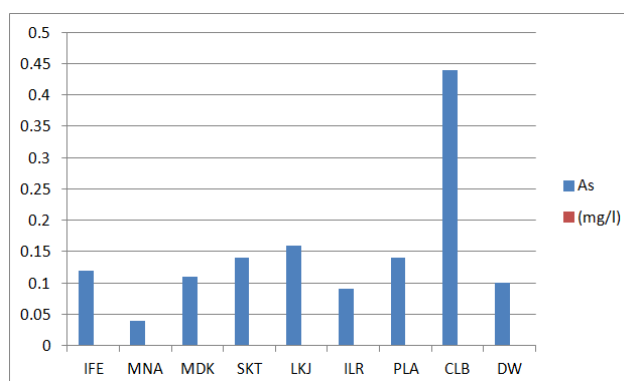

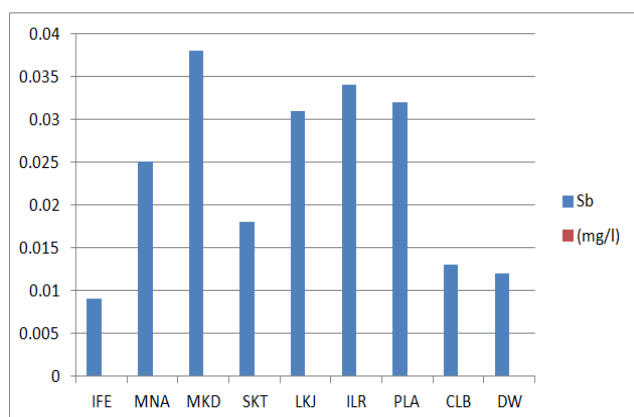**Figure 6** . *Concentration of As water boiled in clay pots*

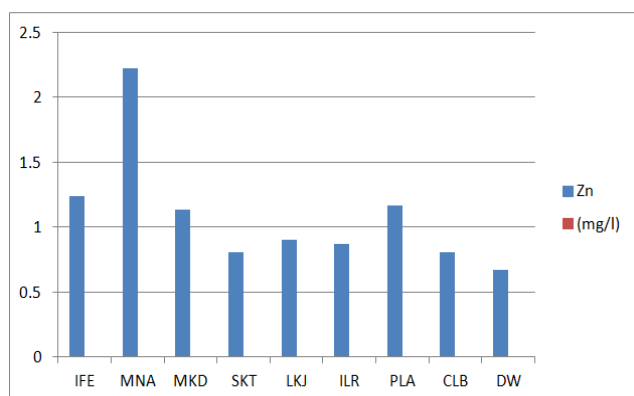Figure 7. Concentrations of Sb in water boiled in clay pots

Figure 8. Concentrations of in Zn water boiled in clay pots

Table 4. Geochemical Results of Water from Metal Pots

|	PLM	NASM	ONIM	KDM	DW
Al (mg/l)	1.79	16.02	14.71	7.689	0.490
As (mg/l)	0.232	0.072	0.109	0.089	0.095
Ca (mg/l)	5.467	14.15	13.32	11.03	6.424
Cd (mg/l)	<DL	<DL	<DL	<DL	<DL
Co (mg/l)	0.005	0.002	0.002	0.006	0.001
Cr (mg/l)	<DL	<DL	<DL	<DL	<DL
Cu (mg/l)	0.009	<DL	<DL	0.005	<DL
Fe (mg/l)	0.002	0.031	<DL	<DL	0.005
K (mg/l)	4.690	5.907	5.665	4.850	<DL
Mg (mg/l)	0.946	1.063	1.063	1.106	0.540
Na (mg/l)	2.909	1.975	1.489	2.891	1.883
Ni (mg/l)	<DL	0.001	<DL	0.001	<DL
Pb (mg/l)	<DL	<DL	<DL	<DL	<DL
Sb (mg/l)	0.047	0.030	0.013	0.015	0.012
Se (mg/l)	0.072	0.017	<DL	0.019	0.031
Tl (mg/l)	0.259	0.129	0.037	0.201	0.104
Zn (mg/l)	0.739	1.113	0.672	0.980	0.669
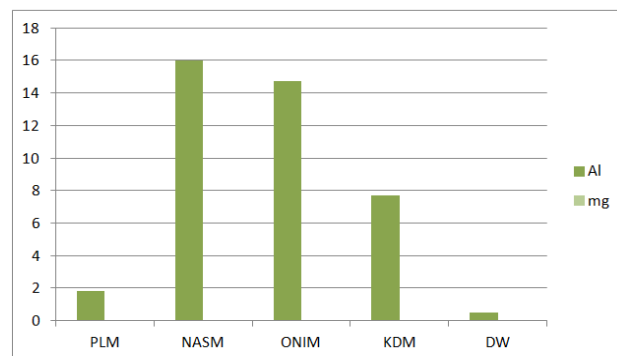
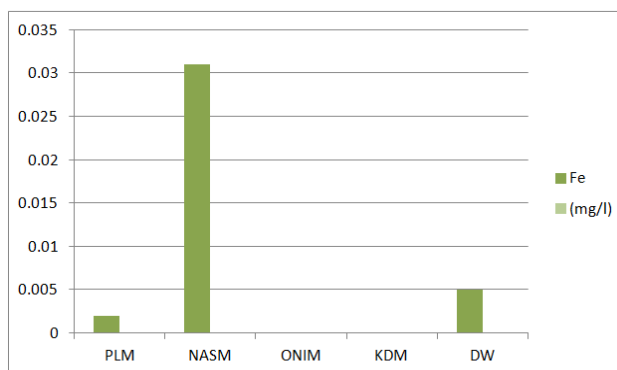Figure 9. Concentrations of Aluminum in water boiled in the metal pots

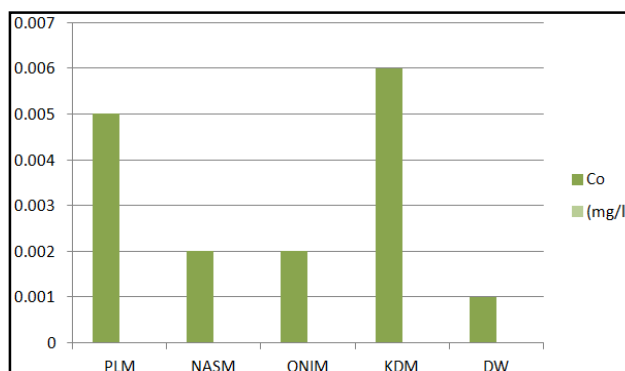Figure 10. Concentrations of Fe in water boiled in the metal pots

Figure 11. Concentrations of Co in water boiled in metal pots
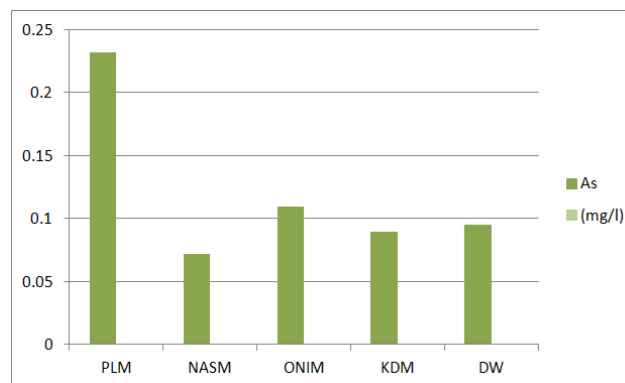

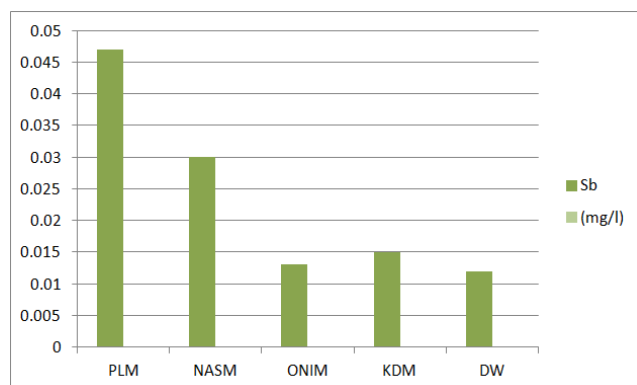Figure 12. Concentrations of As in water boiled in metal pots

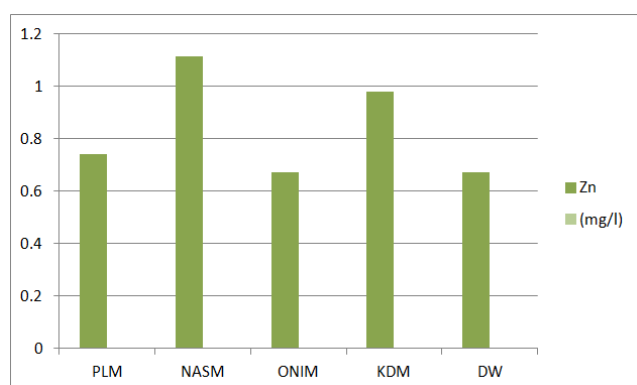**Figure 13.** *Concentrations of Sb in water boiled in metal pots*

Figure 14. *Concentrations of Zn in water boiled in metal pots*

3.1. Contamination Factor (CF)

The level of contamination of the pots by Heavy Metals can be expressed in terms of a contamination factor (CF), which is given as:

CF = Cm/Cb

Where

Cm = Heavy metal concentration from chemical analysis.

Cb = (WHO) maximum recommended intake level.

Hence the contamination factor (CF) can be classified as follows

- CF < 1   Low contamination
- $1 \leq CF < 3$ Moderate contamination
- $3 \leq CF \leq 6$ Considerable contamination
- CF > 6   Very high contamination

Table 5. *Contamination Factor (CF) for As, Sb, and Se from clay pots*

Sample ID and clay type used	As	Sb	Se
IFE (Stoneware and kaolin clay)	11.9	0.45	0
MNA (Earthenware clay)	4.3	1.25	7.3
MKD (Earthenware clay)	10.9	1.9	0.4
SKT (Earthenware clay)	13.5	0.9	1.4
LKJ (Stoneware clay)	6.3	1.5	0
ILR (Stoneware clay)	8.6	1.7	1.8
PLA (Earthenware and kaolin clay)	13.5	1.6	0
CLB (Stoneware clay)	44.0	0.65	0

Table 6. *Contamination Factor (CF) for As, Sb, and Se from metal pots*

Sample ID and State of production	As	Sb	Se
PLM Plateau	23.2	3.35	7.2
NASM Nassarawa	7.2	1.5	1.7
ONIM Anambra	10.9	0.65	0
KDM Kaduna	8.9	0.75	1.9

4. Discussion

4.1. Heavy Metals

a. Clay pots

Heavy metals content in the water boiled in the clay pots are below their concentrations in the reference water (DW=0.490mg/l) with the exception of the water boiled in clay pot produced in IFE and MNA which are higher (0.571 – 0.787mg/l) (see Table 3 and Figure 3 above). The water boiled in all the clay pots has concentration values of Fe (0.025 – 0.550mg/l) which are higher than that of the reference water (0.005mg/l), Table 3 and Figure 4. The water boiled in the clay pots produced in MNA, ILR and CLB have high concentration values of Co (Table3 and Figure5). Water boiled in the clay pot produced in CLB has the highest concentration value of (0.440mg/l) while its values in the other water are similar to that of the reference distilled water (DW) (Table 3 and Figure 6). The concentration value of Sb is high in water boiled in MNA, MKD, SKT, LKT, ILR and PLA with MKD having the highest value ((Table 3 and Figure 7). The concentration of water boiled in clay pot made in MNA has the highest value of Zn (Table 3 and Figure 8).

The MNA clay pot is considerably contaminated by having a CF value for As of 4.3 but all the other clay pots are very highly contaminated (As CF values ranging from 6.3 to 44.0) (Table 5).

The CF of Sb in the clay pots is low in IFE, SKT, and CLB with values ranging from 0.45 to 0.9. the value of Sb is moderate contamination in the clay pots produced in MNA, MKD, LKJ, ILR and PLA with values ranging from 1.3 to 1.9 (Table 5).

The clay pots produced in IFE, LKJ, PLA, and CLB are not contaminated by Se by having a CF value of zero (0). MKD clay pot has low contamination by having CF value of 0.4. The CF values of clay pots produced in SKT and ILR are 1.4 and 1.8 respectively. Clay pot produced in MNA has CF value of 7.3 and this indicate very high contamination with Se (Table 5)

b. Metal pots

The concentration of Al in the water boiled in all the metal pots are higher (1.79 – 16.02mg/l) than that of the distilled water (0.490mg/l), Table 4 and Figure 9). Only the water boiled in the metal pot produced in NASM concentration value (0.031mg/l) which is higher than its value in distilled water (0.005mg/l), Table 4 and Figure 10). In the case of the metal pots, the highest concentration value of As is found in the water boiled in the pots produced in PLM (Table 4 and

Figure 12). The concentration value of Co is high in the water boiled in metal pots produced in PLM and KDM (Table 4 and Figure11). The highest value of Sb is found in the water boiled in metal pot produced in PLM (Table 4 and Figure 13). The highest concentration of Zn is found in the metal pots produced in NASM and KDM respectively (Table 4 and Figure 14).

All the metal pots produced in PLM, NASM, ONIM and KDM are very highly contaminated with As by having CF values ranging from 7.2 to 23.2 (Table 6).

In the case of Sb, the metal pots produced in ONIM and KDM have low contamination by having CF values of 0.65 and 0.75 respectively (Table 6). The metal pot produced in NASM has a CF value of 1.5 and this indicates moderate contamination. The metal pot produced in PLM has the highest CF value of Sb which is 3.35 indicating considerable contamination (Table 6).

The CF value of Se is zero (0) in the metal pot produced in ONIM and this indicate that the pot is not contaminated by Se. the metal pots produced in NASM and KDM have CF values of 1.7 and 1.9 respectively and this indicates moderate contamination.

Considering all the CF values of As, Sb, and Se in the metal pots, PLM pot has the highest level of contamination in all the metal pots.

5. Conclusion

This study brings to the fore the locally made utensils (clay or metal) as sources of heavy metals contamination of water destined for cooking purposes. The continuous use of such pots for cooking could cause immeasurable human health consequences especially for people in poor countries. The metal pots are the highest contributors of these heavy metals relative to the clay pots. The sources of these heavy metals in the clay pots are linked to the composition of the rocks from which the clay raw materials were derived and in the metal pots, to the composition of the scrap metals with which they were made.

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