

Study of Potentially Toxic Metals (PTMS) from Two Nigerian Clays and Related Clay Pottery Used Locally as Foodwares

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ABSTRACT

There is presently lack of data on composition of potentially toxic metals and their leaching from clay based foodwares into food. Therefore, in present study we evaluated the leaching of cadmium, chromium, copper, manganese, nickel, lead and zinc from raw clays and traditional clay pots from two locations, Ara-Ekiti, Ekiti State and Kono-Boue, Rivers State in Nigeria. Samples were digested with aqua regia and analysed using atomic absorption spectrometry and also with energy dispersive X-ray fluorescence. Tap water set at different temperatures (27°C and 100°C) and pH values (4.2 and 9.2) were used to leach the pots. The pH of the raw clays ranges from 2.08–6.50. The order of concentrations is Fe>Mn>Pb>Zn>Ni>Cr>Cu>Cd for both clays and this was consistent with XRF data. The results from this study indicate that Cd, Cr, Cu and Pb were not in leachable forms in clay pots. The concentration ranges of Fe and Mn leached were 0.16–8.37 ppm and 0.08–10.00 ppm, respectively. In all cases the Kono-Boue pots indicated more leached concentrations of metals than Ara-Ekiti pots. It is essential to assess traditional clay pots for leachability of xenobiotics.

1. Introduction

Food and Drug Administration (FDA) compliance programs are not available in most developing countries. Consequently records of toxic elements in food and foodwares are not known to consumers in most countries in Africa. In Nigeria and some other African countries foodwares produced from local clay materials are still very popular. In some of these countries big and popular restaurants and eateries sited major towns advertise the use of local clay based foodware in preparation and serving of meals. Improperly formulated, or fired clay based foodwares may permit unacceptable amounts of toxic elements to leach into food or portable water. Therefore the need to evaluate raw clay employed for clay based foodwares and finished clay based pottery products cannot be over emphasized. Presently, even in some developed countries there are no validated protocols tests for detecting toxic metals in foodwares.

The Council of Europe committee of experts on materials coming into contact with food and the committee of experts on nutrition, food safety and consumer health, and other committees in public health field in justifying their guidelines on metals and alloys used as food contact materials suggested that these metals exceeds recommended exposure limits.

In Nigeria, the clay pottery industry is small-scale and widespread due to the distribution of clay deposits in over eighty (80) different locations. Food processing and storage of portable water in locally made clay pots are common all over the country. For instance, the Kono-Boue and Ara-Ekiti

Communities of Rivers State, South-South Nigeria and Ekiti State, South-West Nigeria, respectively, are among the several locations in Nigeria where clay is mined and used for pottery making. Previous studies have indicated that the constituents and properties of clay soils and clay based products vary from one geographical location to another. Therefore, leachability of the constituent elements may also vary for different locations. The aim of this study is to evaluate the elemental constituent of two different clay deposits in Nigeria and assess their suitability as food and portable water contact materials.

2. Sample Collection and Pre-Treatment

A total of 3 clay deposit samples were collected at a depth of about 1m with soil auger from sites across each of the clay deposit sites at Kono-Boue in Rivers State, South-South Nigeria (KBC) and Ara-Ekiti in Ekiti State, South-West Nigeria (AEC) (**Figure 1**). Clay pot samples produced from Kono-Boue (KBCP) and Ara-Ekiti (AECp) were purchased from potters producing with clay mined from the respective locations. All the samples were labeled accordingly and transported to Chemistry Department Laboratory of the Rivers State University (RSU), Port Harcourt. The clay soil samples spread in plastic trays allowed to dry in the laboratory. The air-dried clay samples were disaggregated and sieved using a 2mm stainless sieve screen. The clay pots were broken into small piece units and then ground in porcelain mortar before sieving with 2mm sieve. The <2mm clay and clay pot samples transferred into labeled poly ethylene bags and stored at room temperature for treatment and analysis.



Fig.1: Map of the study area showing the locations of clay deposits

Determination of pH:

The pH of the samples was determined in CaCl_2 solution and deionized water. About 10g of the <2mm soil samples were weighed into bottles with screw caps and 25ml of water was added and the bottle capped. The resulting suspension was shaken. The cap of the bottle was removed and the pH meter electrode inserted and pH reading recorded. The same procedure was conducted with CaCl_2 solution instead in place of water.

Sample Digestion:

A 0.5g of each of the samples was accurately weighed and transferred into a boiling test tube. Thereafter, 20ml of aqua was added to each sample. A blank solution was prepared by measuring 20ml of aqua regia only into the boiling tubes in order to evaluate the contribution of acid medium in the analysis. The mixture was heated to boiling in a fume-cupboard for 1 hour 30 mins. The resulting digests were allowed to cool and filtered into 50ml flask in the fume cupboard. The filtrate was made to mark with deionized water and preserved for analysis.

Leaching Tests:

Leaching tests were conducted to determine the migration of heavy metals from Kono-Boue Clay Pot (KBPC) and Ara-Ekiti Clay Pot (AECPC) into the food and water stored therein. Normal tap water and simulated food methods were used to conduct the leaching test.

Leaching with Tap Water:

The clay pots were filled with normal tap water to about 90% of its capacity and allowed to stand on a tripod stand for 12 hours at room temperature. Thereafter, the water was filtered and stored in polyethylene bottles for further analysis.

Leaching in Simulated Food:

Leaching of heavy metals in clay pots by simulated food method was carried out according to ASTM 738-94 standard test method for specific metals leaching into 4% Acetic acid solutions at varying temperatures and pH values. A pH of 4.2 was adopted for acidic conditions that are likely to occur in foodstuffs. In recent studies, researchers have shown that

leaching of metals into 4% Acetic acid solution occur similar to the manner in which leaching occurs when preparing foodstuffs of about pH 4.2. A pH of 9.2 adopted to mimic the alkaline conditions in some foodstuffs. Leaching solutions of pH 4.2 and 9.2, at ambient temperature (28°C), and at about 100°C , were each exposed to the clay pots for 1 hour.

Heavy Metals Analysis:

The migrated heavy metals from the clay pot samples were determined using Flame Atomic Absorption Spectrophotometer (FAAS) (Releigh WFX 320 model). For quality assurance and quality control, blank solutions of the normal water were analyzed for heavy metal concentration.

Wavelength Dispersive X-Ray Fluorescence Analysis of Clays:

Details of the principle and instrumentation of the wavelength dispersive X-ray fluorescence has been previously reported by Krishna. In this study samples were pulverized to fine homogeneous size and then pelletized and submitted for quantitative elemental analysis of the clays and clay pots using EDX 3600B Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer (Skyray Instrument Ltd., China) at the NASNI Centre of Excellence, Nanotechnology and Advanced Materials, Akure.

Experimental Quality Control:

Analytical accuracy of aqua regia extractions were assessed against a reference material, BCR 143R (aqua regia certified Sewage sludge amended soil). All digestions were repeated three times. Excellent results were obtained for total concentrations; Cd measured was $69.0 \pm 19\text{mg/kg}$ compared to the certified value of $72.0 \pm 1.8\text{mg/kg}$. Cu measured was $119.0 \pm 5.3\text{mg/kg}$ compared to the certified value of $130.6 \pm 1.5\text{mg/kg}$. Pb measured was $187 \pm 9.0\text{mg/kg}$ compared to the certified value of $174 \pm 5.0\text{mg/kg}$. Mn measured was $834 \pm 18\text{mg/kg}$ compared to the certified value of $858 \pm 11\text{mg/kg}$. Zn measured was $1050 \pm 39\text{mg/kg}$ compared to the certified value of $1063 \pm 16\text{mg/kg}$. Ni measured was $277 \pm 19\text{mg/kg}$ compared to the certified value of $299 \pm 5\text{mg/kg}$. There were no listed values for Cr and Fe.

pH of Clays and Related Clay Pottery:

The pH values of the clay soil and their related clay pot samples, AEC, AECP, KBC and KBCP in water solution and in CaCl_2 solution are as presented in **Table 1**. The pH values, 6.50 ± 0.03 and 5.77 ± 0.11 obtained for Ara-Ekiti Clay sample in water and CaCl_2 solution are within the range. 4.8–6.9 reported for Nigerian soils by Abu and Nwosu and Raji and Mohammed. The pH values, 2.22 ± 0.07 and 2.08 ± 0.14 obtained for Kono-Boue Clay sample in water and CaCl_2 solution are outside the range previously reported for Nigerian soils. The Kono-Boue Clay indicted very low pH values that fall under a class called the ultra-acidic soils. The exceptionally low pH values observed the Kono-Boue Clay deposit is strange. However, a recent study by Obi that surveyed the effect of gas flare on soil pH in selected communities in Niger Delta of Nigeria found that the pH changed from extremely acidic (3.5-4.4) to moderately alkaline (7.9-8.4) as they moved away from the flare points.

Sample ID	pH values	
	Water	CaCl_2 solution
AEC	6.50 ± 0.03	5.77 ± 0.11
AECP	5.20 ± 0.03	4.33 ± 0.14
KBC	2.22 ± 0.07	2.08 ± 0.14
KBCP	4.18 ± 0.21	3.88 ± 0.06

Table 1: Mean and Standard Deviation of pH of Ara-Ekiti and Kono-Boue Clay and related Clay Pots in deionized water and CaCl_2 solution.

Lower pH values of 5.20 ± 0.03 and 4.33 ± 0.14 were obtained for Ara-Ekiti Clay Pot sample in water and CaCl_2 solution respectively. Higher pH values of 4.18 ± 0.21 and 3.88 ± 0.06 were obtained for Kono-Boue Clay Pot sample in water and CaCl_2 solution respectively. The relative decreased and increased pH ranges obtained from the Ara-Ekiti Clay Pot

and the Kono-Boue Clay Pot respectively may have resulted during firing stage of processing the raw clay samples into pottery.

Where, AEC= Ara-Ekiti Clay; AECP= Ara-Ekiti Pot; KBC= Kono-Boue Clay.

Heavy Metal Concentration Clay Soils and Clay Pot Samples:

The concentrations of Cu, Ni, Pb, Cd, Mn, Fe, Cr and Zn obtained from the clay soil and clay pots following acid digestion of samples are provided in Table 2. The order of concentrations is $\text{Fe} > \text{Mn} > \text{Pb} > \text{Zn} > \text{Ni} > \text{Cr} > \text{Cu} > \text{Cd}$ for Ara-Ekiti Clay, Kono-Boue Clay and the Ara-Ekiti Clay Pot (**Table 2**) and this order is consistent with elemental data previously published by Omoniyi and Gbarakoro. The mean concentrations observed in this for Ni, 77.67ppm, Pb, 135.27ppm and Zn, 93.17ppm are within the range of concentrations of Ni, 88-290ppm, Pb, 75-310ppm and Zn, 88-290ppm, previously reported for Ara-Ekiti Clay deposits by Omoniyi. The order of concentrations, $\text{Fe} > \text{Mn} > \text{Zn} > \text{Pb} > \text{Ni} > \text{Cr} > \text{Cu} > \text{Cd}$ for Kono-Boue Clay Pot is different compared to that of Ara-Ekiti Clay Pot, consistent with previous EDX elemental composition count data on Kono-Boue Clay by Gbarakoro. The presence of the potentially toxic metals, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn is also confirmed by the metal peaks indicated on XRF analysis results Ara-Ekiti (**Figure 2**) and Kono-Boue (**Figure 3**) clays. The trend of concentration loading observed from the AAS analysis of the acid digest (**Table 2**) is consistent with the trend indicated in the XRF results (**Figures 2 and 3**).

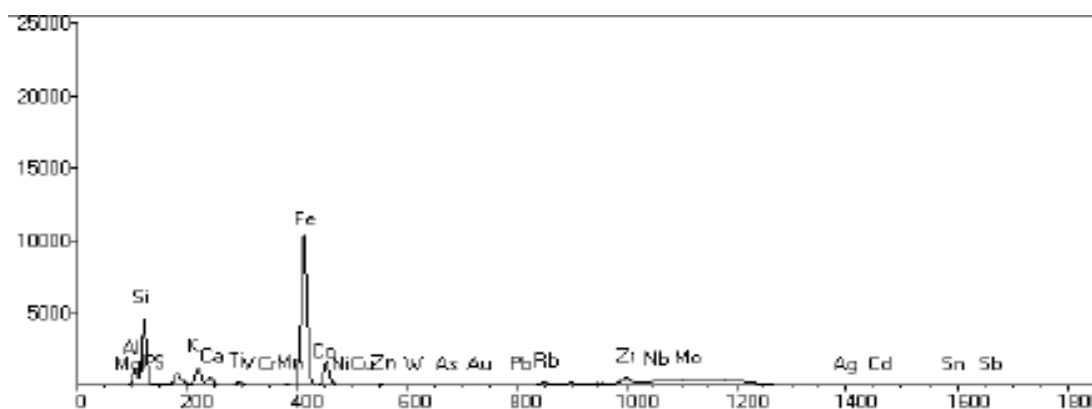


Figure 2: XRF analysis result for Ara-Ekiti Clay

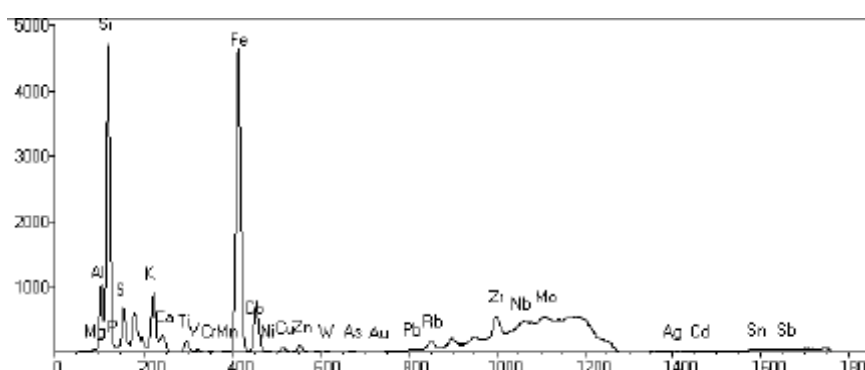


Figure 3: XRF analysis result of Kono-Boue Clay

Samples	Heavy Metals Concentration (mg/kg)							
	Cr	Cd	Ni	Cu	Zn	Fe	Pb	Mn
AEC	69.77±6.55	6.4±1.56	77.67±11.49	17.2±2.30	93.17±6.85	3095±27.00	135.27±48.44	417.47±66.37
AECP	76.27±11.37	8.57±2.31	101.57±8.27	43.13±1.72	113.03±4.88	1202.33±24.05	238.77±46.21	447.73±60.71
KBC	71.93±8.25	14.5±4.39	97.53±2.31	31.2±0.00	136.93±9.79	2022.67±149.72	194±9.69	354.5±28.01
KBCP	52.27±6.81	9.9±0.00	72.37±9.45	33.07±9.45	164.33±5.60	2280.67±92.38	118.5±42.28	212.4±70.73

Table 2: Mean and standard deviation of heavy metals concentration in Ara-Ekiti and Kono-Boue Clay and related Clay Pots.

Determination of Potentially Toxic Metals Leaching:

In order to simulate conditions of storage and cooking of both acidic and alkaline recipes the leaching test were conducted by exposing the clay pots to tap water at room temperature and at 100°C at pH of neutral (7.0), acidic (4.2) and alkaline (9.2). The results from this study indicate that Cd, Cr, Cu and Pb were not in leachable forms in the Ara-Ekiti and Kono-Boue Clay Pots and the poor leachability of certain metals from foodwares has previously been reported by Anderson and Aderemi. The non-leachability of Cd, Cr, Cu, and Pb from the clays even at increased temperatures and pH conditions has previously been highlighted in adsorptions employing the Kono-Boue Clays for removal of Cr and Pb from water by Ajemba.

In both clay pots (Ara-Ekiti and Kono-Boue) Ni was highly non-leachable at neutral and alkaline pH values. Only minimal amount of Ni was leached from Kono-Boue Clay Pots at pH 4.2 when the water was at 100°C and room temperature. It is possible that most of the Ni in the Ara-Ekiti Clay Pot are not leachable since Ara-Ekiti Clay soil indicated higher pH, because soil pH dependent retention of Ni have previously been suggested by Mcbridge and Lasiask. Leaching test for Zn indicated very low migration of Zn (<0.13ppm) from the Ara-

Ekiti Clay Pots irrespective of the pH and temperature changes. The low leachability of Zn may be indicative of the fact that the Zn mineral in the Ara-Ekiti samples are insoluble in water.

The concentrations of Fe leached upon exposure of Ara-Ekiti Clay Pot to water of neutral pH, alkaline pH and acidic pH were 0.16ppm, 0.08ppm and 1.15ppm at room temperature, and 0.19ppm, 0.16ppm and 5.33ppm at 100°C, respectively. The concentrations of Fe leached upon exposure of Kono-Boue Clay Pot to water of neutral pH, alkaline pH and acidic pH were 0.33ppm, 0.41ppm and 2.54 ppm at room temperature, and 0.28ppm, 0.41ppm and 8.37ppm at 100°C, respectively (**Table 3**). In both pots (Ara-Ekiti and Kono-Boue) the trend of leachability indicates a pH dependence tap on water's ability to leach Fe. Leaching test at neutral, alkaline and acidic conditions have indicated more Fe migration of from Kono-Boue Clay Pots into the tap water in spite of the lower Fe total concentration (**Table 2**) in the Kono-Boue Clay. The long time use of Kono-Boue Clay Pots for storage of food and drinking water, cooking of food and serving of cooked food may be a source Fe excessive introduction into human systematic circulation.

Metal	Clay Pot	Leaching Test Conditions of Tap water					
		RM	RM (pH 4.2)	RM (pH 9.2)	100°C	100°C (pH 4.2)	100°C (pH 9.2)
Cd	AECP	ND	ND	ND	ND	ND	ND
	KBCP	ND	ND	ND	ND	ND	ND
Cr	AECP	ND	ND	ND	ND	ND	ND
	KBCP	ND	ND	ND	ND	ND	ND
Cu	AECP	ND	ND	ND	ND	ND	ND
	KBCP	ND	ND	ND	ND	ND	ND
Fe	AECP	0.16	1.15	0.08	0.33	2.54	0.28
	KBCP	0.19	5.33	0.16	0.49	8.37	0.41
Mn	AECP	ND	0.15	0.08	ND	0.75	0.09
	KBCP	2.19	6	0.67	0.14	10	0.35
Ni	AECP	ND	ND	ND	ND	ND	ND
	KBCP	ND	0.07	ND	ND	0.23	ND
Pb	AECP	ND	ND	ND	ND	ND	ND
	KBCP	ND	ND	ND	ND	ND	ND
Zn	AECP	0.03	0.01	0.03	0.07	0.13	0.05
	KBCP	0.05	0.21	0.08	1.71	0.47	0.05

Table 3: Leached heavy metal concentration (ppm) from Ara-Ekiti and Kono-Boue Clay Pots at varying conditions of pH and temperature.

The concentration Mn leached upon exposure of Ara-Ekiti Clay Pot to water of neutral pH, alkaline pH and acidic pH were 0.00ppm, 0.08ppm and 0.15ppm at room temperature, and 0.00ppm, 0.09ppm and 0.75ppm at 100°C, respectively. The concentrations of Mn leached upon exposure of Kono-Boue Clay Pot to water of neutral pH, alkaline pH and acidic pH were 2.19ppm, 0.67ppm and 6.00ppm at room temperature, and 0.14ppm, 0.35ppm and 10.00ppm at 100°C, respectively

(**Table 3**). In both pots (Ara-Ekiti and Kono-Boue) the trend of leachability indicates a temperature and pH dependence on tap water's ability to leach Mn. Leaching test at neutral, alkaline and acidic conditions have indicated more Mn migration of from Kono-Boue Clay Pots into the tap water in spite of the lower Mn total concentration (**Table 2**) in the Kono-Boue Clay. The relatively higher availability of Mn from the Kono-Boue Clay Pots also agrees with our earlier suggestion that some

fractions metals in the Kono-Boue Clays not in mineral form but may have adhered to clay surfaces by weaker bonds.

3. Conclusion

This study has demonstrated the presence of Cd, Cr, Cu, Mn, Ni, Pb, Zn and elevated total concentrations of Fe in raw clays mined for clay pottery and clay pots in Ara-Ekiti and Kono-Boue of Nigeria. Whilst it is typical in the spirit of preserving culture to promote the continued used of traditional

foodwares at homes and public eateries, this study highlights the possibility of undersirable leaching of potentially toxic metals from the traditional foodwares into food. At conditions mimicking food preparation and storage detectable concentrations of Fe, Mn and Zn leached from the clay pots into extraction media. The risk of taking up Fe, Mn and Zn when traditional clay pots are used to prepare food has been highlighted.

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