

## Assessment of Potential Carcinogenic Metals in Palm Wines of Northern Cross River State, Nigeria

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**Abstract:** Palm wine samples collected from five major areas in Northern Cross River State, South-south Nigeria were assessed in triplicates for their contents of five carcinogenic metals including arsenic (As), cadmium (Cd), mercury (Hg), Ni (Ni) and lead (Pb) using Atomic Absorption Spectrophotometer (AAS) following a 2:5 HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> mixture digestion according to standard procedure. The study was repeated in three consecutive years and in each case, the results were compared with WHO acceptable limits of the metals in drinks. The results revealed that As, Cd, Ni and Pb mean contents were significantly above WHO recommended limits at  $\alpha$  (0.0 5) and  $\nu$  (14) in the samples within the three years period of the study. Hg was not detected in 2015 and was found to be slightly above the allowable limit estimated to be statistically insignificant in all the wine samples at  $\alpha$  (0.0 5) and  $\nu$  (14). The observed orders of concentrations of each potential metal carcinogen within the three years were established. Poor packaging and handling of palm wine may be a major potential route to toxic metal poisoning in Northern Cross River State as observed by this study.

**Keywords:** assessments, carcinogens, metals, Nigeria, palm-wine.

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### I. INTRODUCTION

The need for assessments of carcinogenic potential of chemicals on humans and health risk assessments of toxic metals in Nigeria has been recently emphasized [1- 10]. Palm wine is an alcoholic beverage widely consumed in Northern Cross River State, Nigeria. It is produced by the fermentation of oil palm (*Elaeis guineensis*) tree saps [11-12]. Globally, palm tree products have attracted both dietary and food safety attention [13]. However, there is a paucity of data on the status of toxic metals or essential trace metals at chronic levels in palm wine consumed in Northern Cross River State at the moment.

The occurrence of toxic metals in palm wine has been ascribed to a number of factors. These include principal sources such as adsorption (e.g. palm tree leaves) and absorption (e.g. geogenic: soil-borne heavy metals absorbed through palm roots and stems) pathways. Secondary anthropogenic contamination routes include processing, packaging and storage activities [10].

Carcinogenic metals include As Cd, Hg, Ni and Pb [10, 14]. Studies on the toxicity mechanisms for some of these chronic metals indicate food contamination sources. For instance, a survey pointed that the rate of absorption and distribution of lead are mainly influenced by dietary intake storage of calcium, iron, and phosphate in the body. It highlights that Pb is initially carried in red blood cells and distributed to soft tissues; redistributed to bone, hair and teeth as a phosphate salt. The study further discussed the sources of exposure, absorption, toxicity, symptoms, diagnosis and treatment of carcinogenic metals [15]. Another study demonstrated that As, Cr and Ni are capable of inducing post-translational histone modifications and proposed intracellular targets that mediate the toxicity and carcinogenicity of nickel as well as carcinogenesis induced by arsenic [16]. Evaluation of protein binding as a kinetic factor for As, Cd, Hg, Ni (bind to metallothionein) and Pb (sequestered in bones) has been recommended during human health risk assessment. Several other risk assessments of metals ingestion in humans have been suggested [17].

In view of the increase in cancer cases in Nigeria, it is crucial to periodically investigate possible metallic carcinogens as part of diseases monitoring/surveillance in various parts of the country. Hence, this study assessed the level of five potential cancer-causing metals in palm wine widely consumed in Northern Cross State and established the yearly trends of contamination due to the chronic metals contents in the wine samples for three years.

## II. MATERIAL AND METHODS

### 2.1 Sample Collection and Preparation

Replicate palm wine samples were randomly collected from tappers (freshly tapped) and vendors in five major areas of Northern Cross River State namely: Bekwarra, Obanliku, Obudu, Ogoja and Yala. Sample collection was conducted throughout the three years period of the study (2015 – 2017). The samples were labeled as B, O<sub>1</sub>, O<sub>2</sub>, O<sub>3</sub> and Y respectively, preserved at 4 °C prior to analysis.

### 2.2 Sample Preparation and Preparation of Working Solutions

Standard solutions were prepared using serial dilution method. Reference AAS standard solutions (1000 mg/L Fisher Scientific standard solutions of As, Cd, Hg, Ni and Pb) were serially diluted and 25 mL of each solution was transferred into a 250mL volumetric flask and made up to volume using ultra-pure water. Working standards were then prepared by serial dilution and calibration performed.

Each sample was prepared following standard procedure described in literatures [7, 18-19]. A 10ml aliquot of the bulk sample was quantitatively transferred to a 250ml digestion flask and 7ml freshly prepared HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> mixture in the ratio of 2:5 added. This was slowly shaken to mix and then heated between 60 °C to 180 °C for one hour until a clear solution was obtained. The digested solution in the flask was then cooled in a desiccator for ten minutes and quantitatively transferred to a 50ml volumetric flask. This was then diluted to the volume with distilled deionized water and refrigerated pending analysis.

### 2.2 Determinations

All determinations were performed using Atomic Absorption Spectrophotometer (Unicam Model 919) following the standard procedure described by AOAC [20].

## III. RESULTS

Results obtained from the study are presented in TABLES 1.1-1.3 below. Figs. 1.1 – 1.5 illustrate the variations in each toxic metal across the five sample locations as well as variations within the different years that the samples were studied.

**Table 1.1** Mean Concentrations of Toxic Metals in Palm wine Consumed in Northern Cross River State, Nigeria in 2015

Sample designation	N	mean*(mg/L) ± sd				
		As	Cd	Hg	Ni	Pb
B	5	0.013±0.002	0.023±0.001	nd	nd	0.103 ±0.001
O <sub>1</sub>	5	Nd	0.002±0.002	nd	0.147 ± 0.001	0.220 ±0.001
O <sub>2</sub>	5	0.002±0.001	0.014±0.001	nd	nd	0.163 ±0.001
O <sub>3</sub>	5	0.014±0.001	0.012±0.001	nd	0.004± 0.001	0.144±0.001
Y	5	0.011±0.001	0.002±0.001	nd	0.301±0.012	0.241 ±0.001
mean†		0.008±0.003	0.0106±0.006	nd	0.0904±0.014	0.1742±0.001
WHO limits [21]		0.01	0.003	0.001	0.07	0.01

nd =not detected; Fresh palm wine collected from source served as control; mean\* concentration of metals in palm wine obtained from a given location; mean† concentration of metals in palm wine obtained from all the five locations in the study area.

**Table 1.2** Mean Concentrations of Toxic Metals in Palm wine Consumed in Northern Cross River State, Nigeria in 2016

Sample designation	N	mean*(mg/L) ± sd				
		As	Cd	Hg	Ni	Pb
B	5	0.021±0.011	0.031±0.002	0.004±0.011	0.034±0.001	0.203 ±0.031
O <sub>1</sub>	5	0.100±0.014	0.008±0.002	0.003±0.001	0.210±0.053	0.170 ±0.021
O <sub>2</sub>	5	0.047±0.005	0.013±0.001	0.004±0.012	0.178±0.039	0.029 ±0.041
O <sub>3</sub>	5	0.035±0.002	0.021±0.001	0.003±0.002	0.092±0.016	0.131±0.030
Y	5	0.141±0.013	0.035±0.012	0.002±0.002	0.410±0.010	0.273 ±0.010
mean†		0.0688±0.045	0.0216±0.018	0.0032±0.0056	0.1848±0.0238	0.1612±0.0266
WHO limits		0.01	0.003	0.001	0.07	0.01

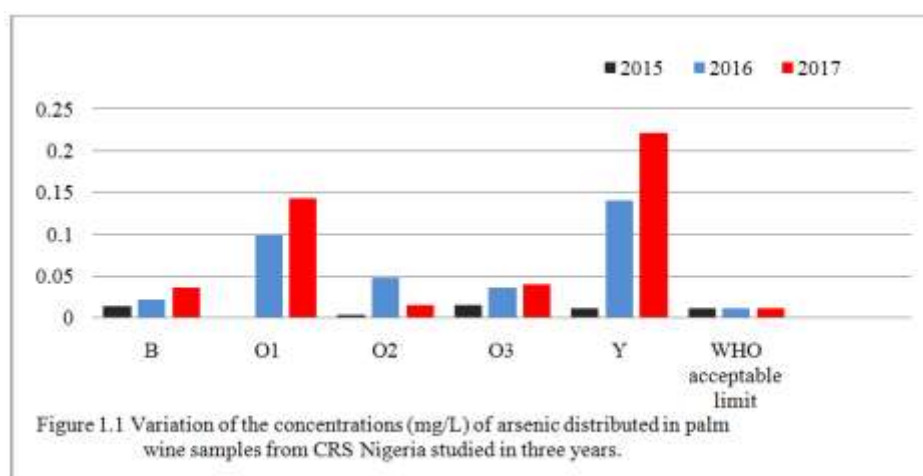
**Table 1.3** Mean Concentrations of Toxic Metals in Palm wine Consumed in Northern Cross River State, Nigeria in 2017

Sample designation	N	mean*(mg/L) ± sd				
		As	Cd	Hg	Ni	Pb
B	5	0.036±0.052	0.044±0.001	0.002±0.220	0.021±0.010	0.310 ± 0.001
O <sub>1</sub>	5	0.143±0.020	0.014±0.032	0.006±0.011	0.074±0.001	0.200 ± 0.001
O <sub>2</sub>	5	0.151±0.011	0.021±0.011	0.003±0.002	0.041±0.022	0.040 ± 0.002
O <sub>3</sub>	5	0.040±0.039	0.030±0.020	0.002±0.031	0.110±0.002	0.220 ± 0.010
Y	5	0.221±0.020	0.051±0.010	0.005±0.001	0.407±0.020	0.326 ± 0.022
mean†		0.1182±0.142	0.032±0.074	0.0036±0.001	0.1306±0.055	0.2192±0.036
WHO limits		0.01	0.003	0.001	0.07	0.01

#### IV. DISCUSSION

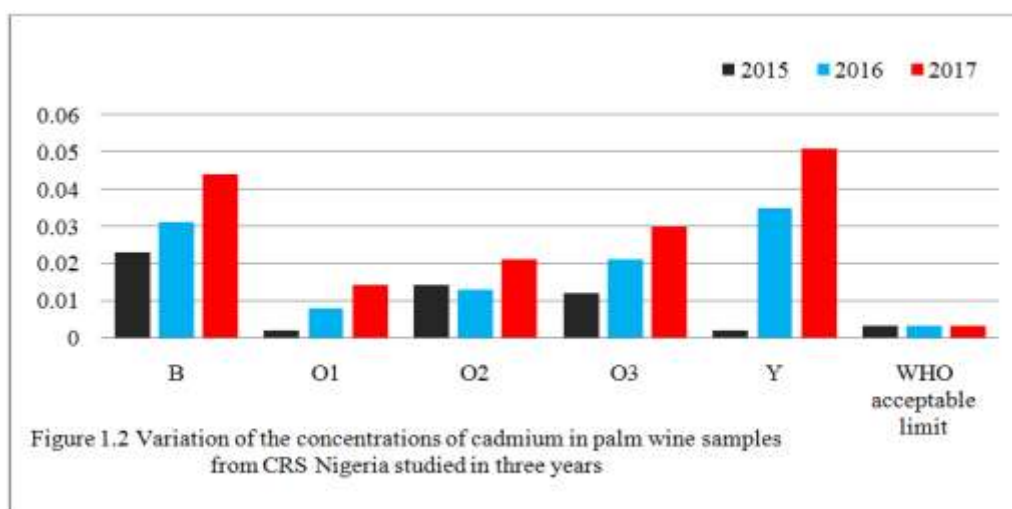
##### 4.1 Arsenic

As shown in TABLE 1.1, arsenic was slightly above the WHO acceptable limits in some samples (B, O<sub>3</sub> and Y) studied in 2015, below the limits in sample O<sub>2</sub> and was not detected in sample O<sub>1</sub>. In 2016 and 2017, its concentration was found to be above the limits in all the palm wine samples studied. Arsenic was distributed in the samples as follows: In 2015: O<sub>1</sub> < O<sub>2</sub> < Y < B < O<sub>3</sub>; in 2016 and 2017: B < O<sub>3</sub> < O<sub>1</sub> < O<sub>2</sub> < Y. (See Fig.1.1 below).



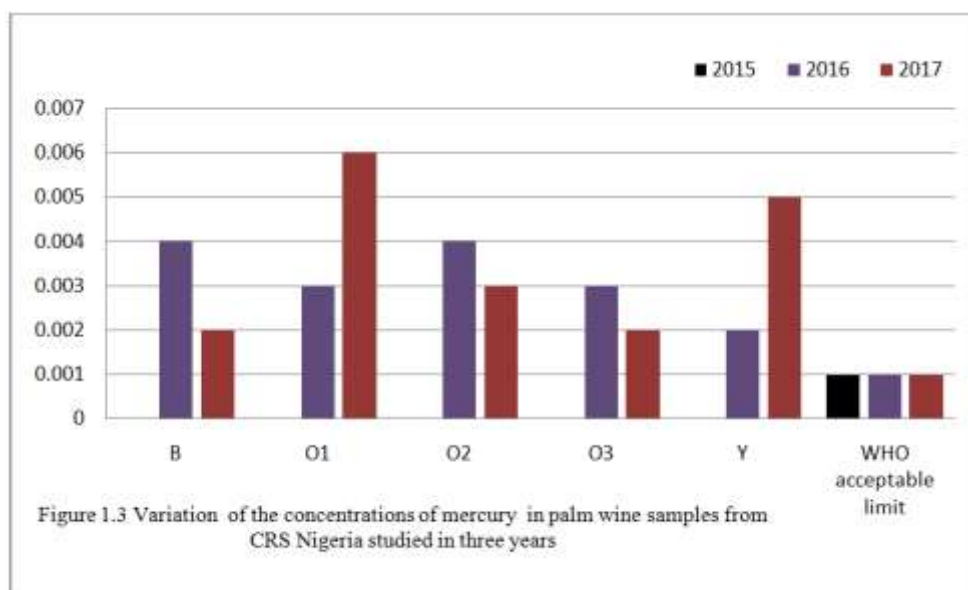
##### 4.2 Cadmium

Cadmium was detected within the WHO limits in all samples studied in 2015 but outside the limits in the 2016 and 2017 samples studied. Fig. 1.2 pictures the distribution of cadmium was distributed in the samples. In 2015: Y < O<sub>1</sub> < O<sub>3</sub> < O<sub>2</sub> < B; in 2016 and 2017: O<sub>1</sub> < O<sub>2</sub> < O<sub>3</sub> < B < Y.



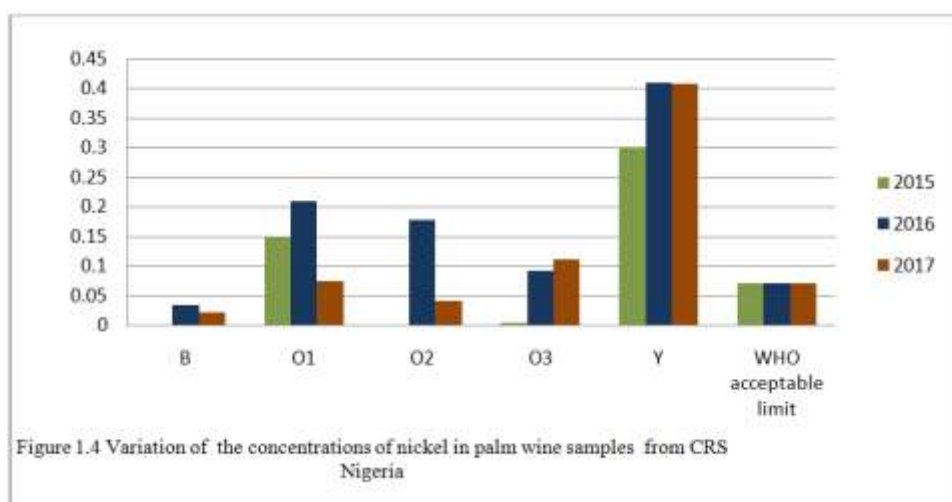
### 4.3 Mercury

Mercury was not detected in all the samples studied in 2015 but was slightly above WHO permissible limits in the 2016 and two samples (O<sub>1</sub> and Y) in 2017. Mercury was distributed in the samples as follows: In 2016: Y < O<sub>1</sub> < O<sub>3</sub> < B < O<sub>2</sub> and in 2017: O<sub>3</sub> < B < O<sub>2</sub> < Y < O<sub>1</sub>. This trend is illustrated in Fig 1.3 below.



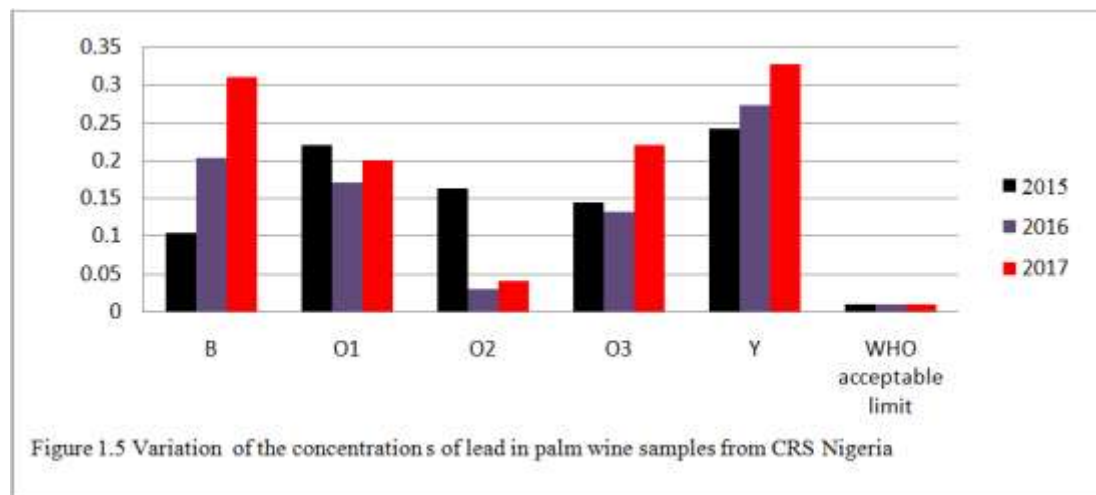
### 4.4 Nickel

In 2015, nickel was not detected in samples B and O<sub>2</sub> but was found to be above the WHO acceptable limit in O<sub>1</sub> and Y. All the samples, except sample O<sub>1</sub> studied in 2016 contained nickel above the set limit. In 2017, the level of nickel dropped in some samples (B, O<sub>1</sub>, O<sub>2</sub>, and Y) and increased in sample O<sub>3</sub>. It was distributed in the samples as follows: 2015: O<sub>3</sub> < O<sub>1</sub> < Y; 2016: B < O<sub>3</sub> < O<sub>2</sub> < O<sub>1</sub> < Y and in 2017: B < O<sub>2</sub> < O<sub>1</sub> < O<sub>3</sub> < Y (see Fig. 1.4 below).



### 4.5 Lead

Lead was found to be at chronic levels (highly above the WHO permissible limits) in all the samples studied in the three years. The orders of distributions of Pb were in the as follows: 2015: B < O<sub>3</sub> < O<sub>2</sub> < O<sub>1</sub> < Y; in 2016: Y < O<sub>2</sub> < O<sub>3</sub> < O<sub>1</sub> < B and in 2017: O<sub>2</sub> < O<sub>1</sub> < O<sub>3</sub> < B < Y. Variations of Pb in the palm wine samples within the three years is illustrated in Fig. 1.5 below



Comparing the level of metal loads in the palm wine samples studied in 2015, 2016 and 2017: the following order was obtained:

Arsenic: 2016 > 2017 > 2015; Cadmium: 2017 > 2016 > 2015; Mercury: 2017 > 2016 > 2015; Nickel: 2016 > 2017 > 2015 and Lead: 2017 > 2015 > 2016.

**Table 2.1** Summary/Descriptive Statistics

Toxic metal	Mean mg/L for 2015 - 2017 (n = 15)	$\mu$ (acceptable value)	Std. Dev.	t calculated
As	0.2954	0.01	0.272	2.346
Cd	0.0214	0.003	0.0095	4.331
Hg	0.0027	0.001	0.0016	0/147
Ni	0.1353	0.07	0.0422	3.460
Pb	0.1849	0.01	0.0259	15.10

t tabulated at  $\alpha(0.05)$  and  $\nu(14) = 2.15$ .

As shown in TABLE 2.1, the levels of As, Cd, Ni and Pb were significantly above WHO recommended permissible limits at  $\alpha(0.05)$  and  $\nu(14)$  in all the samples within the three years period of the study. Although Hg was slightly above the allowable limit, it was statistically estimated to be insignificant in all the wine samples at  $\alpha(0.05)$  and  $\nu(14)$ .

The International Agency for Research on Cancer classifies arsenic, cadmium and nickel as group 1 carcinogens and several studies on the toxicity and carcinogenic mechanisms of As, Cd, Hg, Ni and Pb have been conducted as well as cited [22, 23]. For instance, exposure to Cd via food and drinks is said to cause oxidative stress which accelerates of transcriptional activity of the metallothionein (MT) coding gene. This leads to conformational change of renal tubular cell as well as degradation of glomerular cell function thereby disrupting calcium metabolism and augment the calcium load in the kidney, leading to an increase of kidney stones and cancer [7, 24; 25]. Ni taken through food and drink is said to induce oral epithelium damage [26-28] and oxidative stress via a reduction in expression of antioxidant enzymes and DNA single- and double-strand breaking [7, 29-31].

## V. CONCLUSION

The study detected the following carcinogenic metals: arsenic, cadmium, nickel and lead at levels above acceptable limits in street vended palm wine consumed in Northern Cross River State for three years. Mercury was found slightly above the tolerable limits in two 2016 and 2017. Poor packaging and handling may be a major potential route to toxic metal content in palm wine found in the area. Also, daily consumption of the metals-contaminated palm wines could be a major cause of cancer cases in the area. Further assessments of toxic metal status in human blood samples as well as dietary intake/exposure to carcinogenic metals in palm wine consumed in Cross River State are recommended.

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