International Journal of Research Publication and Reviews

Journal homepage: www.ijrpr.com ISSN 2582-7421

Evaluation of Heavy Metal Concentration in Edible Crops from Selected Artisanal Crude Oil Refinery Communities in Rivers State

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ABSTRACT

This study investigated the heavy metals present in fluted Pumpkin leaf, cassava tubers, Okra and palm oils from artisanal crude oil refinery sites in Elele-Alimini, Rumuekpe and Ndele communities in Rivers State, Nigeria. Control samples were also obtained from Okporo community in Imo State, Nigeria. The results obtained were also compared with FAO/WHO reference standards. The heavy metals were analyzed using Atomic Absorption Spectrophotometry (AAS). The mean Pb levels in studied fluted pumpkin leaf sample harvested from Elele-Alimini, Rumuekpe, Ndele, and Okporo (control) communities were 2.52±0.01 mg/kg, 2.37±0.01 mg/kg, 2.31±0.02 mg/kg, and 0.32±0.01mg/kg respectively, Cd levels were 0.02±0.01mg/kg, 0.02±0.01mg/kg, 0.01±0.01mg/kg, and 0.01±0.01mg/kg respectively while Cr levels were 3.03±0.01mg/kg, 3.19±0.03mg/kg, 1.52±0.01mg/kg, and 0.03±0.01mg/kg respectively, while those of nickel (Ni) were 0.67±0.03 mg/kg, 0.47±0.02 mg/kg, 0.50±0.02 mg/kg, and 0.19±0.01 mg/kg respectively. The mean Pb levels in studied cassava harvested from Elele-Alimini, Rumuekpe, Ndele, and Okporo (control) communities were 1.89±0.02 mg/kg, 3.00±0.01 mg/kg, 2.36±0.02 mg/kg and BDL respectivelywhile those of Ni were 0.19±0.01 mg/kg, 1.56±0.01 mg/kg, 0.12±0.01 mg/kg, and 0.11±0.01 mg/kg respectively. The mean Pb levels in studied Okra samples harvested from Elele-Alimini, Rumuekpe, Ndele, and Okporo (control) communities were 1.44±0.01 mg/kg, 2.01±0.01 mg/kg, 1.78±0.02 mg/kg, and 0.02±0.01 mg/kg respectively, those of Cd were 0.02±0.01 mg/kg, 0.02±0.01 mg/kg, 0.01±0.01 mg/kg, and BLD while those of Ni were 0.04±0.01, 0.04±0.02, 0.03±0.01, and BDL respectively. The mean Pb levels in palm oil from Elele-Alimini, Rumuekpe, Ndele, and Okporo (control) communities were 0.31±0.01, 0.43±0.01, 0.61±0.02, and BDL respectively, those of Cd were 0.01±0.01, 0.01±0.01, 0.01±0.01, and BDL while those of Ni were 0.02±0.01, 0.03±0.01, 0.02±0.01, and 0.01±0.01. The levels of the heavy metals shown in the edible crops analyzed in this study is suggestive of potentials to pose significant health risks to the populace when consumed.

INTRODUCTION

Metals are substances with high electrical conductivity, malleability, and luster, which voluntarily lose their electrons to form cations. Metals are found naturally in the earth's crust and their compositions vary among different localities, resulting in spatial variations of surrounding concentrations. The metal distribution in the atmosphere is monitored by the properties of the given metal and by various environmental factors (Khlifi & Hamza-Chaffai, 2010).

Lead (Pb), cadmium (Cd), chromium (Cr), iron (Fe) nickel (Ni),) and Cupper (Cu) are widely dispersed in the environment. Chromium and iron under low concentrations in living system are beneficial, Pb, Cd and Ni have no beneficial effects in humans, and there is no known homeostasis mechanism for them (Draghici et al., 2010). They are generally considered among the most toxic elements to humans and animals; the adverse human health effects associated with exposure to them, even at low concentrations, are diverse and include, but are not limited to, carcinogenic and neurotoxic actions (Castro-González and Méndez-Armenta, 2008).

Artisanal crude oil refining of stolen oil is one of the major causes of oil spills in Rivers State while other causes include sabotage of oil installations, corrosion of pipelines and storage tanks, and accidents in oil production operations (Efenakpo et al., 2018). Refining the crude oil by this method, yields 2% kerosene, 2% fuel, 41% diesel, and 55% waste and after the desired products are collected, large quantities of residue (waste) produced are dumped indiscriminately on land and water body causing environmental pollution while part of the residue is used as fuel for further refining process (Bello and Amadi, 2019).

The unchecked proliferation of artisanal refineries in regions like the Rivers State elucidates a critical nexus between local economic activities and severe environmental degradation. These makeshift operations, often characterized by substandard extraction and refining practices, contribute disproportionately to environmental pollution, particularly through the release of hydrocarbons and heavy metals into surrounding ecosystems. Elevated concentrations of toxic substances, as observed in the Oturuba river ecosystem, exceed sediment quality guidelines, leading to chronic ecological disturbances (Ezekwe et al.). The resulting contamination not only threatens aquatic biodiversity, with potential repercussions for the entire food web, but also exacerbates health risks for local populations reliant on these water sources. Moreover, the ongoing environmental crises are compounded by ineffective governmental policies that fail to address the sustainability of the regions natural resources (Joab-Peterside et al.).

Soil is the fundamental sustenance of food crops, and it can be greatly perturbed by heavy metals from point sources (e.g., energy-intensive industries, such as thermal power plants and coal mines, and chlor-alkali chemical industries, such as goldmines, smelting, electroplating, textiles, leather, and e-waste processing) and non-point sources (e.g., soil/sediment erosion, agricultural runoff, and open freight storage). In addition to their human health implications, heavy metals adversely affect soil biota through microbial processes and soil–microbe interactions (Gadd, 2010). Beneficial soil insects (especially in agriculture), invertebrates, and small and large mammals are all affected (Rai et al., 2018)

Heavy metals are transferred from soil pores to plants in ionic forms, which can vary by metal (McLaughlin et al., 2011). The biospeciation of heavy metals can also vary by food crop. Vegetables such as iceberg lettuce, cherry belle radishes, Roma bush beans, and Better Boy tomatoes all accumulate heavy metals with different concentrations in the roots, leaves, and fruits (Cobb et al., 2000).

This study investigates the heavy metal concentration in edible crops from the selected artisanal crude oil refinery sites in Rivers State.

MATERIALS AND METHODS

SAMPLING

The crop samples under study were collected from farms situated in Elele-Alimini, Rumuekpe, and Ndele communities where artisanal crude oil refinery activities took place. For the palm oil samples, Palm fruits harvested from the refinery sites were strictly monitored from the point of harvest to the milling process from where palm oil samples were gotten. The results obtained are further compared with control samples from Okporo community (Control) in Imo State as well as with FAO/WHO reference standards for these compounds.

HEAVY METAL ANALYSIS

Finely grounded sample (0.5g) was weighed and then oven-dried (60^0C) in a 30-ml porcelain crucible. The sample was ignited in a muffle furnace for 6-8 hours at a temperature between 450^OC and not exceeding 500^OC. Greyish white ashes was obtained, otherwise indicating incomplete ignition. Another sample was weighed and the ignition was repeated. Incomplete ignition is usually caused by placing too many samples in the furnace, or too fast heating rate. After that, the sample was cooled on top of asbestos sheet and 5ml HNO_3 solution was added and allowed to evaporate to dryness on a steam bath at low heat in a fume cupboard. The samples were returned to the furnace and heated at 400^0C for 10-15min until a perfectly white or grayish white ash was obtained. Then the sample was cooled on top of asbestos sheet, 10ml HCl was added and the solution was filtered into a 50-ml volumetric flask. After that, the crucible and the filter paper were washed with additional 10ml portion of 0.1NHCl three (3) times the volume made up with 0.1NHCl solution. The filtrate was then stored for the determination of the heavy metals of interest.

RESULTS

Table 1 Heavy metal concentrations in studied Pumpkin Leaf samples from Artisanal Crude Oil Refinery Communities In Rivers State State (n=3)

Heavy Metal (mg/kg)	Elele-Alimini	Rumuekpe	Ndele	Okporo (Control)	Permissible Limit For Plants (FAO/WHO, 2007)
Pb	$2.52±0.01^a$	$2.37±0.01^a$	$2.31±0.02^a$	$0.12±0.01^a$	0.3
Cd	$0.02±0.01^a$	$0.02±0.01^a$	$0.01±0.01^a$	$0.01±0.01^a$	0.02
Cr	$3.03±0.01^a$	$3.19±0.03^a$	$1.52±0.01^b$	$0.03±0.01^c$	1.5
Fe	$3.19±0.02^a$	$4.84±0.02^b$	$5.01±0.01^c$	$2.98±0.01^d$	150
Cu	$2.71±0.01^a$	$4.41±0.02^b$	$3.21±0.04^c$	$0.02±0.01^d$	40
Ni	$0.67±0.03^a$	$0.47±0.02^b$	$0.50±0.02^a$	$0.19±0.01^d$	1.12

Values are expressed as means ± standard error of mean (SEM) of three replicates. Values with different superscript in the same row are significantly different while values with the same superscript within a row are not significantly different ($p<0.05$).

Table 2 Heavy metal concentrations in studied cassava tubers from selected Artisanal Crude Oil Refinery sites In Rivers State (n=3)

Heavy Metal (mg/kg)	**Elele-Alimini**	**Rumuekpe**	**Ndele**	**Okporo (Control)**	**Permissible Limit For Plants (FAO/WHO, 2007)**
Pb	1.89±0.02[a]	3.00±0.01 [b]	2.36±0.02 [c]	BDL	0.3
Cd	0.02±0.01[a]	0.02±0.01[a]	0.01±0.01[a]	BDL	0.02
Cr	0.22±0.01[a]	1.76±0.02[b]	0.18±0.01[c]	BDL	1.5
Fe	3.19±0.04[a]	1.37±0.01[b]	3.32±0.02[b]	2.12±0.01[d]	150
Cu	2.71±0.02[a]	6.82±0.02[b]	3.89±0.02[c]	0.02±0.01[d]	40
Ni	0.19±0.01[a]	1.56±0.01[b]	0.12±0.01[a]	0.11±0.01[a]	1.12

Values are expressed as means ± standard error of mean (SEM) of three replicates. Values with different superscript in the same row are significantly different while values with the same superscript within a row are not significantly different ($p<0.05$).

Table 3 Heavy metal concentrations in studied okra from selected Artisanal Crude Oil Refinery sites In Rivers State (n=3)

Heavy Metal (mg/kg)	**Elele-Alimini**	**Rumuekpe**	**Ndele**	**Okporo (Control)**	**Permissible Limit For Plants (FAO/WHO, 2007)**
Pb	1.44±0.01[a]	2.01±0.01 [b]	1.78±0.02 [c]	0.02±0.01[d]	0.3
Cd	0.02±0.01[a]	0.02±0.01[a]	0.01±0.01[a]	BDL	0.02
Cr	0.74±0.01[a]	0.68±0.01[b]	0.62±0.01[c]	0.10±0.01[d]	1.5
Fe	1.63±0.01[a]	3.12±0.02[b]	3.02±0.02[b]	1.02±0.01[c]	150
Cu	0.92±0.01[a]	1.02±0.01[b]	0.62±0.01[c]	0.02±0.01[a]	40
Ni	0.04±0.01[a]	0.04±0.02[a]	0.03±0.01[a]	BDL	1.12

Values are expressed as means ± standard error of mean (SEM) of three replicates. Values with different superscript in the same row are significantly different while values with the same superscript within a row are not significantly different ($p<0.05$).

Table 4 Heavy metal concentrations in palm oil from selected Artisanal Crude Oil Refinery sites In Rivers State (n=3)

Heavy Metal (mg/l)	**Alimini**	**Rumuekpe**	**Ndele**	**Oporo (Control 1)**	**FAO/WHO Standard (2003)**
Pb	0.31±0.01[a]	0.43±0.01 [b]	0.61±0.02 [c]	BDL	0.2
Cd	0.01±0.01[a]	0.01±0.01[a]	0.01±0.01[a]	BDL	9.0
Cr	0.40±0.01[a]	0.31±0.01[a]	0.35±0.01[a]	BDL	0.10
Fe	4.01±0.02[a]	4.24±0.02[a]	3.54±0.04[a]	2.87±0.02[a]	48
Cu	0.52±0.03[a]	1.16±0.02[b]	0.71±0.02[a]	0.08±0.01[a]	30.0
Ni	0.02±0.01[a]	0.03±0.01[a]	0.02±0.01[a]	0.01±0.01[a]	300

Values are expressed as means ± standard error of mean (SEM) of three replicates. Values with different superscript in the same row are significantly different while values with the same superscript within a row are not significantly different ($p<0.05$).

DISCUSSION

The mean Pb, Cd, Fe, Cu, and Ni levels noticed in studied fluted pumpkin leaf harvested from Elele-Alimini, Rumuekpe, and Ndele significantly higher than the permissible limit for plants as reported by (FAO/WHO, 2007) (Table 1). In this study, the mean Pb level noticed in studied fluted pumpkin leaf harvested from Elele-Alimini, Rumuekpe, and Ndele communities significantly higher than the permissible limit for plants as reported by (FAO/WHO, 2007) (Table 1). The Cd levels in Elele-Alimini, Rumuekpe, and Ndele significantly higher than the permissible limit for plants as reported by (FAO/WHO, 2007) (Table 1). The significantly high Pb and Cd levels observed in fluted pumpkin leaf harvested from Alimini, Rumuekpe, and Ndele communities when compared to the control (Okporo community) which also exceed the permissible limits in plants is suggestive that consumption of fluted pumpkin leaf as vegetable over a period of time might result in Pb and Cd-induced poisoning or toxicities. This result is in line with the report of Ogunka-Nnoka et al (2018) on the heavy metal levels in fluted pumpkin leaf.

High levels of heavy metals in tuber crops in a community can have several serious implications, affecting public health, the environment, agriculture, and the local economy (De La Torre-Roche *et al*., 2019). Tuber crops, such as potatoes, yams, cassava, and sweet potatoes, are often staple foods in many communities, so contamination with heavy metals can pose significant risks. High level of heavy metals in tuber crops pose a significant cancer risk due to their carcinogenic properties. Consuming tuber crops contaminated with heavy metals over a long period can increase the likelihood of developing cancers such as lung, skin, liver, and stomach cancer (Fismes *et al.,* 2022). In this study, the mean Pb, Cd, Cr, Fe, Cu, an Ni levels characterized in studied cassava samples harvested from Elele-Alimini, Rumuekpe and Ndele communities were significantly higher than those of Okporo community (control) (Table 2). Also, the mean Pb, Cd, Cu, and Ni levels in studied cassava samples harvested from Elele-Alimini, Rumuekpe, and Ndele communities were significantly higher than the permissible limits as recommended by FAO/WHO (2007) (Table 2). The significantly high Pb, Cd, Cr, Fe, Cu, an Ni observed in the studied cassava sample harvested from Elele-Alimini, Rumuekpe, and Ndele communities when compared to the control (Okporo community) as well as the permissible limits as recommended by FAO/WHO (2007) is suggestive that increases in illegal crude oil and environment contamination in those communities. This result finding is similar to the report of Nwaichi *et al.* (2017) on the heavy metals and some Trace metals in yam, cassava, orange and papaya from two oil and gas flaring impacted communities in Southern Nigeria

In this study, the mean Pb, Cd,Cr, Fe, Cu, and Ni level in studied okra (Table 3) from Elele-Alimini, Rumuekpe, and Ndele were significantly higher than the control (Okporo community). The significantly high mean Pb, Cd,Cr, Fe, Cu, and Ni level in studied okra from Elele-Alimini, Rumuekpe, and Ndele observed is reflective of increases in illegal crude oil activities in those communities. Also, the mean Pb, Cd, Cr, Cr, Fe, Cu, and Ni in studied okra harvested from Elele-Alimini, Rumuekpe, and Ndele communities were statistically less than the the permissible limit as recommended by FAO/WHO (2007). This result is in agreement with the report of Silva *et al.* (2018) on the heavy metal profile in coconut, and tomato.

Some heavy metals such as Cd, Cr, Pb and Ni are known to cause toxicity and are carcinogenic. Regular consumption of palm oil contaminated with high levels of heavy metals can increase the risk of cancers, particularly in organs exposed to dietary intake, such as the liver, skin, and digestive tract (Silva *et al.,* 2018). In this study, the mean Pb, Cd, Cr, and Ni levels were observed in studied palm oil samples purchased from Elele-Alimini, Rumuekpe, and Ndele communities to be significantly higher than the control (Okporo community).

The mean Pb levels in studied palm oil samples (Table 4) in Elele-Alimini, Rumuekpe, and Ndele were significantly above the standard as recommended by FAO/WHOO (2003). The mean Cr levels in studied palm oil samples in Elele-Alimini, Rumuekpe, and Ndele were significantly above the standard as recommended by FAO/WHOO (2003). The significantly high Pb and Cr observed in in studied palm oil samples in Elele-Alimini, Rumuekpe, and Ndele communities when compared to the control (Okporo community) as well as the standard as recommended by FAO/WHOO (2003) are suggestive Pb and Cr contamination arising increases in bunkering activities in those communities. Consumption of palm oil purchased from those communities over a long period of time could pose health risk.

CONCLUSION

This study was based on environmental evaluation of selected illegal oil bunkering sites in Rivers State. Four communities were used for this study. All evaluations were carried based on standard methods. The mean Pb, Cd, Cr, Fe, Cu, an Ni levels in cassava tuber harvested from Elele-Alimini, Rumuekpe, and Ndele communities were significantly higher the control and were significantly higher than the permissible limits as recommended by FAO/WHO (2007). The levels of the heavy metals shown in the edible crops analyzed in this study is suggestive of potentials to pose significant health risks to the populace when consumed.

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