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The notorious daredevils: potential toxic levels of cyanide and heavy metals in cassava flour sold in selected markets—taken Oke Ogun Community, Oyo State as an example

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Pollution spread throughout terrestrial and aquatic ecosystems, and many remain transported around the globe by air transport. Furthermore, food as well as production chains remain dispersed through the global economy. Thus, the current study examined the potentially harmful amounts of cyanide as well as trace metals in cassava flour sold in Oke Ogun community township markets. Its goal was to quantify the degrees of Lead, Cyanide, Arsenic and Chromium, evaluate their health impacts on customers, and evaluate WHO-allowable dietary quantities. Using a stratified sampling strategy, five township markets were visited to obtain samples of finely ground fermented cassava flour (Kishi, Igbeti, Igboho, Iseyin, and Shaki). The materials were properly digested before being examined with an Atomic Absorption Spectrophotometer (AAS). Lead (0.028-0.053 mg/L), Cyanides (0.010-0.018 mg/L), Chromium (0.034-0.065 mg/L) and Arsenic (0.006-0.012 mg/L), were the results obtained. At conclusion, due to the lower content of these metals, the cassava flour sold in Oke Ogun community markets is safe as well as appropriate for human utilization, with no nutritional risk consequences. As a result, it is advised that cassava flour marketed be closely checked and assessed on a continuous basis. Therefore, regular monitoring of toxic metals in Nigeria is strongly advised in order to avoid a significant environmental and public health issue.

KEYWORDS

health risk, cyanide, heavy metals, cassava flour, human consumption, Oyo State

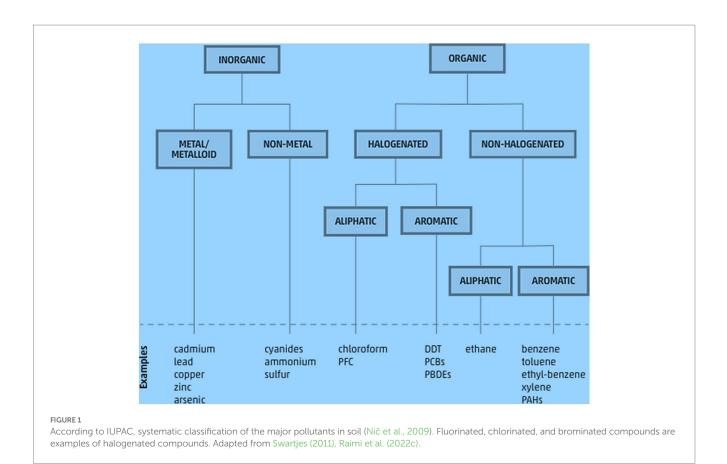
1. Introduction

Cassava (*Manihot spp*) remains a starchy staple with roots that remain high in carbohydrates, which remain a primary energy source. With the possible exception of sugarcane, the cassava plant is the largest generator of carbohydrates among agricultural plants. Palmate lobed leaves, inconspicuous flowers, and a big, starchy, tuberous root with a tough papery brown bark and white to yellow flesh distinguish the plant (Olalekan et al., 2018b). It is one of the most perishable

tuber crops, with significant postharvest loss (Diasolua et al., 2003; Olalekan et al., 2018b). Cassava root is not a tuberous root, but rather a real root that cannot be propagated vegetatively. The mature cassava storage root contains three separate tissues: the bark (periderm), the peel (cortex), as well as the root itself. The parenchyma, which is the edible part of the fresh root, encompasses roughly 85% of the total weight, comprising the xylem vessels, which is radially distributed in a matrix of starch containing cells. The concentration of cyanide in cassava differs depending on the species, age, location, as well as environmental factors (Olalekan et al., 2018b). Cassava flour, generally known as "lafu" in Yoruba, is a common staple processed cassava product diet in Nigeria that includes necessary as well as beneficial minerals required for the body's morphological processes. It is a good carbohydrate source, which is commonly denoted to as the main body tissues fuel (Robert et al., 2000; Olalekan et al., 2018b) since it produces energy that the body requires to function effectively in its everyday activities. Human activities (human induced) may promote the occurrence of harmful pollutants such as cyanide as well as trace metals in cassava flour, rendering it unsafe for human utilization, particularly when they remain present in large concentrations (Raimi and Sabinus, 2017a; Suleiman et al., 2019; Raimi et al., 2019c, 2020a, 2022a; Isah et al., 2020a,b; Morufu Olalekan et al., 2020a; Morufu, 2021; Olalekan et al., 2021, 2022b; Hussain et al., 2021a,b; Morufu et al., 2021a; Asiegbu et al., 2022; Oshatunberu et al., 2023). In urban centers, the predominant cyanide sources as well as metal pollution remain anthropogenic (human actions), whereas contamination resulting from nature sources that predominates in remote areas (Raimi and Sabinus, 2017b; Olalekan et al., 2018b; Ogidi et al., 2021). Toxic pollutants such as cyanide as well as heavy metals remain commonly found in densely populated urban areas with high traffic density as well as industries (Odipe et al., 2018; Premoboere and Raimi, 2018; Raimi et al., 2018, 2020b, 2022a,b; Sawyerr et al., 2019; Deinkuro et al., 2021; Morufu Raimi et al., 2021b,e,f,g; Ifeanyichukwu et al., 2022; Olalekan et al., 2022; Raimi and Sawyerr, 2022; Stephen Olalekan et al., 2023). Cyanide, a harmful pollutant, is found naturally in most plants but is abundant in cassava as well as in bamboo shoot (Olalekan et al., 2018b). It enters the environment via volcanoes as well as nature biogenic procedures involving significant plants, algae, bacteria, tobacco smoke, as well as industries discharges, waste water treatment, fungi biomass burning, wood smoke, burning plastics smoke, vehicular emissions, as well as inadequately processed cassava products (Agency for Toxic Substances and Disease Registry, 1997; Williams et al., 2019; Raimi et al., 2019a; Morufu Olalekan et al., 2019b; Ajibola et al., 2020; Olalekan et al., 2021; Morufu et al., 2021c,f; Clinton-Ezekwe et al., 2022). Chemicals that act as environmental pollutants in soil as well as may provide dangers to human health and the milieu as a result of these include organic and inorganic substances. Figure 1 depicts a structured classification of a number of the most frequent pollutants found in soils based on their chemical features. Because new contaminants may emerge and can be classified in a variety of ways, comprising retention or moving to different environmental matrices, their impacts on biological systems are dictated by the contaminant's intrinsic features as well as local soil factors. Understanding pollution trends and making pollutionremediation decisions require recognizing the sources of trace elements in the environment.

Except for pesticide inputs, most contaminant emissions are difficult to quantify and, as a result, remain very unclear. Industrial pollutants remain introduced into the environment at several stages of their life cycle, including manufacturing, the generation of contaminant-containing commodities, transportation, usage, as well as disposal. As a result, regardless of the route of exposure, exposure to small amounts of cyanide can be fatal. Cyanide is extremely dangerous; it inhibits cellular respiration in the body by blocking an enzyme in mitochondria called cytochrome oxidase. The expression heavy metals refer to a set of metals and metalloids that are connected with pollution plus toxicity, but then also include approximately elements that remain required for living creatures at small quantities. Heavy metals such as chromium, manganese, iron, calcium, copper, selenium, cobalt, magnesium, as well as zinc, remain important trace components for humans, animals, as well as plants but turn out to be toxic if the homeostatic mechanisms that maintain their physiological limits remain interrupted or if their body intensity is extremely high, whereas mercury, cadmium, lead, nickel as well as arsenic remain potentially toxic at certain levels (Kaur and Gupta, 2009; Olalekan et al., 2022; Raimi and Sawyerr, 2022; Raimi et al., 2022a,b; Stephen Olalekan et al., 2023). Antimony (Sb), Arsenic (As), as well as selenium (Se) are examples of trace elements that are not metals. Trace elements have a long-shelf life and aren't eviscerated by metabolic processes. Trace elements can exist in a number of different forms, along with sulphides, organometallic complexes, salts, oxides, as well as ions dissolved in soil solution. Chemical processes like adsorption on particles or pH-dependent dissolution in water drive the partitioning of water, air, and soil (Alloway, 2012). Trace elements remain natural (geogenic) in origin, as several rocks contain significant quantities of trace elements that remain introduced into the milieu via anthropogenic or weathering activity. Despite the fact that some heavy metals remain essential and beneficial, as excessive levels of these metals can induce morphological irregularities, decreased growth, increased rate of human mortality, as well as mutagenic consequences in humans (Morufu and Clinton, 2017; Raimi and Sabinus, 2017b; Olalekan et al., 2018a, 2020; Morufu et al., 2021f). Furthermore, series of studies has shown that excessive heavy metals accumulation in the anatomical and physiological system is typically the result of greater occupational exposure to the metals, which can lead to health snags like anemia, renal dysfunction, cancer, neurological problems, as well as hepatic damage, neuromuscular, hematological, reproductive, renal, as well as central nervous systems (Li et al., 2001; Afolabi and Morufu, 2021; Afolabi and Raimi, 2021; Morufu et al., 2021d,e,f; Olalekan et al., 2022; Raimi and Sawyerr, 2022; Raimi et al., 2022a,b). Several health problems have been linked to regular consumption of sub-lethal amounts of cyanogens, a few of which have caused mortality as well as poisoning as a result of intake of cyanide from improperly processed cassava products (Wheatley and Churel, 1993; Adindu et al., 2003; Nhassico et al., 2008; Olalekan et al., 2018b). In Nigeria, there have been isolated reports of an entire family dying suddenly after consuming a cassava meal laced with a deadly dosage of cyanide as a result of faulty processing (Adindu et al., 2003; Olalekan et al., 2018b). As a result, optimal cassava processing practices are required, as well as ensuring that residual cyanide, arsenic, lead, as well as cadmium levels in cassava flour from carefully chosen markets in Oke Ogun community remain within acceptable standards.

Abbreviations: ATSDR, Agency for Toxic Substances and Disease Registry; AAS, Atomic Absorption Spectrophotometer; HCl, Hydrogen Chloride; IITA, International Institute of Tropical Agriculture; WHO, World Health Organization.



Efforts were made in this study to investigate the potential harmful thresholds of cyanide as well as other heavy metals in some local commercial cassava products collected from selected township markets in Oke Ogun Community, Oyo State, Nigeria. This is to determine the health risk that eating of cassava products can bring to the local residents. Thus, the study's findings are expected to reveal the nutritional properties composition as well as thresholds of harmful heavy metals in cassava to help consumers understand the value as well as potential risks associated with its intake.

2. Description of the study area

Oke Ogun area is in Oyo State and can be found at Latitude 7.33333 and Longitude 4.06667. According to the 2006 census, it has a land area of 13,537km² and a population of 1.4 million people. Oke Ogun area comprises ten (10) Local Government Areas, all of which have land ideal for agricultural as well as allied purposes (Figure 2). The main source of income for the residents of Oke Ogun is agriculture. The climate of the area is favorable for crops cultivation such as maize, cassava, yams, palm produce, and so on. Saki and Kishi have extensive livestock pastures. Oke Ogun region is the state's food basket, accounting for 60% of the state's land mass.

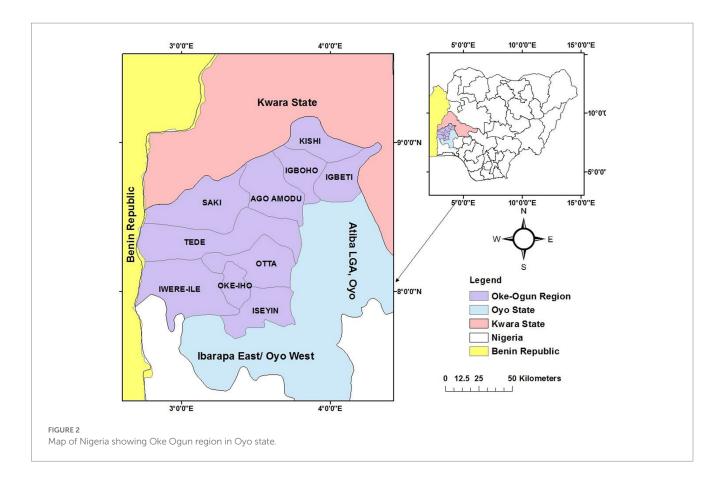
3. Sample collection

Samples of finely ground fermented cassava flour were obtained from various marketplaces in the Oke Ogun town of Oyo State in Southwest Nigeria. Stratified sampling was used to purchase samples from different markets in each town in the following communities: Iseyin, Igbeti, Kishi, Igboho, and Shaki. To prevent additional contamination throughout sampling, shipping, as well as storage, the samples were kept in airtight polyethylene bags that had been rinsed with dilute HCl and dried before use. The specimens were conveyed to the Ibadan Laboratory of the International Institute of Tropical Agriculture (IITA) for further testing.

4. Sample preparation

4.1. Ashing procedure for analysis of samples for lead determination

In a porcelain crucible, 2 g of finely ground fermented cassava flour was weighed, 1 mL of HNO₃ concentration was added, and the sample was burned on an electric hot plate. The charred sample was then burned in a controlled muffle furnace at 450°C until no brown vapors were produced and completely white ash was collected. The ash was allowed to cool in the furnace before adding 5 mL of IM HNO₃ solution and 5 mL of 30% HCl as well as warming the solution on an electric hot plate. After cooling, the solution was decanted into a 10 mL volumetric flask using a funnel and washed with deionized water. The solution was up to the mark with deionized water. The technique remained repeated for each sample as well as the consequential solutions were dispensed into sample bottles for Atomic Absorption Spectrophotometry (AAS) analysis for lead. The methods used for the commercial production of the different dried cassava



products are described by Awoyale et al., (2017). All the analyses were done in duplicate. Extraction procedure of sample for cyanide determination: 2 g of finely powdered fermented cassava flour was ground into a paste and dissolved in distilled water in a corked conical flask overnight. The mixture was filtered into a 50 mL volumetric flask with a funnel and Whatman 44 filter paper, then filled with distilled water to the mark.

4.2. Determination of lead, arsenic and cadmium using atomic absorption spectrophotometry

The amount of arsenic, lead, and cadmium in the sample solutions was analyzed using an atomic absorption spectrophotometer (GBC avanta version model 2.02) with an air acetylene flame at a specified wavelength for the metal. The digested samples were transferred via a mixing chamber into the burner, where the air met the fuel gas (C_2H_2), acetylene was fed to the burner at a given pressure, and the mixture was burned, and the radiations from the ensuing flame were measured.

4.2.1. Determination of cyanide using UV/visible spectrophotometer

5mL of the sample filtrate was placed in a corked test tube, together with 4mL of the alkaline picrate, and the solution was incubated in a water bath for 5min. The absorbance of the corked test tube was read using a Novaspec model 4049 UV/visible spectrophotometer at 490 nm, which is the wavelength of maximum absorption (max) of cyanide, after color development (reddish brown color), and this technique was repeated for each sample. On the calibration graph, the absorbance of a blank solution containing 1 mL pure water and 4 mL alkaline picrate solution was also read and extrapolated.

5. Results and discussion

In the food industry, understanding the concentration as well as pattern of particular metals present in food products is frequently critical to consider. Trace metals are essential for maintaining health throughout life because they are involved in the function of several enzymes (Khurshid and Qureshi, 1984; World Health Organization, 1992; Wheatley and Churel, 1993; Rosling, 1994; Institute of Medicine, Food and Nutrition Board, 2001). This is due to the fact that such metals seem to be inherently contained in foods and thus are nutritionally critical for humans, but they are toxic once consumed in large amounts. These metal insufficiencies are the most serious health and nutrition issue confronting populations in both developed and emerging countries (Olivares et al., 2004). During the sampling period, the greatest proportion of cyanide was found in cassava flour at Station K₃ (0.0019 mg/kg), followed by Station K₁ (0.0018 mg/kg), and lowest at Stations K₂ (0.010 mg/kg) and K₅ (0.010 mg/kg), respectively (Table 1; Figure 3). The mean concentration of cyanide (0.014 mg/kg) in cassava flour sold in marketplaces in Oke Ogun communities was less than the WHO limit (10 mg/kg; Table 2). Small quantities of cyanide, irrespective of exposure method, can be fatal. A dose of 50 to 100 mg taken within 24h by an adult can totally stop cellular respiration, resulting in death. Malnutrition, diabetes, congenital abnormalities, neurological problems, and myelopathy are all long-term complications

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(FSANZ, 2004; Olalekan et al., 2018b; Ogidi et al., 2021). According to Maziya-Dixon et al. (2007), scientists as well as international regulatory agencies have not synchronized on safe cyanide levels for both human as well as animal consumption. However, the SON standard for hydrogen cyanide (10 mg HCN/kg) in cassava products, on the other hand, agrees with the conclusion of the third session of the FAO/WHO Food Standards Program Codex Committee on Contaminants in Foods that a level of up to 10 mg HCN/kg in edible cassava flour (Codex Alimentarius Commission (CAC) 2013). The Joint FAO/WHO Food Standards Programme (Joint FAO/WHO Food Standards Programme Codex Committee on Contaminants in Foods (JECFA), 2009) established 10 mg/kg as the tolerable limit for hydrogen cyanide in food in accordance with this conclusion. As a consequence, if the CNP is less than 10 mg/kg, all of the products are safe for human consumption. The difference in CNP content between products from different locations, on the other hand, could be due to differences in cassava varieties, locations, and processing methods. As stated by the cassava cyanide disease network, cyanide is especially harmful since it binds to cytochrome oxidase and inhibits its action in the electron transport chain, which is a key energy conversion process in the body, and that high levels of cyanide in cassava products could harm consumers. One instance is acute intoxication, which manifests as headache, dizziness, vomiting, stomach pains, and diarrhea is one example" (Cassava Cyanide Diseases Network (CCDN), 2011).

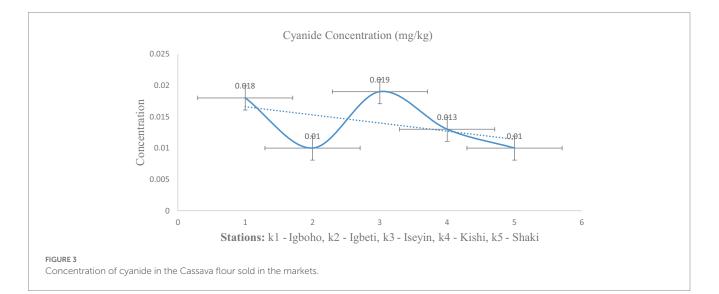
During the sampling, the level of lead in cassava flour was highest at Station K_3 (0.053 mg/kg), followed by Station K_1 (0.049 mg/kg), and

TABLE 1 Cyanide and heavy metal concentrations in Cassava flour sold in selected Oke-Ogun community markets.

| Parameters | | | | | | | |
|------------------------|--------------------|-----------------|--------------------|--------------------|--|--|--|
| Stations | Cyanide (mg/kg) | Lead (mg/kg) | Cadmium (mg/kg) | Arsenic (mg/kg) | | | |
| K ₁ _Igboho | 0.018 | 0.049 | 0.061 | 0.012 | | | |
| K ₂ _Igbeti | 0.010 | 0.029 | 0.036 | 0.007 | | | |
| K ₃ _Iseyin | 0.019 | 0.053 | 0.065 | 0.012 | | | |
| K ₄ _Kishi | 0.013 | 0.036 | 0.045 | 0.008 | | | |
| K₅_Shaki | 0.010 | 0.028 | 0.034 | 0.006 | | | |

lowest at Station K_5 (0.028 mg/kg; Table 1; Figure 4). Furthermore, the mean lead concentration (0.040 mg/kg) in cassava flour sold in marketplaces in Oke Ogun communities was lower than the WHO limit (0.1 mg/kg) for food (Table 2). Because of the reduction in human activities in the Oke Ogun community, the lead concentration was below the WHO standard for food, which will aggravate the presence of lead in the soil. This is consistent with the study of Agency for Toxic Substances and Disease Registry (2006), which found that majority of lead concentrations found in cassava flour are caused by human activities. Long-term contact with lead may harm nervous connections (particularly among young children), as well as cause blood and brain disorders. In women who are pregnant, it could cause miscarriage as well as reduce males' fertility through sperm damage (Agency for Toxic Substances and Disease Registry, 2006; Olalekan et al., 2018b).

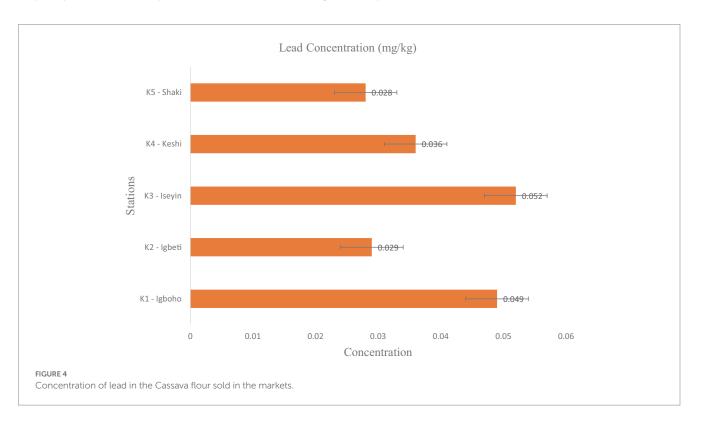
Cadmium concentrations in cassava flour were highest at Station K₃ (0.065 mg/kg), followed by Station K₁ (0.061 mg/kg), and lowest at Station K₅ (0.034 mg/kg) during the sample period, as shown in Table 1; Figure 5. During the sampling period, the mean Cadmium concentration (0.050 mg/kg) in cassava flour sold in Oke Ogun community markets was less than the WHO permitted level for Cassava flour (Table 2). Cadmium is low in the sample stations due to a reduction in the use of cadmium-containing fertilizers, which is the primary cause of the increase in cadmium in the soil with cassava plant, which is consistent with Jensen and Bro-Rasmussen's study (Jensen and Bro-Rasmussen, 1992). Cadmium has a negative impact on essential organs in high levels. Low levels of Cd and Pb in biological systems have also been linked to a variety of human organ disorders, some of which are irreversible (Sawyerr et al., 2019). As a result, lead and cadmium are important elements to consider when it comes to food-chain contamination. The existence of these metals in food, even in trace amounts, poses a risk to health. Similarly, this study found supports with the findings of Emurotu et al. (2012), which state that Pb and Cd levels remained below the limit of detection in all samples tested. As a result, the cassava flour is safe to eat. In terms of food-chain contamination, lead and cadmium are critical elements to consider. The existence of these metals in food, even in trace amounts, poses a significant risk.



| S/N | WHO | Unit | WHO | Mean of the present study | Mean \pm Standard deviation (SD) |
|-----|---------|-------|-----|---------------------------|------------------------------------|
| 1. | Cyanide | mg/kg | 10 | 0.014 | 0.014 ± 0.004 |
| 2. | Lead | mg/kg | 0.1 | 0.040 | 0.039 ± 0.012 |
| 3. | Cadmium | mg/kg | 3 | 0.050 | 0.048 ± 0.014 |
| 4. | Arsenic | mg/kg | 2 | 0.010 | 0.009 ± 0.003 |

TABLE 2 Comparison of present study with WHO standards for Cassava flour.

Analyses of cyanide as well as some heavy metals in cassava flour sold in selected Oke-Ogun Community markets.



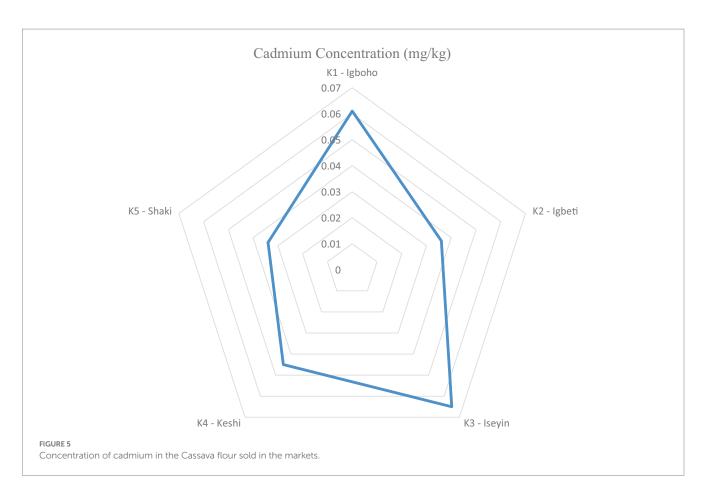
The maximum concentration of arsenic in cassava flour was observed at Stations K1 (0.012 mg/kg) and K3 (0.012 mg/kg), while the lowest value was reported at Station K5 (0.006 mg/kg) during the sample period, as shown in Table 1; Figure 6. Finally, the mean amount of arsenic value (0.010 mg/kg) for Cassava flour sold in markets was less than the WHO standard (2mg/kg; Table 2). According to Saha et al. (1999) this was due to the fact that there were less industrial operations in the research area, which resulted in less arsenic being released into the environment. Excessive arsenic intake from diet will harm a group of cells in the human body, causing malfunctions in cell respiration, cell enzymes, and mitosis. Thus far, environmental chemicals are widely found in food and may have adverse effects on fetal development. As this chemical pose considerable reproductive health risks, the clinical community is being urged to incorporate environmental health awareness as well as assessment as a regular part of preconception and maternity care.

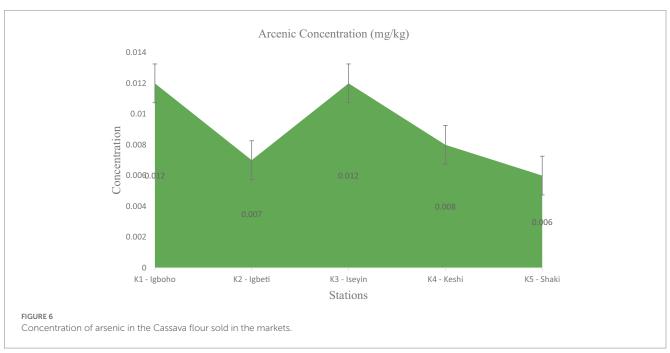
6. Conclusion

Global annual production of industrial chemicals has more than doubled to around 2.3 billion tons since the turn of the century, with an 85 percent increase expected by 2030. Food and environmental degradation are thus projected to worsen until there is a rapid transition in production and consumption habits, as well as a governmental dedication to genuine ecological sustainability that fully appreciates nature. While human activities have released thousands of different synthetic chemical compounds and naturally occurring components with potential toxicity into the milieu since ancient times. These pollutants can persist in the milieu for hundreds to thousands of years and can be found all over the globe. As a result, the study's findings revealed that the dietary concentration threshold of Cyanide, Cadmium, Arsenic as well as Lead in cassava flour sold in selected markets in the Oke Ogun community were lower than the World Health Organization's permissible safe food levels of potentially toxic elements, despite their low concentrations. As a result, cassava flour sold in Oke-Ogun community markets was found to be safe and acceptable for human consumption, with no dietary risk effects. Hence, there is need for continuous surveillance for the specific purpose of food safety, export and certification of origin of all foods.

7. Recommendations

Pollution has no boundaries: toxins are disseminated throughout land as well as aquatic ecosystems, and several are transported





worldwide by air travel. Furthermore, they are circulated across the world economy via food as well as industry networks. Hence, these findings can inform the development of future interventions to prevent or reduce environmental chemicals lifestyle choices due to exposure in our food and food products in order for those recommendations to be successfully translated into behavioral changes. It is suggested, based on the research findings and conclusion that:

• Cassava flour sold in Oke Ogun should be spread to other parts of the community and exported. Also, human daily actions that can increase the concentration of these potentially hazardous metals should be avoided.

- Cadmium-containing fertilizers should be prohibited from being used on cassava farm fields in order to prevent further contaminations.
- Increase spending on tailored research on emerging pollutants, together with detection as well as risk evaluation.
- Develop and improve heavy metal pollution inventories and monitoring at the national, regional, and global levels; Establish and strengthen national biomonitoring and epidemiological surveillance systems toward recognizing, analyzing, and tracking harm and illnesses caused by cyanide and heavy metals in cassava flour, as well as to support preventive activities.
- The government should hire experienced environmental health professionals to monitor and assess environmental media that have the potential to increase the level of these potentially harmful metals in the area on a regular basis.
- The government should advocate for a global commitment to preventing, halting, as well as remediating food contamination as component of the Zero Pollution/Concerning a Pollution-Free World goal, based on municipal, state, national, as well as regional activities and targets such as the European Green Deal.
- The government should conduct a global food pollution awareness campaign geared at the public at large in order to help them comprehend why food pollution is important to everyone and how they can help to solve the problem. Also, to raise public awareness of the importance of environmentally responsible and sustainable usage.
- Encourage citizen research plus observatories in order to expand early warning systems as well as community-based food pollution monitoring. As well as promote the release of material in freely accessible sources and facilitate the sharing of scientific knowledge via global events.
- Establish as well as strengthen monitoring networks for averting, overseeing as well as remediation of dispersed pollution. Also, create a national training program to build capacity on the entire food contamination cycle.

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Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

Author contributions

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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