

Accumulation of Chromium, Lead and Arsenic in Calcium Carbide Induced Ripened Fruits and Their Possible Human Health Risks in Bauchi, Nigeria

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ABSTRACT

The study determined three heavy metal composition of three calcium carbide induced ripened fruits – pineapple, orange and banana bought from local markets within Bauchi Metropolis, Nigeria. The study aimed to compare the heavy metal composition and the estimated daily intake of the metals in these fruits to FOA permissible limits and their Ingestion Reference doses respectively; and to estimate the possible health risks by consuming them. Standard analytical and spectrophotometric methods were used to determine the metal concentrations. Results of the analysis indicated that the studied metals were detected in all the categories of fruits studied. The concentrations ranges (mg/kg) of Cr, Pb and As detected in the NR fruits analysed were 0.001 ± 0.01 – 0.009 ± 0.03 , $.001\pm 0.01$ and 0.001 ± 0.01 – 0.003 ± 0.01 respectively while for the AR, it was 0.003 ± 0.01 – 0.014 ± 0.06 , 0.002 ± 0.0 – 0.004 ± 0.01 and 0.003 ± 0.001 – 0.006 ± 0.03 , though the AR fruits have enhanced levels of these metals compared to the NR fruits. The levels of metals in the fruits were lower than the FOA limits. The Estimated daily intake of the study fruits were below the reference doses of the metals (Cr- 1.5; Pb – 0.004; As – 0.005), while the Hazard index for the metals were all less than 1. All the study fruits are therefore safe for consumption and poses no negative effect on human. However, it is recommended among others, that food science and public health experts in collaboration with regulatory bodies should educate fruit sellers and the general public on the negative effects artificially ripening has on the nutritional values of fruits and the health implications of consuming such fruits over time.

Keywords: Fruit ripening, Calcium Carbide, Metals, Health risk, Bauchi

INTRODUCTION

Fruit ripening is the final and essential stage in the process of fruit maturation. It may occur naturally or artificially. Natural ripening generally occurs when the fruits attain proper maturity and a sequence of irreversible physiological and biochemical process is triggered by the plant hormone (ethene), making the fruit soft, palatable, colourful, flavourful and nutritious. Ripening of fruits naturally usually take several days and most often, the fruits may lack uniformity in peel colour. Artificially, harvested fruits, whether mature or immature are forcefully ripen using ripening agents, which mimics the naturally occurring ethene by controlling different parameters to achieve a faster and uniform ripening, uniform colour and attractive brightness. Although these fruits may appear attractive and appealing to the consumer, the tissue inside remains green and the fruits generally have shorter shelf life (Chandel et al., 2018; Ekanem et al., 2021; Oladipupo et al., 2022). Several artificial fruit ripening agents are used to hasten the fruit ripening process. These include ethylene gas, methanol, ethylene glycol, ethephon, ethereal and calcium carbide (Mursalat et al., 2013; Hassan et al., 2019; Maduwanthi and Marapana, 2021). However, Calcium carbide, CaC_2 is the most commonly used in Nigeria (Ekanem et al., 2021).

CaC_2 produces ethene when it is dissolved in water. This gas is then used as the artificially ripening agent. Though the gas may cause any serious toxic hazards to human, its associated impurities (approx. 3ppm of arsenic) is known to be harmful to humans (Nuhu, Rabi, & Tukur, 2020; Oladipupo et al., 2022). Arsenic in the form of calcium arsenide and phosphorus, in the form of calcium phosphide are impurities found in commercial-

grade CaC_2 . When these compounds react with water, their hydrides (phosphine (PH_3) and arsine (AsH_3) are released. Since these hydrides are fat-soluble, they easily dissolve in any wax layer of fruits and spread from the peel to the pulp (Khan and Abbas, 2015; Chandel et al., 2018; Hassan et al., 2019).

Artificially ripened fruits are also known to pose serious human health risks when consumed. Calcium carbide found to contain some amounts of arsenic and phosphorus has been reported to affect vertebrate's neurological system. The acetylene gas produced from the reaction between Calcium carbide induced persistent hypoxia, leading to headache, dizziness, mood swings, sleepiness, mental confusion, memory loss, cerebral edema, and seizures (Gandhi et al., 2016; Gupta, 2017). Ain et al (2023) measured the concentrations of As in different varieties of mangoes collected from local markets in Abbottabad to assess the potential health risk associated with such contaminated mangoes for humans. They discovered that trader used CaC_2 for the artificial ripening of mangoes and a high concentration of As was found in the peel, followed by the fruit surface and pulp. Though the Health Quotient and Health Risk Index values obtained for As in mangoes did not indicate any significant health risks to the consumers, they warned that frequent consumption of such mango fruits may result in serious effects. Olubiyo et al., (2022) reported the presence of Pb in fruit samples treated with CaC_2 and concluded that the use of CaC_2 for fruit ripening cause a significant loss of fruit nutrients. While most of the agents used for ripening fruits are carcinogenic, impurities such as Pb, Cr and Cd which are known carcinogens are also found in artificial ripening agents. Ingesting these chemicals cause kidney failure, lung failure and skin diseases (Hakim et al., 2012; Basapor and Ngabaza, 2015).

In spite of the toxic effects of treating fruits with CaC_2 and initial warnings from NAFDAC, many vendors have continued to use this chemical at the detriment to human health in Bauchi. Studies have shown that fruits ripening with chemical are widely used in many developing countries because these countries lack strict rules and regulations regarding many banned chemicals (Hassan et al. 2019). The paucity of scientific information and limited public awareness about the related health risks associated with the artificial ripening of fruits in Bauchi State therefore necessitated this study. This study determined the level of Arsenic, Lead and Chromium in CaC_2 induced ripened fruits in order to ascertain the possible health risks this could pose to consumers in Bauchi State.

Sample collection, preparation and treatment

Freshly unripe green but mature pineapples, banana and oranges were bought from three station local markets in Bauchi metropolis with the assistance of fruit vendors within the markets. The fruits were thoroughly cleaned in the laboratory, where they were divided into two equal weighted treatment groups (Naturally ripened and artificially ripened). The naturally ripened (NR) group were allowed to ripen naturally while the other group were ripened artificially (AR) using 10g of Calcium carbide before ripening. Both groups of fruits were kept in a laboratory cupboard and observed under similar environmental condition until signs of ripening were noticed (change of skin colour from green to yellow) (Olubiyo et al., 2022). The ripe fruits were then washed with deionised water, peeled, cut into smaller slices with plastic knife and oven dried at 70°C for 48 hours. The dried samples were ground into powder using a mortar and pestle, sieved and stored in an airtight plastic container (Ain et al., 2023).

Metal Determination

1g of each pulverized fruit samples was placed in a crucible and ignited in a muffle furnace at 550°C for 6 hours. The ash obtained was dissolved in 10ml of 10% HNO_3 and heated for 20 minutes. The mixture was then filtered through Whatman No 1 filter. The filtrate obtained was analyzed in triple for heavy metal content using the Atomic Absorption Spectrophotometer (AAS).

Human Health Risk Assessment

According to the Human Risk Assessment (HRA) model introduced by the USEPA, Human health risks could be carcinogenic and non-carcinogenic (Najmi et al. 2023; Mohammed et al., 2022). Both risks can be determined using the estimated daily intake of the metals.

Estimated daily intake (EDI) of metals

The EDI for humans was calculated using the average concentration in the fruit samples and the daily consumption in grams of fruits from the equation (Antoine et al., 2017; Bayo et al., 2021; Nwankwo et al., 2021).

$$EDI = \frac{\text{Mean concentration of heavy metal in fruit} \times \text{Daily intake of fruit}}{\text{Average body weight}}$$

Average daily intake of fruits is 0.400kg/person/day while Average body weights are 55.9 kg and 32.7kg for adults and children respectively.

Non-carcinogenic risk (NCR) expresses the toxic effect of individual chronic exposure to pollutants such as genetic and teratogenic. NCR is assessed by determining the Hazard Index (HI) which is the sum of the hazard quotient (HQ) of the individual metal.

$$HQ_i = \frac{\text{Mean concentration of heavy metal in fruit} \times \text{Daily intake of fruit}}{RfD \times \text{Average body weight}}$$

RfD is the oral reference dose for metal. To evaluate the potential risk to human health through more than one heavy metal,

$$\text{Hazard Index (HI)} = \sum (THQ_i)$$

Where THQ_i is the target hazard quotient for individual pollutant. It is also referred to the health risk index

$$\text{Target Hazard Quotient (THQ}_i) = EDI / RfD,$$

Heavy metals	Ingestion Reference dose (RfDi)
Cr	1.5000
Pb	0.0040
As	0.0050

(Nwankwo et al. 2021; Bayo et al., 2021; Chioma and Butch, 2024)

RESULTS AND DISCUSSION

Heavy Metal Concentrations in the studied Fruits

The concentrations of heavy metals in the NR and AR fruits studied are shown in Table 1. The results revealed that Cr, Pb and As were detected in all the fruits analysed, though accumulation of the metals in the fruits occurred at different concentrations. The AR fruits were observed to have enhanced level of Cr, Pb and As compared to those of the NR fruits.

The mean Cr values of the NR banana (0.001±0.01mg/kg), pineapples (0.002±0.01mg/kg) and oranges (0.009±0.03mg/kg) respectively were lower than the 0.003±0.01mg/kg, 0.006±0.03mg/kg and 0.014±0.06mg/kg obtained for the metal in their AR samples respectively. The value of Cr detected in the study fruits were lower than the permissible limit of 0.5 stipulated by the FAO. The level of chromium in the fruits in the present study were lower than those (between 0.018 and 0.029 mg/kg) reported in Bayo et al., (2021) for some fruits.

Pb values of the NR banana (0.001±0.01mg/kg), pineapples (0.001±0.01mg/kg) and oranges (0.001±0.02mg/kg) respectively were lower than the 0.004±0.0mg/kg, 0.003±0.0mg/kg and 0.002±0.01mg/kg obtained for the metal in their AR samples respectively. The value of Pb detected in the study fruits were lower than the permissible limit of 0.2 stipulated by the FAO.

Table 1: Levels of Heavy metals concentration (mg/kg) in the Fruit samples

Metals (mg/kg)	Cr	Pb	As
Naturally Ripened Fruits			
Banana	0.001±0.01	0.001±0.01	0.001±0.01
Pineapple	0.002±0.01	0.001±0.01	0.002±0.01
Orange	0.009±0.03	0.001±0.02	0.003±0.01
Artificially Ripened Fruits			
Banana	0.003±0.01	0.004±0.01	0.003±0.01
Pineapple	0.006±0.03	0.003±0.01	0.004±0.01
Orange	0.014±0.06	0.002±0.01	0.006±0.03
FOA (2001)	0.5	0.2	0.5

The concentration of Pb in all the fruits here were lower compared to values in other works. Okeke et al., (2022) detected a mean Pb concentration of $0.05 \pm 0.02 \mu\text{g/g}$ in ripened banana samples but none in naturally ripened samples (control) purchased from markets within Enugu metropolis. Pb values of $0.015 \pm 0.017 \text{ ppm}$ and $0.023 \pm 0.026 \text{ ppm}$ were reported for CaC_2 treated oranges and bananas respectively by Olubiy et al., (2022). However, Pb was not detected in the naturally ripened oranges and bananas in their work. Studies have shown that calcium carbide treated fruits contain high levels of Pb. Bayo et al., (2021) reported a Pb concentration between 0.031 mg/kg and 0.055 mg/kg for various fruit samples purchased from markets in Jos, Nigeria, while Ihesinachi and Eresiya (2014) reported Pb value as high as 1.69 mg/kg in the avocado pear from Rivers State, Nigeria. Pb concentrations in fruits, especially in the NR could be attributed to possible Pb contaminated soils where the fruits were grown, improper storage and poor handling (Okeke et al., 2022). The use of CaC_2 as a ripening agent has been reported as a major source of Pb in fruits. The industrial grade CaC_2 illicitly used by fruit sellers for ripening contains Pb as an impurity. During ripening, Pb can deposit on the fruit surface and be potentially absorbed into the surface and pulp of the fruit (Dibagha and Ogoun 2022; Akolade et al., 2022; Nwankwo et al., 2021).

The mean As level of the NR banana ($0.001 \pm 0.01 \text{ mg/kg}$), pineapples ($0.002 \pm 0.01 \text{ mg/kg}$) and oranges ($0.003 \pm 0.01 \text{ mg/kg}$) respectively were lower than the $0.003 \pm 0.0 \text{ mg/kg}$, $0.004 \pm 0.0 \text{ mg/kg}$ and $0.006 \pm 0.03 \text{ mg/kg}$ obtained for the metal in their AR samples respectively. However, these values were below the FAO permissible limit for the metal in fruits, and may not pose any danger to humans. In comparison to fruits treated by CaC_2 , the AR sample contained As residues of 0.002 mg/kg , 0.002 mg/kg and 0.003 mg/kg in banana, pineapples and oranges. This further shows that As is an impurity found in CaC_2 . Researchers have reported higher levels of As in fruits compared to the ones examined in the present study (Shaheen et al., 2016; Bayo et al., 2023). The concentration of As in this study are consistent with levels in Oluyiyo et al., (2022). Ain et al., (2023) noted that the As residue on the fruit was formed as a result of the reaction of moisture and CaC_2 to form arsine gas. This gas accumulates on the fruit surface, which eventually enters the peel and pulp of fruits.

Health Risk Index

The Estimated Daily Intake (EDI) of metals and individual Health Quotient (HQ_i) for adults and children calculated for the study metals via the consumption of the artificially ripened fruits are shown Table 2. In adults, the EDI values for Cr and As in banana were the same ($2.2\text{E}-5$) but $2.9\text{E}-5$ for Pb. For pineapples, it was between $2.2\text{E}-5$ to $4.3\text{E}-5$ while it was $1.4\text{E}-5 - 0.0001$ for oranges. In children, Cr and As EDI values ($3.7\text{E}-5$) for banana were also observed to be similar. The ranges of the EDI values for the metals for pineapples and oranges were

3.7E-5 – 7.3E-5 and 2.5E-54 – 0.0002 respectively. The EDI for all the three heavy metals in the studied fruits in children are considerably higher than those for adults. However, these values (1.4E-5 - 0.0002) for all the heavy metals are below their reference oral doses (Cr- 1.5; Pb – 0.004; As – 0.005). The exposure to these heavy metals through the consumption of these fruit may not result in any deleterious effects on the consumers.

Table 2: Estimated Daily Intake of metals (EDI) and Health Quotient (HQ) from Artificially Ripened Fruits

Metal	Banana		Pineapple		Oranges	
	EDI	HQ	EDI	HQ	EDI	HQ
<i>Adults</i>						
Cr	2.2E-5	1.4E-5	4.3E-5	2.9E-5	0.0001	7.3E-5
Pb	2.9E-5	0.0072	2.2E-5	0.0054	1.4E-5	0.0036
As	2.2E-5	0.0043	2.9E-5	0.0057	4.3E-5	0.0086
<i>Children</i>						
Cr	3.7E-5	4.9E-5	7.3E-5	4.9E-5	0.0002	0.0005
Pb	4.9E-5	0.0122	3.7E-5	0.0092	2.5E-5	0.0061
As	3.7E-5	0.0073	4.9E-5	0.0098	7.3E-5	0.0147

Hazard Index of Heavy Metals in Artificially Ripened Fruits

Figure 1 shows the hazard index (HI) of the metals of the artificially ripened fruits. The HI calculated for bananas, pineapple and oranges for adults and children respectively are 0.1115, 0.0200; 0.0111, 0.0191 and 0.0123, 0.0213. HI levels were higher in children than in adults.

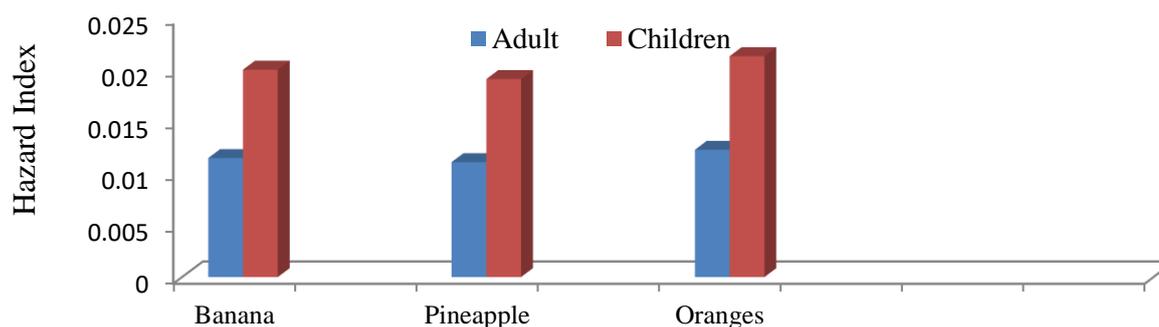


Figure 1: Hazard Index of Heavy metals in studied fruits

The results of the non-carcinogenic risk assessment, Hazard Index (HI) in Figure 1 were less than 1. This also indicates that consumption of these fruits may not constitute any health hazards to consumers. All the HIs derived for each fruit for children were also observed to be higher than those for adults. This shows that children are more likely to be exposed to these metals than adults. The HI values obtained for the artificially ripened fruits in this study are consistent with those reported in Shaheen et al. (2016); Antoine et al. (2017) and Ain et al., (2023) for some fruits ripened using CaC₂. In their studies, HQs and HIs were all less than 1. With these values, mature fruits ripened with CaC₂, probably at lower concentrations are free from heavy metal contamination and may be safe for consumption; so exposed population is unlikely to experience any negative effects for metal

poisoning. There are therefore no potential health risks of accumulating these heavy through the consumption of the fruits in this study.

CONCLUSIONS

The levels heavy metals detected in the fruits varied greatly according to nature of the fruits. The ranges in the concentrations of Cr, Pb and As the fruits were observed to be lower the permissible limits set by the FAO. However, the levels of the metals measured in the AR fruits were higher than the NR fruits. The fruits in this study have very low hazard quotients and hazard index (less than 1), implying that consumers of these the artificially ripened fruits may not face serious health risks. However, the frequent consumption of such fruits may result in serious effects due to possible reduced nutritional benefits. Regulatory bodies like NAFDAC should therefore ensure regular monitoring of the use of CaC₂ and other artificial ripening agents for fruits. They should collaborate with other food and public health experts in to educate fruit sellers and the general public on the health implications of consuming artificially ripened fruits; while encouraging them to use available proven methods to naturally ripen their fruits

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