Evaluation of pesticide residues and heavy metals in common food tubers from Nigeria

AUTHORS:
Kingsley O. Omeje[1]
Benjamin O. Ezema[2,3,4]
Sabinus O.O. Eze[1]

AFFILIATIONS:
[1]Department of Biochemistry, University of Nigeria, Nsukka, Nigeria
[2]The Biochemistry Unit, Department of Science Laboratory Technology, University of Nigeria, Nsukka, Nigeria
[3]Aston Institute of Materials Research, Aston University, Birmingham, UK
[4]Energy and Bioproducts Research Institute, Aston University, Birmingham, UK

CORRESPONDENCE TO:
Benjamin Ezema

EMAIL:
ezema.onyebuchi@unn.edu.ng

DATES:
Received: 17 Apr. 2023
Revised: 28 Oct. 2023
Accepted: 06 Nov. 2023
Published: 27 Mar. 2024

HOW TO CITE:
Omeje KO, Ezema BO, Eze SOO. Evaluation of pesticide residues and heavy metals in common food tubers from Nigeria. S Afr J Sci. 2024;120(3/4), Art. #15969. https://doi.org/10.17159/sajs.2024/15969

ARTICLE INCLUDES:
☒ Peer review
☒ Supplementary material

DATA AVAILABILITY:
☐ Open data set
☒ All data included
☐ On request from author(s)
☐ Not available
☐ Not applicable

EDITOR:
Priscilla Baker

KEYWORDS:
tubers, pesticide residue analysis, heavy metal analysis, gas chromatography–mass spectrometry, atomic absorption spectroscopy, maximum permissible limit

FUNDING:
None

© 2024. The Author(s). Published under a Creative Commons Attribution Licence.

Pesticide residues and heavy metal content of cassava, yam, cocoyam, potato, water yam and carrot were evaluated by gas chromatography–mass spectrometry and atomic absorption spectroscopy. The detected pesticide residues in the samples were 2,4-dichlorophenoxyacetic acid, glyphosate, hexachlorobenzene (HCB), dichlorobiphenyl, aldrin, endosulfan, profenofos, g-chlordane, carbofuran, biphenyl, heptachlor, lindane and t-Nonachlor. The concentration of HCB ranged between 0.0799 ± 0.06 mg/kg and 0.1596 ± 0.00 mg/kg, which was greater than the permitted maximum limit of 0.5 mg/kg established by the US Environmental Protection Agency. The concentration of aldrin and profenofos detected was lower than the predetermined maximum allowed limits. Endosulfan concentrations in cocoyam (0.2500 mg/kg) and potato (0.3265 mg/kg) were higher than the limits allowed by the Canadian Department of Industrial Research. The heavy metals detected in these samples include cobalt, nickel, lead, manganese, chromium, arsenic and mercury in at least one of the samples evaluated. There was not much difference between the concentration of cobalt in yam (0.036 mg/kg) and the maximum allowed concentration (0.043 mg/kg). Lead was detected in potatoes and carrots but was below detectable concentration in cassava, yam, cocoyam and water yam. Similarly, cocoyam was found to have a significant mercury content (0.658 mg/kg), but mercury content was below detectable concentrations in cassava, yam and water yam.

Significance:

Heavy metal pollutants and pesticide residues can impair human health, and their presence in food can cause various illnesses and health issues. It is important to prevent exposure to these contaminants and ensure that food is safe by identifying and monitoring them. Farmers may provide consumers with more assurance that their products are safe by identifying and monitoring pesticide residues and heavy metal contamination in these food crops. Overall, it is crucial to find and monitor pesticide residues and heavy metal contamination in food to safeguard customer confidence, ensure legal compliance and preserve human health.

Introduction

Pesticides are chemicals that are used to control pests which are harmful to humans, plants and the environment.[1] In parallel, pesticide residues are described as substances that are found in foods for consumption by humans or other animals, and are chemical derivatives considered to be toxic to living organisms.[2] Similar to pesticide residues, the entrance of heavy metals into the food chain is their major route into the human system, which could cause autoimmune disorders and inhibit the functions of some biochemical processes.[3] Heavy metal toxicity has been reported regularly in recent times, with some deaths attributed to it. Other effects of heavy metals on humans include cancers, high blood pressure and gene mutation.[2,4,5] Uncontrolled disposal of household and electronic waste, animal dung and abandoned metallic parts are some of the environmental sources of heavy metals.[6] Environmental pollution is a serious problem in today's modern world, with pesticides and heavy metal pollution being the most prevalent due to their ability to contaminate air and water.[7]

Cassava, yam, cocoyam, potato, water yam and carrot are commonly cultivated in Nigeria due to their multiple usage and nutritional values. These tubers are tropical crops consumed by about 2 billion people and are the major sources of carbohydrates providing energy for the roughly 700 million residents of tropical and subtropical regions.[8] The production of these products and their conversion into goods derived from food is expanding, and farmers profit significantly from their market.[8] Their high post-harvest losses, due to contamination by external and internal hazardous substances (such as mycotoxins, heavy metals and insecticides), reduce economic value and income. These roots/tubers have a crude fat content on the fresh weight of 0.1–0.5% and 1–3% on the dry weight, of which 80% is starch. The carbohydrate content of cassava is larger than that of potatoes.[8] Cassava is a potent source of energy despite being deficient in lipids, minerals and proteins.[9] On the other hand, yam provides energy in the range of 80–120 kcal/100 g.[10] Vitamin A is produced from beta-carotene, and it is present in adequate amounts in potatoes.[11] These tubers' essential amino acid composition is higher than that recommended by the Food and Agriculture Organization (FAO) for daily protein intake and greater than that of soybean protein.[12] These tubers may become polluted during cultivation and food processing and also contain certain endogenous antinutrients.

Currently, there are common applications of several agrochemicals in the cultivation of these crops to ward off pests. All the grown food crops are highly vulnerable to various insect attacks, especially on the farm or in the cultivation area, which has a detrimental impact on both the financial and dietary elements of product quality. Pesticides must be used to control pest infestations, which helps to improve the quality of crops and their production on farms.[13] Consequently, these tubers may get contaminated, and the risks associated with consuming these roots can be divided into two groups: those related to potentially harmful substances present in the crop itself, and those related to processing and product development. However, there are some significant concerns regarding food safety and security. A lot of research still needs to be carried out concerning the level of heavy metal and pesticide pollution, especially that seen in Nigerian food crops like the tubers that are commonly consumed, such as cassava, yam and cocoyam.[14,15]

The amount of residues from pesticides and heavy metals in tuber-derived food products varies based on the location of the growing area and the system of farming. In Nigeria, pesticide residues detected in some tubers (cassava and yam) were HCB (0.0247), endosulfan (0.0340 and 0.090) and aldrin (0.0000 and 0.0937) mg/kg, respectively.[15] The concentration of isopropylamine in yam was 0.2165 ± 0.00 mg/kg and in cassava was 0.1649 ± 0.00 mg/kg, while the concentration of t-Nonachlor in yam was 0.1093 ± 0.00 mg/kg and in cassava was 0.0006 ± 0.00 mg/kg, as reported by Omeje et al.[15] Adeyeye and Osibanjo[16] detected high concentrations of organochlorine residues in yam (aldrin = ~5.0 μg/kg; dieldrin = ~24.0 μg/kg and p,p´-DDE = ~13.0 μg/kg) and cassava (aldrin = ~6.0 μg/kg; dieldrin = ~31.0 μg/kg and p,p´-DDE = ~21.0 μg/kg) in their study. Heavy metals have been found in tubers like potatoes, yams and cassava in previous studies. The amount of cadmium (Cd) found in yam was reported to be 0.11 mg/kg, and lead (Pb) and nickel (Ni) were also detected.[17] In addition, 0.21 mg/kg of Pb, 42 mg/kg of copper (Cu), 24 mg/kg of zinc (Zn), 18 mg/kg of manganese (Mn) and 12 mg/kg of Ni were reported by Wilberforce and Nwabue[18]. Arsenic (As) concentration in cassava was detected to be 0.017 mg/kg.[15] According to Onianwa et al.[19], the range reported for Ni concentrations in tubers is 0.93–1.79 mg/kg. Akinyele and Shokunbi[20] detected Mn in yams (~4.42 mg/kg), and Orisakwe et al.[21] reported Pb (~0.33 mg/kg), Cd (~0.10 mg/kg) and Ni (~0.30 mg/kg) in cassava.

To enrich the existing body of information, we assessed the presence and concentration of common food pesticide residues and heavy metal contaminants in essential and commonly consumed tuber crops cultivated in Nigeria using gas chromatography–mass spectrometry (GC–MS) and atomic absorption spectroscopy.

Materials and methods

Chemicals and materials

The chemicals and reagents used were of analytical quality and included chloroform, perchloric acid, sodium sulfate, concentrated sulfuric acid (Sigma-Aldrich), n-hexane (Loba Chemie, India) and concentrated nitric acid, anhydrous sodium sulfate, methanol (Sigma-Aldrich) and benzene. The pesticide standards (purity > 95%) were obtained from Restek (Sigma-Aldrich, USA). With concentrations ranging from 50 ng/mL to 200 ng/mL, stock standard solutions of 47 organochlorine pesticides (OCPs), organophosphorus pesticides (OPPs) and other pesticides were made in ethyl acetate and stored at 4 °C in a dark location until analysis. Pesticides are present in spiking solutions in amounts of 10–50 ng/L. The internal standard was aldrin solution (Sigma-Aldrich) in acetone at a concentration of 50 ng/L.

Samples

In April 2022, fresh tubers weighing 500 g each (cassava, yam, cocoyam, potato, water yam and carrot) were purchased from Nsukka open market situated in Enugu State (6°51’24” N and 7°23’45” E) in southeast Nigeria, and transported to the laboratory of the Department of Biochemistry, University of Nigeria, Nsukka. They were processed and stored at 4 °C for further analysis.

Pesticide residue analysis

The pesticide residues were determined with the help of a GC analysis and prepared following the AOAC method[22], with minor modifications. Ten grams (10 g) of the homogenised sample was mixed with 60 g of anhydrous sodium sulfate in an agate mortar to absorb moisture. The homogenate was transferred into a 500 mL beaker, and the extraction was carried out with 300 mL of n–hexane for 24 h. The obtained crude extract was concentrated using a rotary vacuum evaporator at 40 °C to dryness. The sample residue (1 mL) was measured into 50 mL of chloroform transferred to a 100 mL volumetric flask and diluted. Most of the chloroform was evaporated at room temperature before adding 1 mL of the solvent mixture (20% benzene and 55% methanol). The mixture was sealed and heated at 40 °C using a water bath for 10 min. After heating, the organic sample was extracted with n–hexane and water in a proportion of 1:1. The mixture was shaken vigorously for 2 min, and n-hexane phase was transferred onto a small test tube for injection into a Buck 530 Gas Chromatograph (GC) equipped with an on-column, automatic injector, electron capture detector and an HP 88 capillary column (100 mm X 0.25 μm film thickness) (Agilent Technologies, Santa Clara, CA, USA), with injector and detector temperatures of 180 °C and 300 °C, respectively. Overall, the GC enabled the identification of pesticide residues, which were recorded in mg/kg, as the results emerged.

Heavy metal analysis

The heavy metal analysis (Co, Ni, Pb, Mn, Cr, As, Hg and Cd) was performed using a Varian AA240 Atomic Absorption Spectrophotometer (AAS; Varian Inc., Palo Alto, CA, USA) equipped with an acetylene air flame, adapting the protocol described by Quarcoo and Adotey[23], with slight modifications. The pyrolytic-coated graphite tubes of the AAS were equipped with platform instrument settings and furnace programs that helped to ascertain the peak signals. A known concentration of the sample (~2 g) was put into a digestion flask, along with 20 mL of acid mixture (which consisted of 650 mL concentrated HNO_3; 80 mL perchloric acid; 20 mL concentrated H_2SO_4), and subsequently heated until a clear digest was obtained. The digest was diluted with distilled water to the 100 mL mark. The acid level samples as they came along were monitored by a pH meter. The digestate was quantified, assayed for heavy metals using a Varian AA240 Spectrophotometer, and reported in mg/kg. The reference standards (Fluka Analytical, Sigma-Aldrich Chemie GmbH, Switzerland) for the detected element, blanks and their duplicates were digested using conditions consistent with those of the samples.

Statistical analysis

The emergent heavy metal and pesticide residue data were obtained from triplicate determinations of different samples from a given food crop batch. A one-way analysis of variance (ANOVA), using SPSS for Windows (version 16, SPSS Inc., Chicago, IL, USA), was used to establish differences in heavy metals/pesticide residues across the studied food crop samples. Data are expressed as mean ± standard error (SE). A simple *t*-test was used to compare the heavy metals/pesticide residue concentration data and the established/referenced maximum permissible limits (MPLs). The probability level was set at $p < 0.05$ (95% confidence level).

Results

The concentrations of nickel (Ni), chromium (Cr), cobalt (Co), arsenic (As), manganese (Mn), cadmium (Cd), lead (Pb) and mercury (Hg) in the tubers are shown in Table 1.

All the heavy metals evaluated were present in the samples, except for Cd, which was below the detectable concentration in all the samples studied (Table 1). Among the samples, the maximum level of Ni (0.012 ± 0.00 mg/kg) was found in cassava. The concentration of Ni was 0.009 ± 0.00 mg/kg in cocoyam, 0.006 ± 0.00 in yam, 0.007 ± 0.00 in water yam, 0.001 ± 0.00 in carrot and 0.006 ± 0.00 in potato (Table 1).

Co, one of the common heavy metals in the environment, was among those evaluated. The maximum Co concentration of 0.036 ± 0.00 mg/kg was detected in yam. A Co concentration of 0.026 ± 0.00 mg/kg was detected in cocoyam, 0.016 ± 0.00 mg/kg in water yam, 0.011 ± 0.00 mg/kg in cassava, 0.010 ± 0.00 mg/kg in carrot and 0.002 ± 0.00 mg/kg in potato. According to Leyssens et al.[24], Co is an essential constituent of nature, which is released during many anthropogenic activities and is a cofactor of vitamin B_{12}.

Cr was also detected in all the samples. Cr concentrations of 0.093 ± 0.00 mg/kg and 0.083 ± 0.00 mg/kg were found in cocoyam and cassava, respectively. Potato and water yam had Cr concentrations of 0.073 ± 0.00 mg/kg and 0.078 ± 0.00 mg/kg, respectively. The lowest level of Cr was detected in carrots (0.010 ± 0.00 mg/kg). Similarly, cobalt was detected in all the samples, with the highest concentration (0.036 ± 0.00 mg/kg) found in yam. Co was detected in the potato sample, although at the lowest concentration (0.00 ± 0.00 mg/kg) when compared to those of the other samples.

Similarly, As was found in the samples in various amounts. The amounts found in cassava, yam and cocoyam were 0.045 mg/kg, 0.010 mg/kg and 0.049 mg/kg, respectively. Also, 0.056 ± 0.00 mg/kg, 0.037 ± 0.00 mg/kg and 0.019 ± 0.00 mg/kg As were detected in samples of potato, water yam and carrot, respectively. Potatoes had the highest concentration of As discovered, whereas yam had the lowest concentration (0.010–0.00 mg/kg) (Table 1). The presence of Mn, Cd and Pb was evaluated in the samples. High concentrations of Mn (0.838 ± 0.00 and 0.750 ± 0.00 mg/kg) were detected in water yam and potato. Cassava contained 0.138 ± 0.00 mg/kg of Mn, as shown in Table 1.

Lead was not detected in cassava, yam, cocoyam or water yam. However, higher concentrations of 0.032 mg/kg and 0.028 mg/kg were detected in cassava and carrots, respectively. The World Health Organization (WHO) limit for Mn is not yet established.[15] Mn serves as a cofactor for some enzymes but could cause neurological disorders when above >5 mg/dm^3.[5,25]

The concentrations of Pb were 0.032 ± 0.00 and 0.028 ± 0.00 mg/kg in cassava and carrot, which were below FAO/WHO established MPLs (10 ± 0.00 mg/kg). The concentration of Pb in cassava, yam, cocoyam and water yam was below the detectable range, as shown in Table 1. The concentration of mercury (Hg) was lowest in potato (0.153 ± 0.00 mg/kg) and highest in cocoyam (0.658 ± 0.02 mg/kg), but below the detectable range in cassava, yam and water yam.

Metallic mercury exposure has been reported to cause lung damage.[26] The concentration of Hg in the cocoyam (0.658 ± 0.00 mg/kg) was greater than the 0.5 mg/kg FAO/WHO maximum acceptable limits.[27] However, potatoes showed a Hg concentration below the MPL.[27]

Table 2 shows the concentrations of pesticide residues present in the tubers studied. 2,4-dichlorophenoxyacetic acid, dichlorobiphenyl, HCB, endosulfan, aldrin, profenofos, carbofuran, lindane, g-chlordane, dichlorvos (DDVP), heptachlor, glyphosate, t-Nonachlor and biphenyl were the different pesticide residues detected in the six tubers studied. Aldrin was observed in all the samples studied; the highest amounts were detected in potato (0.1161 ± 0.00 μg/m^3) and cocoyam (0.0779 ± 0.000μg/m^3), followed by carrot (0.0711 ± 0.00μg/m^3), cassava (0.0617 ± 0.00 μg/m^3), water yam (0.0580 ± 0.00 μg/m^3) and then yam (0.0004 ± 0.00 μg/m^3). Similarly, DDVP was found in every sample studied, with the maximum concentration observed in cassava (0.5208 ± 0.00), potato (0.3635 ± 0.05 μg/m^3), followed by carrot (0.3632 ± 0.06), yam (0.1334 ± 0.04) μg/m^3, cocoyam (0.0683 ± 0.00 μg/m^3) and then water yam (0.0562 ± 0.00μg/m^3). Endosulfan (0.2500 ± 0.01 μg/m^3), lindane (0.0914 ± 0.01μg/m^3), g-chlordane (0.0000 ± 0.120 μg/m^3), biphenyl (0.9228 ± 0.00 μg/m^3), 2,4-dichloro phenoxy acetic acid (0.1127 ± 0.00 μg/m^3), HCB (0.1018 ± 0.00 μg/m^3), profenofos (0.2138 ± 0.00 μg/m^3), glyphosate (0.1876 ± 0.00 μg/m^3) and t-Nonachlor (0.1084 ± 0.001 μg/m^3) were detected only in cocoyam. Furthermore, cassava contained 0.0431 ± 0.00 μg/m^3 2,4-dichlorophenoxyacetic acid, 0.1596 ± 0.00 μg/m^3 HCB, 0.1693 ± 0.00 μg/m^3 p'p'-DDD, 0.1476 ± 0.00 μg/m^3 profenofos and 0.0988 ± 0.00 μg/m^3 glyphosate. Also, 0.1285 ± 0.00,

Table 1: Heavy metals and their maximum permissible limits with regulator references

Parameter	Cassava	Yam	Cocoyam	Potato	Water yam	Carrot	MPL	MPL reference
Nickel (mg/kg)	0.012 ± 0.00^A	0.006 ± 0.00^A	0.009 ± 0.00^A	0.006 ± 0.00^A	0.007 ± 0.00^A	0.001 ± 0.00^A	0.10 mg/kg^B	US Environmental Protection Agency[28], Wani et al.[29]
Chromium (mg/kg)	0.083 ± 0.00^A	0.010 ± 0.00^A	0.093 ± 0.00^A	0.073 ± 0.00^A	0.078 ± 0.00^A	0.016 ± 0.00^A	0.10 mg/kg^B	US Environmental Protection Agency[28], Food and Agriculture Organization / World Health Organization[30]
Cobalt (mg/kg)	0.011 ± 0.00^A	0.036 ± 0.00^B	0.026 ± 0.00^A	0.002 ± 0.00^A	0.016 ± 0.00^A	0.010 ± 0.00^A	0.043 mg/kg^B	Institute of Medicine (US) Panel on Micronutrients[31]
Arsenic (mg/kg)	0.045 ± 0.00^A	0.010 ± 0.00^A	0.049 ± 0.00^A	0.056 ± 0.00^A	0.037 ± 0.00^A	0.019 ± 0.00^A	1.4 mg/kg^B	Food and Agriculture Organization / World Health Organization[30], Institute of Medicine (US) Panel on Micronutrients[31]
Manganese (mg/kg)	0.138 ± 0.00^A	0.571 ± 0.00^A	0.172 ± 0.00^A	0.750 ± 0.09^A	0.838 ± 0.11^A	0.516 ± 0.10^A	2.0 mg/kg^B	Onianwa et al.[19], US Environmental Protection Agency[28]
Cadmium (mg/kg)	0.00 ± 0.00^A	0.00 ± 0.00^A	0.00 ± 0.00^A	0.00 ± 0.00^A	0.00 ± 0.00^A	0.00 ± 0.00^A	0.3 mg/kg^B	Food and Agriculture Organization / World Health Organization[30], Institute of Medicine (US) Panel on Micronutrients[31]
Lead (mg/kg)	0.00 ± 0.00^A	0.00 ± 0.00^A	0.00 ± 0.00^A	0.032 ± 0.00^A	0.00 ± 0.00^A	0.028 ± 0.00^A	1.0 mg/kg^A	Food and Agriculture Organization / World Health Organization[30], Institute of Medicine (US) Panel on Micronutrients[31]
Mercury (mg/kg)	0.00 ± 0.00^A	0.00 ± 0.00^A	0.658 ± 0.02^B	0.153 ± 0.00^A	0.00 ± 0.00^A	0.404 ± 0.00^A	0.5 mg/kg^B	US Environmental Protection Agency[28], Institute of Medicine (US) Panel on Micronutrients[31]

The values were triplicate determinations. Values with various superscripts (uppercase [A–D]) are statistically significant ($p < 0.05$) in comparison to the uppermost allowable limits; mean standard error (SE).

Table 2: Pesticide residue concentration (μg/m³) in cassava, yam, cocoyam, potato, water yam and carrot

Parameter	Cassava	Yam	Cocoyam	Potato	Water yam	Carrot	Maximum permissible limit (MPL)	MPL reference
2,4-dichlorophenoxy acetic acid (μg/m³)	0.0431 ± 0.00	0.1285 ± 0.00	0.1127 ± 0.00	BDL	0.0527 ± 0.00	0.0957 ± 0.00		
HCB (μg/m³)	0.1596 ± 0.00	0.0799 ± 0.06	0.1018 ± 0.09	0.1415 ± 0.00	0.0000 ± 0.00	BDL	0.002 mg/m³	Opaluwa et al.[32]
Aldrin (μg/m³)	0.0617 ± 0.00	0.0004 ± 0.00	0.0779 ± 0.00	0.1161 ± 0.00	0.0580 ± 0.00	0.0711 ± 0.00	0.25 mg/m³	Zamora[33]
p'p-DDD (μg/m³)	0.1693 ± 0.00	0.0732 ± 0.00	BDL	BDL	0.0002 ± 0.00	0.1603 ± 0.00		
Profenofos (μg/m³)	0.1476 ± 0.00	0.0000 ± 0.00	0.2138 ± 0.05	0.0817 ± 0.00	BDL	0.0011 ± 0.00	0.25 mg/m³	FAO/WHO[34]
Glyphosate (μg/m³)	0.0988 ± 0.00	0.1098 ± 0.00	0.1876 ± 0.00	0.3130 ± 0.06	BDL	0.1039 ± 0.09		
Dichlorovos (DDVP) (μg/m³)	0.5208 ± 0.00	0.1334 ± 0.04	0.0683 ± 0.00	0.3635 ± 0.05	0.0562 ± 0.00	0.3632 ± 0.06	1.0 mg/m³	International Food Standards/Codex Alimentarius FAO/WHO[35]
Endosulfan (μg/m³)	BDL	BDL	0.2500 ± 0.01	0.3265 ± 0.08	BDL	BDL	0.10 mg/m³	FAO/WHO[34]
Lindane (μg/m³)	BDL	BDL	0.0914 ± 0.01	BDL	BDL	0.0015 ± 0.07	0.50 mg/m³	FAO/WHO[34]
g-chlordane (μg/m³)	BDL	BDL	0.000 ± 0.00	0.0000 ± 0.00	BDL	BDL	0.0020 mg/L	International Food Standards/Codex Alimentarius FAO/WHO[36]
Biphenyl (μg/m³)	BDL	BDL	0.9228 ± 0.20	0.7418 ± 0.00	0.2472 ± 0.00	1.1842 ± 0.44	1.30 mg/m³	FAO/WHO[34]
t-Nonachlor (μg/m³)	BDL	BDL	0.1084 ± 0.06	0.0000 ± 0.00	BDL	BDL	0.040 mg/m³	International Programme on Chemical Safety (IPCS)[37]
Dichlorobiphenyl (μg/m³)	BDL	BDL	BDL	0.1653 ± 0.02	BDL	BDL	0.10 mg/m³	Singh[38]
Carbofuran (μg/m³)	BDL	BDL	BDL	0.2688 ± 0.08	0.1256 ± 0.05	BDL	NA	
Heptachlor (μg/m³)	BDL	BDL	BDL	BDL	BDL	0.0867 ± 0.00	0.050 mg/m³	FAO/WHO[34]

BDL, below detectable limit

0.799 ± 0.00, 0.0732 ± 0.00, 0.0000 ± 0.00 and 0.1098 ± 0.00 μg/m³ were the concentrations of 2,4-dichlorophenoxyacetic acid, HCB, p'p'-DDD, profenofos and glyphosate detected in yam, as shown in Table 2. For potato, 2,4-dichloro and p'p'-DDD were not detected, HCB (0.1415 ± 0.00 μg/m³), profenofos (0.3130 ± 0.00 μg/m³), glyphosate (0.3130 ± 0.00 μg/m³), endosulfan (0.3265 ± 0.08 μg/m³), biphenyl (0.7418 ± 0.00 μg/m³) and dichlorobiphenyl (0.1653 ± 0.02 μg/m³) were detected. Lindane, g-chlordane, t-Nonachlor, carbofuran and heptachlor were also not detected in the sample, as shown in Table 2. Subsequently, 2,4-dichlorophenoxyacetic acid, HCB, p' p'-DDD, profenofos and glyphosate were detected in water yam as 0.0527 ± 0.00, 0.0000 ± 0.00, 0.0002 ± 0.00, 0.0000 ± 0.00 and 0.0000 ± 0.00 μg/m³, respectively. Biphenyl and carbofuran concentrations were 0.2472 ± 0.00 and 0.1256 ± 0.05 μg/m³, respectively. Some pesticide residues found in potatoes include 2,4-dichloro (0.0957 ± 0.00 μg/m³), HCB (0.0000 ± 0.00 μg/m³), p'p'-DDD (0.1603 ± 0.00 μg/m³), profenofos (0.0011 ± 0.00 μg/m³), glyphosate (0.1039 ± 0.00 μg/m³), lindane (0.0015 ± 0.00 μg/m³), biphenyl (1.1842 ± 0.00 μg/m³) and heptachlor (0.0867 ± 0.00 μg/m³). The chemical abstract service (CAS) numbers of some of the pesticide residues tested are listed in Supplementary table 1.

Discussion

Currently, due to the advances in crop production and cultivated food crops, there is an increase in the pollution of heavy metals and chemical residues. Thus, there is a need for continuous evaluation of their presence and concentration to aid in mitigating or preventing any public health issues that could occur as a result.

Several heavy metals, including nickel, lead, cobalt, arsenic, manganese, chromium, cadmium and mercury, were detected in the six samples (cassava, yam, cocoyam, potato, water yam and carrot) using atomic absorption spectroscopy and efficient techniques. The levels of Co in yam did not differ significantly from one another (0.036 ± 0.00 mg/kg) and from the MPL (0.043 mg/kg) established by the US Food and Nutrition Board (2004).

Although Ni was present at varying concentrations in the samples, its concentration was below the MPLs (100 μg/L) as stipulated by the US Environmental Protection Agency and, thus, may not pose any serious health challenges to consumers, such as skin allergies and lung cancer, which are signs of Ni toxicity manifestation. A higher concentration of Ni residue (0.93–0.179 mg/kg) in tubers has been reported by Onianwa et al.[19]. Ni occurs naturally as part of different mineral complexes, with its deficiency in the human system causing retardation of intra-uterine development and reduced iron reabsorption.[20] The highest Co intake in humans occurs through diet. Co has been detected in okra, as reported by Orisakwe et al.[21]

One of the major sources of As in the environment is arsenic-rich fertilisers[36], which are released when applied. Previous researchers have shown high heavy metal accumulation in leafy vegetables.[31] The MPL for Cd is 0.3 mg/kg as set by the FAO/WHO (2006). It has been detected in different food materials such as cassava, yam[15] and cereals. Onianwa

Table 3: The maximum permissible exposure limits (MPLs) of all the pesticide residues based on the US and Canadian country databases

Component	Minimum permissible limits	Institutional body	Reference
Dichlorobiphenyl (also considered among 'polychlorinated biphenyls')	0.1 mg/m³	US Department of Health and Human Services (DHHS), US National Institute for Occupational Safety and Health	Centers for Disease Control and Prevention[39]
HCB (hexachlorobenzene)	0.002 mg/m³	United States OSHA PEL	US Department of Labour[40]
Endosulfan	0.1 mg/m³	California Department of Industrial Relations	Permissible Exposure Limits for Chemical Contaminants[41]
Aldrin	0.25 mg/m³	California Department of Industrial Relations	Permissible Exposure Limits for Chemical Contaminants[41]
Profenofos	0.25 mg/m³	US National Institute for Occupational Safety and Health	The National Institute for Occupational Safety and Health (NIOSH)[42]
DDT	0.5 mg/m³	New Jersey Department of Health and Senior Services	New Jersey Department of Health and Senior Services[43]
Lindane	0.5 mg/m³	California Department of Industrial Relations	Permissible Exposure Limits for Chemical Contaminants[41]
g-Chlordane	0.5 mg/m³	California Department of Industrial Relations	Permissible Exposure Limits for Chemical Contaminants[41]
	0.002 mg/L	U.S. Environmental Protection Agency	US Environmental Protection Agency[44]
Dichlorvos (DDVP)	1 mg/m³	California Department of Industrial Relations	Permissible Exposure Limits for Chemical Contaminants[41]
Heptachlor	0.05 mg/m³	California Department of Industrial Relations	Permissible Exposure Limits for Chemical Contaminants[41]
t-Nonachlor	0.04 mg/kg	Canadian Health Measures Survey	Canadian Health Measures Survey[45]

et al.[19] reported Cd concentrations of 0.03–0.28 mg/kg in tubers. Also, Commission Regulation (EC) No 1881/2006[46] reported the presence of Cd in rice. Due to its slow excretory rate, high Cd levels threaten human health and could damage the kidneys and liver.[46]

Pb is made available to the environment through lead-containing pipes, combustion of leaded gasoline and the use of lead-based paint.[30] Lead is known to affect the cardiovascular, nervous, skeletal, muscular and immune systems, and causes gastrointestinal symptoms and organ damage when ingested or from prolonged exposure.[30] The maximum exposure permissible limits of some pesticide residues established by international regulators are shown in Table 3.

The concentration of HCB was greater than the MPL (0.002 mg/m³) reported by OSHA, the US government's workplace safety and health authority. The concentrations of aldrin and profenofos were below the MPL, as reported by FAO/WHO. The pesticide residual amounts in the tests were lower than the permitted exposure level specified by international organisations such as WHO/FAO, the US Environmental Protection Agency and CDIR. However, care should be taken when consuming these food tubers, as prolonged consumption could lead to their bioaccumulation in the body of organisms.

A similar study by Lien et al.[47] reported high concentrations of organochlorine residues in yam. Some pesticide residues are highly persistent in the environment.[47] Oyinloye et al.[48] also detected different concentrations of aldrin, carbofuran, endosulfan and profenofos in *T. occidentalis.* There are many risks associated with pesticide residue exposure, including effects on human health; thus, concentrations of these residues in food samples should be monitored regularly.

Increased d-glutaric acid metabolism and allergic reactions/skin rashes have both been linked to aldrin and lindane.[15] Aldrin, heptachlor, endosulfan and dieldrin were some of the pesticide residues that were detected by Njoku et al.[49] Jayaraj et al.[50] reported some adverse effects of aldrin, heptachlor and lindane, including neurotoxic effects. This could be why the Nigerian government prohibits their use.

Conclusions

Using AAS and GC–MS, we assessed the levels of heavy metals and pesticide residues in regularly grown tuber crops in Nigeria. In all the samples, 13 different pesticide residues were found. In every sample examined, the Cd concentration was below the threshold for detection.

Similarly, Pb and Hg were below the detectable concentration in cassava, yam and cocoyam. Other heavy metals present were lower than the MPLs established by standard organisations. Aldrin and dichlorvos (DDVP) were present in all the samples, with cassava having the highest concentration. Almost all the pesticide residues were detected in cocoyam, potato and carrot. Thus, there should be continuous monitoring of these staple foods to ensure their consumption does not predispose the consumer to heavy metal toxicities, as continuous consumption could potentially threaten people's health.

Competing interests

We have no competing interests to declare.

Authors' contributions

K.O.O.: Conceptualisation and resources, project administration, writing – original draft, supervision. B.O.E.: Formal analysis, investigation, writing – revision and editing, data curation. S.O.O.: Conceptualisation and resources, supervision, writing – revision and editing, validation. All the authors read and approved the final version of the manuscript.

References

1. Hakeem KR, Akhtar MS, Abdullah SNA. Plant, soil, and microbes: Implications in crop science. Cham: Springer; 2016. https://doi.org/10.1007/978-3-319-27455-3

2. Pathak VM, Verma VK, Rawat BS, Kaur B, Babu N, Sharma A, et al. Current status of pesticide effects on environment, human health and its eco-friendly management as bioremediation: A comprehensive review. Front Microbiol. 2022;13:1–29. https://doi.org/10.3389/fmicb.2022.962619

3. Navish K, Amit KC, Garg VK, Parmod K. Sequestration of heavy metals from contaminated water using magnetic carbon nanocomposites. J Hazard Mater Adv. 2022;6, Art. #100066. https://doi.org/10.1016/j.hazadv.2022.100066

4. Carver A, Gallicchio VS. Heavy metals and cancer. In: Astroshi F, editor. Cancer causing substances. London: InTech; 2018. p. 1–18. https://doi.org/10.5772/intechopen.70348

5. Chen P, Bornhorst J, Aschner M. Manganese metabolism in humans. Front Biosci. 2018;23(9):1655–1679. https://doi.org/10.2741/4665

6. Zheng N, Liu J, Wang Q, Liang Z. Health risk assessment of heavy metal exposure to street dust in the zinc smelting district, Northeast of China. Sci Total Environ. 2010;408(4):726–733. https://doi.org/10.1016/j.scitotenv.2009.10.075

7. Ahmad JU, Goni MA. Heavy metal contamination in water, soil, and vegetables of the industrial areas in Dhaka, Bangladesh. Environ Monit Assess. 2010;166(1–4):347–357. https://doi.org/10.1007/s10661-009-1006-6

8. Peprah BB, Parkes EY, Harrison OA, van Biljon A, Steiner-Asiedu M, Labuschagne MT. Proximate composition, cyanide content, and carotenoid retention after boiling of provitamin a-rich cassava grown in Ghana. Foods. 2020;9(12), Art. #1800. https://doi.org/10.3390/foods9121800

9. Montagnac JA, Davis CR, Tanumihardjo SA. Nutritional value of cassava for use as a staple food and recent advances for improvement. Compr Rev Food Sci Food Saf. 2009;8(3):181–194. https://doi.org/10.1111/j.1541-4337.2009.00077.x

10. Ferraro V, Piccirillo C, Tomlins K, Pintado ME. Cassava (*Manihot esculenta* Crantz) and yam (*Dioscorea* spp.) crops and their derived foodstuffs: Safety, security and nutritional value. Crit Rev Food Sci Nutr. 2016;56(16):2714–2727. https://doi.org/10.1080/10408398.2014.922045

11. Hagenimana V, K'osambo LM, Carey EE. Potential of sweet potato in reducing vitamin A deficiency in Africa. In: Impact on a changing world. Program report 1997–1998. Lima: International Potato Center; 2010. Available from: https://www.sweetpotatoknowledge.org/files/potential-of-sweetpotato-in-reducing-vitamin-a-deficiency-in-africa/

12. De Vries-Ten Have J, Owolabi A, Steijns J, Kudla U, Melse-Boonstra A. Protein intake adequacy among Nigerian infants, children, adolescents and women and protein quality of commonly consumed foods. Nutr Res Rev. 2020;33(1):102–120. https://doi.org/10.1017/s0954422419000222

13. Tudi M, Ruan HD, Wang L, Lyu J, Sadler R, Connell D, et al. Agriculture development, pesticide application and its impact on the environment. Int J Environ Res Public Health. 2021;18(1112):1–23. https://doi.org/10.3390/ijerph18031112

14. Biose E, Amaechi CF, Ahator F. Heavy metal contents of some common tubers sold in Benin metropolis, Benin City, Nigeria. FUTY J Environ. 2020;14(3):84–95. https://doi.org/10.4314/jasem.v25i2.6

15. Omeje KO, Ezema BO, Okonkwo F, Onyishi NC, Ozioko J, Rasaq WA, et al. Quantification of heavy metals and pesticide residues in widely consumed Nigerian food crops using atomic absorption spectroscopy (AAS) and gas chromatography (GC). Toxins. 2021;13(12), Art. #870. https://doi.org/10.3390/toxins13120870

16. Adeyeye A, Osibanjo O. Residues of organochlorine pesticides in fruits, vegetables and tubers from Nigerian markets. Sci Total Environ. 1999;231(2–3):227–233. https://doi.org/10.1016/s0048-9697(99)00067-4

17. Nworu J, Author C, Sunday J. Heavy metal concentrations in yam and cassava tubers from Enyigba lead-zinc mining site in South Eastern Nigeria. IOSR J App Chem. 2019;11(10):39–43.

18. Oti Wilberforce JO, Nwabue FI. Uptake of heavy metals by *Dioscorea rotundata* (white yam) and *Ipomoea batatas* (sweet potato) from Enyigba lead-zinc derelict. Environ Pollut. 2013;2(2):79–84. https://doi.org/10.5539/ep.v2n2p79

19. Onianwa PC, Lawal JA, Ogunkeye AA, Orejimi BM. Cadmium and nickel composition of Nigerian foods. J Food Compos Anal. 2000;13(6):961–969. https://doi.org/10.1006/jfca.2000.0944

20. Akinyele IO, Shokunbi OS. Concentrations of Mn, Fe, Cu, Zn, Cr, Cd, Pb, Ni in selected Nigerian tubers, legumes and cereals and estimates of the adult daily intakes. Food Chem. 2015;173:702–708. https://dx.doi.org/10.1016/j.foodchem.2014.10.098

21. Orisakwe OE, Nduka JK, Amadi CN, Dike DO, Bede O. Heavy metals health risk assessment for population via consumption of food crops and fruits in Owerri, South Eastern, Nigeria. Chem Cent J. 2012;6(1):1. https://doi.org/10.1186/1752-153x-6-77

22. AOAC. Association of official analytical Chemists official methods of analysis. 18th ed. Gaithersburg, MD: AOAC International; 2007.

23. Quarcoo A. Adotey G.Determination of heavy metals in *Pleurotus ostreatus* (oyster mushroom) and *Termitomyces clypeatus* (termite mushroom) sold on selected markets in Accra, Ghana. Mycosphere. 2013;4:960–967. https://doi.org/10.5943/mycosphere/4/5/9

24. Leyssens L, Vinck B, Van Der Straeten C, Wuyts F, Maes L. Cobalt toxicity in humans – A review of the potential sources and systemic health effects. Toxicology. 2017;387:43–56. https://dx.doi.org/10.1016/j.tox.2017.05.015

25. Sanou A, Méité N, Kouyaté A, Irankunda E, Kouamé A, Koffi A, et al. Assessing levels and health risks of fluoride and heavy metal contamination in drinking water. J Geosci Environs Prot. 2022;10:15–34. https://doi.org/10.4236/gep.2022.1011002

26. Okpala COR, Sardo G, Vitale S, Bono G, Arukwe A. Hazardous properties and toxicological update of mercury: From fish food to human health safety perspective. Crit Rev Food Sci Nutr. 2018;58(12):1986–2001. https://doi.org/10.1080/10408398.2017.1291491

27. Howlet JF, Kirkpatrick DC, Kojima K, Meyland I, Modderman JP, Blumenthal H, et al. Evaluation of certain food additives and contaminants. World Health Organ Tech Rep Ser. 1989;(776):7–64.

28. US Environmental Protection Agency. Toxicological review of trivalent chromium; CAS No. 16065-83-1 [document on the Internet]. c1998 [cited 2023 Jan 10]. Available from: https://iris.epa.gov/static/pdfs/0028tr.pdf

29. Wani AB, Wani L, Anjum ARA, Usmani JA. Lead toxicity: A review. Interdiscip Toxicol. 2015;8:55–64. https://doi.org/10.1515/intox-2015-0009

30. Food and Agriculture Organization/World Health Organization. Joint FAO/WHO Expert Committee on Food Additives. Evaluation of certain additives and contaminants [document on the Internet). c2011 [cited 2023 Jan 10]. Available from: https://www.who.int/publications/i/item/9789241209601

31. Institute of Medicine (US) Panel on Micronutrients. Dietary reference intakes for vitamin A, vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium, and zinc. Washington DC: National Academies Press (US); 2001. Available from: https://www.ncbi.nlm.nih.gov/books/NBK222310/

32. Opaluwa OD, Aremu MO, Ogbo LO, Abiola KA, Odiba IE, Abubakar MM, et al. Heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia metropolis, Nasarawa state, Nigeria. Adv Appl Sci Res. 2012;3:780–784. https://doi.org/10.12944/cwe.7.2.04

33. Zamora EU. Hexachlorobenzene. In: Encyclopedia of toxicology. 2nd ed. Amsterdam: Elsevier; 2005. p. 511–513. https://doi.org/10.1016/B0-12-369400-0/00484-1

34. FAO/WHO. Joint meeting on pesticide residues [webpage on the Internet]. c2022 [cited 2022 Nov 23]. Available from: https://www.who.int/publications/i/item/9789240069602

35. International Food Standards/Codex Alimentarius FAO/WHO. Pesticides database search: Profenofos [webpage on the Internet]. No date [cited 2022 Dec 23]. Available from: https://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/pesticide-detail/en/?p_id=171

36. International Food Standards/Codex Alimentarius FAO/WHO. All standards [webpage on the Internet]. No date [cited 2022 Dec 23]. Available from: https://www.fao.org/fao-who-codexalimentarius/codex-texts/all-standards/en/

37. International Labour Organization. International Programme on Chemical Safety (IPCS) [webpage on the Internet]. c2009 [cited 2022 Dec 23]. Available from: https://www.ilo.org/global/topics/safety-and-health-at-work/resources-library/WCMS_111391/lang--en/index.htm

38. Singh K. Human health risks of persistent organic pollutant exposures in the Canadian Arctic [PhD thesis]. Ottawa: University of Ottawa; 2018. p. 236.

39. US Centers for Disease Control and Prevention. The National Institute for Occupational Safety and Health (NIOSH) [homepage on the Internet]. Available from: https://www.cdc.gov/niosh/index.htm

40. US Department of Labour Occupational Safety and Health Administration. OSHA Occupational Chemical Database: Hexachlorobenzene [webpage on the Internet]. No date [updated 2020; cited 2023 Jan 09]. Available from: https://www.osha.gov/chemicaldata/146

41. State of California Department Industrial Relations. Permissible exposure limits for chemical contaminants [webpage on the Internet]. No date [cited 2023 Jan 09]. Available from: https://www.dir.ca.gov/title8/5155table_ac1.html

42. The National Institute for Occupational Safety and Health (NIOSH) [homepage on the Internet]. No date [cited 2023 Jan 09]. Available from: https://www.usa.gov/agencies/national-institute-of-occupational-safety-and-health

43. New Jersey Department of Health and Senior Services. Hazardous substance fact sheet [document on the Internet]. c1996 [updated 2002; cited 2023 Jan 09]. Available from: https://nj.gov/health/eoh/rtkweb/documents/fs/0596.pdf

44. US Environmental Protection Agency [homepage on the Internet]. No date [cited 2023 Jan 09]. Available from: https://www.epa.gov/

45. Canadian Health Measures Survey. Statistic Canada [webpage on the Internet]. No date [cited 2023 Jan 09]. Available from: https://www.statcan.gc.ca/en/survey/household/5071

46. Commission Regulation (EC) No 1881/2006. Setting maximum levels for certain contaminants in foodstuffs; Official Journal of the European Union. Brussels: European Union; 2006. Available from: https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:364:0005:0024:EN:PDF

47. Lien KW, Pan MH, Ling MP. Levels of heavy metal cadmium in rice (*Oryza sativa* L.) produced in Taiwan and probabilistic risk assessment for the Taiwanese population. Environ Sci Pollut Res Int. 2021;28(22):28381–28390. https://doi.org/10.1007/s11356-020-11902-w

48. Oyinloye JA, Oyekunle JAO, Ogunfowokan AO, Msagati T, Adekunle AS, Nety SS. Human health risk assessments of organochlorine pesticides in some food crops from Esa-Oke farm settlement, Osun State, Nigeria. Heliyon. 2021;7(7), e07470. https://doi.org/10.1016/j.heliyon.2021.e07470

49. Njoku KL, Ezeh CV, Obidi FO, Akinola MO. Assessment of pesticide residue levels in vegetables sold in some markets in Lagos State. Nigeria. Nig J Biotechnol. 2017;32(1):53. https://doi.org/10.4314/njb.v32i1.8

50. Jayaraj R, Megha P, Sreedev P. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. Interdiscip Toxicol. 2016;9(3–4):90–100. https://doi.org/10.1515/intox-2016-0012