INVESTIGATION INTO THE PESTICIDES RESIDUES IN SESAME, MILLET, RICE, AND GUINEA CORN GROWN AROUND THE HADEJIA-KOMADUGU-YOBE RIVER AREA IN YOBE STATE, NIGERIA.

S A Shettima¹*, A M Gashinge¹, A A Baffa¹, A K Akinlabi², A S Abdulkadir³

¹Chemistry Department, Federal University Gashua, Yobe State, Nigeria.
²Chemistry Department, Federal University of Agriculture, Abeokuta, Ogun State, Nigeria
³Environmental Toxicology Department, Southern University and A&M College, Baton Rouge, Louisiana, USA

*Corresponding Author’s email: saidusa1961@gmail.com, Tel: +2348035054474

ABSTRACT

Application of pesticides during crop production often results in pesticide residue, a significant source of heavy metals in the harvested crops. This raises concern for consumers' health due to the potentially deleterious effects of pesticides on animals, particularly humans. This study examined the levels of pesticide residues using a gas chromatography-mass spectrometry (GC-MS) system and heavy metal elements concentration using Atomic Absorption Spectrometry (AAS) in four food crops (Sesame, Millet, Rice, and Guinea corn) cultivated in (Gwio-Kura) Gashua and Hadejia towns in Nigeria. The results disclosed that Sesame was the only crop with Dichlorvos from both Gashua and Hadejia, surpassing the WHO's limit for pesticide residue concentrations, and that the Hadejia samples had higher levels than the Gashua samples. The study also detected traces of Cadmium (Cd), Lead (Pb), Nickel (Ni), and Manganese (Mn) in the crops, but they were below the permissible intake levels established by FAO/WHO. However, Arsenic (As) and Chromium (Cr) exceeded the FAO/WHO limits and may entail serious health problems such as kidney damage and cancer. Mercury (Hg) was not detected in any of the crops. Our findings suggest health authorities monitor and regulate heavy elements intake in food crops, especially those with high toxic contamination, to prevent adverse health effects such as the kidney disease on humans and animals, currently prevalent in the area.

Keywords: Sesame, Millet, Rice, Guinea corn, Pesticides, AAS, LCMS

INTRODUCTION

Pesticides are chemical compounds that confer protection to crops from biotic stressors such as insects, weeds, fungi, and bacteria. Consequently, pesticides can augment crop productivity and food security, albeit with potentially detrimental effects on human health and the environment. The application of a pesticide to a target pest entails the exposure of the entire site, encompassing crop plants, soil organisms, and possibly humans and wildlife in the vicinity. Pesticide residues are the trace amounts of pesticides that persist on or in food subsequent to harvesting and processing [1]. The presence of pesticide residues in food can elicit acute or chronic health effects, contingent on the nature, magnitude, and route of exposure. The environmental dispersion of pesticide residues
and the ensuing mortality of various nonhuman biotic entities, such as bees, birds, amphibians, fish, and small mammals, have been substantiated in several studies [2–4]. The seminal work of Rachel Carson in 1962 explicated the behaviour of these chemicals in the environment, their cycling and fate, and their toxicity to biota. It revealed how local utilization of synthetic chemicals for crop protection was engendering contamination not only at the local scale but also at the global scale [5].

Pesticides are also very important sources of Heavy metals [6], naturally occurring elements with high atomic weight and density [7]. Some heavy metals, such as Arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), manganese (Mn), and mercury (Hg), are of particular concern for human health and the environment because of their toxicity, persistence, and bioaccumulation potential. The occurrence of pesticide residues in food can induce acute or chronic health effects, depending on the nature, magnitude, and route of exposure. Hence, the early reports and structured incident reporting systems facilitated the establishment of regulatory frameworks for pesticide applications, encompassing the dosage of chemicals and the optimal periods of application [8,9]. Therefore, it is imperative to monitor and regulate the concentrations of pesticide residues in food to ensure food safety and safeguard public health.

Sesame, millet, Rice, and guinea corn are staple crops extensively cultivated and consumed in Nigeria. These crops are also subjected to intensive pesticide application to control various pests and diseases. However, there is scarce information on the levels and types of pesticide residues in these crops and their potential health impacts on consumers. Moreover, there is mounting concern about the plausible link between pesticide exposure and the high incidence of kidney disease and other related ailments in some regions of Nigeria, especially around the Hadejia-Komadugu-Yobe river basin. This region is characterized by intensive agricultural activities, irrigation schemes, and frequent flooding events that may influence the environment's fate and transport of pesticides. Some of the commonly used pesticides in this area are Dichlorvos, lindane, diazinon, methomyl, and paraquat dichloride. These pesticides belong to different classes and have different modes of action and toxicity profiles. However, they all have the potential to cause adverse effects on human health if ingested or absorbed through the skin or respiratory tract.

A similar study [10] conducted around the same area on some vegetables (spinach and lettuce) using HPLC indicated appreciable presence in the samples studied.

The FAO/WHO has expressed concern over the intake of heavy metals and pesticide residues in food because of their potential adverse effects on human health. Some health effects associated with heavy metals include neurotoxicity, nephrotoxicity, hepatotoxicity, immunotoxicity, carcinogenicity, genotoxicity, reproductive toxicity, developmental toxicity, and endocrine disruption [11]. While acute poisoning, chronic toxicity, neurotoxicity, carcinogenicity, genotoxicity, reproductive toxicity, developmental toxicity, endocrine disruption,
and immunotoxicity are common health effects associated with pesticides [12]. The health effects of heavy metals and pesticides depend on several factors, such as the type, dose, duration, frequency, and route of exposure; the age, gender, genetic susceptibility, nutritional status, and health status of the exposed individual; and the interactions among different contaminants [13].

This study investigated the pesticide residues in Sesame, Millet, Rice, and Guinea corn grown in Hadejia and Gashua towns around the Hadejia-Komadugu-Yobe river area in Yobe state, Nigeria. Identification and quantification of the pesticide residues were carried out using gas chromatography-mass spectrometry (GC-MS) while Atomic Adsorption Spectrometer (AAS) was used to determine the heavy metals, including Cadmium (Cd), Lead (Pb), Nickel (Ni), and Manganese (Mn) in the crops. This study will provide valuable information for policymakers, regulators, farmers, consumers, and researchers on the current status of pesticide residues in food crops and their implications for human health and food security in Nigeria, particularly whether a correlation exists between these toxins and the prevalence of kidney disease in the area.

**MATERIAL AND METHODS**

The equipment and instruments used in this study were all calibrated to check their status in the middle of the experiments. Apparatus such as volumetric flask and measuring cylinder were thoroughly washed with detergents and tap water, then rinsed with deionized water. All glassware were cleaned with about 10% concentrated Nitric acid (HNO₃) to clear out solution contamination on their surfaces and rinsed with distilled water.

**Reagents and chemicals**

The reagents and chemicals used for the laboratory works were all analytical grade; deionized water (chemically pure with conductivity 1.5 s/cm and below) was prepared in the university chemistry laboratory and used for dilution of the sample and preparation of intermediate metal standard solutions prior to analysis and also rinsing glass wares and sample bottles.

**Standard working solution**

100ppm was prepared as a working solution from the 1000ppm already prepared. A simple dilution formula \( C_1V_1 = C_2V_2 \) was used to calculate the volume of the stock solution to be diluted to the new desired concentration. 1mL of concentrated HNO₃ was added to each working standard and finally diluted to the desired volume with deionized water.

**Determination of Elements using Atomic Absorption Spectrometry**

**Preparation of Calibrated Curve**

Calibration curves were prepared to determine the concentration of the metals in the sample solution [13]. The instrument was calibrated using a series of working standards. The working standards of solutions of each metal were prepared from standard solutions of their respective metals, and their absorbance taken
A calibration curve for each metal ion to be analysed was prepared by plotting the absorbance as a function of metal ion standard concentration.

**Determination of Elements in the Samples**

The metal ions’ concentration in the samples was determined by reading their absorbance using AAS (Buck scientific model 210GP) and comparing it to the respective calibration curve. Three replicate determinations were carried out on each sample. The metals were determined by absorption/concentration mode, and the instrument readout was recorded for each solution manually. The same analytical procedure was employed to determine elements in digested blank solutions and the picked samples.

**Study Area**

The study was conducted in two different locations of Gwio Kura, located at latitude 12° 4029.24N and longitude 11° 040.84E, near Gashua in Yobe State, Nigeria, and Hadejia, situated at latitude 12°272.18N and longitude 10°225.47E in Jigawa State, Nigeria.

**Sample Collection**

The samples were collected from two different farmlands in the study areas during harvest in clean and labeled polythene bags for further analysis in the laboratory.

**Sample Preparation And Treatment**

The samples were allowed to dry under natural shade and then ground into a fine powder using a porcelain mortar and pestle. The grounded samples were kept in zip lip bags before digestion.

**Extraction of Samples for Determination of Pesticides**

The extraction of pesticides from Sesame, Millet, Rice, and Guinea corn samples was performed using a modified QuEChERS (quick, easy, cheap, effective, rugged, and safe) method [14,15]. Five grams (5.0 g) of each powdered sample were accurately weighed in a 50 ml Teflon vessel, and 20 ml of acetonitrile were added. The samples were sonicated for 20 min using an ultrasonicator and then centrifuged for 20 min at 6,000 rpm. The supernatants were transferred to separate vessels and mixed with 10 ml each of petroleum ether and dichloromethane. The mixtures were allowed to stand for 5 min and then filtered through a funnel containing 5.0 g of anhydrous sodium sulfate and activated charcoal each. The filtrates were collected in clean Teflon vessels and stored for further analysis [16].

**Digestion Of Samples**

0.5g of samples (Sesame, Millet, Rice, or Guinea corn) were weighed into a thoroughly washed plastic container (microwave tube), and 4 ml of HNO₃: HCl (3:1) was added and allowed to stand for a while. The plastic container was then covered, placed into a microwave digester, and digested. The digestion was carried out at 95°C for 40 mins, followed by cooling at room temperature in the microwave digester. The cooled sample solution was filtered using Whatman (No.1) filter paper into a 50 ml volumetric flask and diluted to a 25 ml mark with
distilled water. The trace element content of the samples was determined using Colorimeter (BUCK SCI.210 VGP USA).

**Pesticides Analysis Using Gas Chromatography-Mass Spectrometry**

The analysis of pesticides was performed using a gas chromatography-mass spectrometry (GC-MS) system consisting of an Agilent 7890B gas chromatograph, a 5977A mass selective detector, and an HP-5MS analytical column (30 m x 0.25 mm). The data acquisition and processing were carried out using a mass hunter GC-MS solution software. The column oven temperature was initially set at 50°C for 1 min and then increased to 210°C at a rate of 45°C/min. The sample injection volume was 1 µl, and the carrier gas was helium at a constant pressure of 8 psi. The separation of the sample components was based on their differential partitioning between the gaseous mobile phase and the stationary liquid phase. The components with higher affinity for the gas phase eluted earlier than those with higher affinity for the liquid phase. The mass spectra of the eluted components were recorded and displayed on the computer software, which allowed their identification and quantification [17].

**RESULTS AND DISCUSSION**

Table 1 presents the results obtained in dried Sesame, Millet, Rice, and Guinea corn samples from both Gashua and Hadejia towns, designated as SG and SH (Sesame), MG and MH (Millet), RG and RH (Rice), GG and GH (Guinea corn) respectively.

<table>
<thead>
<tr>
<th>Concentrations of Pesticides Residues</th>
<th>SG (mg/kg)</th>
<th>SH (mg/kg)</th>
<th>MG (mg/kg)</th>
<th>MH (mg/kg)</th>
<th>RG (mg/kg)</th>
<th>RH (mg/kg)</th>
<th>GG (mg/kg)</th>
<th>GH (mg/kg)</th>
<th>FAO/WHO Limit intake (mg/kg) 2019</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichlorvos</td>
<td>0.548</td>
<td>0.389</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>Lindale</td>
<td>0.011</td>
<td>0.020</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.03</td>
</tr>
<tr>
<td>Diazone</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>Methimyl</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>Paraquat dichloride</td>
<td>0.442</td>
<td>0.548</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

**Keys:** SG = Sesame from Gashua, SH = Sesame from Hadejia, MG = Millet from Gashua, MH = Millet from Hadejia, RG = Rice from Gashua, RH = Rice from Hadejia, GG = Guinea corn from Gashua and GH = Guinea corn from Hadejia.
The analysis revealed that Dichlorvos, lindane, and paraquat dichloride were present in the samples from both locations. The concentrations of Dichlorvos were 0.583 mg/kg and 0.389 mg/kg in SG and SH, respectively. The concentrations of lindane were 0.011 mg/kg and 0.020 mg/kg in SG and SH, respectively. The concentrations of paraquat dichloride were 0.442 mg/kg and 0.548 mg/kg in SG and SH, respectively. Lindane was below the permissible limit of 0.03 mg/kg. In contrast, both dichlorvos and paraquat dichloride surpassed the allowable limit of 0.02 mg/kg and 0.03 mg/kg, respectively, according to WHO/FAO [18]. The traces of pesticide residues in SG and SH samples suggest farmers from both towns may rely on using pesticides/chemical fertilizers to cultivate Sesame.

Table 2 shows concentrations obtained for the analysis of the samples using AAS spectrometry for heavy trace metals in Sesame (SG and), Millet (MG and MH), Rice (RG and RH, and Guinea corn (GG and GH) samples analysed. Heavy trace elements in food should be at low concentrations so as to avoid risk to human health. Human health implications of heavy metals are determined by accumulated concentration levels from ingestion through food. In their natural, unprocessed, whole-grain form, cereals are a rich source of vitamins, minerals, carbohydrates, fats, oils, and protein. The various amount found are discussed below from the results obtained in the study. The section shows results obtained from the samples using AAS and Calorimeter to analyse heavy trace elements.

Table 2 Elemental Concentration (mg/kg) of heavy metal in Crop samples.

<table>
<thead>
<tr>
<th>Heavy Elements</th>
<th>SG (mg/kg)</th>
<th>SH (mg/kg)</th>
<th>MG (mg/kg)</th>
<th>MH (mg/kg)</th>
<th>RG (mg/kg)</th>
<th>RH (mg/kg)</th>
<th>GG (mg/kg)</th>
<th>GH (mg/kg)</th>
<th>FAO/WHO Permissible in take (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>0.007</td>
<td>0.045</td>
<td>0.019</td>
<td>0.022</td>
<td>0.010</td>
<td>0.008</td>
<td>0.011</td>
<td>0.010</td>
<td>0.002</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>0.010</td>
<td>0.069</td>
<td>0.030</td>
<td>0.035</td>
<td>0.014</td>
<td>0.012</td>
<td>0.016</td>
<td>0.013</td>
<td>0.2</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>0.25</td>
<td>0.211</td>
<td>0.104</td>
<td>0.117</td>
<td>0.240</td>
<td>0.43</td>
<td>0.151</td>
<td>0.119</td>
<td>0.05</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.016</td>
<td>0.063</td>
<td>0.015</td>
<td>0.023</td>
<td>0.011</td>
<td>0.010</td>
<td>0.014</td>
<td>0.033</td>
<td>0.3</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>0.007</td>
<td>0.048</td>
<td>0.000</td>
<td>0.000</td>
<td>0.010</td>
<td>0.008</td>
<td>0.011</td>
<td>0.080</td>
<td>1.4</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>0.019</td>
<td>0.112</td>
<td>0.045</td>
<td>0.054</td>
<td>0.025</td>
<td>0.018</td>
<td>0.026</td>
<td>0.028</td>
<td>0.4</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Discussion
The purpose of this study was to investigate the pesticide residues in Sesame, Millet, Rice, and Guinea corn grown around the Hadejia-Komadugu-Yobe river area in Yobe state, Nigeria. In Nigeria, a sizable portion of the population depends largely on the agricultural sector as a primary source of subsistence and livelihood, and Agriculture is one of the country’s main economic drivers [19]. This study found that Dichlorvos on Sesame from both Gashua and Hadejia exceeded the WHO's limit for consumption. Moreover, the concentration of Arsenic (As) and Chromium (Cr) from both locations for all the crops exceeded the WHO's limits. Additionally, although no WHO limit is found for paraquat dichloride exposure in literature, limits from other sources suggest that the concentration detected in all the samples greatly exceeded healthy limits.

The results showed that Dichlorvos, lindane, and paraquat dichloride were detected in the crops from both locations, with dichlorvos and paraquat dichloride exceeding the WHO's limits.

These results indicate that the crops are contaminated with pesticide residues that may pose serious health risks to the consumers and the environment. Dichlorvos is a highly toxic organophosphate insecticide that can affect the nervous system and cause respiratory failure [20]. Lindane is an organochlorine insecticide that can cause skin irritation, seizures, and cancer [21,22]. Paraquat dichloride is a herbicide that can cause lung damage, kidney failure, and death [23]. These pesticide residues may also adversely affect the study area's soil quality, water resources, and biodiversity.

Figure 1; Show Pesticide residues detected in Sesame, Millet, Rice, and Guinea corn samples obtained from Hadejia and Gashua.
Although the direct application of these pesticides on the crops is the most plausible source, other possible pesticide residues may include the drift of these pesticides from nearby fields or the contamination of irrigation water or soil with these pesticides.

Figure 2 Shows the Concentration (mg/kg) of heavy metal detected in Sesame, Millet, Rice, and Guinea corn samples obtained from Hadejia and Gashua, Nigeria

The concentration of Chromium was also found to be above the limit taking in some of the samples analysed, as shown in Table 4. Chromium is a trace element that exists in two main forms: trivalent Chromium (Cr III) and hexavalent Chromium (Cr VI) [24,25]. Trivalent Chromium is found in foods and supplements and is considered an essential nutrient for its role in carbohydrate, lipid, and protein metabolism [26]. On the other hand, Hexavalent Chromium is a toxic by-product of industrial processes and is not naturally present in foods or the environment.

Additionally, for all the crops, the concentration of Arsenic exceeded the WHO’s limits (see Figure 2). Exposure to Arsenic through food can have adverse health effects on various organs and systems in the body. Arsenic can affect the skin, nervous system, respiratory system, cardiovascular system, liver, kidney, bladder, prostate, immune system, endocrine system, and developmental processes [27–29]. The most well-established health effect of arsenic exposure is skin lesions and skin cancer [27–29]. Other health effects include lung cancer, bladder cancer, liver cancer, kidney cancer, prostate cancer [30,31], diabetes mellitus, hypertension,
cardiovascular disease, peripheral neuropathy, cognitive impairment, respiratory infections, anaemia, and adverse pregnancy outcomes [27–29,32].

CONCLUSION

Our results reveal high Dichlorvos and paraquat dichloride residue concentrations in Sesame, while Millet, Rice, and Guinea corn had none or lower concentrations of the pesticides. Moreover, the concentration is higher in the Hadejia samples than in the Gashua samples. Therefore, Sesame cultivated around Gashua and Hadejia towns may necessitate further attention due to the higher pesticide residues detected. Based on the above, it may be inferred that both cities may rely on using pesticides/heavy chemicals in the production of Sesame.

Additionally, traces of some of the heavy elements, namely, Arsenic (As) and Chromium (Cr) were found to surpass the FAO/WHO limited intake [18], which may entail several harms to human health (kidney, cancerous diseases, etc.), and this warrants health caution due to high consumption. Hence, it is vital to mitigate health risks by imposing permissible limit intake on heavy elements in food crops that exhibit higher toxic contamination. This raises concerns about consumer health due to pesticide residues and heavy metals known to have potentially deleterious effects on both humans and animals. These findings have significant implications for public health and environmental sustainability. Further research is needed to corroborate these findings and to explore ways to alleviate this problem.

RECOMMENDATION:

Some recommendations for future research and practice are: to measure the pesticide residues in other environmental media, such as water or soil, which could provide more information on the extent and origin of the contamination. Also, a measurement in processed or cooked products to obtain a more accurate estimate of human exposure; conduct epidemiological surveys and biomonitoring to assess the health effects of pesticides residues among the population; to compare the pesticides residues levels with other regions or countries to identify the factors that influence the variation in contamination; to implement measures to reduce or eliminate the use of harmful pesticides and promote alternative methods of pest control that are safe and effective; and to educate farmers and consumers about the hazards of pesticides residues and how to avoid or minimize them.

REFERENCES


