



## Research Article

### EVALUATION OF SOME HERBICIDE CONTENT IN AGRICULTURAL PRODUCE IN SOKOTO METROPOLIS

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#### ABSTRACT

The effect of herbicide as an environmental pollutant can constitute public health food hazard. It therefore becomes pertinent for regular monitoring of the environment for public health food safety. Herbicide residues content in crop samples from Sokoto, State, Nigeria were determined using Cary 630 FTIR spectrophotometer equipped with diffuse reflectance sampling interface (Agilent Technologies, USA). The concentration of the herbicide residues such as atrazine in food type (rice, potato, bean and groundnut) was 23pg/ml, 67pg/ml, 67pg/ml and 117pg/ml respectively, 2,4-D concentration in crop (rice, potato, bean and groundnut) was 5.6pg/ml, 11pg/ml, 14pg/ml 14pg/ml respectively, Paraquat concentration in food crop (rice, potato, bean and groundnut) was 17pg/ml, 33pg/ml, 33pg/ml and 45pg/ml respectively, Glyphosate concentration in food crop (rice, potato, bean and groundnut) was 10pg/ml, 33pg/ml, 33pg/ml and 45pg/ml respectively. The concentration of herbicide (2,4-D, Paraquat, Glyphosate and Atrazine) in food crop (Rice, Bean, Potato and Groundnut) in this study is generally very low. The relatively low concentration of these residues may be due low usage of herbicide in the farming practice within the study area in which farmers are supplied with very limited quantity of herbicide. The danger associated with herbicide use on human health requires that user should be adequately trained with necessary skills and protective gear in applying the herbicide and other pesticides on farm land.

**Keywords:** Herbicide, Atrazine, 2,4-D, Glyphosate, Paraquat, Foodcrop.

#### Introduction

Herbicides, also commonly known as weed killers, are chemical substances used to control unwanted plants (EPA, 2011). Selective herbicides control specific weed species, while leaving the desired crop relatively unharmed, while non-selective herbicides (sometimes called total weed killers in commercial products) can be used to clear waste ground, industrial and construction sites, railways and railway embankments as they kill all plant material with which they come into contact (Smith, 1995). Apart from selective/non-selective, other important distinctions include persistence (also known as residual action: how long the product stays in place and remains active), means of uptake (whether it is absorbed by above-ground foliage only, through the roots, or by other means), and mechanism of action (how it works). Historically, products such as common salt and other metal salts were used as herbicides, however these have gradually fallen out of favor and in some countries a number of these are banned due to their persistence in soil, and toxicity and groundwater contamination concerns (EPA, 2011). Herbicides have also been used in warfare and conflict. Although research into chemical herbicides began in the early 20<sup>th</sup> century, the first major breakthrough was the result of research conducted in both the UK

and the US during the Second World War into the potential use of herbicides in war (Andrew *et al.*, 2011). The first modern herbicide, 2,4-D, was first discovered and synthesized by W. G. Templeman at Imperial Chemical Industries. In 1940, he showed that "Growth substances applied appropriately would kill certain broad-leaved weeds in cereals without harming the crops." By 1941, his team succeeded in synthesizing the chemical. In the same year, Pokorny in the US achieved this as well (Robert, 2007). Independently, a team under Juda Hirsch Quastel, working at the Rothamsted Experimental Station made the same discovery. Quastel was tasked by the Agricultural Research Council (ARC) to discover methods for improving crop yield. By analyzing soil as a dynamic system, rather than an inert substance, he was able to apply techniques such as perfusion. Quastel was able to quantify the influence of various plant hormones, inhibitors and other chemicals on the activity of microorganisms in the soil and assess their direct impact on plant growth. While the full work of the unit remained secret, certain discoveries were developed for commercial use after the war, including the 2,4-D compound (Quastel, 1950; Robert, 2007). When 2,4-D was commercially released in 1946, it triggered a worldwide revolution in agricultural output and became the first successful selective herbicide. It allowed for greatly enhanced weed control in wheat, maize (corn), rice, and similar cereal grass crops, because it

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kills dicots (broadleaf plants), but not most monocots (grasses). The low cost of 2, 4-D has led to continued usage today, and it remains one of the most commonly used herbicides in the world. Like other acid herbicides, current formulations use either an amine salt (often trimethylamine) or one of many esters of the parent compound (Robert, 2007). These are easier to handle than the acid. Modern herbicides are often synthetic mimics of natural plant hormones which interfere with growth of the target plants (Quastel, 1950). The term organic herbicide has come to mean herbicides intended for organic farming. Some plants also produce their own natural herbicides, such as the genus *Juglans* (walnuts), or the tree of heaven; such action of natural herbicides, and other related chemical interactions, is called allelopathy. Due to herbicide resistance - a major concern in agriculture - a number of products combine herbicides with different means of action. Integrated pest management may use herbicides alongside other pest control methods. In the US in 2007, about 83% of all herbicide usage, determined by weight applied, was in agriculture (EPA, 2011; Lock *et al.*, 1998). In 2007, world pesticide expenditures totaled about \$39.4 billion; herbicides were about 40% of those sales and constituted the biggest portion, followed by insecticides, fungicides, and other types (EPA, 2011; Quastel, 1950; Robert, 2007). Smaller quantities are used in forestry, pasture systems, and management of areas set aside as wildlife habitat.

## Aims

The study is aimed to evaluate the residues of herbicides content in selected stored agricultural produce in sokoto metropolis.

## Justification of the Study

Some herbicides cause a range of health effects ranging from skin rashes to death. The pathway of attack can arise from intentional or unintentional direct consumption, improper application resulting in the herbicide coming into direct contact with people or wildlife, inhalation of aerial sprays, or food consumption prior to the labeled preharvest interval. Research has suggested such contamination results in a small rise in cancer risk after occupational exposure to these herbicides (Kogevinas *et al.*, 1997). Herbicides have widely variable toxicity in addition to acute toxicity from occupational exposure levels with 2,4-D causes cancer in humans Ibrahim *et al.*, (1991), and associated with increased risk of soft tissue sarcoma and non-Hodgkin lymphoma (Howard *et al.*, 1992). Researchers have observed apparent links between exposure to 2,4-D and non-Hodgkin's lymphoma (a blood cancer) and sarcoma (a soft-tissue cancer). But both of these can be caused by a number of chemicals, including dioxin, which was frequently mixed into formulations of 2,4-D until the mid-1990s. Nevertheless, in 2015, the International Agency for Research on Cancer declared 2,4-D a possible human carcinogen, based on evidence that it damages human cells and, in a number of studies, caused cancer in laboratory animals.

## Research Questions

- i. What is the content of 2,4-Dichlorophenoxyacetic acid (2,4-D), atrazine, paraquat and Glyphosate in groundnut?
- ii. What is the content of 2,4-Dichlorophenoxyacetic acid (2,4-D), atrazine, paraquat and Glyphosate in potato?
- iii. What is the content of 2,4-Dichlorophenoxyacetic acid (2,4-D), atrazine, paraquat and Glyphosate herbicide in beans?
- iv. What is the content of 2,4-Dichlorophenoxyacetic acid (2,4-D), atrazine, paraquat and Glyphosate herbicide in rice?

## Specific objectives

- i. To determine the concentration of 2,4-Dichlorophenoxyacetic acid (2,4-D), atrazine, paraquat and Glyphosate in groundnut
- ii. To determine the concentration of 2,4-Dichlorophenoxyacetic acid (2,4-D), atrazine, paraquat and Glyphosate in potato
- iii. To determine the concentration of 2,4-Dichlorophenoxyacetic acid (2,4-D), atrazine, paraquat and Glyphosate in bean
- iv. To determine the concentration of 2,4-Dichlorophenoxyacetic acid (2,4-D), atrazine, paraquat and Glyphosate in rice.

## Materials and Method

### Study Area

Sokoto is one of the seven states that form the North West geopolitical zone of Nigeria. It is bordered to the north by the Republic of Niger, Zamfara State to the east, Kebbi state to the south and west. It is situated in the savannah on the temperature of 44 degree Celsius annually. The city of Sokoto is its capital. Sokoto state traces its origin to the Sokoto Caliphate founded in 1809 by Shehu Usman dan Fodio, the leader of the jihadists who overthrew the Hausa state of Gobir, Kano, Katsina and Kanem-Bornu. Sokoto State covers an area of 28,232.37 square kilometers. The state is located between latitudes 40 to 60 north and longitudes 110 to 130 east has a population of 3,702,676 (2006 census figures). It accounts for 2.3 percent of Nigeria's total population. Prior to the establishment of Sokoto as a ribat (military camp or frontier) in 1809, the area that is modern-day Sokoto state was home to Hausa state with large populations.

### Ethical approval

Ethical approval shall be obtained from Sokoto Agricultural Development Project (SADP) Sokoto State.

### Experimental

#### Samples

A total of four different crops (fresh groundnut, potato, beans and rice) was purchased from farmer in sokoto metropolis.

#### Sample Collection

Fresh samples (approximately 1 kg) of groundnut, potato, beans and rice was be purchased from farmer in Sokoto metropolis. The samples was grinded (with a Hanil grinder) and passed through a 40-mesh sieve; the resultant fine powder was placed in a plastic zipper bag and stored at -24°C until analysis.

#### Standard Solutions

Standard stock solution of 2,4-Dichlorophenoxyacetic acid (2,4-D), Atrazine, Paraquat and Glyphosate of 50pg/ml concentrations was used to prepared five different concentration range of 0.5 to 10 pg/mL. Standard solutions shall be stored at -24°C in amber bottles

pending analysis using Fourier transform infrared spectroscopy (FTIR) Instrumentation Agilent Technologies.

**Fourier transform infrared spectroscopy (FTIR) Instrumentation.**

The FTIR analysis was carried out on Cary 630 FTIR spectrophotometer equipped with diffuse reflectance sampling interface (Agilent Technologies, USA). FTIR spectra were recorded in the wave number range between 4000nm<sup>-1</sup> and 650 nm<sup>-1</sup>, averaging 32 scans per sample using a nominal resolution of 8cm<sup>-1</sup> employing background spectra of gold. The Cary 630 MicroLab software was used for data collection and Agilent Resolution Pro software was used to analyze the data (Bhoomendra *et al.*, 2014).

**Calibration curve:** Calibration curve were prepared for the five different standard of the herbicides (Atrazine, Glyphosate, 2,4-D and Paraquat) of concentration of range 0.5pg- 10pg/ml. the linear equation generated was used to quantify the analyte (Sirotiak *et al.*, 2015). All the statistical calculations and calibration curve plotting in the Cary 630 MicroLab software was used for data collection and Agilent Resolution Pro software was used to analyze the data

**Statistical analysis**

All the statistical calculations and calibration curve plotting in the Cary 630 MicroLab software was used for data collection and Agilent Resolution Pro software was used to analyze the data and stafflex version 6.0 software for window (Artech, Osaka Japan, <http://www.stafflex.net>) (Bhoomendra *et al.*, 2014).

**Results**

Table 1: Atrazine concentration in food crop (rice, potato, bean and groundnut). The concentration of atrazine in rice was 23pg/ml greater than acceptable level 0.2ppm, Potato 67pg/ml greater than acceptable level 0.25ppm, Bean 67pg/ml greater than acceptable level 0.2ppm and Groundnut 117pg/ml greater than acceptable level 0.2ppm (e-CFR, 2015). Table 2: 2,4-D concentration in food crop (rice, potato, bean and groundnut). The concentration of 2,4-D in rice 5.6pg/ml greater than acceptable level 0.5ppm, Potato 11pg/ml greater than acceptable level 0.4ppm, bean 14pg/ml greater than acceptable level 0.2ppm and Groundnut 14pg/ml greater than acceptable level 0.5ppm (e-CFR, 2015). Table 3: Paraquat concentration in food crop (rice, potato, bean and groundnut). The concentration of paraquat in Rice 17pg/ml greater than acceptable level 0.05ppm Potato 33pg/ml greater than acceptable level 0.5ppm, Bean 33pg/ml greater than acceptable level 0.05ppm and in Groundnut 45pg/ml greater than acceptable level 0.05ppm (e-CFR, 2015). Table 4: Glyphosate concentration in food crop (rice, potato, bean and groundnut). The concentration of glyphosate in Rice 10pg/ml greater than acceptable level 0.1ppm, Potato 33pg/ml less than acceptable level 3ppm, Bean 33pg/ml greater than acceptable level 0.1ppm and Groundnut 45pg/ml greater than acceptable level 0.2ppm (e-CFR, 2015).

**Table 1. Atrazine concentration in food crop (rice, potato, bean and groundnut)**

Food type	Concentration(pg/ml)	Accepted food level (e-CFR data, 2019).
Rice	23pg	0.0000002pg(0.2ppm)
Potato	67pg	0.000002.5pg(0.25ppm)
Bean	67pg	0.0000002pg(0.2ppm)
Groundnut	117pg	0.0000002pg(0.2ppm)

The concentration of atrazine in rice was 23 pg/ml greater than the acceptable food level, bean 67pg/ml greater than the acceptable food level, potato 67pg/ml greater than the acceptable food level and groundnut 117pg/ml greater than the acceptable food level (e-CFR data, 2019).

**Table 2. 2,4-D concentration in food crop (rice, potato, bean and groundnut)**

Food type	Concentration(pg/ml)	Accepted food level (e-CFR data, 2019)
Rice	5.6pg	0.00000005pg(0.5ppm)
Potato	11pg	0.0000004pg(0.4ppm)
Bean	14pg	0.0000002pg(0.2ppm)
Groundnut	14pg	0.0000005pg(0.5ppm)

The concentration of 2,4-D in rice 5.6pg/ml greater than acceptable level 0.5ppm, Potato 11pg/ml greater than acceptable level 0.4ppm, bean 14pg/ml greater than acceptable level 0.2ppm and Groundnut 14pg/ml greater than acceptable level 0.5ppm (e-CFR 2019).

**Table 3. Paraquat concentration in food crop (rice, potato, bean and groundnut)**

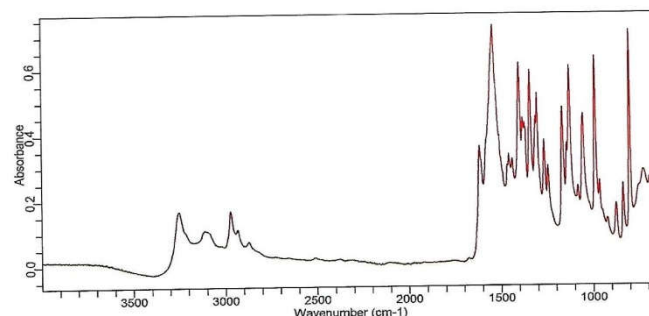
Food type	Concentration( pg/ml)	Accepted food level (e-CFR data, 2019)
Rice	17pg	0.00000005pg (0.05ppm)
Potato	33pg	0.0000005pg( 0.5ppm)
Bean	33pg	0.00000005pg( 0.05ppm)
Groundnut	45pg	0.00000005pg( 0.05ppm)

The concentration of paraquat in Rice 17pg/ml greater than acceptable level 0.05ppm Potato 33pg/ml greater than acceptable level 0.5ppm, Bean 33pg/ml greater than acceptable level 0.05ppm and in Groundnut 45pg/ml greater than acceptable level 0.05ppm (e-CFR 2019).

**Table 4. Glyphosate concentration in food crop (rice, potato, bean and groundnut)**

Food type	Concentration	Accepted food level (e-CFR data, 2019)
Rice	10pg/ml	0.0000001pg(0.1ppm)
Potato	33pg /ml	0.000003(3ppm)
Bean	33pg/ml	0.0000001pg(0.1ppm)
Groundnut	45pg/ml	0.0000002pg(0.2ppm)

The concentration of glyphosate in Rice 10pg/ml greater than acceptable level 0.1ppm, Potato 33pg/ml greater than acceptable level 3ppm, Bean 33pg/ml greater than acceptable level 0.1ppm and Groundnut 45pg/ml greater than acceptable level 0.2ppm (e-CFR 2019).



**Fig. 1. Infrared spectrum of Atrazine**

There was an elevated high intensity absorbance band 700nm<sup>-1</sup> to 800nm<sup>-1</sup>, correspond to C-CL stretch the intensity absorbance band was high at 1100nm<sup>-1</sup> to 1250nm<sup>-1</sup>. The intensity absorbance band

grew from  $1200\text{nm}^{-1}$ ,  $1250\text{nm}^{-1}$ ,  $1300\text{nm}^{-1}$  and  $1350\text{nm}^{-1}$ , the intensity absorbance band slipped down at  $1400\text{nm}^{-1}$  and intensity absorbance band high at  $1500\text{nm}^{-1}$ ,  $3100\text{nm}^{-1}$  and  $3200\text{nm}^{-1}$ . Bhoomendra *et al.*, (2014) reported band at  $1600\text{cm}^{-1}$  that corresponded to the carbonyl (amide) of the herbicide appeared as well as a small shoulder assigned to the  $\text{NH}_2$  deformation band at  $1600\text{nm}^{-1}$  (Undabeytia *et al.*, 2010). The band at  $1050\text{nm}^{-1}$  correspond to the thioether group  $-\text{S}-\text{CH}_3$ , the  $-\text{NH}_2$  group shows both symmetric and asymmetric stretching vibrations at  $3200$  and  $3300\text{nm}^{-1}$ . The C-N absorption is found near  $1520\text{nm}^{-1}$  (Maqueda *et al.*, 2009).

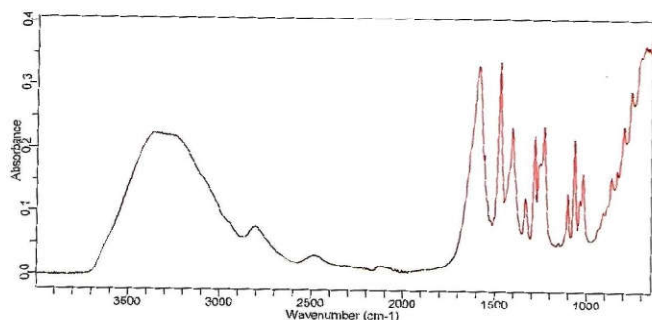


Fig. 2. Infrared spectrum of 2,4-D.

There was a very high intensity absorbance band at  $700\text{nm}^{-1}$  the band slipped down at  $800\text{nm}^{-1}$  and  $900\text{nm}^{-1}$ . There was high intensity absorbance band at  $1200\text{nm}^{-1}$ , the band at  $1200\text{nm}^{-1}$  is attributed to  $\nu(\text{P}-\text{OH})$ , low intensity absorbance band observed at  $1300\text{nm}^{-1}$ . The intensity absorbance band at  $1400\text{nm}^{-1}$  was high, Wave number at  $1400\text{nm}^{-1}$  refers to  $\nu(\text{C}-\text{OH})$  bond, it was higher at  $1500\text{nm}^{-1}$  and  $1600\text{nm}^{-1}$  to  $1700\text{nm}^{-1}$  correspond to C=O stretch band. The intensity absorbance band was high between  $2900\text{nm}^{-1}$  and  $3200\text{nm}^{-1}$ , correspond to C-H stretch band.

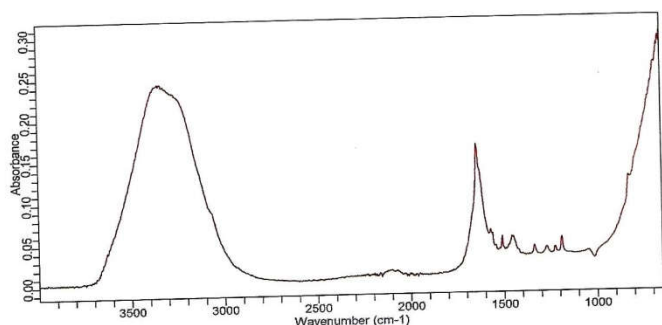


Fig. 3. Infrared spectrum of paraquat

The intensity absorbance band was very high at  $700\text{nm}^{-1}$ ,  $1650\text{nm}^{-1}$  and  $3300\text{nm}^{-1}$ . There was a high intensity absorbance band at  $1550\text{nm}^{-1}$ , there was a generally very low intensity absorbance band between  $1200\text{nm}^{-1}$  to  $1500\text{nm}^{-1}$ . Band observed at  $1400\text{nm}^{-1}$  is assigned as the scissoring mode of  $-\text{CH}_2$  (Bertaux *et al.*, 1998). Bands of hydrocarbons due to  $\text{CH}_2$  twisting and wagging vibrations are observed in the region  $1200 - 1400\text{nm}^{-1}$ . The position of the  $\nu(\text{C}-\text{O})$  stretch band is assigned for phenoxy group is at  $1200$  and  $1300\text{nm}^{-1}$ . The absorption bands at  $3000$  and  $3600\text{nm}^{-1}$  corresponds to interlayer hydroxyl group stretching of kaolinite (Bertaux *et al.*, 1998). The absorption bands observed around  $1400$  and  $1600\text{nm}^{-1}$  corresponds to C-H stretching vibration of organic matter and O-H

deformation of water molecular respectively (Viscarra, *et al.*, 2010; Tcheumi *et al.*, 2012).

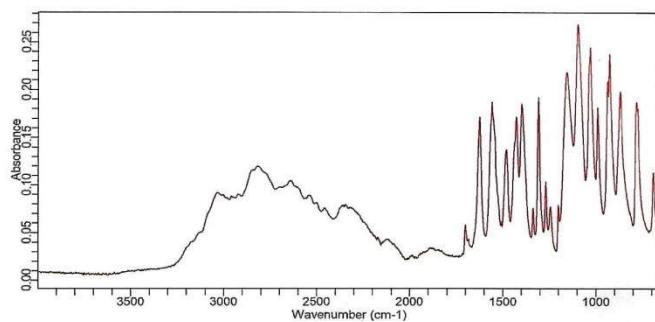
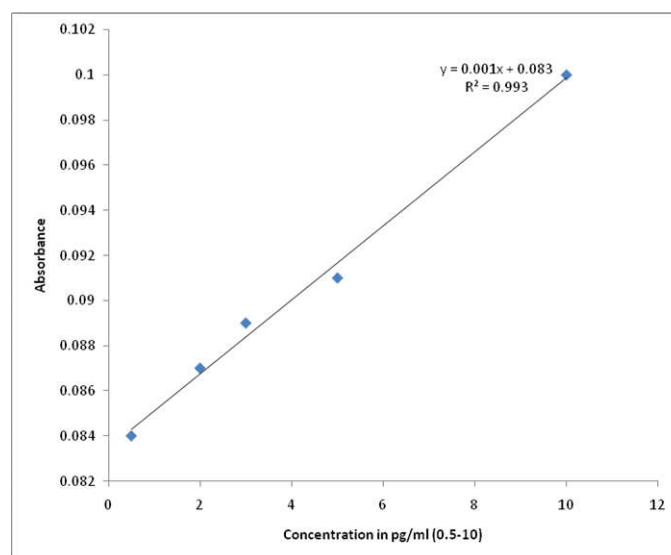
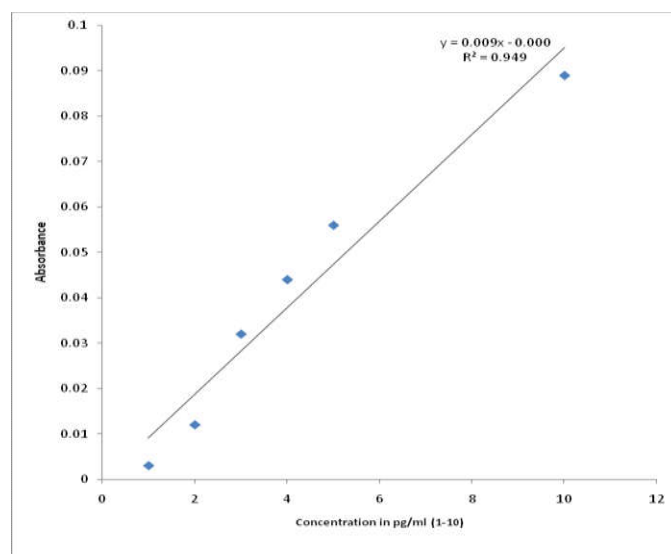


Fig. 4. Infrared spectrum of glyphosate



$y = 0.001x + 0.083$ ;  $R^2 = 0.993$ ;  $y =$  absorbance of sample  $x =$  concentration of the sample.  $R^2 =$  Regression;  $x = Y - 0.083/0.001$

Figure 1. The linear calibration of standard atrazine concentration 0.5-10pg/ml

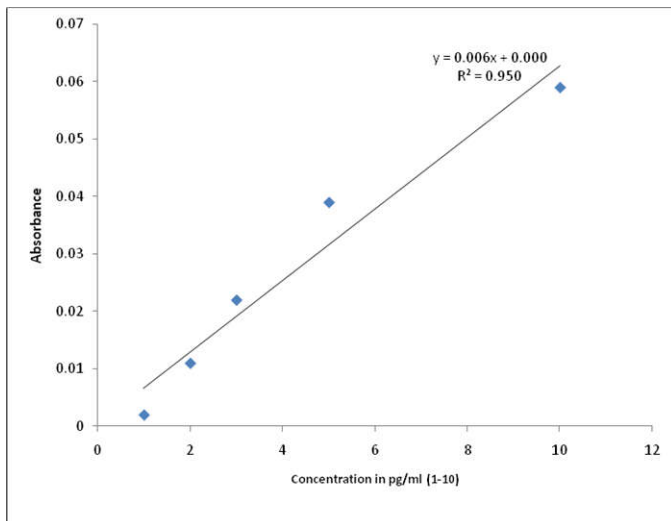


$y = 0.009x - 0.000$ ;  $R^2 = 0.949$ ;  $y =$  absorbance of sample  $x =$  concentration of the sample.  $R^2 =$  Regression;  $x = Y/0.009$

Figure 2. The linear calibration of standard 2,4-D concentration 1-10pg/ml

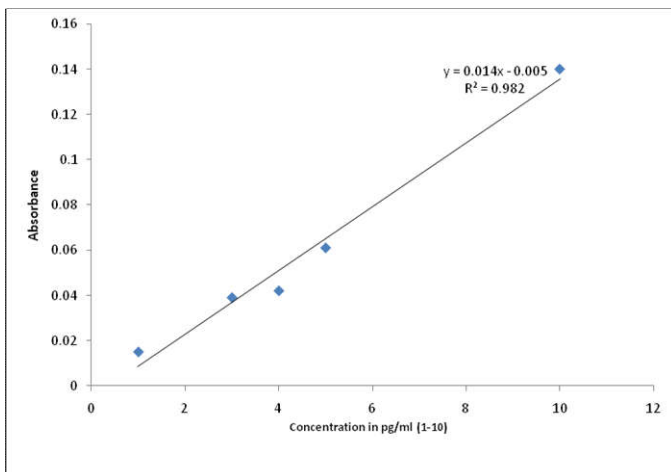


There was a high intensity absorbance band at  $700\text{nm}^{-1}$ ,  $800\text{nm}^{-1}$ ,  $1050\text{nm}^{-1}$ ,  $700\text{nm}^{-1}$ , there was a very high intensity absorbance band at  $1150\text{nm}^{-1}$ . The intensity absorbance band was low at  $1250\text{nm}^{-1}$  while the intensity absorbance band at  $1300\text{nm}^{-1}$ ,  $1400\text{nm}^{-1}$  and  $1600\text{nm}^{-1}$  to  $1650\text{nm}^{-1}$  was high. There was a high intensity absorbance band  $3200\text{nm}^{-1}$  to  $2000\text{nm}^{-1}$ . Sirotiak *et al.*, (2015) reported glyphosate absorption bands at  $1396$ ,  $1317$ ,  $1163$ ,  $1072$  (shoulder) and  $980\text{nm}^{-1}$ , and correspond to the  $\nu(\text{C}-\text{O})$ ,  $\nu(\text{C}-\text{O}-\text{P})$ ,  $\nu(\text{P}-\text{OH})$  (antisymmetric and symmetric) vibration modes, respectively. According to Sheals *et al.*, (2009) these bands reflect the formation of monodentate mononuclear inner-sphere complexes (Waiman *et al.*, 2013). Wavenumber at  $1400\text{nm}^{-1}$  refers to  $\nu(\text{C}-\text{OH})$  bond. Band at  $1200\text{nm}^{-1}$  is attributed to  $\nu(\text{P}-\text{OH})$ .



$y = 0.006x + 0.000$ ;  $R^2 = 0.950$ ;  $y =$  absorbance of sample;  $x =$  concentration of the sample.  $R^2 =$  Regression;  $x = Y/0.006$

**Figure 3. The linear calibration of standard Paraquat concentration 1-10pg/ml**



$y = 0.014x - 0.005$ ;  $R^2 = 0.982$ ;  $y =$  absorbance of sample  $x =$  concentration of the sample.  $R^2 =$  Regression:  $x = y + 0.005/0.014$

**Figure 4. The linear calibration of standard Glyphosate concentration 1-10pg/ml**

## Discussion

The concentration of herbicide (2,4-D, Paraquat, Glyphosate and Atrazine) in food (Rice, Bean, Potato and Groundnut) in this study is

generally low although it is above international accepted level reported by e-CFR (2015), but lower than that of John *et al.*, (2013), who reported an average concentration of the herbicide residues such as atrazine and 2,4-D which were discovered to be more in the root crops and nuts (cassava, yam, potato, groundnuts) are  $0.04\text{mg/kg}$  and  $0.02\text{mg/kg}$  respectively and paraquat concentration in potato which was abnormally high ( $0.67\text{mg/kg}$ ). U.S. Environmental Protection Agency (2016), reported no detectable levels of pesticide residues were found in 52.9% of domestic and 50.7% of imported human food samples analyzed (over 99% of the 2,670 domestic and 90% of the 4,276 imported human foods samples were found to be in compliance with federal pesticide residue standards). The low amount of herbicide found in the food could be influenced by the following factors such as quantity of spray, volatility, temperature, soil type, water solubility and adsorption. Herbicide Volatility generally increases with increasing temperature and soil moisture, and with decreasing clay and organic matter content (Helling *et al.* 1971). The use of a surfactant can change the volatility of a herbicide (Que Hee and Sutherland 1981). In extreme cases, losses due to volatilization can be up to 80 or 90% of the total herbicide applied (Taylor and Glotfelty 1988). 2,4-D and triclopyr can present significant volatilization problems in the field (Taylor and Glotfelty 1988). Water-soluble herbicides generally have low adsorption capacities, and are consequently more mobile in the environment and more available for microbial metabolism and other degradation processes. Esters, in general, are relatively insoluble in water, adsorb quickly to soils, penetrate plant tissues readily, and are more volatile than salt and acid formulations (Que Hee and Sutherland, 1981). The half-life gives only a rough estimate of the persistence of an herbicide since the half-life of a particular herbicide can vary significantly depending on soil characteristics, weather (especially temperature and soil moisture), and the vegetation at the site. Dissipation rates often change with time (Parker and Doxtader 1983). For example, McCall *et al.*, (1981) found that the rate of dissipation increased until approximately 20% of the applied herbicide remained, and then declines. Nonetheless, half-life values do provide a means of comparing the relative persistence of herbicides.

Adsorption is also related to the water solubility of an herbicide, with less soluble herbicides being more strongly adsorbed to soil particles (Helling *et al.*, 1971). Solubility of herbicides in water generally decreases from salt to acid to ester formulations, but there are some exceptions. For example, glyphosate is highly water-soluble and has a strong adsorption capacity. Paraquat and diquat are examples of the second type of photosynthesis inhibitor. They accept electrons from Photosystem I, and after several cycles, generate hydroxyl radicals. These radicals are extremely reactive and readily destroy unsaturated lipids, including membrane fatty acids and chlorophyll (Hutzinger, 1981). Soil pH can also affect the availability of some soil-applied herbicides in crop. This is important for the triazine herbicides. These herbicides are most strongly adsorbed (tied up and unavailable for uptake by weeds and food crop) on clay and organic matter particles at low pH levels. Although the amount of atrazine adsorption increases at all pH levels below 7.0, adsorption is most dramatic at pH levels of 6.0 and below. This is an important indicator that promotes high concentration of atrazine among the food crops when compared to other herbicide. The decline in herbicide concentration in these food crops could also be due to herbicide degradation, dilution within the plant due to plant growth, or translocation of the herbicide to the roots (Anderson, 2004). The availability of herbicide in the soil determines the amount that will

enter food crops especially root crop. Similarly, EPA, (2016), found no detectable levels of pesticide chemical residues in 43.0% of the 242 domestic animal food samples collected, nor in 54.7% of the 225 imported animal food samples. Less than 2% of the animal food samples were found to contain violative pesticide chemical residues. Less than 1% of domestic samples and less than 10% of imported samples were found to be violative. Samples are violative if they have pesticide chemical residues above the EPA tolerance or pesticide chemical residues for which the EPA has not established a tolerance or a tolerance exemption for the specific pesticide/commodity combination (EPA, 2016). In another report of the 760 samples tested for the glyphosate and glufosinate assignment (consisting of 274 grain corn, 267 soybean, 113 milk, and 106 egg samples), 53.7% had no detectable residues of the pesticides. Non-violative levels of glyphosate were found in 173 (63.1%) of the corn samples and 178 (67.0%) of the soybean samples and non-violative levels of glufosinate were found in 4 (1.4%) of the corn samples and 3 (1.1%) soybean samples (U.S. Environmental Protection Agency (EPA, 2016). None of the milk and egg samples had any detectable glyphosate or glufosinate residues, and all the residues detected in the corn and soybean samples were below the tolerance levels set by the U.S. Environmental Protection Agency (EPA, 2016). A new study led by scientists from the Arctic University of Norway has detected "extreme levels" of Roundup, the agricultural herbicide manufactured by Monsanto, in genetically engineered soy (Emily, 2014). The study of Food Chemistry with 31 different soybean plants on Iowa farms and compared the accumulation of pesticides and herbicides on plants in three categories 1) genetically engineered "Roundup Ready" soy, 2) conventionally produced (not GE) soy, and 3) soy cultivated using organic practices (Emily, 2014). They found high levels of Roundup on 70 percent of genetically engineered soy plants (Emily, 2014). Glyphosate based herbicides are the most widely used in the world and residues of glyphosate have been found in tap water, children's urine, breast milk, chips, snacks, beer, wine, cereals, eggs, oatmeal, wheat products, and most conventional foods tested (Zen, 2019). These glyphosate and 2,4-D are herbicide commonly used in this part of the world since it is among agricultural subsidy been rendered to farmer by the government (Zen, 2019). EPA reported that Americans can consume 17 times more glyphosate in our drinking water than European residents. The Environmental Working Group (EWG) asserts that 160 ppb of glyphosate found in breakfast cereal is safe for a child to consume due to their own safety assessments, and yet renowned scientists and health advocates have long stated that no level is safe (Zen, 2019).

## Conclusion

The concentration of herbicide (2,4-D, Paraquat, Glyphosate and Atrazine) in food (Rice, Bean, Potato and Groundnut) in this study is generally very low. The relatively low concentration of these residues may be due low usage of herbicide in the farming practice within the study area in which farmers are supplied with very limited quantity of herbicide.

## Recommendation

- a. The danger associated with herbicide use on human health requires that user should be adequately trained with necessary skills and protective gear in applying the herbicide and other pesticides on farm land.

- b. Provision of basic regulations needed in the effective utilization of these chemical farm inputs.
- c. It was also suggested that there should be a legislation to regulate the use of herbicide within the area covered in this study.

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