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Seasonal variations in the levels of glyphosate in soil, water and crops from three farm settlements in Oyo state, Nigeria

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ABSTRACT

This study investigated the concentration of glyphosate in water (groundwater and surface), soil (top and sub) on cassava and maize farms within 3 farm settlements (Akufo, Ilora and Otiri Ipapo) from Ido, Oyo and Iseyin Local Government Areas of Oyo state, Nigeria. Samples of Top and sub soil were taken from the farms while water was collected from wells (groundwater) and streams (surface water) around each farm settlement using standard methods. Crops (cassava and Maize) samples were collected from each of the selected farm after harvest. The samples were collected over a six-month period to reflect seasonal variation. The glyphosate levels were determined using HPLC-FLD after liquid-liquid extraction technique for water and soxhlet extraction for soil crops The pH, electrical conductivity (EC), total dissolved solids (TDS) values for groundwater were within the WHO limits while values recorded for surface water were above the WHO limits. The phosphate and nitrate values were high in surface water compared to groundwater. High concentration of the exchangeable cations were recorded at the top soil for all the farms with values ranging from 4.0 ± 0.1 to 8.2 ± 0.0 for Ca^{2+}, 2.9 ± 0.0 to 5.1 ± 0.1 for Mg^{2+}, 0.3 ± 0.2 to 0.55 ± 0.0 for Na^{+}, and 0.32 ± 0.0 to 8.2 ± 0.0 for K^{+}. the residual concentration of glyphosate taken from wells and taps (groundwater) were within the maximum concentration of glyphosate in drinking water (0.7 mgL^{-1}). Glyphosate concentrations observed were higher in soil samples from all farm settlements during wet season compared to dry, higher concentrations were also observed in surface water during wet season (August) compared to dry, with Akufo farm settlement having the highest concentrations of 29.40 ± 0.83 mgL^{-1}. The glyphosate residues were also higher in cassava (0.3 ± 0.0 $mgKg^{-1}$) compared to maize (0.07 ± 0.08 $mgKg^{-1}$) across each farm settlement. Generally, the higher concentrations observed during wet season in both soil and water samples were as a result of active farm activities during wet season and run off respectively. If herbicide usage is not properly monitored within these settlements, it can pose a threat to aquatic animals and humans around the settlements, thus a sustainable and conservative farming is advised.

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1. Introduction

The effect of weeds in Agriculture cannot be over emphasized, thus the use of herbicides [1] The ease of application and efficiency of herbicides for weed control have both increased dramatically in Nigeria. This increase has been attributed to the simplicity and efficacy of different herbicides used and difficulties in getting hired labour to carry out the traditional methods of controlling weeds [2]. According to Ref. [3], managing weeds is essential for agricultural production and landscape maintenance, it was also noted that future food production demands will depend significantly on how well weeds are manage. In Nigeria, majority of the farmers that handles these agrochemicals are illiterates and apply these chemicals indiscriminately because of little or no training on the appropriate application of these chemicals [2]. [4] reported farmers' perceptions of the negative effects of agrochemicals application in Karnataka, an activity that resulted in farmlands and waterways contamination. Inappropriate application of chemicals herbicides makes rural farmers more vulnerable to cancer-related illnesses. The detrimental effects of chemical pesticides on both the ecosystem and human health have drawn the attention of numerous researchers [5–7].

These herbicides contaminate water bodies through runoff and aerosol drift during spraying because glyphosate dissolves in water, it slowly evaporates into sediments or suspended particles [2]. The indiscriminate usage of the herbicides has been recorded to poses significant threat to human health, the environment, threat to non-target organisms, destroying soil microorganisms and thus affecting soil fertility [2], similarly [8], reported that Nigerian rural farmers who misuse herbicides have a propensity to harm the soil's natural ability to regenerate nutrients and the efficiency of the farmlands' water retention systems. Among these herbicides, glyphosate [N-phosphonomethyl) glycine, GP] has been displaying potent efficacy [9]. Several herbicide products, including Roundup, contain the active component glyphosate, which is also commercially accessible in the salt forms of isopropylamine, ammonium, potassium, and trimesium. Across the world, it is use to control broadleaf, grasses, and sedges on field and farms. Also, it is being used in urban, rural, forestry, and aquatic environments [10]. It works by stopping 5-enolpyruvylshikimate-3-phosphate synthesis (EPSPS) in the shikimate acid pathway, this prevents glyphosate-exposed plants from producing aromatic amino acids [11].

Generally, glyphosate has showed positive role in agricultural production for growing quality crops and enhanced the quality of seed [11]. Several studies have reported increased in the residual level of glyphosate and other agrochemicals in water bodies close to farmlands during the wet season in comparison to the dry season [12,13]. In Nigeria [14], reported increase in the concentrations of glyphosate in Kuti stream Abuja during the wet season (April to June) with values ranging from (0.15 $\pm$ 0.02 mgL^{-1} to 0.1 $\pm$ 0.01 mgL^{-1}). Some nations have set maximum allowable levels for glyphosate in various sources of water. The Ministry of the Environment Canada defined a long-term cutoff point for the preservation of freshwater aquatic life at 800 μgL^{-1} [CCME [15] and establish the highest permissible concentration in drinking water at 280 μgL^{-1} The United States Environmental Protection Agency established standards for aquatic life between 1800 and 49,900 μgL^{-1} and made the decision to limit the concentration in drinking water to be 700 μgL^{-1} [16]. However, in the European Union, the list doesn't include glyphosate as top contaminants in surface water but anticipated maximum concentration will be 398.6 μgL^{-1} when it joins [17].

Glyphosate concentrations have increased in various environmental matrices as a result of its extensive use. Numerous studies have shown that glyphosate is readily absorbed by clay and other elements in the soil after application [18]. Nonetheless, studies have found glyphosate in various water bodies. Glyphosate pollution was reported in southeast Brazil due to flooding into surface water and underground water, stream water had a concentration of 5.8 mgL^{-1} while drinking water had a concentration ranging from 0.5 to 8.7 mgL^{-1} [19]. The concentrations of glyphosate vary widely, different concentrations have been reported such as 0.1–100 $mgKg^{-1}$, 0.1–25 $mgKg^{-1}$, 0.1–28 $mgKg^{-1}$ and 1–344 $mgKg^{-1}$ in legumes, grain crops, oil seed crops and in various types of fodder respectively [20]. The estimated residual values of glyphosate are mostly less than 5 $mgKg^{-1}$ but sometimes 20 $mgKg^{-1}$ when glyphosate is applied prior to maturation of crops [21,22]. Administration of glyphosate on a regular basis in small dosages have resulted in negatively impact in the fertility of male rats [23], whereas a single treatment at a high dosage also had a harmful impact on fertility of male laboratory rats at 500 mg kg^{-1} [9]. Male rats who were treated with soymilk at 100 $mgKg^{-1}$ had fewer spermatids and more aberrant sperm morphology than those who consumed the control soymilk [24]. The World Health Organization (WHO) presently lists glyphosate in category 2A as a potential human carcinogen [25].

There is an increase in the yield of agricultural productions up to 55% as a result of increased use of the glyphosate in Nigeria [1]. According to Ref. [26] glyphosate was reported to be the second most used herbicides in Oyo state, Nigeria. Many towns, states, and nations have taken action to either limit or outright ban glyphosate usage in agricultural practices except Nigeria. Additionally, little or no work has been done on the seasonal variations of glyphosate in Oyo State Nigeria. Therefore, the objectives of this study were to determine the physico-chemical parameters and seasonal concentrations of glyphosate in soil and water within Akufo, Otiri-Ipapo and Ilora farm settlements, in Oyo State. Glyphosate residues were also determined in crops (Cassava and maize) after harvest from these selected farm settlements. it is imperative to carry out this study as the effect of this herbicide might pose threat to the communities and human health especially uneducated farmers and their families that are in direct contact with glyphosate-based agrochemicals.

2. Materials and methods

2.1. Study area and sampling stations

The study sites were in Oyo State, which is surrounded by Kwara State to the north, Osun State to the east, Ogun State to the south, and the Republic of Benin to the west [26]. Three (3) Farm settlements; Akufo, Ilora and Otiri Ipapo located in 3 different local government areas; Ido, Oyo and Iseyin were selected for this study. The selection of these regions were founded on the fact that they are the main locations in Oyo State that grow food crops [26]. Two farms (maize and cassava farm) were selected from each farm settlement based on the most planted crops common within the settlement, resulting in six farms overall. (Fig. 1).

2.2. Water, soil and crop collection

Surface and groundwater samples were collected from each farm settlement. The surface and ground water were collected into a pre-clean amber bottles. Samples of the soil were taken from maize and cassava farm from the studied farm settlements. Samples were collected as composite from 0 to 15 cm and 15–30 cm for top and sub soil respectively using a clean soil auger into foil paper, wrapped and placed in polyethylene bags. The samples were well labeled and taken to the laboratory for further analysis. Soil and water were collected for six months (January, February, March, April, June and August) representing dry and wet season while crops (maize and cassava) were collected from each of the farm after harvest.

2.3. Physico-chemical of soil and water samples

Using a 2.0 mm mesh, soil samples were sieved and air-dried at room temperature in the laboratory. The pH of soil samples were measured with a pH meter using a ratio of 1:1 (soil to water w/v); particle size analysis of the soil was determined using hydrometer method as outlined by Ref. [27], Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} which are the exchangeable cations were determined using the method of [28]. The total organic carbon of soil were analyzed using the wet digestion method as described by Ref. [29] while total nitrogen was investigated using Kjeldahl [30]. The available phosphorus was analyzed by methods of Bray P1 [31]. Water samples were tested on-site for temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS) using Hanna combo Meter HI 98129.

2.4. Chemicals and reagents used for analysis

Glyphoste standard 99.3% purity was obtained from superclo (United States) for qualitative and quantitative analysis of analytical samples. Pesticides-grade Dichloromethane (CH_2Cl_2) 99% Methanol (CH_3OH) 99.9%, anhydrous Sodium Sulphate (Na_2SO_4) 99.5%, distilled water was obtained from milliq water distiller.

2.5. Extraction of soil, water and crops for glyphosate residue

2.5.1. Water sample extraction

Five hundred milliliter of water taken from sites was measured and poured into a 1 L capacity separatory funnel. 50 mL of dichloromethane (CH_2Cl_2) and 15 mg of sodium chloride (NaCl) was added to the seperatory funnel containing the water samples the sodium chloride solution was added to prevent emulsion formation. The content was shaking vigorously for 3 min with intermittent opening to release pressure. The organic layer was allowed to settle and the dichloromethane (CH_2Cl_2) extract was drained and

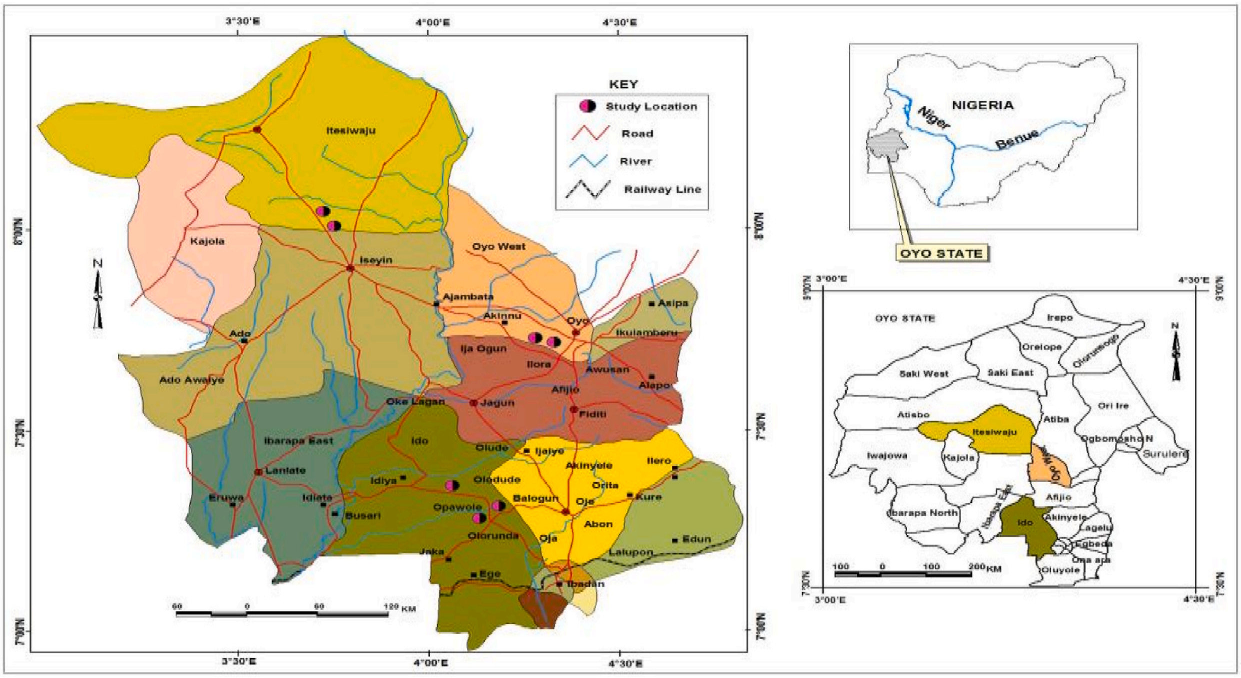

Fig. 1. Map of study area.

collected over dried anhydrous sodium sulphate (Na_2SO_4) through Whatman® 0.50 μm filter paper to remove water. The extraction was repeated twice and the extract combined. The combined extracts left to near dryness (1 mL) using a rotary evaporation (mini lab QYINS, China). The extract was cleaned using silica gel conditioned with 5 mL methanol and extract was eluted with 5 mL methanol and concentrated to 1 mL. The cleaned-up sample was then transferred into GC-MS vial using Pasteur pipette and analyzed using HPLC fluorescence detector (FLD).

2.5.2. Soil and crops sample extraction

The soil samples were extracted for glyphosate residue using soxhlet extractor following the methods of Association of Official Analytical Chemists [32]. Five gram (5 g) of each sample was weighed with an analytical weighing balance and 5 g of anhydrous sodium sulphate was added to each sample and thoroughly mixed. The samples were placed in cellulose thimble and extracted for 12 h using 150 mL of dichloromethane (DCM) in a soxhlet apparatus. The extracts were concentrated by evaporation overnight in a fume cupboard while covering with a perforated aluminum foil. Five (5) mL of DCM was used to reconstitute the dried extract in the round-bottomed flask for clean-up. Maize and cassava tubers from each of the experimental farms were harvested when they were deemed ripe enough and prepared for analysis. Three maize cob and cassava tubers were harvested from experimental farm randomly from each settlement. These were well labeled and taken immediately to the laboratory. Maize grains were removed and air dried while the cassava tubers were peeled and cut to smaller pieces and also air dried. Further extraction were carried out as specified by the Food and Agriculture Manual for the evaluation of pesticide residues in food and feed [33].

2.6. Clean-up procedure

Glass wool was placed into a 15 cm column, 7.5 g of activated silica gel was added. To remove any water or solvent that might have been in the sample or solvent, Anhydrous sodium sulphate (5 g) were added to the top of the column. 15 mL of DCM was used for pre-elution. The extracts were run through the column down to the sodium sulphate layer. This was carried out thrice, the eluate was collected into 100 mL round bottom flask and were dried by rotary evaporator to a final volume of 1 mL [34].

2.7. Stock solution preparation and equipment conditioning

A concentrated stock solution (100 ppm) of the Glyphosate standard was prepared by weighing 10 mg of the chemical into a glass beaker (100 mL), and 10 mL of methanol was used to dissolve it (50/50 v/v). An Agilent 1260 Infinity High Performance Liquid Chromatogram (HPLC) equipped with Agilent fluorescence detector (FLD: Agilent 1046A) which was set at Excitation 242 nm, Emission = 388 nm. The volume of standard injected was 25 μL, Analytical column Discovery C18 SUPELCO (15 cm × 4.6 mm × 5 μm) column (Supelco Analytical, USA), temperature 40 °C, the isocratic mobile phase 2% H_3PO_4 in water: methanol (70/30, v/v) at flow rate of 0.35 mL/min retention time 2.267. Analytes identification was based on their retention times to the retention time of the prepared standard.

Table 1
Physical and chemical properties of soil in selected farm settlements in Ido, Iseyin and Afijio LGA.

LGA	Farm settlement	Soil depth (cm)	pH	EC (μs/cm)	OC (%)	OM (%)	SAND (%)	SILT (%)	CLAY (%)
IDO	Akufo (Maize)	0–15	5.9 ± 0.14^a	645 ± 0.00^b	2.23 ± 0.35^a	3.86 ± 0.61^b	84.30 ± 0.01^a	10.50 ± 0.00^a	5.2 ± 0.01^b
		15–30	6.93 ± 0.60^a	615 ± 21.21^a	2.05 ± 0.07^a	3.54 ± 0.12^a	85.4 ± 0.01^a	11.3 ± 0.001^b	3.3 ± 0.00^a
	Akufo (Cassava)	0–15	5.5 ± 0.57^a	880 ± 14.14^b	1.90 ± 0.14^b	3.29 ± 0.24^b	78.5 ± 0.01^b	20.4 ± 0.07^a	1.1 ± 0.07^a
		15–30	6.85 ± 0.07^b	754 ± 5.66^a	1.75 ± 0.35^a	3.03 ± 0.61^a	73.5 ± 0.00^a	22.3 ± 0.04^b	4.2 ± 0.02^b
ISEYIN	Otiri (Maize)	0–15	6.70 ± 0.14^a	988 ± 2.12^a	1.62 ± 0.23^b	2.80 ± 0.40^b	72.8 ± 0.01^a	25.8 ± 0.01^b	1.4 ± 0.00^a
		15–30	6.5 ± 0.42^a	968 ± 31.11^a	1.1 ± 0.14^a	1.90 ± 0.24^a	71.4 ± 0.00^a	19.5 ± 0.00^a	9.1 ± 0.07^b
	Otiri (Cassava)	0–15	6.70 ± 0.14^a	1562 ± 3.54^b	1.90 ± 0.00^b	3.29 ± 0.00^b	69.43 ± 0.01^b	24.8 ± 0.002^a	5.77 ± 0.00^b
		15–30	6.45 ± 0.35^a	1005 ± 7.07^a	1.50 ± 0.14^a	2.60 ± 0.24^a	65.72 ± 0.00^a	30.2 ± 0.07^b	4.08 ± 0.01^a
AFIJIO	Ilora (Maize)	0–15	5.83 ± 0.04^a	1245 ± 63.64^b	2.5 ± 0.08^b	4.32 ± 0.14^b	88.41 ± 0.00^b	7.7 ± 0.00^a	3.89 ± 0.02^a
		15–30	6.54 ± 0.60^b	1205 ± 7.07^a	2.22 ± 0.31^a	3.84 ± 0.54^a	76.32 ± 0.01^a	14.3 ± 0.05^b	9.38 ± 0.01
	Ilora (Cassava)	0–15	5.51 ± 0.01^a	830 ± 56.59^b	1.67 ± 0.16^b	2.89 ± 0.28^a	70.50 ± 0.00^a	19.5 ± 0.01^b	10 ± 0.00^b
		15–30	6.45 ± 0.21^b	600 ± 0.00^a	1.42 ± 0.18^a	2.46 ± 0.31^a	79.8 ± 0.01^b	10.4 ± 0.01^a	9.8 ± 0.01^a

2.8. Statistical analysis of data

Version 20.0 of the software [Statistical Package for Social Sciences (SPSS)] was used to generate the means of physical parameters of water, soil, and glyphosate residue levels. A 1-way analysis of variance (ANOVA) was also used to identify the significant differences and similarities between physical and chemical parameters and glyphosate residues in water, soil and crops from the study area.

3. Results and discussion

3.1. Physical and chemical properties of soil in studied farm settlements

The mean values for the soil pH across the study sites are presented in Table 1. The pH values ranged from acidic to neutral for all the soil samples. Acidic pH values were recorded at the top soil for Ilora and Akufo cassava and maize farm (Table 1). The acidic nature may be as a result of acidic cations and high organic matter content present in the soil [35]. Similar report by Ref. [36] revealed that some communities in Ondo State, Nigeria that have been exposed to herbicides had soil pH ranges from slightly acidic to neutral. So, at this pH level, less pesticide will be absorbed at the soil's surface. Herbicide adsorption is pH-dependent, with low pH being the optimal pH for adsorption. The mean values of EC are presented in Table 1. Ilora maize and cassava, as well as the Otiri cassava farm, had the highest EC values above 1000 μscm^{-1} Pesticide residue mobility and persistence in the soil can be affected by the electrical conductivity of the soil. A measurement of a soil's capacity to conduct electricity is its electrical conductivity. The increase in the levels of EC may be associated with the high levels of dissolved ions in the soil.

The values obtained for organic carbon (OC) and organic matter (OM) are presented in Table 1. Soil organic matter (SOM) is made up of plant and animal remains, soil organism's cells and their by-products [37]. Higher OC and OM values were recorded at the top soil compared to sub soil. The majority of herbicides in soil adsorb more readily when the levels of organic content is high. Organic matter affects the microbial population in soil, which is crucial for the breakdown of herbicides in soil [38]. [39] found that soil organic matter significantly contributed to herbicide persistence. It has been determined that the presence of organic matter and herbicide persistence in soil are positively correlated [40]. Herbicides remain on the surface longer when there is more organic carbon in the surface soil than when there is less [41].

The mean values of sand, silt and clay are presented in Table 1. The soil detected inside the examined sites belonged to the textural class of sandy-loamy. The soils' high concentration of sand may be a result of Nigeria's typically sandy, humid tropical soils [42].The sandy nature of the soil encourages the leaching of numerous soil properties into the groundwater, rivers, lakes, and streams nearby during the rainy season when herbicide treatment occurs [36]. Soils that have a significant amount of sand particles are referred to as Sand, loamy sand, or sandy loam soils and are considered to be coarse in texture. Herbicides drain more quickly through coarse-textured (sandy) [43].

The mean values for total nitrogen content (N) are presented in Table 2. The total nitrogen levels in the soil within the studied farms were measured at medium levels. According to Singh et al. (2011) nitrogen content between 0.15 and 0.20% was rated medium while above 0.20% high. In a lengthy field study in Argentina, the impact of glyphosate on soil nitrogen content was examined with its effect

Table 2
Physical and chemical properties of soil in selected farm settlements in Ido, Iseyin and Afijio LGA continued.

LGA	Farm settlement	Soil depth (cm)	Textural class	N (%)	P ($mgKg^{-1}$)	K^+ ($mgKg^{-1}$)	Ca^{2+} ($mgKg^{-1}$)	Na^+ ($mgKg^{-1}$)	Mg^{2+} ($mgKg^{-1}$)
IDO	Akufo (maize)	0–15	Sandy-loamy	0.12 ± 0.07^a	4.34 ± 0.47^b	0.54 ± 0.02^a	4.88 ± 0.04^b	0.41 ± 0.01^b	5.10 ± 0.09^b
		15–30	Sandy-loamy	0.09 ± 0.00^a	3.89 ± 0.15^a	0.46 ± 0.08^a	3.78 ± 0.16^a	0.34 ± 0.06^a	3.22 ± 0.01^a
	Akufo (Cassava)	0–15	Sandy-loamy	0.15 ± 0.07^a	3.34 ± 0.13^a	0.44 ± 0.23^b	4.16 ± 0.23^b	0.32 ± 0.01^a	2.12 ± 0.00^a
		15–30	Sandy-loamy	0.18 ± 0.02^a	3.29 ± 0.40^a	0.32 ± 0.01^a	3.95 ± 0.07^a	0.29 ± 0.03^a	1.89 ± 0.01^a
ISEYIN	Otiri (maize)	0–15	Sandy-loamy	0.15 ± 0.22^a	3.99 ± 0.01^a	0.93 ± 0.04^b	5.23 ± 0.04^a	0.41 ± 0.03^a	3.97 ± 0.19^b
		15–30	Sandy-loamy	0.17 ± 0.13^a	3.62 ± 0.06^a	0.69 ± 0.13^a	5.11 ± 0.01^a	0.40 ± 0.07^a	3.00 ± 0.02^a
	Otiri (cassava)	0–15	Sandy-loamy	0.13 ± 0.18^b	4.14 ± 0.07^b	0.84 ± 0.01^b	5.39 ± 0.09^a	0.29 ± 0.16^a	2.87 ± 0.04^b
		15–30	Sandy-loamy	0.14 ± 0.02^a	3.89 ± 0.01^a	0.68 ± 0.00^a	5.76 ± 0.31^a	0.19 ± 0.11^a	2.17 ± 0.01^a
AFIJIO	Ilora (maize)	0–15	Loamy-sandy	0.15 ± 0.02^b	3.56 ± 0.01^a	0.64 ± 0.02^b	5.03 ± 0.04^b	0.48 ± 0.01^a	3.87 ± 0.13^a
		15–30	Loamy-sandy	0.18 ± 0.11^a	3.99 ± 0.01^a	0.32 ± 0.01^a	$4.78 \pm 0.39a$	0.44 ± 0.17^a	3.81 ± 0.22^a
	Ilora (cassava)	0–15	Sandy-loamy	0.16 ± 0.07^a	3.84 ± 0.06^a	0.97 ± 0.01^b	8.23 ± 0.03^b	0.55 ± 0.00^b	4.89 ± 0.02^b
		15–30	Sandy-loamy	0.14 ± 0.04^a	3.85 ± 0.07^a	0.75 ± 0.01^a	5.98 ± 0.01^a	0.23 ± 0.04^a	4.02 ± 0.02^a

on the soil nitrogen cycle. It was reported that glyphosate use decreased the total nitrogen content of soil, microbial biomass, and increased soil nitrate leaching [44]. Also, some recent researches have emphasized the possible harm that glyphosate residues may cause to soil microbial populations and nitrogen levels [45].

The mean values for available phosphorous (P) from the studied farm sites are presented in Table 2 The availability of important elements such as phosphorous can be impacted by glyphosate residue in the soil, which may have an impact on soil fertility. The impact of glyphosate residue on microbial soil communities and nutrient cycling in a soybean field were examined, and it was reported that glyphosate residue decreased the amount of available phosphorous and the microbial populations in the soil which could be detrimental to growth of plant and health of soil [46,47].

The values for potassium ($K^{+)}$ calcium (Ca^{2+}), sodium ($Na^{+)}$, and magnesium (Mg^{2+}) are also presented in Table 2. Generally low levels were recorded at the sub soil compared to top soil. The macronutrients K^+, Ca^{2+}, Na^+, and Mg^{2+} are necessary for plant development and for preserving the health of the soil. Keeping track of their presence in the soil is essential for sustainable agricultural methods. The impact of glyphosate treatment on soil K^+, Ca^{2+}, Na^+, and Mg^{2+} concentrations was studied by Ref. [48] they discovered that glyphosate application reduced the concentrations of K^+ and Ca^{2+} in soil, while Na^+ and Mg^{2+} concentrations were not significantly affected. This suggests that glyphosate residue may have negative impacts on plant development and growth and soil health by decreasing the availability of crucial macronutrients. Another study by Ref. [49] investigated into how long-term use of glyphosate affected soil K, Ca^{2+}, Na^+, and Mg^{2+} concentrations, they discovered that while Na^+ and Mg^+ concentrations were not significantly impacted by long-term glyphosate usage, K^+ and Ca^{2+} concentrations in soil decreased. This study emphasizes the necessity for sustainable herbicide use as well as possible long-term consequences of glyphosate use on soil health. Furthermore, effects of various K^+ fertilization rates on maize development and yield in a calcareous soil were studied by Ref. [50], higher K^+ fertilization rates were observed to increase the levels of K^+ in soil, which helps to improve plant growth, and boost maize yields. Additionally, in sandy loam soils, it has also been shown that Mg^+, K^+, and Ca^{2+} increase the glyphosate adsorption coefficient. these cations can stabilize glyphosate in agricultural soils by continuously creating insoluble compounds with glyphosate for an extended period of time [51].

3.2. Physical and chemical properties of water within studied farm settlements

The pH values of water from the studied farm settlements for groundwater (wells) ranged from slightly acidic to near neutral while values for surface water (streams and lake) were slightly acidic (Table 3). The mean pH values recorded for all groundwater falls within the 6.5 to 8.5 acceptable limits for drinking and domestic chores [52] while the values for surface water fall below the acceptable limit making it unfit for drinking [53]. also reported a pH range of 6.42–7.40 in a similar study. The slightly acidic mean values recorded for surface water at all study farmland may be linked to the concentrations of organic matter in soil zones and the amounts of acidic cations in the adjacent soil oxidize to release CO_2 that reacts with H_2O to form H_2CO_3 [35].

The EC values of the water samples (Table 3) recorded across the farmlands falls within the allowable limit of 1000 μS/cm for potable water [52]. However, higher values were recorded in surface water compared to ground water samples. Several reports have investigated the relationship between water's electric conductivity and pesticide residue levels. According to a [54] electric conductivity and the amount of pesticide residue in water were positively correlated. In this case, it is possible that water with higher electric conductivity levels may contain more pesticides. Also, the connection between electric conductivity and pesticide residues in water was also studied by Ref. [55], It was reported that some pesticides, like atrazine and simazine, had a positive correlation between electric conductivity and their concentrations, In addition [56], discovered a positive correlation between electric conductivity and the levels of specific pesticides, such as carbofuran and chlorpyrifos, in water samples.

The temperature for water samples from each studied farm settlements varied between 28.00 and 32.0 °C for all the water samples (Table 3). The temperature for groundwater samples were between 28.00 and 31.0 °C while surface water ranged from 30.0 to 32.0 °C thus, groundwater samples had relatively lower temperatures compared to surface water. All ground water samples fall within the permissible limit of WHO temperature range for drinking water 22 °C and 29 °C [57] except for groundwater at Akufo farm settlement which had slightly higher value of 31.00 °C. The surface water values exceeded the WHO permissible limit. Weather patterns during the sampling period and the groundwater inflow may contribute to high value in both surface and groundwater samples. Temperature contributes a crucial part in water's physical and chemical properties as well as the metabolic functions of living things. The varying difference in values reported may also be attributed to the various water sample sources used and the timing of the sampling [35].

The levels of TDS of the sampled water are presented in (Table 3). Surface water's TDS was within the acceptable range from WHO (2004) of 1000 mgL^{-1} [58]. An assessment of the concentration of all organic and inorganic components dissolved in water is called TDS. Akufo water recorded a much higher TDS of 1685 ± 0.07 mgL^{-1} this could be linked to the nature of the water being a lake [59].

Table 3
Physical and chemical properties of water samples from selected farm settlements.

LGA	Farm settlement	Water body	Distance (m)	pH	EC μS/cm	Temp °C	TDS (mgL^{-1})	Phosphate (mgL^{-1})	Nitrate (%)
Ido	Akufo	Lake	100	5.8 ± 001^a	707 ± 0.07^b	30.00	1685 ± 0.07^e	$15.6 \pm .12^d$	4.89 ± 0.02^c
		well	500	6.8 ± 0.02^c	546 ± 0.24^a	31.00	577 ± 0.17^a	2.90 ± 0.00^b	0.56 ± 0.77^a
Iseyin	Otiri	Stream	200	5.4 ± 0.17^b	899 ± 0.05^d	32.00	1538 ± 0.00^d	5.9 ± 0.02^c	1.83 ± 0.17^{bc}
		Well	800	7.2 ± 0.02^c	780 ± 0.00^c	29.00	640 ± 0.07^b	3.67 ± 0.01^{cb}	0.3 ± 0.77^a
Afijio	Ilora	Stream	100	5.3 ± 0.24^a	976 ± 0.07^e	31.00	840 ± 0.07^c	7.89 ± 0.02^c	1.7 ± 0.02^b
		Well	50	6.1 ± 0.00^b	720 ± 0.00^c	28.00	532 ± 0.00^a	1.77 ± 0.07^a	0.2 ± 0.01^a

studied the effects of TDS on the persistence and degradation of a widely used insecticide in water it was discovered that greater TDS levels caused the insecticide to persist in the water longer, indicating that increased TDS may result in larger quantities of pesticide residues in the water. The connection between TDS and pesticide residues in water from various sources in Iraq was examined by Ref. [60], they discovered a positive correlation between TDS levels and pesticide residue levels, suggesting that increase in TDS levels may be a contributing reason to increased levels of pesticide residue in water. The mean values of phosphate in groundwater (Table 3). were within the allowable level of 3.5 mg/L by Ref. [61] and 5.0 mgL^{-1} by Ref. [52] while surface water exceeded these limits [62]. reported how phosphate affected the degradation of herbicide in water, they discovered that higher phosphate levels reduce the rate of the herbicide's degradation, which led to increased pesticide residue levels in the water. This implies that higher phosphate levels may result in higher pesticide residual levels in water. Also, reported a high concentration in a River in India. Similar trend was reported for phosphates in a study carried out in Indonesia [63].

The mean values for nitrate (Table 3). in surface water was higher compared to groundwater. High concentration of nitrate can be attributed to the usage of fertilizers which contains high levels of Nitrogen derived from farmlands. The high concentrations of both phosphate and nitrate in surface water around the farm settlements can be attributed to Insufficient water inflow during the dry season and the buildup of nutrients during the rainy season as a result of household and farming operations near the shores of the sampled water bodies that serve as sources for people who reside in the farm settlement [64]. In their research in a wetland in India, discovered a significant concentration of phosphate, which they attributed to agricultural runoff from fields, particularly during the rainy season [65]. also noted that at Gilgel Gibe Catchment, Southwest Ethiopia, agricultural and urban streams had higher nitrate concentrations than did forest streams and this was linked to intensive cultivation of crops and intensive usage of fertilizers with high nitrogenous content [66]. also reported that the increase level of NO_3^- in River Jinsha in China were as a result of nitrogenous fertilizers usage from farms on the bank of the sampled river. Agricultural runoff contributed to 54% of nitrogen and phosphorous load in Taihu lake Basin in China according to Ref. [67].

3.3. Seasonal concentration of glyphosate in top soil and sub soil from the studied farm settlements

The mean concentration of glyphosate residue in Akufo, Otiri and Ilora farm settlements for dry and wet season are presented in Table 4 Akufo cassava farm recorded a much higher value of glyphosate during wet season compared to maize farm. (Table 4).

The mean concentration values recorded in Ilora farm settlement also recorded higher values in wet season for both cassava and maize farm compared to dry season.

The rainy season plays a crucial role in determining agricultural productivity and ultimately, the livelihoods of millions of smallholder farmers [68]. Recently, there have been growing concerns regarding the abundance, availability and effects of glyphosate on soil during raining season [69]. When glyphosate is applied during the time of land preparation, the majority of it is absorbed on the soil while a small amount is absorbed into the plant's stalk. When this occurs, microbial degradation cannot take place, so there is a release of this herbicide during the process of leaf senescence, which increases its availability in the soil [70]. Furthermore, activities of microorganisms reduces at wet season, which has a negative impact on how microorganisms degrade glyphosate [71,72] as a result, allowing glyphosate to persists longer in the soil during raining seasons [73]. also reported the half-life of glyphosate in soil varies from a few days to months, and some data indicate that glyphosate can stay in the soil for years [14]. also reported high levels of glyphosate in Kuti stream, Abuja during raining season which was linked to high concentrations of glyphosate in soil of nearby farm close to the stream. Samples of were taken from a region in Tasik Chini, Pahang, Malaysia, which produces oil and their concentrations of glyphosate and its primary metabolite were assessed, values ranged from not detected (ND) to 6.0 mg kg^{-1} in soils and sediments [74].

3.4. Seasonal concentration of glyphosate in surface water within the studied farm settlement

Glyphosate residues detected in surface water samples are presented in Table 5. The water samples from Otiri, Ilora and Akufo farm

Table 4
Glyphosate concentration ($mgkg^{-1}$) in soil (top and sub soil) of maize and cassava farms in Akufo, Otiri and Ilora farm settlement.

Month	Akufo				Otiri				Ilora			
	Maize		Cassava		Maize		Cassava		Maize		Cassava	
	Top soil	Subsoil	Top soil	Subsoil	Top soil	Subsoil	Top soil	Subsoil	Top soil	Subsoil	Top soil	Subsoil
January	1.29 ± 0.00^{a}	1.12 ± 0.01^{a}	1.42 ± 0.01^{a}	1.95 ± 0.01^{a}	1.78 ± 0.16^{a}	1.65 ± 0.14^{a}	1.82 ± 0.16^{a}	1.69 ± 0.21^{a}	1.76 ± 0.09^{a}	1.58 ± 0.09^{a}	1.11 ± 0.00^{a}	1.15 ± 0.01^{a}
February	1.38 ± 1.36^{a}	1.18 ± 0.00^{a}	1.92 ± 0.01^{a}	1.84 ± 0.24^{a}	1.73 ± 0.25^{a}	1.59 ± 0.20^{a}	1.55 ± 0.30^{a}	1.67 ± 0.18^{a}	1.67 ± 0.03^{a}	1.88 ± 0.00^{a}	1.71 ± 0.00^{a}	1.60 ± 0.08^{a}
March	5.85 ± 0.16^{b}	5.23 ± 0.08^{b}	7.66 ± 0.02^{b}	6.28 ± 0.06^{b}	1.76 ± 0.03^{a}	1.64 ± 0.13^{a}	1.70 ± 0.04^{b}	1.56 ± 0.18^{a}	4.92 ± 0.11^{b}	5.13 ± 0.06^{b}	4.66 ± 0.02^{b}	4.77 ± 0.77^{b}
April	9.49 ± 0.06^{ab}	9.16 ± 0.14^{ab}	10.61 ± 0.36^{c}	10.15 ± 0.04^{c}	17.11 ± 0.52^{c}	14.41 ± 1.69^{b}	17.56 ± 1.05^{c}	15.93 ± 2.27^{b}	8.53 ± 0.00^{c}	6.44 ± 0.25^{b}	6.61 ± 0.36^{b}	6.45 ± 0.18^{ab}
June	13.40 ± 0.39^{c}	13.51 ± 0.01^{c}	19.98 ± 0.00^{d}	19.17 ± 0.01^{d}	14.89 ± 0.38^{b}	14.11 ± 0.15^{b}	15.34 ± 0.48^{b}	14.60 ± 0.71^{b}	13.40 ± 0.39^{d}	10.91 ± 0.01^{c}	11.38 ± 0.13^{c}	11.47 ± 0.42^{c}
August	22.34 ± 0.00^{d}	22.32 ± 0.01^{d}	25.19 ± 0.02^{e}	25.11 ± 0.00^{e}	19.40 ± 0.38^{d}	18.54 ± 0.50^{c}	17.36 ± 0.31^{ab}	17.41 ± 0.69^{c}	15.89 ± 0.06^{d}	14.3 ± 0.12^{d}	18.78 ± 0.14^{cd}	14.62 ± 0.69^{d}

Table 5
Glyphosate concentration (mgL^{-1}) in surface water of Otiri, Ilora and Akufo farm settlements.

Month	Otiri Farm (Stream)		Ilora Farm (Stream)		Akufo Farm (Lake)	
	Upstream (200 m)	Down stream	Upstream (300)	Downstream	Upstream (100 m)	Downstream
Jan	1.83 ± 0.15^{a}	1.39 ± 0.21^{ab}	1.57 ± 0.02^{a}	1.02 ± 0.00^{a}	1.77 ± 0.02^{a}	1.22 ± 0.00^{a}
Feb	2.84 ± 0.46^{a}	2.67 ± 0.14^{a}	2.05 ± 0.00^{a}	1.97 ± 0.28^{a}	3.00 ± 0.07^{b}	3.00 ± 0.00^{a}
Mar	7.87 ± 0.04^{ab}	6.94 ± 0.09^{b}	3.17 ± 0.04^{a}	3.12 ± 0.00^{b}	5.92 ± 0.31^{ab}	5.707 ± 0.06^{b}
Apr	15.76 ± 0.02^{c}	9.65 ± 0.15^{c}	13.86 ± 0.00^{b}	8.12 ± 0.00^{c}	15.33 ± 0.62^{c}	10.32 ± 0.14^{c}
Jun	18.60 ± 0.39^{c}	10.09 ± 0.13^{d}	19.16 ± 0.05^{d}	8.45 ± 0.03^{c}	21.05 ± 0.24^{cd}	13.40 ± 0.53^{cd}
Aug	20.87 ± 0.07^{d}	10.21 ± 0.01^{d}	15.55 ± 0.00^{ab}	15.53 ± 0.00^{d}	26.18 ± 0.83^{d}	22.54 ± 0.00^{cd}

settlement recorded highest concentrations of glyphosate at the upstream level between April to August (wet season) compared to dry season. Also, Surface water in Ilora and Akufo farm settlements recorded the highest concentration both at dry and wet season at the upstream levels. while the least concentration was recorded in Otiri farm settlement (downstream) for dry season.

Generally, the highest concentrations were observed in August and lowest January. However, the values recorded were above the allowable contaminant level of 0.7 mgL^{-1} [75]. The high level of glyphosate observed during the wet season at all studied farm settlements could be attributed to farming activities which is majorly carried out during this season, usage and heavy application of glyphosate-based herbicides (GBH) on the farmlands to remove weeds. This can be washed by heavy down pour of rain through agricultural runoff and drift into water bodies around the farm settlements. Also, the proximity of the farm settlements to water bodies can also increase the level of glyphosate in water [14]. Akufo farm settlement has a lake that provides water for farmers for planting and for domestic usage, the presence of slope around the lake encourages easy run-off into it. However, numerous studies have found glyphosate and its metabolite in various water bodies Surface water in Alberta, a western Canadian region where grain is grown, contained concentrations between 0.2 and 6.079 μgL^{-1} [76]. Investigations into the herbicide's existence in the United States have been reported in various states. Samples were gathered in spring ponds and nearby streams during pre and post herbicide application to some crops, concentrations of up to 328 μgL^{-1} were discovered in these areas that were higher than the freshwater aquatic life standards of 65 μgL^{-1} [77]. Glyphosate has been found in various water sources close to planted crops in Colombia, including streams and reservoirs, primarily during the months of June and July (wet seasons). Concentrations between 201 and 2777 μgL^{-1} were discovered [78].

3.5. Seasonal concentration of glyphosate in groundwater within the studied farm settlement

The concentration of glyphosate in groundwater within the farm settlements are presented in Fig. 2. Generally, higher concentrations were observed during wet season at all studied farm settlements which are within the Canadian maximum permissible limit of 0.7 mgL^{-1} [75]. Spillage of glyphosate through runoff and leaching into water bodies pose a threat to people's health or the biota that live within the ecosystems where such herbicides are used [79]. According to the research carried out around some agricultural localities in Mexico for abundance of glyphosate in groundwater and sealed water it was reported that ground water had the highest concentration of 1.42 μgL^{-1} [79]. Additionally, the site conditions, dimension of the water table and proximity of the water to farm site could be a contributory factor for the leaching process [80]. Presence of glyphosate in water bodies may also be attributed to farmers mixing and preparing their herbicides besides the well. Well water within the farm settlements are the major resources of water used by the settlements for drinking, irrigation, and animal husbandry [14,35]. also reported values within the maximum permissible limit of 0.7 mgL^{-1}. A study by Ref. [81] in Chiapas, Mexico observed increase in the quantities of glyphosate (0.04 mgL^{-1}) in the groundwater close to agricultural crops, According to Ref. [82], 0.04 mgL^{-1} of glyphosate was discovered groundwater, in a rural place in Canada.

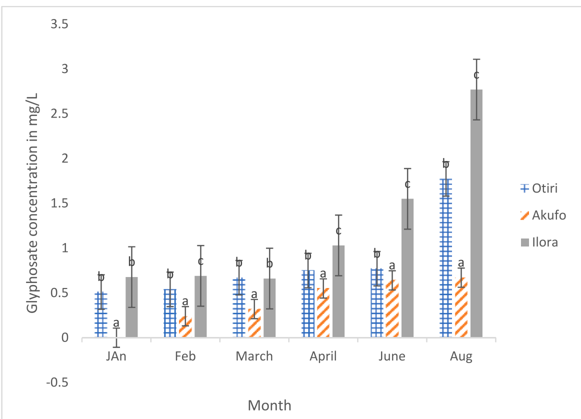

Fig. 2. Glyphosate concentration (mgL^{-1}) in groundwater of Otiri, Ilora and Akufo farm settlements.

Preferential flow could transport glyphosate to water ways, as well as intensive rainfall soon after application of glyphosate which makes this herbicide run a high possibility of entering the groundwater in substantial levels. Also, herbicide may also accumulate through infiltration into wells in crop fields where pesticides are applied [79].

3.6. Seasonal concentration of glyphosate in harvested crops (maize and cassava)

Glyphosate concentration of cassava and maize collected after harvest from the 3 different farm settlement are presented in Fig. 3. Generally, the mean values of glyphosate in cassava were higher than concentrations found in maize Nonetheless, the concentrations were within the USEPA 2002 glyphosate daily chronic Reference Dose (cRfD) of 1.75 $mgKg^{-1}$ bodyweight (mg/kg bodyweight/day) for human exposures [83]. [2,84] recorded high mean values of herbicide residue in cassava, yam, potato and groundnuts compared to grain crops. In most cases glyphosate is used in weed management in root crops especially when tubers of these crops are formed and matured, this leads to absorption of the herbicides and their derivatives in the harvested crop, thus the high concentration of glyphosate recorded in cassava. Several studies have revealed the presence of glyphosate and its metabolite (AMPA) in some crops which were within the USEPA 2002 cRfD limit [85]. investigated how much glyphosate was present in the soil of a mango orchard and how much was absorbed by the fruit. glyphosate residue levels were below the threshold that could be detected in ripe fruits because the chemical is strongly absorbable by the soil, which is practically immobile and highly degradable. Also [86], investigated the availability of glyphosate and AMPA in a total of 243 samples of various fruits, and reported that all samples were within the maximum permissible limit. However [87], reported that glyphosate and its metabolite, AMPA, were not detected in cassava within the cover crops in the Amazon ecosystem even with five applications per year. While glyphosate levels in soybeans were reported to be 1.8 $mgKg^{-1}$ for three times applications of glyphosate which is above the cRfD allowable dose, it was concluded that glyphosate and AMPA concentrations were higher when sprayings were done later in the growing season, close to time of blooming [83]. The crop and the region where it was cultivated can have a significant impact on the residue level.

3.7. Research limitations

There are some other farm settlements within the state which need to be evaluated for a longer period of time, however lack of funding limited the research to just three (3) farm settlements for six (6) months. A long-term investigation will provide a compounded effect of glyphosate on the well-being of soil, the purity of water, and the harmony of ecosystems at large. Also, historical data is unavailable, which made it difficult to differentiate whether the detected residues are an outcome of recent applications or a repercussion of prior glyphosate usage.

4. Conclusion and recommendations

The application of herbicides in agricultural farmlands have increased marginally due to its benefits in crop yield and reduced cost of labor. However, the benefits cannot be compared to the deleterious impact on human health. This research revealed that there are glyphosate residues in soil, water and crops (maize and cassava) within the studied farm settlements. The presence of these residues are attributed to the intense agricultural activities within the farm settlements. The amount of glyphosate in the groundwater was quite low compare to the concentrations observed in surface water which were above the Canadian permissible limit of 0.7 mg/L. High concentration values of glyphosate were also recorded in soil. values observed in cassava were higher compared to maize but were all within the daily chronic Reference Dose. With the development of glyphosate-tolerant crops, repeated applications of glyphosate will soon become standard practice. This could affect how glyphosate is distributed as well as how this herbicide behaves throughout its sorption and desorption processes in soil.

Nonetheless, there is a need to embrace an eco-friendly agricultural practice which include, conservation tillage, ecological ditches, removal of weeds biologically and also, sensitization of farmers in the use of glyphosate in land clearing and its impact on water bodies within the farms and crops planted. Further studies should be carried out to cover more local government areas and farm settlements within the state, Government should also consider funding of researches like this as data obtained can be used in policy formulation and revision.

Author contribution statement

Olanrewaju Olusoji Olujimi: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper. Rhoda Titilope Ayoola: Performed the experiments; Analyzed and interpreted the data; Wrote the paper. Babtunde Saheed Bada; Gabriel Adewunmi Dedeke: Analyzed and interpreted the data; Wrote the paper.

Data availability statement

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to

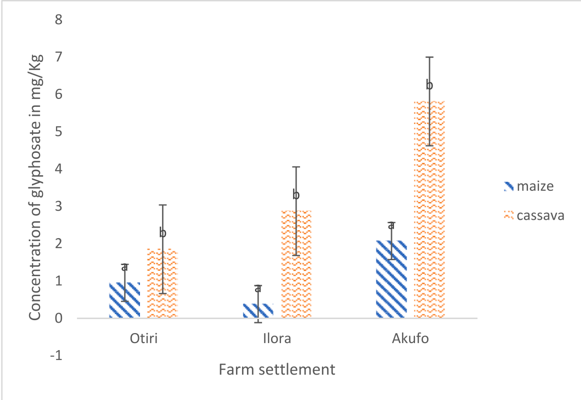

Fig. 3. Glyphosate concentration (mgKg^{-1}) in harvested maize and cassava from Otiri, Ilora and Akufo farm settlements.

influence the work reported in this paper.

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