



Assessment of persistent organic pollutants in soil and water of kara bisichi, barkin ladi lga of Plateau state, Nigeria

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Abstract

Persistent organic pollutants (POPs) are organic compound that remain intact for exceptionally long periods of time in the environment as they resist photolytic, chemical and biological degradation. Environmental impacts from POPs continue to generate global concern and attract attention especially in urban centers, Some POPs compounds which are toxic, mutagenic, or carcinogenic and can bio-accumulate by aquatic organisms, plants and human from polluted water and soil. The study aims to identify and quantify the presence of POPs in soil and water of Kara Bisichi of Barkin Ladi Local Government Area of Plateau State, Nigeria. Soils and water sample were randomly collected at five points within the study area. The pesticide residual levels of the POPs were determined using Gas chromatography- electron capture detector (GC/ECD). The soil samples of both the treated and control had concentrations range of :aldrin (0.008-0.054mg/kg), dieldrin (0.004-0.012mg/kg), heptachlor epoxide (0.009-0.013 mg/kg), paraquat (ND – 0.014 mg/kg), dichlorvos (0.008-0.010 mg/kg), sulprofos (0.002-mg/kg), endosulfan II (ND – 0.0104 mg/kg), all falls within the USEPA and UK MRL standard value of 0.02mg/kg and 0.01mg/kg, except for glyposate (0.0189-0.656mg/kg), dimethoate(0.0132-0.049mg/kg), chlorpyrifos (ND-0.209mg/kg) and cypermethrin (ND-0.176mg/kg) which falls above. And for the water sample had the concentration of: aldrin (0.013mg/l), dieldrin (0.003mg/l), Paraquat (0.010mg/l), dichlorvos (0.077mg/l), glyphosate (0.004mg/l), sulprofos (0.173mg/l). Dimethoate (0.035mg/l), propyzamine (0.712mg/l), atrazine (0.568mg/l), heptachlor epoxide (0.077mg/l), chlorpyrifos (0.173mg/l), *p,p*-DDT (0.010mg/l) and (0.021mg/l), which all falls within the USEPA, WHO, Australia, Canadian and EU standard value for pesticides in water respectively except for Heptachlor epoxide and chlorpyrifos whose values (0.774mg/l and 0.173mg/l) were above the MRL set by WHO/Australian as (0.03mg/l and 0.05mg/l).

Keywords: persistent organic pollutants, soil, water, kara bisichi

Introduction

Soil is a mixture of organic matter, minerals, gases, liquids and organisms that together support life. The earth's body of soil is the pedosphere which has four important functions; it is a medium for plant growth; it is a means of water storage, supply and purification; it is a modifier of earth's atmosphere; it is a habitat for organisms; all of which, in turn, modify the soil. Soil interfaces with lithosphere, the hydrosphere, the atmosphere, and the biosphere [1].

Soil pollution is defined as the presence of toxic chemicals (contaminants) in soil, in high concentrations that can pose a risk to human health and /or the ecosystem. Soil contaminants occur naturally in soil, their levels are not high enough to pose a risk and soil pollution is said to occur if the levels of the contaminants in soil exceed the levels that should naturally be present [2].

A clean water is colourless, transparent, odourless. Water is a compound of oxygen and hydrogen (chemical formula; H₂O) with higher distinctive physical and chemical properties: it is able to dissolve many other substances. its solid form (ice) is less dense than the liquid form; its boiling point; viscosity, and surface tension are unusually high for its molecular weight, and it is partially dissociated into hydrogen and hydroxyl ions, [3].

Surface water is used to describe a collection of freshwaters on land (rivers, streams, creeks, lakes and reservoirs). They are

vitaly important to our everyday life. The main uses of surface water include drinking, and other public uses like irrigation, power generating industry to produce electricity for powering equipment [4]

Persistent organic pollutants (POPs) are organic compounds of natural or anthropogenic origin that possess a particular combination of physical and chemical properties such that, once released into the environment, they remain intact for exceptionally long periods of time as they resist photolytic, chemical and biological degradation [5].

At the United Nations Environment Program Stockholm convention 2001 [6], legislature from 92 republic approved the Stockholm convention on POPs to decrease and/ or eradicate the discharge of 12 unique POP substances; the substances are referred to as the "dirty dozen" or "legacy POPs". Although additional pollutants have been identified, the key concern is these unique 12. The group include 10 intentionally produced pollutants; aldrin, endrin, chlordane, dichloro diphenyl trichloro ethane (DDT), dieldrin, heptachlor, mirex, toxaphene, hexachlorobenzene (HCB), and polychlorinated biphenyls (PCBs), and two unintentionally generated contaminants, polychlorinated dibenz-o-dioxins (PCDDs) and polychlorinated dibenofurans (PCDFs) [7]. Polycyclic aromatic hydrocarbons (PAHs) are categorized as persistent organic pollutants as well,

and combustion and burning of organic contaminants produces these substances unintentionally.

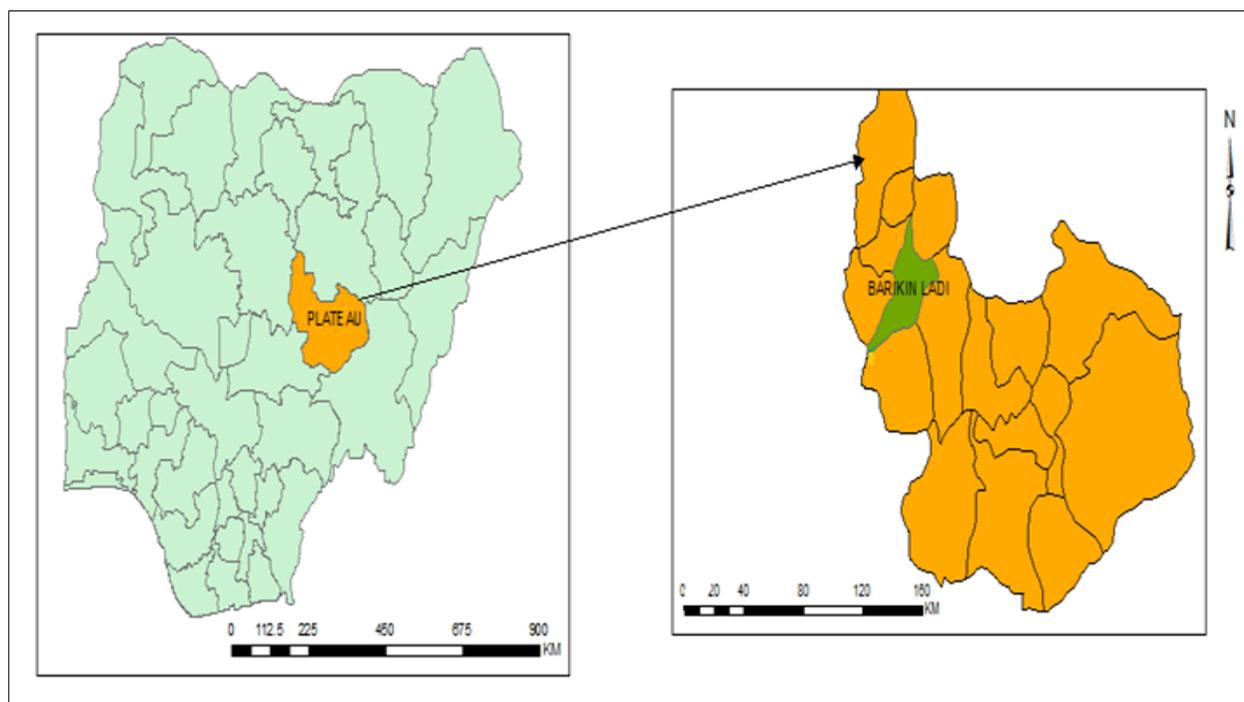
POPs like PCBs (Polychlorobiphenyls) are excellent dielectric fluids in electrical capacitors and transformers because their light resistant to degradation and fire. A single application of chlordane, an organochlorine-termiticide, provides household termite protection for years. DDTs has the ability to repel and injure or kill malaria carrying mosquitoes can provide several months of household protection, POPs like DDT, Aldrin, Deldrin has been widely used in agricultural activities to augment the crop production and yield. Mirex is still used in the USA mainly as a flame-retardant in plastics, rubbers, paints, paper, and electronics. Despite the wonder uses of POPs, they can also have serious detrimental effects on the environment and humans. Birth defects, certain cancers and tumors at multiple sites, immune-system disorders, and reproductive problems, reducing ability to fight diseases, stunted growth, and permanent impairment of brain function. POPs are suspected carcinogens and have been implicated in disease such as endometriosis (a painful, chronic gynecological disorder that affects uterine tissue), increased incidence of diabetes, and neurobehavioral impairment, including learning disorders, reduced performance on standard tests, and changes in temperament. PCBs are known to induce vitamin A deficiency in mammals, an effect that may be associated with impairment of the immune system, reproduction and growth. The entire ecosystems are affected by the use of pesticides - not only by POPs pesticides birds, mammals, insects and all other living creatures are poisoned either directly or indirectly by feeding upon poisoned food, they experience reductions in food supply and habitat for both themselves and their prey due to the extensive use of pesticides. POPs can have serious environmental and human effects that includes, birth defects, certain cancers and tumors at multiple sites, immune-system disorders, and reproductive problems, reducing ability to fight diseases, stunted

growth, permanent impairment of brain function. POPs are suspected carcinogens and have been implicated in disease such as endometriosis (a painful, chronic gynecological disorder that affects uterine tissue), increased incidence of diabetes, and neurobehavioral impairment, including learning disorders, reduced performance on standard tests, and changes in temperament. PCBs are known to induce vitamin A deficiency in mammals, an affect that may be associated with impairment of the immune system, reproduction and growth. Environmental symptoms such as a shift in sex ratios, cancer in wildlife animals, impaired fertility and/or other physical abnormalities can barely be explained at the current stage of scientific knowledge due to the presence of POPs.

This paper therefore aims to address the environmental impacts of persistent organic pollutants as it continues to generate global concern and attract attention especially in the urban areas. It is therefore, important to monitor the presence of persistent organic pollutants in water and soil and also ascertain their concentration levels in crops grown around prone areas. This will help cope the menace of these pollutants as regard their carcinogenic characteristics. This study, would provide information about the presence, concentration as well as give an indication of the toxicity levels of persistent organic pollutants in water and soil samples from Kara Bisichi of Barkin Ladi Local Government Area of Plateau state

Study area

Kara Bisichi is located 27.9 kilometers from Jos, Plateau State capital. It is situated in Barkin Ladi local Government Area on longitude 9o32'N and latitude 8o55'E The common crops grown there are maize, cabbage, sweet and irish potato, acha, millet, sorghum, pepper and beans.



Source: Center for Remote Sensing.

Fig 1: Map of Nigeria Showing Plateau State and Barkin Ladi Local Government Area



Fig 2: Satellite Map of Kara Bisichi Showing Sampling Area (Google Map)

Methodology

Sample Collection

Soil auger was used for collection of soil samples by method adopted by Dodo,^[8] Trenchard, Joseph, Anthony and Ivara^[9] and Onyeonwu^[10]. The soil samples were then transported to the laboratory, exposed for air drying for seven days. The samples were crushed and sieved through a mesh size of 2 mm and 0.5 mm respectively and for further analysis.

The water sample was collected beside the farmland on which the soil sample were collected. According to standard methods. The temperature was taken using a mercury glass thermometer on sampling site before transported to the laboratory. The pH and conductivity of the water samples were taken immediately using pH meter and a conductivity meter on arrival at the laboratory. The samples were coded as follows; KT = Soil sample treated with both herbicides and pesticides.

Kc = Soil control sample.

Kw = Water sample near farmland treated with herbicides or pesticides.

All chemicals and reagent used were of analytical grade, distilled water was used throughout. The soil samples collected on the farmland where herbicides and pesticides have been applied for at least three years and above and under cultivation. The soil pH samples were determined by pH meter, Electrical Conductivity was determined by using the conductivity cell (model Hanna HI86304) with the range of 0.00-19.99 mS/cm, soil particle-size analysis was by Bouyoucos Hydrometer Method^[11] Soil texture class was based on the soil textural triangle. Organic Matter Content by Walkley-Black Method^[12] Organic Nitrogen Content was determined using the method described by Ibitoye.^[13] determination of Phosphorus was by Bray -P1 Method^[14], Exchangeable Ca and Mg were by EDTA Titration^[15], potassium (K) and sodium (Na) were determined by Flame photometer, Turbidity of Water Sample was taken at 450 nm using HACH Spectrophotometer, Dr

/2000. Determination of Total Dissolve Solid (TDS) and Total Suspended Solids (TSS) in water was determined by standard methods. Extraction of soil and water sample(s) for GC/ECD analysis was done using a mixture of methanol and hexane in a ratio of 2:3v/v after soaking in acetone for 30 minutes. It was then filtered using Whatman No. 1 filter paper. The filtrate was shaken using a ZD speed Adjusting multi – purpose vibration shaker for 30 minutes. It was then transferred to a separating funnel and allow to settled. The non - aqueous layer was collected and cleaned through a column containing 24g of silica gel topped with 6g of anhydrous sodium sulphate while methanol and hexane mixture was used to elute the extract. This is a modification of the method used and suggested by^[8]. The extracts were allowed to evaporate and packed in sample bottles at 20 oC for GC/ECD analysis. GC/ECD analysis of soils and water sample were carried out on a Hewlett Packed (HP) 6890 GC/ECD technologies. Network GC/ECD system, equipped with dual injector, column, and electron capture detector capabilities, model number of the column with specification RTX-XLB 3.0 millilitres/minute (ml/Min). The carrier gas used was Helium at a flow rate of 1.0 ml/min. The inlet temperature was programmed to increase to 285 oC ending with 10 minutes. The ECD transfer line was maintained at a temperature of 250 oC, source temperature was also maintained at 300 oC.

Results

The results obtained for the physico-chemical parameters of the soil samples are presented in Table 1. The pH, Cation exchanges capacity, electrical conductivity, moisture content, organic matter, organic carbon, particle size of the soil is presented. The macro-element content, Nitrogen, Phosphorus, Sodium, Calcium, Magnesium, Potassium, Nitrogen, and phosphorus of the soil samples in (mg/100g), are also as indicated for both treated and control samples.

Table 1: Physico-Chemical Properties of the Soil Samples at Kara Bisichi, Barkin Ladi LGA.

Parameters	KT	Kc
pH	5.580±0.010	5.960±0.040
CEC (meq/100g)	4.060±0.030	3.820±0.010
EC(Ms/cm)	40.000±0.100	30.200±0.520
Moisture content (%)	4.900±1.000	4.883±1.000
Organic matter	4.180±0.200	0.440±0.020
Organic carbon	2.100±0.010	0.240±0.010
Clay content (%)	20.160±0.020	20.160±0.010
Silt content (%)	18.000±0.040	18.000±0.100
Sand content (%)	61.840±0.020	61.840±0.010
Nitrogen content (%)	0.120±0.001	0.012±0.001
Phosphorus content (%)	9.330±1.520	4.000±1.000
Sodium content (mg/100g)	2.760±0.010	2.300±0.100
Calcium content (mg/100g)	683.000±1.000	672.100±1.050
Magnesium content (mg/100g)	130.000±1.000	114.000±2.000
Potassium content (mg/100g)	78.000±1.000	20.360±0.570

KT = treated samples,

Kc = control samples.

Physical Parameters of the Water Sample

The results obtained for the physical parameter of the water sample is presented in Table 2; The pH is 7.04±0.23 of the water sample. The electrical conductivity is 30.00± 10.00 mS/cm and temperature of the

ranged 22 oC to 23 oC of the water sample. The turbidity is 3.00±0.40 NTU, TDS is 20.10±0.20 ppm and while 4.00±0.10 ppm is the TSS for the water sample.

Table 2: Physical Parameters of Water Sample at Kara Bisichi, Barkin Ladi LGA

Parameter	KW
pH	6.17±0.23
Temperature (oC)	23.00±0.08
TDS (ppm)	20.10±0.20
TSS (ppm)	4.00±0.10
Turbidity (NTU)	3.00±0.40

Kw = water sample.

Quantitation of Persistent Organic Pollutants using GC-ECD

Tables 3 and 4 shows the level of concentration of persistent

Organic pollutants detected in both soil and water samples from the study area.

Table 3: Organic Pollutants and their Concentration Levels in Soil Samples of Kara Bisichi, Barkin Ladi LGA.

S/N	Residues Available	RT (Min)	KT Conc. (mg/kg)	KC Conc. (mg/kg)	Maximum Residues Level in Soil (USEPA/UK) (mg/kg)
1.	Paraquat	2.674	0.014±0.002	ND	0.200
2.	Dichlorvos	4.158	0.010±0.003	0.008±0.002	0.010
3.	Glyphosate	5.432	0.656±0.020	0.019±0.001	0.020
4.	Sulprofos	9.456	0.029±0.001	0.002±0.001	0.010
5.	Dimethoate	9.797	0.049±0.010	0.013±0.001	0.010
6.	Propyzamide	12.453	ND	0.006±0.002	0.010
7.	Ethion	15.022	0.011±0.001	ND	0.010
8.	Atrazine	18.890	0.427±0.020	ND	0.010
9.	Aldrin	8.991	0.005±0.001	0.008±0.001	0.030
10.	Heptachlor epoxide	9.797	0.013±0.001	0.009±0.002	0.030
11.	Dieldrin	12.631	0.012±0.002	0.004±0.001	0.030
12.	Chlorpyrifos	13.051	0.209±0.010	ND	0.030
13.	Endosulfan II	15.950	0.010±0.001	ND	0.010
14.	Cypermethrin	18.520	0.176±0.020	ND	0.030

RT = Retention time, KT = treated soil samples, Kc = control soil samples, ND = Not detected.

Table 4: Organic Pollutants and their Concentration Levels in Water Sample of Kara Bisichi Barkin Ladi LGA

S/N	Residues Available	RT (Min)	Kw Conc. (mg/l)	Maximum Residues Level in Water (WHO/Australian) (mg/l)
1.	Paraquat	2.674	0.010±0.001	1.000
2.	Dichlorvos	4.158	0.077±0.030	1.000
3.	Glyphosate	5.432	0.004±0.001	10.000
4.	Sulprofos	9.456	0.173±0.010	10.000
5.	Dimethoate	9.797	0.035±0.002	20.000
6.	Propyzamide	12.453	0.712±0.040	2.000

7.	Atrazine	18.890	0.568±0.030	2.000
8	Aldrin	8.991	0.013±0.002	0.030
9.	Heptachlor epoxide	9.797	0.077±0.020	0.030
10.	Dieldrin	12.631	0.004±0.001	0.030
11.	Chlorpyrifos	13.051	0.173±0.003	0.050
12.	<i>p,p</i> - DDT	15.022	0.010±0.001	0.060
13.	Cypermethrin	18.520	0.021±0.002	0.0002

RT = Retention time, Kw = treated water samples

Discussion

Residues in Soil Sample

Soil samples and water sample from the study area were analyzed for their physicochemical properties. Results indicate that the soil is slightly acidic, organic matter content is low, both in the treated and the control (4.18± 0.20 – 0.44± 0.02). The soil had more of sand (61.84%) than clay and silt with moisture content of 4.883± 1.000 – 4.9000± 1.000%) for both the treated and untreated. The nitrogen and phosphorus content were all low compared to the require quantity for agricultural soils, therefore the soil need fertilization for better yield. Some selected organochlorines (OCs) and organophosphorus (OPs) pesticides /Herbicides residues were assess using GC/ECD. Most common pesticides applied to food crops on field and during storage are organochlorines [16]. Organophosphorus pesticides have been extensively used throughout the world for crops protection and orchard treatment due to their high efficiency of pest control and low costs [17]. The major pesticides/Herbicide residues detected in the study were paraquat, glyphosate, atrazine, propyzamide, aldrin, chlorpyrifos, heptachlor epoxide, dieldrin, cypermethrin, endosulfan II, *p,p* – DDT, dichlorvos, sulprofos, dimethoate and ethion respectively, out of which Aldrin, Dieldrin, Dichlorvos, Chlorpyrifos and Heptachlor are POPs. Their concentrations even though, some lower and some higher than USEPA concentrations, they are capable of bioaccumulating over time (Table 3). The concentration of paraquat residue is about 0.014mg/kg in the treated soil sample and not detected in the control soil sample, which may be as a result of previous application. Paraquat is very persistent in soil [18]. It binds readily to both clays and organic matter, with adsorption increasing with clay content but not mobile in silt loam, silt clay loams and is slightly mobile in sandy loam [19]. In Thailand 5.83% desorption was found in sandy loam soils (only 0.17% clay soil) [20]. Adsorption increases with increasing pH, and decreases with increasing acidity [21]. Field studies have found that half-life (DT50) of paraquat is between 7-8 years in the UK and 10-20 years in the USA. DT90 value (90% degradation) was never reached. Monitoring for residues in the soil in Europe found residues of between <0.2 and 15mg/kg [22]. Therefore, the results indicate low concentration of the paraquat residue, but with field dissipation studies it showed that paraquat accumulate slightly with application [18], implying that the concentration falls below the maximum acceptable limit of 0.2 mg/kg suggested US Environmental Protection Agency [23]. Glyphosate was detected at a high concentration of 0.656 mg/kg in treated soil sample due to frequent application on the farm and low concentration of 0.019 mg/kg in control soil sample as reported in Table 3. Thus, the median half – life of glyphosate in soil has been widely studied, values between 2 and 197 days have been reported in the literature [23, 25]. Soil and climate condition affect glyphosate persistence in soil [26]. It is also relatively stable to chemical and photo-decomposition [27]. The primary pathway of glyphosate degradation in soil is by microbial action, which yields aminomethyl phosphonic acid (AMPA) and glyoxime acid. Both products are further degraded to carbon dioxide [28]. The concentration of glyphosate in this result is above the maximum acceptable limit of 0.02 mg/kg suggested by USEPA [23] in the treated soil sample but falls below the Maximum Concentration Limit in the control sample. Atrazine was detected to be slightly higher in concentration of 0.427 mg/kg in the treated soil sample but not detected in the control soil sample, it could be attributed to its frequent application on the farmland. The

concentration of Atrazine in this result, fall above the UK maximum residue limit of 0.01 mg/kg of pesticides in soil. The fate of atrazine after it enters the soil is dependent on its sorption properties, water solubility, polarity and its ionic nature. The physicochemical characteristic and other factors that influence atrazine stability in soil are its texture, organic matter content, water content, the presence of micro-organisms and the pH [29]. Various concentrations of dichlorvos, sulprofos, dimethoate, ethion and propyzamide all organophosphate were also detected in the treated and control soil samples. The concentration of dichlorvos detected at the range of 0.010 mg/kg for the treated soil sample and 0.008 mg/kg for the control soil sample. The low concentration may be as a result of its inability to bind to soil particles; therefore, it can move through soil fairly rapidly. The breakdown in soil is less rapid than in air or water and most rapidly in moist soils with low acidity [30]. Dichlorvos falls within the UK Maximum Residue limit (MRL) of 0.01 mg/kg in soil. Sulprofos concentration was in the ranged of 0.020 mg/kg – 0.002 mg/kg in both the treated and control soil sample. The concentration of sulprofos in treated soil sample was slightly above the UK MRL of 0.01mg/kg and that of control soil sample was within the UK MRL of 0.01 mg/kg in soil. Thus, based on classification scheme of Swann *et al.*, [31], Koc values of 12,000 [32] and 13,500, Kordel *et al.*, [33], measured in soil, indicated that sulprofos is expected to have no mobility in soil given an estimated Henry's Law constant of 8.6x 10⁻⁷ atm- cm/mole derived from its vapour pressure of 6.3 x 10⁻⁷ mmHg and water solubility of 0.3 mg/l [34].

Concentration of dimethoate was detected to be 0.049 mg/kg in treated soil sample and 0.013 mg/kg in control. The concentration in treated sample is above the UK MRL of 0.01mg/kg while the control was within the limit. Dimethoate absorbs only very weakly to soil particles, it may be subjected to considerable leaching and degradation occur by hydrolysis, especially in alkaline soils, and it can evaporate from soil surfaces. Losses due evaporation of 23 to 40% of applied dimethoate have been reported [35] dimethoate does not persist. It has a soil half – live of 4 to 16 days, but high half-life of 122 days has been reported. Half – lives between 2.5 and 4 days were reported during drought and moderate rainfall condition [35]. It also breaks down faster in moist soil and rapidly by most soil microorganisms. Ethion concentration was detected in the treated soil sample at 0.011 mg/kg and not detected in the soil control sample, which falls within the UK MRL of 0.01 mg/kg ethion absorbs strongly to soil particle and it is nearly insoluble in water. It is therefore unlikely to leach or contaminate groundwater (35) this suggest or explain why it was not detected in the water sample. In soil, ethion is subject to microbial degradation. It is resistant to hydrolysis, except in alkaline conditions (pH 9 or above), [35]. The concentration of propyzamide was detected to be 0.006 mg/kg in the soil control sample but absent in the treated soil sample, which the concentration falls within the UK MRL of 0.01 mg/kg. Propyzamide biodegrades at a moderate rate in soil with half – lives of 18 to 50 days under field conditions and also moderately to slightly mobile in soil and has a limited potential to move through soil to contaminate ground or surface water. And also, more mobile in soils with low organic matter and clay content (KERB FLO, Environmental Information Sheet [36] Pronamide Tolerance Reassessment Eligibility Decision; TRED, [37]. Table 3 shows various concentrations of pesticide residues in the treated and control soil samples which are aldrin, dieldrin, heptachlor epoxide, chlorpyrifos, endosulfan II and cypermethrin respectively. Aldrin residues was

detected and concentrations range of 0.005 mg/kg to 0.008 mg/kg of both the treated and control soil samples. Due to its persistent nature and hydrophobicity aldrin is known to accumulate and/or bio-concentrate mainly as its conversion product dieldrin^[38]. Dieldrin, a metabolite of aldrin was also detected and concentration of 0.004 mg/kg to 0.012 mg/kg of all the soil samples. Thus, an increasing in the concentration of dieldrin from this study may imply that, aldrin may have been recently applied directly on the farm. However, when compared, the concentrations of aldrin and dieldrin falls within the US maximum residues limit (MRL) of 0.03 mg/kg. The concentrations of aldrin and dieldrin residues level in this study falls below the average concentration of total aldrin + dieldrin residues from 2-17 mg/kg in surface soil and from 2-15 mg/kg in sub-surface soil reported by^[39]. Heptachlor epoxide residue was detected and concentration of 0.013 mg/kg and 0.009 mg/kg in soil samples. Thus, the low concentration level of heptachlor epoxide detected in the soil sample, since heptachlor is only converted to heptachlor epoxide in plant and insect tissues. The epoxide is more chemically potent than heptachlor itself^[40]. The concentration of heptachlor epoxide residue in this study falls within the US maximum residents limit (MRL) of 0.03 mg/kg, according to Ademola *et al.*,^[40], the concentration value of heptachlor epoxide ranges of 28.076 to 109.901 mg/kg in soils from selected cocoa farms in Akure- South local Government Area are higher than the concentration value detected in this study. Chlorpyrifos residue concentration was detected at 0.209 mg/kg of the treated soil sample, however was comparable falls higher than the US maximum residues limit of 0.03 mg/kg of pesticide residue in the soil. Chlorpyrifos is a broad-spectrum organophosphorus pesticide, the concentration of chlorpyrifos residue level (0.209 mg/kg) recorded in this study was for lower than the range of 0.52-0.97 mg/kg reported by Mohammed *et al.*,^[41] in soil samples from Gashua, Bada local Government Area Yobe State. This may be due to difference in the geology and extent of soil pollution by pesticides. Endosulfan II residue concentration was detected at 0.010 mg/kg of the treated soil sample which falls within the US MRL of 0.01 mg/kg. Endosulfan II is unstable and may be slowly be converted to endosulfan I in the environment^[40]. The concentration of endosulfan II residue level recorded in this study was a less value than the range of 0.011-1.133 mg/kg in soils from selected cocoa farms in Akure South Local Government Area reported by Ademola *et al.*,^[40]. Cypermethrin residue in the treated soil sample was detected and concentration of 0.176 mg/kg which when, compared is greater than the US maximum residue s limit of 0.03 mg/kg.

Residues in Water Sample

Pesticide residues reach the water body through direct runoff, leaching, careless disposal of empty containers, equipment washing etc. The number of pesticides lost from agriculture fields and transported to surface water depends on several factors, including soil characteristics, topography weather agricultural practices, and chemical and environmental properties of individual pesticides, Hossana *et al.*,^[42]. The pH mean value ranged of 6.17 ± 0.23 was obtained which falls slightly below the guideline limit of 6.5 -8.5; indicating slight acidity. The world Health Organization^[43] recommends a pH value of 6.5 or 8.5 for drinking water to prevent corrosion. The electrical conductivity of the water sample is shown in Table 2, indicating the ability to carry electric current in the presence of dissolved solids such as calcium, chloride, and magnesium in water sample. The result shows that the measured conductivity value mean is $30 \pm 10.00 \mu\text{S/cm}$ which falls within the maximum allowable level of $1000 \mu\text{S/cm}$ according to National Drinking water quality standard^[44]. Turbidity is the cloudiness of water caused by a variety of particles and is another key parameter in drinking water analysis. It is also related to the content of diseases causing organisms in water, which may come from soil runoff. The turbidity mean value of $3.00 \pm 0.40\text{NTU}$ was recorded from the water sample and the standard recommended maximum turbidity limit, set by WHO^[44] and NDWQS^[44], for drinking water is 5 NTU. The results

indicate that the turbidity of the water sample studied was below the maximum standard limit of 5 NTU. Total Dissolve Solids (TDS) constitute ions of inorganic salts which determine the saline behaviour of the water and small amount of organics matter that may be dissolved in it^[45]. The TDS value for the water sample was $20.10 \pm 0.20 \text{ mg/l}$ which falls below the WHO^[43] recommended value of 1000mg/l. low TDS is said to be a characteristic of hills and upland areas that represent areas of recharge according to Olobaniyi *et al.*,^[46]. This is an apt description of the study area topographically. Water containing TDS less than 1000mg/l could be considered to be "Fresh "water" and good enough both for drinking and irrigational purposes, as this would not affect the osmotic pressure of soil solution according to Oyem *et al.*,^[47]. The mean value of TSS for the water sample studied is $4.00 \pm 0.10 \text{ mg/l}$ which still well below the maximum standard limit of 25 mg/l set and recommended by NDWQS^[44]. The paraquat residue concentration was detected to be 0.010 mg/l in Table 4 is the water sample which it is below the drinking water g value of 1 mg/l for pesticides in Australia. The low concentration of paraquat residue in the water sample may be as a result of its resistance to hydrolysis^[48]. According to Eisler^[49], loss of paraquat from the water phase is rapid; about 50% in 36 hours and 100% in 4 weeks from fresh water ecosystem; and in marine ecosystems, 50-70% loss of paraquat for sea water was usually recorded within 24 hours. However, is likely to enter surface waters bound to soil particle as a result of erosion and runoff, and subsequently be re-deposited onto the beds of surface water bodies or low land^[18]. The concentration of dichlorvos in water sample was found to be 0.008 mg/l which is the lowest concentration among the pesticide detected, this may be as a result of its ability to dissolve in water and some evaporate into the air, but most of it will be broken down when it reacts with the water^[50]. The less acidic the water is, the more rapidly dichlorvos is broken down. Bacterial and other micro-organism (Microscopic plant and animals) in lakes and river can also break down dichlorvos^[50]. According to^[50] dichlorvos was applied to a pond, 50% of the chemical was degraded in 24-36 hours. This result indicates that, the concentration of dichlorvos in the water sample is less than 1 mg/l of Australia drinking water guideline value for pesticides. The concentration of glyphosate was 0.656 mg/l in the water sample which also equal to the amount concentration of glyphosate present in treated soil sample, but however, glyphosate does have the potential to contaminate surface water, due to its aquatic use pattern and through erosion, as it adsorbs to soil particles suspended by runoff (51), if glyphosate reaches surface water, it would not be broken down readily by water or sunlight^[51]. In this study, the concentration of glyphosate is below the Australia drinking standard of 10 mg/l for pesticides and 700 mg/l Maximum Contamination Level (MCL) of USEPA^[18]. Sulprofos, dimethoate, propyamide and atrazine were detected in various concentration in the water sample. Sulprofos had concentration of 0.022 mg/l, which is lower than the standard Australian standard value of 10mg/l, whereas dimethoate had a concentration of 0.035 mg/l, which falls lower than the Canadian interim maximum concentration (IMAC) of 20 mg/l. Propyzamide was 0.712 mg/l which is also lower than the Australian standard of 2 mg/l. And on the other hand, Atrazine was detected and concentration of 0.568mg/l which was lower when compared to WHO standard of 2 mg/l. The water sample also had aldrin, dieldrin, heptachlor epoxide, chlopyrifos, *p,p*-DDT and cypermethrin all detected various concentrations respectively as shown in Table 4. An isomer of DDT, *p,p*-DDT was also detected with a concentration of 0.010 mg/kg in the water sample, which is within the Australia guideline value of 0.06 mg/kg for drinking water. Cypermethrin had a concentration of 0.021 mg/l which falls within the Swedish standard value of 0.0002 mg/l for cypermethrin and European Union (EU) regulatory value of 0.0068 mg/l for cypermethrin in stagnant water systems, Wijngaarden *et al.*,^[52]. Cypermethrin is a hydrophobic organic compound which can be adsorbed to sediment, they can leach and cause long term contamination of water sources, Turgut *et al.*,^[53]. Major reported sources of cypermethrin contamination are surface water

include agricultural and urban runoff from rainstorms, spray drift, urban landscape, irrigation and release of agricultural tail waters^[54].

Conclusion

The study has provided data on the level of contamination of soils and water by pesticides applied within the study area. Varied concentrations of paraquat, dichlorvos, glyphosate, sulprofos, dimethoate, propyzamide, atrazine, ethion, aldrin, dieldrin, chlorpyrifos, heptachlor epoxide, *p,p*-DDT, cypermethrin and endosulfan II were detected. From the results, the concentration of glyphosate, propyzamide and atrazine are higher in the treated soil and water sample compared to World Health Organization maximum residues limit value for pesticide residues in soil and water. The result revealed that, virtually all the pesticide residues detected in the water soil samples were also found in the water sample except for Ethion which was detected only in the treated soil sample only. The concentration of chlorpyrifos, and cypermethrin are higher compared to US MRL/ WHO standard value for pesticides residue in soil and water, both detected in the treated soil and water sample. Endosulfan II was detected in the treated soil sample but absence in the water sample and isomer of *p,p*- DDT was detected in the water sample but was not found in the soil samples which could be as a result of runoff from other farmlands, leaching or erosion from around the study area. However, apart from the potential danger they may pose to the soil organisms, their possible translation into edible parts of crops and emission into surrounding water bodies have generated a great deal of interest as these are currently being investigated.

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