

Chapter

Riparian-Buffer Loss and Pesticide Incidence in Freshwater Matrices of Ikpoba River (Nigeria): Policy Recommendations for the Protection of Tropical River Basins

Azubuike Victor Chukwuka and Ozekeke Ogbeide

Abstract

The unregulated use of watersheds for agriculture negatively impacts the quality of river basins. In particular, the reduced quality of surface-waters, have been attributed to absence or poorly-decided riparian-buffer specifications in environmental laws. To demonstrate suitable buffer-width for protection of surface water, sediment and benthic fish populations, five riparian areas with different vegetation richness and buffer-width were selected within an organochlorine pesticide (OCP)-impacted watershed using the Normalized Differential Vegetation Index (NDVI) and multiple buffer analysis respectively. Mean OCP levels in surface water, sediment and fish sampled at each riparian stations showed site-specific differences with markedly higher levels of α -BHC, β -BHC, δ -BHC, p,p'-DDD and total pesticide residues at stations with least riparian cover. The principal component analysis further revealed more OCPs associating with sediment and fish from stations having smaller buffer-width and sparse riparian vegetation. Stations with wider buffer-width of at least 120 m provided greater protection to adjacent surface water and benthic fish populations. While this study recommends riparian buffer-widths for a typical tropical environment, further research which assesses other contaminant types in aquatic matrices adjacent to different riparian environments would be valuable and informative for regulatory guidance and strategic protection of ecosystem services.

Keywords: riparian reserve, labile pesticides, watershed, environmental policy, unsupervised imagery classification, NDVI

1. Introduction

The ecological integrity of watersheds is critical for normal ecosystem functioning of associated river systems [1, 2]. Riparian areas of fluvial systems consist of natural buffer vegetation which spans both sides of the stream bank and function in mitigating the impact of flood, sedimentation, and nutrient run-off from adjoining cultivated land areas [3, 4]. However, the dynamics of rapid urbanization, lack of environmental education among the citizenry, and outright government negligence which have put such environments under anthropogenic pressure is an issue of growing concern [5, 6].

River basins are typically exposed to anthropogenic pressure via agricultural land-use in which attempting to harness fertile areas of alluvial deposits around fluvial systems, have accelerated the depletion of riparian vegetations [2, 7]. Such disruption of riparian landscape increases access of contaminants of anthropogenic origin into adjacent surface water, thus putting biodiversity and human populations at risk [8]. The use of organochlorine pesticides as a choice chemical for agricultural applications in tropical developing countries despite its ban still constitutes a concern due to its persistence and toxicity to non-target species [9, 10]. In agricultural catchments, the fate of pesticides including the uptake, accumulation and persistence within environmental matrices depends on its hydrophobicity or n-octanol-water partition coefficient ($\log K_{ow}$) [11]. Several studies have demonstrated the ability of wide riparian vegetation areas to buffer adjacent surface water by filtering pesticide-laden runoff and top-soil originating from agricultural catchments [12, 13], with small buffer widths conferring little protection [13, 14].

Recent advances in spatial analysis and fluvial remote sensing, allow better assessment of such extraction of information regarding river basins behavior under natural and human-induced disruptions on a larger scale compared to *in situ* assessments alone [15]. Data ranging from low, medium and high-resolution imagery obtained from Earth Observation (EO) satellites [16, 17], have enabled the complementary use of indices to efficiently identify degraded riparian areas and allow prioritization of river basins for strategic protection [18–20]. In developing climes, the effective management of riparian ecosystems has been limited by weak, poorly constituted or outright non-existent policies, which have aggravated issues of riparian exploitation and its imminent loss [21, 22]. In Nigeria, the National Environmental (Watershed, Hilly, Mountainous and Catchment Areas) Regulations, 2009, is the major watershed-specific regulatory instrument used by the National Environment Standards and Regulations Enforcement Agency (NESREA), to monitor and enforce national laws and domesticate international agreements on the watershed [21]. Although this regulatory document describes watershed as ‘the total land area that drains directly or indirectly into a particular stream or river’, it makes no mention of key parameters like riparian zone or buffer width. Such documents exemplify regulatory instruments with limited scientific scope and coverage of their subjects’ focus. Existence of such laws in developing countries has been attributed to limited research information and empirical data necessary for developing context-specific guidelines for such environments [5]. Similar cases of laws and regulations with forest and watershed specifications not backed by empirical studies or proof of its suitability for the environment concerned have also been documented [6, 23].

Anthropogenic pressures which accelerate the degradation of river basins are particularly severe in African urban environments [8, 24]. A critical feature of river basin resilience is its lateral connectivity between the river channel and its watershed [25]. The connecting stream network and volume of lateral connectivity (stream orders) within a river basin landscape, is a reliable proxy for discerning watershed disruption [26] and is greatly reduced via agricultural activities including soil leveling for irrigation [27]. Loss of riparian areas and altered pollution dynamics within watersheds due to agriculture and the use of pesticides is also typical of sub-Saharan areas, including Nigeria [9]. Evidence of recent use of banned pesticides, including OCPs, with environmental concentrations that portend risks to both humans and aquatic wildlife, has spotlighted the Ikpoba agricultural catchment within Edo area [28, 29]. This study explores the complementary use of medium resolution (Landsat 8, OLI) and high resolution (Google earth) imageries to describe riparian loss within the Ikpoba watershed. Besides, we also sought to demonstrate effective riparian buffer-width by relating pesticide incidence in

adjacent surface water, sediment and benthic fish to buffer-width within the agrarian catchment of Ikpoba. We hypothesize that an effective buffer-width and density of riparian cover within the Ikpoba watershed will limit the incidence of pesticides in adjacent surface water, sediment and fish.

2. Materials and methods

2.1 Study area

Ikpoba River is a sixth-order river located between Lat. 6° 19' 12" N, long 5° 24' 0"E and Lat. 6° 22' 48"N, long 5° 51' 7.2"E in Benin City, Edo State, Nigeria (**Figure 1**) [30]. The Ikpoba catchment area which extends laterally along the rivers longitudinal continuum is a notable urban watershed within the heart of Benin city, Edo state. Ikpoba's river riparian area offers local communities with diverse resources including fisheries and domestic water supply. The study section has a width of 10 to 12 meters' watercourse and characterized by a predominance of indigenous plant species i.e. bamboo trees (*Bambusa vulgaris*) that make up the riparian vegetation [31]. However, most of this vegetation has been lost due to massive deforestation for agricultural practices and other anthropogenic activities. The favorability of the landscape area for agricultural purposes could be attributed to its rich alluvial landscape.

2.2 Geospatial analysis

To demonstrate the role of riparian vegetation in preserving the quality of adjacent surface water, a prior spatial description of the area and determination of riparian areas that exemplify the different degree of riparian alteration was required. To achieve this, the geospatial analysis workflow is detailed sequentially by sections. The schematic representation of the workflow is given in Appendix I.

2.2.1 Data acquisition

Viable spatial patterns of land-use and land cover of the Ikpoba riparian area were first visualized within the google earth database before acquisition using the snapshot tool of Google earth 7.1 software. The images offered by the software originate from both satellites and aerial photography with a repeatability update ranging from 6 months to 5 years [32]. This repetitive frequency of updating images over time makes them an effective and reliable alternative to non-updated hard-copies of maps and surveys available at the local and state government repositories.

The watershed and riparian area of Ikpoba river were mapped at a fine spatial scale from Google Earth Imagery with discernable land use and landcover features particularly the river course and aquatic vegetation within the watershed. Confirmatory ground-truthing was carried out using expert knowledge of the area to ascertain the general layout, and interspersed anthropogenic activities including farming activities and built-up areas (**Figure 1a**). Detailed photographs of the area were also taken as evidence of riparian features (Appendix II).

2.2.2 Land-use land cover classification

To improve the spatial visualization of the watershed and riparian extent of Ikpoba river, and highlight the finer details of land use/cover features-classes, high spatial resolution raster image acquired from Google Earth was subjected to Iso

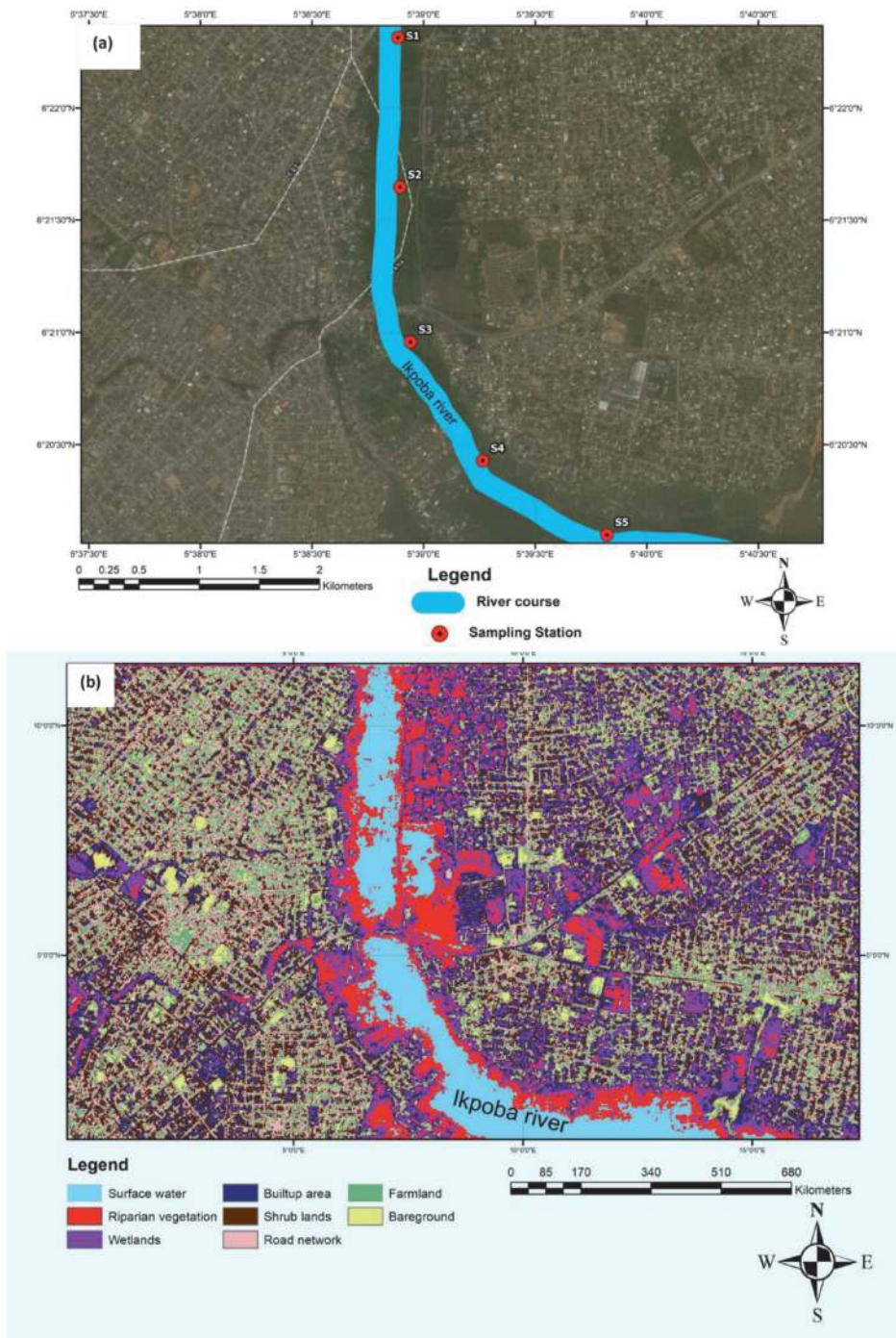


Figure 1. Map of Ikpoba River, showing (a) sampling stations and (b) land-use land-cover classes.

cluster unsupervised classification in ArcMap 10.4 [33]. The choice of google earth imageries over traditional Landsat imageries for land-use land-cover classification is attributable to its relatively lesser cost of acquisition [34], better discriminating capacity of google earth imageries compared to Landsat and parallel classification testing which rates the classification accuracy of google earth imagery to be within range attainable by other high-resolution imagery like QuickBird [35]. The output from the unsupervised classification highlighted the riparian extent of the Ikpoba area and revealed eight land-use land-cover features i.e. surface water, riparian

vegetation, wetlands, built-up area, shrublands, road-network, farmland and bare-ground (**Figure 1b**).

2.2.3 Vegetation analysis

To quantify the vegetation richness of the riparian area and establish an empirical basis for the difference in riparian vegetation along the Ikpoba river, the Normalized Difference Vegetation Index (NDVI) was calculated. For this purpose, Landsat 8 imagery was acquired from the United States Geological Survey (USGS) website. The index was calculated by imputing the red band (R) and near-infrared band (PIR) contained therein into the raster calculator of ArcGIS version 10.4., using Eq. 1 below.

$$NDVI = (B4 - B3)/(B4 + B3) \quad (1)$$

Where B3 and B4 is the red band and near-infrared band respectively.

This standardized vegetation index is sensitive to plant vigor and abundance by illustrating the disparity between the visible red band and the near-infrared band. The output of this analysis highlighted the rich and depleted riparian areas within the watershed, where green, yellow and red pixels extending laterally to the fluvial course was considered to be gradients of richness or depleted-ness of riparian vegetation (**Figure 2**) [36].

2.2.4 Creating stream orders

In addition to measures of riparian disruption and watershed dynamics, the stream order network for the Ikpoba area was assessed by processing digital

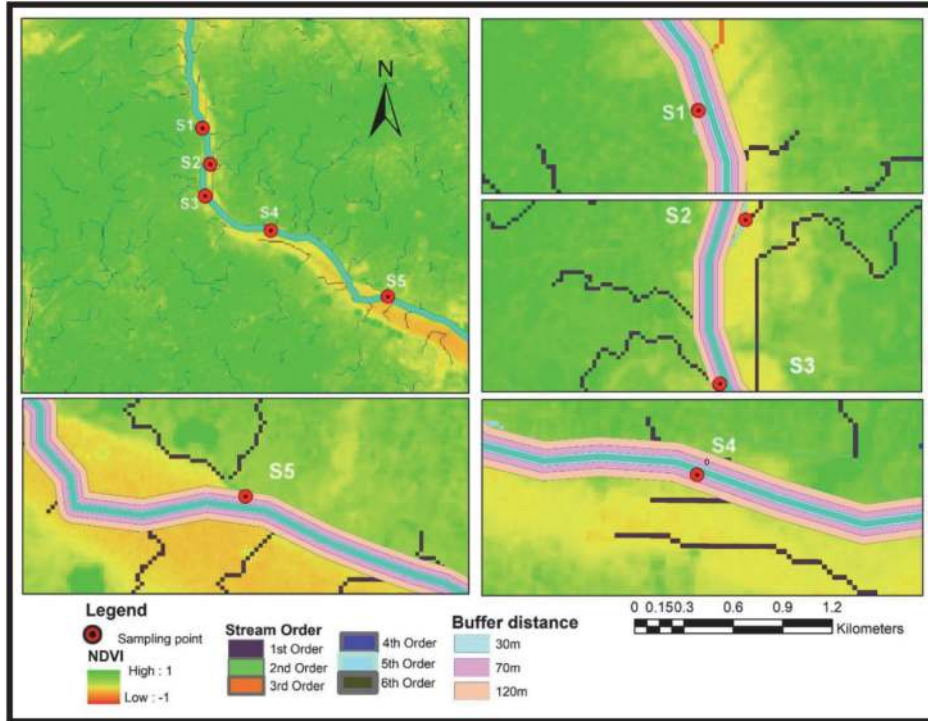


Figure 2. NDVI analysis of riparian vegetation along Ikpoba river where station 1 (dense riparian vegetation on both sides of the river+ higher-order tributary), 2 (sparse riparian vegetation on one side of the river+2 lower-order tributaries), 3 (sparse vegetation buffer on one side of the river + one lower-order tributary), station 4 (moderate vegetation buffer on one side of the river+3 lower-order tributaries), station 5 (sparse vegetation buffer on both sides of the river+3 lower-order tributaries).

elevation models (DEMs) of the Ikpoba area in ArcMap® version 10.4 using ArcGIS Hydrology tools (Appendix I) [37, 38]. The DEMs of the Ikpoba area were also downloaded from the United States Geological Survey (USGS) website. The classification of stream order offered a standardized approach for defining the volume/size of the river (i.e. reaching length x width x depth under average flow conditions) and the potential hydrological ability of each stream within the catchment. Using the “Strahler” method available under hydrological tools in the ESRI ArcGIS 10.4 software, [39, 40] very small streams were categorized as a stream order of “1–3”, while larger rivers were designated a stream order of “4–6”. Stream order used as a measure of landscape connectivity and watershed disruption highlighted large incidences of lower-order streams entering the river system indicating a disconnectivity from headwaters and vulnerability to pollutants from overland runoff [8, 26]. Incidence of higher-order rivers emptying into the Ikpoba river (6th order stream) was taken as indices of relative connectivity to headwaters from the watershed and lesser vulnerability to overland runoff and pollutant-laden discharge.

2.2.5 Riparian station delineation

Using the color gradient scale of the NDVI analysis to establish richness and sparseness of riparian vegetation along Ikpoba river, control station was assigned to an area with ecologically desirable features i.e. dense riparian vegetation on both sides of the river+ higher-order tributary (station 1). Station 2 was assigned to an area of the watershed having sparse riparian vegetation on one side of the river+2 lower-order tributaries. Station 3 was assigned to an area characterized by sparse vegetation buffer on one of the rivers + one lower-order tributary. Station 4 was located within an area having moderate vegetation richness on one side of the river +3 lower-order tributaries, station 5 (sparse vegetation buffer on both sides of the river+3 lower-order tributaries) (Table 1). In total, five different predetermined stations/areas of the watershed approximately 1 km apart, with different degree of altered riparian vegetation were selected.

2.2.6 Buffer analysis

For this study, riparian buffer [41] is “a strip or area of vegetation adjacent to a river or stream of sufficient width necessary to remove nutrients, sediment, organic matter, pesticides, and other pollutants from surface runoff and subsurface flow by deposition, absorption, plant uptake, and other processes, thereby reducing

Sampling station	Riparian Feature description	Coordinates	Distance to the next sampling area
1 (control site)	Rich riparian vegetation on both sides of the river	6°22'18.76"N 5°38'53.10"E	1.2 km
2	sparse riparian vegetation on one side of the river+2 lower-order tributaries	6°21'38.81"N 5°38'53.62"E	1.29 km
3	sparse vegetation buffer on one of the rivers + one lower-order tributary	6°20'57.38"N 5°38'56.46"E	1.13 km
4	moderate vegetation buffer on one side of the river+3 lower-order tributaries	6°20'25.70"N 5°39'15.88"E	1.19 km
5	sparse vegetation buffer on both sides of the river+3 lower-order tributaries	6°20'5.83"N 5°39'49.27"E	

Table 1.
Sample site designation for different riparian features along the Ikpoba watershed.

pollution and protecting surface water and subsurface water quality, which are also intended to provide shade to reduce water temperature for improved habitat for aquatic organisms and supply large woody debris for aquatic organisms and habitat for wildlife”.

To determine the width of riparian buffer at each station, and to allow comparison with the minimum recommended riparian widths specified for the protection of water quality and improvement of in-stream biodiversity i.e. 30 m, 70 m and 120 m [4], a multiple buffer ring features was created around the stream feature using the ‘multiple buffer’ command in ArcGIS version 10.4.

To extract total vegetation richness around each riparian station, NDVI raster was clipped for each station within a 120 m buffer radius. Mean pixel threshold values for each area within the 120 m buffer zone was extracted from the attribute table of the clipped NDVI raster image. The difference in mean vegetation richness of the riparian stations was confirmed using mean pixel thresholds extracted for each station within the 120 m buffer radius and subjected to one-way ANOVA analysis (Appendix III).

Table 1: Sample station designation for different riparian features along the Ikpoba watershed.

2.3 Sample collection and analysis

2.3.1 Water, sediment and biota samples collection

Every fourth night, from January 2016 to June 2016, samples of water (n = 60, 12 samples per station) and sediment (n = 60, 12 samples per station) were obtained from the five predetermined points along the river. As earlier specified, the predetermined points were runoff generating points long the watershed having different riparian features. Samples were gathered using an Eckman grab from three riverbeds at depths of 5 m for sediment and a hydro-bios sampler at depths of 0.3 m in a pre-cleaned 1 L glass bottle for water samples [42]. Impurities in water samples were eradicated using fiber-glass filters. Five (5) samples of *Clarias gariepinus*, were collected monthly from each riparian station. A total of 150 fishes (n = 30 per station) were collected for 6 months, January –June 2016. The Catfish, *Clarias gariepinus*, was caught using gillnets with 50–55 mm meshes between opposite knots. All samples were properly labeled and placed in an ice-chest at 4 °C afterwards transported to the laboratory for further analysis.

2.3.2 Extraction of samples

A method described by Hladik and McWayne [43] and Steinwandter [44] was used for the extraction of OCP residues in sediment samples and fish samples respectively. In summary, 15 g of the homogenized sediment samples were obtained by air-drying and sieving through a 2-mm sieve, while 25 g of edible portions of *Clarias gariepinus*, with 100 ml of acetone was homogenized for 20 min at 100 rpm. Homogenized samples were mixed with dichloromethane (DCM) and n-hexane (10:90) and sonicated for about 20–25 min at 50 °C. Similarly, OCP residues in water samples were extracted using the same solvent mix (n-hexane and dichloromethane (DCM) (50:50)), based on a method vividly described by USEPA [45]. Here, a volume of 250 ml water samples was mixed with 60 ml of the prepared solvent mix. The resulting solution was filtered with a separator funnel and then concentrated to 10 ml in a water bath at 35–40 °C with the aid of a rotary evaporator. Clean up of water, sediment and fish extracts was achieved using a florisil solid-phase extraction (SPE) method [45]. This florisil column was equipped

with 15% hexane as an eluting mixture. Elutes were then transferred in vials to gas chromatography and later concentrated into a final volume of 1 mL using a rotary evaporator operating at six mbar at 30 °C.

2.3.3 Analysis of samples

All extracts were analyzed for OCPs using the EPA 8081 pesticide standard mix containing the following pesticides (aldrin, endrin, dieldrin, (α , β , γ , δ), endosulfan (I, II & sulfate), chlordane (α and γ -chlordane), isomers of DDT (p,p'-DDD, p,p'-DDE, p,p'-DDT), endrin aldehyde and heptachlor and heptachlor epoxide. Choice of pesticides analyzed was informed from a previous study which revealed predominant use of OCPs within the same catchment area [28]. Concentrations of these OCPs were determined using Gas chromatography (Hewlett-Packard (hp) 5890 Series II) equipped with a 63 Ni electron capture detector (ECD). Conditions of this instrument were as follows: chromatographic separation was obtained using a VF-5 ms capillary column of 30 mm x 0.25 mm internal diameter x 0.25 μ m film thicknesses with a 1 m retention gap (0.53 mm, deactivated). The carrier gas for this instrument was helium and it was used to run 1.5 μ L aliquot of the sample with a splitless injection mode. At standard pressure, the flow rate was kept constant at 29 ml/min while the temperature of 250 °C. The initial oven temperature was set at 60 °C for 2 min and ramped at 25 °C /min to 300 °C for 5 min and allowed to stay for 15 min giving a total run time of 58 min. The detector temperature was 320 °C and was held for 5 min.

2.3.4 Quality assurance

To ensure the reliability and precision of the tests, all analyzes are subject to strict quality control, quality assurance and precautionary procedures. All materials used for the collection of water samples was pre-cleaned with ethanol. The research used double-distilled deionized water and analysis grade reagents while glassware was properly purified before the experiment. Instruments were calibrated using blank reagents determinations. The validity, as well as reliability of extraction and cleanup methods, was ensured by the recovery of an internal standard. For this research, analytical grade decachlorobiphenyl was purchased from Sigma Aldrich and used as an internal standard. Overall, with 10 ng/g level of fortification, the pesticide recovery rate was 85–90% for all matrices, with method detection limits (MDL) of 0.005 μ g/g/dw, 0.01 μ g/g/dw and 0.01 μ g/l for sediment, fish and water respectively.

2.4 Statistical analysis

Statistical analysis was carried out on the data obtained from across each station. Analyses were performed by the use of Statistica® 12.0 (Stat Soft Inc. USA) and Microsoft Excel 2013 for Windows. One-way ANOVA test compared values and significant differences in mean were determined using Duncan's test ($p < 0.05$). Following the large number of inter-related pesticide variables in fish, sediment and surface water, Principal Components Analysis (PCA) was used to organize variables into sets of rotated inter-correlated variables (principal components or PCs) on the basis of a correlation matrix. The interrelated output of variables from the PCA are also referred to as linear combinations of the original variables that form the axes, used to construct a biplot. Each of the PCs or axes account for the variances in data, and only axes accounting for large variances (mostly PC 1 and PC 2) were considered for interpretation [46]. Biplots were used to visualize the association of pesticides in fish, sediment or water with particular riparian areas. Close proximity of pesticides species with particular riparian stations within the ordination space of the

biplot was termed strong association and was indicative of high concentrations of that pesticide in that riparian area [47].

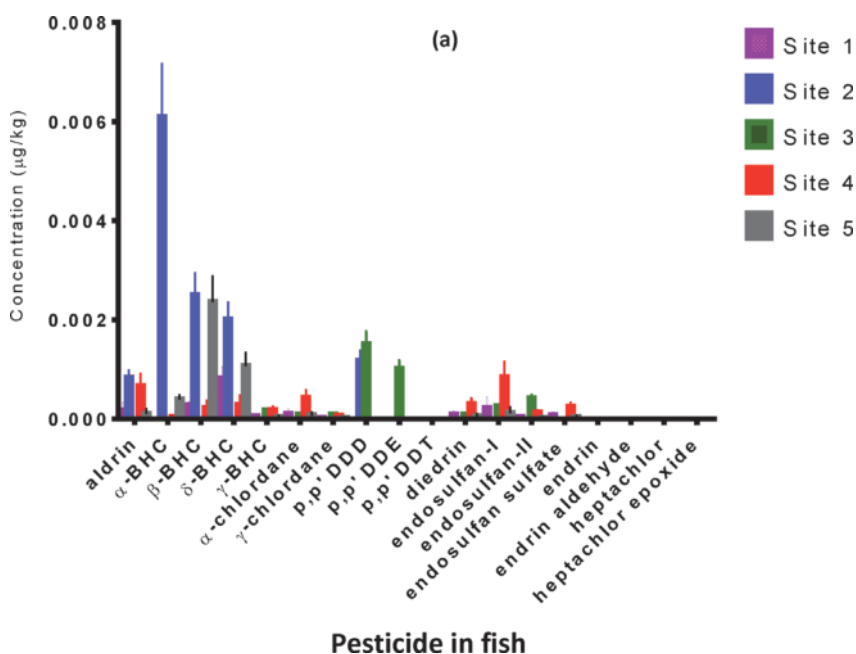
3. Results

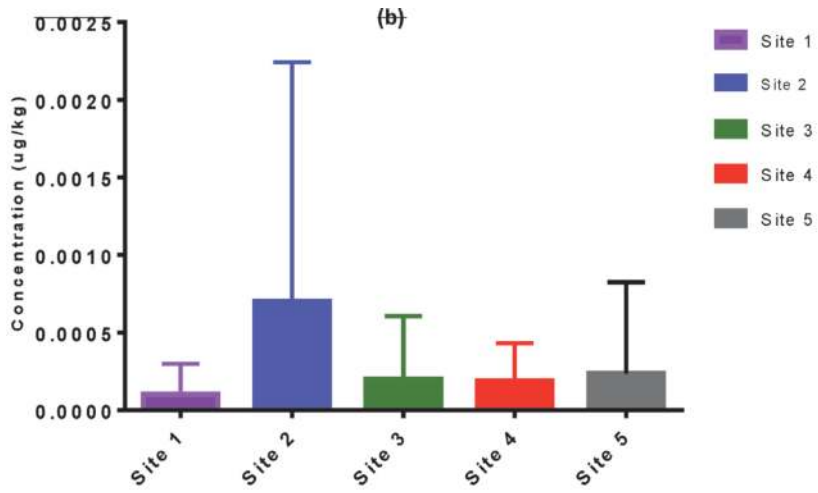
3.1 Pesticide concentration in environmental matrices across riparian stations

Results of pesticides residues in fish samples obtained from Ikpoba river shows that station 2 had the highest concentration of total pesticide residues. There was no significant difference ($p \leq 0.05$) in total pesticide concentration in fish samples from all stations. δ -BHC ($0.00082 \pm 0.00024 \mu\text{g/kg}$), α -BHC ($0.00608 \pm 0.00108 \mu\text{g/kg}$), p,p'-DDD ($0.00150 \pm 0.00027 \mu\text{g/kg}$), endosulfan-1 ($0.00084 \pm 0.00032 \mu\text{g/kg}$), and β -BHC ($0.00236 \pm 0.00052 \mu\text{g/kg}$) were observed to have the highest concentrations in stations 1,2,3,4, and 5 respectively. Pesticide levels in fish across sampling stations of riparian stations showed marked levels of α -BHC and β -BHC in fishes from station 2. Again, total pesticide concentration was higher at station 2, followed by station 5 and station 3. i.e. station 2 > station 5 > station 3 > station 4 > station 1 (**Figure 3a,b**).

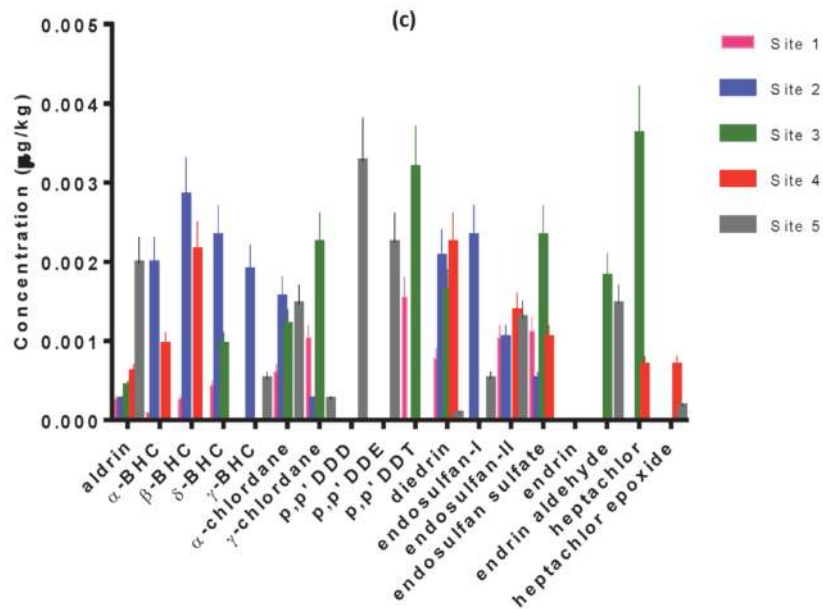
In sediment samples, it was observed that concentrations of p,p'-DDT ($0.00155 \pm 0.00026 \mu\text{g/kg}$), BHC ($0.00284 \pm 0.00048 \mu\text{g/kg}$), heptachlor ($0.0036 \pm 0.00061 \mu\text{g/kg}$), dieldrin ($0.0022 \pm 0.00038 \mu\text{g/kg}$) and p,p'-DDD ($0.0033 \pm 0.00055 \mu\text{g/kg}$) were highest for stations 1, 2, 3, 4 and 5 respectively. Overall Station 2 and 3 had higher concentrations of total pesticide residues compared with the other stations although there was no significant difference in total pesticide residues between the five stations. In sediment, total pesticide concentration was markedly high at station 2 and station 3, with lowest values at station 4 i.e. station 2 = station 3 > station 5 > station 1 > station 4 (**Figure 3c,d**).

For water samples, the highest concentration of total pesticide residues was observed at station 2. At station 1 ($0.00041 \pm 0.00006 \mu\text{g/L}$) and 2 ($0.00086 \pm 0.00014 \mu\text{g/L}$), α -BHC had the concentration of pesticides while δ -BHC and β -BHC were highest at stations 4 ($0.00024 \pm 0.00006 \mu\text{g/L}$) and

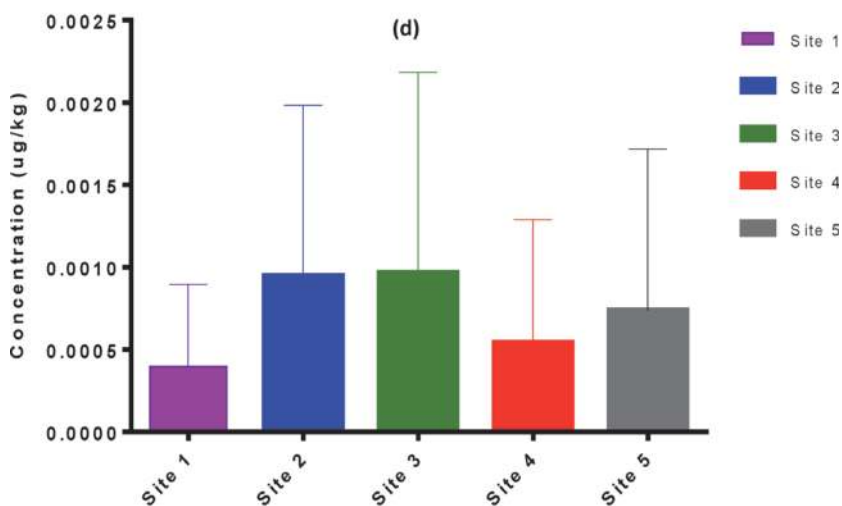




Pesticide in fish



Pesticide in sediment



Pesticide in sediment

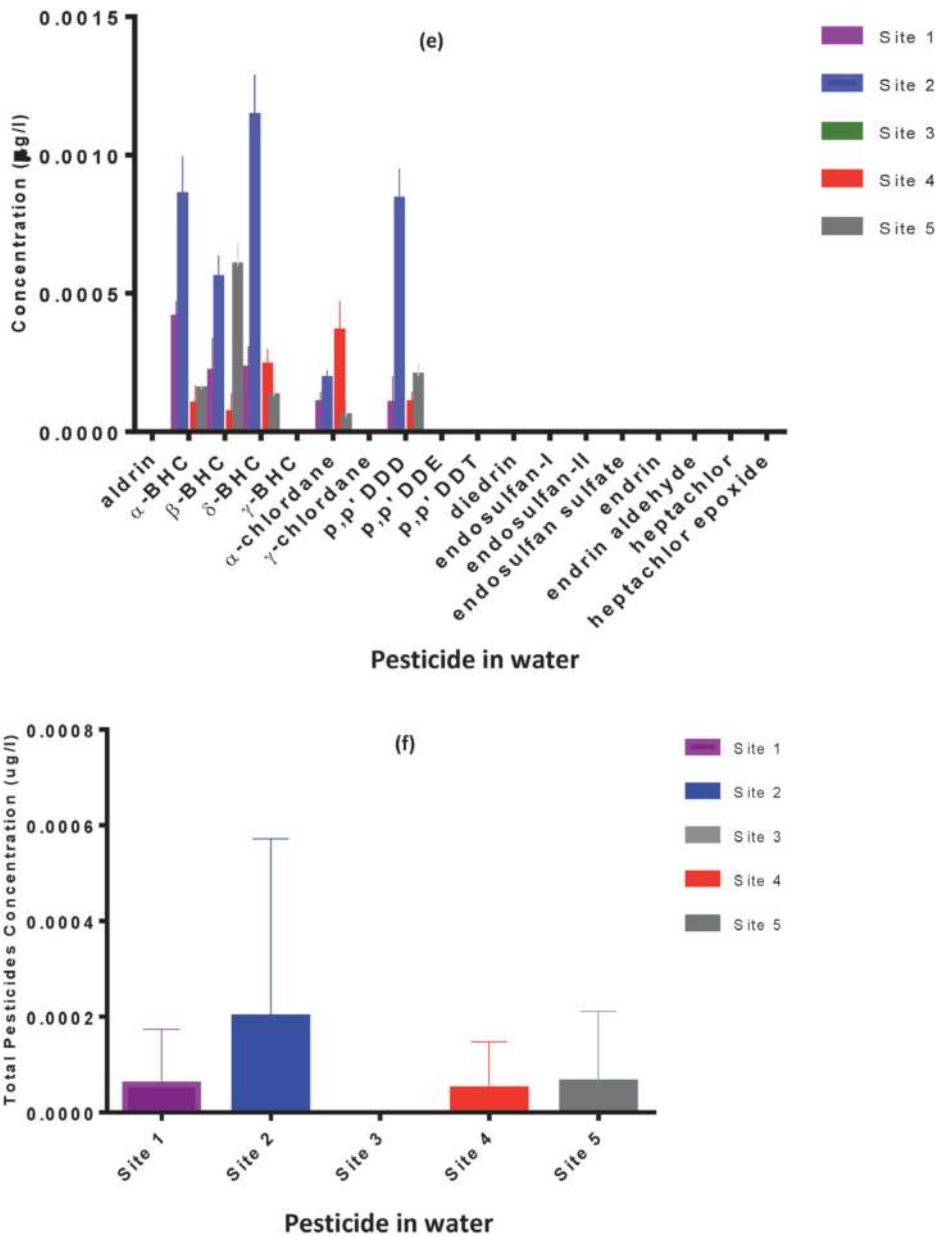


Figure 3. Single pesticides and total pesticide concentrations respectively for (a-b) fish (c-d) sediment (e-f) water across riparian sites.

5 (0.00060 ± 0.00008 µg/L). Pesticide concentration in surface water across riparian stations in this study, revealed markedly high levels of α-BHC, β-BHC, δ-BHC, and p,p'-DDD at station 2, while other stations showed markedly lower values (Figure 3e,f).

3.2 Multivariate relationship between riparian profile and pesticide incidence

Multivariate tests using principal component analysis (PCA), recorded varying patterns of associations between riparian stations and incidence of pesticides in sediment, surface water and fish across riparian stations. Describing occurrence of pesticides according to n-octanol–water partition coefficient ($\log K_{ow}$) i.e. hydrophilic (>4.5) or hydrophobic (<4.5) (Appendix IV), gave better insight into

pesticide mobility and occurrence within environmental matrices of the Ikpoba catchment.

For sediment, station 2 showed strong positive associations with the greatest number of pesticide types (α -BHC, β -BHC, γ -BHC, Endosulfan 1, δ -BHC and dieldrin). Five of them were hydrophilic pesticides while dieldrin was the only hydrophobic pesticide (5:1). Contrastingly, Station 3 showed a strong positive association with a greater number of hydrophobic pesticides (3:1), while endosulfan was the only hydrophilic pesticide detected in this area. Station 4 also showed a positive association with a greater number of hydrophobic (2:1), with endosulfan II as the only hydrophilic pesticide strongly associated with sediment from this area. All three pesticides positively associated with sediments at station 5 were all hydrophobic pesticides. While endrin aldehyde did not show any station-specific association or pattern of occurrence, sediments from station 1 did not show any marked association with any pesticide type (Figure 4).

For pesticide incidence in fish across riparian stations, the PCA revealed a strong positive association between station 2 and fish with the predominant occurrence of high labile pesticides (β -BHC, α -BHC, δ -BHC); station 4 showed positive associations with both low labile (dieldrin, a-chlordane and Aldrin) and high labile (endosulfan 1, endosulfan sulfate) pesticides. Fish samples from station 3 were only strongly associated with p,p'-DDE (a low labile pesticide). Station 1 and 5 showed no marked or weak association with any pesticide species (Figure 5).

PCA for pesticides in surface water across riparian stations revealed that surface water from station 2 was strongly associated with the greatest number of pesticides consisting of both high labile (α -BHC, δ -BHC) and low labile (p,p'-DDD) pesticides. Station 4 surface water samples showed a strong association with single pesticide a-chlordane. Surface water samples from station 1, 3 and 5 did not show any strong association with any of the pesticide species detected in this study, indicating a generally low level/incidence in surface water from these stations (Figure 6).

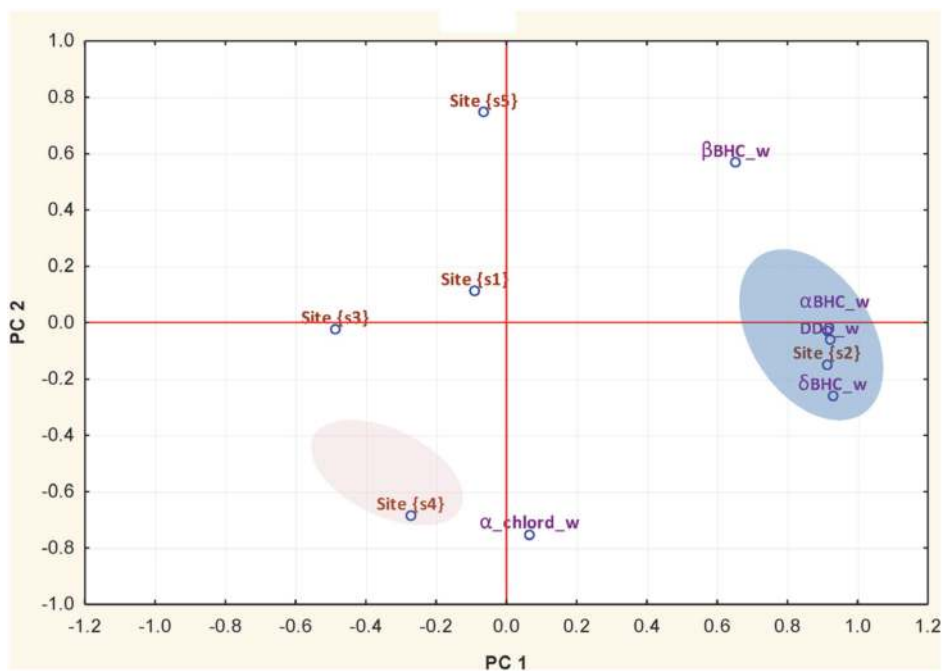


Figure 4. PCA biplot for contaminants in sediment across sites along the Ikpoba watershed.

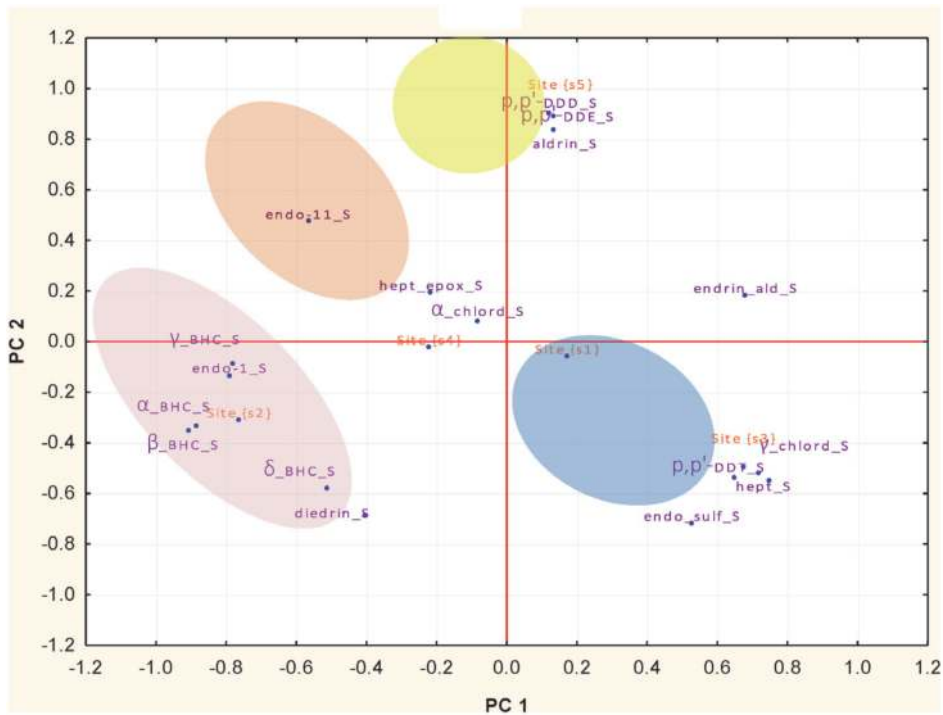


Figure 5.
 PCA biplot for contaminants in fish across sites along the Ikpoba watershed.

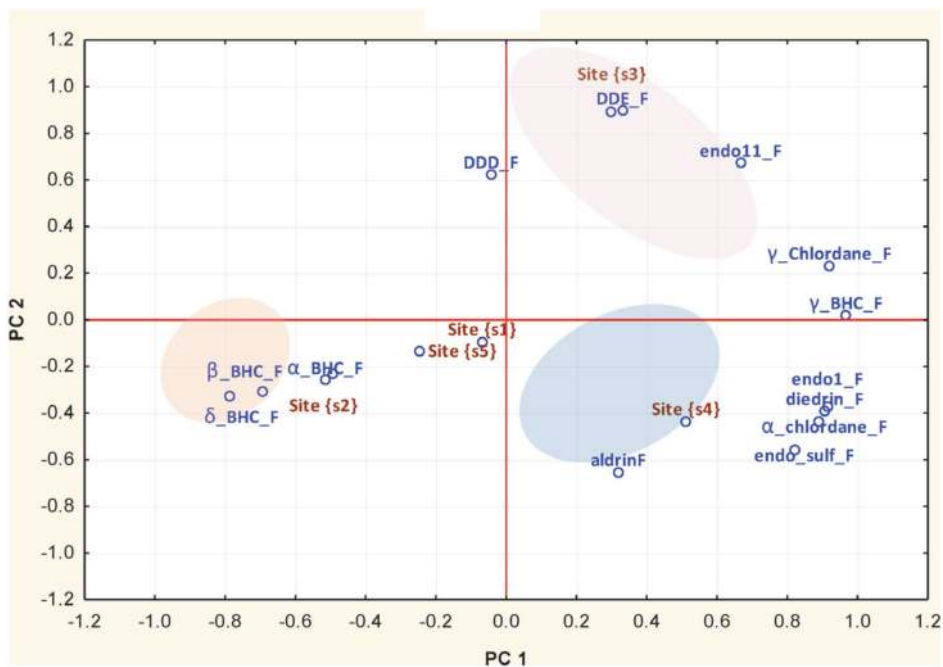


Figure 6.
 PCA biplot for contaminants in surface water across sites along the Ikpoba watershed.

From the combined PCA plot for pesticide concentrations in fish, sediment and water, there was a notable incidence of low labile pesticides, γ -chlordane and p,p'-DDE in fish flesh sampled from station 3 that was positively associated with γ -chlordane and DDT in sediment (**Figure 7**).

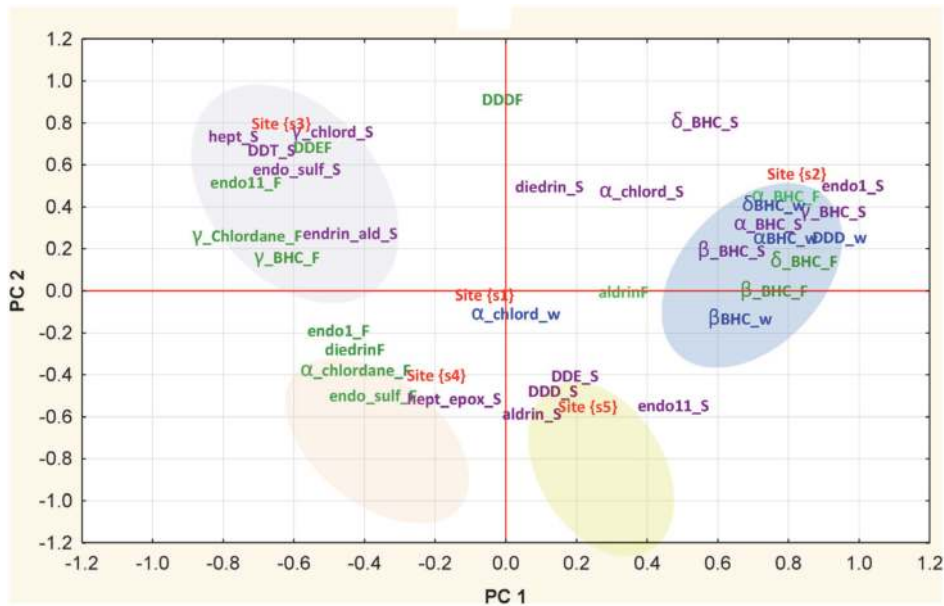


Figure 7. PCA biplot for contaminants in water, sediment and fish combined across sites along the Ikpoba watershed.

4. Discussion

Riparian buffers are vital links between terrestrial and aquatic ecosystems and they regulate the flow of species, energy, and various materials including contaminants between these ecosystems [48]. Under normal conditions of sufficient buffer-width and vegetation density, riparian vegetation buffers have the potential to remove and detoxify pesticides in runoff [13], however, only a few studies have examined the fate of pesticides in riparian areas [49].

4.1 Pollutant incidence in sediment and surface water

The patterns of pesticide incidence in surface water and sediment across different riparian profile areas of the watershed give a first impression of the role of riparian vegetation in preserving water quality. Station 2 with over 120 m of sparse vegetation only on the west side of the river, showed the highest incidence of pesticide species and total pesticide concentration in surface water. Higher incidence of pesticides in surface water adjacent to agricultural catchments has been attributed to recent and probably ongoing pesticide applications within the area [11, 50].

Sparse riparian vegetation cover increases the likelihood of soil compaction/bank shearing and ultimately, increased runoff into surface water from the affected area [51], thus, the sparse riparian cover on the west side of the river at station 2 may be implicated in the high occurrence of pesticides at this station. The lower pesticide incidence in surface water recorded for other riparian stations with <120 m rich vegetation suggests the absence of recent pesticide applications within that axis of the watershed. Surface water adjacent to buffer strips with intact riparian vegetation has been found to have better water quality compared to stations adjacent to buffer strips with little or no vegetation [52].

The difference in OCP concentration and types in sediments sampled at the five riparian stations are also relatable to the narrow riparian buffer (< 120 m) and sparse vegetation cover. Higher magnitude of above-ground sediment flow and the

erosion of streambanks has been associated with bare topsoil in watersheds covered by little or no vegetation [40]. This, in turn, amounts to the loss of valuable soil and acreage and the resultant loss in quality of adjacent surface water [53]. While efficient buffer widths have been shown to differ in application, wider buffers are considerably more useful for ecosystem protection than narrow ones. The 120 m buffer-width highlighted in this study for the Ikpoba watershed is consistent with some national guidelines with width recommendation of 10–100 m on each river-bank depending on hydrology and vulnerability of landscape [5].

4.2 Pollutant incidence in fish

From this study, the varied occurrence of OCPs in the flesh of the catfish (benthic fish) across riparian stations was relatable to the size of riparian-buffer widths. From the combined PCA plot, the high incidence of high labile OCPs (β -BHC, α -BHC, δ -BHC) in fish at station 2 was strongly associated with the same labile pesticide species in surface-water and sediment. This observation readily suggests that the smaller buffer-width at station 2, allowed greater OCP transport via runoff into surface water, and sediment, and eventual uptake by benthic fish. The co-occurrence of high labile OCPs in sediment and surface water portends increase risks to aquatic species because they are readily taken up by gills [11, 54]. Ecological risk assessment based on observed concentrations in water and sediment in Ikpoba river showed potential for risk to the different trophic levels (algae, daphnia and fish) inhabiting the river [28].

Also, from the combined PCA plot, the incidence of low labile pesticides, γ -chlordane and p,p'-DDE (a metabolite of DDT) in fish flesh sampled from station 3 was positively associated with γ -chlordane and DDT in sediment. The low labile (hydrophobic) characteristics of these OCPs readily suggests that incidence of these OCPs into the river sediment may have largely occurred via sediment erosion, and washing away of topsoil into adjacent regions of the river [11]. The coincidence of the same labile OCPs in sediment and flesh portends that uptake by benthic fish could be more likely to occur via benthic trophic interactions within its habitat range [54]. Such uptake in local fish fauna could culminate to reduced growth, altered reproduction and recruitment in local populations, and major shifts in community structure and health of local fauna [40, 55, 56]. Freshwater habitats in wet tropics support significant aquatic biodiversity [57], thus shrinking riparian vegetation would disrupt local assemblages of biodiversity, macro-invertebrates, and vertebrates that feed on them [58].

The clear discrimination between fish sampled from different stations based on OCPs in flesh, not only depicts that the predetermined areas of the watershed are indeed experiencing different pollutant traffic and transport but also establishes that the fish population from the different stations are not intermingling populations. This discrete uptake of OCPs depicts site-fidelity of species. It an ecological feature that prevents the additional physiological costs of exploring new areas [59], and is advantageous for increased individual survival and recruitment [60, 61] and better population viability [62]. The distances between the Ikpoba riparian stations (i.e. having a minimum of 1 km intervals) juxtaposed with the discrete OCP uptake by the catfish populations, and inferences of site-fidelity are consistent with studies that have proposed linear home range distance of approximately 1 km in similar benthopelagic fish [63]. The realization of site-fidelity for the catfish, a predominant benthic fish within the Ikpoba watershed portends that strategic conservation of different fish populations via designs of protected areas or implementations of fishing closures could be achieved if and when deemed necessary.

In general, the incidence of OCPs in fish, reveals that riparian stations with less than 120 m of buffer-width, cannot confer protection on biota in adjacent surface water. This finding demonstrated within a typical tropical catchment, is consistent with biodiversity studies in Latin America (tropical environment) and Southeast Asia that have recommended width thresholds of 40–200 m [5]. While our study corroborates other studies that attribute greater pesticide filtering capacity to wider buffer-width in riparian areas [13, 14], the use of NDVI, highlights vegetation vigor as a necessary feature to confer surface water protection. Many riparian studies have solely emphasized buffer width as a criterion for river protection [53, 55] while just a few have highlighted vegetation density or vigor [64, 65]. However, this study is a first report relating remotely sensed vegetation index to the filtering capacity and river protective features of riparian buffers in a typical tropical environment.

4.3 Stream order indices as a cofactor of riparian vulnerability

From this study, it was observed that riparian stations with the lowest occurrence of OCPs (station 1), not only had wide riparian buffer-width exceeding 120 m on both sides of the riverbank, and rich vegetation but received watershed drainage input from higher-order tributaries. Although, there was no linear relationship between the number of lower-order tributaries that characterized each riparian station, riparian stations with a greater incidence of OCPs in matrices received drainage from lower to intermediate-order tributaries. The association of lower-order drainage tributaries with narrow buffer-width areas and sparse vegetation presents a situation of altered hydrology due to disrupted watershed and loss of riparian vegetation. Such disrupted hydrology and tributary connectivity in agricultural catchment could have ecological implications, including limited dispersal corridors for biota and altered downstream delivery of substances within the watershed [66]. Hydraulic interactions during baseflows in watersheds of riparian areas allow the concentration of upstream flows, creating higher-order tributaries [67, 68]. As such, disrupted watersheds, allow predominance of lower-order or ephemeral tributaries which lack concentrated upstream flow and dominated by overland water flow [69]. As a result, these low-order tributaries are most prone to non-point sources of pollution, and increased pollutant load, and could significantly influence the quality of the receiving waters [70].

4.4 Riparian ecosystem services and policy advocacy

The occurrence of OCPs in sediments and fish adjacent to particular sampling stations indicates that the watershed has experienced a significant loss of riparian buffer-width and vegetation density resulting in what could be described as ‘remnant riparian’ vegetation. Findings have revealed that climes with well-formulated regulation for watershed and riparian protection would have classified such remnant vegetation as either “Endangered” or “Of Concern” e.g. Vegetation Management Act 1999 [71]. This brings to bear the need to urgently address the regulatory deficit for riparian protection in developing countries, to save remnant riparian vegetation and foster its restoration by reducing anthropogenic assault.

The occurrence and association of OCPs in sediments with each riparian station indicate that smaller buffer-areas experienced greater sediment mobility, and thus more transport of hydrophobic/low labile pesticides. Riparian vegetation plays an important role in slowing down the flow velocity, decreasing erosion and stabilizing stream banks. In addition to the bank stabilization offered by well-developed root systems, the amount of vegetation present in the riparian region often influence other riparian system functions [40, 72]. Aside from trapping sediment and

nutrients, the presence of riparian vegetation protects soil compartments from erosion, compaction, evaporation as well as reduce water and soil temperature [13]. In terms of ecosystem services, riparian rich areas typically provide several important functions, including water purification from riparian vegetation, improved water quality, improved water esthetics for visitors and also improve the abundance of native fish and wildlife; which not only enhance ecological health but also have financial and economic benefits [40, 73]. However, the urgency for appropriate management of riparian areas will be a product of the information on their current condition and health.

4.5 Socio-economic implication of riparian area loss

The degradation of river basins and watersheds as seen in the Ikpoba river carries tangible economic, fiscal and social costs because the cost of environmental degradation goes hand in hand with the adverse health and lowering the productivity of citizens. The increased incidence of pesticides in surface water could result in acute pesticide poisoning for consumers increasing the likelihood of morbidity and mortality that could debilitate a significant part of the community workforce [74]. However, improving the quality of a deteriorated Ikpoba river system via appropriate policy and sufficient resource allocation will significantly improve the economic and fiscal future of the Ikpoba area and Edo state at large.

5. Conclusion

This study used the agrarian riparian area of Ikpoba river to demonstrate the capacity of riparian vegetation to protect adjacent river systems from pesticide-laden runoff. The spatial distribution of OCPs in water, sediment and fish matrices were consistent with the relative depletion of riparian vegetation and buffer-width across the stations studied. It is a first report to demonstrate within any sub-Saharan area that, buffer-width and density of vegetation are critical aspects of the filtering capacity of riparian areas. While this study highlights dense riparian vegetation and wide buffer-width of 120 m as suitable for protection of surface water quality and aquatic species, more studies of this nature but of larger scope are recommended to inform contextual management of tropical agrarian watersheds. It is also recommended that extant regulatory instruments be reviewed to reflect strategies and practices needed to improve the ecological functions of existing riparian areas and encourage the restoration of depleted riparian areas. Focused action on addressing policy issues and regulatory gaps on watershed protection are necessary to change the current trajectory of deteriorating river basins within urban African areas. Also, strengthening regulatory requirements for pollutant-filtering buffer zones along agricultural catchments to limit risks to adjacent surface water.

Competing interests' statement

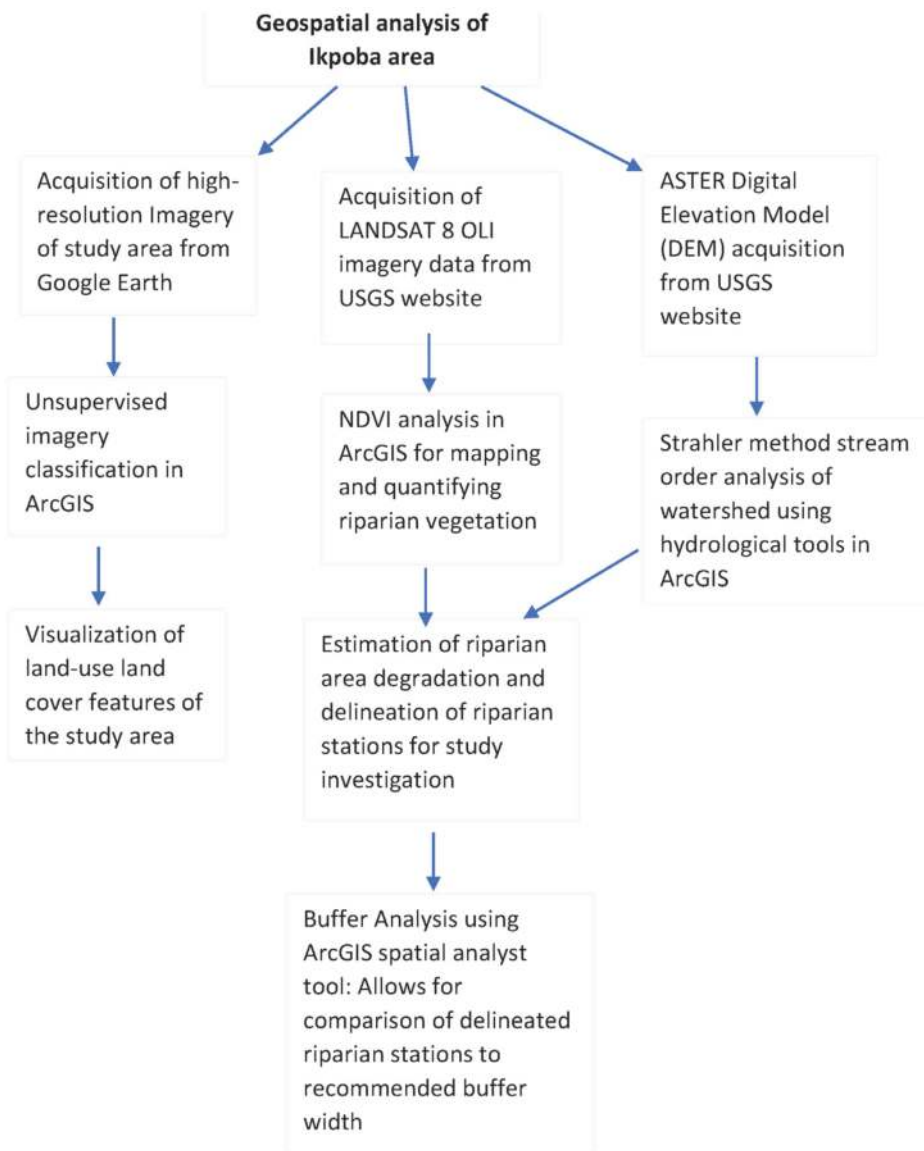
The authors declare that they have no conflict of interest.

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A. Appendix I

Overall geospatial methodological scheme of the study.



B. Appendix II (RIPARIAN STATIONS)

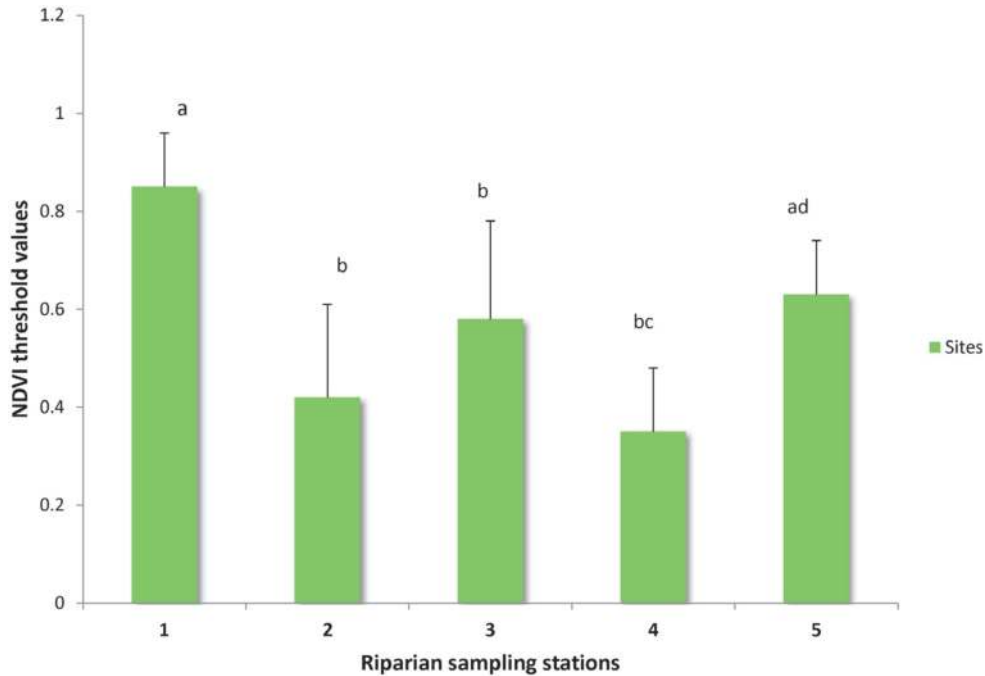




(a) Full riparian buffer on both sides of river (b) sparse riparian cover on one side of the river with agricultural activity (c) Sparse riparian cover on one side of the river (d) moderate riparian vegetation cover on both sides of the river (e) moderate riparian vegetation cover on both sides of the river (f) sparse riparian cover on both sides of the river

C. Appendix III

Normalized difference vegetation index (NDVI) for predetermined riparian stations within the Ikpoba watershed.



*Stations with the same alphabet are not significantly different

D. Appendix IV

n-octanol–water partition coefficient ($\log K_{ow}$) of pesticides detected within the Ikpoba river catchment.

Pesticide	Log K_{ow}
γ BHC	3.73
α BHC	3.8
β BHC	3.81
Endosulfan-I	4.1
Endosulfan-II	4.1
Endos_aldehyde	4.1
Endos_sulfate	4.1
Hept_Epoxyde	5
Endrin	5.06

Pesticide	Log K _{ow}
<i>Dieldrin</i>	5.37
<i>Chlordane</i>	5.5
<i>Heptachlor</i>	6.26
<i>Aldrin</i>	6.5
<i>DDT</i>	6.53

Author details

Azubiike Victor Chukwuka^{1*} and Ozekeke Ogbeide^{2,3}

1 Environmental Quality Control Department, National Environmental Standards and Regulations Enforcement Agency (NESREA), Nigeria

2 Ecotoxicology Research Laboratory, Afromontane Research Unit, Department of Zoology and Entomology, University of the Free State (Qwa qwa Campus), South Africa

3 Environmental Management and Toxicology, University of Benin, Nigeria

*Address all correspondence to: zubbydoo@gmail.com

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