



Distribution of heavy metals and pesticides residues in sediments of some rivers in Ekiti state, Southwest Nigeria

Olayinka D. Akodu^{1,2*}, Ademola F. Aiyesanmi¹, Bolaji W. Tomori^{1,3}

1. Department of Chemistry, Federal University of Technology, Akure, Ondo State, Nigeria

2. Department of Pollution Control, Ekiti State Environmental Protection Agency, Ado-Ekiti, Ekiti State, Nigeria

3. Department of Chemistry, Nigeria Defence Academy, Kaduna Nigeria

*Corresponding author E-mail: <u>yinkaakodu@gmail.com</u>

Article info

Received 4/5/2023; received in revised form 17/5/2023; accepted 15/6/2023 DOI: <u>10.6092/issn.2281-4485/16969</u> © 2023 The Authors.

Abstract

Sediments are habitats and major sources of nutrients for benthic organisms. High concentration of pollutants can impact negatively on the lives of such organisms and ultimately on the lives of human beings who may feed on them. This study was carried out in order to evaluate some environmental pollutants' load: heavy metals and pesticide residues in Irintan, Omi-Eye and Egbigbu river sediments in Ekiti State, Southwest Nigeria. Sediment samples were taken at upper, middle and lower courses of each river relative to the farm used for the study. The samples were air-dried in the laboratory, disaggregated, sieved and analysed for heavy metals and organochlorine pesticides (OCP) residues using standard methods. The heavy metal range at floodplains (mg/kg) was: Cr (0.25-2.08), Cu (0.19-14.28), Zn (BDL-2.53), Cd (BDL-0.87), Pb (BDL-0.32), Fe (0.38-22.35) while for OCP residues, the range (μ g/kg) was α -BHC (0.15-0.33), β -BHC (0.19-14.28), δ -BHC (0.25-1.09), lindane (BDL-1.23), chlorothalonil (0.87-1.44), heptachlor (BDL-1.04), heptachlor epoxide (BDL-1.96), endosulfan I (0.20-1.98), endosulfan II (BDL-0.67), aldrin (BDL-1.93), endrin (BDL-0.37), dieldrin (BDL-0.42), p,p-DDE (BDL-0.52), p,p-DDT (BDL-1.20), methoxychlor (0.21-0.88). The pollutants' concentrations in the sediments were generally low at all the sites when compared with international guidelines for each pollutant. Governments in Nigeria should checkmate indiscriminate dumping of refuse most of which end in our rivers in order to reduce pollutants' concentration in rivers/sediments so as to protect the lives of benthic organisms.

Keywords

Benthic, ecosystem, sediments, PAHs, pesticides, pollutants

Introduction

The industrial revolution of 19th century came with increased pollution of the earth's environment. Since then, rivers from all over the world have received significant amounts of pollutants from industrial effluents (Perey, 2006). Sediment is a matrix of materials which composed of detritus, inorganic and organic particles and it is relatively heterogeneous in terms of its physical, chemical and biological characteristics (Kumar *et al.*, 2011). It serves as habitat and major nutrient source for benthic organisms (Davies and Abowei, 2009). It is a known fact that pollutants dropped in water bodies eventually settle to the bottom sediment. Therefore, sediment acts as sink for pollutants like heavy metals, pesticide residues and polycyclic aromatic hydrocarbon (PAHs) amongst others (Amadi *et al.*, 2016). Pollutants are of environmental concern in aquatic ecosystems due to their environmental persistence, toxicity, bioaccuDOI: 10.6092/issn.2281-4485/16969

cumulation and biomagnification in the food chain (Saria, 2016). Though heavy metals may be discharged into aquatic ecosystem in low amounts, the constant deposits through anthropogenic activities can raise their concentration, creating environmental problems in lakes, rivers, streams as well as households (Saria, 2016). According to (Nfon et al., 2008), sources of heavy metals in sediments include industrial effluents, municipal sewage, mining and agricultural activities among others. Pesticides, in particular organochlorine pesticides (OCPs), can enter the aquatic environment through paths like runoff from contaminated soil, industrial effluents and atmospheric deposition. In water, hydrophobic OCPs (such as DDTs and HCHs) tend to adsorb to particulate organic matter and deposit in sediments (Ivanova et al., 2021).

As a result of their persistence and bio-accumulative nature, these pollutants can enter the food chain thereby creating health issues to man (Vesel *et al.*, 2013). Thus, there is the need to determine sediment qualities of rivers especially in a developing country like Nigeria where, as a result of her large population, great amount of wastes are generated daily without good management practices and technology to treat such wastes effectively (Howard *et al.*, 2021).

A lot of research works have been done on heavy metal, pesticide residues in sediments worldwide (Mahugija *et al.*, 2017; Skorbiloicz *et al.*, 2018, El-Alfy *et al.*, 2019). However, only scanty reports are seen on state of sediment pollution in developing countries, Nigeria inclusive. The aim of this study therefore is to evaluate the distribution of heavy metals and pesticide residues in sediments of some rivers in Ekiti State, Southwest Nigeria in order to present, perhaps for the first time, a multipurpose environmental data as an index for environmental evaluation.

Materials and Methods

Study Area

The Ekiti State is mainly an upland zone rising over 250 meters above sea level. The state is located between longitudes 4045' and 5045' East of Greenwich Meridian and between latitudes 7015' and 8050' North of Equator. It is generally undulating with a characteristic landscape that consists of old plains broken by step sided outcrops or ridges. The state enjoys tropical climate with distinct wet and dry seasons (Akinyemi *et al.*, 2013). The state is the source of many notable rivers in the South western Nigeria.



Sample collection and preparation

Three rivers with floodplains used for dry season farming (FGN Fadama project) were selected for the study; these were Irintan river, tributary of Ogbese River in Ogbese Town, Ise-Ekiti; Omi-Eye River at Erio-Ekiti and Egbigbu River at Ayetoro-Ekiti in southern, central and northern parts of the state respectively. The coordinates of the farm locations taken with GPS

e-trek 10 are: Longitude - 05º 22.019'E, Latitude - 07º 30.528'N (Altitude - 420m); Longitude - 04⁰ 52.882' E Latitude - 07º 43.450'N (Altitude - 417m); Longitude -05º 09.131'E, Latitude - 07º 55.457'N (Altitude - 531m) respectively. Sediment sampling at the three rivers took place between October 2019 and April 2020 which were dry season months during which the rivers could be accessed to obtain the samples. Sediment samples were obtained at upper, middle and lower parts of each river relative to the FADAMA farm. All samples were put in separate polythene bags, appropriately labeled and transported to the laboratory under a sealed box. They were subsequently air dried, disaggregated with agarte mortal and pestle, sieved with 2.0mm (BS) stainless steel mesh and kept in polyethylene terephthalate (PET) bottles pending analysis.

Sample analyses

Heavy Metals Analysis. One gram of sample was placed in a 250 mL digestion tube and 10 mL of Conc. HNO₃ was added. The mixture was boiled gently in a fume cupboard for 30-45 minutes to oxidize all easily oxidizable matter. After cooling, 5 mL of 70 % HClO₄ was added and the mixture was boiled gently until dense white fumes appeared. It was cooled again before 20 mL of deionised water was added and the mixture was boiled further to release any fumes. The solution was finally cooled, filtered through Whatman No 42 filter paper and transferred quantitatively to a 25 mL volumetric flask and made up to mark using deionised water (Zang-Yei, 2004). The heavy metals were analyzed with Atomic Absorption Spectrophotometer (AAS) Perkin Elmer Analyst 400 model.

Pesticides Analysis. The reagents used were all of analytical grade and glasswares used were cleaned as prescribed by USEPA method 1699 (USEPA, 2007). The extraction of organochlorine pesticides in the sediments was carried out using the method described by (Ize-Iyamu and Egwakhide, 2007). Twenty five grammes of the dry sediment sample was mixed with fifty grammes of granular sodium sulphate, ground carefully into fine particles using pestle and mortal after which it was extracted using 150 mL mixture of n-hexane and acetone (1:2) in a 250 mL Erlemeyer flask. The extract was transferred into a round bottomed flask and concentrated to 20mL on a water bath with temperature maintained at 55 °C. The concentrated extract was further concentrated using a rotary evaporator to 5 cm³.

The concentrated extract was transferred to centrifuge tube and concentrated on a centrifuge tube where it was concentrated on a nitrogen evaporator to 0.5 cm^3 and diluted to 2 cm^3 in hexane before analysis.

Pesticide extract clean-up

A 15 cm (length) x 1cm (internal diameter) column plugged at its lower end with glass wool was packed with 5 g activated silica made in slurry form in dichloromethane. Two grams (2 g) of anhydrous sodium sulphate (Na2SO4) was placed on top of the silica gel to absorb water in the sample or solvent in the clean-up extract. Pre-elution was done with 15 cm³ dichloromethane without exposing the sodium sulphate layer to air, in order to prevent the drying up and cracking of the packed silica gel adsorbent. The extract was then introduced into the column and allowed to sink below the sodium sulphate layer. Elution was done three times each with 10 cm³ portions of dichloromethane (DCM). The combined eluate was evaporated to dryness on a rotary evaporator at about 45 °C using a gentle stream of pure nitrogen (99.99 %). The dried eluate was reconstituted with 1 cm3 trimethylpentane and transferred into glass GC vials in readiness for gas chromatographic analysis.

Gas Chromatographic operating conditions

The sample (1 μ L) was injected into the injection port of an Agilent 7980 Autosampler Gas Chromatograph system equipped with an Electron Capture Detector. The oven temperature started at 150 °C and increased to 280 °C at 6 °C per minute. The run time was 21.67 min. The individual OCPs were identified by comparing the elution time of standard OCPs with those in the samples, while each OCP was quantified by comparing the peak areas of the OCPs in the samples with those in standard.

Quality Assurance

All glass wares were first soaked in 14% HNO₃ for 24 hours to remove possible contaminants, washed with detergent and rinsed with de-ionised water before commencing analysis. Quality control was assured through replicate samples, use of pure analytical grade reagents and procedural blanks, limit of detection and limit of quantification (Olawale *et al.*, 2017). Other methods adopted in order to further ensure that the result obtained in this study is valid and reliable included determination of percentage recoveries of organochlorine pesticides residues from spiked and unspiked samples which were found to be within the 70-120% range approved by the European Commission (EC) for evaluating the efficiency and precision of an analytical method (EU, 2017).

Data Analysis

The data obtained from this study were statistically tested for analysis of variance (ANOVA), t-test, Pearson correlation using SPSS 16.0 package. The interpretation of statistical results was done using one level confidence limit (p<0.05).

Results and Discussion

Heavy Metals in Sediment

The results of heavy metal concentration in sediments at Irintan (Ogbese), Omi-Eye (Erio) and Egbigbu (Ayetoro) rivers are presented in Table 1. All the metals studied were detected in the sediments samples The concentration ranges (mg/kg) are: Cr (0.25-0.79), Cu (0.19-0.77), (1.54-1.74), Cd (0.54-0.87), Pb (0.09-0.29), Fe (0.38-1.14) with the highest value recorded in $Zn (1.74\pm0.39 mg/kg)$ at middle course and the lowest value recorded in Pb (0.09±0.03mg/kg) at upper course for Irintan floodplain; Cr (0.46-0.73), Cu (0.74-1.84), Zn (2.17-2.53), Cd (BDL-0.28), Pb (BDL-0.25), Fe (7.45-18.88) with the highest value recorded in Fe (18.88±4.16mg/kg) at upper course and the lowest concentration obtained in Pb and Cd (BDL) at upper course for Omi-Eye floodplain and Cr (1.59-2.08), Cu (7.03-14.28), Zn (BDL-3.83), Cd (BDL-0.03), Pb (0.14-0.32), Fe (6.17-22.35) with the highest values obtained in Fe $(22.35\pm1.29 \text{ mg/kg})$ at middle course and lowest values recorded in Zn at upper course and Cd at upper and middle course (BDL) for Egbigbu floodplain.

Table 1. Heavy metal comcentration (mg/kg) in Sediments at the study sites and Mean comparison with USEPA Guidelines.

Site	R/Course	Cr	Cu	Zn	Cd	Pb	Fe			
Irintan	Upper	0.25 ± 0.01	0.19 ± 0.08	1.56 ± 0.04	0.65 ± 0.02	0.09 ± 0.03	0.38 ± 0.06			
	Middle	0.55 ± 0.04	0.36 ± 0.03	1.74 ± 0.39	0.54 ± 0.17	0.11 ± 0.01	1.05 ± 0.10			
	Lower	0.79 ± 0.04	0.77±0.19	1.54 ± 0.05	0.87 ± 0.12	0.29 ± 0.06	1.14 ± 0.03			
Omi-Eye	Upper	0.46 ± 0.03	1.84±0.00	2.17±0.11	BDL	BDL	7.45±1.62			
	Middle	0.58 ± 0.09	1.56 ± 0.07	2.37 ± 0.07	0.11 ± 0.02	0.25 ± 0.06	16.12±3.97			
	Lower	0.73 ± 0.00	0.74 ± 0.05	2.53 ± 0.31	0.28 ± 0.08	0.14 ± 0.02	18.88±4.16			
Egbigbu	Upper	1.59 ± 0.14	14.28±1.03	BDL	BDL	0.32±0.03	18.48±3.62			
	Middle	1.75 ± 0.02	7.03±0.13	1.69 ± 0.11	BDL	0.15 ± 0.00	22.35±1.29			
	Lower	2.08 ± 0.11	9.95±0.81	3.83 ± 0.33	0.03 ± 0.01	0.14 ± 0.05	6.17±0.32			
Irintan	Mean Values	0.53±0.27	0.44±0.30	1.61±0.11	0.69 ± 0.14	0.16±0.11	0.86±0.42			
Omi-Eye	Mean Values	0.59 ± 0.14	1.38±0.85	2.35 ± 0.18	0.13±0.02	0.13±0.12	14.15±5.96			
Egbigbu	Mean Values	1.81 ± 0.25	10.42±3.65	1.84±0.92	0.01±0.02	0.20±0.10	8.33±8.45			
USEPA Metal Guideline	Not polluted	40-60	<25	<90	NA	<40	NA			
	Moderately polluted	>60	25-75	90-200	NA	40-60	NA			
	Heavily polluted	>75	>75	>200	>60	>60	NA			
Values with different superscripts on the same row are significant (p<0.05). Source of USEPA Guidelines: (Ogbeibu et al., 2014)										

The range of the metal concentration (mg/kg) along the courses at Irintan equally reveal that Zn recorded the highest value (1.56 ± 0.04) while the least value was obtained in Pb (0.09 ± 0.03) at upper course, highest value in Zn (1.74 ± 0.39) and lowest value in Pb (0.11 ± 0.01) at middle course and the highest value in Zn (1.54 ± 0.05) while lowest value was recorded in Pb (0.29 ± 0.06) at the lower course. At Omi-Eye, thehighest value was recorded in Fe (7.45 ± 1.62) and lowest was recorded in Cd and Pb (BDL) at upper course, the highest value was obtained in Fe (16.12 ± 3.97) and lowest value recorded in Cd (0.11 ± 0.02) at the middle course and highest concentration in Fe (18.88 ± 4.16) and lowest value in Pb (0.14 ± 0.02 at the lower course of the floodplain. Finally at Egbigbu, the highest was recorded in (18.48 ± 3.62) and lowest recorded in Zn and Cd (BDL) at the upper course, the highest value obtained in Fe

DOI: 10.6092/issn.2281-4485/16969

(22.35±1.29) and lowest concentration obtained in Cd (BDL) in middle course and highest concentration recorded in Cu and lowest value recorded in Cd (0.03 ± 0.01) at the lower course of the floodplain. The values obtained in this study are within the ones obtained by Adeyemi et al. (2019) in their study of heavy metal pollution in sediments from Ologe lagoon, Agbara, Lagos, Nigeria but far less than those obtained by Onoyima et al. (2021) in sediment of River Kaduna, Nigeria and those obtained by Algul and Beyhan (2020) from sediment of Bafa Lake in Turkey. The order of Cr in Irintan, Omi-Eye and Egbigbu was lower course>middle course>upper course. However, the order of Cu in Irintan was lower course>middle course>upper course, at Omi-Eye it was upper course>middle course>lower course while at Egbigbu it was upper course>lower course>middle course. In the case of Zn, the order was middle course>upper course>lower course at Irintan, while it was lower course>middle course>upper course at both Omi-Eye and Egbigbu. Cd has the order of lower course>upper course>middle course in Irintan, lower course>middle course>upper course at Omi-Eye while the order at Egbigbu was lower course>upper course/middle course.

For Pb, it was lower course>middle course>upper course in Irintan, middle course>lower course>upper course in Omi-Eye and upper course>middle course>lower course in Egbigbu. Iron has the order lower course>middle course>upper course in Irintan and Omi-Eye while it was middle course>upper course>lower course at Egbigbu.

Metals with higher values at upper courses may be as a result of contributions from outside the farm while metals with higher values at the lower course may be attributed to anthropogenic activities on the farm especially the use of agrochemicals like pesticides and fertilizers.

The results obtained in this report show the sediments were not polluted when compared with USEPA guidelines (Table 1). The values obtained at upper, middle and lower courses were significantly

different for some metals as observed in Cr and Cu in Omi-Eye while they were not significantly different for others at as observed in Zn at Irintan and Pb in Egbigbu p<0.05.

Table 2 shows the concentration of organochlorine pesticide residues measured in Irintan River (Ogbese), Omi-Eye River (Erio) and Egbigbu River (Ayetoro) sediments.

 Table 2. Organochlorine residues concentrations in sediments at the study sites and comparison with Sediment Quality Guidelines

F/plain	Irintan			Omi-Eye			Egbigbu			Sediment Quality Guidelines			
R/course	Upper	Middle	Lower	Upper	Middle	Lower	Upper	Middle	Lower	ERL ^a	ERMª	TEL ^b	PEL ^b
α-BHC	0.15 ^a ±0.03	$0.33^{b} \pm 0.05$	$0.34^{b}\pm0.00$	$0.25^{a} \pm 0.07$	$0.25^{a} \pm 0.00$	0.33ª±0.05	0.24ª±0.03	$0.30^{b} \pm 0.04$	0.31 ^b ±0.04	NA	NA	0.94	1.38
β-ВНС	BDL	BDL	BDL	$0.42^{a} \pm 0.07$	$0.54^{a} \pm 0.02$	$0.97^{b} \pm 0.31$	BDL	$1.20^{a} \pm 0.17$	$1.20^{a} \pm 0.14$	NA	NA	NA	NA
δ-ВНС	$0.72^{a} \pm 0.04$	$0.80^{b} \pm 0.07$	$0.92^{c} \pm 0.00$	$0.25^{a} \pm 0.00$	$0.52b \pm 0.00$	1.09 ^c ±0.07	0.64ª±0.05	$0.65^{a} \pm 0.03$	$0.87^{b} \pm 0.21$	NA	NA	NA	NA
Lindane	BDL	BDL	BDL	$0.26^{a} \pm 0.04$	$0.23^{a} \pm 0.00$	$0.35^{b} \pm 0.13$	$1.23^{b} \pm 0.57$	$0.23^{a} \pm 0.02$	BDL	NA	NA	NA	NA
Chlorotha	$0.90^{a} \pm 0.06$	$1.05^{b} \pm 0.53$	1.44 ^c ±0.20	$1.18^a \pm 0.02$	1.13ª±0.57	$1.06^{a} \pm 0.25$	$0.87^{a} \pm 0.11$	$1.30c\pm0.20$	$1.16^{b} \pm 0.05$	NA	NA	NA	NA
Heptachlor	$0.35^{a} \pm 0.08$	$0.35^{a} \pm 0.10$	$1.04^{b} \pm 0.23$	$0.22^a \pm 0.03$	$0.23^{a} \pm 0.07$	$0.30^{b} \pm 0.00$	BDL	BDL	BDL	NA	NA	NA	NA
H/Epoxid	BDL	BDL	BDL	1.96°±0.73	$1.47^{b} \pm 0.13$	$0.54^{a} \pm 0.11$	BDL	BDL	BDL	NA	NA	0.6	2.74
E/Sulfan I	$0.20^{a} \pm 0.06$	$1.55^{b} \pm 0.32$	$1.87^{c} \pm 0.20$	1.98°±0.55	$1.40^{b} \pm 0.09$	$0.47^{a} \pm 0.15$	$0.21^{a} \pm 0.05$	$0.39^{a} \pm 0.08$	$1.41^{b} \pm 0.33$	NA	NA	NA	NA
E/Sulfan II	BDL	BDL	BDL	$0.45^{b} \pm 0.04$	$0.28^{a} \pm 0.00$	BDL	$0.67^{b} \pm 0.09$	$0.32^{a} \pm 0.00$	$0.29^{a} \pm 0.00$	NA	NA	NA	NA
Aldrin	$0.24^{a} \pm 0.09$	$1.40^{b} \pm 0.02$	1.93°±0.04	1.57¢±0.10	$0.48^{b} \pm 0.00$	$0.29^{a} \pm 0.08$	BDL	1.91ª±0.75	BDL	NA	NA	NA	NA
Endrin	BDL	BDL	BDL	$0.32^{a} \pm 0.02$	$0.36^{b} \pm 0.00$	$0.36^{b} \pm 0.05$	$0.37^{a} \pm 0.02$	BDL	$0.36^{a} \pm 0.00$	0.02	45	2.67	62.4
Dieldrin	BDL	BDL	$0.21^{b} \pm 0.02$	$0.34^{b} \pm 0.09$	$0.33^{b} \pm 0.01$	$0.24^{a} \pm 0.00$	0.42°±0.13	$0.35^{b} \pm 0.01$	$0.24^{a} \pm 0.07$	0.02	8	2.85	2.85
p,p-DDE	BDL	BDL	BDL	BDL	$0.32^{a} \pm 0.00$	$0.52^{a} \pm 0.00$	BDL	BDL	BDL	2.2	2.7	1.42	6.67
p,p-DDT	BDL	BDL	BDL	BDL	$0.63^{a} \pm 0.03$	$0.96^{b} \pm 0.13$	$1.20^{\mathrm{b}} \pm 0.39$	$0.62^{a} \pm 0.06$	$0.60^{a} \pm 0.09$	1	7	1.79	NA
Methoxy	$0.58^{a} \pm 0.11$	$0.55^{a} \pm 0.07$	$0.66^{c} \pm 0.15$	$0.21^{a} \pm 0.02$	$0.49^{b} \pm 0.05$	$0.51^{\mathrm{b}} \pm 0.00$	$0.88^{\rm b}{\pm}0.07$	$0.23^{a} \pm 0.00$	$0.23^{a} \pm 0.00$	NA	NA	NA	NA
$\sum BHCs$	0.87	1.13	1.36	1.18	1.54	2.74	2.11	2.15	2.38	NA	NA	NA	NA
$\sum DDTs$	BDL	BDL	BDL	BDL	0.95	1.48	1	0.62	0.6	1.58	46.1	7	4450

BHC= Benzene hexachloride, Chlotha= Chlorothalonil, H/Epoxide= Heptachlor Epoxide, E/sulfan= Endosulfan, DDE= Dichlorodiphenyldichloroethene, DDT= Dichlorodiphenyltrichloroethane, Methoxyc= Methoxychlor. Values with different superscripts on the same row are significant (p<0.05). ERL= Effect Range Low, ERM= Effect Range Medium, TEL= Threshold Effect Low, PEL= Probable Effect Level, Source: a=(Long et al., 1995) b=(MacDonald et al., 2000). Values with different superscripts on the same row are significant (p<0.05)

DOI: <u>10.6092/issn.2281-4485/16969</u>

All the sediments studied were detected with exception of a few at some sites. The concentration $(\mu g/kg)$ ranged observed were as follows: for Irintan viz:- α - BHC (0.15-0.34), β - BHC (BDL), δ -BHC (0.72-0.92), lindane (BDL), chlorothalonil (0.90-1.44),heptachlor (0.35-1.04), heptachlor (BDL), endosulfan I epoxide (0.20-1.87),endosulfan II (BDL), aldrin (0.24-1.93), endrin (BDL), dieldrin (BDL-0.21); dichlorodiphenyldichloroethylene (p,p-DDE) (BDL), dichlorodiphenytrichloroethane (p, p' - DDT) (BDL), methoxychlor (0.55-0.66); for Omi-Eye viz:- α – BHC (0.25-0.33), β – BHC (0.42-0.97), δ – BHC (0.25-1.09), lindane (0.23-0.35), chlorothalonil (1.06-1.18), heptachlor heptachlor (0.22 - 0.30),epoxide (0.54 - 1.96),endosulfan I (0.47-1.98), endosulfan II (BDL-0.45), aldrin (0.29-1.57), endrin (0.32-0.36), dieldrin (0.24-0.34), p,p'-DDE (BDL-0.52), p, p' - DDT) (BDL-0.96), methoxychlor (0.21-0.51) and for Egbigbu viz:- α – BHC (0.24-0.31), β – BHC (BDL-1.20), δ – BHC (0.64-0.87), lindane (BDL-1.23), chlorothalonil (0.87-1.16), heptachlor (BDL), heptachlor epoxide (BDL), endosulfan I (0.21-1.41), endosulfan II (0.29-0.67), aldrin (BDL-1.91), endrin (BDL-0.37), dieldrin (0.24-0.42), p, p'-DDE (BDL), p, p' - DDT (0.60-1.20) and methoxychlor (0.23-0.88). The total OCPs concentration at upper, middle and lower courses respectfully is 3.14, 6.03 and 8.41 µg/kg at Irintan, 9.41, 8.66 and 7.99 µg/kg at Omi-Eye and 6.73, 7.50 and 6.67 μ g/kg at Egbigbu floodplain.

The OCPs values obtained in this study are within the values obtained by Okoya et al. (2013) in their study of OCP residues in sediments from cocoa producing Areas of Ondo State, Southwest Nigeria but lower than the ones obtained by Olofinsoye and Senkele (2016) in their study of OCPs in sediment obtained from Lagos Lagoon, Nigeria. Generally, the trend was upper course<middle course<lower course for most of the pesticide values except for methoxychlor at Irintan river; lindane, heptachlor epoxide, aldrin, dieldrin in Omi-Eye river and methoxychlor in Egbigbu river. The observed trend may imply that the OCPs were still being used by the farmers at the farm sites despite ban on their usage. The values obtained at upper, middle and lower courses were significantly different for some pesticide residues while they were not significantly different for others at p<0.05. For example, chlorothalonil showed significant difference between

the three courses in Irintan and Egbigbu but shows no significance at Omi-Eye floodplain. The OCP values obtained at the three sites were generally low when compared with probable effect level (PEL) (MacDonald et al 2000) (Table 2). This implies that the benthic organisms living on the sediment may not be at risk as far as the OCP residue concentrations are concerned. The only exception to the above generalization were p,p'-DDT at Egbigbu river (Ayetoro) upper course which was above effect range low (ERL) and heptachlor epoxide at Omi-Eye river (Erio) upper and middle courses where the values were above the threshold effect low (TEL) but less than probable effect level (PEL). The concentrations of the two OCP residues call for concern in those respective regions.

Conclusions

The results of the pollutant concentrations in the sediments of Irintan, Omi-Eye and Egbigbu Rivers shows that the rivers are not polluted when established sediment quality compared with guidelines. The values obtained for heavy metals and pesticide residues are lower than effect range low of the guidelines of each pollutant which is the concentration above which aquatic organisms could be affected negatively by the pollutants. This implies that the organisms may not be negatively impacted by the concentrations of the pollutants. However, there is the need to watch the concentration of p,p'-DDT at Egbigbu river (Ayetoro) upper course which was above effect range low (ERL) and heptachlor epoxide at Omi-Eye (Erio) upper and middle courses where the values were above the threshold effect low (TEL) but less than probable effect level (PEL). This implies the concentrations of the two pesticide residues may impact the lives of the benthic organisms negatively if the trend is not checked. It is therefore recommended that regulatory agencies should constantly monitor the sediments to safeguard the organisms feeding on the sediments which apart from being affected negatively by the concentration of the pollutants, can equally bio-accumulate the pollutants and ultimately transfer them to man. Waste management practices should equally be improved upon by government to prevent indiscriminate dumping of refuse/wastes into rivers and thereby save the lives of benthic organisms.

Conflict of Interest: The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgement: The authors deeply appreciate the farmers who allowed their farms to be used for this study and the staff of Department of Chemistry, Federal University of Technology, Akure for their useful pieces of advice and technical assistance during the laboratory work.

Funding: This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

ADEYEMI M.O., OLUSOLA J.A., AKPOBASAH O., ADIDI N.E., SHELLE R.O.D. (2019) Assessment of heavy metals pollution in sediments from Ologe Lagoon, Agbara, Lagos, Nigeria. Journal of Geoscience and Environment Protection, 7(7):61-73. <u>https://doi.org/10</u>. 4236/gep.2019.77006.

AKINYEMI O., AYENI O.A., FAWEYA O., IBRAHEEM A.G. (2013) Statistical Study of Annual and Monthly Rainfall Patterns in Ekiti State, Nigeria, International Journal of Pure and Applied Science & Technology, 15(2):1-7. <u>https://doi.org/10.31901/</u> 24566608.2021/74.1-3.3307

ALGUL F., BEYHAN M. (2020) Concentrations and sources of heavy metals in shallow sediments in Lake Bafa, Turkey. Scientific Reports, 10: 11782. <u>https://doi.org/10:1038/s41598-020-68833-2.</u>

AMADI A.N., EBIEME E.E., MUSA A., OLASEHINDE P.I., UNEVHO C.I., AMEH I.M. (2016) Stream sediment as pollution indicator within Shikira Gold Mining Site, Niger State, North Central Nigeria", Journal of Mining and Geology, 54(2): 119-131. http://repository.futminna.edu.ng:8080/jspui/handle/12 3456789/577

EUROPEAN UNION (EC) (2017) Guideline document on analytical quality control and method validation procedures for pesticides residues and analysis in foods and feeds. Santi/11813/2017, <u>https://ec.europa.</u> <u>eu/food/sites/food/files/plant/docs/pesticidesmriguidel</u> ineswrkdoc2017-11813.pdf

EL-ALFY M.A, HASBALLAH A.F., EL-ZAINY A.M. (2019) Toxicity assessment of heavy metals and organochlorine pesticides in freshwater and marine environments, Rosetta area, Egypt using multiple approaches. Sustainable Environment Research, 29:19. https://doi.org/10.1186/s42834-019-0020-9 HOWARD I.C., OKPARA K.E., TECHATO K. (2021) Toxicity and risk assessments of polycyclic aromatic hydrocarbons in river bed sediments of an Artisanal Crude Oil Refining Area in the Niger Delta, Nigeria, Water, 13: 1-19. https://doi.org/10.3390/w13223295

IVANOVA A., WIBERQ K., AHRENS L., ZUBCOV E., DAHLBERG A. (2021) "Spatial distribution of legacy pesticides in rivers sediment from the Republic of Moldova", Chemosphere, 279: 130923. <u>https://doi.org/10.1016/j.2021.130923</u>

IZE-IYAMU O.K., ASIA I.O., EGWAKHIDE P.A. (2007) "Concentrations of residues from organochlorine pesticides in water and fish from some rivers in Edo State, Nigeria", *International Journal of Physical Sciences*, 2(9): 237–241. ISSN: 1992-1950, <u>https://doi.org/10.5897/IIPS.9000141</u>

KENDZIERSKA H., MATUZSZEWSKA K.L., BURSKA D., JANAS U. (2020) Benthic fluxes of oxygen and nutrients under the influence of macrobenthic fauna on the periphery of intermittent hypoxic zone in the Baltic Sea. Journal of Experimental Marine Biology and Ecology, 530-531,151439. <u>https://doi.org/10.1016/j.</u> j.jembe.2020. 151439

KUMAR B., GAUR R., GOEL G., MISHRA M., PRAKASH D., SINGH S.K., LAL R.B., KUMAR S., SHARMA C.S. (2011) Distribution of Pesticides in Sediments from Municipal drains in Delhi, India, Asian Journal of Scientific Research, 4(3): 271-280. https://doi.org/10.3923ajsr.2011.271.280

LONG E.R., MACDONALD D.D., SMITH S.I. & F. D. CALDER F.D. (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments, Environmental Management, 19(1): 81-97. https://goi.org/10.1007/BF02472006

MCDONALD D.D., INGERSOIL C.G., BERGER T.A. (2000) Development and Evaluation of Concensus-Based Sediment Quality Guidelines for Fresh Water Ecosystems. Archives of Environmental Contamination and Toxicology, 39: 21-31. <u>https://doi.org/10.1007s_002440</u>010075

MAHUGIJA J.A.M., NAMBELA L., MMOCHI A.J. (2017) Level and distribution of pesticide residues in soil and sediments in Eastern Lake Tangayika environs, International Journal Biological and Chemical Sciences, 11(5):2537-2547. https://doi.org/10.4314/ijbcs.v11i5.46

NFON E., COUSINS I.T., BROMAN D. (2008) Biomagnification of organic pollutants in benthic and pelagic marine food chains from Baltic Sea, Science of the Total Environment, 397:190-204. ISSN: 0048-9697 DOI: <u>10.6092/issn.2281-4485/16969</u>

OGBEIBU A.E., OMOIGBERALE M.O., MAXEWELL I. (2014) Using Pollution Load Index and Geoaccumulation Index for the Assessment of Heavy metal Pollution and Sediment Quality of the Benin River, Nigeria, Natural Environment, 2(1):1-9. <u>https://doi.otg/</u> 10.12966/nc.05.01.2014

OKOYA A.O., OGUNFOWOKAN A.O., ASUBIOJO O.I., TORTO N. (2013) Organochlorine pesticide residue in sediments and waters from cocoa producing areas of Ondo State, Southwestern Nigeria. International Scholarly Research Notices., Article ID 131647, 12 pages. https://doi.org/10.1155/2013/131647

ONOYIMA C.C., OKIBE F.G., OGAH E., DALLATU Y.A. (2021) Heavy metal pollution and ecological risk assessment in the sediment of River Kaduna, Nigeria. Journal of Research in Forestry, Wildlife and Environment, 133(4):205-214. ISSN: 2141-1778

OLAFISOYE O.B., SENKALE T.M., OSIBOTE A.O. (2016) Determination of level of pesticides in sediments and water from Lagos lagoon. Journal of Advanced Agricultural Technologies, 3(3): 222-225. <u>https://doi.org/10.18178/joaat.3.3.222-225</u>

OLAWALE F. P., AIYESANMI F. A., ADEKOYA O. A., OLADELE S. J. (2017) Assessment of heavy metal enrichment and level of contamination of floodplain soils in Ondo State, Nigeria. Journal of Geography Environment and Earth Science International, 10 2):1-11. https://doi.org/10.9734/JGEESI/201732278 PEKEY H.(2006) Heavy metal pollution assessment in sediments of the Izmit Bay, Turkey. Environmental Monitoring and Assessment, 123: 219-231. https://doi.org/10.1007/s1066-006-9192-y

SARIA J.A.M. (2016) Health Risk Assessment of Heavy Metals via consumption of contaminated vegetables cultivated at Dar Es Salam and Morogoro Regions in Tanzania. Journal of Multidisplinary Engineering Science Studies, 2(11):1133-1139. ISSN: 2458-925X

SKORBILOWICZ M., SKORBILOWICZ E., GORSKA M. (2018) "The content of Heavy metals in Botton Sediments of Selected City Rivers of Podlaise Province. Journal of Ecological Engineering, 19(4): 197-206. https://doi.org/10.12911/22998993/89650

USEPA UNITED STATE ENVIRONMENTAL PROTECTION AGENCY (2007) Method ID 1699 Pesticides in water, soil, biosolids and tissue by High Resolution Gas Chromatography with High Resolution Mass Spectrometry. 821-R-08-001. <u>http://www.epa.gov/</u><u>waterscience</u>

VESEL O., MOSTEO R., ORMAD M.P., OVELLEIRO J.L. (2013) Sediment quality assessment of two industrialized areas of Spain. International Journal Environmental Research, 7(4):1039-1046. ISSN: 1735-6865

ZANG-YEI H. (2004) Evaluating heavy metal contents in mine composts using four digestion method. Bioresource Technology, 95:53-59. <u>https://doi.org/</u> 10.1016/j.biortech.2004.02.008