ISSN: 0975-833X

Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 8, Issue, 02, pp.26599-26608 February, 2016

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

RESEARCH ARTICLE

ECOLOGICAL RISK ASSESSMENT AND CONTAMINATION LEVELS OF HEAVY METALS AND PESTICIDE RESIDUES IN WATER AND SEDIMENT FROM ONDO COASTAL REGION, NIGERIA

[1,*]Akinnawo Solomon, [1]Olajide Ayodele and [2]Edward Olanipekun

[1]Department of Chemistry, Federal University of Technology, P.M.B 704, Akure, Nigeria
[2]Department of Chemistry, Ekiti State University, P.M.B 5363, Ado-Ekiti, Nigeria

ARTICLE INFO

Article History:
Received 27th November, 2015
Received in revised form
15th December, 2015
Accepted 29th January, 2016
Published online 27th February, 2016

Key words:

Contamination, Pesticide, Heavy metals, Organochlorine, Organophosphorus.

ABSTRACT

Contamination levels of heavy metals and pesticide residues were studied in water and sediment samples from Ondo coastal region of Nigeria. Pesticide residues were extracted from water and sediment and analysis was done using gas chromatography coupled with mass spectrometer. Heavy metals in water and sediment was obtained by digestion, the digestate was analyzed using atomic absorption spectrometer. The result shows that the water and sediment samples is contaminated with levels of organ chlorine and organophosphorous pesticide residues while the sediment is not contaminated with the analyzed heavy metals by using calculated data obtained from enrichment factor, geoaccumulation index, ecological risk code, contamination degree and ecological risk index.

Citation: **Akinnawo Solomon, Olajide Ayodele and Edward Olanipekun, 2016.** "Ecological risk assessment and contamination levels of heavy metals and pesticide residues in water and sediment from Ondo coastal region, Nigeria", *International Journal of Current Research,* 8, (02), 26599-26608.

INTRODUCTION

Heavy metals and pesticides play an important role in the contamination of the aquatic environment as a result of the chemical relationship between heavy metals and pesticides. Pesticides are used extensively in agriculture and horticulture and some of these pesticides contain substantial concentrations of metals. For instance in the recent past, about 10% of the chemicals approved for use as insecticides and fungicides in UK were based on compounds which contain Cu, Hg, Mn, Pb, or Zn. Examples of such pesticides are copper-containing fungicidal sprays such as *Bordeaux mixture* (copper sulphate) and copper oxychloride (1-2). Heavy metal pollution represents an important environmental problem due to the toxic effects of metals, and their invasion in to the food chain leads to serious ecological and health problems. Heavy metals contamination is a major concern because of their toxicity and threat to human life and his environment. Heavy metals in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota which generally exist in low levels in water and attain considerable concentration in sediment and biota (3-6).

Heavy metals are universal environmental pollutants that arise from a variety of industrial, commercial, and domestic activities. Heavy metals are not biodegradable and can lead to accumulation in living organisms, causing various diseases and disorders. It is well known that some metals are harmful to life (7-9). The influence of environmental geochemistry on human health is extremely important above all if some heavy metals, such as lead (Pb), appear to cause ill health through either deficiency or toxicity or both. Soil in urban environment has a direct influence on public health not related directly with production of food. Urban soil acts as a sink for heavy metals and many other pollutants. Sources of heavy metals and other pollutants are related to human activities, such as vehicular emissions, industrial discharges and urban development. Among these sources, a vehicular emission is commonly known to be significant and increasing source of soil pollution in urban environment (10-16). Organochlorine pesticides (OCPs) are synthetic, non-polar, toxic and environmentally persistent dichlorodiphenylethanes, cycodienes or chlorinated benzenes that are used for pest control. Synthetic pesticides were introduced into the Nigerian markets in the 1950s and farmers have been using them for control of weeds; weevils of cotton, beans and cereals; borers of plant stalks and yams; and disease vectors like tsetse flies and mosquitoes. The persistent nature of the OCPs is advantageous for the control of pests

---

**Corresponding author: Akinnawo Solomon,*
[1]Department of Chemistry, Federal University of Technology, P.M.B 704, Akure, Nigeria.

such as termites around buildings (17-18). These compounds are characterised by high persistent, low polarity, low aqueous solubility and high lipid solubility (lipophilicity). They are ecotoxic non-biodegrable and able to bioaccumulate and biomagnify in living organisms. The use of OCPs such as DDT has been outlawed since 1990 in Nigeria. Meeting the minimum requirements of health standards is generally regarded as one of the elements of sustainable agricultural development (19-.20).

The manufacture and use of chlorinated pesticides have been banned or restricted in developed countries. Although these bans and restrictions were enacted during the 1970s and 1980s, some developing countries are still using OCPs for agricultural and public health purposes because of their low cost and versatility in controlling various pests. Again, they are being used in most developing countries, including Nigeria, due to a lack of appropriate regulatory control and management of the production, trade and use of these chemicals (21-24). Organophosphates have been found in sewage sludge in Sweden and Norway with maximum concentrations in the milligrams per kilogram range. Organophosphates were also detected in river water in relatively high concentrations. Wastewater does not seem to be the only source. Organophosphates were also detected in rain and snow from Germany with concentrations up to micrograms per liter. Moreover, there is evidence for global occurrence in the atmosphere. It is thus no surprise that Organophosphates were also detected in soils that had no history of sewage sludge application or irrigation (25-30). The aim of this research is to determine the contamination levels of heavy metals and pesticide residues in the water and sediment in the dynamic aquatic environment of the Ondo coastal area which is subjected to anthropogenic inputs from activities such oil exploitation, transportation, farming practice, domestic and cottage industrial effluents into the water ways in the Ondo coastal area which finally emptied into Atlantic Ocean in the southern part. In the present study, in order to evaluate the levels of sediment contamination, Enrichment factor (EF), index of geoaccumulation (I*geo*), ecological risk index, risk assessment code and contamination degree (C*d*) for each of the metals was calculated.

MATERIALS AND METHODS

Study area

The Ondo coastal area consist of Ilaje and Ese-Odo, it is located on Latitude $5^0$50'N-$6^0$09'N and on Longitude $4^0$45'E-$5^0$05'E, The Ondo coastal area is a deltaic region boarders with the Atlantic Ocean, the Ondo coastal region play a major role in fishing, farming, crude oil exploration and serves as settlement for a large group of people in the region.

Sampling and Pre-treatment of Samples

Sampled were collected from 2 sampling site during the dry and rainy seasons using a GPS, Water samples were collected in a 2L glass bottles, while top (0-15cm) and bottom (15-30cm) sediment samples were collected using a soil hugger. Water and sediment samples were collected during the dry season and rainy season of 2015 from the study area. The sediment samples were air dried for two weeks and pulverized using laboratory mortar and pestle. It was later sieved using a 2 mm mesh size sieve. Extraction of organochlorine and organophosphorous pesticide residues in water and sediment samples was carried out using liquid-liquid extraction and solid-liquid extraction respectively. All chemicals used were of analytical grade.

Liquid-liquid extraction for water samples

The water samples were subjected to liquid-liquid extraction using Method 3510 as described by USEPA (31). 50 mL of dichloromethane was introduced into a separating funnel containing 100mL of the water sample and shaken vigorously for 5 minutes. The sample was allowed to settle for 30 minutes to facilitate effective separation of the organic and aqueous phases. After separation, the organic layer was filtered into a 250 mL volumetric flask through anhydrous sodium sulphate (Na2SO4) that has been prewashed with dichloromethane. The extraction was repeated twice using 50 mL of dichloromethane. The extracts were later combined to make a whole. The extracts were concentrated to 5 mL using a rotary evaporator, during concentration the solvent is exchanged with n-hexane. The level of organochlorine and organophosphorous pesticide residues in the water samples were determined using gas chromatography coupled with Electron capture detector (GC-ECD).

Solid-liquid extraction for sediment samples

The sediment samples were subjected to solid-liquid extraction using Method 3550C as described by USEPA (32). A mixture of 20 g of sediment samples and 20 g of anhydrous sodium sulphate (Na2SO4) was thoroughly mixed with a mixture of acetone and n-hexane (1:1 v/v). The mixture was sonicated for 30 minutes in a high frequency ultrasonic bath at 600C, the organic extract was decanted. The extraction process was repeated twice using 50 mL of a mixture of acetone and n-hexane (1:1 v/v). The extracts were later combined to make a whole. The extracts were concentrated using a rotary evaporator.

Clean up procedure for sediment samples

The sediment samples were subjected to a cleanup process in order to avoid interferences. The extracts from the sediment samples were clean up using a column packed with 2 g of activated silica gel and 2 g of anhydrous sodium sulphate (Na2SO4). Prior to the clean up, the column was conditioned with 20 mL of n-hexane. The extract was introduced into the column and eluted using a mixture of n-hexane and diethyl ether (1:1 v/v).The elute was concentrated to 5 mL using a rotary evaporator, during concentration the solvent is exchanged with n-hexane.

Gas chromatographic conditions

The following instrumentals conditions were maintained. Gas pressure was 60 psi and injector temperature was 220°C, GC column temperature was 190°C, detector temperature was

270°C, the carrier gas was nitrogen (at 30 ml/min), column length 200 cm, id 2 mm, the glass spiral column packed with 1.5% 0V – 17 and 1.95% 0V-210 on chromosorb WHP 80/100 mesh. There were no peaks when solvents and blanks were chromatographed, before the samples were analyzed under the same condition. Known standards, were also chromatographed, the retention time were used to identify the compounds present in the samples.

Heavy metal analysis

One hundred milliliter of water samples were digested using 10 mL of HNO_3, while 1 g of air dried sediment sample was digested using 20 mL of a mixture of HNO_3, HF and $HCLO_4$, (3:2:1) to near dryness. The digest of water and sediment samples was analyzed for heavy metals using an atomic absorption spectrophotometer (AAS BUCK SCIENTIFIC 210).

Assessment of sediment contamination and ecological risks

In this study, 5 different indices were used to assess the degree of heavy metal contamination and ecological risks in the top and bottom sediments of the Ondo coastal area of Nigeria. For the comparison purpose, the concentrations of average shale given by Turekian and Wedepohl (33, 34) have been adopted as the background value for heavy metals in this study. Hakanson potential ecological risk assessment method was used to determine the pollution levels of metals in the sediment. However, naturally occurring heavy metal pollution is in the form of combined pollution. The potential ecological risk index developed by Hakanson is based on the assumption that the sensitivity of the aquatic system depends on its productivity. Hakanson method is the most scientific and comprehensive approach to assessing heavy metal contamination in soils. The method comprises a single contamination coefficient, a comprehensive contamination measure, the toxic response factor for heavy metals, and a potential ecological risk index of an aquatic system through a toxic-response factor for a given substance (35)

Risk assessment code (RAC)

RAC which was originally developed by Perin *et al.*, (36) is widely used in ecological risk assessments of heavy metals in sediments. RAC determines the availability of heavy metals in sediments by applying a scale to the percentage of heavy metals in the exchangeable and carbonate fractions. RAC is defined as:

$$RAC = Exc\% + Carb\%$$

Exc% and Carb% are percentages of metals in exchangeable and carbonate fractions (i.e., acid soluble fractions in the present study). According to RAC values, each sample falls into one of the five tiers: i) $RAC \leq 1\%$ (no risk); ii) $1\% < RAC \leq 10\%$ (low risk); iii) $10\% < RAC \leq 30\%$ (medium risk); iv) $30\% < RAC \leq 50\%$ (high risk); v) $50\% \leq RAC$ (very high risk).

Ecololgical Risk Index (RI)

Ecological risk index (RI) is defined as the summation of the change occurred in metals with respect to background values considering toxicological factor. The mathematical expression of RI can be shown as; $E = T_i \text{ x } C_i / C_0$

$$RI = \sum_{i=1}^{n} \left(T_i \times \frac{C_i}{C_o} \right)$$

Where, n is the number of heavy metals, Ti is the toxic-response factor for a given substance (e.g., Cd = 30, Pb = Ni = Cu = 5, Cr = 2, Zn = 1), C_i represents metal content in soil and C_0 is the regional background value of heavy metals. As the regional background values of measured heavy metals were unavailable, the metal concentrations for the world shale average were chosen as the background value (37).

Enrichment Factor (EF)

Enrichment factor (EF) of an element in the studied samples was based on the standardization of a measured element against a reference element. Fe is the reference metal used in this study. The EF is expressed below as

$$EF = \frac{(Cx/Fe)_{soil}}{(Cx/Fe)_{background}}$$

Where (Cx/Fe)soil is the metal to Fe ratio in the samples of interest, and (Cx/Fe)background is the natural background value of the metal to Fe ratio. In this study, admittedly, as Fe background values for the study area are not available, the average continental shale metal values have been adopted (38). There is no accepted pollution ranking system or categorization of degree of pollution on the enrichment ratio and/factor methodology. The proposed EF classes along with the sediment quality at various values are shown below

Geo-accumulation Index (I*geo*)

The geo-accumulation index (I*geo*) method was used to calculate the metal contamination level. Where, Cx represents the measured concentration of the element x and Bx is the geochemical background value of the element in fossil argillaceous sediment (average shale). The constant 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to litho logic variations in the sediments (38, 39). The classification is given, as shown in Table 4, for geo accumulation index.

$$I_{geo} = \log_2 \left(\frac{C_x}{1.5 B_x} \right)$$

Contamination Factor and Degree of Contamination

The contamination degree is estimated to assess the contamination levels of contaminants in sediment using the concentration of substance and the background value (40)

$$Cd = \sum_{i=1}^{m} Cfi$$

C*d*= contamination degree, C*f*= contamination factor

Cf= *Ce/Cb*, where *Ce* = concentration of the element in sediment samples, *Cb* = background value for the element taken from average shale, m are multiple metals. The following four classes have been used to define the degree of contamination of each creek in the present study. *C*d <8 (low degree of contamination), 8 ≥ Cd < 16 (moderate degree of contamination), 16 ≥ Cd <32 (considerable degree of contamination), Cd ≥ 32 (very high degree of contamination) (41).

The exchangeable and carbonate fraction used in the calculation of the Risk Assessment Code was obtained from report presented by Solomon *et al*., (42). From the result obtained in table 5, the heavy metals from the two sampling sites during the dry and rainy seasons falls in the region of medium risk code, except Zn occurring in the top sediment at site A during the dry season which has a low risk code. This indicates that the sediments collected from the Ondo coastal area does not contain heavy metal at a high risk level. This result agrees with the report on Ecological risk assessment of heavy metals in sediments of Xiawan Port based on modified potential ecological risk index (43).

Table 1. Categorization of Ecological risk index

E_i	Ecological risk of single metal	RI	Ecological risk of all metals
$E_i < 40$	Slightly	$RI < 150$	Slightly
$40 \le E_i < 80$	Moderately	$150 \le RI < 300$	Moderately
$80 \le E_i < 160$	Strongly	$300 \le RI < 600$	Strongly
$160 \le E_i < 320$	very strongly	$600 \le RI$	Very strongly
$320 \le E_i$	Extremely		

Table 2. Categorization of Enrichment Factor

EF value	EF class	Level of enrichment
> 40	6	extremely high enrichment [a]
20-40	5	very high enrichment [a]
5-20	4	significant enrichment [a]
2-5	3	moderate enrichment [a]
1.5-2	2	minimal enrichment [a, b]
0.5-1.5	1	enrichment entirely from crustal materials [b]
< 0.5	0	enrichment from point and non-point sources (E_p) [b]

Table 3. Categorization of Geo-accumulation index

I_{geo} value	I_{geo} class	Designation of soil quality
> 5	6	extremely contaminated
4-5	5	strongly to extremely contaminated
3-4	4	strongly contaminated
2-3	3	moderately to strongly contaminated
1-2	2	moderately contaminated
0-1	1	uncontaminated to moderately contaminated
0	0	Uncontaminated

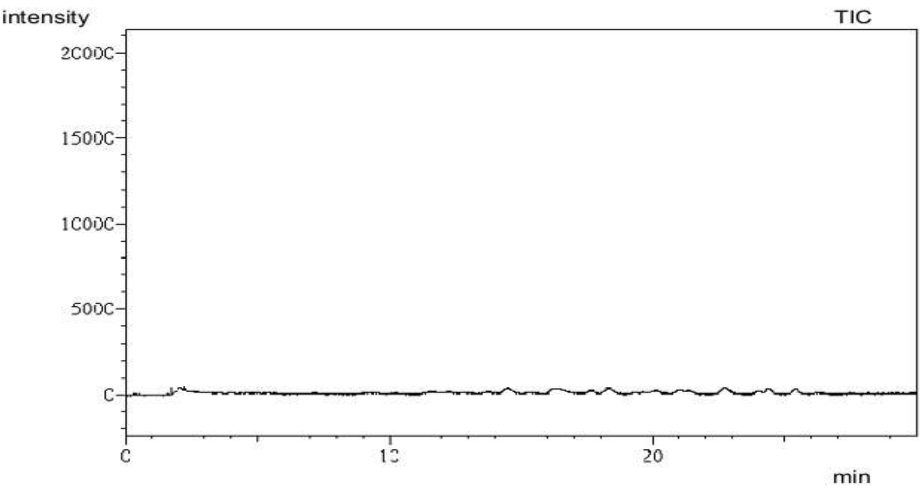


Fig. 1.Chromatogram of the blank solution with no peak for organochlorine or organophosphorous pesticide

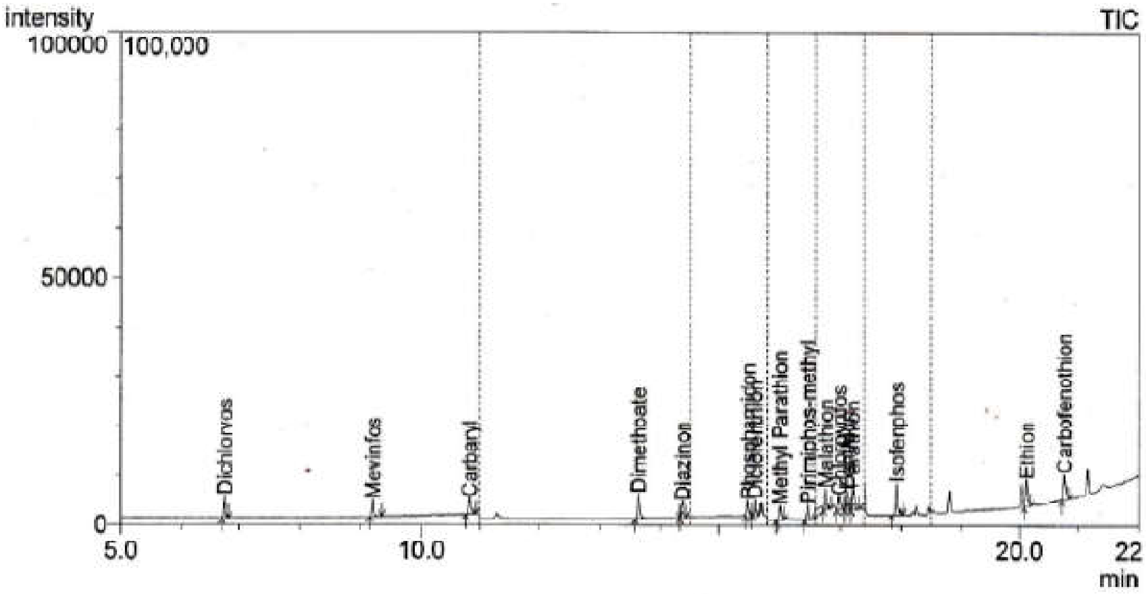


Fig. 2. Chromatogram of the standard used for the analyzed organophosphorous pesticide residues

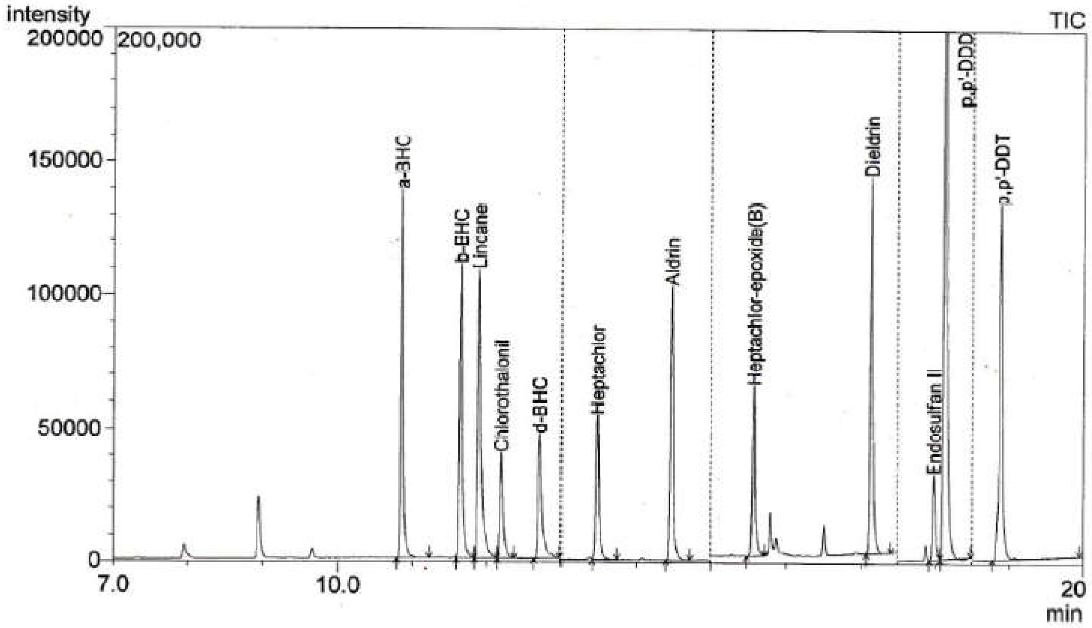


Fig. 3. Chromatogram of standard used for the analyzed organochlorine pesticide residues

Table 4. Organophosphorous and organochlorine and retention times

Organophosphorous	Retention time	Organochlorine	Retention time
Dichloros	6.765	a-BHC	10.851
Mevinfos	9.207	b-BHC	11.645
Carbaryl	10.836	Lindane	11.890
Dimethoate	13.630	Chorothalonil	12.194
Diazinon	14.362	d-BHC	12.709
Phosphamidon	15.479	Heptachlor	13.473
Diclofenthion	15.600	Aldrin	14.469
Methyl Parathion	16.010	Heptachlor-epoxide (B)	15.569
Primiphos-methyl	16.465	Dieldrin	17.135
Malathion	16.755	Endosulfan (II)	17.977
Chlorpyrifos	16.980	p,p'-DDD	18.117
Fenthion	17.111	p,p'-DDT	18.878
Parathion	17.205		
Isofenphos	17.938		
Bromophos-ethyl	18.467		
Ethion	20.124		
Carbofenothion	20.755		

RESULTS AND DISCUSSION

Table 5. Risk Assessment Code (%)

		Site A (dry)	Site A (rainy)	Site B (dry)	Site B (rainy)
Zn	Top	9.47	19.08	11.60	19.25
	Bottom	10.22	20.86	10.26	20.27
Cr	Top	27.09	13.42	24.01	27.22
	Bottom	25.04	28.80	15.78	27.24
Cd	Top	21.21	32.08	26.67	27.96
	Bottom	31.82	28.87	25.72	28.57
Cu	Top	32.39	23.58	16.33	34.86
	Bottom	18.31	21.95	27.40	35.33
Pb	Top	10.81	31.02	15.21	11.73
	Bottom	17.81	27.82	15.07	31.75

Table 6. Geoaccumulation index

		Site A (dry)	Site A (rainy)	Site B (dry)	Site B (rainy)
Zn	Top	-5.04	-4.45	-5.05	-4.42
	Bottom	-4.81	-4.50	-5.09	-4.30
Cr	Top	-4.42	-2.34	-4.54	-2.37
	Bottom	-4.59	-2.27	-4.91	-2.07
Cd	Top	-0.45	1.24	-0.59	1.05
	Bottom	-1.03	1.11	-0.74	1.12
Cu	Top	-6.26	-5.66	-6.11	-5.95
	Bottom	-6.57	-5.78	-6.53	-5.49
Pb	Top	-4.76	-3.80	-4.13	-2.63
	Bottom	-5.36	-3.50	-5.36	-3.83

Table 7. Enrichment factor (EF)

		Site A (dry)	Site A (rainy)	Site B (dry)	Site B (rainy)
Zn	Top	81.80	130	69.68	145.67
	Bottom	96.82	124.02	79.91	123.28
Cr	Top	125.83	564.77	99.04	613.18
	Bottom	112.44	563.40	90.60	575.78
Cd	Top	33500.63	6713.90	1539.47	6549.69
	Bottom	1325.17	5842.78	16307	5276.75
Cu	Top	35.09	56.58	33.53	51.18
	Bottom	28.51	49.39	29.39	53.84
Pb	Top	99.61	205.22	131.63	513.41
	Bottom	65.96	240.34	66.13	170.42

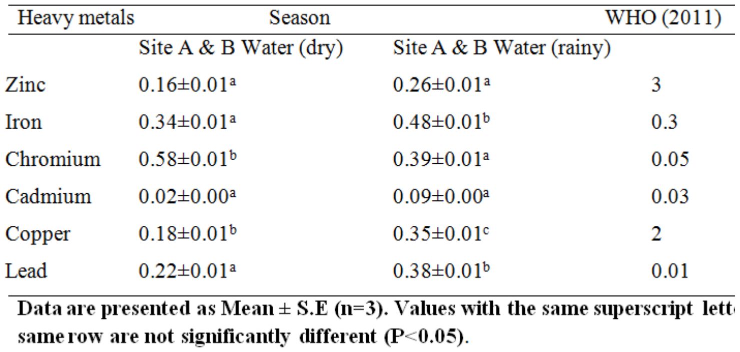
Table 8. Contamination Degree

		Site A (dry)	Site A (rainy)	Site B (dry)	Site B (rainy)
Zn	Top	0.05	0.07	0.05	0.07
	Bottom	0.05	0.07	0.04	0.08
Cr	Top	0.07	0.29	0.06	0.29
	Bottom	0.02	0.31	0.05	0.36
Cd	Top	1.10	3.53	1.00	0.31
	Bottom	0.73	3.23	0.90	3.27
Cu	Top	0.02	0.03	0.02	0.02
	Bottom	0.02	0.03	0.03	0.03
Pb	Top	0.06	0.11	0.09	0.24
	Bottom	0.04	0.13	0.04	0.11

Table 9. Ecological Risk Index

		Site A (dry)	Site A (rainy)	Site B (dry)	Site B (rainy)
Zn	Top	0.05	0.07	0.05	0.07
	Bottom	0.05	0.07	0.04	0.08
Cr	Top	0.14	0.59	0.13	0.56
	Bottom	0.12	0.64	0.10	0.71
Cd	Top	33	106	30	93
	Bottom	22	97	27	98
Cu	Top	0.10	0.15	0.11	0.12
	Bottom	0.08	0.14	0.08	0.17
Pb	Top	0.28	0.54	0.43	1.22
	Bottom	0.18	0.67	0.18	0.53

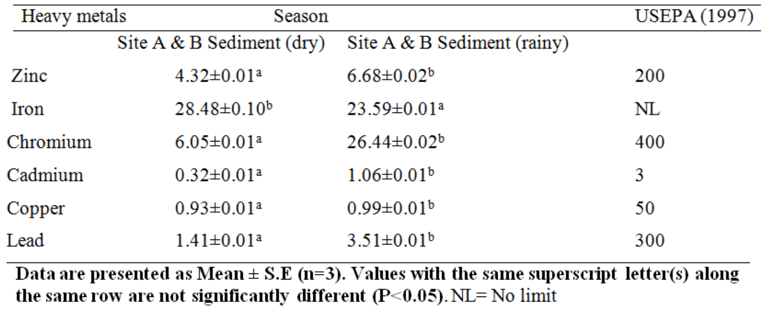
Table 10. Total concentration (mg/L) of heavy metals in water samples



Heavy metals	Season		WHO (2011)
	Site A & B Water (dry)	Site A & B Water (rainy)	
Zinc	0.16±0.01^{a}	0.26±0.01^{a}	3
Iron	0.34±0.01^{a}	0.48±0.01^{b}	0.3
Chromium	0.58±0.01^{b}	0.39±0.01^{a}	0.05
Cadmium	0.02±0.00^{a}	0.09±0.00^{a}	0.03
Copper	0.18±0.01^{b}	0.35±0.01^{c}	2
Lead	0.22±0.01^{a}	0.38±0.01^{b}	0.01

Data are presented as Mean ± S.E (n=3). Values with the same superscript lett
same row are not significantly different (P<0.05).

Table 11. Total concentration (mg/L) of heavy metals in sediment samples



Heavy metals	Season		USEPA (1997)
	Site A & B Sediment (dry)	Site A & B Sediment (rainy)	
Zinc	4.32±0.01^{a}	6.68±0.02^{b}	200
Iron	28.48±0.10^{b}	23.59±0.01^{a}	NL
Chromium	6.05±0.01^{a}	26.44±0.02^{b}	400
Cadmium	0.32±0.01^{a}	1.06±0.01^{b}	3
Copper	0.93±0.01^{a}	0.99±0.01^{b}	50
Lead	1.41±0.01^{a}	3.51±0.01^{b}	300

Data are presented as Mean ± S.E (n=3). Values with the same superscript letter(s) along the same row are not significantly different (P<0.05). NL= No limit

Table 12. Concentration (mg/L) of organophosphorus pesticide residues in water samples

Organophosphorus	Site A (dry)	Site A (rainy)	Site O (dry)	Site O (rainy)
Dichlorvos	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Mevinfos	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Carbaryl	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.27±0.01^{b}
Dimethoate	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Diazinon	0.48±0.00^{b}	0.48±0.00^{b}	1.46±0.01^{c}	0.09±0.00^{a}
Pirimicarb	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Phosphamidon	2.13±0.01^{b}	3.63±0.02^{c}	7.09±0.00^{d}	1.04±0.01^{a}
Dichlofenthion	0.10±0.01^{c}	0.00±0.00^{a}	1.58±0.01^{d}	0.07±0.00^{b}
Methyl parathion	0.48±0.00^{a}	0.54±0.02^{b}	1.34±0.01^{d}	1.05±0.01^{c}
Pirimiphos-methyl	0.77±0.02^{b}	0.38±0.02^{a}	0.92±0.01^{c}	0.35±0.01^{a}
Fenthion	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.22±0.01^{b}
Parathion	0.51±0.01^{b}	0.22±0.00^{a}	0.63±0.02^{c}	0.25±0.01^{a}
Isofenphos	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Bromophos-ethyl	0.70±0.00^{b}	0.92±0.02^{c}	0.00±0.00^{a}	1.98±0.02^{d}
Ethion	0.91±0.00^{c}	4.45±0.02^{d}	0.00±0.00^{a}	0.66±0.00^{b}
Carbofenothion	1.17±0.00^{c}	0.00±0.00^{a}	0.00±0.00^{a}	0.64±0.00^{b}
Malathion	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
TOPP	6.08±0.02^{a}	6.81±0.01^{c}	7.32±0.01^{d}	4.10±0.00^{b}

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same row are not significantly different (P<0.05).

Table 13. Concentration (mg/L) of organophosphorus pesticide residues in water samples

Organophosphorus	Site A (dry)	Site A (rainy)	Site O (dry)	Site O (rainy)
Dichlorvos	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Mevinfos	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Carbaryl	0.00±0.00^{a}	0.27±0.00^{a}	0.00±0.00	0.00±0.00
Dimethoate	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Diazinon	0.97±0.00^{b}	0.29±0.00^{b}	0.54±0.01^{b}	0.14±0.00^{as}
Pirimicarb	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Phosphamidon	4.61±0.01^{b}	2.34±0.02^{c}	0.40±0.00^{b}	1.70±0.02^{d}
Dichlofenthion	0.84±0.01^{c}	0.07±0.00^{a}	0.30±0.01^{c}	0.10±0.01^{b}
Methyl parathion	0.91±0.00^{a}	0.79±0.02^{b}	0.51±0.01^{d}	0.31±0.01^{b}
Pirimiphos-methyl	0.85±0.02^{b}	0.35±0.02^{a}	0.43±0.01^{c}	0.14±0.01^{b}
Fenthion	0.00±0.00^{a}	0.22±0.01^{b}	0.00±0.00	0.00±0.00
Parathion	0.56±0.01^{b}	0.24±0.00^{a}	0.26±0.01^{b}	0.54±0.02^{c}
Isofenphos	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Bromophos-ethyl	0.70±0.00^{b}	0.92±0.02^{c}	0.00±0.00	0.00±0.00
Ethion	0.91±0.00^{c}	2.61±0.02^{d}	0.00±0.00	0.00±0.00
Carbofenothion	1.17±0.00^{c}	0.64±0.00^{b}	0.00±0.00	0.00±0.00
Malathion	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
TOPP	6.66±0.02^{a}	5.46±0.01^{c}	2.10±0.01^{b}	1.63±0.01^{c}

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same row are not significantly different (P<0.05).TOPP= total organophosphorous pesticide

The result obtained from table 6, shows that Zn, Cr, Cu and Pb fall in the I*geo* class of 0, as most of the values were less than 0. This indicates that the top and bottom sediment samples collected during the dry and rainy seasons were not contaminated with Zn, Cr, Cu and Pb. While Cd in the top and bottom sediment during the dry and rainy seasons falls in the I*geo* class of 1, which means the sediment is free from Cd contamination. This result indicates that the sediment collected from the Ondo coastal area in Nigeria is not contaminated with the analyzed heavy metals. The geoaccumulation result of this study agrees with the report on integrated assessment of heavy metal pollution in the surface Sediments of the Laizhou Bay and the coastal waters of the Zhangzi Island (44). From the result obtained from Table 7, all the heavy metals analyzed from the two sampling sites during the dry and rainy seasons have EF class of 6. This indicates that the top and bottom sediment samples collected from Ondo coastal area in Nigeria during the dry and rainy seasons have an extremely high enriched with the analyzed heavy metals. The result on the enrichment factor of the analyzed heavy metals agrees with the report on assessment of heavy metal contamination in incinerated medical waste (45).

Table 8 shows that the values of the contamination degree of the analyzed heavy metals in the top and bottom sediment falls below 7, this indicate that the analyzed heavy metals in the top and bottom sediment during the dry and rainy seasons have a low degree of contamination. This result agrees with the report on Assessment of heavy metal contamination of agricultural soil around Dhaka export processing zone (DEPZ), Bangladesh: Implication of seasonal variation and indices (46). From Table 9 above the result shows that Zn, Cr, Cu and Pb in the top and bottom sediment samples were at low ecological risk of water body pollution while Cd in the top and bottom sediment was at low to strongly ecological risk of water body pollution. This result indicate that the top and bottom sediment samples collected during the dry and rainy seasons were not strongly or extremely polluted with the analyzed heavy metals. This result agrees with the report on Pollution and Potential Ecological Risk Assessment of Heavy Metals in a Lake (47). The concentration of heavy metals in water samples varies during the dry and rainy seasons, it was observed that the concentration of Zn and Cu were below the maximum permissible limit for drinking water (WHO Standards), while Fe, Cr, Cd and Pb were above the WHO standard for drinking water (48).

The concentration of heavy metals in the sediment varies during the dry and rainy season. Zn, Cr, Cd, Cu and Pb have a higher concentration during the rainy season, while Fe has a lower concentration during the rainy season when compared to the dry season. The concentrations of the analyzed heavy metals were lower than the maximum permissible limit (USEPA Standards) (49-50). From the analyzed organophosphorus pesticide residues, Diazinon, Phosphamidon, Dichlofenthion, methyl parathion, Pirimiphos- methyl, parathion, Bromophos-ethly, Ethion, and Carbofenothion were detected in the water and sediment samples at various concentrations during dry and rainy seasons. The TOPP was higher in the dry season when compared to the rainy season for both water and sediment samples, this variation can be attributed to the dilution factor as a result of the heavy rainfall during the rainy season which leads to an increase in the volume of water in the river at the sampling site which is far from the point source pesticide application area in the farmlands, dilution factor plays a major in the seasonal variation of the concentration of pesticide residue in surface water when comparing the dry and wet seasons (51,52). The TOPP exceeded the 0.5µg/L of the WHO standard for drinking water.

From the results of organochlorine pesticide residue analyzed in water samples from Ondo coastal area of Nigeria, it was observed that organochlorine pesticide residues were not detected (N.D) in the water samples, this shows that the water may be free from organochlorine pesticide contamination. The sediment samples collected during the dry season were contaminated to some degree with Lindane in the range of 0.303-0.344 µg/g, while the sediment samples collected during the rainy season were free from organochlorine pesticide residues. The sediment samples collected during the dry season has the highest degree of organochlorine pesticide contamination in the following order Lindane (0.217 - 0.391 µg/g) Endosulfan II (0.176 µg/g) Dieldrin (0.103 µg/g). While Alpha BHC, beta BHC, Chlorothalonil, Delta Lindane, Heptachlor-expoxide, pp'-DDD, PCB-153, pp'-DDT, Endosulfan-sulphate, d-BHC and Aldrin were not detected in the water and sediment samples from the 2 sites. Although the water samples are free from organochlorine pesticide contamination but could be later contaminated by organochlorine pesticide residues due to water runoff or leaching as a result of the bioaccumulation of organochlorine pesticide residue in the sediment of some of the sampling sites

Conclusion

The result shows that the water and sediment samples collected for analysis is contaminated with organophosphorus and organochlorine pesticide residues. Zn and Cu were below the maximum permissible limit in the water sample while the other metals exceed the maximum permissible limit in the water samples. From the calculation using enrichment factor, geoaccumulation index, contamination degree, ecological risk index and risk assessment code shows that the sediment is not contaminated with the analyzed heavy metals.

REFERENCES

1. Raymond A.W., Okieimen F.E. Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. Hindawi., 2011;20 http://dx.doi.org/10.5402/2011/402647
2. Jones L.H, Jarvis S.C, fate of heavy metals," in the Chemistry of Soil Processes, D. J. Green and M. H. B. Hayes, Eds., p. 593, John Wiley & Sons, New York, NY, USA;1981.
3. Dilna D, Gummadi S, Raj M. Bioremediation of Soil by removing heavy metals using Saccharomyces cerevisiae. 2011 2nd International Conference on Environmental Science and Technology IPCBEE vol.6 (ACSIT Press, Singapore; 2011

4. Malami, D.I, Zakaria, Z.I, Mohammed M.I, Audu A.A. Coparison of the levels of some metals in the water and sediment from Challawa Gorge Dam, Kano, Nigeria. Bayero Journal of Pure and Applied Sciences, 2014;7(1):80–84. http://dx.doi.org/10.4314/bajopas.v7i1.15 ISSN 2006 – 6996
5. Camusso, M.V, Baitstrini L.R. Bioaccumulation of Trace Metals in rainbow trout, *Ecotox. Environ. safe*., 1995;31:133-141.
6. Namming, H.N, Wilhm J. Effects of high discharge and oil refinery cleanup Operation, Heavy Metals in Water and Sediments in skeleton creek. Proceedings of the Oklahoma *Academy of Science*, 1976;56: 133-138.
7. Aslam M, Malik M, Baig M, Qazi A, Iqbal J. Treatment performances of compost-based and gravelbased vertical flow wetlands operated identically for refinery wastewater treatment in Pakistan. *Ecol. Eng*., 2007;30: 34–42.
8. Renge V.C, Khedkar S.V, Pande S.V. Removal of heavy metals from wastewater using low Cost adsorbents: a review. *Sci. Revs. Chem. Commun*., 2012;2(4):580-584 ISSN 2277-2669
9. Akinnawo S, Abiola C, Olanipekun E. Seasonal variation in the physicochemical and microbial characterization of sediment and water samples from selected areas in Ondo coastal region, Nigeria. *Journal of Geography, Environment and Earth Science International*, 2016;5(1):1-12, ISSN: 2454-7352 DOI: 10.9734/JGEESI/2016/22413 www.sciencedomain.org (in press)
10. Ilaria G.A, Gabriele B.B, Domenico C.A, Rosanna D.C. Assessment of lead contamination in urban soils in an area of southern Italy. 19th World Congress of Soil Science, Symposium 3.5.1 Heavy metal contaminated soils Soil Solutions for a Changing World, Brisbane, Australia; 2010
11. Oliver M.A. Soil and human health. *European Journal of Soil Science*, 1997;48, 573-592.
12. Rossini O.S, Fernandez A.J. Monitoring of heavy metals in top soils, atmospheric particles and plant leaves to identify possible contamination sources. *Microchemical Journal*, 2007;86, 131-139.
13. Madrid L, Diaz-Barrientos E, Madrid F. Distribution of heavy metal contents of urban soils in parks of Seville. Chemosphere. 2002;49, 1301-1308.
14. Biasioli M, Barberis R, Ajmone-Marsan F. The influence of a large city on some soil properties and metals content. *Science of the Total Environment*, 2006;356, 154-164.
15. Lee C, Li X, Shi W, Cheung S, Thornton I. Metal contamination in urban, suburban and country park soils of Hong Kong: A study based on GIS and multivariate statistics. *Science of the Total Environment*, 2005;356, 45-61
16. Wong CSC, Li XD, Thornton I. Urban environmental geochemistry of trace metals. Environmental Pollution. 2006;142, 1-16.
17. Adeyeye, A, Osibanjo O. Residues of organochlorine pesticides in fruits, vegetables and tubers from Nigerian markets. Sci. Total Env. 1990;231:227-333.
18. Ogunfowokan O, Oyekunle J, Torto N, Akanni S. A study on persistent organochlorine pesticide residues in fish tissues and water from an agricultural fish pond. *Emir. J. Food Agric*., 2012;24 (2): 165-184 http://ejfa.info/
19. Afful, S, Arim K, Sertor-Armah Y. Spectrum of organochlorine pesticide residues in fish samples from Dense basin. *Research Journal of Environmental Earth Sciences,* 2010;2(3), 133-138.
20. Olayinka A.I, Ademola F.A, Emmanuel I.A, Albert O.A. Persistent Organochlorine Pesticide Residues in Water, Sediments and Fish Samples from Ogbese River. *Environment and Natural Resources Research*, 2015; 5:3 ISSN 1927-0488 E-ISSN 1927-0496
21. Darko G, Acquaah O. Levels of organochlorine pesticides residues in meat. *Int. J. Environ. Sci. Technol*., 2007;4: 521-524.
22. Xue N, Zhang D, Xu X. Organochlorinated pesticide multiresi-dues in surface sediments from Beijing, Guanting reservoir. Water Res. 2006; 40: 183-194.
23. Ize-Iyamu O.K, Asia I.O, Egwakhide P.A. Concentrations of residues from organochlorine pesticide in water and fish from some rivers in Edo State Nigeria. *Int. J. Phys. Sci*., 2007;2(9):237-241.
24. Akan B.W. Residue analysis of organochlorine pesticides in water and sediments from Agboyi Creek, Lagos. African *Journal of Environmental Science and Technology*, 2013;7:267-273 Doi:10.5897/AJEST12.214 ISSN 1996-0786
25. Marklund A, Andersson B, Haglund P. Organophosphorus flame retardants and plasticizers in Swedish Sewage Treatment Plants. Environ Sci Technol 2005;39:7423–7429
26. Thomas K, Langford K, Muthanna T, Schlabach M, Borgen A, Ghebremeskel et al. Occurrence of selected organic micropollutants and silver at wastewater treatment plants in Norway. NIVA report no. 2011;6157–2011.
27. Regnery J, Püttmann W. Organophosphorus flame retardants and plasticizers in rain and snow from Middle Germany. Clean. 2009;37(4–5):334–342
28. Andresen J, Grundmann A, Bester K. Organophosphorus flame retardants and plasticisers in surface waters. *Sci Total Environ*., 2004; 332:155–166
29. Mihajlovic I, Miloradov V, Fries E. Application of Twisselmann extraction, SPME, and GC-MS to assess input sources for organophosphate esters into Soil. *Environ Sci Technol*., 2011;45:2264–2269
30. Möller A, Sturm R, Xie Z, Cai M, He J, Ebinghaus R. Organophosphorus flame retardants and plasticizers in air borne particles over the Northern Pacific and Indian Ocean toward the Polar Regions: Evidence for global occurrence. *Environ Sci Technol*., 2012. doi:10.1021/es204272v
32. US Environmental Protection Agency (USEPA). Method 3510, Revision C, Washington DC: USEPA; 2007.
32. US Environmental Protection Agency (USEPA). SW-847 Test methods for evaluating solids waste. 3rd ed. Washington DC: USEPA; 2000.
33. Turekian K. K, Wedepohl K. H. Distribution of the elements in some major units of the earth’s crust. *Bulletin of Geological Society of America*, 1961;72: 175-192.
34. Lina F, Nayak G, Ilangovan D. Geochemical Assessment of Metal Concentrations in Mangrove Sediments along Mumbai Coast, India. *International Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering*, 2012;6(1). waset.org/Publication /180

35. Hakanson L. An ecological risk index for aquatic pollution-control—A sedimentological approach. Water Res. 1980; 14:975–1001.
36. Perin G, Craboledda L, Cirillo M, Dotta L, Zanette ML et al., Heavy metal speciation in the sediments of Northern Adriatic Sea: a new approach for environmental toxicity determination. In: Lekkas TD, editor. Heavy Metal in the Environment. CEP Consultant, Edinburgh. 1985;2:454–456.
37. Jing L. Risk Assessment of Heavy Metals in Surface Sediments from the Yanghe River, China. Int. J. Environ. Res. Public Health. 2014;11:12441-12453; doi:10.3390/ijerph111212441
38. Nastja S., Vrho T. Dolenec T. Serafimovski G, Dolenec M. Assessment of the heavy metal contamination in the surficial sediments of Lake Kalimanci (Macedonia): a preliminary study. *RMZ – Materials and Geoenvironment*. 2009;56(4):437–447
39. Krzysztof L, Jan C, Jacek P, Danuta W, Jerzy K. Use of enrichment, and contamination factors together with geo accumulation indexes to evaluate the content of Cd, Cu, and Ni in the Rybnik water reservoir in Poland. Water, Air and Soil Pollution. 1997;93(1–4):347–365.
40. Abrahim S, Parke R. Environ. Monit. Assess, 2008; 136(1):227.
41. Jinman W, Weihong L, Ruixuan Y, Ling Z, Jianjun M. Assessment of the potential ecological risk of heavy metals in reclaimed soil at an opencast coal mine. Disaster Advances. 2013; 6:366-377
42. Akinnawo S, Kolawole R, Olanipekun E. Spatial Distribution and Speciation of Heavy Metals in Sediment of River Ilaje, Nigeria. IRJPAC. 2015; 10(2): 1-10, Article no.IRJPAC. 22031. ISSN: 2231-3443, NLM ID: 101647669. www.sciencedomain.org
43. Zhu H, Yuan X, Zeng G, Jiang M, Liang J, Chang et al., Ecological risk assessment of heavy metals in sediments of Xiawan Port based on modified potential ecological risk index. Trans. Nonferrous Met. Soc. China. 2012; 2:1470 1477. Elsevier. www.sciencdirect.com
44. Zhuang W, Gao X. Integrated Assessment of Heavy Metal Pollution in the Surface Sediments of the Laizhou Bay and the Coastal Waters of the Zhangzi Island, China: Comparison among Typical Marine Sediment Quality Indices. PLoS ONE. 2014;9(4): e94145. doi:10.1371/journal.pone.0094145
45. Tanjim S, Sourav R, Kabir M, Purkayastha T. Assessment of Heavy Metal Contamination in Incinerated Medical Waste. *ARPN Journal of Science and Technology*, 2012;2;10(904-911). ISSN 2225-7217
46. Syed H, Dilara K, Tanveer M, Mohammad S, Mohammad A and Mohammad A. Assessment of Heavy Metal Contamination of Agricultural Soil around Dhaka Export Processing Zone (DEPZ), Bangladesh:Implication of Seasonal Variation and Indices. Appl.Sci. 2012;2:584-601 doi:10.3390/app2030584 ISSN:2076-3417www.mdpi.com/journal/applsci
47. Theoneste N, Gang D, Jing-song G, Xu G, Lei H. Pollution and Potential Ecological Risk Assessment of Heavy Metals in a Lake. *Pol. J. Environ. Stud.*, 2013;22(4):1129-1134
48. World Health Organization. Drinking water standards and health advisories office of water. U.S Environmental Protection Agency Washington, D.C; 2011
49. USEPA (US Environmental Protection Agency). Exposure Factor Handbook, Volume II- Food ingestion Factors. EPA/600/P-95/002Fa. Office of Research and Development. Washington, DC, USA; 1997
50. Chipo M, Loveness M, Stenly M, Revai M. Assessment of heavy metal accumulation in wastewater irrigated soil and uptake by maize plants (Zea Mays L) at Firle Farm in Harare. *Journal of Sustainable Development*, 2011;4(6):132-137. www.ccsenet.org/jsddoi:10.5539/jsd.v4n6p132
51. Ismail B.S, Siti H.H, Mohd T.F. Pesticide residue levels in the surface water of the irrigation canals in the Muda Irrigation Scheme Kedah, Malaysia. IJBAS-IJENS. 2012;12(6):85-89
52. Aaron D, Stephen L, Zoe B, Jon B, Evan S. Pesticide Residues in waterways of the lower Burdekin Region: Challenges in ecotoxicological interpretation of monitoring data. *Australasian Journal of Ecotoxicology*, 2008;14:89-108.

****