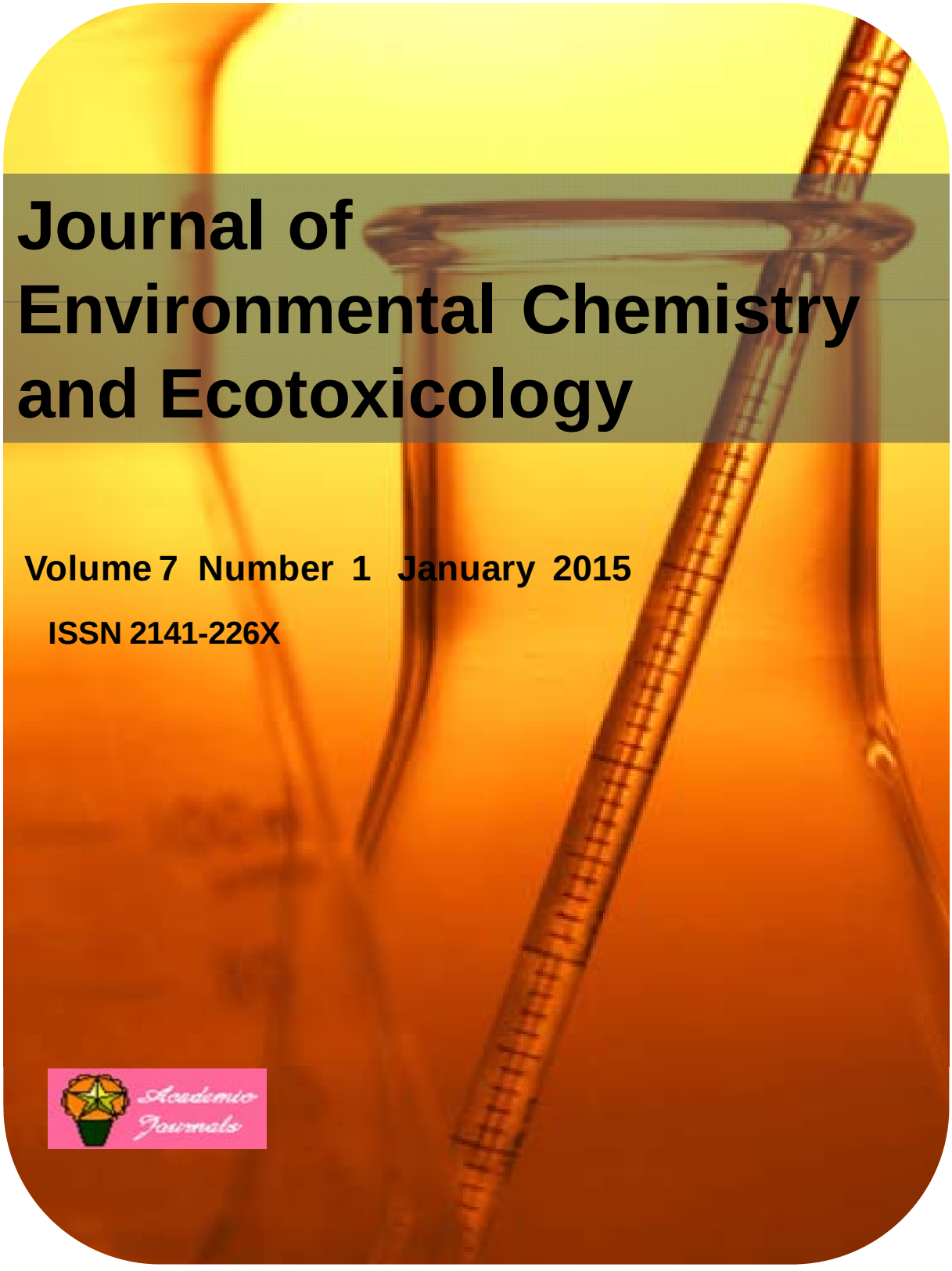

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Full Length Research Paper

Nondestructive analysis of dumpsite soil and vegetable for elemental composition

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In this study, dumpsite soils and vegetables were analyzed for total elemental composition using a 5SDH Tandem Pelletron accelerator available at Centre for Energy Research and Development, Obafemi Awolowo University Ile-Ife. The results at a 2.5 MeV energy revealed the presence of elements: Cu, Cr, Ni,Al, Si, P, S,Cl, K, Ca, Ti, Mn, Fe, Zn, Rb, Sr, Y, Zr and Pb in the dump site soil, with the exception of Cu, Cr,Ni, Zr and Y; other elements with Mg in addition were found in the vegetables around the dump site soil, majority of the elements were at lesser concentrations. However, there was a sharp difference in the concentrations of Mg, Ca and K being present at higher concentrations in the vegetables than in the soil. The result showed no significant difference in the concentration of elements analyzed on each site with the control site, both in the vegetable and the soil samples at 95 and 99% confidence interval. The analysis of variance (ANOVA) for the soil and vegetable samples also confirmed no significant differences. The relationship among the sites was determined in either direction (positive and negative, 2-tailed analysis) using correlation coefficient, the R^2 values among sites were all above 0.5 in vegetable and > 0.9 in the dumpsite soil, showing that all sites were well related depicting common components. Fe, Zn and Pb were within the range of concentration of metals in plant but were higher than the permissible limit of International Organization (WHO/FAO, 2007; EU, 2006). High concentrations coupled with high standard deviation values of some elements suggest influence of anthropogenic activities.

Key words: Dumpsite soil, vegetable, elemental composition, PIXE.

INTRODUCTION

Open dump disposal system of waste has been on for a long time in developing countries with its associated risk. The increase in urbanization and industrialization increases waste generation at homes, in industries and market places with little consideration of its impact on environmental health. Since waste sorting and separation are uncommonly practiced, anything that has lost its value is deposited at dump sites, from home, municipal and small scale workshops (Odia et al., 2008). The constituents of these wastes include scraps from mechanic workshops, household materials such as, papers, food wastes and many more. Open dump site is believed to be rich in organic fertilizer as a result of decayed and composted organic materials that enrich soil

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fertility (Ogunyemi et al., 2003). The random deposition of these wastes, consequently leads to adjacent lands getting enriched in elemental composition and salts of such wastes (Lawan et al., 2012). Studies on municipal waste have shown that heavy metals concentration ranges were high and that waste sites can accumulate heavy metals in the soil at toxic level hence the risk of vegetable grown in the areas getting contaminated with heavy metals and consequently endangering the human health (Purves, 1973; Carlson, 1976).

Amaranthus *spinosus is* a common vegetable that grows naturally on soil but appears leafy and greenish on and around dumpsite. Grubben and Denton (2004) considered it as valued food in Africa. Due to the greenish and leafy nature of the vegetable (Amaranthus *spinosus*) around the dump site, many people living below poverty line collect this vegetable for food and sales for economic gain with or without the full implications on the people's health.

Particle-induced X-ray emission or proton-induced X-ray (PIXE) is a technique used in determining elemental make-up of a material or sample. It is based on the ionization of the sample atoms by the incidence of a particle beam; when a material is exposed to an ion beam, atomic interactions occur that give off electromagnetic radiation that is characteristic of the elements present in the sample (Joansson et al., 1970). It analyzes solids down to 10^{-4} g and 1 ml of liquids. It is multi elemental and analyzes elements in samples simultaneously. It is a routine analytical technique employed by chemists, physicists, geologists, archaeologists and art conservators. Vegetables (especially *Amaranthus spinosus*) consumed in many areas within Ile-Ife metropolis have their sources attached to dumpsites, hence the need to identify the major heavy metals present at various dumpsites, ascertain their levels of concentration in vegetables which could have resulted from the up-take from the soil and to know the contamination level and health risk of direct consumption of vegetables grown on these dumpsites.

MATERIALS AND METHODS

Collection of samples and pre-treatment

Soil and vegetable samples were collected from three different major dumpsites around Ile-Ife and the fourth one that serves as the control site was not a dump site. Each site was divided into four parts, soil samples were taken to a depth of 0 to 20 cm soil level from each quadrant, and vegetables were also collected likewise. Soil and vegetable samples from each quadrant were mixed together to form composite samples that adequately represent each site. This was so because wastes were concentrated on some part than the others. The vegetable samples were rinsed separately with water to remove dust and sand particles and later rinsed with distilled water. The rinsed vegetable and the soil samples were air dried for several days in an aerated cupboard to prevent cross contamination. The air-dried soil and vegetable samples were oven dried for 2 to3 min at 103 to105°C to remove moisture content until constant weight was achieved. Triplicate analyses were carried out on the samples, and the mean value taken as the concentration per site. The grid location of the sample sites is shown in Table 1. The Google Earth search (Figure 1) was used to locate the grid of the sampling site.

Table 1. The grid location of the sample sites.

Sites	Latitude (N)	Longitude (E)
A	7°30'07.14"N	4°33'10.91"E
B	7°29'58.11"N	4°33'17.64"E
C	7°29'52.87"N	4°32'31.11"E
D**	7°29'44.40"N	4°33'08.70"E

Samples preparation and methods

The dried samples were ground in agate mortar and mixed with 10% by weight of ultra pure graphite powder and prepared into thick pellets of 11 mm diameter without binder.

The PIXE experiments were performed using 2.5 MeV proton beam obtained from CERD ion beam analysis (IBA) facility. The facility is centered on a NEC 5SDH 1.7 MV Pelletron Accelerator, equipped with a radiofrequency charge exchange ion source. The end-station consists of an Aluminium chamber of about 150 cm diameter and 180cm height. It has four ports and a window. Port 1 at 165° is for the RBS detector, port 2 at 135° is for PIXE detector, port 3 at 30° is for the ERDA detector, the window at 0° is for observing the beam position and the size, while port 4 at 270° is for PIGE. The chamber has a turbo pump and a variable beam collimator to regulate beam size, and an isolation value. The measurements were carried out with a beam spot of 4mm in diameter and a low beam current of 3 to 6 nA, depositing a charge of 0.5 µC on target. The irradiation was for 10 to 20 m, a Canberra Si(Li) detector Model ESLX 30-150, beryllium thickness of 25µm, with full width half maximum (FWHW) of 150 eV at 5.9 keV, with the associated pulse processing electronics, and a Canberra Genie 2000(3.1) MCA card interfaced to a PC were used for the X- rays data acquisition. With respect to the beam director, the sample's normal was located at 0° and the Si(LI) detector at 45°.

Analytical validation

The PIXE set-up was calibrated using some pure element standards and the National Institute of Standards and Technology (NIST) geological standard, NBS278. The accuracy of the method was studied by analyzing the Certified Reference Material. Apple Leaves (NIST 1515) and (IAEA- SOIL7) were used for the determination of the H- value which was subsequently used for analyzing the soil and vegetable samples and to assure the accuracy of the experimental procedure (Tables 2 and 3).

Statistical analysis

Statistical Package for the Social Sciences (SPSS, version 16.0, Inc., Chicago, USA) was used for data analysis. The significant differences between groups were compared using analysis of independent t-test and analysis of variance at probability level of 95 and 99% confidence level. Correlation coefficient was performed on the data to test the relationship among the elements and factor analysis was carried out to classify the element into groups for possible identification of its sources.

Figure 1. Imagery of the sampling site. Source: Google Earth Search.

Table 2. The result of the analysis of Apple leaves (NIST 1515).

Z	Symbol	Observed values	Certified values
12	Mg (%)	2.72± 0.07	0.271 ±0.008
13	Al (ppm)	286.6 ±23.53	286±9
14	Si (ppm)	214.0±21.23	-
15	P (%)	0.150± 0.020.	0.159±0.011%
16	S (%)	0. 18±0.007%	0.18%
17	Cl (ppm)	757.4±41.88	579±23 ppm
19	K (%)	0.161±0.004	1.61±0.02
20	Ca (%)	1.526±0.006	1.526±0.015%
22	Ti (ppm)	25.9 ±6.74	-
25	Mn (ppm)	36.7 ±3.19	54±3
26	Fe (ppm)	87.8 ±3.60	83±5
30	Zn (ppm)	13.5±2.33	12.5±0.3
37	Rb (ppm)	10.5±9.13	10.2±1.5
82	Pb (ppm)	616.0 ±65.11	-

RESULTS AND DISCUSSION

Tables 2 and 3 showed the result of the method validation for sample analysis, the observed values were comparable with the expected values and adjudged good for precision and accuracy of the work. Tables 4 and 5 were the mean and standard deviation of the elements analyzed, the result showed no significant difference in the concentration of elements analyzed both in the vegetable and the soil samples at 95 and 99% confidence interval. The analysis of variance both for the soil and vegetables samples also confirmed no significant differences. The relationship among the sites was determined in either direction (positive and negative,

Table 3. Result of analysis of soil reference material, International Atomic Energy Agency (IAEA-SOIL7).

Element	Observe value (ppm)	Certified/Expected value (ppm)
Mg	9247.2	9040
Al	37564.8	37600
Si	143791.3	144000
Cl	88.7	-
K	9687.5	9680
Ca	130744	130400
Ti	2409.7	2400
Cr	63.0	48
Mn	512.6	504.8
Fe	20591.6	20560
Ni	25.2	20.8
Zn	79.8	83.8
As	13.6	10.72
Rb	42.2	40.8
Sr	90.0	86.4
Y	17.5	16.8
Zr	149.5	148
Pb	49.5	48

2-tailed) using correlation coefficient, the r-values among sites were all above 0.5 in vegetable and >0.9 in the dumpsite soil, showing that all the sites were well related. Fe, Zn and Pb were within the range of concentration of metals in plants as stipulated in Opaluwa et al. (2012); but were higher than the permissible limit of Standard organizations as stipulated by the WHO/FAO (2007) and EU (2006).

High concentrations coupled with high standard deviation values of some elements suggest influence of anthropogenic activities (Manta, 2012). This showed that the control soil site in this study probably bear some imprint of anthropogenic activities or occurrence of diffuse pollution and do not reflect purely natural conditions. Dhrubajyoti et al. (2011) carried out similar work on municipal waste soil with EDXRF and similar pattern was observed. Mineral elements such as Fe, Ca, K were higher than other elements (Cr, Mn, Ni, Cu, Zn, Rb, Sr, Zr, and Pb) analyzed. However, the work of Opaluwa et al. (2012) carried out on dumpsite soil of Nassarawa State Nigeria, using AAS showed relatively low concentration compared with this work. Considering the concentration of elements in unpolluted soil of Italy (Palumbo et al., 2000) and calculation based on world scale range (Fergusson, 1990) shown in Table 5, all the soil sites were polluted except site A that was not polluted with Cu.

Multivariate statistical procedures were used to identify the pattern in the data sets of these elements in the soil and the vegetable found on them. Cluster analysis of the vegetable data gave two groups with three distinct clusters (Figure 2) which was complemented by principal component analysis (Figure 3) (all loading taken into consideration), with three components extracted for distribution of the elements and possible interpretation in relation to the sources of the elements in the vegetable. Factor I consisting of Al, Si, Ti, Zn, S and Ca (cluster I) contributed 9.097 with 60.65% variance, these are likely to be from soil natural materials.

Factor II associated with factor III and made of P, Cl, Rb and Sr (cluster II) with contribution of 3.692 and 24.616% variance, these elements could possibly be from the waste dumped on the soil and picked by vegetables. Factor III contributed 2.210 with 14.734% variance and was loaded mainly with Mn and Rb with Mg, K having a low positive loading value. Fe and Pb were negative meaning that they were not fulfilling same mission with Mn, Rb, Mg and K that has positive value in factor III but were in the same cluster, therefore, Pb and Fe are likely to be from the waste because of their positive values in factor II. These elements with positive component values (Mn, Mg and K) in factor III that clustered with Pb and Fe in the cluster III were majorly mineral elements. The vegetable is likely to derive these nutrients from the wastes and formed its mineral components. This is likely to have accounted for the association of cluster II and III; they were likely from the same source.

The principal component graph of factor I and II which are the main contributor showed clearly that the elements are from the lithogenic waste (upper part), mineral constituents of the vegetable (lower Part) taken from the

Table 4. Concentration of elements in the vegetables from different sites (mg/kg) and values from Opaluwa et al. (2012).

Elements	WHO/FAO	NAFDAC	EU	NR in plant	A		B		C		D	
					Mean	SD	Mean	SD	Mean	SD	Mean	SD
Mg				*2000	10703.50	240.00	13610.00	4910.00	18916.00	2560.00	8436.00	1270.00
Al				-	446.00	4.50	586.00	76.00	799.00	108.70	5050.00	4530.00
Si				-	518.75	37.65	629.00	144.00	778.00	169.90	5560.00	15.00
P					5447.65	1291.35	5468.80	1215.00	4230.00	727.00	2650.00	2020.00
S				*2000	4848.20	475.60	3719.55	113.00	3683.00	160.00	5660.00	0.00
Cl				*1000	6376.20	0.00	6877.90	1259.00	5640.00	6.00	5160.00	10.00
K				*100	46053.40	591.45	71193.00	17612.50	101568.00	4030.00	29930.00	23970.00
Ca				*10000	25185.60	533.40	20396.00	5661.00	10976.00	140.00	40758.00	17060.00
Ti				-	50.35	9.35	58.00	17.00	76.00	0.00	11440.00	11370.00
Mn				*50	45.15	2.25	135.90	70.10	162.00	10.00	60.00	2.00
Fe	48	-	-	400 - 500	410.5	30.80	285.00	83.30	351.00	50.00	201.00	149.00
Zn	60	50	<50	20 - 100	56.30	1.90	102.70	33.60	94.00	10.00	192.00	130.00
Rb				-	65.20	2.60	85.45	2.25	49.00	3.00	66.00	5.00
Sr				-	258.00	34.50	177.60	68.90	BDL	-	178.00	89.00
Pb	2-5	2	0.3	0.5 - 30	34.10	0.00	BDL	-	29.00	0.00	BDL	-

D: Control site; BDL: Below detection limit; NR: Normal range; *, Epstein (1965).

Table 5. Concentration of elements in the dumpsite soil (mg/kg).

Element	*Unpolluted soil (Italy)	**World scale range	A		B		C		D	
			Mean	SD	Mean	SD	Mean	SD	Mean	SD
Al	-	-	200665.00	33852.00	341049.30	82162.70	296397.50	2484.75	354985.60	61060.45
Si	-	-	688469.00	76906.10	593368.30	237611.30	792015.50	44311.11	728160.70	153863.50
P	-	-	BDL	-	4025.55	1756.95	1799.00	269.80	BDL	-
S	-	-	470.65	182.45	1295.60	300.10	797.75	171.45	840.95	159.95
Cl	-	-	892.80	176.50	606.90	91.90	380.05	12.85	380.40	54.70
K	-	-	12059.50	2304.35	15028.50	1017.10	9215.25	155.85	9778.90	583.60
Ca	-	-	12358.70	93.35	20143.15	978.05	6721.85	97.95	19042.95	458.95
Ti	-	-	10837.90	1639.50	9710.80	1160.20	7324.95	578.05	9387.20	816.30
Cr	83	12 - 83	345.35	200.85	190.10	5.10	170.45	23.05	312.60	11.50
Mn	1728	270 - 525	1128.55	85.25	1061.00	24.00	825.20	42.90	1347.60	48.50
Fe	-	-	59775.90	4652.70	54941.10	2575.00	56582.90	649.40	90526.20	4235.60
Ni	-	12 - 34	26.95	16.35	16.25	0.35	14.15	1.65	BDL	-
Cu	34	13 - 21	6.96	5.90	119.10	15.70	56.90	9.30	135.40	4.00

Table 5. Contd.

Zn	122	25-100	450.95	245.65	465.25	8.65	247.85	44.45	608.85	53.45
Rb		-	83.05	26.75	34.70	22.80	55.25	10.95	51.30	33.10
Sr		-	64.00	2.40	73.70	9.00	102.35	8.45	51.10	5.40
Y			BDL	-	68.60	1.60	BDL	-	33.73	5.80
Zr			358.90	86.20	208.30	142.70	186.95	19.55	173.80	22.00
Pb	44	22-44	125.95	41.65	BDL	-	BDL	-	67.85	17.45

* Mean values of different natural soils of Sicily (Palumbo et al., 2000). ** Mean ranges calculated to the world scale (Fergusson, 1990). D: Control site; BDL: Below detection limit.

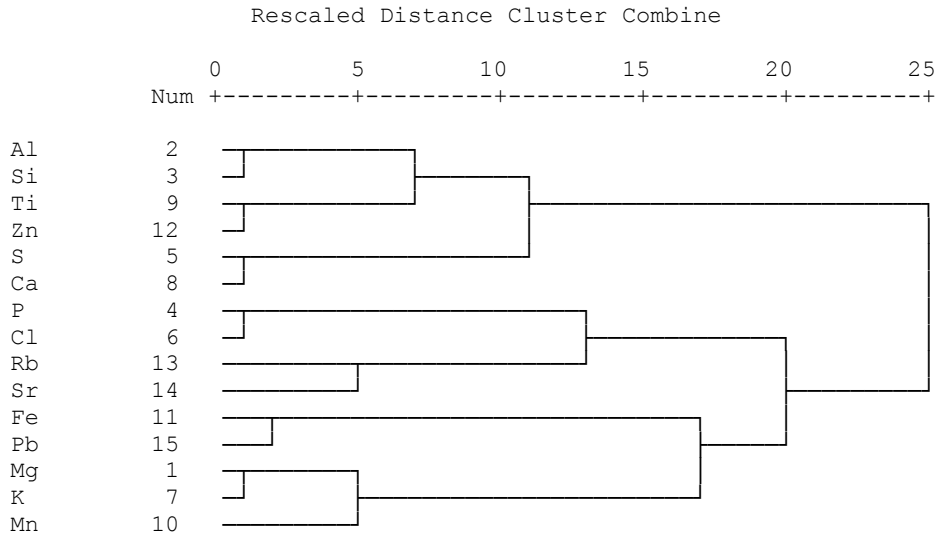

Figure 2. Cluster analysis of elements in vegetable.

polluted soil with Pb from aerial deposition. An explorative hierarchical cluster analysis performed on the dumpsite soil data set (Figure 4), showed two main groups of elements clustered at three levels of similarity as shown in Figure 5, discriminating Mn, Zn, S, Y, P, Ca, Fe, Al and Cu (Group I) from Cl, Zr, Ni, Cr, Pb, Rb, Sr and Si (Group II). These two groups discriminated the elements into natural origin- elements from the parent material and other soil-forming factors that may have added or removed some elements from the soil. Group II could be classified as elements from the waste in association with elements from anthropogenic activities with some natural elements from the soil. This result is consistent with elemental relationships indicating that the elements in Factor I (Figure 4) do not correlate with Al and Si (Figure 3), meaning that they are not from alumino-silicate phases of the soil and as such, not from the natural origin and possibly from the waste and anthropic inputs.

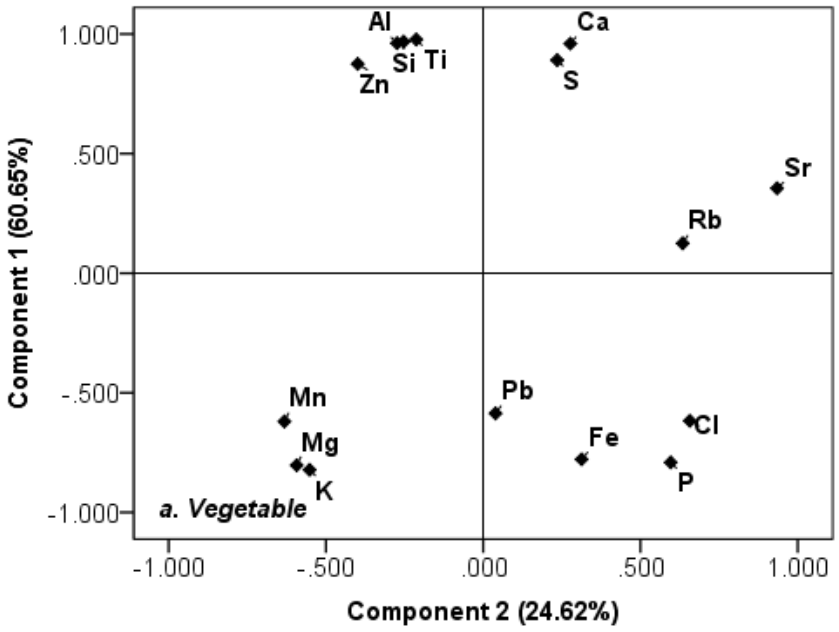

Figure 3. Principal component analysis of the vegetable.

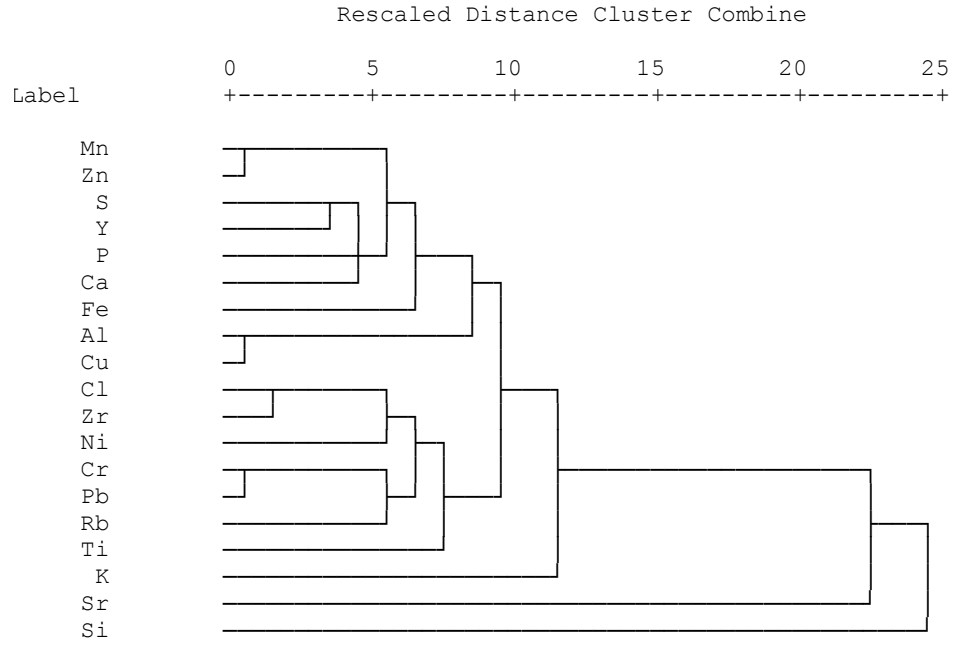

Figure 4. Cluster analysis of elements in the soil.

Factor II has its major elements from the natural sources and weathering processes with changes that would have occurred as a result of the wastes. Al correlated with Ca (0.5) and positively correlated with Fe (0.4) as shown in Table 6; these pointed to the parent rock to likely be from CaO, Al_2O_3,Fe_2O_3 (Manta et al., 2002). Factor III consists of Ti, K, Y, P, S and Ca. It is likely to be a combination of elements released from agricultural wastes with remnants of fertilizers such as NPK and CaO together with P_2O_5 soil components. Plant ability to take up chemical elements from growth media is evaluated by a ratio of element concentration in plants to element concentration in soils and is called Biological Absorption Coefficient (BAC), Index of Bioaccumulation

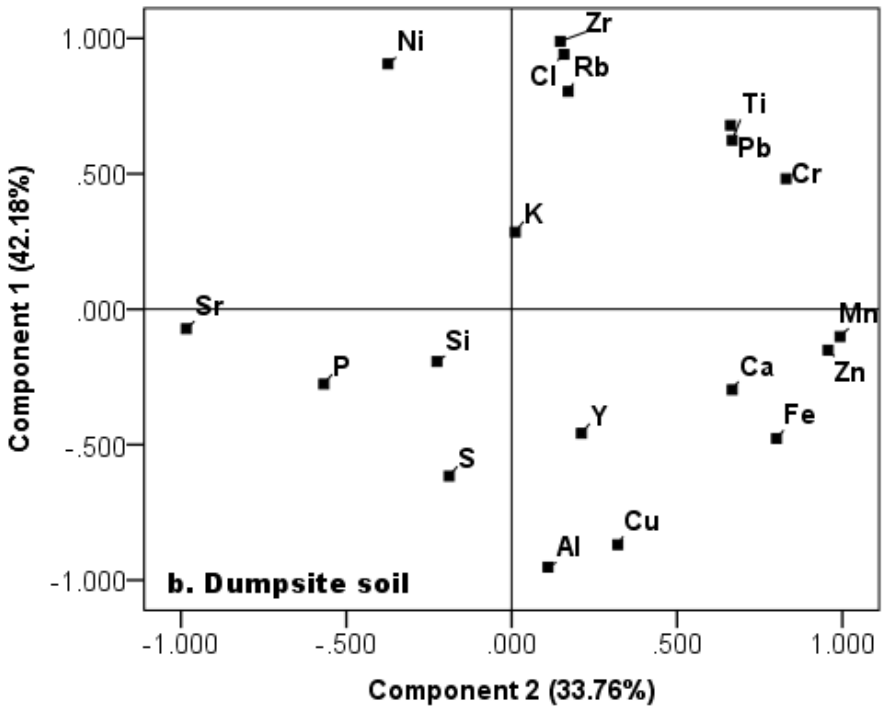

Figure 5. Principal component analysis of soil.

(IBA), or Transfer Factors (TF). Some elements are more susceptible to phytoavailability than others.

In this study, elements such as P, S, Cl, K, Ca, Sr, Mg were phytoavailable in the vegetable than the soil. These are essential elements in relation to photosynthesis and normal growth of the plants. Trace elements (TEs) concentrations in plants are highly associated with the chemical composition of growth media. Plant responses to TEs in soils depend on several factors; however some general trends expressed by plant/soil, Transfer Factor (TF) can be presented as generalized values: 10: Cd, 1: B, Br, Cs, Rb, 10^{-1}: Ag, Co, Cu, Ge, Hg, Mo, Pb, Sr, Te, Zn, 10^{-2}: Be, As, Li, F, I, Mn, Ni, Sb and 10^{-3}: Ba, Bi, Ga, Fe, Se, V, Tl, Zr (Kabata-Pendias, 2011).

The transfer factor of elements were calculated and shown in Table 7; it was found that TF were not within the range provided as normal above. The TF of Al and Si (<0.1) mg/kg; P and Ca < 2.50 mg/kg, S and K were <15.00 mg/kg, while Cl and K were < 20.00 mg/kg. Only Rb and Fe in the control site were within the normal range of TF among the elements analyzed. Ernst (2007) reported that Asian herbal medicinal plants sampled from polluted soils, have elevated contents of TE mainly of Hg, Pb, and As. Therefore, the main source of the elevated concentration in the vegetable could be the polluted soil, comprising lithogenic elements, inherited from mother material and wastes that both form the growth media and probably atmospheric deposition.

Animals including humans generally get exposed to elemental toxicity through food contaminants as the case of this study. Opaluwa et al. (2012) and Epstein (1965) gave the normal range of elements in plants, only the concentrations of Fe in the vegetables fulfilled this condition. Others deviated and well above the stipulated values (Table 4). The tolerable/ permissive values for metals in food as given by WHO/FAO (2007) was fulfilled only in Zn(Sites A,B,C) and was above the value in site D. Heavy metals have health implication in human because they bioaccumulate and are not biodegradable in the body, and the rate of excretion differ from individuals. The tolerable limits of transition elements were not provided.

In this study, heavy metals such as Pb, Al, Zn were above the WHO tolerable limits in food. Lead is a neurotoxic metal, in adults, lead poisoning can cause poor muscle coordination, nerve damage to the sense organs and nerves controlling the body, increased blood pressure, hearing and vision impairment, reproductive problems (e.g., decreased sperm count), retarded fetal development even at relatively low exposure levels. In children, lead poisoning can cause damage to the brain and nervous system, behavioral problems, anemia, liver and kidney damage, hearing loss,hyperactivity, developmental delays, in extreme cases, death. Although the effects of lead exposure are a potential concern for all humans, young children (less than seven years old) are most at risk (Reagan and Silbergeld, 1989).

As for many food components, the intake of metal ions can be a double edged sword. Both their excesses and deficiencies can cause diseases. Redox-Active Metal

Table 6. Correlation table of soil elements.

Element	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Rb	Sr	Y	Zr	Pb
Al	1																		
Si	-0.116	1																	
P	0.422	-0.559	1	0.															
S	0.785	-0.569	0.870	1											*				
Cl	-0.793	-0.502	-0.118	-0.381	1														
K	0.005	-0.973*	0.658	0.556	0.556	1													
Ca	0.552	-0.746	0.232	0.580	0.029	0.578	1												
Ti	-0.404	-0.659	-0.237	-0.200	0.814	0.574	0.537	1											
Cr	-0.448	-0.013	-0.822	-0.668	0.501	-0.122	0.220	0.741	1										
Mn	0.225	-0.269	-0.484	-0.073	0.082	0.047	0.739	0.627	0.756	1									
Fe	0.438	0.256	-0.604	-0.134	-0.431	-0.473	0.429	0.090	0.536	0.819	1								
Ni	-0.847	-0.279	0.116	-0.336	0.853	0.443	-0.384	0.396	0.071	-0.449	-0.803	1							
Cu	0.970*	-0.264	0.349	0.763	-0.656	0.117	0.729	-0.176	-0.258	0.431	0.536	-0.833	1						
Zn	0.320	-0.425	-0.309	0.103	0.083	0.207	0.853	0.645	0.652	0.982*	0.748	-0.445	0.532	1					
Rb	-0.909	0.351	-0.761	-0.963*	0.613	-0.316	-0.514	0.384	0.689	0.050	-0.040	0.552	-0.858	-0.100	1				
Sr	-0.085	0.389	0.455	0.108	-0.271	-0.185	-0.745	-0.767	-0.807	-0.981*	-0.696	0.271	-0.313	-0.971*	-0.135	1			
Y	0.707	-0.784	0.676	0.903	-0.140	0.700	0.866	0.205	-0.288	0.314	0.075	-0.323	0.790	0.486	-0.824	-0.312	1	-	
Zr	-0.926	-0.220	-0.359	-0.639	0.953*	0.280	-0.198	0.714	0.599	0.045	-0.353	0.841	-0.814	-0.010	0.822	-0.215	-0.425	1	
Pb	-0.665	0.024	-0.810	-0.786	0.648	-0.104	0.022	0.736	0.966*	0.567	0.321	0.305	-0.498	0.451	0.840	-0.650	-0.447	0.770	1

Table 7. Transfer factor of elements from soil to vegetable.

Element	Site A			Site B			Site C			Site D		
	Soil	Vegetable	Transfer factor	Soil	Vegetable	Transfer factor	Soil	Vegetable	Transfer factor	Soil	Vegetable	Transfer factor
Al	200665.00	446.00	0.0022	341049.30	586.00	0.0017	296397.50	799.00	0.0026	354985.60	5050.00	0.014
Si	688469.00	518	0.0008	593368.30	629	0.0010	792015.50	778.00	0.0009	758160.70	5560	0.0073
P	BDL	5447.65	-	4025.55	5468.80	1.3585	1799.00	4230.00	2.3513	BDL	2650.00	-
S	470.65	4848.2	10.3010	1295.60	3719.55	2.8709	797.75	3683.00	4.6167	840.95	5660.00	6.7304
Cl	892.80	6376.20	7.141	606.90	6877.90	11.3328	380.05	5640.00	14.8401	380.40	5160.00	13.564
K	12059.50	46053.40	3.818	15028.50	71193.00	4.7371	9215.25	101568	11.0217	9778.90	29930.00	3.060
Ca	12358.70	25185.60	2.0378	20143.15	20396.00	1.0125	6721.85	10976.00	1.6329	19042.95	40758.00	2.140
Ti	10837.90	50.35	0.0046	9710.80	58.00	0.0059	7324.95	76.00	0.0103	9387.20	11440.00	1.218
Mn	1128.55	45.15	0.0400	1061.00	135.90	0.1280	825.20	162.00	0.1963	1347.60	60.00	0.044
Fe	59775.90	410.00	0.0068	54941.10	285.00	0.0051	56582.90	351.00	0.0062	90526.20	201.00	0.00022

Table 7. Contd.

Zn	450.95	56.30	0.1248	465.25	102.74	0.2208	247.85	94.00	0.3792	608.85	192.00	0.3153
Rb	83.05	65.20	0.7850	34.70	85.45	2.4625	55.25	49.00	0.8868	51.30	66.00	1.2865
Sr	64.00	258.00	4.0312	73.70	177.60	2.4097	102.35	-	-	51.10	178.00	3.4833
Pb	125.95	34.10	0.2707	BDL	-	-	BDL	29.00	-	67.85	-	-

plants/vegetable as stipulated by the WHO/FAO (2007). The elements in the soil were inflated by the waste deposition on the soil and other anthropogenic sources, changes in soil formation play important roles in interrelationship of the elements and its discrimination.

The uptake of these elements by Amaranthus *spinosis* caused increases in the metal levels above acceptable limits in the vegetable. This is because the concentrations of metals in the dumpsites were higher than the international permissive limits in soil. Redox active metals such as Fe, Zn, Mn, Al are capable of catalyzing oxidative stress processes, thereby causing chronic inflammatory diseases, cancer, Alzheimer's disease and premature ageing.

Conflict of Interests

The authors declare that there was no conflict of interests associated with this study.

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REFERENCES

Aliev G, Smith MA, Seyidov D, Neal ML, Lamb BT, Nunomura A, Gasimov E K, Vinters HV, Perry G, LaManna JC, Friedland RP (2002). The role of oxidative stress in the pathophysiology of cerebrovascular lesions in Alzheimer's disease. Brain Pathol. 12:21-35.

Carlson CW (1976). Land application of waste materials. Soil Conservation Society of America, Ankeny, Iowa, pp. 3-7.

Dhrubajyoti G, Rita G, Ajoy KM, Subinit R, Manoranjan S, Subhajit C, Asit B, Ujjal M, Shila M, Chul-Un R (2011). Nondestructive Characterization of Municipal-Solid-Waste-Contaminated Surface Soil by Energy-Dispersive X-ray Fluorescence and Low-*Z* (Atomic Number) Particle Electron Probe X-ray Microanalysis. J. Air Waste Manage. 61:1102–1114.

Epstein E (1965). 'Mineral metabolism', In Plant Biochemistry. Eds J. Bonner and J. E. Varner, pp. 438-466. Academic Press: London.

Ernst E (2007). "Herbal medicines: balancing benefits and risks". *Novartis Found. Symp*. Novartis Foundation Symposia 282:154–67; discussion 167–72, 212–218. doi:10.1002/9780470319444.ch11

EU (2006). Commission regulation (EC) No. 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. OJL 364, p. 5.

Fergusson JE (1990). The heavy elements: chemistry, environmental impact and health effects. Pergamon Press, 379 pp.

Grubben GJH, Denton OA (2004). Plant Resources of Tropical Africa 2. Vegetables. PROTA Foundation, Wageningen; Backhuys, Leiden; CTA, Wageningen.

Halliwell B, Gutteridge JM (1999). Free radicals in biology and medicine. Oxford University Press.

Kabata-Pendias A (2011). Trace elements in soils and plants, 4th ed. CRC Press, pp. 93-95.

Lawan IB, Stephen SH, Goni AD, Muhammad T (2012). Study of Vertical Migration of Heavy Metals in Dumpsites Soil. ARPN J. Sci. Technol. 2(2):50-55.

Naughton DP, Petroczi A (2008). The metal ion theory of ageing: Dietary target hazard quotients beyond radicals. Immun. Ageing 5(3).

Odia SN, Ebenezer M, Dela S, Shoji R, Esi A (2008). Heavy Metals uptake by vegetables cultivated on Urban Waste Dumpsite: Case study of Kumasi, Ghana. Res. J. Environ. Toxicol. 2(2):92-99.

Ogunyemi S, Awodoyin RO, Opadeji T (2003). Urban agricultural production: Heavy metal contamination of *Amaranthus cruentus* L. grown on domestic refuse landfill soils in Ibadan, Nigeria. Emir. J. Agric. Sci. 15(2):87–94.

Opaluwa OD, Aremu MO, Ogbo LO, Abiola KA, Odiba IE, Abubakar MM, Nweze NO (2012). Heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis, Nassarawa State, Nigeria. Adv. Appl. Sci. Res. 3(2):780-784.

Palumbo B, Angelone M, Bellanca A, Dazzi C, Wilson J, Neri R, Hauser S (2000). Influence of inheritance and pedogenesis on heavy metal distribution in soils of Sicily, Italy. Geoderma 95:247–266.

Powers KM, Smith-Weller T, Franklin GM, Longstreth WT, Swanson PD, Checkoway H (2003). Parkinson's disease risks associated with dietary iron, manganese, and other nutrient intakes. Neurology 60:1761-1766.

Purves D (1973). Solid wastes and the environment- land. Institute of Public Cleansing 75th Annual Conference Great Britain. Abstracted by C.G. Golueke. Compost. Sci. 14:4-5.

Reagan PL, Silbergeld EK (1989). Establishing a health based standard for lead in residential soils. In: Hemphill and Cothern, eds. Trace substances in environmental health. Supplement to Volume 12, (1990) of Environmental Geochemistry and Health.

Valko M, Rhodes CJ, Moncol J, Izakovic M, Mazur M (2006). Free radicals, metals and antioxidants in oxidative stress-induced cancer. Chem. Biol. Interact. 160:1-40.

WHO/FAO (2007). Joint FAO/WHO Food Standard Programme Codex Alimentarius Commission 13th Session. Report of the Thirty Eight Session of the Codex Committee on Food Hygiene. Houston, United States of America, ALINORM 07/30/13.

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Heavy metal bioaccumulation and oxidative stress in *Austroaeschna inermis* (Dragon fly) of the Lagos Urban ecosystem

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Urban ecosystems are often characterized by the receipt of pollutants, especially heavy metals from diverse anthropogenic activities. To better understand the distribution of heavy metals (Cd, Cu, Pb, Mn and Zn), *Austroaeschna inermis* from five different sites (Unilag, Mile 12, Olushosun Dump site, Imoshe and Badagry) in Lagos, sediments from the respective sites were assessed. This was followed by assessment of lipid peroxidation product; Malondialdehyde (MDA) and antioxidative stress enzymes; superoxide dismutase (SOD), catalase (CAT), glutathione S-transferase (GST) and reduced glutathione (GSH) in *A. inermis*. The results indicate widespread heavy metal distribution with Mn and Zn having the highest concentrations of 13.369±0.800 mg/kg and 21.473±2.001 mg/kg in sediment samples from Mile 12 and Olushosun Dump site respectively. Only Cd was bioaccumulated at two sites (Unilag and Badagry) with biota to soil accumulation factor (BSAF) of approximately 2. The oxidative stress biomarkers assessment in the insects did not indicate any trend to link heavy metal concentrations with respective sites. However there was strong (r ≥ 0.5 < 0.7) to very strong (r ≥ 0.7) positive correlation between Pb concentrations in *A. inermis* and most biomarkers. All enzymes and MDA showed negative correlation with the other heavy metals with values mostly between strong (r ≥ -0. 5< -0.7) to very strong (r ≥ -0.7) negative. The findings from this study reaffirms the ubiquity of heavy metals in the City of Lagos and the relevance of the insects as pollution indicators were discussed.

Key words: Biomonitoring, urban ecology, pollution, biomagnification.

INTRODUCTION

Heavy metals are among the most problematic causes of water and soil pollution, a situation heightened by their ubiquity and evolving knowledge of the biological effects. Although most metals occur naturally in rocks, ores, soil, water, and air, their levels are usually low and widely dispersed (Otitoloju, 2000). Metals that are of environmental concern fall into three classes: suspected carcinogens, those that are readily in soil and those that move through the food chain (Hodgson, 2011). Anthropogenic activities are the major culprits in the

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release of heavy metals in recent times.

Abiotic indices such as soil, air and water analysis alone are inadequate for the assessment of the availability and potential toxicity of contaminants to humans and wildlife (Talmage and Walton, 1991). Metal accumulation in the soil can cause harm to biota, by altering physiological activities and causing many genotoxic effects (Sanita di Toppi and Gabbrieli, 1999; Panda and Panda, 2002), disruption of reproductive potential and endocrine system (Drevnick and Sandheinrich 2003; Kasperczyk et al., 2008), immunosuppression (Carey and Bryant, 1995), induction of stress proteins (Piano et al., 2004) and oxidative stress (Soundararajan et al., 2009; Farombi et al., 2007).

Health risk due to heavy metal contamination of soil has been reported (Eriyamremu et al., 2005; Muchuweti et al., 2006). But the biotoxic effects of heavy metals depend upon the concentrations and oxidation states of heavy metals, kind of sources and mode of deposition (Duruibe et al., 2007). Most studies on metal accumulation and toxicity have focused on vertebrates, but recent works has revealed both negative and positive effects of heavy metals on the host defense response systems of marine invertebrates (Oweson and Hernroth, 2009; Vijayavel et al., 2009) and terrestrial insects (Sorvari et al., 2007; Van Ooik et al., 2008).

Insects are strategic to the welfare of man (Ewuim, 2004) and constitute a major component of the earth's biodiversity with their species richness or diversity exceeding that of any group of extant organisms. They account for 20,000 species (90.54%), many of which contribute significantly to the maintenance of life support systems, with 99.90% of the insect species being beneficial or neutral to man (Ivbijaro, 2003). They are abundant in a wide range of habitats including both terrestrial and aquatic ecosystems (especially fresh water) and including wetlands, either as aquatic or sub-aquatic species, even though they have never adapted to a typical marine environment (Cheng, 1976).

Insects inhabiting coastal areas receiving multiple pollution sources by urban, industrial, and agricultural activities are exposed to complex mixtures of different types of contaminants; while some are found in moist soil littered with dead organic matters (Fukul, 1996).

Dragonflies are amphibious in nature, with adults which fly about on land while their larvae are aquatic. Odonates are very sensitive to changes in habitat quality and as such they are used for monitoring impairments resulting from anthropogenic activities and long term climatic changes (Corbet, 1999; Oertli et al., 2002; Dijkstra, 2007).

The dispersal capabilities of dragonflies correspond to their ecological requirements (Adu and Ogunjobi 2014). Due to the sensitivity of these insects to environmental changes, both the larvae and adults may be used as bio-indicators of environmental conditions (USEPA, 2012).

In keeping with the recent trend in the use of arthropods for biomonitoring, we investigated heavy metal burden of dragonfly (*Austroaeschna inermis*) - ubiquitous in the City of Lagos as well as the correlation between oxidative stress markers and heavy metal levels in dragonfly (the most ubiquitous of the three) so as to draw conclusions which may provide vital insights for future investigations.

MATERIALS AND METHODS

Study design

Five sites in the urbanized western section of Lagos mainland, including Unilag, Imoshe, Olushosun Dumpsite, Mile 12 and Bagdagry (Figure 1) were selected for this study on the basis of the spread in the kind and level of anthropogenic influence in the area. The simple random sampling method was further used to pick triplicate insect samples from the sample sites.

Classification of study sites

The detailed description of the five study sites are as follows:

(i) Owode in Mile 12 (06° 36. 252'N and 003° 24.457'E) characterized by very high human and vehicular density as well as automobile emissions;
(ii) Imoshe (06° 32.348'N and 003° 12.632'E), a relatively less dense area characterized by the presence of a flowing stream where transportation and fishing activities occur;
(iii) Bagdagry (06° 30.664'N and 002° 57.543'E) characterized by farming activities with low industrial and transportation activities;
(iv) Olusosun Dumpsite (06° 35.791'N and 003° 22.766'E), established in 1991 and became operational in 1992, believed to be the largest landfill in Lagos State and Nigeria and managed by Lagos state waste management authority (LAWMA). The site is about 42 hectares of land and in terms of capacity it receives between 40-45% of solid waste generated in Lagos State (9000metric tons of waste per day);
(v) Unilag (University of Lagos) - (06° 32.352'N and 003° 23.854'E), busy campus with high population and vehicular density.

Sampling operations

Sediment samples from fresh and dried ponds from the five sites were collected using a 10 kg soil auger in triplicates and pulled into one for each of the sites making a total of five samples. Samples were kept in flasks lagged with ice packs until they were transferred to the laboratory where they were stored at 4°C prior to analysis.

The insects were caught using sweep nets and transferred in properly aerated cages made with wire gauze, with floors lined with moist soil samples from different locations. The insects were collected by sweeping across vegetations at three different locations within each site in the early hours of the day. They were transported to the laboratory in plastic bottles containing soil from collection sites. Within 24 h of collection, they were frozen at -20°C for preservation prior to analysis.

Heavy metal analysis for sediment samples

The sediment samples were allowed to dry at room temperature and passed through a 2 mm sieve. 5 g of the sieved sample were

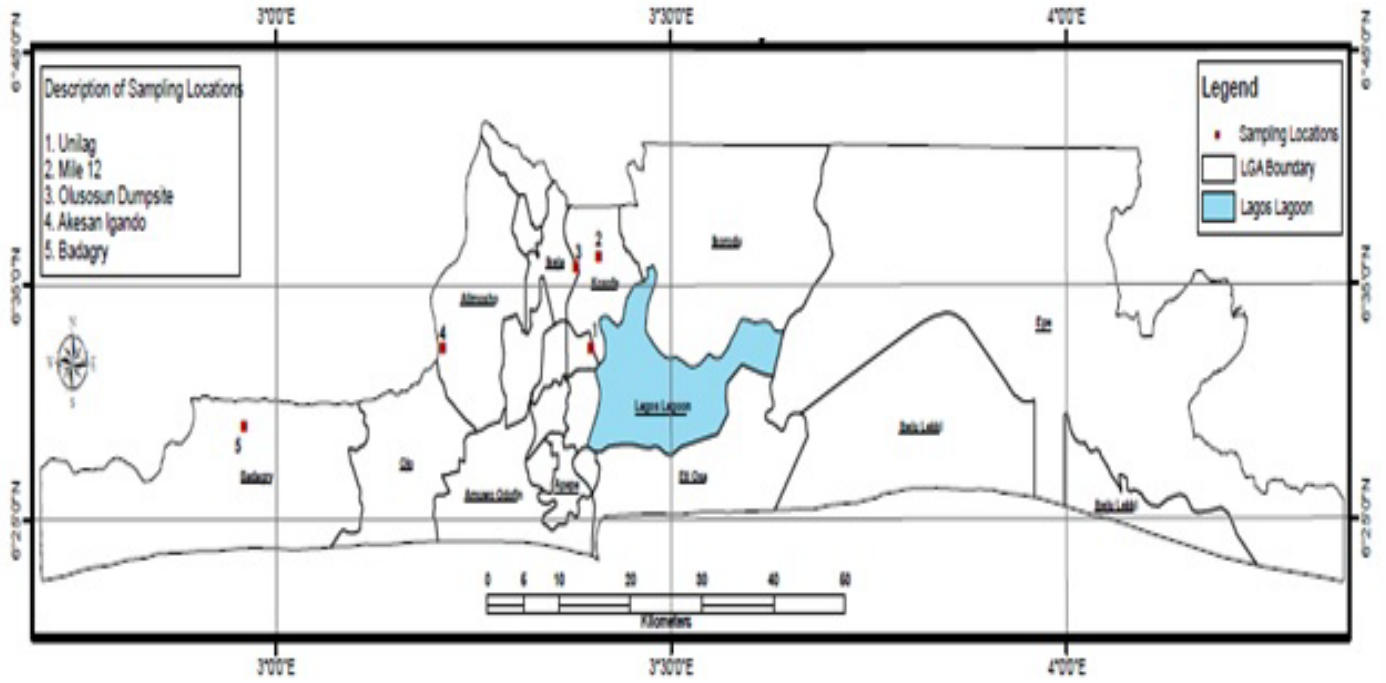

Figure 1. The distribution of sampling sites for the study in Lagos State.

weighed and 10 ml concentrated nitric acid added. The mixture in a beaker was covered with a watch glass and refluxed for 45 min. The watch glass was then removed and the content in the beaker evaporated to dryness. 5 ml aqua regia was added and evaporated to dryness after which 10 ml, 1 M nitric acid was added and the suspension filtered. The filtrate was then diluted to volume with distilled water in a 50 ml volumetric flask. The Concentrations of heavy metals - Cd, Cu, Mn, Zn and Pb - were determined using a Perkin Elmer 403 Atomic Absorption Spectrophotometer (AAS) at wavelengths specific to each metal based on the method reported by Don-Pedro et al. (2004).

Determination of heavy metal content in these insects

About 0.5 g of the insects were weighed into a Teflon bomb and 5ml of aqua-regia (1:3 of HNO_3: HCl) was added and then 5ml of Hydrogen fluoride. The Teflon bomb was sealed and heated in an oven for 6 h at 165°C. After the digestion, 10 ml of saturated boric acid solution was added to the mixture and allowed to cool at room temperature about 2 h. The resulting solution was properly mixed and transferred into a 50 ml standard flask and made up to the mark with distilled water. The digest solutions were used to analyze for the metals in an AAS as in sediment analysis

Determination of Lipid peroxidation levels and Antioxidative stress enzyme activities

Dragonflies collected for biochemical assays were removed from the refrigerator and allowed to defrost. They were first homogenized as whole insects and then the protein content determined by Biuret method (Gonall et al., 1949). The level of lipid peroxidation was determined based on the thiobarbituric acid (TBA) reactivity assay (Yagi, 1998).

Superoxide dismutase was determined as described by Sun and Zigma (1978) at absorbance at 480 nm for 5 min. The catalase activity was determined according to the method of Beers and Sizer as described by Usoh et al. (2005) by measuring the decrease in absorbance at 240 nm due to the decomposition of Hydrogen peroxide (H_2O_2) in a UV recording spectrophotometer with the specific activity of catalase was expressed as moles of H_2O_2 reduced per minute per mg protein.

Reduced glutathione (GSH) was determined as non-protein sulphydryls estimated according to the method of Sedlak and Lindsay (1968) while glutahthione-s-transferase (GST) activity was measured using the method of Habig et al. (1974) using 1-Chloro-2, 4-Dinitrobenzene (CDNB) as substrate.

Data analysis

The Data obtained for assessment of heavy metal concentrations were presented as mean ± SD. Statistical analysis was performed using the SPSS statistical package, with significance level determined at $p<0.05$. Two-way analysis of variance (two-way ANOVA) was applied to determine differences between sites and sampling periods. Kolmogorov- Smirnoff test and Levene's test were applied to test normal distribution and homogeneity of variance, respectively.Data were log-transformed where necessary. Correlations between biomarkers and heavy metals were examined by Pearson's correlation coefficient. Determination of Biota to soil accumulation factor (BSAF) was as reported in Idowu et al. (2014).

$$BSAF = \frac{Concentration\ of\ heavy\ metal\ in\ insect\ tissue}{Concentration\ of\ heavy\ metal\ in\ sediment\ sample}$$

Table 1. Heavy metal concentration in soil samples (mean ± S.D) and *Austroaeschna inermis* across the five sampling sites in Lagos State.

Sampling sites	Heavy metals (mg/kg)				
	Cd	Cu	Mn	Pb	Zn
Unilag	-	-	-	-	-
Sediment	0.027±0.007	0.997±0.225	8.395±0.696	0.227±0.139	20.743±1.686
A. inermis	0.050[a]	0.181[a]	2.929 [a]	ND	3.893[a]
Mile 12					
Sediment	0.109±0.061	1.278±0.216	13.369±0.800	2.820±0.370	18.327±2.210
A. inermis	0.028[b]	0.113[a]	1.914[b]	0.007[a]	1.383[a]
Olushosun Dump site	-	-	-	-	-
Sediment	0.1±0.078	1.038±0.085	10.081±1.260	4.723±0.409	21.473±2.001
A. inermis	0.011	0.014	3.100	0.004	0.448
Imoshe					
Sediment	0.02±0.014	0.165±0.153	4.73±0.812	0.0153±0.010	5.39±0.848
A. inermis	0.008[a]	0.011[a]	0.757[a]	ND	0.230[b]
Badagry	-	-	-	-	-
Sediment	0.012±0.006	0.859±0.203	5.923±0.794	3.497±0.634	17.73±1.323
A. inermis	0.024[b]	0.036[b]	1.376[a]	0.007[a]	0.759[a]

*ND: metal not detected, different alphabets indicate significant difference ($p<0.05$).

RESULTS

Heavy metal accumulation

Heavy metals were ubiquitous occurring at varying concentrations in the sediments and insects at varying sampling sites (Table 1). The heavy metal with the least concentration in the sediments was Cd, was the second lowest, with its highest concentration recorded at Mile 12 while the least at Badagry sampling site. With respect to Cu, Mile 12 had the highest sediment concentration while Imoshe had the least.

Among the insect, the least concentration was also detected at Imoshe while the highest concentration of Cu as well at Mile 12. Overall, Mn had the second highest concentration in sediments and the highest concentration in the insect. Specifically, the highest Mn concentration was detected at sediments from Mile 12, followed by Olushosun Dump site while the least was recorded at Imoshe. The least insect Mn burden was measured at Imoshe. Lead although detected in all sediment samples was not detected in most insects caught. Its concentration was highest in sediments from Olushosun Dump site, followed by Badagry and Mile 12 while Imoshe had the least concentration. Zn had the highest concentration of heavy metals among the sediments analyzed, with the highest recorded at Olushosun Dump site and the lowest at Imoshe.

The heavy metal analysis in the insect clearly showed a higher mean concentration of Mn and Zn in all the insects across all the sites. The trend entails Mg>Zn>Cu>Cd>Pb in most of the sampling sites. The analysis of variance test carried out on metals found on the insect for the various sites considered does not show significant differences (Table 1). Cd was the only heavy metal that was bioaccumulated and this occurred Unilag and Badagry, having BSAF values of 1.85 and 2.00 respectively (Table 2).

Oxidative stress biomarkers in Dragonflies

The relative levels of oxidative stress enzyme activities as well as the levels of lipid peroxidation product, MDA in the insects are presented in Table 3. MDA levels in the dragonflies was highest at Imoshe and least in those caught around the Olushosun Dump site. With respect to the antioxidative stress enzymes, dragonflies at Olushosun dumpsite had the least activity of SOD while those at Badagry recorded the highest. Catalase activity was however least in those caught at Unilag and highest in those around Imoshe site. The highest level of the reduced glutathione (GSH) was recorded in grasshoppers from Imoshe, followed by Badagry and least in those caught at Olushosun Dump site. Glutathione-s transferase (GST) activity was also highest at Imoshe, followed by Badagry and least Unilag.

Correlation of heavy metal burden with Oxidative stress biomarkers in Dragonflies

The assessment of the overall relationship between mean biochemical biomarker levels with heavy metal

Table 2. The biota to soil accumulation factor (BSAF) for the heavy metals in *Austroaeschna inermis* at the sampling sites

Sampling sites	Heavy metals				
	Cd	Cu	Mn	Pb	Zn
Unilag	1.85	0.18	0.35	ND	0.19
Mile 12	0.026	0.09	0.14	0.00	0.08
Olushosun Dump site	0.11	0.01	0.31	0.00	0.02
Imoshe	0.4	0.07	0.16	*	0.04
Badagry	2.00	0.04	0.23	0.00	0.04

* No data for BSAF calculation.

Table 3. Mean antioxidant enzyme activity and level of lipid peroxidation product, MDA (u/mg pro) in *Austroaeschna inermis* across the sampling sites in Lagos

Sampling sites	SOD[b]	CAT[b]	GSH[b]	GST[b]	MDA[b]
Unilag	2.65	3.34	0.21	26.31	0.028
Mile 12	5.85	4.05	0.36	38.67	0.026
Olushosun dumpsite	0.64	4.15	0.17	40.20	0.020
Imoshe	3.02	7.15	0.95	49.96	0.067
Badagry	9.51	6.14	0.55	44.09	0.034

*Similar alphabets (b) imply no significant difference across sampling sites using Chi squre analysis.

concentrations in the *A. inermis* showed that most had weak to very strong negative correlation (Figure 2). Except for SOD activity, Cd was negatively correlated with all other biomarkers. Lead was positively correlated with CAT and GST activities and very strongly and positively correlated ($r \geq 0.7$) with MDA, SOD and GSH. Except for MDA levels, anti oxidative enzyme activities correlated either strongly negatively ($r \geq -0.5 < -0.7$) or very strongly and negatively ($r \geq -0.7$) with Cu in the dragonflies. Mn was at least strongly negatively correlated with all biomarkers. Zn showed very strong negative correlation with GST and strong negative correlation with CAT and GSH.

DISCUSSION

The ubiquity of heavy metals and their relative importance as pollutants of concern is once again brought to the fore by findings from this study. The mean metal concentration of the sediment samples across the sites was generally less than the limits for heavy metals in the soil (USEPA, 2012). Diverse human activities continually increase environmental concentrations of these toxicants to levels where widespread threat to human and animal health can result (Kurdland, 1960; Pereira et al., 2006).

The concentrations of Zn and Mn were particularly high across the sediments and together with Pb were highest at Unilag, Mile 12 and Olushosun Dump site, three areas that are highly impacted by human activities. Lead was particularly highest at Olushosun dump site, followed by Mile 12. While the former may be associated with leachates from the assorted wastes which its collects, the latter may be associated with the high vehicular density and deposits from diver activities. Of all the dumpsites in Lagos state, Olusosun is the most active in terms of traffic and quantity of waste recovery daily at the dumpsite (Odunaiya, 2002).

The soil is the primary recipient of solid wastes (Nyle and Ray, 1999) as well as tons of wastes from a variety of sources; industrial, domestic and agricultural find their way into the soil. Apart from interacting with the soil system thereby changing the physical and chemical properties (Piccolo and Mbagwu, 1997) as well as productivity, an important cause for concern is the possibility of bioaccumulation of these metals.

The accumulation of contaminants is aided by the capacity of soil to bind with clay minerals and organic substances. Their accumulation has multiple effects on the usability and functions of soil in the ecosystem. The stable nature of soils enables the metals to remain for long periods, enhancing changes of uptake.

Mile 12 recorded the highest level of Cd, Cu and Mn while appreciable amounts of Pb and Zn were also found. This high heavy metal concentration may be due to the emission of atmospheric pollutants by vehicles. Mile 12 is a major junction community and the most important route

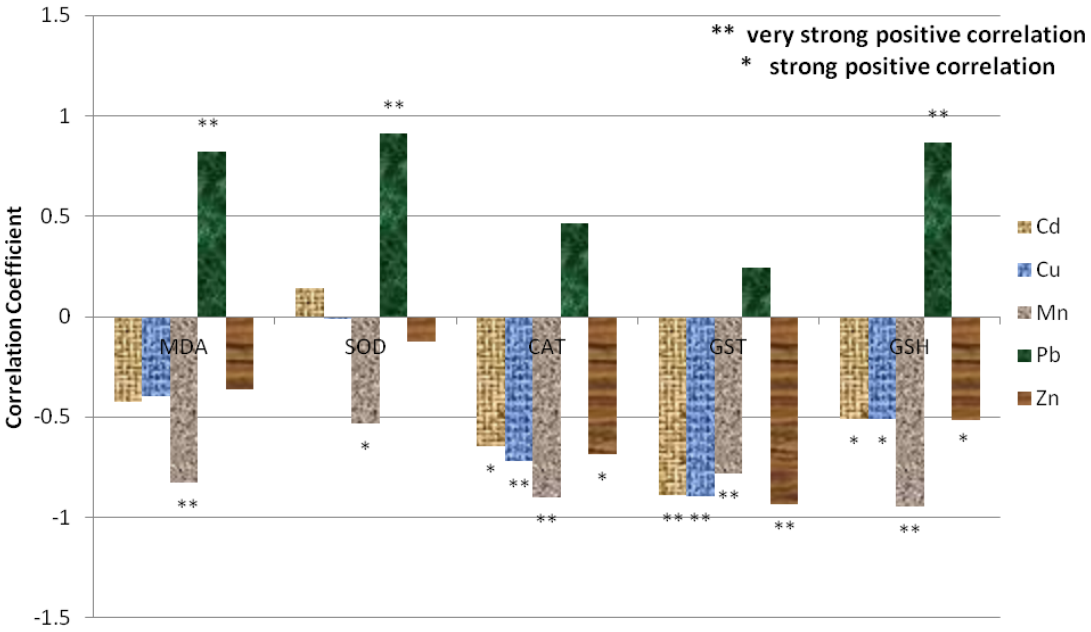

Figure 2. Relationship between heavy metal burden and oxidative stress markers in *A. inermis.*

conveying traffic to and from the Ikorodu axis of Lagos. Road transports contaminate the atmosphere, water and soil near the highway via atmospheric fallout containing potentially toxic metals like lead, cadmium and zinc (ATSDR, 1994, 1999). The least heavy metal concentration was recorded at Imoshe and this could be attributed to the relatively lower level of anthropogenic activity in the area. Imoshe is a coastal community whose primary preoccupation is fishing and crop cultivation. Thus there is limited level of polluting activities in the area. Considerable amount of heavy metals were detected in the insects especially Mn and Zn.

The findings from this study indicates that heavy metal burden were often higher in insects collected at more polluted sites. However, only Cd was bioaccumulated and this can be inferred from the fact that Cd being a very toxic metal as categorized by Walker et al. (2001) is often not found in high concentrations in the environment. These insects acquire heavy metals mostly in ingested food, via water or such as leaf litter, plant material and captured prey, or rarely through dermal absorption (Heliövaara and Väisänen, 1993).

Although comparism is made with the sediments in this study as environmental store of these metals, they are not the most important source of the heavy metals to the insects. Feeding is a much more important route of entry into their system. This therefore may imply that the true BSAF levels is likely to be higher than was recorded in this study because most other sources of the metal are likely to contain lower concentrations than the sediment.

The findings from this study indicate that there was no significant difference between oxidative stress markers in dragonflies across the sampling sites. However there were overall strong positive or negative correlation between heavy metals concentrations in the dragonflies and respective oxidative stress markers in them.

Metals might increase the production of reactive oxygen species, and directly or indirectly cause oxidative damage by inhibiting antioxidant activity (Migula et al., 2004). High concentrations of Cu acts directly, causing an increase in reactive oxygen species, while Cd acts indirectly leading to an increase in cellular iron levels or directly inhibiting the antioxidant activity of glutathione-related enzymes and deplete cellular glutathione (Kang, 1997). Lead recorded strong positive correlation with MDA levels implying that increases in its concentration may be linked with increased cell membrane damage in the insect and subsequently oxidative stress. Metals can enhance oxidative stress and lipid peroxidation in insects especially when other per-oxidant constituents are present in their diet (Ahmad, 1995; Felton and Summers, 1995; Chrascina et al., 1996).

Lead also had strong positive correlation with SOD and GSH, implying that the concentration in the insects was not high enough to inhibit SOD activities or that its mechanism of action does not relate directly with SOD activities. Mn on the other hand had negative correlation with the antioxidative stress enzymes including MDA levels. This also raises questions about their mechanism of action in the insect, the threshold for toxic action and

the possibility of an inherent detoxifying mechanism in the insects. Both enhancement and inhibition have been reported for the activity of antioxidant enzymes such as SOD, CAT or GST, depending on the metal levels, form and period of exposure, and insect species (Zaman et al., 1994; Migula and Glowacka, 1996).

Insects waxy cuticle and fatty tissues may also hold these metals in inactive forms, thereby preventing metal penetration and toxic action. Earlier studies on the reactive oxygen species and antioxidant defense mechanism in insects suggested that there exists a regulatory mechanism for balancing pro-oxidants and antioxidants (Ahmad, 1992). Controversially, relatively higher MDA levels in dragonflies were recorded in Imoshe and Bagdagry where the lowest heavy metal values were recorded reflecting stress possibly due to factors other than metal intoxication.

The activity of the enzyme SOD was much lower in dragonflies found in the Dump site compared to the other sampling sites, implying some level of inhibition. The enzyme SOD is known to provide cyto-protection against free radical induced damage by converting superoxide radicals (O^{-2}) generated in peroxisomes and mitochondria to hydrogen peroxides. The hydrogen peroxide is then removed from the system by the enzyme CAT, which converts it to water and molecular oxygen (O_2). The inhibition of the enzyme SOD by the presence of pollutants will therefore lead to increased oxidative stress in the tissues as a result of the damaging effects of the superoxide radicals (O^{-2}). Although CAT was not equally lowest at the Dump site, its link with SOD activities is well established. The inhibition of the enzyme SOD is believed to result in a reduction in the activity of the enzyme CAT, due to a decrease in H_2O_2 generation from SOD activities. Similar observation of a decrease in CAT activity following an inhibition of the activity of enzyme SOD has been reported by Fatima and Ahmad (2005).

GST response to toxic chemicals follows a similar bell-shaped trend as CAT (Viarengo et al., 2007) hence increased and decreased enzyme activities have been reported in polluted areas (Regoli et al., 2004). Thus describing a trend for the activities of these enzymes over large study areas and variables is often difficult as observed in this study. Glutathione transferases however plays an essential role in the overall fitness of insects exposed to potentially toxic exo- or endogenous substances and are induced by organic contaminants as part of the phase II biotransformation pathway (Sheehan and Power, 1999). It has been reported to respond differently to different compounds, for example, Hamed et al. (1999) reported that the enzyme was strongly inhibited by dimethoate, while Zhang et al. (2004) reported statistically significant enhancement in GST in animals exposed to oxidative stress of 2,4-dichlorophenol.

The highest levels of MDA in the dragonflies, the key indicator of lipid peroxidation damage was found in the least disturbed sites; Imoshe and Bagdagry. Increased or elevated levels of MDA is due to an inhibitory effect on mitochondrial electron transport system leading to stimulation in the production of intracellular ROS (Stohs et al., 2001).

Elevated ROS level in tissues leads to cellular damage when the rate of its generation surpasses the rate of its decomposition by antioxidant defense systems. The measurements of lipid peroxides levels in plants and animal tissues exposed to different pollutants have been recognized as reliable early warning signal of exposure to environmental stress and therefore often integrated to environmental monitoring programs (Avci et al., 2005; Fatima and Ahmad, 2005; Valavanidis et al., 2006).

Conclusion

The findings from this study reaffirm the varied and dispersed concentrations of heavy metals in Lagos as reported earlier by Idowu et al. (2014). The heavy metal concentrations in the insects with respect to the sediment samples did not reflect widespread bioaccumulation. This may imply that a feeding route of bioaccumulation assessment may be more important for terrestrial insects than absorption through their cuticle and other passive processes. Although there was either at least strong positive or negative correlation between heavy metal burdens and oxidative stress markers in the insects, further explanation is needed as to why these activities were not higher in areas with higher metal contamination. Thus the use of oxidative stress markers for biomonitoring of heavy metal contamination in field studies with insects appears a difficult and controversial subject given the numerous other environmental factors and contaminants that may interplay.

Conflict of Interest

The authors declare that there are no conflicts interest regarding this article.

REFERENCES

Adu BW, Ogunjobi JA (2014). Assessment of dragonflies and damselflies of Owena Forest Southwestern, Nigeria. Int. J. Agri. Sci. 4(3):153-159.

Ahmad S (1992). Biochemical defense of pro-oxidant plant allelochemicals by herbivorous insects. Biochem. Sys. Ecol. 20:269-296.

Ahmad S (1995). Oxidative stress from environmental pollutants. Arch. Insect Biochem. Physiol. 29:135-157.

ATSDR (1994). Toxicological profile for zinc. US Department of Health and Human Services, Public Health Service, Atlanta, GA.

ATSDR (1999). Toxicological profile for cadmium. US Department of Health and Human Services, Public Health Service, Atlanta, GA.

Avci A, Kaçmaz M, Durak I (2005). Peroxidation in muscle and liver tissues from fish in a contaminated river due to a petroleum refinery industry. Ecotoxicol. Environ. Saf. 60:101-105.
Carey C, Bryant CJ (1995). Possible interrelations among Environmental Toxicants, Amphibian Development and Decline of Amphibian Population. Environ. Health Perspect. 103 (4): 13-17.
Cheng L (1976). Marine insects. Scripps Institution of Oceanography Research, Scripps Institution of Oceanography.
Chrascina M, Kafel A, Migula P (1996). Patterns of detoxifying enzymes in larval stage *Smerinthus ocellatus* L. exposed to cadmium, tocopherol or quercetin. St. Soc. Sci. Torun 4: 31-37.
Corbet PS (1999). Dragonflies: Behaviour and Ecology of Odonata. Harley Books, Colchester.
Dijkstra K-DB (2007).Demise and rise: The biogeography and taxonomy of the Odonata of tropical Africa. PhD Thesis, Leiden University.
Don-Pedro KN, Oyewo EO, Otitoloju AA (2004). Trend of heavy metal concentrations in Lagos lagoon ecosystem, Nigeria. WAJAE 5:103 - 114.
Drevnick PE, Sandheinrich MB (2003). Effects of dietary methyl mercury on reproductive endocrinology of Fathead minnows. Environ. Sci. Technol. 37: 4390-4396.
Duruibe JO, Ogwuegbu MDC, Egwurugwu JN (2007). Heavy metal pollution and human biotoxic effects. Int. J. Phys. Sci. 2: 112-118.
Eriyamremu GE, Asagba SO, Akpoborie A, Ojeaburu SI (2005). Evaluation of lead and cadmium levels in some commonly consumed vegetables in the Niger-Delta oil area of Nigeria. Bull. Environ. Contam. Toxicol. 75: 278- 283.
Ewuim SC (2004). A study of the insect fauna of the Permanent Site of Nnamdi Azikiwe University, Awka, Ph.D. Thesis. Nnamdi Azikiwe University Awka.
Farombi EO, Adelowo OA, Ajimoko YR (2007). Biomarkers of Oxidative Stress and Heavy Metal Levels as Indicators of Environmental Pollution in African Cat Fish (Clarias gariepinus) from Nigeria Ogun River. Int. J. Environ. Res. Public Health 4(2):158-165.
Fatima RA, Ahmad M (2005). Certain antioxidant enzymes of Allium cepa as biomarkers for the detection of toxic heavy metals in wastewater. Sci. Total. Environ. 346(1-3):256-73.
Felton GW, Summers CB (1995). Antioxidant systems in insects. Arch. Insect Biochem. Physiol. 29:187-197.
Fukul M (1996). Notes on the larval stages of *Oligoaeshna pryeri* Martin Aeshna 32:9-13.
Gonall AG, Bardawill CJ, Davd MM (1949). Glutathione transferases. The first step in mecapturic acid formation. J. Biol. Chem. 77:751-760.
Habig WH, Pabst MJ, Jakoby WB (1974). Glutathione *S*-transferases. The first enzymatic step in mercapturic acid formation. J. Biol. Sci. 249:7130-7139.
Hamed RR, Elawa SE, Farid NM, Ataya FS (1999). Evaluation of detoxificationenzyme levels in Egyptian catfish, *Clarias lazera*, exposed to dimethoate. Bull. Environ. Contam. Toxicol. 63:789-796.
Heliövaara K, Väisänen R. (1993). Insects and Pollution. CRC Press, Ann Arbor, 393 pp.
Hodgson E (2011). A Textbook of Modern Toxicology. Wiley Publishers.
Idowu ET, Amaeze NH, Adie PI, Otubanjo OA (2014). Heavy metal bioaccumulation and biomarkers of oxidative stress in the wild African tiger frog, *Hoplobatrachus occipitalis.* AJEST 8(1):6-15.
Ivbijaro MFA (2003). Insect and the environment. A key note address presented at the 34th Annual Conference of the Entomological Society of Nigeria (ESN). University of Lagos.
Kang YJ (1997). Alteration of antioxidant system In: Masaro, E. (ed.) Handbook of human toxicology, CRC Press, Boca Raton, Florida, USA, pp. 275-284.
Kasperczyk A, Kasperczyk S, Horak S, Ostalowsk A, Grucka-Mamczar E, Romuk E, Olejek A, Birkner E (2008). Assessment of semen function and lipid per oxidation among lead exposed men. Toxicol. Appl. Pharmacol. 228:378-384.
Kurdland L (1960). Minamata disease. World Neurol. 1:370-385.
Migula P, Glowacka E (1996). Heavy metals as stressing factors in the red wood ants (*Formica polyctena*) from industrially polluted forests. Fresenius J. Anal. Chem. 354: 653-659.
Migula P, Laszczyca P, Augustyniak M, Wilczek G, Rozpedek K, Kafel A, Woloszyn M (2004). Antioxidative defence enzymes in beetles from a metal pollution gradient. Biol. Brat. 59: 645-654.
Muchuweti M, Birkett JW, Chinyanga E, Zvauya R, Scrimshaw MD, Lester JN, (2006). Heavy metal content of vegetables irrigated with mixture of waste water and sewage sludge in Zimbabwe: Implications for human health. Agric. Ecosystem aEnviron. 112: 41-48.
Nyle CB, Ray RN (1991). The Nature and Properties of soils. 12th Ed. United State of America. pp. 743-785.
Odunaiya CO (2002). Repositioning solid waste management practices in cosmopolitan Lagos state Polytechnic Inaugural Lecture Series No. 6 (26 th June 2002) P. 66.
Oertli B, Joye DA, Castella E, Juge R, Cambin D, Lachavanne JB (2002). Does size matter? The relationship between pond area and biodiversity. Biol. Cons.104:59-70.
Otitoloju AA (2000). Joint action toxicity of heavy metals and their bioaccumulation by benthic animals of the Lagos Lagoon. Ph.D Thesis, University of Lagos, Lagos, Nigeria. P. 231.
Oweson C, Hernroth B (2009). A comparative study on the influence of manganese on the bactericidal response of marine invertebrates. Fish Shellfish Immunol. 27:500-–507.
Panda BB, Panda KK (2002). Genotoxicity and mutagenicity of metals in plants. Prasad, K.N.V. and Strzalka, K., (Ed.), Physiology and BioChemistry of Metal Toxicity and Tolerance in Plants, Kluwer Academic Publishers, Netherlands. pp. 395-414.
Pereira R, Pereira ML, Ribeiro R, Goncalves F (2006). Tissues and hair residues and histopathology in wild rats (*Rattus rattus* L.) and Algerian mice (*Mus spretus* Lataste) from an abandoned mine area (Southeast Portugal). Environ. Pollut. 139:561-575.
Piano A, Valbonesi P, Fabbri E (2004). Expression of cytoprotective proteins, heat shock protein 70and metallothioneins, in tissues of *Ostrea edulis* exposed to heat and heavy metals. Cell Stress Chaperon. l9(2):134-142.
Piccolo A, Mbagulu JSC (1997). Exogenuos humic substances as conditions for the rehabilitation of degraded soil agro Foods Industry Hi-Tech. March/April 21-28.
Regoli F, Frenzilli G, Bocchetti R, Annarumma F, Scarcelli V, Fattorini D, Nigro M (2004). Time-course variations of oxyradical metabolism, DNA integrity and lysosomal stability in mussels, *Mytilus galloprovincialis*, during a field translocation experiment. Aquat. Toxicol. 68: 167-178
Sanita di Toppi L, Gabbrieli R (1999). Responses to cadmium in higher plants. Environ. Exp. Botany 41(2):105-130.
Sedlak J, Lindsay RH (1968). Estimation of total protein bound and non-protein sulfhydryl groups in tissues with Ellman's reagent. Anal. Biochem. 25:1192-1205.
Sheehan D, Power A (1999). Effects of seasonality on xenobiotic and antioxidant defence mechanisms of bivalve molluscs Comp. Biochem. Physiol. C 123:193-199.
Sorvari J, Rantala LM, Rantala MJ, Hakkarainen H, Eeva T (2007). Heavy metal pollution disturbs immune response in wild ant populations. Environ. Pollut. 145:324-328.
Soundararajan M, Veeraiyan G, Samipillai SS (2000). Arsenic-induced oxidative stress in fresh water tilapia (*Tilapia mossambica*). J. Phytol. 1(4):267-276.
Stohs SJ, Bagchi D, Hassoun E, Bagchi M (2001). Oxidative mechanisms in the toxicity of chromium and cadmium ions. J. Environ. Pathol. Toxicol. Oncol., 20:77-88.
Sun, M, Zigma, S (1978). An improved spectophotometric assay of dismutase based on epinephrine antioxidation. Anal. Biochem. 90:81 - 89.
Talmage SS, Walton BT (1991). Small mammals as monitors of environmental contaminants. Rev. Environ. Contam. T. 119: 47-145.
USEPA (2012). Water: Monitoring and Assessment. Macro invertebrates and Habitats. United States Environmental Protection Agency. http://water.epa.gov/type/rsl/monitoring/vms40.cfm
Usoh FI, Akpan EJ, Etim EO, Farombi EO (2005). Antioxidant actions of dried flower of *Hibiscus sabidariffa* L. on sodium arsenite- induced oxidative stress. Pak. J. Nutr. 4: 135-141.
Valavanidis A, Vlahogianni T, Dassenakis M, Scoullos M (2006).

Molecular Biomarkers of Oxidative Stress in Aquatic Organisms in Relation to Toxic Environmental Pollutants. Ecotox. Environ. Saf. 64:178-189.
Van Ooik T, Pausio S, Rantala MJ (2008). Direct effects of heavy metal pollution on the immune function of a geometrid moth, *Epirrita autumnata*. Chemosphere 71: 1840-1844.
Vijayavel K, Gopalakrishnan S, Thiagarajan R, Thilagam H (2009). Immunotoxic effects of nickel in the mud crab *Scylla serrata*. Fish Shellfish Immunol. 26:133-139.
Viarengo A, Lowe D, Bolognesi C, Fabbri E, Koehler A (2007). The use of biomarkers in biomonitoring: A 2-tier approach assessing the level of pollutant induced stress syndrome in sentinel organisms. Comp. Biochem. Physiol. C 146:281- 300.
Walker CH, Hopkin RM, Sibly RM, Peakall DB (2001). Principles of Ecotoxicology. Taylor and Francis, New York.
Yagi K (1998). Simple procedure for specific enzyme lipid hydroperoxidases in serum or plasma. Methods Mol. Biol. 108:107-110.
Zaman K, Macgill RS, Johnson JE, Ahmad S, Pardini RS (1994). An insect model for assessing mercury toxicity: Effect of mercury on antioxidant enzyme activities of the housefly (Musca domestica) and the cabbage looper moth (*Trichoplusia ni*). Arch. Environ. Contam. Toxicol. 26:114-118.
Zhang J, Shen H, Wang X, Wu J, Xue Y (2004). Effects of chronic exposure of 2,4 dichlorophenol on the antioxidant system in liver of freshwater fish *Carassiu sauratus* . Chemosphere 55: 167-174.

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