International Journal of Scientific World, 5 (1) (2017) 38-46

International Journal of Scientific World

Website: www.sciencepubco.com/index.php/IJSW
doi: 10.14419/ijsw.v5i1.6710
Research paper

Accumulation and toxicological risk assessment of Cd, As, Pb, Hg, and Cu from topsoils of school playgrounds at Obio-Akpor LGA Rivers State Nigeria

Okereke Chioma Joy [1], Agomuo Emmanuel Nnabugwu[2], Amadi Peter Uchenna[1]*

[1] *Department of Biochemistry, University of Port Harcourt, Choba, Rivers State, Nigeria*
[2] *Department of Biochemistry, Imo State University, Owerri*
**Corresponding author E-mail: peter_amadi@uniport.edu.ng*

Abstract

The adverse health effects associated with heavy metal pollution have become a subject of topical discussion. Using standard methods, this study evaluated the accumulation and toxicological risks of heavy metal deposition on top soils of school playgrounds in Obio-Akpor LGA. Results obtained from the top soils, sampled from 10 different schools showed that the concentration of heavy metals assessed, followed the trend; Hg<As<Cd<Pb<Cu. Marginal differences between the test and control samples were observed for the geoaccumulation index of the heavy metals except for copper. For the contamination factor, FCUA had the least results for cadmium (0.31) but highest in arsenic (0.016) while OPS, UDPS and RBPS recorded the highest contamination factor for lead, mercury, and copper respectively. The results for the pollution load index and degree of contamination of the test sites showed that the sites were unpolluted and had low contamination status, while the enrichment factors showed the deposition of only cadmium to be of a natural origin, and the rest of the heavy metals resulted from anthropogenic sources. The trend from the hazard quotient was Pb>Hg>Cu>Cd>As while the highest (0.0213) and least (0.0162) total hazard index value occurred at RBPS and MOM respectively. These values obtained for this study indicate that the school playground's soils are still within the recommended heavy metal content safe levels.

Keywords: *Geoaccumulation Index; Contamination Factor; Pollution Loads Index; Total Hazard Index; Hazard Quotient*.

1. Introduction

Heavy metals are regarded as natural components of the earth crust. Soils serve as a natural sink for heavy metals, and are regarded as a critical environment where water, air and rock interface [20] [29]. In urban areas, dusts and top soils are natural indicators of heavy-metal pollution whereas locations close to the road are mostly affected by heavy-metal contamination as a result of traffic [24] [62]. Some of the heavy metals that frequently occur in contaminated soils and potentially cause health problems include Fe, Cr, Cd, Zn, Cu, and Pb [7]. Others include As, Hg, Co, Ni, Mn, Mg, etc. Sources like waste water in agricultural land, atmospheric deposition, fertilizer application, waste disposal, industrial sources, by product combustion, and traffic are the major sources of anthropogenic input. In addition, properties such as soil classification, texture and mineralogy which condition the relative mobility of these heavy metals, climatic conditions and state of the parent materials all influence the distribution of these heavy metals [32]. Also, the availability and accumulation of these heavy metals into the soil are equally affected by some of the physicochemical properties of the soil like pH and temperature [43]. The distribution of heavy metals occurs in several ways that include precipitation and complexation, ion exchange, adsorption, etc. [45]. The contamination of heavy metals in top soils has posed serious worldwide challenges, as reported by Alloway, [10] and Nriagu, [36]. Some heavy metals at minute quantities found in soils, water, dusts and air, play a crucial role in the functioning of biological systems [28]. Due to their toxic effects and bioaccumulation, and recalcitrance to biodegradation, they are noted as more serious environmental contaminants. In organisms, accumulation of these heavy metals occurs as a result of direct uptake from the environment, food or from respiration [26]. Heavy metals exert their toxic effects through the disruption of metabolic activities that relates to growth, repair of tissues, oxygen consumption and reproduction [14]. The occurrence of cadmium into the environment preempts an occupational and environmental concern [49]. It is used for many industrial purposes like production of batteries, pigments and alloys [89]. However, the main cadmium exposure routes are by food ingestion, cigarette smoke, or inhalation [49]. Tchounwou et al., [49] reported that the circulatory system was the main distribution route of calcium, whereas its toxicity is mostly exerted on the blood vessels. Though the mechanism by which cadmium exerts its toxic effects is poorly understood, it has been suggested by Stohs, [47] that cadmium exerts its toxic effect via the production of reactive oxygen species (ROS) that damages the single-strand DNA, thus disrupting protein and nucleic acid synthesis. Also, direct or systemic exposure to cadmium has been reported by Waalkes and Rehm [59] to cause proliferatives lesions like adenocarcinomas. Further, Singhal et al., [46] found that chronic exposure to cadmium reduces the levels of acetylcholine, serotonin, and norepinephrine, while Baselt and Cravey [13], Åkesson et al., [6], and Gallagher et al., [22], reported a relationship between reduction in osteoporosis and bone mineral density, and acute low-level exposure to exposure to cadmium. Several symptoms are associated with acute ingestion of cadmium, and

Copyright © 2017 Okereke Chioma Joy et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

they include a 15minutes to 30-minute convulsion, vertigo, abdominal pain, vomiting, and salivation [13].

Arsenic, an element that is found in several environmental matrices at low concentrations [4] occur either in the organic form as methylated metabolites or in inorganic forms as pentavalent or trivalent arsenate. Tchounwu et al., [51], and Centeno et al., [15] have reported that arsenic compounds form part of the therapy used for the treatment of trypanosomiasis, syphilis, amoebic dysentery, and other parasitic diseases. A lot of factors like genetic and nutritional factors, individual proneness, gender, age, and biological species all influence arsenic toxicity. Tchounwu et al., [49] observed that trivalent arsenic can cause the loss of activity of more than two hundred (200) enzymes by binding to their sulfhydryl groups, and substitution of their phosphate groups. Wang and Rossman, [61] also found that arsenic exerts its toxic effects by disrupting cellular respiration through rendering mitochondrial enzymes inactive, thereby impairing oxidative phosphorylation. Many authors have proposed mechanisms for the carcinogenic potency of arsenic. Arsenic has been found to cause the hypomethylation of DNA thus facilitating aberrant gene expression. Trouba et al., [53] reported that the alterations in mitogenic signal proteins resulting from acute long-term exposure to arsenic might be responsible for arsenic induced carcinogenesis.

Some adverse health effects have been associated with the acute exposure to lead, and they include gastrointestinal diseases, kidney and brain damage, while some other studies have reported that chronic exposure induces health defects related to blood and blood pressure, cholecalciferol metabolism, and kidney [3], [2], [55], [31], [12]. Specific mechanism of toxicity of lead centered on the mimicry or inhibition of cadmium activities has been reported by ATSDR, [3]. Lead can also bind to amide and sulfhydryl groups of enzymes causing the alteration of their configuration and activities [49].

Humans come in contact with mercury through food contamination, accidents, medical practices, environmental pollution, dental care, occupation-related operations, and agricultural and industrial operations [41]. The mechanism of mercury toxicity centers on oxidative stress [58]. Mercury has been observed to cause elevated levels of ROS formation by disrupting the ubiquinone-cytochrome b5-step during oxidative phosphorylation [37].

Copper is quite toxic to aquatic organisms. Impairment of zinc homeostasis and antioxidant function has been reported to result from excess amount of free copper in the system [40]. Curtis [17] found that symptoms of acute ingestion of copper include hypotension, hematemesis, gastrointestinal distress, coma, vomiting, and jaundice. Also, it has been noted by Environmental Fact Sheet [16] that kidney and liver damages have been caused by chronic exposed to copper.

Elevated heavy-metal content in children has been associated with various anthropogenic activities [9] [27]. Irrespective of the source of heavy-metal contamination, i.e. anthropogenic or natural, their deposition on children playground soils establishes potent toxic tendency resulting from their bioaccumulative properties. In general, the environmental characteristics of urban soils influence the health status of its inhabitants, so people have become particularly conscious of soil contamination around them. A few studies have accounted for the heavy metals' content, and toxicities associated with their contamination in some school playground soils in Nigeria. However, no study has been conducted yet for soil samples from school children playground in Obio-Akpor LGA, Rivers State. Hence, this study was carried out to evaluate the contents and accumulation of heavy metals as well as assess the risk associated with the level of deposition on these soil samples.

2. Materials and methods

2.1. Study area

Ten schools situated at Obio-Akpor LGA Rivers State Nigeria were used for this study. Soil samples used for this study were collected in two parts, representing the test and control samples. The test soil samples were obtained at the respective playgrounds, while the control soil samples were obtained 100m away from the playgrounds. The schools used for this study include:

- Choba State Primary School (CSPS)
- Mother of mercy primary school (MOM)
- Universal primary education model primary school (UPE)
- Rock base primary school (RBPS)
- Olobo primary school Choba (OPS)
- Alekahia state primary school (ASPS)
- University demonstration secondary school (UDSC)
- State school Umuokpo-aluu (SCUA)
- Foundation comprehensive school Umuokpo-aluu (FCUA)
- University demonstration primary school (UDPS)

2.2. Sample collection and preparation

Soil samples obtained from the study sites during the dry season were collected in triplicates. At each study site, the composite top surface soil samples from the 0-15cm layer were randomly collected using an Auger, and then transferred to a clean air tight aluminum plastic container. After the manual removal of debris from the samples, they were taken to the laboratory for further preparations. At the laboratory, the soil samples were air dried at room temperature for 3days, ground and sieved using a 2mm stainless steel mesh.

2.3. Sample analysis

The content of heavy metals (Cadmium (Cd), Arsenic (As), Lead (Pb), Mercury (Hg), and Copper (Cu) in the soil samples were determined using an Atomic Absorption Spectrophotometer. One (1) gram of soil sample was weighed out and transferred into an empty 250ml beaker. To this soil sample, a mixture of 15 ml of HNO_3, H_2SO_4, and $HClO_4$ in a ratio of 5:1:1 was added. The mixture was gently stirred and placed on a heating mantle up to a temperature of 80^0C till a clear solution was obtained. The mixture was cooled and made up to 30ml with 2% HNO_3 and filtered. The concentrations of the heavy metals were obtained using an atomic absorption spectrophotometer (Shimadzu AA-670, Japan) after the preparation of a reference solution.

2.4. Geoaccumulation index (IGEO)

The index of geoaccumulation (I_{geo}) was calculated using the following relationship:

$$I_{geo} = \text{Log}_2 \frac{Cn}{1.5Bn}$$

Where,

Cn stands for the concentration of heavy metal in the school playgrounds. Bn stands for standard background value of element n. In this study, the standard background value was derived from the average of three widely accepted baselines (average shale [54], crustal average content and worldwide mean values for soils [30]). The factor 1.5 is used for the possible variations of the background data due to lithological variations. I-geo was classified into seven grades: I-geo ≤ 0 (grade 0), unpolluted; 0< I-geo ≤1 (grade 1), slightly polluted; 1 < I-geo ≤ 2 (grade 2), moderately polluted; 2< I-geo ≤3 (grade 3), moderately severely polluted; 3< I-geo ≤4 (grade 4), severely polluted; 4< I-geo ≤5 (grade 5), severely extremely polluted; I-geo > 5 (grade 6), extremely polluted [34].

2.5. Contamination factor (C^if)

The contamination factor was calculated using the following relationship:

$$C^if = \frac{Cn}{Bn}$$

Cn represents the measured concentration of heavy metal in the school playgrounds. Bn stands for standard background value of element n. In this study, the standard background value was derived from the average of three widely accepted baselines (average shale [54], crustal average content and worldwide mean values for soils [30]. $C^i f$ values are classified into four categories: $C^i f < 1$ represents low contamination factor indicating low contamination, $1 \leq C^i f < 3$ represents moderate contamination factor, $3 \leq C^i f < 6$ represents considerable contamination factor, and $6 \leq C^i f$ represents very high contamination factor [25].

2.6. Estimation of enrichment factor (EF)

The enrichment factor was computed using the following relationship:

$$EF = \frac{\text{Heavy metal concentration in the soil at the playground}}{\text{Heavy metal concentration in the soils at the control site}}$$

The EF values < 1 or close to unity indicate a natural source or crusted origin, and a possible mobilization or depletion of metals, whereas EF>1.0 indicates that the element is of anthropogenic origin [69].
Five further contamination categories are generally recognized on the basis of the enrichment factor: EF<2, depletion to mineral enrichment; 2≤EF<5, moderate enrichment; 5≤EF<20, significant enrichment; 20≤EF<40, very high enrichment; and EF>40, extremely high enrichment [48].

2.7. Pollution load index (PLI)

The PLI is obtained as a concentration factor of each heavy metal with respect to the background value in the soil. The PLI can give an estimate of the metal contamination status and the necessary action that should be taken. The pollution load index (PLI) was proposed by Tomlinson et al., [52], for detecting pollution which permits a comparison of pollution levels between sites and at different times. The PLI value of > 1 is polluted, whereas <1 indicates no pollution. Pollution load index (PLI) is calculated using the equation:

$$PLI = n\sqrt{(CF1xCF2xCF3x\ldots xCFn)}$$

Where, CF represents the contamination factor, and n represents number of metals.
The sum of contamination factors for all elements examined represents the contamination degree (C_{deg}) of the environment and four classes are recognized [25]. $C_{deg} < 8$ low degree of contamination $8 \leq C_{deg} < 16$ moderate degree of contamination $16 \leq C_{deg} < 32$ considerable degree of contamination $32 \leq C_{deg}$ very high degree of contamination

2.8. Health risk assessment

For the assessment of health risks through ingestion of the top soils at the individual school playgrounds by children, the daily intake of metal (DIM) (that estimates the total dose entering the human body through oral ingestion of contaminated soil), and systemic toxicity or non-carcinogenic hazard for each metal were calculated using the following equations:

$$\text{Daily oral intake of soil (DI) (mg/kg/day)} = \frac{C \times IR \times EF \times ED}{BW \times AT}$$

Where C represents concentration of the metal in the school playground soils (mg/kg), IR represents ingestion rate (mg/kg), EF represents exposure frequency (day/year), ED = exposure period (year), AT represents average time for non-carcinogens and BW = body weight (kg) [33]. This gives the total dose entering the human body through oral ingestion of contaminated soil.
The systemic toxicity or non-carcinogenic hazard for a single element is expressed as the hazard quotient:

$$\text{Non-cancer Hazard Quotient (HQ)} = \frac{DI(mg/kg/day)}{ORfd}$$

Where DI represents the daily oral intake of soil ORfd represents is oral reference dose for the element. In the case where ORfd is not available for a particular metal, the ORfc (oral reference concentration) is utilized.
Total chronic hazard index which is the summation of all the individual hazard quotients is represented as below:

$$\text{Total Chronic Hazard Index (THI)} = \sum_{i=1}^{n} HQ$$

The greater is the value of HQ and THI above 1, the greater is the level of concern since the accepted standard is 1.0 at which there will be no significant health hazard [23]. The probability of experiencing long-term health hazard effects increases with the increasing THI value [60].

3. Results

Table 1: Mean Content of Heavy Metals at Different School Study Sites at Obio-Akpor LGA Rivers State

		CSPS	MOM	UPE	RBPS	OPS	ASPS	UDSC	SCUA	FCUA	UDPS
Cd	Test	0.54±.045	0.56±0.13	0.74±0.10	0.52±0.09	0.67±0.16	0.66±0.03	0.66±0.20	0.67±0.15	0.49±0.13	0.73±0.08
	Control	0.68±0.15	0.79±0.15	0.91±0.08	0.59±0.35	0.94±0.16	0.88±0.03	0.94±0.25	0.96±0.03	0.56±0.40	0.93±0.10
	Standard	1.56±1.36	1.56±1.36	1.56±1.36	1.56±1.36	1.56±1.36	1.56±1.36	1.56±1.36	1.56±1.36	1.56±1.36	1.56±1.36
As	Test	0.09±0.04	0.11±0.02	0.10±0.01	0.05±0.01	0.10±0.02	0.06±0.02	0.05±0.01	0.11±0.05	0.13±0.05	0.05±0.01
	Control	0.06±0.01	0.10±0.04	0.07±0.01	0.04±0.01	0.04±0.02	0.04±0.00	0.02±0.00	0.05±0.01	0.06±0.02	0.03±0.01
	Standard	8.33±10.3	8.33±10.3	8.33±10.3	8.33±10.3	8.33±10.3	8.33±10.3	8.33±10.3	8.33±10.3	8.33±10.3	8.33±10.3
Pb	Test	6.62±0.41	5.23±0.23	7.26±0.12	6.94±0.08	8.34±0.23	7.05±0.37	5.88±0.91	6.57±0.42	6.25±0.17	5.07±0.85
	Control	5.04±1.48	4.14±0.24	3.35±0.48	7.64±0.74	5.82±0.18	4.77±0.56	3.13±0.70	5.41±0.67	4.64±0.65	2.79±0.71
	Standard	19.66±5.50	19.66±5.50	19.66±5.50	19.66±5.50	19.66±5.50	19.66±5.50	19.66±5.50	19.66±5.50	19.66±5.50	19.66±5.50
Hg	Test	0.05±0.01	0.04±0.00	0.05±0.00	0.09±0.00	0.06±0.02	0.06±0.01	0.07±0.00	0.04±0.02	0.05±0.00	0.11±0.03
	Control	0.05±0.02	0.05±0.01	0.03±0.00	0.06±0.00	0.02±0.00	0.02±0.00	0.04±0.01	0.03±0.00	0.03±0.01	0.06±0.00
	Standard	0.49±0.47	0.49±0.47	0.49±0.47	0.49±0.47	0.49±0.47	0.49±0.47	0.49±0.47	0.49±0.47	0.49±0.47	0.49±0.47
Cu	Test	13.81±0.54	15.04±1.91	14.98±0.70	15.96±1.89	14.05±1.77	12.74±0.43	13.78±0.85	14.51±1.33	14.09±0.96	12.77±1.26
	Control	4.81±1.58	5.62±1.39	5.03±0.42	5.74±0.67	5.93±1.43	5.75±0.54	6.73±1.06	6.36±1.16	6.21±1.47	6.34±0.76
	Standard	38.0±21.3	38.0±21.3	38.0±21.3	38.0±21.3	38.0±21.3	38.0±21.3	38.0±21.3	38.0±21.3	38.0±21.3	38.0±21.3

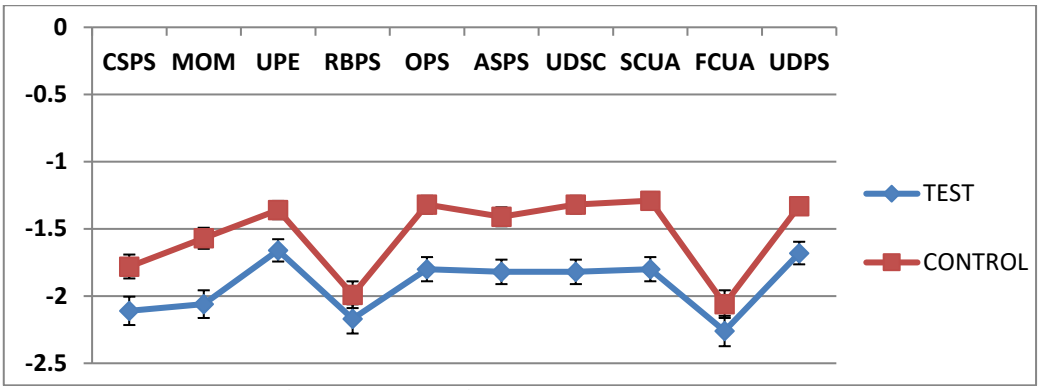

Fig. 1: Index of Geoaccumulation of Cadmium in Soil Samples at Obio-Akpor LGA.

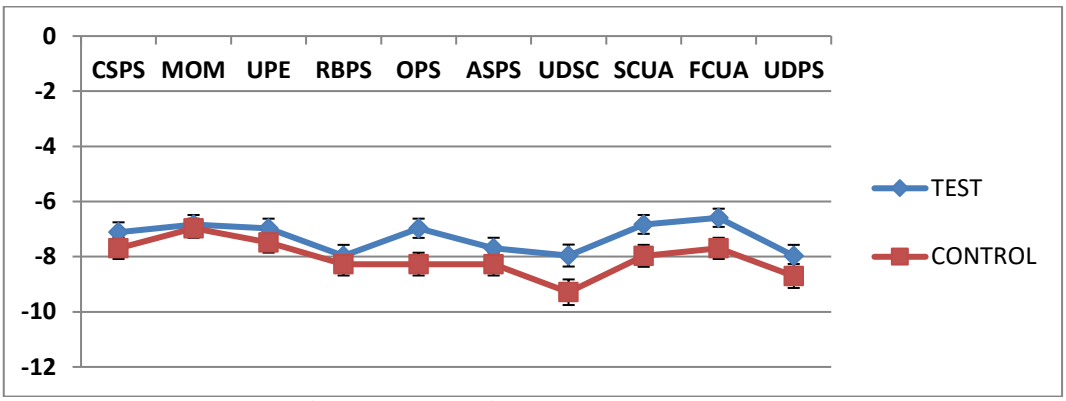

Fig. 2: Index of Geoaccumulation of Arsenic in Playgrounds at Obio-Akpor LGA.

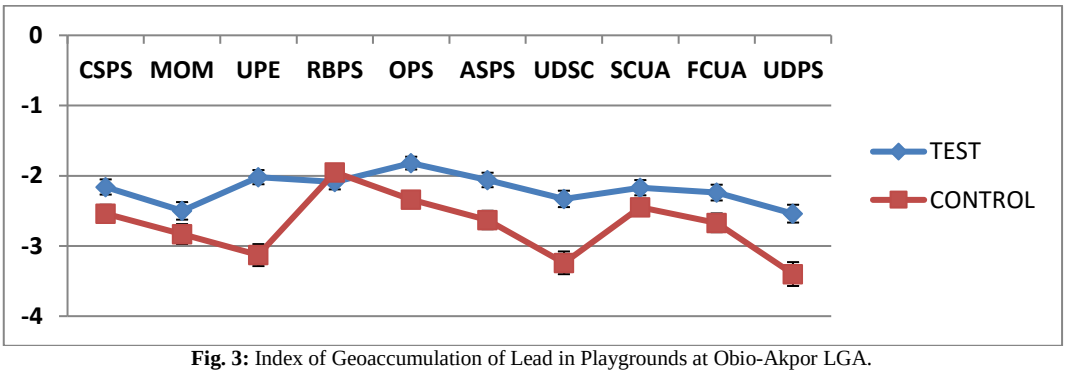

Fig. 3: Index of Geoaccumulation of Lead in Playgrounds at Obio-Akpor LGA.

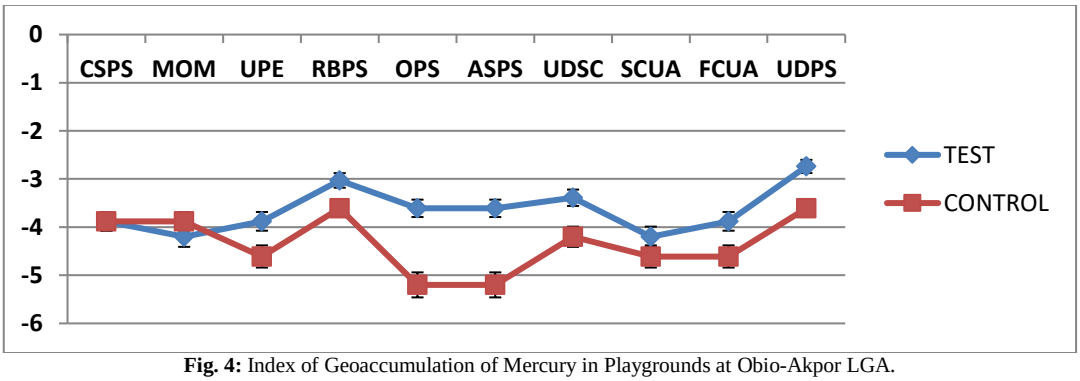

Fig. 4: Index of Geoaccumulation of Mercury in Playgrounds at Obio-Akpor LGA.

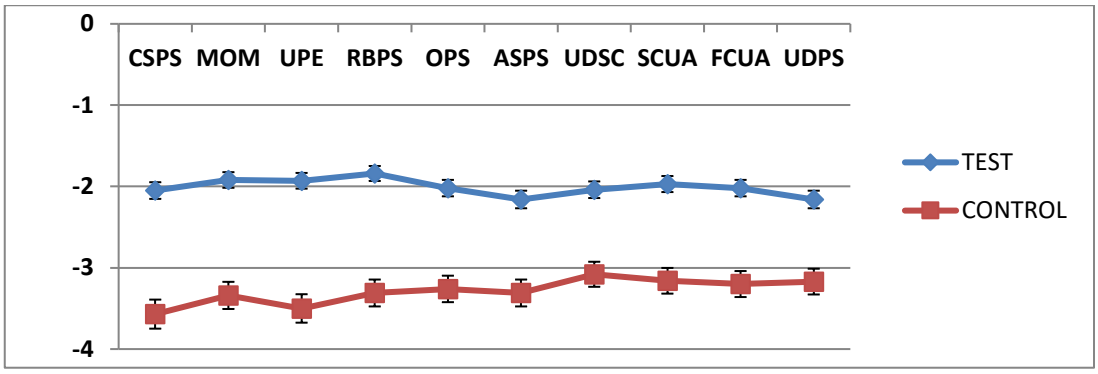

Fig. 5: Index of Geoaccumulation of Copper in Playgrounds at Obio-Akpor LGA.

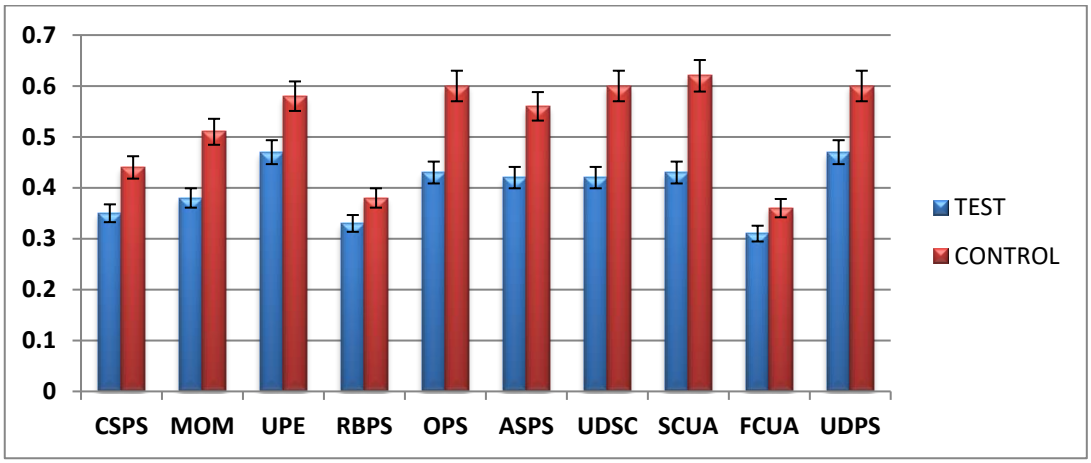

Fig. 6: Contamination Factor of Cadmium in Playgrounds at Obio-Akpor LGA.

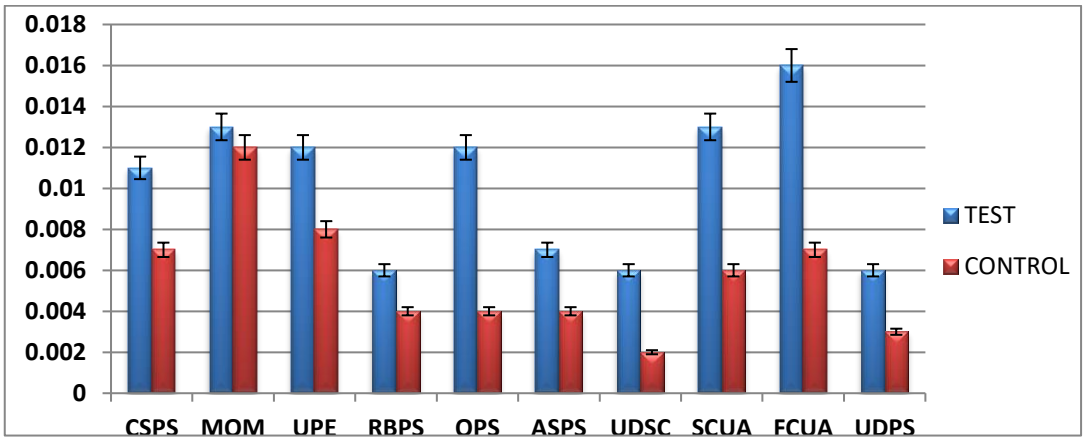

Fig. 7: Contamination Factor of Arsenic in Playgrounds at Obio-Akpor LGA.

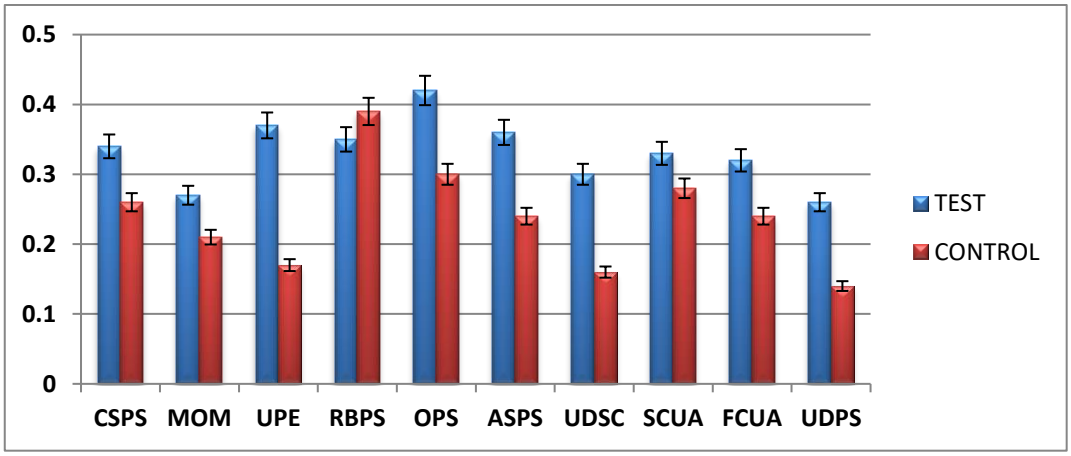

Fig. 8: Contamination Factor of Lead in Playgrounds at Obio-Akpor LGA.

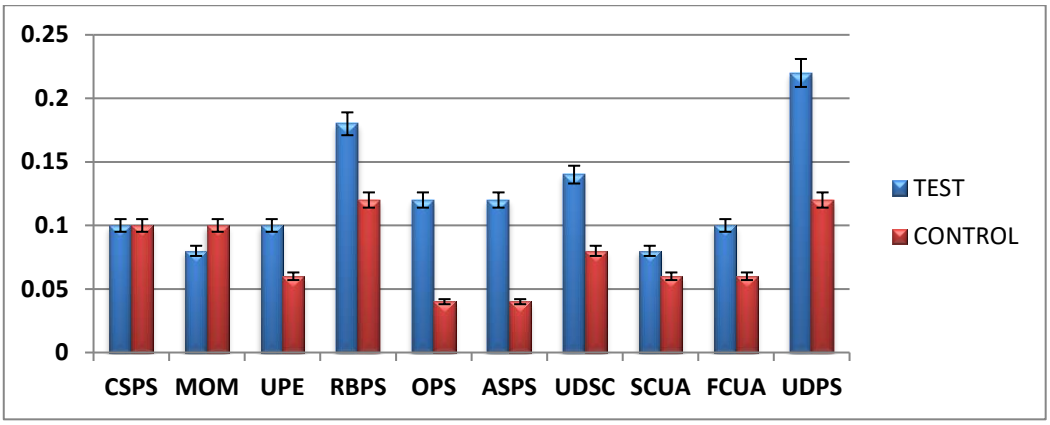

Fig. 9: Contamination Factor of Mercury in Playgrounds at Obio-Akpor LGA.

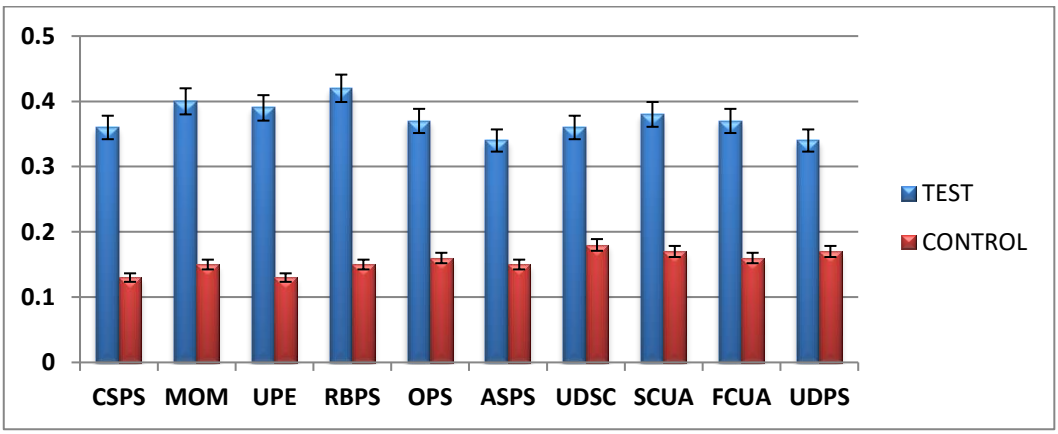

Fig. 10: Contamination Factor of Copper in Playgrounds at Obio-Akpor LGA.

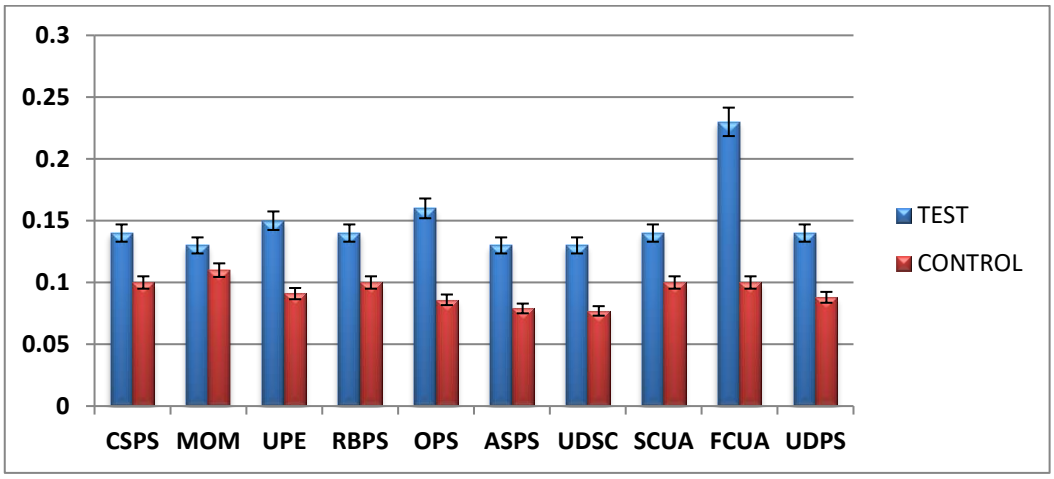

Fig. 11: Pollution Load Index of School Playgrounds in Obio-Akpor LGA.

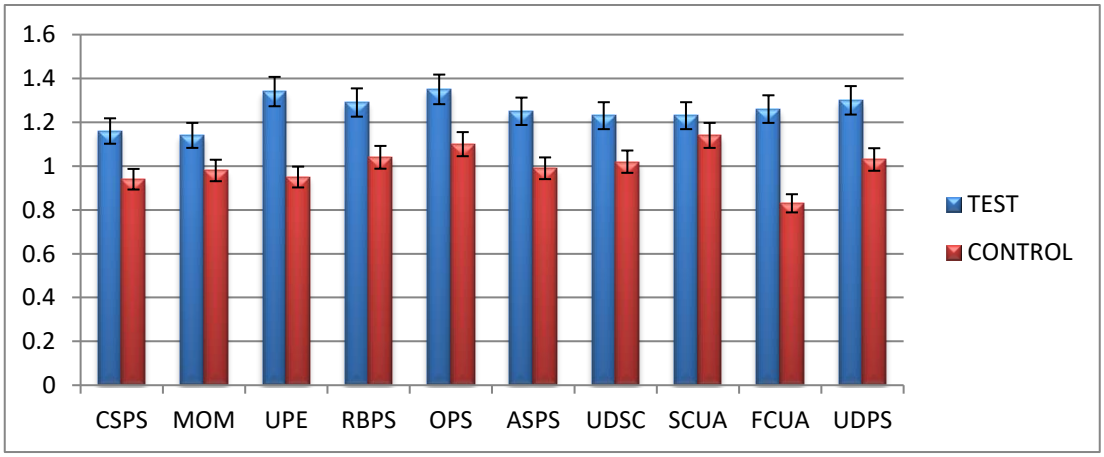

Fig. 12: Degree of Contamination of Heavy Metals at School Playgrounds in Obio-Akpor LGA.

Table 2: Enrichment Factor of Heavy Metals at School Playgrounds in Obio-Akpor LGA

Heavy Metals	CSPS	MOM	UPE	RBPS	OPS	ASPS	UDSC	SCUA	FCUA	UDPS
Cd	0.79	0.71	0.81	0.88	0.71	0.75	0.70	0.69	0.88	0.78
As	1.5	1.1	1.43	1.25	2.5	1.5	2.5	2.2	2.17	1.67
Pb	1.31	1.26	2.17	0.91	1.43	1.48	1.88	1.21	1.35	1.82
Hg	1.00	0.8	1.67	1.50	3.00	3.00	1.75	1.33	1.67	1.83
Cu	2.87	2.68	2.98	2.78	2.37	2.21	2.05	2.28	2.27	2.01

Table 3: Average Daily Intake of Heavy Metals at School Playgrounds in Obio-Akpor LGA

Heavy Metals	CSPS $x10^{-6}$	MOM $x10^{-6}$	UPE $x10^{-6}$	RBPS $x10^{-6}$	OPS $x10^{-6}$	ASPS $x10^{-6}$	UDSC $x10^{-6}$	SCUA $x10^{-6}$	FCUA $x10^{-6}$	UDPS $x10^{-6}$	Reference mg/kg/day
Cd	1.77	1.84	2.43	1.71	2.20	2.17	2.17	2.20	1.61	2.40	1 $x10^{-3}$ (ORfD) [51]
As	0.30	0.36	0.33	0.16	0.33	0.20	0.16	0.36	0.42	0.16	3 $x10^{-4}$ (ORfD) [53]
Pb	21.77	17.21	23.89	22.83	27.44	23.19	19.35	21.62	20.56	16.68	3.5 $x10^{-3}$ (ORfD) [1]
Hg	0.16	0.13	0.16	0.29	0.20	0.20	0.23	0.13	0.16	0.36	4 $x10^{-5}$ (ORfC) [53]
Cu	45.43	49.48	49.28	52.50	46.22	41.91	45.34	47.73	46.36	42.01	1 $x10^{-2}$ (ORfD) [2]

*ORfD: Oral Reference Dose, ORfC: Oral Reference Concentration.

Table 4: Non Cancer Hazard Quotient and Total Hazard Index of Heavy Metals at School Playgrounds in Obio-Akpor LGA

Heavy Metals	CSPS	MOM	UPE	RBPS	OPS	ASPS	UDSC	SCUA	FCUA	UDPS
Cd $x10^{-3}$	1.77	1.84	2.43	1.71	2.20	2.17	2.17	2.20	1.61	2.40
As $x10^{-2}$	0.10	0.12	0.11	0.0533	0.110	0.0667	0.0533	0.120	0.140	0.053
Pb $x10^{-3}$	6.22	4,92	6.83	6.52	7.84	6.63	5.53	6.18	5.87	4.77
Hg $x10^{-1}$	0.040	0.0325	0.040	0.0725	0.050	0.050	0.0575	0.0325	0.040	0.090
Cu $x10^{-4}$	45.43	49.48	49.28	52.50	46.22	41.91	45.34	47.73	46.36	42.01
THI	0.0175	0.0162	0.0193	0.0213	0.0207	0.0187	0.0185	0.0176	0.0175	0.0209

4. Discussion

The results of the heavy metal contents of the different soil samples are shown in Table 1. The mean cadmium content in the test soil samples were lower than the values for the control samples and baseline values shown in Table 1. The average cadmium content of the soil samples was relatively lower than the contents of cadmium in sands from Rabka's Zdrój playgrounds [8].

The levels of arsenic for the playgrounds were found within the range 0.05mg/kg±0.01 to 0.13mg/kg±0.05 which was below the standard baseline values used for arsenic as shown in Table 1. The arsenic content of the control values were slightly lower than the values recorded for the playgrounds, and were also within the baseline values. The playground soil sample at FCUA recorded the highest arsenic content, and was observed greater than two of the sampling sites at Rabka's Zdrój playgrounds reported by Alicja and Agnieszka, [8]. However, the mean contents of arsenic in soil samples in urbanized area soils of Dongguan [65], and soils in Beijing [66] were found to occur higher than the cadmium content of soil samples reported in this study.

Similarly, the concentration of lead recorded in Table 1 for both the test and control samples were found lower than the baseline values. The lead content of minor roads within Suleja town, reported by Yisa et al., [68] were higher than the lead contents of the playground soil samples evaluated in this study. Also, the lead content of most popular cities like Oslo [18], Hong Kong [67], Shangai [44], and N. Zealand [21], were all found greater than the concentration of lead in both test and control samples reported in this study. The high levels of lead found in UPE and OPS might have resulted from the falling off of paint chippings on the playground soils due to diminished longevity of the paints on the walls of these schools. Lead from house paints has been found to confer a major influence on the blood levels of lead in cadmium between the ages of 6-35 months [64].

The mercury content of playground soils at UDPS was found greater than the remaining study sites. However, the amount of mercury deposition on this site was still below the baseline values as shown in Table 1. Mercury deposition on these soil samples may have resulted from electrical materials such as thermostats, switches, and some preservatives, on or around the study sites. Mercury has been reported to induce neurotoxicity, nephrotoxicity, and gastrointestinal toxicity [50]

The range of copper contents of the playground soil samples were between 12.74mg/kg±0.43 to 15.96mg/kg±1.90 as shown in Table 1, and these values were within the baseline values for copper. The copper content of the soil samples of four study sites reported by Yisa et al., [68] were observed to be greater than the copper content of the playground soils. However, the copper content of Abdulahi Zuba road reported by Yisa et al., [68] were found lower than the values of playground soils presented in this study but were comparable to the values for the control samples.

Further, from the data presented in Fig. 1, the index of geoaccumulation of cadmium in the test sites were lower than their corresponding control sites, with the least cadmium contamination occurring at FCUA and RBPS. There was an observable slightly marginal difference in the geoaccumulation index of arsenic (Fig. 2), lead (Fig. 3), and mercury (Fig. 4), between the test and control samples. Only the geoaccumulation index of copper at the playgrounds conspicuously differed from the geoaccumulation index of copper at the soil samples obtained 100m away (control) as shown in Fig. 5. From the classification of Nriagu, [35] since none of the evaluated soil samples in this study exceeded zero for the geoaccumulation index, then both the test and control study sites are regarded as unpolluted with the evaluated heavy metals.

The extent of contamination of these soil samples were evaluated using the contamination and enrichment factors initially applied to ascertain the source of elements found in seawaters, precipitation, or atmosphere [19], but now used for the analysis of the extent of contamination of soil sediments, tailings, lakes, and peats. The contamination factors of the heavy metals at the different study sites were shown in Fig. 6, Fig. 7, Fig. 8, Fig. 9, and Fig. 10. All the contamination factors occurred below 1 implying that the study sites had low contamination of these heavy metals.

The pollution load index for the study sites was shown in Fig. 11, to ascertain the overall pollution status. The pollution load index for all the study sites were less than 1, indicating that the study sites were unpolluted with the heavy metals assessed. In addition, the data presented in Fig. 12 shows that the degree of contamination of the study sites were below 2, meaning that the study sites had a low degree of contamination with respect to the classification of Hankanson, [25].

The enrichment factors of the heavy metals were presented in Table 2. In addition to the application of enrichment factors for the determination of the magnitude of contamination, they are equally used to ascertain the source of the heavy metal contamination. The enrichment factors for cadmium at all the study sites in this study were less than 1. Then, from the classification of Zsefer et al., [69] the source of deposition of cadmium on the top soils of all the study sites was purely of natural or crusted origin. Further, the enrichment factors of arsenic lead, mercury, and copper at all the study sites were greater than 1, indicating that the source of deposition of these heavy metals was purely of anthropogenic origin.

Also, applying the classification of Sutherland [48], only the enrichment factors of mercury in OPS and ASPS, and copper at all the study sites had moderate enrichment, whereas all other heavy metals at their respective study sites had depletion to mineral enrichment.

The daily oral intakes of cadmium, arsenic, lead, mercury, and copper are presented in Table 3. The cadmium and arsenic daily intake levels were found lower than their respective oral reference doses shown in Table 3. It is very imperative to have a daily intake level of these heavy metals below their oral reference doses. Cadmium is a widely recognized metal that promotes different kinds of reproductive toxicities. Rossman et al., [38] have observed the alterations of male reproduction in mice at administration of 1mg/kg body weight of cadmium. Furthermore, some products of arsenic have been reported to induce alterations of male leukocytes [39], and in human lymphocytes [11]. In addition, the daily intake levels of lead, mercury, and copper evaluated in this study were observed to have occurred below their respective oral reference doses presented in Table 3. The non-carcinogenic quotient of these heavy metals, and the total hazard index of the study sites are presented in Table 4. The results of the hazard quotient pointed out that lead in general, portends the greatest toxic hazards of oral exposure to the school children. This could have resulted from the common usage of lead batteries, metal products, paint coatings, and pipes around the playgrounds. However, by the guide provided by Wang et al., [61] no heavy metal indicated any carcinogenic risk as the entire hazard quotient values for the heavy metals was less than 1.

5. Conclusion

In this study, the concentration of Cd, As, Pb, Hg, and Cu was evaluated in top soils of children playgrounds at schools in Obio-Akpor LGA Rivers State. Index analysis using enrichment, contamination factor and degree, metal pollution and geoaccumulation index, non-cancer and total hazard index were applied successfully to assess the heavy-metal contamination of the top soils at the study sites. In comparison with the standard baseline values, the results in general showed that the sites were unpolluted and had low contamination of the evaluated heavy metals. Consequently, the risk assessment carried out showed no potent toxic risks associated with the level of occurrence of these heavy metals on the children's playgrounds. Since anthropogenic activities were found to be the major source of majority of the heavy metals on the playground soils, it is recommended that the assessments of the playgrounds for heavy metals be regularly undertaken.

References

[1] Agency for Toxic Substances and Disease Registry (ATSDR) (2005) Toxicological profile for lead—draft for public comment, Atlanta, GA

[2] Agency for Toxic Substances and Disease Registry (ATSDR). (1992). Case Studies in Environmental Medicine - Lead Toxicity. Atlanta: Public Health Service, U.S. Department of Health and Human Services.

[3] Agency for Toxic Substances and Disease Registry (ATSDR). (1999). Public Health Service. Atlanta: U.S. Department of Health and Human Services. Toxicological Profile for Lead.

[4] Agency for Toxic Substances and Disease Registry (ATSDR). (2000). Toxicological Profile for Arsenic TP-92/09. Georgia: Center for Disease Control, Atlanta.

[5] Agency for Toxic Substances and Disease Registry, (ATSDR) (2004). https://www.atsdr.cdc.gov/ mrls/mrllist.asp# 37tag

[6] Åkesson, A., Bjellerup, P., Lundh, T., Lidfeldt, J., Nerbrand, C. and Samsioe, G. (2006). Cadmium-induced effects on bone in a population-based study of women. Environ Health Perspect.; 114:830–834. [PubMed: 16759980] https://doi.org/10.1289/ehp.8763.

[7] Akoto, O., Ephraim, J.H. and Darko, G. (2008). Heavy metal pollution in surface soils in the vicinity of abundant railway servicing workshop in Kumasi, Ghana. *Int. J. Environ. Res.* 2(4):359-364

[8] Alicja K. and Agnieszka K. (2015). Risk assessment of heavy metals in children's playgrounds in the Rabka Zdrój health resort. *Environmental protection and natural resources*, 26 4(66): 15-19.

[9] Aliyu, M., Zakari, Y.I., Ibeanu, I.G.E. and Akpa T.C. (2009) Evaluation of lead concentration levels of children's playground in Kaduna state schools, Bayero. *Journ. of Pure and Appl. Sc.,* 2(2), 105–109

[10] Alloway, B.J. (1995). Heavy Metals in Soils, Blackie Academic and Professional, London. https://doi.org/10.1007/978-94-011-1344-1.

[11] Anderson, D., Yu, T.W., Phillips, B.J. and Schemezer, P. (1994). The effect of various antioxidants and other modifying agents on oxygen-radical-generated DNA damage in human lymphocytes in the Comet assay. *Mutation Res*. 307:261–271. [PubMed: 7513806] https://doi.org/10.1016/0027-5107(94)90300-X.

[12] Apostoli, P., Kiss, P., Stefano, P., Bonde, J.P. and Vanhoorne, M. (1998). Male reproduction toxicity of lead in animals and humans. *Occup Environ Med*. 55:364–374. [PubMed: 9764095] https://doi.org/10.1136/oem.55.6.364.

[13] Baselt, R.C. and Cravey, R.H. (1995). Disposition of Toxic Drugs and Chemicals in Man. 4th Edn. Chicago, IL: Year Book Medical Publishers. p. 105-107.

[14] Biasioli M, Grcman H, Kralj T, Madrid F, Dıaz- Barrientos E and Ajmone-Marsan F., Potentially toxic elements contamination in urban soils: A comparison of three European cities, J. Environ. Qual., 36, 70–79 (2007) https://doi.org/10.2134/jeq2006.0254.

[15] Centeno, J.A., Tchounwou., P.B., Patlolla, A.K., Mullick, F.G., Murakat, L., Meza, E., Gibb, H., Longfellow, D. and Yedjou, C.G. (2005). Environmental pathology and health effects of arsenic poisoning: a critical review. In: Naidu, R.; Smith, E.; Smith, J.; Bhattacharya, P., editors. Managing Arsenic In the Environment: From Soil to Human Health. Adelaide, Australia: CSIRO Publishing Corp.

[16] Environmental Fact Sheet. (2005). Copper: Health Information Summary. New Hampshire Department of Environmental Services, ARD-EHP-9, Available Online at: http://des.nh.gov/organization/commissioner /pip/factsheets/ard/documents/ard-ehp-9.pdf

[17] Curtis D. Klassen, Casarett & Doull's Toxicology, the Basic Science of Poisons, Fifth Edition, McGraw-Hill, New York. pp 715

[18] De Miguel, E., Llamas, J.F., Chacon, E. Berg, T. Larssen, S. R›yset, O. and Vadset, M. (1997). Origin and patterns of distribution of trace elements in street dust: unloaded petrol and urban lead. *Atmos Environ*., 31: 2733-2740. https://doi.org/10.1016/S1352-2310(97)00101-5.

[19] Duce, R.A., Hoffmann, G.L., Zoller, W.H. (1975). Atmospheric trace metals at remote northern and southern Hemisphere sites: Pollution or natural? *Science*.187: 59–61 https://doi.org/10.1126/science.187.4171.59.

[20] Facchinelli, A., Sacchi, E. and Malleri, L. (2001). Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. *Enviro. Pollut*. 114:313-324. https://doi.org/10.1016/S0269-7491(00)00243-8.

[21] Fergussion, J.E. and Kim, N.D. (1991). Trace elements in street and house dusts: Source and Speciation. *Sci. Total Environ*, 100: 125-150 https://doi.org/10.1016/0048-9697(91)90376-p.

[22] Gallagher, C.M., Kovach, J.S. and Meliker, J.R. (2008). Urinary cadmium and osteoporosis in U.S. women ≥ 50 years of age: NHANES 1988–1994 and 1999–2004. *Environ Health Perspect*. 116:1338– 1343. [PubMed: 18941575] https://doi.org/10.1289/ehp.11452.

[23] Grzetic, I. and Ghariani, R.H.A. (2008). Potential health risk assessment for soil heavy metal contamination in the central zone of Belgrade (Serbia). *J. Serb. Chem. Soc*., 73 (8-9): 923-934 https://doi.org/10.2298/jsc0809923g.

[24] Guvenc, N., Alagha, O. and Tencel, G. (2004). Investigation of soil multielement composition in Antalya, *Turkry. Environ. Int*. 29:631-640. https://doi.org/10.1016/S0160-4120(03)00046-1.

[25] Håkanson, L. (1980). An ecological risk index for aquatic pollution control-a sedimentological approach. *Water Res.*, 14: 975-1001. https://doi.org/10.1016/0043-1354(80)90143-8.

[26] Horsfall, M. J. (2011). Chemistry and heavy metals are Janus faced, An inaugural lecture series no. 81st, Department of pure and Industrial chemistry, university of Port Harcourt, November

[27] Information for Advocacy and Action. (1997). UNICEF Childhood Lead Poisoning. 3 UN Plaza, New York, NY 10017, U.S.A.

[28] Isaac, R., Santos, E.V., Silva-Filho, C.E., Schaefer, M.R. and Albuquerque- Filho, L.S. (2004). Heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. Marine Pollution Bulletin (in press).

[29] Jonathan, M.P., Ram-Mohan, V. and Srinivasalu, S. (2004). Geochemical variation of major and trace elements in recent sediments of the Gulf of Mannar the southeast coast of India. *Environ. Geol.* 45(4):466-480. https://doi.org/10.1007/s00254-003-0898-7.

[30] Kabata-Pendias, A. and Mukherjee, A.B. (2007). Trace Elements from Soil to Human, Springer-Verlag, Berlin. https://doi.org/10.1007/978-3-540-32714-1.

[31] Kaul, B., Sandhu, R.S., Depratt, C. and Reyes, F. (1999). Follow-up screening of lead-poisoned children near an auto battery recycling plant, Haina, Dominican Republic. *Environ Health Perspect*. 107(11):917–920. [PubMed: 10544160] https://doi.org/10.1289/ehp.99107917.

[32] Krishna, A.K. and P.K. Govil, (2007). Soil Contamination due to Heavy Metals from an Industrial Area of Surat, Gujarat, Western India. *Environ Moni Assess*, 124: 263-275. https://doi.org/10.1007/s10661-006-9224-7.

[33] Lack, J.A. andStuart-Taylor, M.E. (1997) Calculation of drug dosage and body surface area of children. *British Journal of Anaesthesia*, 78, 601–605 https://doi.org/10.1093/bja/78.5.601.

[34] Muller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. *J. Geol*. 2:108-118

[35] Nriagu, J.O. (1989). A global assessment of natural sources of atmospheric trace metals. *Nature*. 338:47–49 https://doi.org/10.1038/338047a0.

[36] Nriagu, J.O. (1996). A history of global metal pollution. *Science, New Series*. 272(5259):223-224.

[37] Palmeira, C.M. and Madeira, V.M.C. (1997). Mercuric chloride toxicity in rat liver mitochondria and isolated hepatocytes. *Environ Toxicol Pharmacol*. 3:229–235. [PubMed: 21781782] https://doi.org/10.1016/S1382-6689(97)00018-5.

[38] Rossman, T.G., Roy, N.K., Lin, W.C. (1992). Is cadmium genotoxic? IARC Sci Publ. 118:367–375. [PubMed: 1303963]

[39] Saleha Banu, B., Danadevi, K., Kaiser, J., Ahuja, Y.R., Visweswara, R.K. and Ishap, M. (2001). In vivo genotoxic effect of arsenic trioxide in mice using comet assay. *Toxicol*. 162:171–177. https://doi.org/10.1016/S0300-483X(01)00359-6.

[40] Sandstead, H.H. (1995). "Requirements and toxicity of essential trace elements, illustrated by zinc and copper". *Am. J. Clin. Nutr*. 61 (3 Suppl): 621S–624S. PMID 7879727

[41] Sarkar, B.A. (2005). Mercury in the environment: Effects on health and reproduction. *Rev Environ Health*. 20:39–56. [PubMed: 15835497]

[42] Schutte, R., Nawrot, T.S., Richart, T., Thijs, L., Vanderschueren, D. and Kuznetsova, T. (2008). Bone resorption and environmental exposure to cadmium in women: a population study. *Environ Health Perspect.* 116:777–783. [PubMed: 18560534] https://doi.org/10.1289/ehp.11167.

[43] Shakery, A., Farid, M. and Razikordmahalleh, L. (2010) Distribution of soil heavy metal contamination around industrial complex zone, Shiraz, Iran 2010 19th World Congress of Soil Science, Soil Solutions for a Changing World 1 – 6 August, Brisbane, Australia. Published on DVD.

[44] Shi, G., Chen, S. Xu, S. Zhang, J. Wang, C. and Bi, J. (2008). Potentially toxic metal contamination of urban soils and roadside dust in Shanghai, China. *Environ. Potential*, 156: 251-260

[45] Silveira, M. L., Luís, R. F. and Guilherme L. (2003). Biosolids and heavy metals in soils. *Scientia Agricola*, 60 (4), p.793-806. https://doi.org/10.1590/S0103-90162003000400029.

[46] Singhal, R.L., Merali, Z., Hrdina, P.D. (1976). Aspects of the biochemical toxicology of cadmium. Fed Proc.; 35(1):75–80. [PubMed: 173584]

[47] Stohs, B. (1995). Oxidative mechanisms in the toxicity of metal ions. *Free Radic Biol Med*. 18:321–336. [PubMed: 7744317] https://doi.org/10.1016/0891-5849(94)00159-H.

[48] Sutherland, R.A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*.39: 611–627 https://doi.org/10.1007/s002540050473.

[49] Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K. and Sutton, D. J. (2012) "Heavy metal toxicity and the environment,"Molecular, *Clinical and Environmental Toxicology Experientia Supplementum*, 101, pp. 133–164. https://doi.org/10.1007/978-3-7643-8340-4_6.

[50] Tchounwou, P.B., Ayensu, W.K., Ninashvilli, N. and Sutton, D. (2003). Environmental exposures to mercury and its toxicopathologic implications for public health. *Environ Toxicol*.; 18:149–175. [PubMed: 12740802] https://doi.org/10.1002/tox.10116.

[51] Tchounwou, P.B., Wilson, B. and Ishaque, A. (1999). Important considerations in the development of public health advisories for arsenic and arsenic-containing compounds in drinking water. *Rev Environ Health*. 14(4):211–229. [PubMed: 10746734] https://doi.org/10.1515/REVEH.1999.14.4.211.

[52] Thomilson, D.C., Wilson, D.J., Harris, C.R. and Jeffrey, D.W. (1980). Problem in heavy metals in estuaries and the formation of pollution index. *Helgol Wiss Meeresunlter*, 33(1-4):566-575. https://doi.org/10.1007/BF02414780.

[53] Trouba, K.J., Wauson, E.M. and Vorce, R.L. (2000). Sodium arsenite-induced dysregulation of proteins involved in proliferative signaling. *Toxicol Appl Pharmacol*. 164(2):161–170. [PubMed: 10764629] https://doi.org/10.1006/taap.1999.8873.

[54] Turekian, K.K. and Wedepohl, K.H. (1961). Distribution of the elements in some major units of the earth's crust. *Bull. Geo. Soc. Am*., 72, 175–192. https://doi.org/10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2.

[55] United States Environmental Protection Agency (U.S. EPA). (2002). Lead Compounds. Technology Transfer Network- Air Toxics Website.. Online at: http://www.epa.gov/cgi-bin/ epaprintonly.cgi

[56] United States Environmental Protection Agency (USEPA). (1987). Integrated Risk Information System (IRIS), Washington, DC 20005, Available from http:// www.epa.gov/ncea/iris/

[57] United States Environmental Protection Agency (USEPA). (1995). Integrated Risk Information System (IRIS), Washington, DC 20005, Available from http:// www.epa.gov/ncea/iris/

[58] Valko, M., Morris, H. and Cronin, M.T.D. (2005). Metals, Toxicity, and oxidative Stress. *Curr Medici Chem*. 12:1161–1208. https://doi.org/10.2174/0929867053764635.

[59] Waalkes, M.P. and Rehm, S. (1992). Carcinogenicity of oral cadmium in the male Wistar (WF/NCr) rat: effect of chronic dietary zinc deficiency.*Fundam Appl Toxicol*.; 19:512. [PubMed: 1426709] https://doi.org/10.1016/0272-0590(92)90089-Z.

[60] Wang, X., Wang, F., Chen, B., Sun, F., He, W., Wen, D., Liu, X. and Wang, Q. (2012). Comparing the health risk of toxic metals through vegetable consumption between industrial polluted and non-polluted fields in Shaoguan, South China. *Journal of Food, Agriculture & Environment*, 10(2): 943-948

[61] Wang, Z. and Rossman, T.G. (1996). The Toxicology of Metals. Cheng, LW, editor. Vol. Vol. 1. Boca Raton, FL: CRC Press;. p. 221-243.

[62] Wilson, B., Lang, B. and Pyatt, B.F. (2005). The dispersion of heavy metals in the vicinity of Britannia Mine, British Columbia, Canada. *Ecotoxicol. and Environ. Safety*, 60(3):269-276. https://doi.org/10.1016/j.ecoenv.2004.04.005.

[63] Wilson, D.N. (1988). Association Cadmium. Cadmium - market trends and influences; London. Cadmium 87 Proceedings of the 6th International Cadmium Conference;. p. 9-16.

[64] Wright, N.J., Thacher, T.D. Pfitzner, M.A. Fischer P.R. and Pettifor, J.M. (2005). Causes of lead toxicity in a Nigerian city. *Arch Dis. Child*, 90: 262-626. https://doi.org/10.1136/adc.2003.043562.

[65] Wu, S., Siqing, P., Xuexia Z., Duilin, W., Wei L., Tianbin Z., Shungui Z., Guoyi Y., Hongfu W. and Leqin W. (2014). Levels and health risk assessments of heavy metals in urban soils in Dongguan, China *Journal of Geochemical Exploration*. S0375-6742(14), 00296-9. https://doi.org/10.1016/j.gexplo.2014.08.009.

[66] Yang, L. and Wu, S. (2012). Ecological risk assessment of heavy metal pollution in soil of Beijing. *Advanced Materials Research Vols 450-451 pp 827-831* https://doi.org/10.4028/www.scientific.net/amr.450-451.827.

[67] Yeung, Z.L.L., Kwok, R.C.W. and Yu, K.N. (2003). A multi-elemental profile of street dust using energy dispersion XRF. *Appl. RadiatIsot.*, 58: 339-346. https://doi.org/10.1016/S0969-8043(02)00351-2.

[68] Yisa, J., Jacob, J. and Onoyima C.C. (2012). Assessment of Toxic Levels of Some Heavy Metals in Road Deposited Sediments in Suleja, Nigeria *American Journal of Chemistry*, 2(2): 34-37 https://doi.org/10.5923/j.chemistry.20120202.08.

[69] Zsefer, P., Glasby, G.P., Sefer, K., Pempkowiak, J. and Kaliszan, R. (1996). Heavy-metal pollution in superficial sediments from the southern Baltic Sea off Poland. Journal Environmental Science Health, Part A*: Environmental Science and Engineering and Toxicology*.31:2723-2754.