



ORIGINAL ARTICLE

Distribution and Toxicological Risk Evaluation of Pb, Cd, As and Zn from Surface Soils of Selected Marts in Port Harcourt, Rivers State, Nigeria

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KEYWORDS

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ABSTRACT: It is very pertinent to carry out environmental studies for the assessment of human health risks associated with heavy metal accumulation of frequently visited environments. By Atomic Absorption Spectrophotometry, Lead (Pb), Zinc (Zn), Cadmium (Cd) and, Arsenic (As) were analyzed in top soil samples from Rumuokoro mart (RUM), Choba mart, Mile 3 mart, Mile 1 mart, Town mart (TM), Trans-Amadi mart (TRANS), Boundary mart (BOUND), Oil mill mart (OIL M), Eleme mart (ELE). The concentration of zinc was highest in the mart sites among the other metals. There was pollution with some of the heavy metals at some mart sites. The highest I_{geo} was found for cadmium at TRANS. The study further established contamination with some of the metals in some of the mart sites as very high contamination with arsenic was observed in RUM. The enrichment factor result obtained revealed that all the metals in all the mart sites occurred as a result of anthropogenic origin except that of lead in MILE 3 that was from natural activities. The levels of average daily intake of all the metals in all the sites were found to be below their respective reference doses. The highest average daily intake of all the metals investigated was observed in zinc at BOUND. No significant health hazard could result from the levels of the metals deposited in the study sites as they did not exceed the reference level at 1.0. RUM is observed as the likely mart site vulnerable to significant health hazards of all sites assessed. Regular environmental assessment should be performed in order monitor and regulate these metals in order to minimize health risks.

INTRODUCTION

Oil exploration, mineral exploitation, food processing, agricultural activities and other human activities have contributed greatly in endangering the environment and hence threaten the survival of humans and other organisms

[1]. Heavy metal deposition on water bodies and top soils is one of the implications of these activities. All over the world, heavy metal contamination poses a severe challenge because of their detrimental effects on ecosystem, animals

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and plants and their background concentration differs as a result of environmental factors and distinct characteristics across regions [2].

For the evaluation of heavy metal pollution, the soil is considered as a preeminent alternative because of prevalence of deposition of heavy metals on top soils. The soil entertains enormous sum of pollutants from diverse sources, for this reason it serves as reservoir for contaminants. In recent times, due to an elevation in the rate of heavy metal utilization for industrial and commercial purposes, exposure of humans to these metals is on the increase [3], and through this medium, they become part of animal and human food chain thus affecting them. Contamination of food products by heavy metals is a global phenomenon. Fruits and vegetables are more predisposed to heavy metal contamination from soil, waste water and air according to the findings of Adekunle *et al.* [4]. The increase in consumer consciousness about the implications of use of agrochemicals on human health is culpable for the shift in customers' fanaticism about the safety and quality of food materials. The trepidations for consumers on food safety and quality were motivated by food trade globalization and exhaustive agricultural pollution as a result of natural and anthropogenic activities [5]. However, apart from possible initial contamination of food products before transportation and/or perhaps during haulage to the mart, numerous activities in the mart vicinity as well as colossal environmental decay evident in the marts pose a troublesome confront to the consumers.

Rivers state is one of the states in Southern Nigeria predominantly known as the Niger Delta region. This region is known for abundance of crude oil and it accounts for majority of the country's revenue. An open mart system is adopted in this region where traders sample their goods openly and sell to consumers. These marts are characterized with numerous commercial activities and have been faced with a high proportion of infrastructural

putrefy, ridiculous refusal disposal system and lack of drainage due to lack of proper maintenance and management by the retailers and state government. These have threatened the safety of the populace who come in contact with these marts daily. Since some of the marts are located close to locations where huge industrial activities go on, heavy metal exposure from those sources is also feasible.

Taking into consideration, the activities that go on in these marts daily, this investigation was carried out to evaluate the heavy metal composition and health risks posed to the populace.

MATERIALS AND METHODS

Study area

Nine marts located within Port Harcourt, Obio Akpor and Eleme metropolis in Rivers State, Nigeria were used for this study (Figure 1). The soil samples were randomly collected in triplicates in two different segments tagged A and B. The test sample (sample A) was obtained at a point where substantial activities are carried out in the mart while sample B were obtained 100m away from the test site and constituted the control for comparison as reported by Agomuo and Amadi [6]. The marts used for this investigation include:

- Rumuokoro mart (RUM)
- Choba mart
- Mile 3 mart
- Mile 1 mart
- Town mart (TM)
- Trans-Amadi mart (TRANS)
- Boundary mart (BOUND)
- Oil mill mart (OIL M)
- Eleme mart (ELE)

high contamination, and $6 \leq C^i f$ represents very high contamination [10].

Estimation of enrichment factor (EF)

The enrichment factor was estimated as follows:

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

The EF values < 1 or close to unity indicate a natural source or crustal origin, and a possible mobilization or depletion of metals, whereas $EF \geq 1.0$ indicates that the element is of anthropogenic origin [11]. Five further contamination categories are generally recognized on the basis of the enrichment factor: $EF < 2$, depletion to mineral enrichment; $2 \leq EF < 5$, moderate enrichment; $5 \leq EF < 20$, significant enrichment; $20 \leq EF < 40$, very high enrichment; and $EF > 40$, extremely high enrichment [12].

Health risk assessment

For the assessment of health risks through ingestion of the mart top soils, 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 mart 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). The values for IR, EF, ED, BW and AT were as given in the study of Qing *et al.* [13]. The DI thus 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 [14], and is given as;

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

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. The probability of experiencing long term health hazard effects increases with the increasing THI value [15].

Statistical analysis

SPSS Software 20 (Chicago, IL, USA) was used for statistical analysis of obtained triplicate data. Mean values \pm SD were calculated and One-Way ANOVA test was performed. Significance level was calculated at 95% confidence level ($p < 0.05$) as reported by [16].

RESULTS AND DISCUSSION

The heavy metal contents of top soils of some marts in Port Harcourt, Rivers State, Nigeria are shown in Table 1. The concentration of lead was elevated in all the mart soil when compared to the control sites but they did not exceed the baseline values. A study by Ekere and Ukoha, [17] revealed that lead levels in the soil dust of an industrial mart ranged from 87.0 to 4.8 mg/kg, greatly higher than some earlier reported works by Rashad and Shalaly, [18] and Ayodele and Gaya, (19). By the actions of soldering workers and electrical smelting, lead enters soil dust. Lead has adverse effects on humans and animals and is noted as a toxin [20]. Its accumulation in the body organs like in the brain may lead to plumbism (poisoning) or worse, death. The central nervous system, gastrointestinal tract (GIT) and kidneys have been known to be affected by the presence of lead. For instance, mental deterioration, impaired development, hyperactivity, shortened attention span and lower IQ are suffered by children exposed to lead. Children who are below six years old are those at substantial risk [21, 22, and 23]. For adults, exposure to lead causes reproductive

dysfunctions, dementia (temporary loss of memory), irritation, decreased reaction time, anorexia, inhibition of haem synthesis, nausea, tumor production, insomnia and weakness of the joints [24, 21]. Zinc content was the highest among the metals in the mart sites studied. Its levels exceeded the baseline in all the marts except those of ELE, RUM and MILE 1 but were comparable to the control sites. Zinc concentrations in soil samples SA, SB and SC of 810.53 mg/kg, 899.90 mg/kg and 860.17 mg/kg respectively exceeded the new Dutch list intervention value of 720 mg/kg. In comparison to Zn levels reported by Leung *et al.* [25], the concentrations recorded for the study were higher because of the differences in the sampling sites and the method used in recycling the metal. The sampling site 102 contained the highest level of zinc among the sites studied [26]. This collaborated with the findings in some of the marts according to this present study. According to this present study, the uncoupling activities which occur to recycle various metals and the uncontrolled/indiscriminate burning of electronic wastes could have lead to the elevation in zinc concentrations as some of the marts deal on metal scrap. Also, the old worn out zinc sheets found all over these marts could have played a profound role in deposition of zinc on the top soils of these marts. Elevated concentrations of zinc can also interfere with the activities of earthworms and microorganisms thereby stunting the biodegradation of organic matter [23]. The cadmium levels in some of the marts (ELE, RUM, OIL M., TRANS, CHOBA and BOUND) exceeded the baseline value. The cadmium level of MILE 3 mart site was below the baseline value. However, there was no significant difference when compared to the control sites. Furthermore, the cadmium levels of MILE 1 and TM were below detection levels. The concentrations of Cadmium ranged from 2.3 to 0.2 mg/kg. Cadmium presence in the soil dusts results from industrial works such as battery and other electrical works [17]. A study by Marfo, [26] revealed that the concentration of cadmium in soil sample SA of 13.80 mg/kg of the metal scrap mart exceeded the new Dutch list intervention value of 12 mg/kg. The levels of cadmium even though low were still higher than the levels reported by Leung *et al.* [25]. This could have been as a result of the vigorous condition

of uncoupling at the study site. The Ni/Cd batteries discarded in the area and the burning of plastics in order to recover metals could have increased the level of cadmium in the sites [22]. Generally, the low concentrations of cadmium observed when compared to the other heavy metals in the sites could be ascribed to the high mobility of cadmium via the soil layers. When compared to other heavy metals, cadmium is liable to be more moveable in soil systems [24]. Anaemia, severe pains in the joints, lung and kidney problems could occur as result of exposure to high amounts of cadmium [22]. It has also been as a causal factor in hypertension and cardiovascular diseases, reduces birth weight and affects sperm [24, 21]. Furthermore, exposure to cadmium could lead to conditions like vomiting, liver dysfunction and neurotoxin, loss of consciousness, teratogenicity, nausea, carcinogenicity, respiratory difficulties, hypertension and cramps [24, 27]. The concentrations of arsenic in ELE, RUM, TRANS and BOUND exceeded the baseline value whereas the levels in OIL M., CHOBA and MILE 3 did not exceed the baseline value. Also, the concentrations in MILE 1 and TM were below detection level. There was however no significant difference when compared to the control sites. The elevated concentration of arsenic in some of the mart soils when compared to the baseline values could have been because of automobile parts that are sold in these marts. Arsenic is an element which is found in several environmental matrices at low quantities. It occurs either as methylated metabolite in the organic form or as pentavalent or trivalent arsenate in inorganic forms [28]. The therapy used for the treatment of parasitic diseases such as amoebic dysentery, trypanosomiasis, syphilis, etc are partly composed of arsenic. Arsenic toxicity is influenced by several factors which include age, individual proneness, genetic and nutritional factors, gender and biological species [29, 30]. By substituting their phosphate groups and binding to their sulfhydryl groups, trivalent arsenic can result in the loss of activity of over two hundred enzymes [31]. A study by Wang and Rossman, [32] also revealed that toxic effects of arsenic are exerted by the disruption of cellular respiration through the inactivation of mitochondrial enzymes with consequent impairment of oxidative phosphorylation.

Mechanisms have been proposed by several authors for arsenic's carcinogenic efficiency. It has been found to facilitate aberrant expression of gene by causing the hypomethylation of DNA. Arsenic induced carcinogenesis

could be caused as revealed in Trouba *et al.*, [33]'s study by mitogenic signal proteins' alterations due to severe prolonged exposure to arsenic.

Table 1. Heavy metal contents (mg/kg) of top soils of marts in Port Harcourt, Rivers State, Nigeria

Metals	Sites	ELE	RUM	MILE 1	OIL M	TM	TRANS	CHOBA	MILE 3	BOUND
Pb	Test	4.11±0.62 ^a	1.02±0.15 ^a	0.31±0.09 ^a	1.44±1.07 ^a	0.63±0.05 ^a	2.57±0.45 ^a	0.79±0.08 ^a	0.76±0.41 ^a	2.53±0.11 ^a
	Control	1.84±0.65 ^b	0.66±0.23 ^a	0.23±0.04 ^a	0.76±0.13 ^a	0.47±0.31 ^a	0.18±0.15 ^a	0.41±0.20 ^a	0.91±0.12 ^a	1.14±0.25 ^a
Zn	Test	33.46±7.75 ^a	59.33±21.83 ^a	31.86±4.36 ^a	82.26±6.10 ^b	43.53±4.67 ^a	77.73±22.05 ^a	77.56±2.02 ^a	72.46±32.75 ^a	82.53±2.38 ^a
	Control	20.90±5.31 ^b	28.13±3.21 ^b	19.46±4.11 ^b	39.33±6.00 ^b	21.40±7.52 ^b	29.73±6.78 ^b	37.90±9.78 ^b	32.10±6.27 ^b	24.36±10.87 ^b
Cd	Test	0.83±0.40 ^a	1.44±0.84 ^a	BDL	0.54±0.42 ^a	BDL	0.86±0.17 ^a	0.38±0.41 ^a	0.14±0.14 ^a	0.60±0.47 ^a
	Control	0.30±0.04 ^a	0.77±0.32 ^a	BDL	0.06±0.04 ^a	BDL	0.13±0.06 ^a	0.09±0.08 ^a	0.13±0.06 ^a	0.16±0.08 ^a
As	Test	1.81±0.71 ^a	6.28±0.82 ^a	BDL	0.14±0.06 ^a	BDL	2.20±0.63 ^a	0.18±0.09 ^a	0.20±0.03 ^a	1.19±0.27 ^a
	Control	0.17±0.19 ^a	0.29±0.28 ^a	BDL	0.04±0.04 ^a	BDL	0.08±0.01 ^a	0.06±0.01 ^a	0.05±0.03 ^a	0.33±0.50 ^a

Values are means and standard deviations of triplicate determinations. For each metal, values bearing similar superscript letter(s) "a" down the column denote that the mean difference is not significant at 0.05 level. BDL means Below Detection Level.

Table 2 reveals the contamination status of the mart sites investigated. There was no contamination with Lead (Pb) in all the sites. There was low contamination with Zinc (Zn) in ELE, RUM, MILE 1 and TM but there was moderate contamination in OIL M., TRANS, CHOBA, MILE 3 and BOUND. Also, there was considerably high contamination with Cadmium (Cd) in RUM, moderate contamination in OIL M. and CHOBA. However there was no contamination with cadmium in MILE 3. Furthermore, OIL M., CHOBA and MILE 3 had low contamination with Arsenic (As).

There was considerably high contamination with arsenic in ELE and TRANS, very high contamination in RUM but moderate contamination in BOUND. Generally, several studies indicate that the predominant sources of heavy metal contamination in urban soil include wastes from industries (from metallurgic industry, chemical plants, power plants, coal combustion, automobile repair plants, etc), transport emissions (tire wear debris particles, exhaust, by-products of weathering streets, etc) [34].

Table 2. Contamination Factor (CF) for mart soils in Port Harcourt, Rivers State, Nigeria.

Metals	ELE	RUM	MILE 1	OIL M.	TM	TRANS	CHOBA	MILE 3	BOUND
Pb	0.20	0.05	0.01	0.07	0.03	0.12	0.03	0.03	0.12
Zn	0.47	0.83	0.45	1.16	0.61	1.10	1.09	1.02	1.16
Cd	4.15	7.20	-	2.70	-	4.30	1.90	0.70	3.00
As	3.01	10.46	-	0.23	-	3.66	0.30	0.33	1.98

The enrichment factor result obtained (Table 3) reveals that all the metals in all the mart sites occurred as a result of

anthropogenic origin except that of lead in MILE 3 that was from natural activities. According to the observations of

Bini and Bech, [35], the deposition of each metal is site-specific based on a point-like mode of contamination

varying from site-to-site.

Table 3. Enrichment Factor (EF) for mart soils in Port Harcourt, Rivers State, Nigeria.

Metals	ELE	RUM	MILE 1	OIL M.	TM	TRANS	CHOBA	MILE 3	BOUND
Pb	2.23	1.54	1.34	1.89	1.34	14.27	1.92	0.83	2.21
Zn	1.60	2.10	1.63	2.09	2.03	2.61	2.22	2.25	3.38
Cd	2.76	1.87	-	9.00	-	6.61	4.22	1.07	3.75
As	10.64	21.65	-	3.50	-	27.50	3.00	4.00	3.60

Table 4 shows the I_{geo} levels of the metals at the mart sites. There was no pollution with lead and zinc in all the sites. BOUND, ELE, OIL M. and CHOBA were slightly polluted with cadmium. RUM and TRANS were moderately severely polluted with cadmium. There was however no pollution with cadmium in MILE 3. There was no pollution with arsenic in ELE, OIL M., CHOBA and MILE 3 but RUM was moderately severely polluted with arsenic, TRANS was moderately polluted and BOUND was slightly polluted, all with arsenic. The highest I_{geo} obtained for cadmium at TRANS. Cadmium is a vital heavy metal contaminant in the soil. Through the application of phosphoric fertilizers, cadmium is introduced to soils. With the application of massive quantities of compound and phosphate fertilizers as have been shown by several studies,

the available amount of cadmium taken by plants increases since there is an increase in the amount of uptake by the soils. Recently, mulching has been promoted and used in large areas resulting in soil pollution. This is because cadmium and lead contained in heat stabilizers are usually components of the production process of mulch. Heavy metal contamination of soils thereby increases [36]. Cadmium may lead to membrane damage; influence the photosynthetic activities of plants, the synthesis of proteins, etc [37, 38]. Cadmium may disrupt calcium metabolism, resulting in calcium deficiency, bone fractures, cartilage disease etc. Cadmium has been listed as the sixth most toxic substance that damages human health by Agency for Toxic Substances Management Committee.

Table 4. Index of geoaccumulation (I_{geo}) for mart soils in Port Harcourt, Rivers State, Nigeria.

Metals	ELE	RUM	MILE 1	OIL M.	TM	TRANS	CHOBA	MILE 3	BOUND
Pb	-2.86	-4.87	-6.59	-4.38	-5.57	-3.54	-5.24	-5.30	-3.56
Zn	-1.66	-0.83	-1.48	-0.36	-1.28	-0.44	-0.45	-0.54	-0.36
Cd	1.46	2.26	-	0.84	-	1.51	0.34	-1.09	1.00
As	-0.15	2.80	-	-2.68	-	1.28	-2.32	-2.16	0.40

The results shown in Table 3.5 reveal the daily intake levels of heavy metals from the mart sites. As provided by ASTDR, [39], these levels were found to be below their respective reference doses. The highest average daily intake of all the metals investigated was observed in zinc at BOUND. As none of the levels exceeded the reference

level at 1.0, no significant health hazard could result from the levels of the metals deposited in the study sites as shown in the non cancer quotient results in Table 3.6. According to Figure 2 (THI), RUM is observed as the likely mart site vulnerable to significant health hazards of all sites assessed.

Table 5. Average Daily Intake (ADI) (Mg/kg/day) of heavy metals on mart soils in Port Harcourt, Rivers State, Nigeria.

Metals	ELE x10 ⁻⁶	RUM x10 ⁻⁶	MILE 1 x10 ⁻⁶	OIL M. x10 ⁻⁶	TM x10 ⁻⁶	TRANS x10 ⁻⁶	CHOBA x10 ⁻⁶	MILE 3 x10 ⁻⁶	BOUND x10 ⁻⁶	Reference Dose
Pb	7.05	1.74	0.53	2.47	1.08	4.40	1.35	1.30	4.33	3.5 x10 ⁻⁶
Zn	57.39	101.77	54.65	141.10	74.67	133.33	133.04	124.29	141.57	3 x10 ⁻¹
Cd	1.42	2.47	-	0.92	-	1.47	0.65	0.24	1.02	1 x10 ⁻³
As	3.10	10.77	-	0.24	-	3.77	0.30	0.34	2.04	3 x10 ⁻⁴

Table 6. Non-Cancer Hazard Quotient of heavy metals on mart soils in Port Harcourt, Rivers State, Nigeria.

Metals	ELE	RUM	MILE 1	OIL M.	TM	TRANS	CHOBA	MILE 3	BOUND
Pb x10⁻³	2.01	0.49	0.15	0.70	0.30	1.25	0.38	0.37	1.23
Zn x10⁻⁵	19.13	33.92	18.21	47.03	24.89	44.44	44.34	41.43	47.19
Cd x10⁻³	1.42	2.47	-	0.92	-	1.47	0.65	0.24	1.02
As x10⁻²	1.03	3.59	-	0.08	-	1.25	0.10	0.11	0.68

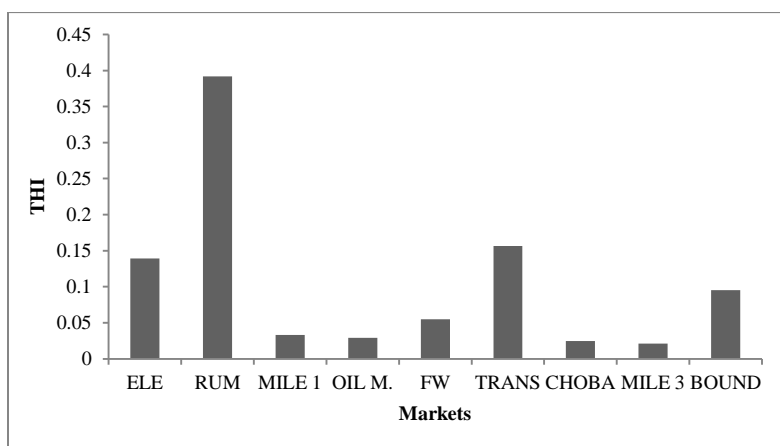


Figure 2. Total Hazard Index (THI) of heavy metals on top soils of marts in Port Harcourt, Rivers State, Nigeria.

CONCLUSIONS

This study investigated the concentration, pollution, contamination, enrichment, ingestion and health risks of some heavy metals in some mart sites in Port Harcourt, Rivers State, Nigeria. It established that the concentration of zinc was highest in the mart sites among the other metals. There was pollution with some of the heavy metals at some mart sites. The highest I_{geo} was found for cadmium at TRANS. The study further established contamination with some of the metals in some of the mart sites as very high contamination with arsenic was observed in RUM. The enrichment factor result obtained revealed that all the metals in all the mart sites occurred as a result of anthropogenic origin except that of lead in MILE 3 that was

from natural activities. The levels of average daily intake of all the metals in all the sites were found to be below their respective reference doses. The highest average daily intake of all the metals investigated was observed in zinc at BOUND. No significant health hazard could result from the levels of the metals deposited in the study sites as they did not exceed the reference level at 1.0. RUM is observed as the likely mart site vulnerable to significant health hazards of all sites assessed. Although the presence of these metals in these marts poses no health threat to the environment, prolonged accumulation and further exposure of the environment to these metals may eventually constitute serious health risks to humans. Therefore regular

environmental assessment should be performed in order monitor and regulate these metals in order to minimize health risks.

CONFLICT OF INTERESTS

The authors declare no conflict of interest regarding this manuscript.

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