Toxic metals in soil depths from selected abandoned sites: Occurrence, sources, ecological and human health risk

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Abstract. This study provides a comparative assessment of cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), copper (Cu), manganese (Mn), zinc (Zn), and iron (Fe) pollution occurrence, sources, and exposure risk in soils from selected abandoned sites. The concentrations of metals were determined using atomic absorption spectrophotometry. The metals occurrence ranged from 0.02 (Zn) to 16600 mg kg⁻¹ (Fe) in the order of subsoil > topsoil with petroleum tank farm and fuel/gas service station exhibiting high metal loading. The sources of metals are anthropogenic and geologic. The hazard index values for infants' were higher than that of adults, and the inhalation risk for adults' was considerably higher than for infants' exposure. The ecological risk of Cd, Pb, Cr, Ni, and Zn falls in the contamination to pollution index. This study revealed the need for clean-up and restoration of abandoned site soils.

Keywords: land-use; toxic metals; anthropogenic; abandoned sites; exposure risk.

1. Introduction

Soil is a significant portion of the aquatic and terrestrial ecosystem that acts as a sink for priority pollutants and plays a vital function in the occurrence and fate of toxic metals [1]. Several studies depict the significant concentration of Cd, Pb, Cr, Ni, Cu, Mn, Zn, and Fe in environmental matrices and food above target and intervention value and accumulate in fatty tissues. Depending on the concentrations and exposure duration, the occurrence of toxic metals in food above target and intervention values may cause optimum regulation dysfunction in living cells and exhibit human and ecological health hazards [2]. Naturally, the source of metals in soils is from parent rock materials, atmospheric-particle deposition, emissions from a volcanic eruption, oceans, lakes, and forests. However, exceeding the natural geochemical concentrations is the human-induced sources such as waste incineration, mining, emissions from fossil energy, leaded-fuel combustion engine, solid waste dump, metal and plastic scrap sites, lead-batteries, crude oil spills, use of fertilizers and pesticides, and industrial processing sites [3-5].

The study sites are selected abandoned sites characterized by the influence of different anthropogenic activities such as asphalt processing, petroleum tank farms, solid waste, auto-mechanic workshops, and fuel/gas service stations situated in Nigeria. Abandoned sites are known for spilled waste engine-oil and petroleum products, paint-metals deposits, metal and plastic scrap dump, pieces of equipment, machinery and trucks, equipment containing electrical appliances, fire resistance materials, PCBmetal oil and Pb-Cd batteries, and domestic and commercial solid waste dump. These sites have been recognized as potential point and non-point sources of priority pollutants and have contributed significant concentrations of toxic metals to soils [6-9]. The study area aquifers have a high vulnerability to pollution because of the closeness of the water table to topsoil (< 10 m depth) and the unconsolidated nature of sediments [10].

In Nigeria, abandoned facilities are converted to residential, institutional, recreational, commercial, and agricultural catchments without proper site and soil clean-up actions. The non-compliance to standard guidelines for use in these catchments for other purposes may lead to considerable pollution load of the immediate and adjacent soils, surface, and groundwater aquifers [11]. Most environmental studies are connected with functional industrial sites and abandoned sites with single anthropogenic activity. Hence, data gaps showing the concentrations origin and associated risks of metals in soil depths from abandoned sites with different landuse. Over the years, several human and environmental health concerns about metals inputs in soils [12-18]. The concentrations of metals in abandoned sites are vital for evaluating the sources and human and environmental health hazards on the immediate and adjacent environment matrices. The concentration and associated health risks of Cd, Pb, Cr, Ni, Cu, Mn, Zn, and Fe, were determined in soil depths from selected abandoned sites of different land use. The results provided insights on the pollution concentrations ecological and human health risks from metals in soil depths from selected

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abandoned sites and can assist policy and decisionmakers to take action. This study represents a similar work environment, valuable in sustainable management of abandoned sites clean-up action for residential, commercial, recreational, institutional, and agricultural catchments.

2. Experimental

2.1. Description of the study area

The study sites are located in the Niger Delta, Nigeria, situated between latitudes $5^{\rm o}-8^{\rm o}\,E$ and $3^{\rm o}-6^{\rm o}\,N.$ The land use operations were abandoned between 10-20 years ago and there is no evidence of natural restoration of soil. The weather and climatic conditions include the Oligocene-Pliestocene Benin Formation that constitutes the aquiferous zone, and annual rainfall above 200 mm. The water table varies from 0.7 to 10 m depth (in some areas, shallow dug wells serve as primary water supply), an atmospheric temperature of 23 to 28 °C, a subequatorial climate, high humidity, and long wet season. [19, 20]. The sample codes are APS1 - asphalt processing site APS2 - asphalt processing site, PTF1 petroleum tank farm, PTF2 - petroleum tank farm, SWD1 – solid waste dump, SWD2 – solid waste dump, AMW1 - auto mechanic workshop, AMW2 - auto mechanic workshop, FSS1 - fuel service station, and FSS2 -fuel service station, Figure 1.



Figure 1. Map of Nigeria showing selected abandoned landuse sites (adapted in part from Emoyan *et al.* [37]).

2.2. Sample collection

After removal of debris from the topsoil, twenty samples were collected with a 2.5 cm diameter probe stainless steel auger at the top (0-15 cm) and subsoil (15-30 cm) from ten abandoned sites of different land use. A composite sample was derived from a quadruplet using standard quality control procedures. Glassware was soaked in 10% HNO₃ for 12 hours, washed twofold with deionized water, and dried in an oven.

2.3. Sample digestion and analysis

Upon removal of twigs and stones, the samples were airdried and sieved using a 2.0 mesh. The USEPA 3050B method was adopted for the digestion, thus 1 g of the sample was weighed into a 250 mL digestion tube, and addition of 15 mL of *aqua regia* 1:3 (HNO₃:HCl). In a heating plate, the mixture was heated at 120 °C for 30 minutes. The digest was filtered using a Whatman No. 41 filter paper, diluted to 25 mL with 0.25 M HNO₃, and stored in a pre-cleaned polyethylene container at 4 $^{\circ}$ C before analysis [1, 21]. The concentrations of Cd, Pb, Cr, Ni, Cu, Mn, Zn, and Fe in the digested samples were determined using a Varian SpectrAA200 flame atomic absorption spectrophotometry (Rikakikai Co. Ltd, Tokyo, Japan). The calibration line technique was adopted for the analysis, and the detection limit of the AAS was 0.001 mg L⁻¹.

2.4. Quality control and assurance

The quality control and assurance were attained by adhering to the standard analytical practice of the manufacturer's recommendations in the preparation and analysis of samples. The sample containers and glassware were pre-cleaned with 10% nitric acid, and the reagents for metal digestion were of analytical grade. The validation of the analytical method was by the method blank and sample matrix, field blank, and spike recovery method. Samples were analyzed in triplicates.

2.5. Human health risk assessment

The human health risk was determined using the hazard index (HI) and the total cancer risk (TCR) models. The rationale behind the human health risk evaluation is exposure hence reported for the topsoil depth. The human health risk evaluation was by the assumption that the routes of exposure; are through ingestion, inhalation, and dermal (IID), [22, 23]. The definition and values of variables used in the non-cancer and cancer risks are presented in the supplementary materials (Table SM1 and SM2).

2.6. Ecological risk evaluation

2.6.1. Contamination and pollution index (CPI). The CPI was determined as stated by Emoyan *et al.* [1].

The reference target value of metals used is the Department of Petroleum Resources-Environmental standards and guidelines for the petroleum industry in Nigeria [24]. The definitions and values of variables used are presented supplementary material (Table SM3).

2.6.2. Index of geoaccumulation (Igeo). The Igeo quantity was applied to determine the contamination of metals by comparing current and pre-concentration levels [1, 25].

The crustal abundance values for metals were applied as the geochemical background levels. The value of 1.5 allows for natural fluctuations in the levels of a given metal in the soil matrix and very minimal anthropogenic impact. The *Igeo* classification is presented in the supplementary material (Table SM3).

2.6.3. Enrichment factor (EF). The EF of metals was determined using the expression by Reimann and De Caritat [26] and Loska and Wiechula [27]. In this study, iron was selected as the reference metal for the EF evaluation because of its natural abundance relative to other metals. The crustal abundance values of metals were used as the background levels for the assessment of the EF. The categories of EF are shown in the supplemental material (SM3).

2.6.4. Ecological risk factor and potential ecological risk index. The ecological risk of metals was determined using expression by Turekian and Wedepohl [28] and Hakanson [1, 29].

The CAV of the metals were adopted as the background concentrations, and the quantitative definition of the ecological risk is presented in the supplementary material (Table SM4).

2.6.5. Soil quality guidelines (SQGs). The ecological effect range low (ERL), the biological effect range medium (ERM), the threshold effect level (TEL), and the probable effect level (PEL) are the SQGs applied for the determination of ecological risk [30, 31]. The values of ERL, ERM, TEL, and PEL used are presented in the supplementary materials (Table SM5).

2.7. Data analysis

The statistical package for the social sciences (SPSS) version 22 was applied for the evaluation of descriptive statistical. The ANOVA was used to determine the significant difference in the concentration of metals, while Pearson's correlation coefficient was used to

determine if there is significant relationship among the metals.

3. Results and discussion

3.1. Quality control and assurance

The relative standard deviation ranged from 8 to 12%. The average recoveries from the spiked sample matrix ranged from 96.7 to 101.4% of metals. The concentration of metals in the procedural blanks (n = 3) was below the limit of quantification, and the r^2 for the calibration curves ranged from 0.9992 to 0.9999. The relative standard deviation of triplicate analysis ranged from 8 to 12%.

3.2. Concentrations and compositional pattern

The concentrations and summary statistics of the measured toxic metals are presented in Tables 1 and 2.

Sites	Depth	Cd	Pb	Cr	Ni	Cu	Mn	Zn	Fe
APS1	Top soil	2.98	0.25	7.53	0.28	23.1	13.6	0.02	28.6
	Sub soil	8.33	0.75	8.03	126	12.7	51.1	1.24	24.9
APS2	Top soil	3.23	1.50	12.0	12.8	25.3	41.1	1.47	43.4
	Sub soil	19.2	1.25	9.25	53.2	0.75	26.0	1.50	32.1
PTF1	Top soil	3.18	0.75	8.28	19.4	125	128	5.05	102
	Sub soil	3.40	4.00	5.40	26.5	54.3	71.9	4.68	166
PTFS2	Top soil	3.08	0.50	7.91	9.84	74.1	70.8	2.54	65.3
	Sub soil	5.87	2.38	6.72	76.3	33.5	61.5	1.37	95.5
SWD1	Top soil	3.16	1.00	9.95	11.3	49.7	56.0	2.00	83.7
	Sub soil	12.5	1.81	7.98	64.7	17.1	43.8	1.44	63.8
SWD2	Top soil	3.17	0.88	9.12	15.4	87.3	92.0	3.53	92.8
	Sub soil	7.97	2.91	6.69	45.6	35.7	57.8	1.40	115
AMW1	Top soil	3.12	0.69	8.51	12.6	80.7	81.4	3.03	79.1
	Sub soil	6.92	2.64	6.70	60.9	34.6	59.7	1.40	105
AMW2	Top soil	3.14	0.84	9.23	12.0	65.2	68.7	2.52	81.4
	Sub soil	9.72	2.23	7.34	62.8	25.9	51.7	1.42	84.5
FSS1	Top soil	3.15	0.86	9.17	13.7	76.3	80.3	3.02	87.1
	Sub soil	8.85	2.57	7.02	54.2	30.8	54.8	1.40	99.7
FSS2	Top soil	3.14	0.77	8.84	13.1	78.5	80.9	3.03	83.1
	Sub soil	7.88	2.60	6.86	57.6	32.7	57.2	1.41	102

Table 1.	Concent	rations o	f metals i	in the	top and	subsoil	from	abandone	d sites	(mg	kg ⁻¹)
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Table 2. Summary statistics of metals in the top and subsoil from abandoned sites (n = 10)

			Topso	il			Subsoil					
	MEAN	SD	MEDIAN	MIN	MAX	%CV	MEAN	SD	MEDIAN	MIN	MAX	%CV
Cd	3.13	0.07	3.15	2.98	3.23	2.13	9.07	4.29	8.15	3.40	19.2	47.3
Pb	0.81	0.32	0.81	0.25	1.50	40.4	2.31	0.90	2.47	0.75	4.00	38.9
Cr	9.05	1.25	8.98	7.53	12.0	13.8	7.20	1.04	6.94	5.40	9.25	14.4
Ni	12.0	4.87	12.7	0.28	19.4	40.5	62.8	25.8	59.3	26.5	126	41.1
Cu	68.5	30.1	75.2	23.1	125	44.0	27.8	14.7	31.7	0.75	54.3	53.0
Mn	71.3	30.6	75.6	13.6	128	42.9	53.5	12.2	56.0	26.0	71.9	22.7
Zn	2.62	1.32	2.78	0.02	5.05	50.4	1.73	1.04	1.41	1.24	4.68	60.2
Fe	7464	2269	8222	2860	10200	30.4	8889	4110	9756	2490	16600	46.2

The concentration profile of Cd, Pb, Cr, Ni, Cu, Mn, Zn, and Fe ranged from 0.02 (Zn) to 16600 mg kg⁻¹ (Fe), and the mean concentrations ranged from 0.81 ± 0.32 mg kg⁻¹ (Pb) to 8889 \pm 4110 mg kg⁻¹ (Fe). The coefficients of variation are greater than 1, and the median values are less sensitive to the skewness, suggesting a complex origin of metals in the abandoned land-use sites [32, 33]. The concentration of metals show considerable values between sample sites and varied significantly (p < 0.05). The concentrations depict an irregular trend in occurrence concerning soil depths and show pollution profile in the order of subsoil > topsoil, and PTF > FSS > AMW > SWD > APS. The results depict the highest concentration of Cd, Pb, Cr, Ni, Cu, Mn, Zn, and Fe at APS2, PTF1, PTF2, SWD1, SWD2, SWD2, PTF1, and AMW1, Table 1 and Figure 2. The high concentration of metals in petroleum tank farms and fuel service stations could be adduced to spilled waste engine-oil and leaded petroleum products, solid waste containing metallic materials, buried metallic components, Cd, Pb, and Ni containing paints, and coat-plating against corrosion in high-stress structures, metal scrap dump, machinery and trucks, equipment containing electrical appliances, fire resistance materials, PCB-metal oil, and Pb-Cd batteries [1, 34, 35]. The percentage concentrations of these metals in the top and subsoil is in the order of Ni < Pb < Cd < Fe < Cr < Mn < Zn < Cu and Cu < Zn < Mn < Cr < Fe < Pb < Cd < Ni respectively.



Figure 2. Peak concentrations of metals in the top and subsoil (mg kg⁻¹)

The concentration pattern of metals suggests a common trend in leaching and infiltration from the top to subsoil, input sources [20, 36, 37]. This is adduced to common; soil physicochemical characteristics, biochemical reactions within soil depths, reduced soils cohesion due to physical, biological, mechanical, and chemical factors, and vertical rather than the horizontal movement of metal mobility, thereby exposing bottom soil layers to contaminants [38]. In addition, the concentration of Fe could increase the rate of geochemical mobility and leaching of metals from active soil sites [39, 40]. In this study, 100% (Cd), 40% (Ni), and 40% (Cu) values surpassed the maximum target value prescribed by DPR respectively (DPR-EGAPSIN, 2002). The concentrations of metals were relatively comparable to the concentrations in some studies from different anthropogenic impacted soils [1, 4, 8, 9, 14, 15, 17, 18, 41-43].

Upon exposure, the observed Pb and Ni concentration may cause oxidative stress toxicity in living cells, microorganisms could suffer severe growth decline, suppress the overall growth of plants, reduce biomass, and catalyze huge imbalance in ion uptake by plants, and considerable metabolic alteration in photosynthetic ability in plants around the abandoned sites upon reuse for agricultural production. Also the influence of biomagnifications, water-soluble Zn can contaminate groundwater aquifer and the food chain;

disrupt the physiological activity of earthworms and microorganisms in soils, thus retarding the regular breakdown of organic materials in the soil around the abandoned land-use sites [44-47]. In addition, microbial metabolisms could be limited by C and P resulting from Cd, Pb, and Zn pollution, and the caused stress considerably increased the microbial C limitation, hence microorganisms may increase the energy value in metabolism to resist metal tension and thus activate C release [48].

Due to infiltration, diffuse and direct migration, and accumulation of pollutants, the unconsolidated nature of the sediments, abundant thick sandy sequence, and shallow water table of the study area, the observed concentration of metals may contaminate adjacent soils, ground and surface water resources in the monsoon season [10]. However, this scenario may be determined by the water chemistry and water-rock interaction [20. 25, 49, 50]. In addition, based on the concentrations, duration, and routes of exposure, the observed Cd, Pb, Cr, Ni, Cu Mn, and Zn concentrations depict significant ecological and human health challenges if accumulated concentrations surpass the allowable standard values [51]. However, these health hazards may be negligible if the metals present are restricted to the insoluble, inert, and immobile species such as Pb(PO₄)₃Cl, PbS, PbSO₄, Pb₃(PO₄)₂, Ni₂O₃, NiO₂, Cr(OH)₃ [52-54]. The reuse of the abandoned sites for agricultural, residential, recreational, institutional, and commercial purposes may increase the potential for onsite occupational exposure risk.

3.3. Pearson correlation coefficients and ANOVA

The Pearson correlation matrix of metals in soil, (Table 3) shows a moderate correlation between Cd and Mn, Zn, Fe; Pb and Ni, a good correlation between Cd and Cr, Ni; Ni and Mn, Fe; Cu and Fe, Zn, strong correlations between Cd and Pb, Cr; Pb, Cr; Cu and Mn, Zn, Fe; Mn and Fe; Zn and Fe. The marked variability in correlation among metals suggests a common trend in their physicochemical properties and reactivity in soils [55]. The correlationbetween metals could be adduced to common sources attributed to the presence of metal equipment; trucks containing Pb-Cd batteries, metallic materials, metal scrap, and asphalt dump in the abandoned sites [56, 57]. The values of t-test and ANOVA depict no significant difference between the total concentration of metals and soil depths (Table SM7 and SM8).

				1			
Cd	Pb	Cr	Ni	Cu	Mn	Zn	Fe
1.00							
0.90*	1.00						
0.76*	0.97*	1.00					
0.84*	0.52**	0.29	1.00				
0.30	-0.15	-0.39	0.77*	1.00			
0.50**	0.06	-0.19	0.88*	0.98*	1.00		
0.54**	0.11	-0.13	0.91*	0.96*	1.00*	1.00	
0.51**	0.13	-0.10	0.83*	0.86*	0.90*	0.90*	1.00
1.00							
-0.66	1.00						
	Cd 1.00 0.90* 0.76* 0.84* 0.30 0.50** 0.54** 0.51** 1.00 -0.66	Cd Pb 1.00 0.90* 1.00 0.76* 0.97* 0.84* 0.30 -0.15 0.50** 0.50** 0.06 0.54** 0.51** 0.13 1.00 -0.66 1.00	Cd Pb Cr 1.00 0.90* 1.00 0.76* 0.97* 1.00 0.84* 0.52** 0.29 0.30 -0.15 -0.39 0.50** 0.06 -0.19 0.54** 0.11 -0.13 0.51** 0.13 -0.10 1.00 -0.66 1.00	Cd Pb Cr Ni 1.00 0.90* 1.00 0.90* 1.00 0.76* 0.97* 1.00 0.00 0.30 -0.15 -0.39 0.77* 0.50** 0.06 -0.19 0.88* 0.54** 0.11 -0.13 0.91* 0.51** 0.13 -0.10 0.83* 1.00 -0.66 1.00	Cd Pb Cr Ni Cu 1.00 0.90* 1.00 0.90* 1.00 0.76* 0.97* 1.00 0.30 0.15 -0.39 0.77* 1.00 0.30 -0.15 -0.39 0.77* 1.00 0.50** 0.06 -0.19 0.88* 0.98* 0.54** 0.11 -0.13 0.91* 0.96* 0.51** 0.13 -0.10 0.83* 0.86* 1.00 -0.66 1.00 -0.10 0.83* 0.86* 1.00	Cd Pb Cr Ni Cu Mn 1.00 0.90* 1.00 0.90* 1.00 0.90* 1.00 0.90* 1.00 0.90* 1.00 0.30 0.52** 0.29 1.00 0.30 -0.15 -0.39 0.77* 1.00 0.50** 0.06 -0.19 0.88* 0.98* 1.00 0.54** 0.11 -0.13 0.91* 0.96* 1.00* 0.51** 0.13 -0.10 0.83* 0.86* 0.90* 1.00 -0.66 1.00 -0.66 1.00 -0.66 1.00 -0.66 1.00 -0.66 1.00 -0.66 1.00 -0.66 1.00 -0.66 -0.00 -0.66 -0.00 -0.66 -0.00 -0.66 -0.10 -0.83* 0.86* 0.90* -0.90* -0.66 -0.90* -0.66 -0.90* -0.66 -0.90* -0.66 -0.90* -0.66 -0.90* -0.66 -0.90* -0.66 -0.90* -0.66 -0.90* -0.66 -0.66 </td <td>Cd Pb Cr Ni Cu Mn Zn 1.00 0.90^{*} 1.00 0.90^{*} 1.00 0.76^{*} 0.97^{*} 1.00 0.76^{*} 0.97^{*} 1.00 0.30 -0.15 -0.39 0.77^{*} 1.00 0.30 -0.15 -0.39 0.77^{*} 1.00 0.50^{**} 0.06 -0.19 0.88^{*} 0.98^{*} 1.00 0.54^{**} 0.11 -0.13 0.91^{*} 0.96^{*} 1.00^{*} 1.00 0.51^{**} 0.13 -0.10 0.83^{*} 0.86^{*} 0.90^{*} 0.90^{*} 1.00 -0.66 1.00 0.90^{*} 0.90^{*} 0.90^{*}</td>	Cd Pb Cr Ni Cu Mn Zn 1.00 0.90^{*} 1.00 0.90^{*} 1.00 0.76^{*} 0.97^{*} 1.00 0.76^{*} 0.97^{*} 1.00 0.30 -0.15 -0.39 0.77^{*} 1.00 0.30 -0.15 -0.39 0.77^{*} 1.00 0.50^{**} 0.06 -0.19 0.88^{*} 0.98^{*} 1.00 0.54^{**} 0.11 -0.13 0.91^{*} 0.96^{*} 1.00^{*} 1.00 0.51^{**} 0.13 -0.10 0.83^{*} 0.86^{*} 0.90^{*} 0.90^{*} 1.00 -0.66 1.00 0.90^{*} 0.90^{*} 0.90^{*}

	Cd	Pb	Cr	Ni	Cu	Mn	Zn	Fe
Cr	0.92*	-0.90	1.00					
Ni	0.06	-0.79	0.24	1.00				
Cu	-0.88	0.94*	-1.00	-0.53	1.00			
Mn	-0.99	0.77*	-0.97	-0.21	0.94*	1.00		
Zn	-0.43	0.76*	-0.60	-0.54	0.72*	0.50**	1.00	
Fe	-0.73	1.00	-0.94	-0.72	0.97*	0.82*	0.76*	1.00

3.4. Human health risk assessment

Cancer and non-carcinogenic risk assessment were based on exposure; hence, the hazard index and total cancer risks were reported for the topsoil.

3.4.1. Non-carcinogenic risk. The hazard index for infants' and adults' exposure to metals (Table SM9 and Figure 3), depicts that the hazard quotient for human exposures to the metals is in the order of HQIng > HQDerm > HQInh. The hazard index and hazard quotient values for the exposure routes suggest no adverse non-carcinogenic health risk for human exposure to metals in soils around the abandoned sites. The hazard index values for infants' exposure were greater than for adults' exposure; this is attributed to exposure duration and smaller body load of infants' to soil and/or dust particles at play hours [58].



Figure 3. Hazard index of metals for infants and adults in topsoil. (The HI value < 1 and > 1 depicts no adverse noncarcinogenic risk and adverse non-carcinogenic risk respectively)

3.4.2. Total cancer risk. The carcinogenic risk evaluated as a total cancer risk for human exposures to metals in the topsoil (Table SM10 and Figure 4), ranged from 9.38 $\times 10^{-6}$ to 1.54×10^{-5} for the infants' exposure, and 3.98×10^{-6} to 6.84×10^{-6} for adults' exposure, suggesting that soils around the abandoned land-use sites are within acceptable safe limits. The total cancer risk values for infants and adults in the exposure pathways are in the order of HQDerm < HQInh < HQIng. The risk through inhalation exposure for infants was considerably less than for adults' exposure, suggesting a longer exposure duration for adults [59-61].



Figure 4. The total cancer risk of metals for infants and adults in topsoil. (The TCR value $< 1 \times 10^{-6}$ and $> 1 \times 10^{-6}$ depict no cancer risk and cancer risk respectively)

3.5. Ecological risk assessment

3.5.1. Contamination/pollution index. The results of *contamination/pollution index* and MPI (SM11 and Figure 5) show that CPI values for Cd were greater than 1, depicting pollution range. The CPI values for Pb Cr

and Zn were less than 1 and falls in the contamination range. The contamination/pollution index values for Ni and Zn were 45% greater than 1 and falls in the contamination range. The multiple pollution index values ranged from 3.73 to 25.5 with considerable contribution from Cd.



Figure 5. The contamination/pollution index values for Cd were greater than 1, for Pb, Cr and Zn were less than 1, and for Ni and Zn were 45% greater than 1.

3.5.2. Enrichment factors. The enrichment factors value of metals (SM11 and Figure 6) depict that Cd values were greater than 10 and ranged from 32 to 937, and 96% of the samples fall in the extremely high enrichment category. The enrichment factors of Cd suggest non-crustal anthropogenic input as a source of Cd. The enrichment factors values for Pb, Cr, Mn and Zn ranged from 0.2 to 0.8, 0.17 to 1.68, 0.24 to 0.69 and 0.06 to 0.25 respectively. The enrichment factors values of Pb, Cr, Mn, and Zn suggest crustal source and deficiency to minimal enrichment category. The enrichment factor for Ni and Cu ranged from 0.07 to 34.98 and 0.24 to 12.80 respectively. This depicts extremely high enrichment, very high enrichment, significant enrichment, moderate enrichment, and deficiency to minimal enrichment categories. The enrichment factors of Ni and Cu were less than 10 in 90% and 85% of the samples indicating a crustal source.



Figure 6. The enrichment factors of Cd and Pb, Cr, Mn, and Zn suggest non-crustal anthropogenic and crustal source and deficiency to minimal enrichment category respectively. The enrichment factor for Ni and Cu falls in minimal to extremely high enrichment category

3.5.3. Geoaccumulation index (Igeo). The *Igeo* values for metals (SM12 and Fig. 7) were less than 0 except

Cd and Cu, depicting class 1 category for Pb, Cr, Ni, Mn, and Zn. However, in the *Igeo* in 30% of the samples, Cu falls in the moderately polluted class. The *Igeo* values for Cd fall in the severe contamination to the slight pollution class. The *Igeo* values indicate that soils around the abandoned sites are polluted with Cd and Cu, and their occurrence depicts geologic and anthropogenic sources.



Figure 7. The geoaccumulation index of metals falls in class 1 to severe pollution category

3.5.4. Contamination factor (Cf) and degree of contamination. The contamination factor of metals

ranged from 9.93 to 64, 0.01 to 0.15, 0.06 to 0.13, 0.14 to 1.85, 0.02 to 2.78, 0.02 to 0.11, and 0.01 to 0.05 respectively, (Table SM13). The average contamination factor is in the order of: Cd > Cu > Ni > Pb > Cr > Mn > Zn, suggesting that Cd contributed a considerable amount to metals contamination of the abandoned sites. The degree of contamination ranged from 10.56 to 65.01, indicating considerable to high contamination index.

3.5.5. Ecological risk factor and potential ecological risk index. The ecological risk factor of metals ranged from 298 to 1920, 0.06 to 1, 0.12 to 0.27, 0.02 to 9.26, 0.08 to 13.89, 0.02 to 0.15, and 0.01 to 0.04 respectively, (Table 4). The ecological risk factor of Cd and Pb, Cr, Ni, Cu, Mn, and Zn, falls in the low-risk and the very high-risk categories respectively. The average ecological risk factor is in the order of: Cd > Cu > Ni > Pb > Cr > Mn > Zn. The potential ecological risk index ranged from 301 to 1925 with Cd showing a significant risk index, and the average ecological risk for the abandoned sites.

Table 4	 Ecological risk 	factor, pote	ential ecological risk	index and pollution	degree of metals in	top and subs	soil from abandoned sites
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Ecological Risk Factor (Er ⁱ)									Potential Risk	Risk Level
Site	Depth	Cd	Pb	Cr	Ni	Cu	Mn	Zn	Index (RI)	
APS1	Top soil	298	0.06	0.17	0.02	2.57	0.02	0.00	301	Very high
	Sub soil	833	0.19	0.18	9.26	1.41	0.06	0.01	844	Very high
APS2	Top soil	323	0.38	0.27	0.94	2.81	0.05	0.02	327	Very high
	Sub soil	1920	0.31	0.21	3.91	0.08	0.03	0.02	1925	Very high
PTF1	Top soil	318	0.19	0.18	1.43	13.89	0.15	0.05	334	Very high
	Sub soil	340	1.00	0.12	1.95	6.03	0.08	0.05	349	Very high
PTFS2	Top soil	308	0.13	0.18	0.72	8.23	0.08	0.03	317	Very high
	Sub soil	587	0.59	0.15	5.61	3.72	0.07	0.01	597	Very high
SWD1	Top soil	316	0.25	0.22	0.83	5.52	0.07	0.02	322	Very high
	Sub soil	1253	0.45	0.18	4.76	1.90	0.05	0.02	1261	Very high
SWD2	Top soil	317	0.22	0.20	1.13	9.70	0.11	0.04	328	Very high
	Sub soil	797	0.73	0.15	3.35	3.97	0.07	0.01	805	Very high
AMW1	Top soil	312	0.17	0.19	0.93	8.97	0.10	0.03	323	Very high
	Sub soil	692	0.66	0.15	4.48	3.85	0.07	0.01	701	Very high
AMW2	Top soil	314	0.21	0.21	0.88	7.24	0.08	0.03	323	Very high
	Sub soil	972	0.56	0.16	4.62	2.87	0.06	0.01	981	Very high
FSS1	Top soil	315	0.21	0.20	1.00	8.47	0.09	0.03	325	Very high
	Sub soil	885	0.64	0.16	3.99	3.42	0.06	0.01	893	Very high
FSS2	Top soil	314	0.19	0.20	0.97	8.72	0.10	0.03	324	Very high
	Sub soil	788	0.65	0.15	4.23	3.63	0.07	0.01	797	Very high

3.5.6. Comparison of the metals with SQG. The ecological risk was evaluated by comparing observed heavy metals concentrations with SQGs values (Table SM5). The results show that 0.0 to 100% and 0.0 to 100% of the samples have metal values less than their TEL and ERL values respectively. Also, 0.0 to 85% and 0.0 to 85% of the samples have concentrations of heavy metals between TEL-PEL and ERL-ERM respectively. However, 0.0 to 40% and 0.0 to 45% of the samples have metals concentrations greater than their respective ERM and PEL respectively. This suggests a low ecological risk to biota on exposure to the soil around the abandoned sites.

3.6. Source apportionment

3.6.1. Principal component analysis. In this study, two PCA component factors were identified in the top and

subsoil, (Table 5). The topsoil depicts high loading of Ni, Cu, Mn, Zn, and Fe, and Cd, Pb, and Cr in factors 1 and 2 respectively, and Factor 1 accounted for 60.627% of the total variation. The subsoil shows high loading of Cu and Mn, and Pb, Zn, and Fein factors 1 and 2 respectively, and Factor 1 accounted for 55.207% of the total variation. The values of the principal component analysis of metals are attributed to common physicochemical properties, origin, and mobility potential in the soil profiles [62].

 Table 5. PCA of metals in top and subsoil from abandoned sites

	Тор	osoil	Subsoil			
	Comp	onent	Component			
	1	1 2		2		
Cd	0.466	0.884	-0.997	-0.075		
Pb	0.036	0.999	0.608	0.783		

	Тор	osoil	Subsoil			
	Comp	onent	Component			
	1	2	1	2		
Cr	-0.209	0.978	-0.891	-0.450		
Ni	0.869	0.489	0.011	-0.981		
Cu	0.979	-0.187	0.844	0.532		
Mn	0.996	0.026	0.975	0.221		
Zn	0.993	0.077	0.361	0.682		
Fe	0.931	0.094	0.682	0.723		
Variance %	60.267 37.816		55.207	38.782		
Cumm Var. %	60.267 98.083 55.207		93.989			

3.6.2. Cluster analysis. The homogeneity and relationship between metals and the samples were determined using cluster analysis (Figure 8 and 9). The dendrogram between metals depicts that Cd, Pb, Cr, Ni, Cu, Mn, and Zn formed a cluster, and Fe is an independent entropy member. The dendrogram between the samples shows that four clusters were formed with a linkage at FSS1A, PTF2A, FSS1B, and APS1B, with PTF1B, an independent entropy member. The proneness of the metals and samples to a cluster is an attribute of physicochemical common properties, origin, degradation pattern, and mobility potential in the soil matrix [58, 63].



Figure 8. The dendrogram of Cd, Pb, Cr, Ni, Cu, Mn, and Zn formed a cluster, and Fe is an independent entropy member



Figure 9. The sample site dendrogram formed four clusters with a linkage at FSS1A, PTF2A, FSS1B, and APS1B, with PTF1B, an independent entropy member

4. Conclusions

The concentrations, sources, and human and ecological health risks of Cd, Pb, Cr, Ni, Cu Mn, Zn, and Fe in soils around abandoned sites of different land use were determined. The results show variable and considerable concentrations of metals in the order of subsoil > topsoil and PTF > FSS > AMW > SWD > APS, with petroleum tank farm and fuel service station exhibiting high metal concentrations. This study revealed that Cd, Ni, and Cu concentrations exceeded the target limits, and the source

of metals is mainly geologic and anthropogenicinduced. The risk through inhalation exposure for adults' was significantly higher than for infants, and the hazard index values for infants' exposure were higher than for adults' exposure. The ecological risk of Cd, Pb, Cr, Ni, and Zn was significant and falls in the contamination to pollution class. This study demonstrated the need for clean-up and restoration of soils of abandoned sites.

Acknowledgments

This work was supported and funded by the authors. Special thanks to the laboratory personnel, Department of chemistry, Delta State University, Abraka for their technical support.

Conflict of interest

The authors have no conflict of interest, hence none declared.

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Received: 26.01.2022 Received in revised form: 16.02.2022 Accepted: 18.02.2022