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Assessment of heavy metals contamination of soil and groundwater around selected petrol stations in Abeokuta Metropolis, Nigeria

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Abstract

This study investigated heavy metals contamination of soil and groundwater in selected petrol stations with the following codes: CNP, JKO, CDA, EP, NMS, MRS, FAG, LJO, DRL, and MNP in Abeokuta Metropolis. The metals were analysed in twenty composite soil samples collected at depth 0-15 cm and 15-30 cm using soil auger. Groundwater samples were collected into 2 litre pre-cleaned sample bottles from six hand-dug wells and four boreholes respectively. Heavy metals in all samples were analysed using atomic absorption spectrophotometer. Concentrations of heavy metals in the soil were in the order of Pb>Cr>Ni>Cu>Cd. Mean Pb concentrations in soils around the petrol stations ranged from 13.75 ± 0.50 in CDA and 209.25±0.66 mgL^{-1} in LJO Petrol Station. Index of geo-accumulation (*Igeo*) indicated that LJO Petrol Station was the most polluted by Pb with I*geo* of 10.5 in the topsoil. The soils around the petrol stations had potential ecological risk index (RI), which were above 200 showing high toxicity. The average concentrations of Pb were 0.19±0.03, 1.31±0.01, 3.52±0.61 mgL^{-1} for water from hand dug wells at JKO, NMS and MRS respectively, which were higher than the WHO permissible limit. Sources of contamination of soil and groundwater around the petrol stations were spillage from dispensing of petrol and leakages or seepages from the underground petrol tankers. Pollution from the petrol stations in Abeokuta Metropolis contributes to heavy metal concentrations in the soil and groundwater, which is a potential threat to human health.

Keywords: Environmental risk; fuel leakages; ingestion; metal contamination; urban soil.

Introduction

In many Nigerian cities, as the population increases progressively, there is the growing demand for essential products such as petrol, diesel, and kerosene, which are needed for transporting goods, people and services and for cooking. Petroleum-filling stations within the urban environment are known as one of the existing and potential dangers in the cities [1] due the spilling petroleum products and leakages from underground storage tanks, which causes soil and groundwater contamination [2-3] This combined with the perceived lucrative nature of the business has led to the establishment of petrol stations in many parts of Nigerian cities. Proliferation of petrol stations to supply the much-needed energy to drive the economic activities especially in cities have however led to the increasing pollution of the environment. Pollution often occurs because of leakages from underground tanks or spills from the stations are deposited on soil and may percolate into groundwater sources thus increasing the potential risk of health. Lead is used as an antiknock compounds in petrol and can easily leak into the soil and groundwater.

Soil and groundwater pollution around petrol stations by heavy metals poses great threat to food safety and human health even in low concentrations [4] that even 1-2 mgL^{-1} for lead [5]. Metals such as lead, cadmium, chromium and copper are known for their persistent behaviour in the environment with consequent environmental, human and animal damage [6-8]. Some of these metals are associated with various human ailments like cardiovascular, nervous system, blood and bone diseases, kidney failure, gingivitis, tremors and among others [9, 10]. Since majority of the petrol stations in major cities in many parts of Nigeria like Abeokuta were indiscriminately established without compliance to Department of Petroleum Resources (DPR) rules and regulations, measures must be taken to investigate the concentrations of pollutants from the activities for proper environmental management and to safeguard the health of the people. There is the need for thorough investigation of the level of pollution of the soil and groundwater around fuel station, and the data would serve as baseline for management of urban pollution and proper planning. Therefore, the objective of this study was to assess heavy metals pollution in soil and groundwater around selected petrol stations in Abeokuta Metropolis, Nigeria.

Materials and methods

Study area

Abeokuta is located in southwest Nigeria and lies between Latitude 7° 102′ N and 7° 152′ N and Longitudes 3° 172′ E and 3° 262′ E. It covers an approximate area of about 808 km^2 (Figure 1) with a population of about 593,100 [11]. Abeokuta is within the rain forest zone of Nigeria: and enjoys a tropical climate with distinct wet and dry seasons with dry period of about 130 days.

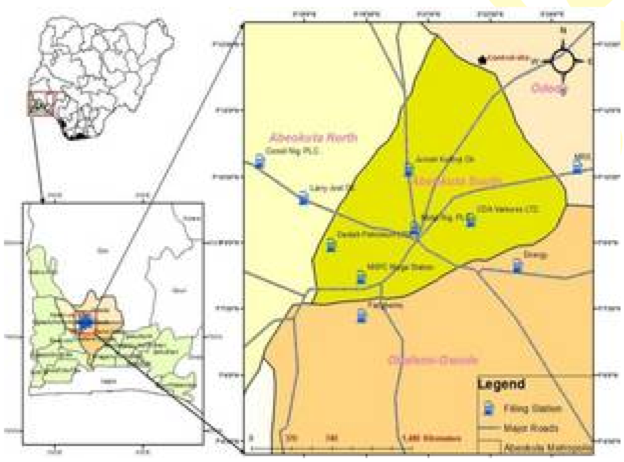

Figure 1. Map showing selected sampling points within Abeokuta Metropolis.

As the capital city of Ogun State, Nigeria, Abeokuta has witnessed tremendous in growth in terms of population and size due to increasing economic and industrial activities. As a result, several petrol stations have emerged within the metropolis that contravenes as the established rules and regulations. Presently, there are about one hundred and twenty petrol stations in Abeokuta dispensing petroleum products such as petrol, diesel, and lubricating oil. Most of these petrol stations are located within residential areas in defiance to planning rules and regulation thus putting the health and safety of the people at risk.

Sampling

The sampling locations covered the 10 petrol stations: CNP, JKO, CDA, EP, NMS, MRS, FAG, LJO, DRL, and MNP which were randomly selected as the study-points. These represent about 10 per cent of the total of number of 120 petrol stations in the metropolis. Soil samples each were taken from both the topsoil (0-15 cm) and subsoil (15-30 cm) around each of the selected petrol stations using stainless steel soil auger. Triplicate soil samples per petrol station were taken and composited to form one sample. This was done for both top soil and subsoil which implied 2 samples per station making 20 composite samples in all. In addition, three groundwater samples were collected each from six hand-dug wells and four boreholes located at about 5 to 20 m away from each of the petrol stations. Control samples for soil and water were taken from uncontaminated locations about 500-1,000 metres away from the petrol stations. All samples were taken twice a month for three months.

Sample preparation

The soil samples were air-dried at room temperature for 10 days and ground in a porcelain mortar with a pestle. The ground soil sample was sieved through a 2 mm sieve to remove large debris, stones and pebbles. The composite soils were stored in glass jars at 4ºC for further analysis in the laboratory. The pH of the soil samples was determined with pH meter Hanna (Model H1991000) and electrical conductivity (EC) was determined with conductivity meter. The organic carbon content was determined according to Walkey-Black and digestion method as described by [12]. Organic matter content in the soil samples was determined by multiplying the organic carbon content with 1.724 using the assumption that organic matter content is approximately 58% carbon. Particle size distribution was determined by the hydrometer method as described by [2] while CEC was determined according to [13]. Heavy metals in the soil samples were determined following the method used by [14].

Plastic bottles used for collection of the water samples were thoroughly washed, rinsed with deionised water and soaked for 48 hours in 50% HNO_3, then rinsed thoroughly with deionized water and air-dried. Samples of total hardness, Cl^-, NO_3^- and SO_4^{2-} were refrigerated and analyzed within 24 hours. Temperature, EC, pH and DO were determined at the time of sampling in the field with HATCH portable meter. The portable meter had been previously calibrated with buffer solutions of 4 and 9 for pH determination and potassium chloride solution for determination of EC. Water quality parameters were determined using standard methods [15]. Heavy metals were determined using Atomic Absorption Spectrometry (AAS 6300, Shimadzu, Japan) following [16].

Assessment of heavy metal in soils

The level of pollution of soils around the petrol stations by heavy metals were assessed by pollution indices namely the Index of Geo-accumulation (I_{geo}) and the Potential Ecological Risk Index (RI).

Index of geo-accumulation (Igeo)

The Index of Geo-accumulation (I*geo*) introduced by [17] computed to make a qualitative assessment of metal contamination levels of the soils around the selected petrol filling station. It is a widely used method to assess the pollution levels of heavy metals in sediment, urban soil, agriculture soil and urban road dusts [18]. Index of Geo-accumulation (I*geo*) was computed using the equation:

$$I_{geo} = \log_2 \left(C_n / 1.5 B_n \right) \quad \ldots (1)$$

where *Cn* is the concentration of the element in the tested soil, while *Bn* is the geochemical background value in the average shale of element [17, 18] and the constant 1.5 compensates for natural fluctuations of a given metal and for minor anthropogenic impacts [18]. The seven classes of *Igeo* as proposed by [17] are as follows: < 0 = practically unpolluted, 0–1 = unpolluted to moderately polluted, 1–2 = moderately polluted, 2–3 = moderately to strongly polluted, 3–4 = strongly polluted, 4–5 = strongly to extremely polluted and >5 = extremely polluted.

Potential Ecological Risk Index (RI) of heavy metal pollution in the soil

Potential ecological risk index (RI) as proposed by [19] was used in this study to assess the risk posed to the environment by the toxicity of the metals from the petrol stations. The RI was used to evaluate heavy metal pollution in soils and associate ecological and environmental effects with their toxicity [20-21]. Potential ecological risk index (RI) is expressed as:

$$RI = \Sigma E_i \quad \ldots . 2$$

$$E_i = T_i f \quad \ldots . 3$$

$$f_i = C_i / B_i \quad \ldots . 4$$

where RI is calculated as the sum of all risk factors for the selected heavy metals (Cd, Co, Cu, Ni, and Pb) in the soils, E_i is the monomial potential ecological risk factor, T_i is the developed metal toxicity factor [21]. Also in the equation, f_i is the metal pollution factor, C_i is the practical concentration of metals in soil, and B_i is the background value for metals. The toxicity factor for Cd is 30, while Cu, Ni, and Pb are all 5 [21]. The adjusted evaluation criteria for the potential ecological risk index were RI d” 50, low pollution; 50 < RI d” 100, moderate pollution; 100 < RI $\leq$ 200, considerable pollution; RI > 200, high pollution [21].

Results and discussion

Physical and chemical parameters of soil

The physical and chemical parameters of top and sub-soil samples from the petrol stations are presented in Table 1. pH values were 7.05±0.31, 7.84±0.11, 7.89±0.07, 8.01±0.07, 8.18±0.26, 7.78±0.27, 8.01±0.08, 8.50±0.17, 8.07±0.19 and 8.35±0.05 for CNP, JKO, CDA, EP, NMS, MRS, FAG, LJO, DRL and MNP petrol stations respectively for the topsoil. The soil lithological materials from the filling stations were either alkaline or slightly neutral. EC values varied between 132.67±6.03 (CNP) to 659.59±66.89 µS/cm (DRL) in topsoil, while in subsoil 119.33±1.15 in EP to 363.67±14.98 µS/cm in NMS respectively for the petrol stations (Table 1).

The high EC values for soils around the petrol stations could possibly be attributed to the uptake of soluble electrolyte from the spilled petroleum products on the soil around the petrol stations vicinity. Soils of the studied-areas were high in sand content, moderate in silt content and low in clay content. The sand-content in the soil samples decreased with an increasing depth. High sand-content in soil samples promotes the infiltration of heavy metals downwards, biodegradation, and an increase of oxygen supply. The study revealed

Table 1. Physical and chemical parameters for top-soil (0-15 cm) and sub-soil samples (15-30 cm).

Petrol station	pH	TEMP (^{O}C)	EC(µS/cm)	% OC	% OM	% SAND	% CLAY	% SILT	CEC (Cmolkg^{-1})
CNP Top	7.05±0.31	26.96±0.06	132.67±6.03	1.05±0.03	1.80±0.05	79.57±1.15	5.81±1.15	14.61±1.15	45.86±1.29
Sub	7.36±0.11	26.93±0.15	222.67±3.06	1.18±0.05	2.03±0.09	85.91±0.58	3.81±1.15	10.28±1.00	68.18±0.76
JKO Top	7.84±0.05	26.97±0.06	266.67±12.66	2.25±0.03	3.87±0.05	86.91±1.15	1.15±1.15	11.95±1.15	110.66±0.90
Sub	8.02±0.03	27.27±0.31	248.67±6.66	2.34±0.06	4.02±0.10	85.57±1.15	3.48±1.00	10.95±0.58	103.87±1.53
CDA Top	7.89±0.07	27.00±0.10	121.33±4.16	0.93±0.03	0.60±0.06	92.91±1.15	3.15±1.15	3.95±1.15	42.93±1.19
Sub	7.93±0.07	26.73±0.31	159.00±3.61	0.95±0.04	1.64±0.07	87.57±1.15	3.75±1.10	8.61±1.15	40.15±0.99
EP Top	8.01±0.07	27.03±0.06	153.00±4.58	0.78±0.04	1.35±0.06	88.91±1.15	2.47±0.01	8.61±1.15	47.12±1.O3
Sub	8.20±0.18	27.07±0.1	119.33±1.15	0.93±0.03	1.61±0.06	88.57±2.52	3.48±1.00	7.95±3.06	63.78±1.32
NMS Top	8.18±0.26	26.97±0.06	302.00±2.00	0.47±0.05	0.79±0.08	81.57±2.31	11.15±1.15	7.28±2.00	38.93±1.28
Sub	8.18±0.08	27.07±0.29	363.67±14.98	0.96±0.03	0.65±0.05	84.91±1.15	3.07±1.02	11.35±0.12	63.65±1.33
MRS Top	7.78±0.27	26.93±0.06	429.00±22.11	1.52±0.05	2.61±0.08	83.57±1.15	3.81±1.15	13.95±1.15	46.31±0.63
Sub	7.96±0.04	27.33±0.31	237.33±3.06	1.52±0.03	2.63±0.07	81.57±2.31	4.41±0.12	14.01±2.19	41.37±2.03
FAG Top	8.01±0.08	26.93±0.06	203.33±4.04	0.74±0.05	1.27±0.10	91.57±1.15	3.15±1.15	5.28±2.00	115.75±1.80
Sub	8.15±0.17	27.13±0.42	202.00±4.00	0.33±0.03	0.56±0.05	88.91±1.15	3.08±1.22	8.01±1.27	81.52±1.48
LJO Top	8.50±0.17	27.40±0.40	171.67±6.50	0.64±0.05	1.09±0.06	90.24±2.00	3.15±1.15	5.28±2.00	72.82±2.06
Sub	8.05±0.31	27.13±0.23	273.00±6.00	0.46±0.06	0.79±0.11	78.91±1.15	7.15±2.31	13.95±1.15	87.27±1.34
DRL Top	8.07±0.19	27.34±0.35	659.59±66.89	0.97±0.03	1.09±0.06	70.91±1.15	9.81±1.25	19.28±2.00	73.08±0.42
Sub	8.39±0.08	27.00±0.20	354.33±6.51	1.32±0.03	2.28±0.06	81.57±2.31	8.81±1.15	12.61±1.15	110.30±1.14
MNP Top	8.35±0.05	27.27±0.31	361.67±6.03	1.48±0.05	2.55±0.08	84.91±1.15	3.15±1.15	11.95±1.15	70.57±1.18
Sub	8.11±0.24	27.00±0.10	216.33±9.29	1.69±0.08	2.92±0.14	88.24±2.00	3.81±1.15	7.95±1.15	63.96±3.70
Control Top	6.55±0.20	25.60±0.30	100±1.20	3.26±0.68	5.30±1.34	83.30±0.05	3.80±0.10	12.90±0.20	105.07±4.50
Sub	6.20±0.13	25.30±0.20	80±0.80	0.98±0.35	1.68±1.00	85.80±0.02	5.10±0.20	9.10±0.70	85.35±3.65

Electrical Conductivity =EC; Organic Carbon = OC; Organic Matter = OM; Cation Exchange Capacity = CEC.

low organic carbon contents in the soils taken from all the petrol stations. Most of the soil-samples studied from the petrol stations had organic carbon values of less than 2.0 % except for JKO with value of 2.25±0.03 (Table 1). Cation exchange capacity (CEC) for the topsoil ranged from 38.93±1.18 cmol kg^{-1} at NMS petrol station to 115.75±1.80 cmol kg^{-1} at FAG petrol station, while CEC ranged from 40.15±0.99 at CDA Petrol Station to 110.30±1.14 cmol kg^{-1} at DRL Petrol Station for the sub-soil.

Heavy metal concentrations in soil

The following heavy metals were identified in the study-points: Cd, Cr, Cu, Ni and Pb (Tables 2). Soils around all the ten selected petrol stations exhibited varying degree of heavy metal concentrations and were much higher than the concentration in the control. Heavy metal concentrations were higher in the topsoil compared to the sub-soil except for Pb at CNP and EP, Ni at JKO, FAG and DRL, and Cu at DRL. Cd was found at low concentration in all the soil samples with the highest concentration in the top-soil at CDA and CNP Petrol Stations with mean values of 0.33±0.14 mg/kg. In the top-soil, Cr concentrations ranged from 11.08±0.63 mgL^{-1} at DRL petrol station to 27.83±0.63 mgL^{-1} at LJO petrol station (Table 2). The values of Cr from all the sampling stations were higher than the guideline values for residential/park (6.40 mg/kg) land uses [22]. The concentrations of Cu in the top-soil ranged from 5.12±0.27 mgL^{-1} at NMS Petrol Station to 15.42±0.52 mgL^{-1} at LJO Petrol Station. Also ranges from 4.83±0.38 mgL^{-1} at MMP Petrol Station to 13.67±0.52 mgL^{-1} at JKO Petrol Station for the sub-soil (Table 2).

Cu normally accumulates in the surface zone of soil, a phenomenon explained by the bioaccumulation of the metal through anthropogenic sources [23]. Concentrations of Cu in the soils were higher than

Table 2. Heavy metal concentrations in top and sub-soil samples around selected petrol stations in Abeokuta Metropolis (*n*=3).

Petrol station		Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)
CNP	Top	0.33±0.14	17.42±0.63	10.92±0.38	19.25±0.50	46.50±0.50
	Sub	0.29±0.19	18.50±0.50	11.58±0.52	5.08±0.63	55.75±0.50
JKO	Top	0.13±0.01	16.25±0.25	13.33±0.63	6.58±0.38	56.33±0.63
n = 3	Sub	0.13±0.01	16.83±0.38	13.67±0.52	4.83±0.63	42.17±0.52
CDA	Top	0.29±0.19	13.33±0.38	6.25±0.25	3.00±0.43	13.75±0.50
	Sub	0.33±0.14	6.75±0.50	5.17±0.38	7.00±0.50	10.50±0.50
EP	Top	0.13±0.01	13.58±0.38	6.25±0.50	8.33±0.38	31.50±0.50
	Sub	0.13±0.01	11.75±0.25	5.08±0.58	3.75±0.50	66.92±0.38
NMS	Top	0.22±0.01	15.50±0.50	5.12±0.27	5.40±0.52	20.33±0.38
	Sub	0.13±0.01	2.67±0.29	1.67±0.52	0.33±0.38	5.50±0.43
MRS	Top	0.13±0.01	14.33±0.29	6.92±0.29	3.08±0.80	30.50±0.50
	Sub	0.10±0.01	15.25±0.25	6.75±0.25	0.25±0.25	25.42±0.52
FAG	Top	0.13±0.01	16.33±0.25	11.58±0.38	3.33±0.38	68.83±0.63
	Sub	0.09±0.01	3.42±0.52	6.25±0.50	8.42±0.52	49.00±0.50
LJO	Top	0.37±0.01	27.83±0.63	15.42±0.52	9.00±0.50	209.25±0.66
	Sub	0.220.01	12.42±0.29	13.08±0.76	8.00±0.50	143.83±0.38
DRL	Top	0.13±0.01	11.08±0.63	8.42±0.38	11.08±0.63	44.57±0.63
	Sub	0.11±0.01	15.33±0.38	10.33±0.38	11.25±0.25	33.33±0.29
MNP	Top	0.09±0.01	12.00±0.66	7.83±0.29	11.33±0.38	41.17±0.14
	Sub	0.07±0.01	9.75±0.50	4.83±0.38	3.42±0.52	30.83±0.76
Control	Top	0.04±0.01	2.75±0.02	1.02±0.01	0.21±0.03	0.75±0.02
	Sub	0.02±0.01	1.02±0.01	0.50±0.02	0.11±0.01	0.23±0.01

WHO maximum limit of 0.05 mgkg^{-1} for soils [24] but below the normal threshold value (20-30 mg/kg) as prescribed for soil [24]. Heavy metals such as Cu and Cd are released in different particles sizes [25] in the urban environment and this is due primarily to anthropogenic activities associated with traffic-related emissions due to incomplete fossil-fuel combustion from vehicles or industrial processes. Nickel concentrations in the top-soil were low ranging between 3.00±0.45 mgL^{-1} at CDA Petrol Station to 19.25±0.50 mgL^{-1} at CNP Petrol Station, which corroborated the findings of [1] in their research on heavy metals assessment of soil near petrol stations in some selected local government areas of Benue State, Nigeria.

Mean concentrations of Pb in the top-soil obtained from each of the petrol station ranged from 13.75±0.50 mgL^{-1} at CDA petrol station to 209.25±0.66 mgL^{-1} at LJO Petrol Station; while in the subsoil it ranged from 10.50±0.50 mgL^{-1} at CDA Petrol Station to 143.0.83±0.38 mgL^{-1} at LJO Petrol Station. Pb concentrations in the soil, which was greater than 1.0 mgL^{-1} generally, indicate a local source of pollution [1]. This could be attributed to leakage of fuel from the storage tanks or corroded metallic storage tanks. In addition, Pb increased with decreasing depth at CNP and EP Petrol Stations. Pb concentration recorded for some of the petrol stations were higher than the worldwide soils value of 17 kg/mg reported by [26].

Furthermore, Pb concentration of 209.25±0.66 mgL^{-1} for top soil sample at LJO Petrol Station was higher than Pb Tanzania Bureau of Standards threshold limit of 200 mgL^{-1} for soil [27]. Excessive Pb in the soil medium has effects on children's developmental and can cause adverse situation and toxicity to adults [28-29]. High concentrations of the heavy metal in soils were observed in this study; also geochemical composition of parent material and natural processes have great influence on the concentrations and distribution of metals in the environment [29]. Soils located close to a point source such as the petrol stations are known to have remarkably high metals concentrations [30]. Human activities and atmospheric deposition of entrained particulates from vehicle and industry exhausts can increase heavy metal concentrations in the soils [31] Heavy metal in high concentration around the petrol stations could influence public health via ingestion, direct dermal contact with soil or by inhalation. This is because virtually all the petrol stations were found in residential areas where people could easily be exposed to the potential risk of fuel spillage or fuel tank leakages. Children are particularly the most sensitive target group exposed to the contaminated soils [32] due to their higher sensitivity, as well as characteristic behaviours such as hand-to-mouth activity and deficient hygienic habits.

Index of Geo-accumulation (Igeo)

Contamination levels of heavy metals in soils around the selected petrol stations were computed using the index geoaccumulation (*Igeo*) according to [17]. Table 3 shows the values obtained for each heavy metal in the top-soils and sub-soils. The I*geo* values for Cu and Pb were very high ranging from 2.193 (moderately to strongly polluted) to 3.784 (strongly polluted) for Cu in the topsoil. Pb in the topsoil had I*geo* values that ranged from 6.55 to10.48, which indicated extremely polluted soil (Table 3). The I*geo* values all other metals were less than zero indicating that the soils around the petrol stations are practically unpolluted with this metals except for Ni in CNP, which had an *Igeo* value of 0.038 indicating unpolluted to moderately polluted. The results obtained revealed that soils around LJO Petrol Station is the most polluted by Pb as shown by their I*geo* of 10.475 and 9.954 in the top-soil and sub-soil respectively. The I*geo* for Cu in the sub-soil was the highest at the JKO Petrol Station followed by the LJO Petrol Station.

Table 3. Index of geoaccumulation in topsoil and subsoil around selected petrol stations in Abeokuta Metropolis.

Index of Geoaccumulation *(Igeo)*										
Parks	**Top-soil**					**Sub-soil**				
	Cd	Cr	Cu	Ni	Pb	Cd	Cr	Cu	Ni	Pb
CNP	-7.828	-1.521	3.286	0.038	8.305	-8.015	-1.434	3.371	-1.884	8.566
JKO	-9.172	-1.621	3.574	-1.511	8.581	-9.172	-1.571	3.610	-1.884	8.164
CDA	-8.015	-1.907	2.481	-2.644	6.547	-7.828	-2.889	2.207	-1.421	6.158
EP	-9.172	-1.880	2.481	-1.171	7.743	-9.172	-2.089	2.182	-2.322	8.830
NMS	-8.413	-1.690	2.193	-1.796	7.111	-9.172	-4.227	0.577	-5.828	5.225
MRS	-9.172	-1.803	2.628	-2.606	7.696	-9.551	-1.713	2.481	-6.229	7.433
FAG	-9.172	-1.614	3.371	-2.493	8.871	-9.703	-3.870	2.481	-1.155	8.380
LJO	-7.663	-0.845	3.784	-1.059	10.475	-8.413	-2.009	3.547	-1.229	9.934
DRL	-9.172	-2.174	2.911	-0.759	8.244	-9.413	-1.706	3.206	-0.737	7.824
MNP	-9.703	-2.059	2.806	-0.727	8.129	-10.065	-2.358	2.109	-2.455	7.712

Potential Ecological Risk Index (RI)

Figure 2 shows the potential ecological in the top and sub soil in the selected petrol stations in Abeokuta Metropolis. The results show that the soils around the petrol stations examined have potential ecological risk as indicated by their RI values, which were above 200 (high pollution) [21]. In the top-soil, LJO Petrol Station had the highest RI value of 5915.944 while CNP Petrol Station had the highest RI of 3,906.371 in the sub-soil. This implies that soil around the petrol stations potentially pose ecological and health risk to the people around the area because of expose through ingestion, inhalation and dermal absorption [21, 33-34]. Children around the locations of the petrol stations can easily ingest soil laden with heavy metals due to their tendency to play on the floor and habit of putting things in their mouth [35].

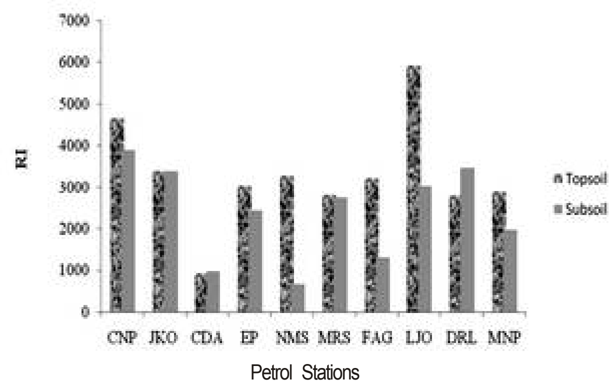

Figure 2. Potential ecological risk index (RI) for top and sub soil in the selected petrol stations in Abeokuta Metropolis.

Physical and chemical parameters in groundwater

Mean pH values of groundwater ranges from 8.26±0.23 at JKO Petrol Station to 9.27±0.35 at LJO petrol station (Table 4). The pH values indicate that

Table 4. Physical and chemical parameters for groundwater.

Petrol Station	pH	Temp (^{O}C)	EC (µS/cm)	DO (MgL^{-1})	TDS (MgL^{-1})	TSS (MgL^{-1})	TH	Cl^-	NO_3^-	SO_4^{2-}
CNP	8.33±0.25	28.35±0.64	252.50±20.51	2.65±0.92	117.50±2.12	0.18±0.03	146.00±5.66	24.00±1.41	30.42±2.14	14.72±1.07
JKO	8.26±0.23	27.80±0.85	423.50±37.48	2.60±0.14	157.50±13.44	0.03±0.01	93.00±1.41	69.00±1.41	9.68±0.30	27.83±0.80
CDA	8.58±0.32	27.55±0.35	265.00±4.24	3.25±0.92	190.00±5.66	0.05±0.01	141.00±9.90	71.50±2.12	7.18±0.11	11.15±0.21
NMS	9.00±0.13	28.05±0.49	250.50±5.66	3.45±0.21	107.00±1.41	0.24±0.11	91.00±7.07	34.00±2.83	0.25±0.07	3.12±0.39
MRS	8.90±0.35	27.15±0.64	391.00±1.41	2.90±0.14	193.50±9.19	0.90±0.10	151.00±1.41	64.50±2.12	17.74±0.70	30.21±1.39
LJO	9.03±0.35	27.60±0.28	772.00±408.71	2.25±1.91	431.00±151.32	0.40±0.37	298.00±2.83	114.50±26.16	8.46±0.36	16.15±0.21
DRL	9.29±0.35	27.65±0.07	167.50±4.95	3.90±0.42	85.50±2.12	0.11±0.07	79.00±4.24	26.50±2.12	2.57±0.35	49.20±1.36
MNP	8.78±0.29	27.75±1.20	490.00±4.24	2.95±1.06	234.00±2.83	0.34±0.03	160.00±2.83	60.00±2.83	38.27±2.19	43.01±0.32
Control	7.65±0.03	26.30±0.35	60.03±18	2.02 ±0.08	57.52±1.09	0.09±0.03	45.00±2.35	16.20±1.03	3.05±0.07	1.92±0.53

Electrical Conductivity = EC; Dissolved Oxygen = DO; Total Dissolve Solid = TDS. Total Suspended Solid = TSS; Total Hardness = TH.

the water is alkaline in nature. pH affects the water quality metal solubility and hardness of the water [7] and the metabolic activities of aquatic organisms are pH dependent. The average pH values of water samples for most of petrol stations exceeded WHO standard of 6.00-9.00 for drinking water [36]. The temperatures of the water from the ten petrol stations were ranged from 26.70 and 28.80^{0}C, and were within the normal range for aquatic lives [37]. Electrical conductivity (EC) of the groundwater samples was very high with the LJO Petrol Station having the highest average EC value of 772 ±408 ìS/cm. The high values of EC obtained from the petrol stations could be attributed to the high loads of conducting ions. These values were higher than WHO [36] standard of 200 ìS/cm for drinking water. Total dissolved solid (TDS) values were quite high in the groundwater samples (Table 4). TDS values of groundwater from the ten petrol stations ranged from 85.50±2.12 mgL^{-1} at DRL petrol station to 431±151 mgL^{-1} at LJO Petrol Station, TDS are known to be negatively charged and attract more heavy metal ions, reducing their concentrations in water [38]. There is a positive correlation ($r = 0.834$) between TDS and electrical conductivity and this agreed with the findings of [7] that established linear relationship between TDS and EC in a study on water quality and bacteriological assessment of slaughter-house effluent on urban river in Nigeria.

The concentrations of chloride and total hardness from the studied petrol-stations were within the WHO standards for drinking water. Concentration of nitrate in groundwater at different sampling locations varies with the highest average concentration of 38.27±2.19 mgL^{-1} was recorded at MNP Petrol Station, while the lowest concentration of 0.25±0.07 mgL^{-1} was recorded at NMS Petrol Station. The presence of nitrate in water indicates the presence of fully oxidized organic matter [38]. The sharp increase of NO_3^- at MNP Petrol Station may be attributed to its closed proximity to Itoku Market where textiles and fabrics materials are produced. The concentration of sulphate ranged from 3.12±0.39 mgL^{-1} at NMS Petrol Station to 49.20±1.36 mgL^{-1} at DRL Petrol Station. However these values were below the WHO standard limit of 250 mgL^{-1} for drinking water [61]. Dissolved oxygen (DO) in groundwater samples from the petrol stations ranges from 2.25±1.91 mgL^{-1} at LJO Petrol Station to 3.90±0.42 mgL^{-1} at DRL Petrol Station (Table 4). Low level of dissolved oxygen may be attributed to presence of large amount of organic loads, which required high level of oxygen for chemical oxidation and breakdown, thereby resulting in the depletion of oxygen [7].

Heavy metals concentration in groundwater

The average concentrations of Pb were 0.19±0.03, 1.31±0.01, 3.52±0.6 mgL^{-1} for JKO, NMS and MRS Petrol Stations respectively (Table 5). These values were higher than the [36] WHO permissible limit of 0.01 mgL^{-1} for drinking water. The high concentration of Pb across the sampling points could be due to leaking of petrol from the petrol stations and the exposure of groundwater to metallic objects and rusted materials [39]. The average concentration of Cu in the ground-water was low across the sampling points. CDA, LJO and MNP Petrol Stations recorded the highest average concentrations of 0.03±0.01, 0.03±0.01 and 0.03±0.01 mgL^{-1} respectively. These values were lower than the WHO maximum permissible levels [36].

However, accumulation of Cu in drinking water could be debilitating to human health. It was reported that Cu is toxic to aquatic organisms and the ecosystem and it binds strongly to organic matter in sediment [7].

The concentrations of Cr were quite high in the groundwater samples with LJO Petrol Station having the highest average concentrations of 0.13±0.01 mgL^{-1} while EP petrol station recorded the lowest average concentration of Cr 0.02±0.01 mgL^{-1}. According to [40], chromium compounds were released to the environment via leakage, poor storage, or improper disposal practices and are very persistent in water. The concentrations of Cd in the sampling locations were higher than World Health Organization standard (0.005) [36] for drinking water. The metals were below detection limit in the control samples.

Variations in heavy metal concentrations in the water and soil samples studied were a consequence of a wide range of human activities [38]. Leaking fuel tanks and spills at petrol stations have contaminated drinking water sources for nearby communities, and have become costly for owners to clean up [40]. Pearson correlation for the metals in the soil samples was conducted to observe interrelations among the metals examined. There were positive correlations between pairs of Pb/Cr (0.982) at 0.01 significant levels, and Pb/Cu (0.998) at 0.05 significant levels for top soil samples (Table 6). This implies that the heavy metals in the soils around the petrol stations were from the same sources, which was mostly due to activities in the stations.

Table 5. Heavy metal concentrations in groundwater samples.

Petrol Station	Cu (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Ni (mg/kg)
CNP	0.02±0.01	0.05±0.01	0.02±0.01	0.05±0.01	0.06±0.01
JKO	0.02±0.01	0.04±0.01	0.02±0.01	0.19±0.03	0.05±0
CDA	0.03±0.01	0.03±0.01	0.21±0.01	0.05±0.01	0.06±0.01
EP	0.02±0.01	0.02±0.01	0.02±0.01	0.11±0.01	0.06±0.01
NMS	0.02±0.01	0.10±0.01	0.02±0.01	1.31±0.01	0.06±0.01
MRS	0.02±0.01	0.11±0.01	0.02±0.01	3.52±0.6	0.06±0.01
FAG	0.02±0.01	0.08±0.01	0.02±0.01	0.05±0.01	0.05±0.06
LJO	0.03±0.01	0.13±0.01	0.02±0.01	0.21±0.01	0.06±0.01
DRL	0.02±0.01	0.06±0.02	0.02±0.01	0.05±0.01	0.06±0.01
MNP	0.03±0.01	0.07±0.02	0.02±0.01	0.31±0.02	0.06±0.01
Control	ND	ND	ND	ND	ND

ND= Not detected.

Table 6. Pearson correlation analysis of heavy metals in topsoil samples of the petrol station.

	Cd	Cr	Cu	Ni	Pb
Cd	1				
Cr	0.655	1			
Cu	0.500	0.982**	1		
Ni	0.866*	0.189	0.000	1	
Pb	0.500	0.982*	0.998**	0.000	1

Conclusion

The study revealed contamination of soil and groundwater around petrol stations with heavy metals such as Pb, Cr and Cu. Pb concentration of 209.25 mgL^{-1} for top-soil sample at LJO Petrol Station was the highest and this was above the Pb threshold limit of 200 mgL^{-1} for soil as reported by Tanzania Local Standards. LJO Petrol Station was the most polluted by Pb as shown by their I*geo* of 10.48 and 9.95 (delete) in the top-soil and sub-soil respectively. The I*geo* values of all other metals were less than zero indicating that the soils around the petrol stations are practically unpolluted with these metals except for Ni in CNP, which had an I*geo* value of 0.038 indicating unpolluted to moderately polluted.

However, the soils around the petrol stations examined had high potential ecological risk as indicated by their RI. Heavy metal pollution poses potential threat to humans and critical environmental media such as water bodies. Sources of pollution might be from the spillage from dispensing of petrol, leakages or seepages from the underground petrol tankers.

Concerned government authorities need to improve on the regulation and monitoring of the petrol stations in the metropolis to reduce the environmental and health risks associated with the activities.

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