

Full Length Research Paper

Assessment of heavy metals concentration in soils around oil filling and service stations in the Tamale Metropolis, Ghana

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This study was conducted to assess the level of heavy metals contamination of soil around oil filling and service stations in the Tamale Metropolis. Soil samples were collected from various oil filling and service stations. Elemental analysis of samples was conducted using atomic absorption spectrometer at Atomic Energy Laboratory, Accra. The metals concentrations ranged from 2.37 to 15.00 mg/kg for Cr; 0.01 to 0.03 mg/kg for Hg; 3.2 to 22.68 mg/kg for Cu; 0.12 to 6.63 mg/kg for Cd and 4.93 to 74.20 mg/kg for Pb. The mathematical models: Index of geoaccumulation (Igeo), enrichment factors (EF), contamination factor and degree of contamination were employed to identify possible levels of pollution from anthropogenic sources. The enrichment factor means places the elements in a decreasing order as Cd > Pb > Cr > Cu > Ni > Fe > Zn > As > Hg > Mn that agreed with others models such as contamination factor, pollution load index and degree of contamination. Elements such as chromium (Cr), copper (Cu), lead (Pb) and manganese (Mg) gave enrichment factor values ranging from 2-5 signifying moderate enrichment. The study revealed that soil contamination by the metals originated from a common anthropogenic source such as the oil filling activities, brake wear, tyres wear and corroded vehicles engine materials since these sources are noted to contribute one or two correlated metals to the natural environment. Hence, pose potential threat to humans and critical environmental media such as water bodies. It is therefore recommended that Environmental Protection Agency (EPA) should regularly monitor the oil filling and service stations to check the levels of heavy metals in the metropolis.

Key words: Oil filling, service station soils, enrichment factor, heavy metals, cadmium, Tamale Metropolis.

INTRODUCTION

Heavy metals are among the more serious pollutants in our natural environment due to their toxicity, persistence

and bioaccumulation potential (Caeiro et al., 2005). Following the introduction of heavy metal contaminants

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into a river, whether via natural or anthropogenic sources, they partition between aqueous (pore water, overlying water) and solid phases (sediment, suspended particulate matter and biota) (Prudencioa et al., 2007; Zhang et al., 2007). Heavy metals are natural constituents of the earth crust. A number of these elements are biologically essential and are introduced into aquatic enrichments by various anthropogenic activities (Al-Khashman, 2004). The main anthropogenic sources of heavy metals are the industrial point sources, the present and former mining activities, foundries, smelters and diffuse sources such as piping, constituents of products, combustion of by products, traffic and human activities (Nilgun et al., 2004).

Heavy metals at trace levels present in natural water, air, dusts, soils and sediments play an important role in human life (Isaac et al., 2004). Soils are critical environment where rock, air and water interface (Facchinelli et al., 2001; Jonathan et al., 2004). Topsoil and dusts in urban areas are indicators of heavy metal contamination from atmospheric deposition. It has been noted that location close to roads are severally polluted by heavy metals such as Pb, Zn, Cu, Cd among others from traffic (Guvenc et al., 2004; Wilson et al., 2005).

With the rapid industrialisation and economic development, heavy metals are continuously introduced to soils and sediments via several pathways, including fertilisation, irrigation, rivers, runoff, atmospheric deposition and point sources, where metals are produced as a result of metal mining, refining and refinishing by-products. Soils are usually regarded as the ultimate sink for heavy metals discharged into the environment (Banat et al., 2005), and sediments can be sensitive indicators for monitoring contaminants in aquatic environments (Pekey et al., 2004). Therefore, the environmental problem of soil and sediment pollution by heavy metals has received increasing attention in the last few decades in both developing and developed countries throughout the world (Zhang et al., 2007).

Pollution of the natural environment by heavy metals is a universal problem because these metals are indestructible and most of them have toxic effects on living organisms when permissible concentration levels are exceeded. Heavy metals frequently reported in literature with regards to potential hazards and occurrences in contaminated soils are Cd, Cr, Pb, Zn, Fe and Cu (Akoto et al., 2008). Environmental contamination by hydrocarbons and petroleum products constitute nuisance to the environment due to their persistent nature and tendency to spread into ground and surface waters. Environmental pollution with petroleum and petrochemical products has attracted much attention in recent decades. The presence of various kinds of automobiles and machinery vehicles has caused an increase in the use of motor oil. Oil spillages into the environment have become one of the major problems. Used motor oils such as diesel or jet fuel contaminate

natural environment with hydrocarbon (Husaini et al., 2008).

The environment can potentially be affected by numerous operations in petroleum exploration, production and transportation, with common sources of contamination being leaking underground storage tanks (Nadim et al., 2000). The chemical composition of soil, particularly its metal content is environmentally important, because toxic metals concentration can reduce soil fertility, can increase input to food chain, which leads to accumulate toxic metals in food stuffs and ultimately can endanger human health. Metals occur naturally in the earth's crust and their contents in the environment can vary between different regions resulting in spatial variations of background concentrations. The distribution of metals in the environment is governed by the properties of the metal and influences of environmental factors (Khlifi and Hamza-Chaffai, 2010).

People living in industrial cities are particularly exposed to this decline in environmental quality leading to human health problems. Urban environments are affected by natural cycles, where air, water and soil are altered by products ultimately returned to the environment in the form of nuisance. The main sources of pollution is fumes from vehicles, sediments from service stations and oils washed into water bodies, organic matter of plant and animal origin, industrial and sewage effluents. In recent times, many investors are into the oil vending (petrol and diesel) business, resulting into uncontrolled sprouting of oil filling and service stations. Some of these oil filling and service stations fails to go through environmental impact assessment process due to cost, political reasons and bureaucratic nature of the process. Hence, due to improper siting of the stations, improper storage tanks or material use for storage and mishandling of fuel during delivery can leach or contribute heavy metals concentrations that can pose threat to environmental media. The objective of this study was to assess the levels of heavy metal concentration around the oil filling and service stations in the Tamale Metropolis.

MATERIALS AND METHODS

Study area

Tamale is the capital of Northern Region of Ghana (Figure 1). Tamale is the third most populous settlement in Ghana with 537,986 inhabitants according to the 2012 census (GhanaWeb.com). The town is located 600 km north of Accra. The metropolis experiences one rainy season from April to September or October with a peak in July and August. The mean annual rainfall is 1100 mm within 95 days of rainfall in the form of tropical showers. Consequently, staple crop farming is highly restricted by the short rain season. The dry season is usually from November to early April. It is influenced by the dry North-Easterly (Harmattan) winds while the rainy season is influenced by the moist South Westerly winds. The mean day temperatures range from 28°C (December and mid-April) to 43°C (March, early April) while mean night temperatures range from 18°C (December) to 25°C

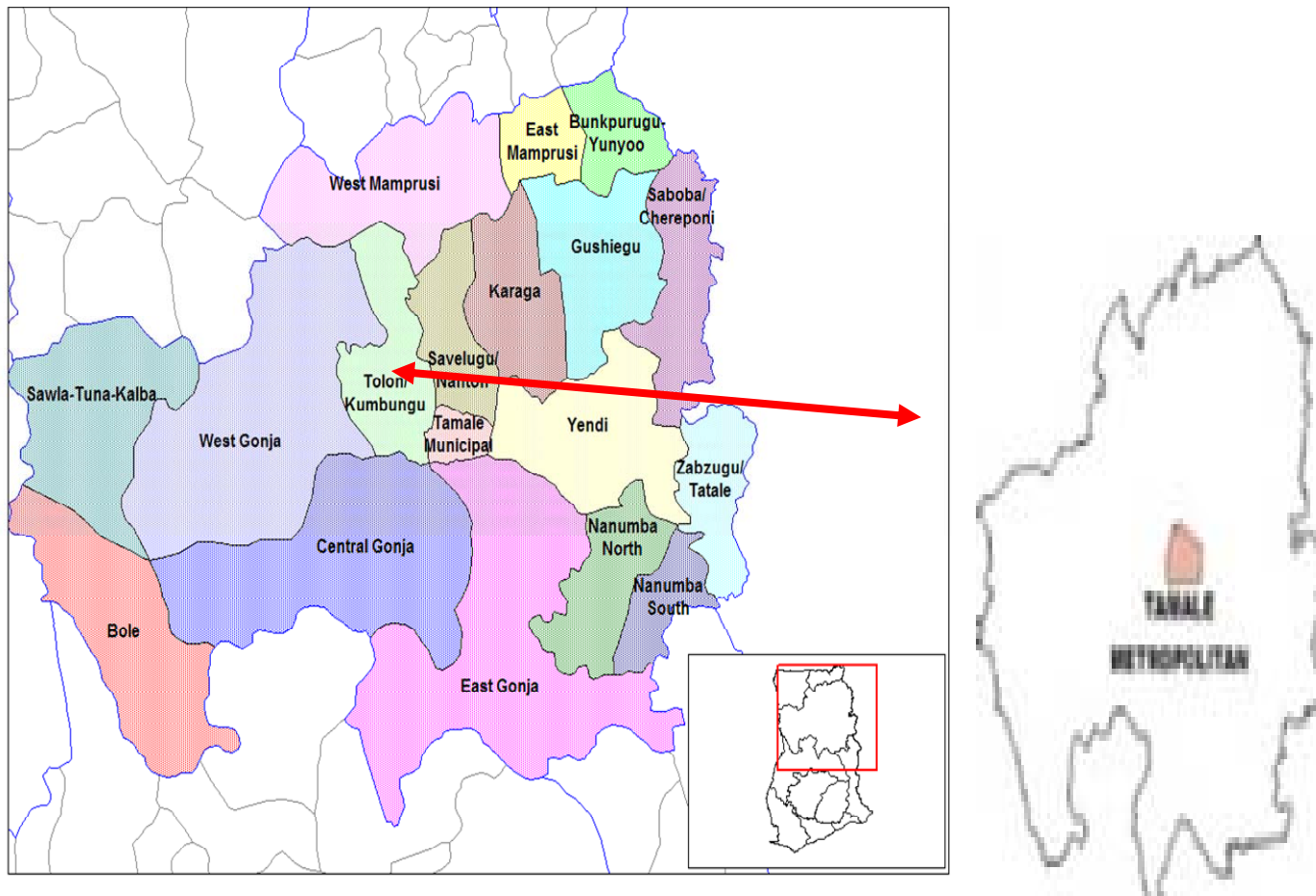


Figure 1. Map of the northern region with Tamale Metropolis singled out.

(February, March). The mean annual day sunshine is approximately 7.5 h.

Sampling techniques

Soil samples were taken from twenty one (21) oil filling and service stations in the Tamale Metropolis. At the sampling sites, about 500 g of soil sample were collected by sweeping using soft touch brush, scoop, trowel and plastic containers. One sample was collected from each filling or service station. The oil filling and service station soil samples were stored in sealed plastic containers, carefully labelled and taken to National Nuclear Research Institute of the Ghana Atomic Energy Commission laboratory for elemental analysis.

Digestion of oil filling and service stations soil samples and analysis

Determination of heavy metals was done in accordance with protocols at National Nuclear Research Institute of the Ghana Atomic Energy Commission. The soil samples collected were air dried to a constant weight in the laboratory under room temperature for 24 hours and then sieved using 200 μm mesh. Sample of 0.5 g was weighed into a tuffin bucket and 6 ml H_2NO_3 acid, 3 ml HCl with 5 drops of H_2O_2 added to the samples on a hot plate (this step was carried out in the hood). The tuffin buckets was tightened and

fixed in the rotar. The rotar was placed in the microwave oven and the machine programmed to commence the digestion process (Each sample had its own programme). The digested samples were diluted to 20 ml and transferred into the appropriate test tube. The concentrations of trace metals such as Cr, Hg, Cu, Zn, Mn, Fe, Pb, Ni, As, Co and Cd in the filtrate were determined using atomic absorption spectrometer.

Quality assurance

Strict QA/QC measures were adopted to ensure reliability of the results. All chemicals and reagents used were of high purity. Glassware used was cleaned thoroughly with detergent and rinsed several times using deionized water. Deionized water was used for all dilution purposes. For the purposes of detection and quantification limits of the AAS, a blank solution was read 25 times, and the standard deviations were calculated for the noise levels generated for each of the elements of interest. The detection limit (LOD) for each element was achieved as follows:

$$\text{LOD} = \frac{3 \times S}{m}$$

Where S is the standard deviation of the blank readings and m represents the gradient of the calibration curve for each element. The limit of quantification was calculated using 10 s/m. The

accuracy and reproducibility of the analytical procedure was determined by spiking and homogenizing three replicates of each of three samples selected at random. Triplicate of each sample was spiked with three different concentrations of the element of interest as follows: Cd (0.5, 2.0 and 3.0 mg/l), Cr (1.0, 2.0 and 5 mg/l), Ni (2.0, 5.0 and 10.0 mg/l), Co (2.0, 5.0 and 8.0 mg/l), Fe (2.0, 5.0 and 10.0 mg/l), Zn (0.25, 0.5, and 1.0 mg/l) and Pb (2.0, 5.0, and 10.0 mg/l) and treated in a similar manner as the samples. The absorbances measured by the AAS were converted to concentrations using standard calibration curves. One thousand milligrams per liter single element standards of the elements of interest, obtained from Fluka Analytical (Sigma Aldrich Chemie GmbH, Switzerland), were diluted using 10 % HNO and used to generate the calibration curves for the AAS analysis.

The oil filling and service station's soil contamination were assessed using various indices: contamination factor (CF) (degree of contamination), pollution load index (PLI), enrichment factor (EF) and index of geoaccumulation (Igeo).

Contamination factor

To assess the extent of contamination of heavy metals in oil filling and service station soils, contamination factor and degree of contamination was used (Rastmanesh et al., 2010). The Cf is the single element index which is determined by the relation:

$$Cf = \frac{C_{o-1}^i}{C_n^i} \quad (1)$$

Where Cf is the contamination factor of the element of interest, C_{o-1}^i is the concentration of the element sample, C_n^i is the background concentration, in this study the continental crustal average was used (Taylor and Meclenan, 1985). Cf is defined according to four categories: <1 low contamination factor, 1-3 moderate contamination factors, 3-6 considerable contamination factors and > 6 very high contamination factor.

Degree of contamination

The sum of the contamination factors of all the elements in the sample gives the degree of contamination as indicated in the equation below:

$$C_{deg} = \sum Cf \quad (2)$$

Four categories has been defined for the degree of contamination as follows: <8 low degree of contamination, 8-16 moderate degree of contamination, 16-32 considerable degree of contamination and > 32 very high degree of contamination.

Pollution load index

Each oil filling and service station soil was evaluated for the extent of metal pollution by employing the method based on the pollution load index (PLI) developed by Thomilson et al. (1980) as follows:

$$PLI = \sqrt[n]{CF1 \times CF2 \times CF3 \times \dots \times CFn} \quad (3)$$

where n is the number of metals studied and CF is the contamination factor calculated as described in an earlier equation. The PLI provides simple but comparative means for assessing a site quality, where a value of PLI < 1 denote perfection; PLI = 1 shows that only baseline levels of pollutants are present and PLI > 1 indicate deterioration of site quality (Thomilson et al., 1980).

Enrichment factor

Enrichment factor (EF) of an element in the studied samples is based on the standardization of a measured element against a reference element. A reference element is often the one characterized by low occurrence variability. It is used to differentiate heavy metals originating from human activities and those of natural sources. This is determined by the relation:

$$EF_x = [X_s / E_{s(ref)}] / [X_c / E_{c(ref)}] \quad (4)$$

where EF_x is the enrichment factor for the element X, X_s is the concentration of element of interest in sample, E_{s (ref)} is the concentration of the reference element used for normalization in the sample, X_c is the concentration of the element in the crust and E_{c (ref)} is the concentration of the reference element used for normalization in the crust (Taylor and Meclenan, 1985). Five contamination categories were recognized on the basis of the enrichment factor: EF < 2 deficiency to minimal enrichment, EF = 2-5 moderate enrichment, EF = 5-20 significant enrichment, EF = 20-40 very high enrichment and EF > 40 extremely high enrichment (Yongming et al., 2006; Kartal et al., 2006).

Index of geoaccumulation

The index of geoaccumulation (Igeo) is widely used in the assessment of contamination by comparing the levels of heavy metal obtained to a background levels originally used with bottom sediments (Muller, 1969). It can also be applied for the assessment of oil filling and service station soil samples contamination. It is calculated using the equation:

$$Igeo = \log_2 (C_n / 1.5B_n) \quad (5)$$

C_n is the measured concentration of the heavy metal in oil filling and service station soil and B_n is the geochemical background concentration of the heavy metal (crustal average) (Taylor and Meclenan, 1985). The constant 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments (Lu et al., 2010). The following classification is given for geoaccumulation index (Huu et al., 2010; Muller, 1969): < 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.

Statistical analysis

The heavy metals concentrations in oil filling and service station soils were subjected to Pearson's significant correlation analysis using SPSS version 16 to determine the relationship and characteristic between the metals.

RESULTS AND DISCUSSION

Heavy metal concentration in oil filling and service station

Heavy metals enter the environment by natural and anthropogenic means such as natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents, pest and disease control agents applied to plants, air pollution fallout, oil leaking

Table 1. Mean concentration of heavy metals (mg/kg) in soils within oil filling and service stations.

Elements	Minimum	Maximum	Mean	Std. Deviation	Soils worldwide
Cr	2.37	15	7.35	2.6	80
Hg	0.01	0.03	0.02	0.01	-
Cu	3.29	22.68	7.86	4.79	25
Zn	3.15	10.43	5.57	2.02	70
Mn	0.23	3.69	2.54	0.75	9
Fe	1.5	1.68	1.53	0.04	35
Pb	4.93	74.2	19.51	15.13	17
Cd	0.12	6.63	2.29	3.76	0.3
Ni	1.79	5.29	2.82	0.87	20
As	0.13	0.71	0.33	0.16	-

from underground storage tanks, corroded metallic storage tanks among others. The mean concentration of the elements obtained from soil samples from oil filling and service stations in the Tamale Metropolis shows decreasing order of Pb > Cu > Cr > Zn > Ni > Mn > Cd > Fe > As > Hg. The concentration of chromium (Cr) ranged from 2.37 to 15.00 mg/kg with a mean of 7.35±2.60 mg/kg (Table 1). Variety of small large scale industrial activities for example metal plating, anodizing, dyes, pigments, ceramic, glues, tanning, wood preserving and textiles are reported to contribute to Cr levels (Alloway, 1995). The concentration of mercury (Hg) ranged from 0.01 to 0.03 mg/kg with a mean of 0.02±0.01 mg/kg (Table 1). Exposure to high levels of metallic, inorganic or organic mercury can permanently damage the brain, kidneys and developing fetus.

Concentrations of copper (Cu) ranged from 3.2 to 22.68 mg/kg with a mean of 7.86±4.79 mg/kg (Table 1). Cu is an essential element, but may be toxic to both humans and animals when its concentration exceeds the safe limits. Cu is used in numerous applications because of its physical properties. The toxicity for humans is not very high (Poggio et al., 2009). Cu normally accumulates in the surface horizons, a phenomenon explained by the bioaccumulation of the metal and recent anthropogenic sources (Abdul Hameed et al., 2013). The observed values of the Cu content did not exceed the normal threshold value prescribed in soil (20 - 30 mg/kg) (Alloway, 1995). Manganese (Mn) recorded concentration levels ranging from 0.23 to 3.69 mg/kg with a mean of 2.54±0.75 mg/kg (Table 1). Manganese deficiency in the human body can produce severe skeletal and reproductive abnormalities in mammals. High doses of manganese can cause adverse effects primarily on the lungs and on the brain. The concentration of Zinc (Zn) ranged from 3.15 to 10.43 mg/kg with a mean of 5.57±2.02 mg/kg (Table 1).

Environmental contamination of Zn is mainly related to anthropogenic input. The anthropogenic sources of Zn are related to industries and the use of liquid manure, composted materials and agrochemicals such as

fertilizers and pesticides in agriculture (Romic and Romic, 2003). Presence of Zn may be due to oil leaking from underground storage tanks. Iron (Fe) concentration ranged from 1.50 to 1.68 mg/kg with mean of 1.53±0.04 mg/kg. Iron is vital for almost all living organisms, participating in a wide variety of metabolic processes, including oxygen transport, DNA synthesis and electron transport. It is known that adequate iron in a diet is very important for decreasing the incidence of anaemia. The concentration of lead (Pb) ranged from 4.93 to 74.20 mg/kg with a mean of 19.51±15.13 mg/kg (Table 1). Some of the lead concentration recorded in some of the oil filling and service stations exceeded the worldwide soils value of 17 mg/kg for lead. This can be attributed to leakage of oil (petrol, diesel among others) from the storage tanks or corroded metallic storage tanks. This therefore poses a potential threat to humans and critical environmental media such as water bodies. Food is one of the major sources of lead exposure; the others are air (mainly lead dust originating from petrol) and drinking water. Lead as a toxicologically relevant element has been brought into the environment by man in extreme amounts, despite its low geochemical mobility and has been distributed worldwide (Oehlenschläger, 2002).

The concentration of cadmium (Cd) ranged from 0.12 to 6.63 mg/kg with a mean of 2.29±3.76 mg/kg as compared to worldwide soil value of 0.3 mg/kg. Widespread distribution of Cd and its high mobility makes it a potential contaminant in a wide range of natural environments. Generally, soil Cd concentrations exceeding 0.5 mg/kg are considered evidence of soil pollution (McBride, 1994). Cadmium is naturally present in the environment: in air, soils, sediments and even in unpolluted seawater. Cadmium is emitted to air by mines, metal smelters and industries using cadmium compounds for alloys, batteries, pigments and in plastics, although many countries have stringent controls in place on such emissions (Harrison, 2001). Human and environmental safety cannot be guaranteed from Cd exposure as it is obvious that the operation of some of these oil filling and service stations in the metropolis are contributing to Cd

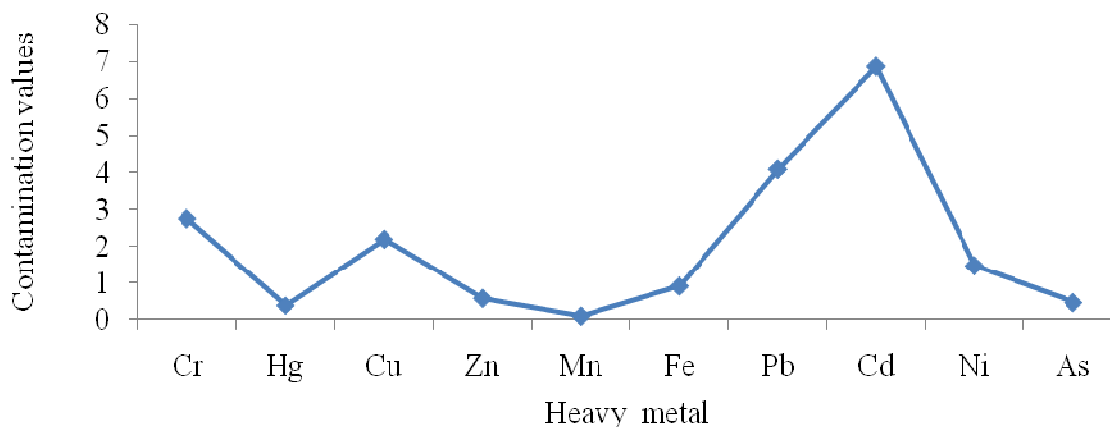


Figure 2. Degree of contamination of soil sampled from oil filling and service stations.

concentration in the soils. Many anthropogenic activities within the metropolis can increase Cd concentrations in soils well above background levels, such as sewage sludge, oil leaking from underground storage tanks and phosphate fertilizer application. Cadmium accumulates in the human body affecting negatively several organs: liver, kidney, lung, bones, placenta, brain and the central nervous system (Castro-González and Méndez-Armenta, 2008).

The concentration of Nickel (Ni) ranged from 1.79 to 5.29 mg/kg with a mean of 2.82 ± 0.8 mg/kg (Table 1). Nickel has many common industrial uses due to its unique chemical properties. Industrially, it is used in electroplating, electroforming, in circuitry, and in nickel-cadmium batteries. Metallic nickel is non-carcinogenic to humans; however, all other nickel compounds, such as nickel sulfides, oxides, and silicates and other soluble salts are carcinogens. Carcinogenic nickel exposure is greatest through the inhalation of nickel-containing particulates. The burning of fossil fuels as well as the refining of metals such as copper introduces considerable amounts of nickel into the atmosphere (Lee et al., 2005). Ni is widely used in electroplating and in the manufacture of batteries. Ni toxicity for human beings is not very high, but it can cause respiratory diseases (Poggio et al., 2009).

The concentration of arsenic (As) ranged from 0.13 to 0.71 mg/kg with a mean 0.33 ± 0.16 mg/kg (Table 1). Arsenic is quite widely distributed in natural waters and is often associated with geological sources, but in some locations anthropogenic inputs, such as the use of arsenical insecticides and the combustion of fossil fuels, can be extremely important additional sources. Inorganic arsenic is considered carcinogenic and is related mainly to lung, kidney, bladder and skin disorders (ATSDR, 2003). Arsenic is a contaminant of public concern since it is highly toxic and carcinogenic. It may be accumulated in plants and eventually be transferred to humans through the food chain.

Contamination factor and degree of contamination

Based on the results presented in Table 2, the mean contamination factor of heavy metals shows a decreasing order as follows: Cd > Pb > Cr > Cu > Ni > Fe > Zn > Hg = As > Mn. The study observed highest contamination factor of 2.29 (Cd) from only one station and least contamination factor of < 0.002 (Mn) from about sixteen oil filling stations sampled. The contamination factor for elements such as Cr, Hg, Cu, Zn, Mn, Fe, Pb, Ni and As were less than 1 signifying low contamination from anthropogenic sources (Taylor and Meclenan, 1985).

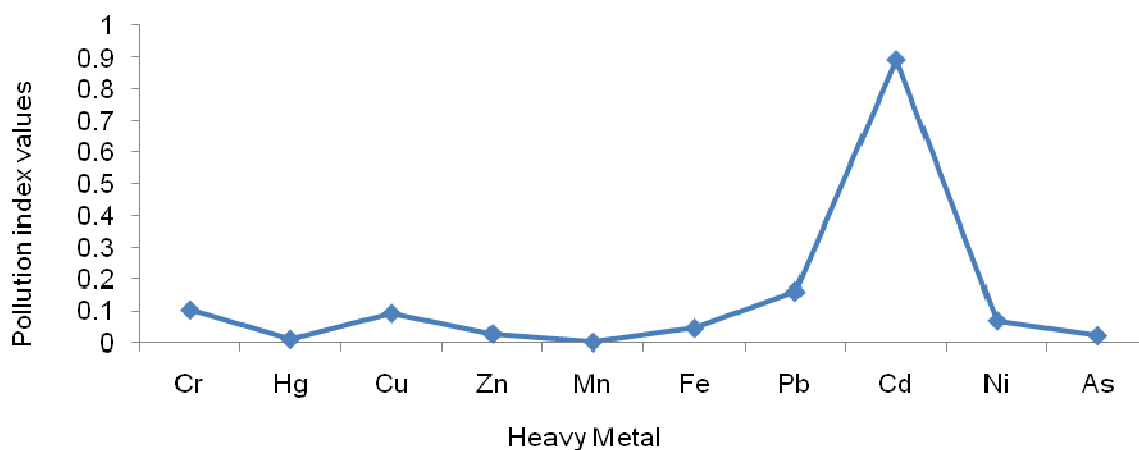
Moderate contamination was obtained in Cd (2.29) in one of the oil filling station. This might be due to oil leaking from underground storage tanks or rusted fuel tanks. The degree of contamination of soil samples from various oil filling and service stations are presented in Figure 2. Generally, the study obtained degree of contamination factors less than 8 mg/kg signifies that the samples from the oil filling and service stations have low degree of contamination (Taylor and Meclenan, 1985). The study reveals that the variability in the range of all the metal distributions as compared to their degree of contamination respectively is an indication of low pollution of the sample. The degree of contamination of heavy metals shows a decreasing order as follows: Cd > Pb > Cr > Cu > Ni > Fe > Zn > As > Hg > Mn.

Pollution load index

The study recorded pollution load index less than 1 mg/kg for all the heavy metals parameters considered which denotes perfection (Thomilson et al., 1980). Based on the results presented in Figure 3, the decreasing trend of pollution load index of heavy metal levels was as follows: Cd > Pb > Cr > Cu > Ni > Fe > Zn > As > Hg > Mn. This suggests that oil filling and service stations within the various sites have not contributed to the heavy metal concentrations in the soils. Possible inputs of heavy

Table 2. Contamination factor of soil sampled from oil filling and service stations.

Location	Cr	Hg	Cu	Zn	Mn	Fe	Pb	Cd	Ni	As
Naagamni	0.03	0.03	0.1	0.02	0.01	0.05	0.2	6.63	0.06	0.03
Sky Petrol	0.06	0.05	0.21	0.02	0.01	0.04	0.2	0.12	0.06	0.03
Petrol Bay Oil Ltd	0.14	0.03	0.1	0.04	0.01	0.04	0.2	0.12	0.07	0.03
Frimps Oil	0.11	0.03	0.05	0.02	0	0.04	0.1	<0.002	0.08	0.01
Total Oil	0.08	0.05	0.07	0.02	0.01	0.04	0.7	<0.002	0.05	0.04
LP Oil	0.11	0.03	0.3	0.04	0.01	0.04	0.3	<0.002	0.08	0.04
Shell Kunain Road	0.11	0	0.04	0.02	0	0.04	0.1	<0.002	0.06	0.03
Deliman Oil	0.13	0.03	0.08	0.03	0.01	0.04	0.2	<0.002	0.07	0.02
Shell Hospital Rd	0.2	0.03	0.1	0.03	0.01	0.05	0.1	<0.002	0.13	0.02
Total Kum Avenue	0.11	0.03	0.07	0.03	0	0.04	0.2	<0.002	0.07	0.05
Goil Hsp Road	0.11	0	0.07	0.03	0	0.04	0.1	<0.002	0.09	0.02
Goil Tamale Cent.	0.1	0	0.05	0.02	0	0.04	0	<0.002	0.05	0.01
Shell Yendi Road	0.09	0	0.07	0.02	0	0.04	0.1	<0.002	0.08	0.01
Quantum Oil	0.05	0	0.11	0.02	0.01	0.04	0.1	<0.002	0.06	0.01
Star Oil	0.1	0.03	0.12	0.04	0.01	0.05	0.2	<0.002	0.08	0.02
Gbanzaba Sev. Sta	0.06	0	0.21	0.04	0.01	0.04	0.1	<0.002	0.06	0.02
Sky Petrol No 2	0.11	0	0.12	0.05	0.01	0.05	0.3	<0.002	0.07	0.02
Nasona	0.08	0.05	0.1	0.03	0.01	0.04	0.2	<0.002	0.06	0.02
Shell	0.11	0	0.11	0.03	0.01	0.04	0.4	<0.002	0.12	0.02
Total	0.78	0	0.06	0.02	0	0.04	0.1	<0.002	0.05	0.01
Goil	0.08	0	0.07	0.02	0	0.04	0.1	<0.002	0.05	0.01
Mean	0.13	0.02	0.1	0.03	0	0.04	0.2	2.29	0.07	0.02

**Figure 3.** Pollution index of soils within oil filling and service stations.

metals from anthropogenic sources such as oil leaking from underground storage tanks, rusted storage tanks and corroded engines from vehicles that take fuel from the oil filling and service stations were less within the soil samples from the oil filling and service stations using the continental crust average where Fe (Iron) was used as reference element for normalization. The results of the enrichment factor calculations shows enrichment of some elements in the soil samples from the oil filling and ser-

vice stations. Based on the results presented in Table 3, the mean enrichment factor of the heavy metals such as Hg, Mn, Fe, Zn, Ni and As gave values less than 2 signifying deficiency to minimal enrichment (Taylor and Meclenan, 1985). Hence, oil filling and service station activities and other human actions contribution to the release of these metals into that environment were minimal. Elements such as Cr, Cu, Pb and Mg gave enrichment factor values from 2–5 signifying moderate

Table 3. Enrichment factor of soils within oil filling and service stations.

Location	Cr	Hg	Cu	Zn	Mn	Fe	Pb	Cd	Ni	As
Naagamni	0.67	0.54	2.08	0.50	0.15	1	3.90	138	1.29	0.67
Sky Petrol	1.46	1.23	4.80	0.50	0.14	1	4.90	2.73	1.39	0.71
Petrol Bay Oil Ltd	3.19	0.61	2.26	0.84	0.16	1	5.00	2.79	1.70	0.63
Frimps Oil	2.47	0.61	1.07	0.42	0.09	1	2.50	0.05	1.77	0.23
Total Oil	1.91	1.26	1.58	0.54	0.12	1	17.0	0.05	1.19	0.91
LP Oil	2.57	0.59	6.86	1.00	0.14	1	6.50	0.05	1.71	0.82
ShellKunain Road	2.63	0.05	1.02	0.37	0.07	1	2.10	0.05	1.37	0.65
Deliman Oil	2.98	0.61	1.79	0.79	0.12	1	4.90	0.05	1.56	0.56
Shell Hospital Rd	4.44	0.58	2.27	0.60	0.13	1	2.90	0.04	2.93	0.33
Total Kum Avenue	2.54	0.61	1.44	0.58	0.09	1	4.80	0.05	1.51	1.09
Goil Hsp Road	2.63	0.05	1.67	0.61	0.09	1	3.30	0.05	1.98	0.47
Goil Tamale Cent.	2.26	0.05	1.09	0.37	0.07	1	1.10	0.05	1.09	0.21
Shell Yendi Road	2.16	0.05	1.61	0.42	0.09	1	1.50	0.05	1.95	0.28
Quantum Oil	1.21	0.05	2.58	0.49	0.12	1	2.40	0.05	0.14	0.33
Star Oil	0.05	0.58	2.64	0.82	0.13	1	3.60	0.04	1.82	0.53
Gbanzaba Sev. Sta	1.44	0.05	4.89	1.02	0.12	1	2.70	0.05	1.30	0.37
Sky Petrol No 2	2.47	0.05	2.58	1.16	0.13	1	5.80	0.04	1.58	0.47
Nasona	1.93	1.26	2.28	0.74	0.12	1	3.90	0.05	1.40	0.40
Shell	2.41	0.05	2.59	0.59	0.11	1	9.50	0.05	2.68	0.48
Total	18.2	0.05	1.49	0.49	0.09	1	2.60	0.05	1.16	0.28
Goil	1.95	0.05	1.61	0.54	0.00	1	2.60	0.05	1.05	0.33
Mean	2.93	0.42	2.39	0.64	0.11	1	4.45	6.88	1.55	0.51

enrichment (Table 3). Basically, as the EF values increase the contribution of anthropogenic origins also increase (Surthland et al., 2000). According to Zhang and Liu (2002), the EF value between 0.5-1.5 indicates the metal is entirely from crusted material or natural processes, whereas EF greater than 1.5 suggests the source is more likely to be anthropogenic. This indicates that the concentration of some of the elements in the soil is as a result of the oil filling, service stations activities and other human action close to the stations. Cadmium (Cd) recorded enrichment factor from one of the sampling site to be greater than 5 indicating very extreme enrichment (Taylor and Meclenan, 1985). The high level is attributed to the fact that storage materials might have rusted and/or leakages of some amount of oil from underground storage tanks on the soil and perhaps due to runoff of agricultural waste to the station site.

Index of geoaccumulation

Table 4 shows the index of geoaccumulation of the soil samples from the various oil filling and service stations. The decreasing trend of averages of metal levels was as follows: Pb > Cr = Cu > Ni > Fe > Zn > As > Hg > Mn = Cd. The result from Table 4 shows that all the heavy metal parameters recorded index of geoaccumulation less than 0.00 which signifies that the samples from the oil filling and service stations were practically unpolluted. Only Cd

recorded geoaccumulation index of 2.14 from only one oil filling station which indicates a moderately to strongly polluted site (Huu et al., 2010; Muller, 1969). This can be attributed to oil leaking from underground storage tanks, corroded metallic tanks and from the exhaust of vehicles that come to the stations or ply roads close to them. Most of these stations are located close to major roads in the metropolis.

Correlation matrix

Table 5 shows the correlation matrix of heavy metals in soil samples from various oil filling and service stations. The study observed strong positive correlations between some elements such as Cr/Ni (0.65), Cu/Zn (0.59), Mn/Fe (0.58) and Pb/As (0.58) at 1% significant levels. The strong positive correlations signify that each paired elements have common contamination sources.

The study observed strong positive correlation between Zn and Mn (0.51) at 5% significant levels indicating common contamination sources. While Pb and Cd shows a strong negative correlation of -1.0 at 1% significant level. The correlation analysis indicates that soil contamination by the metals originated from a common anthropogenic source such as leaking of diesel, petrol, brake wear, tyres wear and corroded vehicles engine materials since these sources are noted to be contributing one or the pair correlated metals to the

Table 4. Index of geoaccumulation of soils within oil filling and service stations in the Tamale metropolis.

Location	Cr	Hg	Cu	Zn	Mn	Fe	Pb	Cd	Ni	As
Naagmi	-5.6	-5.9	-3.9	-6.0	-7.8	-5.0	-3.0	2.1	-4.6	-5.6
Sky Petrol	-4.5	-4.8	-2.8	-6.1	-8.0	-5.1	-2.8	-3.6	-4.6	-5.6
Petrol	-3.4	-5.9	-4.0	-5.4	-7.8	-5.1	-2.8	-3.6	-4.4	-5.8
Frimps Oil	-3.8	-5.9	-5.0	-6.4	-8.4	-5.1	-3.8	-9.6	-4.3	-7.3
Total	-4.2	-4.8	-4.5	-6.0	-8.3	-5.1	-1.0	-9.6	-4.9	-5.3
Lp Oil	-3.7	-5.9	-2.3	-5.1	-8.1	-5.1	-2.4	-9.6	-4.3	-5.4
Shell Kum Rd	-3.7	-9.6	-5.1	-6.6	-8.8	-5.1	-4.0	-9.6	-4.7	-5.8
Deliman Oil	-3.5	-5.9	-4.3	-5.5	-8.1	-5.1	-2.8	-9.6	-4.5	-6.0
Shell Hsp Rd	-2.9	-5.9	-3.9	-5.8	-8.0	-5.1	-3.5	-9.6	-3.5	-6.6
Total Kum. Rd	-3.8	-5.9	-4.5	-5.9	-8.5	-5.1	-2.8	-9.6	-4.5	-5.0
Goil Hsp Rd	-3.7	-9.6	-4.4	-5.9	-8.5	-5.1	-3.4	-9.6	-4.1	-6.3
Goil Tam Cen	-4.0	-9.6	-5.0	-6.5	-8.8	-5.1	-4.9	-9.6	-5.0	-7.4
Shell Yen Rd	-4.0	-9.6	-4.4	-6.3	-8.4	-5.1	-4.6	-9.6	-4.1	-7.7
Quantum Oil	-4.9	-9.6	-3.8	-6.2	-8.3	-5.1	-3.9	-9.6	-4.6	-6.7
Star Oil	-4.0	-5.9	-3.7	-5.3	-8.0	-5.1	-3.2	-9.6	-4.2	-6.0
Gbanzaba Ss.	-4.6	-9.6	-2.8	-5.1	-8.2	-5.1	-3.7	-9.6	-4.7	-6.6
Sky Pet No 2	-3.8	-9.6	-3.7	-4.8	-7.9	-5.1	-2.5	-9.6	-4.4	-6.2
Nasona	-4.2	-4.8	-3.9	-5.6	-8.2	-5.1	-3.2	-9.6	-4.6	-6.5
Shell	-3.8	-9.6	-3.7	-5.9	-8.4	-5.1	-1.8	-9.6	-3.7	-6.1
Total	-4.3	-9.6	-4.6	-6.2	-8.6	-5.1	-3.8	-9.6	-4.9	-7.0
Goil	-4.2	-9.6	-4.4	-6.1	-12	-5.1	-3.7	-9.6	-5.1	-6.7
Mean	-4.0	-7.5	-4.0	-5.8	-8.4	-5.1	-3.2	-8.4	-4.5	-6.3

Table 5. Correlation matrix of heavy metals in soils around oil filling and service stations in the Tamale metropolis.

	Cr	Hg	Cu	Zn	Mn	Fe	Pb	Cd	Ni	As
Cr	1									
Hg	-0.42	1								
Cu	-0.13	0.08	1							
Zn	0.17	-0.31	0.59**	1						
Mn	0.06	-0.17	0.41	0.51*	1					
Fe	-0.16	-0.35	0.24	0.21	0.58**	1				
Pb	-0.02	0.50	0.13	0.17	0.20	0.03	1			
Cd	-0.74	-0.50	-0.48	-0.36	0.80	0.98	-1.0**	1		
Ni	0.65**	-0.47	0.08	0.12	0.33	0.25	0.05	-0.41	1	
As	-0.04	0.10	0.27	0.18	0.29	0.29	0.58**	0.63	-0.09	1

** Correlation is significant at the 0.01 level (2-tailed); *correlation is significant at the 0.05 level (2-tailed).

natural environment. However, their contribution is minimal.

Conclusion

The study employed four contamination indexes namely, EF, Igeo, CF, degree of contamination and PLI in the assessment of level of metal contamination in the

metropolis. The results of all the contamination indexes used agreed well in explaining the contaminated levels and possible sources of the metals present in the oil filling and service station soil samples. For instance, enrichment factor proved to be an effective tool in differentiating a natural origin from anthropogenic source of contamination for the various elements investigated under the study. The mean value of the enrichment factor

places the elements in a decreasing order as Cd > Pb > Cr > Cu > Ni > Fe > Zn > As > Hg > Mn. The degree of contamination, pollution index and mean contamination factor provided the same trend of contamination levels as in the case of the enrichment factor. While index of geoaccumulation placed the metals in a decreasing order of Pb > Cr = Cu > Ni > Fe > Zn > As > Hg > Mn = Cd. The study revealed that there were elevated concentrations of certain metals (Cr, Cu, Pb and Cd) in terms of enrichment of the soil in some of the oil filling and service stations. For instance, the cadmium recorded enrichment factor of 138 from one of the filling station indicating very extreme enrichment. At the same oil station, geoaccumulation index for cadmium (Cd) was recorded as 2.14 signifying a moderate to strongly polluted. The correlation analysis indicates that soil contamination by the metals originated from a common anthropogenic source such as leaking of diesel, petrol, brake wear, tyres wear and corroded vehicles engine materials since these sources are noted to be contributing one or the pair correlated metals to the natural environment. However, their contribution is minimal. Hence, there is a need for concern since some of these metals pose potential threat to humans and critical environmental media such as water bodies. Based on the findings of this study, it is recommended that Environmental Protection Agency (EPA) should regularly monitor the oil filling and service stations to check the levels of heavy metals in the metropolis. The EPA should also ensure that, oil filling and service stations owner's use proper storage tanks or facilities to avoid leaking of oil from tanks.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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