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Determination of the Levels of Lead and Cobalt from Soils of an Irrigated Farmland in Lafia Nasarawa State-Nigeria Using Two Different Methods of Digestion

Augustine U. A. (Corresponding Author)
Department of Chemistry, Faculty of Science, Federal University of Lafia-Nigeria
Email: abelloves@yahoo.com

Akpomie T. M.
Department of Chemistry, Faculty of Science, Federal University of Lafia-Nigeria

Balarabe S.
Department of Chemistry, Faculty of Science, Federal University of Lafia-Nigeria

Ishaq B.
Department of Chemistry, Federal University of Technology, Owerri-Nigeria

Abstract

Washing of vehicles (lorries, cars, buses and motor-bikes), clothes and kitchen utensils, bathing and the release of smoke from exhausts of motor-vehicles and other anthropogenic sources continuously increase the levels of heavy metals in water bodies, especially the Amba river of Lafia used for the irrigation of farmlands thereby resulting to contamination and elevation of heavy metals uptake by crops. This study was carried out to provide information on heavy metals concentration in soils of an irrigated vegetable farmland in Lafia. Soil samples were collected at surface levels of 0-30 cm depth. Samples were analyzed for pH, organic matter, electrical conductivity and soil particle sizes. The soil samples were digested using Aqua regia and Nitric acid methods of digestion. The concentrations of lead (Pb) and cobalt (Co) were determined by Atomic Absorption Spectrophotometric (AAS) technique. The values of soil pH ranged between 5.60 and 6.35, organic carbon between, 1.40-1.49 %, organic matter content between, 2.40 and 2.57 %, electrical conductivity between 100 and 240 $\mu S\ cm^{-1}$ and clay, sand and silt content between 10.4-11.4 %, 82-85 % and 4.6-6.6 % respectively. Total concentration of extractable Pb and Co (Aqua regia method) ranged between 0.083–0.105 and 1.473 – 1.573 $mg\ kg^{-1}$ respectively. The concentrations of heavy metals for Nitric acid method were as follows: Pb: 1.363-1.512 and Co: 0.060-0.086. Concentrations of heavy metals in both methods were all below DPR-EGASPIN (2002) and US EPA. (2014) recommended limits. The results showed that aqua regia method was more efficient than the Nitric acid Method of digestion.

Keywords: Cobalt; Lead; Nitric acid; Aqua-regia; Irrigated farmland.

1. Introduction

Potentially Toxic Elements (PTEs) pollution has caused widespread concern around the world [1]. Even the so called essential elements can be toxic to organisms at some elevated levels. The accumulation of PTEs in soil is becoming more and more serious due to human activities such as industrial wastes, the unreasonable application of chemical fertilizers and pesticides, and landfill. Minamata disease and Itai-itai diseases for instance, were found to be caused by Hg and Cd pollution respectively since 1950's. Accumulation in the soil, biological toxicity, and the irreversibility of heavy metal elements will not only cause serious damage to the ecological security leading to the decrease of the quality of the crops but also give rise to long-term hazards through soil, skin contact, respiratory inhalation, and other exposure toxicity to human health (especially children) and even cause serious harm to human health through food chains [1].

Lead is a metal that belongs to group IV and period 6 of the periodic table with atomic number 82, atomic mass 207.2, density 11.4 $g\ cm^{-3}$ melting point 327.4 ^{O}C, and boiling point 1725 ^{O}C. It is a naturally occurring, bluish gray metal usually found as a mineral combined with other elements, such as sulphur (i.e., PbS, $PbSO_4$), or oxygen ($PbCO_3$), and ranges from 10 to 30 $mg\ kg^{-1}$ in the earth's crust [2]. Typical mean Pb concentration for surface soils worldwide averages 32 $mg\ kg^{-1}$ and ranges from 10 to 67 $mg\ kg^{-1}$ [3]. It ranks fifth behind Fe, Cu, Al, and Zn in industrial production of metals.

Lead is one of the potentially toxic heavy metal, which can be taken up by plant from the soil, there by interfering with the food chain [4]. It is the industrial metal which is extensively present in the air, water, soil and food. It is easily soluble in the water and transported through atmosphere. It behaves like calcium in body and accumulates in bone, liver, kidney and other tissues. It is a cumulative tissue poison and gets stored in different parts of the body especially in bones, liver, kidney and brain [5]. In these days lead is considered as an effective soil and environment pollutants. Lead is emitted from the industries, motor vehicles, stationary fuel, road dust composition

and traffic roads. Lead is not only a toxic element but also can be accumulated in plant organs and agricultural products [6, 7]. For the Pb used in U.S., about half of them are coming from manufacturing Pb storage batteries. Other uses of Pb include bearings, solders, ammunition, caulking, cable covers and plumbing pigments, etc. [8]. The general form of lead released in the surface water, ground water and soil are Lead oxides, hydroxides and ionic lead (II), and lead metal oxyanion complexes. Ingestion and inhalation are the two routes of Pb exposure and from both the effects are same. Accumulation of Pb in the body organs (i.e. brain) may cause poisoning and may lead to death. Its presence can also affect the central nervous system, kidneys and gastrointestinal tract. Exposure of children to lead is at risk for poorer IQ, reduced development, mental deterioration and hyperactivity. Under the age of six children are at a more substantial risk. Lead, Pb exposure to adult can cause insomnia, nausea, memory loss, weakness of joints and anorexia [9].

Cobalt is found in group IX row transition metal, in period 4, of the periodic table, with atomic number 27, mass number 58.93, density 8.90 g/cm^3, melting point 1495 ^{O}C, boiling point, 2927 ^{O}C [10]. The occurrence of cobalt in the earth's surface varies greatly. This element does not exist in its native form and is encountered only in meteorites. Cobalt is most often found in the form of arsenides and sulphides. The most important cobalt minerals are cobaltite CoAsS, linnaet Co_3S_4, smaltyn $CoAs_2$ and karrolit $CuCo_2S_4$. The source of cobalt pollution (apart from industrial waste) is the burning of cobalt. Cobalt may occur at oxidation levels of from -1 to +4, but in nature it occurs usually as a double-valenced cation Co^{2+} (cobalt compounds). In erosive environments it easily undergoes oxidation from Co^{2+} to Co^{3+} and creates the complex anion $Co(OH)_3^{-3}$. It relatively easily becomes mobile in acidic oxidizing environments, but does not undergo extensive aqueous migration, since it combines with the hydroxides of iron and manganese as well as silty minerals [11, 12]. The word cobalt was derived from the German *kobalt*, from kobold meaning goblin, a superstitious term used for the ore of cobalt by miners first attempt to smelt those ores for copper or nickel failed, yielding simply powder (cobalt (II) oxide) instead. Because the primary ores of cobalt always contain arsenic, smelting the ore oxidized the arsenic into the highly toxic and volatile arsenic oxide, adding to the notoriety of the ore [13].

Chronic cobalt ingestion has caused serious health problem at doses far less than the lethal dose. In 1966 the addition of cobalt compounds to stabilize beer foam in Canada led to a peculiar form of toxin-induced cardiomyopathy known as beer drinkers' cardiomyopathy [14]. After nickel and chromium, cobalt is the major cause of contact dermatitis [15].

Occupational exposure to cobalt in humans has been reported to cause several effects on the nervous system, including memory loss (Wechsler Memory Scale-Revised), nerve deafness, and a decreased visual acuity. Congestion in the vessels of the brain/meninges was reported in rats and mice exposed to 19 mg cobalt/m^3 or greater as cobalt sulphate over 16 days [16].

Several studies have evaluated the effects of inhalation of cobalt-containing compounds on possible carcinogenicity in humans. The mortality of a cohort of 1,143 workers in a plant that refined and processed cobalt and sodium was analyzed; the French national population mortality data were used as a reference population. An increase in deaths due to lung cancer was found in workers exposed only to cobalt (standardized mortality ratio [SMR] of 4.66; four cases in the exposed group versus one case in the controls). In a study within the cohort that controlled for date of birth, age at death, and smoking habits, 44 % (four workers) in the group exposed to cobalt and 17 % (three workers) in the group not exposed to cobalt died of lung cancer. The authors, however, indicated that the difference was not statistically significant and that the workers were exposed to arsenic and nickel as well as cobalt. The non neoplastic lung diseases commonly found in cobalt-exposed workers were not reported in this group. These lung diseases may have been present in these workers, but if they were not listed as the cause of death on the death certificate, they would not have been mentioned. Inhalation was probably a prominent route of exposure to cobalt; however, oral and dermal exposure probably occurred as well. No adjustments were made for smoking habits in the larger study, and the exposure levels of cobalt were not reported for either study. However, a follow-up study of this cohort did not report significant increases in mortality due to respiratory or circulatory diseases [16].

Four mortality studies, one in Sweden and three in France, of hard metal industry workers exposed to tungsten carbide, cobalt, and small amounts of other metals found an increased risk of death from lung cancer. The three French studies were not independent. Mortality studies of cobalt production workers and of workers exposed to cobalt during porcelain production found no increased lung cancer risk. Rats and mice exposed to cobalt sulfate heptahydrate by inhalation developed a dose-related lung tumour response, and cobalt metal administered by injection was found to produce injection-site sarcomas [16].

Cobalt has been shown to be mutagenic in somatic and germ cells in in vivo and in vitro experiments. Increased sister chromatid exchange was observed in male workers exposed to cobalt and other metals. Clastogenic effects in bone marrow cells were observed in mice orally exposed to cobalt. Intraperitoneal injection of cobalt produced an increase in micronuclei in mice and oxidatively damaged DNA in rats. Cobalt has been found to cause genotoxic effects in mammalian test systems. Cobalt (III) was positive, but cobalt(II) produced mixed responses, in bacterial mutagenicity tests. Cobalt ions in the presence of oxidants can cause increased levels of DNA damage in vitro. Cobalt sulfate and other soluble cobalt(II) salts are possibly *carcinogenic* to humans [16].

Noorikh, *et al.* [17], conducted a research to determine the levels of heavy metal pollution. Samples taken from Ishaqi River bank and adjacent agricultural soils area, in ten sites, distributed along 48 km of the Ishaqi River, north Baghdad. The evaluated metals were Zinc, Copper, Manganese, Iron, Cobalt, Nickel, Chromium, Cadmium, Vanadium and Lead. pH and Electric Conductivity (EC) were measured to evaluate the acidity and (EC). Results showed that most sites were contaminated with metals evaluated. Among these metals, Zn, Mn, Fe and Ni were consistently higher in all the samples (both river bank and adjacent soil) followed by Pb, Cu, V, Cd, Co and Cr. The

concentration levels of river bank were almost higher than that of adjacent soil. The concentrations of Nickel, Zinc, Manganese and Iron in river bank and agricultural adjacent soil were more than the permissible levels. The average mean levels were (Ni 66.36 mg/kg, Zn 42.59 mg/kg, Mn 26.78 mg/kg, Fe 25.15 mg/kg) in river bank and (Ni 46.31 mg/kg, Zn 33.06 mg/kg, Mn 20.78 mg/kg Fe 16.28 mg/kg) in agricultural adjacent soil. Overall, Nickel had the highest concentrations in the ecosystem [17].

The aim of this research work was to determine the concentrations of lead (Pb) and cobalt (Co) and some physicochemical properties from soils of an irrigated farmland in Lafia; and to investigate the relationship between extractable nitric acid (HNO_3) and aqua-regia heavy metals (Pb and Co) concentrations.

2. Materials and Methods
2.1. Description of the Study Area

Lafia is the state capital and also a Local government area (LGA) in Nasarawa state (Figure 1). It has a Tropical climate with an average annual temperature and rainfall of 34.2 ^{O}C and 108 mm respectively. The highest amount of precipitation occurs around August with an average of 344.8 mm. the highest average temperature of 38 ^{O}C occurs between March and April. The minimum average temperature of about 19.3 ^{O}C occurs around December. The variation in temperatures throughout the year is 5.9 ^{O}C [18].

Figure-1. Map of Showing Study Area and Surrounding Locations
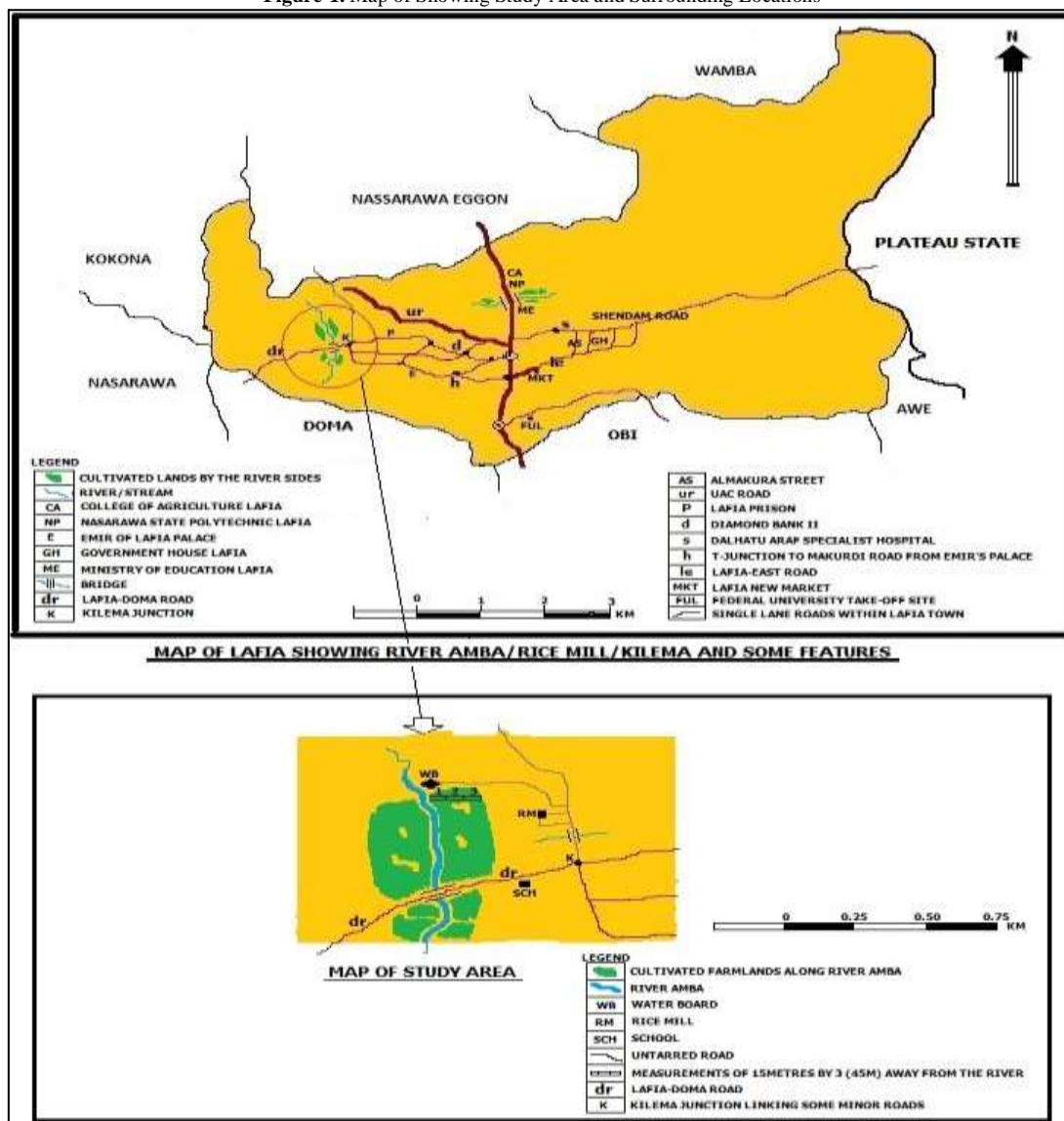
2.2. Reagents/Apparatus

All the chemicals used for this work were of analytical standards. Doubly distilled water was used throughout the work. All glass wares used were soaked in 10 % HNO_3 over night and then washed with detergent, thoroughly rinsed with tap water and then with doubly distilled water.

2.3. Sampling, Sample Collection and Sample Preparation

The research was carried out on soil sample collected from a vegetable irrigated farmland in Tundun Amba close to the intake of the State water board in Lafia metropolis (Figure 1). The sampling site was close to a source of

water (River Amba). Soil samples were collected randomly at the sampling points. Three sub-samples from the top layer were collected at a depth of 0-30 cm at a distance of 15 m each using a stainless steel auger and a measuring tape. The collected samples at each distance (0-15, 15-30 and 30-45 m,) make up three representative samples of the farmland (Figure 1). The samples were then pooled together to form a homogenous composite samples for the farmland, the source of water used for the irrigation is close to the farmland. The samples were collected in a clean polythene bag, labeled and transported to the laboratory for further processing [19].

Table-1. Sample collection codes and Distances

Sample code	Distance (m)
A	0-15
B	15-30
C	30-45

2.4. Sample Pre-Treatment

The homogenized soil samples were air-dried in the laboratory for a week to avoid possible effect of sunlight on the sample, pounded in a clean mortar and pestle, after which each of the was pulverized and passed through a 2.0 mm alumina mesh sieve, then preserved in washed clean plastic bottles for analysis. This is for pH and Total Metal while for Organic Matter; some portion of the sieved soil sample was further pulverized to fine powder and passed through 0.5 mm sieve [19].

2.5. Determination of Soil pH

A 10.0 g of the soil sample was weighed into two different 100.0 mL beaker. A 25.0 mL of distilled water was added for pH in water, in one of the beakers and 25.0 mL of 0.01N Calcium chloride ($CaCl_2$) was added in the second beaker, the suspension was allowed to stand for 30 minutes and stirring occasionally with a glass stirring rod. This was to allow the soil aggregate to breakdown so that the solution can equilibrate with the atmospheric oxygen CO_2. The pH of the soil was read using a pH meter [20].

2.6. Determination of Organic Carbon and Organic Matter Content

A 1.0 g of the prepared sample was weighed into a 250.0 mL conical flask, followed by 10.0 mL of 1N potassium dichromate ($K_2Cr_2O_7$) and swirled gently to disperse the soil. A 20.0 mL of concentrated sulfuric acid (H_2SO_4) was added using a measuring cylinder directing the stream into the suspension and swirled immediately until the reagents were mixed, swirled more vigorously for one minute and allowed the suspension to stand for 30 minutes, followed by 100.0 mL of distilled water after standing for 30 minute, then 3 drops of indicator (Barium diphenylsulphonate ($Ba(C_6H_5)_2SO_2$) was added, and titrated with 0.5 N ferrous sulphate solution. As the end point is approached, the solution takes on a greenish cast and then changed to dark green. At this point, ferrous sulphate was added drop by drop until the colour changed sharply from blue to red (maroon color) in reflected light against a white background. The blank titration was done following same procedure but without the soil sample and the result calculated! (Walkly and Black, 1934).

Calculation: $\% \, OC = \frac{(Me \, K_2Cr_2O_7 - Me \, FeSO_4 \times 0.3 \times f)}{Of \, soil \, (g)} \times 100$ (1)

Where:

Correction factor F= 1.33, M = Normality of solution x ml of solution used.

Organic matter calculated from the result of organic carbon multiply by a constant

$\% \, OM = \% \, OC \times 1.72$ (2)

2.7. Determination of Electrical Conductivity (EC)

A 50.0 g of the soil was weighed and dissolved in 100.0 mL of distilled water into a 250.0 mL glass beaker, the mixture was stirred gently for 30 seconds and allowed to stand for 30 minutes. The solution is stirred gently again before taking the E.C reading. The E.C meter was inserted into the soil and swirled round gently in the soil-water extract. After 30 seconds the E.C reading stabilized and was read in the digital display meter [17].

2.8. Determination of Particle Size of the Soil Samples

A 50.0 g of the air-dried sample was weighed into a 250.0 mL beaker, followed by addition of 50.0 mL of the prepared calgon into the sample and add 10.0 mL of deionized water. The suspension was stirred vigorously for one minute using a glass rod and allowed to stand for 30 minutes, and was transfered to the sedimentation cylinder and mixed for 15 minutes at a medium speed with a plunger and made up to 1liter with deionized water. The cylinder was placed in a flat surface and set the time immediately the hydrometer is placed into the suspension. The first reading on the hydrometer (H_1) was taken at 40 seconds after it has settled down. The hydrometer was removed and the first temperature (T_1) was recorded in (^{O}F). The suspension was allowed to stand for 3 hours and the second hydrometer (H_2) and temperature (T_2) in (^{O}F) readings were taken [21].

2.9. Determination of Exchangeable acidity

A 3.0 g of the prepared sample was weighed into a folded filter paper, placed on a conical flask and 50.0 mL of 1.0 N potassium chloride (1.0 N KCl) was poured gently into the solution through the soil in the filter paper and the

leachate collected followed by the addition of 5 drops of phenolphthalein indicator in the leachate and titrated with 0.05N sodium hydroxide (NaOH) to pink end point, then the volume (mL) of NaOH used was recorded.

Calculations

$$\text{Meg}/100 \text{ g} = \frac{V \times 0.05 \times}{w} 100 \tag{3}$$

Where: V = titer value of the reagent used for titration (0.05 N),

W = wt of sample used (3.0 g)

2.10. Sample Preparation for the Determination of the Metals (Pb and Co)
2.10.1. Aqua regia (3:1 HCl /HNO₃) digestion method

A 30.0 mL of HCl and 10.0 mL HNO$_3$ (3:1 v/v) was added to 1.0 g each of the dried sieved (2 mm) soil sample and left to stand for 24 h. The mixture was then heated on a hot plate at 140 ^{O}C to near dryness. The residue was filtered through Whatman No. 41. The solution was then transferred into 50 cm^3 volumetric flask and made to mark with distilled water, then preserved for metal analysis [22].

2.10.2. Nitric Acid Digestion Method

A 1.0 g of each sample was placed in a 250.0 mL conical flask and 10 .0 mL HNO$_3$ was added, and then heated for about 45 minutes. A 10.0 mL of HNO$_3$ was then added and heated at a constant temperature of about 120 ^{0}C until a clear solution was obtained and the volume was reduced by evaporation to about 5 mL. The flask was cooled at room temperature and the mixture was filtered through a Whatman No. 41.filter paper and transferred quantitatively to a 50.0 mL volumetric flask by adding distilled water to the mark [23].

2.10.3. Analysis of Soil Samples

Appropriate working standards were prepared for each of the metal solution by serial dilution of the stock solutions. Each of the sets of serial dilutions was then aspirated one after the other into the Atomic Absorption Spectrometry (AAS) and their absorbance recorded. The sample solutions were also aspirated one after the other and the absorbance recorded. Calibration curves were plotted for each of the trace metals standard using absorbance against concentrations (ppm) and the actual concentration of the metal interpolated from the curves [19].

3. Results and Discussion
3.1. Soil pH Electrical Conductivity Particle Sizes Exchangeable Acidity Organic Carbon and Matter Contents

Table-2. Physicochemical parameters of soil samples

Sample code	Sample A	Sample B	Sample C
pH-H$_2$O	6.35	5.81	5.60
pH-CaCl$_2$	5.23	5.35	4.78
E.C(µS/cm)	100	240	210
E.A (Meq/100g)	0.83	1.0	0.50
% O.C	1.40	1.49	1.45
% O.M	2.40	2.57	2.50
% clay	11.4	11.4	10.4
% Silt	6.6	5.6	4.6
% Sand	82	83	85
texture class	SL	SL	LS

Table 2 showed the results of the physicochemical parameters of the soils. The pH values ranged from 5.60-6.35 at the varying distances in the farmland from moderately to weakly acidic. This might be as a result of the chemicals that are flushed into the water body from the treatment plant of Lafia water works and other activities carried out around the farmland that may contribute to the soils acidity. Soil pH regulates almost all biological and chemical reactions in soil [3, 24]. Thus the distribution of soil pH may provide a useful index for the potential soil holding capacity for heavy metals, nutrients and fertility of soil types. The pH of most mineral soils ranged from 5.5-7.5 [25]. Radujevic [25], explained that acidic soils with pH 4.0-5.5 can have high concentrations of soluble aluminium and manganese ions which may be harmful to the growth of plants Winterhalder [26] stated that toxicity may occur if soil pH is below 5 and also reported that a pH of approximately 6-7 can release most readily available plant nutrients. The exchangeable acidity value is in the range of 0.5-1.0. The samples organic carbon and organic matter content ranges from 1.40-1.49 and 2.40 to 2.57 respectively. These values are lower than the critical levels required by soils for agricultural use as suggested by Odu *et al*., (1985). Soil accumulation and availability of heavy metals are affected by soil OM, soil pH, grown crop species and crop rotation (IPNI, 2008). The soil particle size analysis showed the soil to be sandyloam-loamysand. Clay ranged between 10.4-11.4 %, sand between 82.0-85.0 % and silt between 4.6-7.6 %.and electrical conductivity values ranged from 100-240 µS/cm.

3.2. Heavy Metals (Pb and Co) Concentrations

Table-3. Heavy Metal Concentrations of the Samples (mg /kg) using Aqua regia (HCl: HNO_3) method of Digestion

Sample code	Pb	Co
A_1	1.473±0.0006	0.105±0.0001
B_1	1.551±0.0003	0.089±0.0008
C_1	1.573±0.0001	0.083±0.0009

A_1-C_1=aqua regia extraction, from 0-15 m to 30-45 m.

Table-4. Heavy Metal Concentrations of the samples (mg /kg) using Nitric Acid (HNO_3) method of Digestion

Sample code	Pb	Co
A_2	1.451±0.0005	0.086±0.0006
B_2	1.363±0.0002	0.060±0.0001
C_2	1.512±0.0007	0.078±0.009

A_2-$C_{2=}$Nitric acid Digestion from 0-15 m to 30-45 m

The results of heavy metals (Co and Pb) concentrations in the irrigated farmland soil are as presented in Table 3. The concentration of the heavy metals   ranged as follows in (mg/kg): Co and Pb were 0.083-0.105 and 1.473-1.573 respectively, for Aqua regia extraction at varying distances from 0.-15 to 30-45 m.

For Nitric acid extraction, the results ranged as follows: 0.060-0.086 and 1.363-1.512 for Co and Pb respectively.

The results showed that Pb in both digestion methods had the higher concentrations than Co. The order of concentration of the heavy metals is: Pb > Co for both methods of digestions, i.e. Aqua regia and Nitric acid methods of digestions.

The high concentration of Pb in the soil might be as a result of the activities that is carried out in on the Amba River, i.e. washing of automobiles, discharge into the water body from the water treatment plant of Lafia water works and other anthropogenic activities. This is in line with work done by Hong, *et al.* [27].

The results indicated that Aqua regia digestion method (A_1, B_1, and C_1) extracts better compared to Nitric Acid digestion Method (A_2, B_2, and C_2). McGrath and Cunliffe [28], reported that using Aqua regia and block digesters, digest faster, more economical and can be very simply modified to suit different types of soil. Aqua regia (ratio 3:1 or 4:1 v/v) has been said to extract effectively trace metals in sediments [22]. Sastre *et al.* (2002) stated that Nitric acid digestion was an optimum method for estimating heavy metal content in soil samples with high organic matter content, being superior to microwave-assisted and aqua regia digestions.

The concentration levels of all the heavy metals (Pb and Co) analyzed in the soil samples at the various distances were below the maximum tolerable limits of soils farmland recommended by DPR-EGASPIN [29] and US EPA [30].

4. Conclusion

The results of this present study indicated the presence of Pb and Co analyzed in the samples at the various distances (0-15, 15-30 and 30-45 m) of the irrigation farmland. Lead ranked higher than Cobalt in both digestion methods used (Aqua regia and Nitric acid methods).

The overall results showed that aqua regia method is a better extracting method for the metals under present study than Nitric acid. The results were all below the maximum tolerable limits for heavy metals in soils of farmland recommended by DPR-EGASPIN [29] and US EPA [30] guidelines.

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