PHYSICOCHEMICAL PARAMETERS AND HEAVY METALS CONTENT OF SOIL SAMPLES FROM FARMS IN MINNA

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ABSTRACT. Physico-chemical properties and heavy metals content of soils were determined from seven farms in Minna, central Nigeria. Conventional analytical methods were employed to determine the physico-chemical properties and the heavy metals were analysed by atomic absorption spectrometry. The result showed that pH values ranged from 6.64 - 7.70 indicating slight acidity to slight alkalinity of the soils. The total organic carbon values ranged from 0.95-2.25 % resulting in the presence of organic matter (1.63-3.87). The electrical conductivity values ranged from 17-37 $\mu\text{S}/\text{cm}$. The cation exchange capacity of the soil samples ranged from 3.68-5.15 cmol/kg . The heavy metals levels were in the following range: Cd (0.00018-0.00134 mg/g), Cu (0.0069-0.0476 mg/g), Fe (1.942-2.2059 mg/g), Mn (0.1825-0.3696 mg/g), Ni (0.0065-0.0069 mg/g) and Zn (0.0157-0.2252 mg/g). The concentration of the metals in the soil samples varied according to the following trend: $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu} > \text{Ni} > \text{Cd}$. The average concentration of all the metals in each farm also gave the trend $\text{Farm B} > \text{Farm G} > \text{Farm E} > \text{Farm C} > \text{Farm F} > \text{Farm D} > \text{Farm A}$. The findings indicate the presence of heavy metals in all the farms but only Fe was above the FAO/WHO standards.

1. INTRODUCTION

Heavy metals like iron tin copper, manganese and vanadium occur naturally in the environment and could serve as plant nutrients depending on their concentrations. Mercury, lead, cadmium, silver, chromium and many others that are indirectly distributed as a result of human activities could be very toxic even at low concentrations (Opaluwa *et al.*, 2012). Those most commonly found at contaminated sites are lead, chromium, arsenic, zinc, cadmium, copper, mercury, and nickel (GWR TAC, 1997).

Heavy metals are extremely persistent in the environment because of their non-biodegradable nature, thermal stability and potential to accumulate to toxic levels, even at low concentrations. These metals can pose a significant health risk producing damaging effects on man and animals because there is no good mechanism for their elimination from the body (Arora *et al.*, 2008; Yusuf *et al.*, 2009).

There is a growing concern about the possibility of agricultural soil's contamination by heavy metals resulting in uptake by plants and their introduction in vital food chains affecting food safety (Pujar *et al.*, 2012). The contamination is often a direct or indirect consequence of anthropogenic activities from urban and industrial wastes, mining and smelting of non-ferrous metals and metallurgical industries (McLaughlin *et al.*, 1999, Singh, 2001). Other ways of metal accumulation in soil is by irrigating farmland with poor quality water, weathering of rocks, transportation and disposal of high metal waste on farmland and leaching from refuse dumpsite (Dosumu, *et al.*, 2005).

Soils may also become contaminated by the accumulation of heavy metals and metalloids from leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, coal combustion residues, and spillage of petrochemicals (Khan *et al.*, 2008 and Zhang

et al., 2010). Knowledge of the total metal concentration provides limited information about their potential mobility and bioavailability (Bashir *et al.*, 2014). The movement and availability of the important micronutrients such as Mn, Fe, Zn and Cu change due to soil conditions which are controlled by plant species and a number of soil parameters like the nature of complexes in which the metal is present in soil, pH, cation exchange capacity, amount of organic matter and particle size (Adriano, 1986).

Top soil and road side soil near heavy traffic in urban areas are indicators of heavy metal contamination from atmospheric deposition. Metals such as Cd, Cu, Pd and Zn are good indicators of contamination in soils because they appear in gasoline, car component, oil lubricants and industrial incinerator emissions (Popoola *et al.*, 2012, Olukanmi and Adeoye 2012).

This study examined the physicochemical properties and the levels of Cd, Cu, Fe, Mn Ni and Zn in soils from farms around Minna, central Nigeria resulting from possible anthropogenic activities. Minna lies on latitude 9° 37' North and longitude 6° 33' East and at an elevation of 356 m (841 Ft). The selected farms for this research are situated by the road sides, near dumpsites, mechanic workshops, car parks and thus have an elevated risk of potential contamination.

2. MATERIALS AND METHOD

2.1 Sampling Sites

The samples that were used for the research were taken from seven selected farms in the following areas of Minna: (A) Okada Road, (B) Kpakungu, (C) Dutsen kura, (D) Keteren gwari (E) Chanchaga (F) Mandela (G) Sauka ka huta.

2.2 Samples Collection and Preparation

Soil samples were collected from a depth of 10 to 15 cm, from the surface as described by Allen (1974). From each farmland, ten soil samples were collected from ten different spots, which were pooled together to form a composite of each individual sample. They were placed in clean dried polythene bags, labelled and transported to the laboratory for analysis. The soil samples were air dried, disaggregated with porcelain pestle and mortar and finely powdered to pass through 2 mm mesh sieve for homogeneity. Soil samples were analysed for the following parameters: pH, electrical conductivity, particle size, organic matter, organic carbon, cation exchange capacity and heavy metals.

2.3 Determination of Physico-chemical Parameters

All the chemicals and reagents used were of analytical standard. The determination of particle sizes of the soil samples was carried out using Bouyoucos Hydrometer method. The pH of the soil samples was determined using pH meter in 1:1 soil water suspension, electrical conductivity was determined in the filtrate of the water extract using Conductivity meter. The Percentage Organic carbon/matter was determined by using chromic acid wet oxidation method by Walkey and Black (1934). Ca and Mg were determined by complexometric titration with EDTA, Na and K by flame photometry, exchangeable acidity by acid-base titration while cation exchange capacity was obtained by summing up the exchangeable bases.

2.4 Determination of Heavy metals

The digestion procedure used for determining heavy metals was as recommended by AOAC, described by Omojola, (1993). 1g of the dried pulverized samples was weighed each and poured into a 100ml beaker. 10 cm³ of concentrated nitric acid was added to sample and heated at 40 °C. After the evolution of brown fumes, heating was continued until a clear solution was obtained. De-ionized water was added at intervals to prevent drying of the digest. The clear solution was diluted to 40 cm³ and filtered with a whatman filter paper No. 41 into a 100 cm³ volumetric flask. The beakers were rinsed thoroughly and then the solution was made up to the mark with de-ionized

water. It was poured into a 100 cm³ polypropylene bottles and stored in the refrigerator at 4 °C for analysis. 1000 ppm stock solutions were prepared from the salts of the metals under investigation and deionized water. Standard solutions were also prepared by serial dilution of the 1000 ppm stock solution of each metal. All metals were determined with a Thermo Scientific ICE 3000 series atomic absorption spectrophotometer. Each sample solution was run in triplicate and the result was corrected by subtracting the blank reading from the value for each metal.

3. RESULTS AND DISCUSSION

3.1 Soil pH and Electrical Conductivity

The pH of a soil has a major effect on metal dynamics because it controls adsorption and precipitation, which are the main mechanisms of metal retention in soils. As pH decreases, the solubility of cationic forms of metal in the soil solution increases and therefore become more readily available to plants. Table 1 gives the result for pH, EC, OM and OC for all the soil samples. The pH value for normal soil is 5.5–7.5, pH of soil below this range can cause low availability of some essential minerals needed by the soil (Brady and Weil, 2000). The pH values of all the soil samples analysed from the seven farms ranged from 5.77 to 7.70 showing slightly acidic to slightly basic. This also shows the soil samples are within the range for normal soil pH. Such pH values are characteristic of soils in areas where leaching is less pronounced due to low precipitation, resulting in the concentration of base forming cations in the place of acid contributing cations such as Al³⁺ and H⁺ (Ajai *et al.*, 2014). These values are in the same range of (5.0-7.5) reported by Iyaka and Kakulu (2009) and 6.20-6.70 reported by (Sumaila, 2014) for soils from the same area. The pH values are also lower than values 7.2 - 8.3 for soil samples in India (Kiran, 2013). Farm E with a lowest pH value of 5.77 may have greater solubility for metals, therefore becoming more readily available for plants.

Conductivity measurements shows farm G with the lowest value of 17 µS/cm and farm C has the highest value of 37 µS/cm. These values indicate the relative water-soluble salt content of the soil. Electrical conductivity depends on the amount of dissolved minerals and gives the ability of a substance to conduct an electric current at a specific temperature (25 °C). There is no regular pattern of variation in conductivity between sandy, loamy sand or silt loam soil samples. Boulding (1994) classified EC of soils as: non saline <2; moderately saline 2-8; very saline 8-16; extremely saline >16. Based on this classification, the EC results for this study may be classified as extremely saline.

3.2 Soil Organic Matter (SOM)

Soil organic matter has influence on soil structure, water holding capacity, nutrient contributions, biological activity, water and air infiltration rate and pesticide activity. A soil with high level organic matter is an indication of high cation exchange capacity, holds more water and increases biological activities (Horwath, 2005)

The presence of SOM is regarded as being critical for soil function and soil quality, it increases soil fertility by providing cation exchange sites and acting as reserve of plant nutrients like N, P, and S, along with micronutrients, SOM also acts as the major sink and source of soil carbon. Although the Carbon content of SOM is known to vary considerably (Perie and Ouimet, 2008, Jain *et al.*, 1997). The concentration of SOM in soils generally ranges from 1 % to 6 % of the total topsoil mass for most upland soils. Soils whose upper horizons consist of less than 1% organic matter are mostly limited to desert areas, while the SOM content of soils in low-lying, wet areas can be as high as 90 %. Soils containing 12-18 % soil organic carbon are generally classified as organic soils (Troeh and Louis, 2005). The SOM for the soil samples analysed was 1.63-3.87 %, which is within the range for upland soils. The organic carbon (OC) is in the range of 0.95-2.25 % which is lower than 12-18 % for organic soils.

Table 1 pH, conductivity, organic matter and organic carbon of soil samples

Farm	pH	Conductivity ($\mu\text{S}/\text{cm}$)	Organic matter (%)	Organic Carbon (%)
A	7.59	24	2.44	1.42
B	6.64	29	3.87	2.25
C	7.25	37	2.95	1.72
D	7.70	20	2.06	1.20
E	5.77	18	3.09	1.80
F	6.73	21	1.92	1.12
G	7.35	17	1.63	0.95

3.3. Soil Particle Size

The results for particle size and texture of the soil samples is as shown in table 2. The textural class of the soil samples were sandy to loamy sandy, with the exception of farm E which was silty loam. The particle size distribution of the soil showed that the soil contained higher composition of sand than silt and clay in all the sampling sites. Trace metals have preferential accumulation in the clay and silt fraction of soil. Generally, the concentration of heavy metal in soil increase with decrease in the sizes of the soil particles (Ajai, *et al.*, 2014).

Table 2 Particle Size (g/kg) and Texture of Soil Samples

Farm	Soil	Silt	Clay	Texture
A	95.80	1.60	4.65	Sand
B	85.60	12.80	1.60	Loamy Sand
C	95.20	2.80	2.00	Sand
D	93.20	5.00	1.80	Sand
E	65.00	33.60	1.40	Silty Loam
F	87.00	7.00	6.00	Loamy Sand
G	89.60	9.80	0.60	Loamy Sand

3.4 Cation Exchange Capacity (CEC)

Table 3 shows the result for the effective cation exchange capacity obtained by summing up the values of the exchangeable bases and exchangeable acidity. Cation exchange capacity (CEC) is a measure of the soil's ability to hold positively charged ions. It is a very important soil property influencing soil structure stability, nutrient availability, soil pH and the soil's reaction to fertilisers (Hazleton and Murphy 2007).

The CEC of soils varies according to the percentage of clay in the soil, the type of clay, soil pH and amount of organic matter. Organic matter has a very high CEC ranging from 250 to 400 meq/100 g (Moore 1998). Soils with a low CEC are more likely to develop deficiencies in potassium, magnesium and other cations while high CEC soils are less susceptible to leaching of these cations (CUCE 2007). The result from table 3 shows that farm D has the highest CEC value of 5.15 cmol/kg while farm G has the least value of 3.68 cmol/kg. A higher CEC usually indicates more clay and organic matter is present in the soil resulting in greater water holding capacity. The soil of farm D with the highest value of CEC will be less susceptible to leaching of cations (CUCE, 2007)

Table 3 Exchangeable Bases and Cation Exchange Capacity (CEC) of soil Samples (cmol/kg)

Farm	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	CEC
A	0.62	0.23	0.15	3.36	4.65
B	1.64	0.05	0.11	2.57	4.33
C	0.86	0.45	0.15	3.36	4.85
D	0.48	0.10	0.31	4.21	5.15
E	1.06	0.12	0.12	2.50	3.83
F	0.48	0.08	0.22	3.56	4.37
G	0.95	0.29	0.11	2.30	3.68

3.5 Heavy Metals

The concentrations of Cd, Cu, Fe, Mn, Ni and Zn in soil samples are given in figures 1 to 7. The concentrations of the heavy metals in the samples showed that all the studied metals were present in all soil samples except Cd and Ni. Cd was detected in only two farms (D and G) and the concentration is very insignificant as shown in figure 1. This result is in agreement with the study on heavy metals in soils from central, Nigeria conducted by Sumaila (2014) where Cd was not detected in all farms. It is also similar to results of heavy metals analysis of soils of Bijapur taluka in India where out of the ten farms analysed, Ni and Cd were not detected in two farms (Pujar *et al.*, 2012). Distribution of heavy metals in soil is continuously altered due to various soil processes and is under the influence of environmental factors. A large share of general cadmium pollution is caused by dumping and incinerating cadmium-polluted waste (Jarup, 2003), these activities may be absent around the farms analysed.

Cu metal in agricultural soils absorbed by plants becomes especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses it can cause harm (Abbas *et al.*, 2010). The average concentrations of Cd, Cu and Fe metal in soil of all farms was as follows: Cd (0.76 mg/kg), Cu (23.60 mg/kg), Fe (2065.90 mg/kg). The FAO/WHO maximum permissible limits (2007) and the EU standards (2002) (Adah *et al.*, 2013) of metals in soil samples from farmlands are (Cu-265, Cd-3.0, Fe-1000). These heavy metals detected in the soil samples were below the permissible limits but the iron contents of the samples which ranged from 1942.13 to 2205.9 mg/kg (figure 3) were above the permissible limits of 1000 mg/kg. Fe has been found to occur at high concentrations in Nigerian soil (Adefemi *et al.*, 2007). The high level of Fe could be as a result of the natural basic rock material of the soil (Qian, *et al.*, 1996).

Figure 1: Concentrations in mg/g of cadmium metal in soil samples

Figure 2: Concentrations in mg/g of copper metal in soil samples

Figure 3: Concentration in mg/g of iron metal in soil samples

Mn is the second most abundant heavy metal after Iron and can find its way into soil from combustion products of motor vehicles, coal burning, pesticides, fertilizers and methylcyclopentadienyl manganese tricarbonyl (MMT) a gasoline additive ((ATSDR, 2000). Nickel is an element that occurs in the environment only at very low levels, its major sources of contamination in the soil are metal plating industries, combustion of fossil fuels, and nickel mining and electroplating (Khodadoust *et al.*, 2004). The result of the study reveals that Ni was absent in farms A, D and F (figure 5), Ni usually take long time for it to be removed from air to other parts of the environment and often leaches down to adjacent groundwater (Wuana and Okieimen, 2011). The average concentrations of Mn, Ni and Zn metal in soil of all farms was as follows: Mn (292.76 mg/kg), Ni (3.59 mg/kg) and Zn (129.24 mg/kg). The FAO/WHO maximum permissible limits (2007) and the EU standards (2002) of these metals in soil samples from farmlands are Mn-500, Ni-75 and Zn-600 mg/kg).

Figure 4: Concentration in mg/g of manganese metal in soil samples

Figure 5: Concentration in mg/g of nickel metal in soil samples

Figure 6: Concentration in mg/g of zinc metal in soil samples

Figure 6 shows that Zn was present in all farms analysed, this may be because it is present in most rocks, weathered out and deposited into the soil. The fate and transport of zinc in the environment is dependent on cation exchange capacity, pH, organic matter content, nature of complexing ligands, and the concentration of the metal in the soil. As pH increases, there is an increase in negatively charged binding sites on soil particles, which facilitates the adsorption of zinc ions and removal from solution (ATSDR 1994).

The range for Cu level (6.71 – 47.59 mg/kg) obtained was found to be within the range of 5.67 – 15.17 mg/kg reported by Sumaila, (2014) for soils around the same area. Iyaka and Kakulu, (2011) also recorded 11.0-26.0 for soil samples from farms around the same geographical region in raining season. This difference could be due to the season this study was conducted (dry season). Concentration of metals in soil vary in dry season and wet season due to the run off effect that is capable of removing high metals from the road side soil and the effect of rain may also facilitate the leaching of the soil and contributes to the dilution of the soil solution (Yahaya *et al*, 2009, Anhwange, 2009).

In general the concentration of the metals in the soil samples varied according to the following trend Fe>Mn>Zn>Cu>Ni>Cd, indicating that all the soil sample had highest level of iron and Cd was the lowest. The average concentration of all the six metals in each farm also gave the following trend B>G>E>C>F>D>A, showing that farm B has the highest average concentration of all the metals combined while farm A has the least. Physico-chemical analysis results also reveals that Farm A had the highest % of sand particles and concentration of heavy metal in soil decrease with increase in the sizes of the soil particles (Ajai, et al., 2014)

Farm B is in a densely populated area with motor parks, petrol stations, vehicle repair garages and dumpsites, which suggest possible mobility of metals from the dumpsites to farmlands

through leaching and runoffs (Opaluwa *et al.*, 2012). Farm G is also close to the main road and aerial deposition could also contribute to metal contents of soils. This is because there is a positive relationship between atmospheric metal deposition and elevated concentrations of heavy metals in top soil (Arora *et al.*, 2008, Debopam *et al.*, 2010).

4. CONCLUSION

The physicochemical study of parameters is important for plants growth and soil management. These studies gives information about the acidity or alkalinity of the soil, the soil texture, nutrient content and the soil's ability to hold positively charged ions. Heavy metals were also detected in the soil samples from all farms investigated. The level of Cd, Cu, Mn Ni and Zn were below the FAO/WHO and EU standards except for Fe. These heavy metals could be picked up by foodstuffs grown on these farms and pose danger to humans as a result of bioaccumulation. The high level of Fe may constitute health hazards due to its toxicity. Routine physico-chemical and heavy metals analysis of soil samples of agricultural farmlands should be carried out in order to maintain the quality of crops grown on farms.

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