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Evaluation of Bioavailable Contents of Arsenic, Copper and Zinc in Some Poultry Farms Soils in Osun State, Nigeria

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ABSTRACT: This work evaluated the mobility and bioavailability of arsenic, copper and zinc in chosen poultry farmlands situated within Osun State, Nigeria in respect to the soil physico-chemical characteristics. The site was split into 12 zones of about equal sites. Soil samples were collected over a period of four months from each zone for analysis of soil physico-chemical characteristics and As, Cu and Zn contents in sequential fraction of the soil sample. Sequential fractionation of soil samples were conducted utilizing reworked Tessier technique, utilizing Flame Atomic Absorption Spectrophotometer. Mean of total content (mg/kg) and percentage bioavailability were: As 470.48±48 (31.16%), Cu 62.95±10.61 (29.02%) and Zn 125.58±20.74 (26.67%), respectively. Analysis of variance and correlation analyzes indicated that soil pH, % clay, % organic carbon, cation exchange capacity, and metal speciation in soil control metal mobility and bioavailability in the poultry farm soil. The mean contents of As, Cu and Zn in soil in the sampling area were usually more than those of the control site, indicating some degrees of contamination of the poultry farm soil by these metals. Also, the mean contents of As in some zones were considerably greater ($p < 0.05$) than stipulated world guidelines like Food and Agriculture Organization/World Health Organization maximum limit of 40 mg/kg in arable land. The elevated contents of As in the soil of the poultry farms in some zones and the elevated bioavailability calls attention to as this could cause a threat to the consumers of the food crops cultivated on these farms.

KEYWORDS: Bioavailability; heavy metals speciation; fractionation; poultry farmlands; soil physico-chemical parameters; potential mobility

1. Introduction

The buildup of heavy metals and metalloids in soil, water and plants, specifically As, Cd, Cu, Pb, Ni, and Zn, causes numerous risks to human and environmental health. People are exposed to potential harmful agents either via the feeding level (soil, water)-plant-human or soil (water)-plant-animal-human or via direct exposure by cutaneous contact or ingestion of soil pollutants (soil-human) or soil-water-human [1]. Ecological risks are described as phytotoxicity or ecotoxicity to soil, plants, and animals. Risks emanating from pollution of soils via heavy metals are well known, and several key assays have been published on this matter [1-4]. While several investigators have endeavored to develop associations between the contents of pollutants in soils or plants and the impacts on plants or organisms (such as humans), it is important to enumerate or determine the main risk routes for some of the elements of interest [1]. All toxic heavy metals can threaten public health with low contact; the crucial organs they target in the body vary from one metal to another. Numerous metals are reportedly carcinogenic; these consist of As, Cd, Hg, Pb, and hexavalent chromium [5]. Harmful health effects of As toxicity comprise several skin lesions that show up (after many years of slight As contact): hyperpigmentation, e.g. dark spots; hypopigmentation, e.g. white spots; keratoses of the hands and feet. After a lot or more years, skin cancer is likely. Prolonged exposure may result in cancers of the lungs, kidneys, liver, and bladder [6].

With the wider use of metals not merely as growth enhancers but also as feed preservatives to prevent diseases in the concentrated poultry industry, poultry manure use has come into view as a significant source of ecological contamination with some of these metals. Metals like As, Co, Cu, Fe, Mn, Se, and Zn are included in feeds with a view to combating disease, enhancing fattening up and food conversion, and amplifying egg production [5]. In general, animals can only absorb 5-15 percent of the metals they consume.The bulk is thus emitted in manure. Heavy metals are taken up in part by the soil, but they can also end up in bodies of water, where they become more concentrated.Arsenic may buildup in soils as a result of farming methods like the utilization of As-containing pesticides and herbicides, chicken manure, pig manure, and phosphorus fertilizers, thus raising issues regarding the risk of As to the ecosystem and health of the people. The absorbed As in soils can be distributed amidst various soil constituents like organic matter, Fe and Mn oxides, carbonates, and sulfides, and such distribution could influence its mobility, bioavailability, and toxicity [7]. Thus, analytical soil estimations for As should concentrate on analyzing its translocation to edible crops with ecotoxicity and phytotoxicity as secondary attention [5].

Copper and Zn are quintessential metals but are also among the heavy metals that are regarded as ecologically significant in cultivated soils. Elevated contents are indicative of man-made inputs, such as excessive use of inorganic fertilizers and pesticides, irrigation with contaminated water, animal feeding, waste disposal, waste incineration, urban effluent, traffic emissions, and industrial and poultry activities [5].Considerable and constant chemical testing of cropland soil samples could act as a databank for signifying potential micronutrient deficiencies and excesses or accumulation, enabling safety measures to be adopted. The complexity of metal polluted sites has been interpreted and continues to be interpreted as a measure of total metal level.While total metal level is an important indicator of polluted sites, it does not provide analytical information on the bioavailability, mobility, and fate of the metal pollutant.Detailed information about soil metal availability is needed to evaluate the risk of soil pollution and to determine the effect of waste management methods. Soil physicochemical forms such as hydrated metal oxide content, organic matter content, cation exchange capacity (CEC), redox potential, pH, and clay content all have different effects on metal mobility, pathways, and thus bioavailability.

Due to urban sprawl and growing human-related activities, the heavy metal contamination of air, soil, dust, sediment, water, and vegetation signifies an increasing ecological issue confronting food safety and the health of the population in towns and cities.

Poultry farming is a common practice in the universe and, presently, several accounts have been published on poultry farm soils contaminated with heavy metals [5,8-11].

As an aspect of a present study program on the evaluation of soil pollution in poultry farmland, our main aim concentrates on the chemical partitioning of heavy metals because the possible effect of soil pollution is better evaluated by the insight of the forms in which a specific metal is found instead of the use of its total content. There is a paucity of databases on the speciation of metals in the poultry farmland of Osun State. Thus, identification and quantification of the various species or forms of phases in which the heavy metals are present is very significant to evaluate their bioavailability in the ecosystem. In this study, three mega poultry farms within the state (Agboola, Odunola, and Worgor), where industrial, farming, and commercial activities persist en masse, were selected to evaluate the geochemical partitioning of As, Cu, and Zn. To evaluate the binding of heavy metals to the major fractions in soils, a five-step sequential extraction method [7], depending on the potential of some extracting reagents to extract the heavy metals retained from the soil chemical phases, has been utilized. The three heavy metals are chosen because they are of significance in farming as micro-nutrients (Cu, Zn) but also because of their toxicity (As). The purpose of this research was to conduct a speciation analysis of As, Cu, and Zn in the soil of poultry farms within Osun metropolis. This was for the purpose of evaluating their bioavailability based upon the soil physicochemical forms and the potential health effects on consumers of food crops grown on the poultry farms. There is, therefore, a need to study the bioavailable levels of heavy metals in the soil ecosystem, hence this study.

2. Materials and Methods

2.1. Description and suitability of the sampling sites.

The study area is located within longitudes 004°16.095’ to 004°30.826’ E and latitudes 07°45.195’ and 07°53.96’ N, while the ground level is within 311.81 to 357.23 m above water level. The study region experiences two distinct climates, known as the dry and wet (rainy) seasons. The wet season begins in March and ends in October and is characterized by frequent, high-volume rainfall, moderately low temperatures, and high relative humidity. The dry season begins in November and ends in February and is characterized by infrequent rainfall, high temperatures, and low relative humidity. Temperatures range from 20 to 32°C during the dry season and 20 to 28°C during the rainy season. The area's average temperature is around 27°C during the day and 21°C at night [12]. The average monthly rainfall varies from 0.31 cm in January to 27 cm in July. The average annual rainfall ranges between 125 and 200 cm [13]. Osun State lies within one of the three vegetation zones in Nigeria. Regionally, the vegetation type is a tropical dry forest and derived savanna environment. In line with [12], topography, drainage, and rainfall influence the vegetation. The vegetation type of the Osun area is parkland; this is attributed to stunted trees and pockets of derelict timberland and secondary forest, including a few shrubs with scattered large trees and climbers [13]. Its vegetation, in most localities, is densely populated with grasses and trees of various sizes. The area is distinguished by an undulated range of shale outcrops which are either greyish or reddish brown in color depending on the shale content and status of weathering. It is identified with Precambrian crystalline basement complex rocks. The prevalent rocks represent groups of gneisses and quartzite [12]. The soil falls under the heavily ferruginous tropical red soils intrinsic to basement complex rocks. Due to the dense, humid tree cover in the area, the soils are usually deep and of two types; viz., deep clayey soils formed on low, smooth hillcrests and upper slopes; and the sandier hill wash soils on the lower slopes. The vegetation has generally been altered by the farming, poultry, quarrying, mining, and construction practices of the people in the area under study. The poultry farms chosen have been involved in commercial poultry production for several years. Agricultural chemicals (inorganic fertilizers, pesticides, antibiotics), accidental spills of hydrocarbons applied as fuel from poultry machines, pollution emanating from maintenance activities demanding the usage of chemicals, like weed and insect control compounds, are commonly utilized on the farms adjoining the soils. There is a likelihood of the emission of toxic metals and other hazardous chemicals into the poultry farm soil from surface run-off. These trace metals were chosen for this study for many reasons. Arsenic poses serious health risks to humans by direct ingestion of soil or by plant uptake and feeding level pollution. Copper and Zn are of great significance because they are necessary plant micronutrients [5] that are also capable of causing health risks at elevated concentrations.

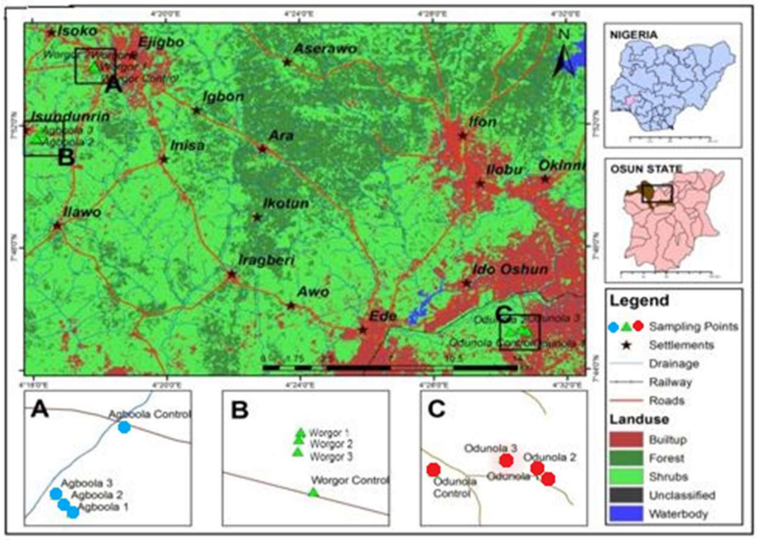

Figure 1. Map of the sampling area displaying study sites.

2.2. Sampling.

The sampling site was divided into 12 zones for the purpose of this work (Fig. 1). Composite samples of soil of approximately 2.0 kg constituted of at least five sub-samples were taken from three farms and gardens for each zone, once a month for a period of four months (June, July, August and September 2020). Samples were taken with a Dutch soil auger, graduated within 0–15 cm. The subsamples were taken along an independent zigzag pattern to obtain randomness. The Dutch soil auger was carefully cleaned after each sampling to prevent cross-contamination. The soil sampling spots were cleared of debris before sampling [12]. Samples were also collected from three rural villages as controls about 3 km away from the farm (Zones 4, 8 and 12).

2.3. Sample preparations.

Soil samples were air-dried for 7 days in the laboratory to prevent microbial deterioration. Prior to analysis, soil samples from each zone were mixed appropriately and re-dried in an oven at

110oC for approximately 3 hours before being ground in a porcelain mortar and sieved through a 2 mm plastic sieve to achieve fine soil particles [12].

2.4. Analysis of soil physicochemical parameters.

The most significant soil physico-chemical parameters controlling the mobility and bioavailability of metals in soil were evaluated. These are soil pH (conducted in water by utilizing a digital pH meter), particle size (through the hydrometer procedure), organic matter content (through the Walker-Black procedure) and cation exchange capacity (through Neutral KCl saturation and Neutral CH_3COONH_4 Displacement procedure) [12]. All parameters were conducted in triplicate. For the analysis of metals, homogenized soil samples were digested in aqua regia, a mixture of 25% HNO_3 and 75% HCl. Solutions from digested soil samples were kept in 100 mL high-density polyethylene sample bottles at 4 C until analysis. Speciation analysis was conducted by the sequential extraction method on 1 g of soil by utilizing a Flame Atomic Absorption Spectrophotometer (SOLAAR 9 SERIES) model AA 6800. The following solution was assayed for heavy metals utilizing a Flame Atomic Absorption Spectrophotometer (SOLAAR 9 SERIES) model AA 6800 equipped with a Zeaman background setting and graphite furnace. Standard solutions of each of the metals were aspirated to standardize the Atomic Absorption Spectrophotometer before aspiration of the samples. The heavy metal content was performed utilizing an Atomic Absorption Spectrophotometer at the Department of Chemistry and Industrial Chemistry Laboratory, Bowen University, Iwo, Nigeria. The equipment and operational settings were in line with the manufacturer's recommendations. The content, obtained after three measurements for each element, is reported in mg/kg. Operational standards for chemical assays were prepared from Zeaman stock solutions.

2.5. Sequential extraction method.

The Tessier method was chosen because it is well recognized, has wide application [3,7,14], and it has been calibrated for the analysis of soils, sediments, dust, and sewage sludge [3,15]. Thus, this five-step method enables comparison of the findings obtained. Problems like variability in extraction efficiency, inaccuracy in differentiation among geochemical fractions, and overlapping of the chemical partitioning between the various extraction stages are notable, and they have been broadly expressed in the literature. However, the sequential method is extremely useful in informing about the fair bonding of metals in various solid stages and thus the forms that may be liberated in soil solution under various ecological settings [3,7,14,15]. Subsequent to the sequential extraction method of Tessier, the chemical partitioning of heavy metals enables the differentiation of five phases [3,7,14] signifying about to be specified chemical fractions: exchangeable metals, associated with carbonates, associated with Fe–Mn oxides, associated with sulfides and organic matter, and residual fraction. The method was conducted with an initial weight of 1 g of the sieved dry soil sample. Deionized water was utilized in preparing stock solutions and for each phase of the leaching method that was found in a Millipore Milli-Q plus system. To check the results of the sequential extraction, the sum of the various phases per element was compared to the results found from the total digestion. The recovery rates were very good for Cu and Zn (about 90%), while the least recovery rates (75%) were found for As. For quality assurance, duplicate assays, inclusive of assays at an external laboratory, were done on three chosen samples. The sequential extraction method is further explained.

2.5.1. Fraction 1- exchangeable fraction.

Samples (1 g) of soil were extracted at ambient temperature for 1 hour with 20 mL of magnesium chloride solution (1 M $MgCl_2$) at pH 7. Soil and extraction solution were carefully stirred all through the extraction. This is primarily an adsorption-desorption method. Metals extracted in the exchangeable fraction comprise weakly adsorbed metals and can be liberated via an ion-exchange system. Alterations in the ionic constituent of the water would highly control the ionic exchange method of metal ions with the main compositions of the samples like clays, hydrated oxides of iron, and manganese [7]. The extracted metals were then decanted from the residual soil.

2.5.2. Fraction 2 - associated with carbonates.

The metals associated with the carbonate phase are controlled by ion exchange and modifications of pH. The residue of Fraction 1 was extracted with 20 mL of 1 M sodium acetate/acetic acid buffer at pH 5 for 5 hours at ambient temperature. At a suitable pH, a significant amount of trace metals can be coprecipitated with carbonates, and the extracted metal solution was decanted from the residual soil. The residual soil was applied for the specified extraction.

2.5.3. Fraction 3 - associated with oxides.

The residue from Fraction 2 was extracted under moderate reducing conditions. 13.9 g of hydroxyl amine hydrochloride ($NH_2OH \cdot HCl$) was dissolved in 500 mL of distilled water to prepare 0.4 M $NH_2OH \cdot HCl$. The residue was extracted with 20 mL of 0.4 M $NH_2OH \cdot HCl$ in 25% (v/v) acetic acid with shaking at 96 °C in a water bath for 6 hours. Iron and manganese oxides, which can be found between particles or coatings on particles, are excellent substrates with large surface areas for absorbing trace metals. Under reducing settings, Fe (III) and Mn (IV) could liberate adsorbed trace metals. The extracted metal solution was decanted from the residual soil, which was employed for further extraction.

2.5.4. Fraction 4 - associated with organics.

The residue from Fraction 3 was oxidized in this manner: 3 mL of 0.02 M HNO_3 and 5 mL of 30% (v/v) hydrogen peroxide, which had been changed to pH 2, were put on the residue from Fraction 3. The mixture was heated to 85°C in a water bath for 2 hours with intermittent shaking and allowed to cool down. Another 3 mL of 30% hydrogen peroxide, changed to pH 2 with HNO_3, was then included. The mixture was heated again at 85°C for 3 h with intermittent stirring and allowed to cool down. Then 5 mL of 3.2 M ammonium acetate in 20% (v/v) nitric acid were included, and after that, dilution to a final volume of 20 mL with de-ionized water. Trace metals can be bound by various forms of organic matter, living organisms, and mineral particle coatings via complexation or bioaccumulation. These substances can be decomposed through oxidation, releasing soluble metals. The extracted metal solution was decanted from the residual soil, which was utilized for hereunder extraction.

2.5.5. Fraction 5 - residual or inert fraction.

Residue from Fraction 4 was oven dried at 105 °C. Digestion was done with a mixture of 5 mL of HNO_3 (HNO_3, 70% w/w), 10 mL of hydrofluoric acid (HF, 40% w/w), and 10 mL of perchloric acid ($HClO_4$, 60% w/w) in Teflon beakers. Fraction 5 generally includes mineral compounds, where metals are strongly bonded within the crystal structure of the minerals, including the soil. After each sequential extraction, the solution was centrifuged at 4500 rpm for 15 min. The supernatant was removed with Whatman No. 42 filtered paper and the residue washed with distilled water, followed by vigorous handshaking before the next extraction. The volume of the distilled water for rising residue was kept to a minimum. To verify the method, the equipment was programmed and it performed metal detection by showing three absorbance readings, and what was recorded was the average. Blanks were also utilized for the correction of background and other sources of error. In addition to standardizing the instrument before it was used, quality checks were also done on it by checking the absorbance after every ten sample runs.

2.6. Quality control of data

Validation of analytical results was tested by recovery experiments because there was no standard reference material (SRM), which is more preferential or required to check the accuracy of the sequential extraction method studied in our laboratory. The recovery of metal was 93% for Cu, 90% for Zn and 75% for As, and the coefficient of variation was between 3% and 42% when assayed in triplicate (Table 1). An internal check on the results of the microwave extraction method and the sequential extraction method was done by comparing the sum of the 5 steps (adsorbed + acid-soluble + reducible + oxidizable + residual) from the sequential extraction method with the total metal level from the microwave-assisted acid digestion method (Tables 3–5). The recovery of the sequential extraction method was computed in this manner:

$$Recovery = \frac{F1 + F2 + F3 + F4 + RES}{Total\ digestion} X100$$

2.7. Reagents.

Nitric acid was purchased from Riedel-deHaen (Germany). Acetic acid, perchloric acid, sulphuric acid, hydrochloric acid were obtained from Sigma-Aldrich (Germany). Ammonium acetate, hydroxylamine chloride, magnesium chloride, potassium dichromate pellets, and hydrofluoric acid were purchased from British Drug House (Poole, England), From the list above, reagent I (25% of HOAc comprising 0.04 M $NH_2OH.HCl$ filled in to 500 mL) and reagent II (3.2 M CH_3COONH_4 and 1.0 M $MgCl_2$) were formulated. These were applied to formulate stock solutions [7].

3. Results and Discussion

The validity of the analytical methods utilized in this study was verified in reference to sensitivity, recovery, precision, and accuracy. Table 1 shows the FAAS measuring specifications, detection limit (LD), and percentage recovery determination (%R) for the sums of the five fractions. Under the analytical methods employed, the standard calibration curves obtained indicated a high proportionality level with correlation levels (r^2) ranging between

0.9820 and 0.9916. Recoveries of heavy metals varied between 75% in As and 93% in Cu. These detected levels were within acceptable levels. The computed LD contents (Table 1), which ranged from 0.002 mg Zn/kg to 0.200 mg As/kg, were in good harmony with the contents indicated by Ogunwale [7]. The mean physico-chemical parameters of the soil samples are displayed in Table 2. The results of the mean sequential extraction of soil samples carried out from June to September 2020 are summed up in Tables 3 to Table 5. The mean percentages of metals in the fractions are indicated in Table 6 and Table 7 relates the total metal contents in soil with the bioavailable contents. Tables 8 and 9 show the analysis of variance (ANOVA) and Pearson correlation coefficient between soil properties and bioavailability of metals in the five geochemical phases of the sequential extraction for soil samples.

Table 1: FAAS measuring specifications, detection limit and % recovery for heavy metals in the soil.

Metal species	Current (mA)	Measuring Stipulations Wavelength	Silt Width (nm)	Calibration Curve (r^2)	Computed LD * (mg/kg)	Amount Spiked	Amount Quantified	% Recovery
As	12	193.70	0.50	0.9850	0.200	25.00	18.75	75
Cu	6	324.80	0.50	0.9820	0.020	25.00	23.25	93
Zn	8	213.90	0.70	0.9916	0.002	25.00	22.50	90

3.1. Physico-chemical Parameters Soil Samples.

Table 2 indicates mean values of the physico-chemical parameters of surface soil samples from the poultry farm area. Soil pH is primarily derived from constituents constituting the parent material. pH values varied from neutral to slightly alkaline (6.60–8.10). The pH was neutral at (S2, S3, S8, and S12), but slightly alkaline at (S1, S6, S9, S10, and S11).The organic carbon percentages were in a narrow range and the organic matter values were below 5%. According to FAO standards, the soil at the location can be classified as medium in organic matter [16]. The CEC signifies the capability of the soils to take up or liberate cations and, thus, is an essential variable in sites polluted by heavy metals. Organic matter and clay minerals are accountable for the CEC. Cation exchangeable capacity ranged from 0.88 to 1.80 Cmol/kg.In line with Ogunwale et al. [12], pH and ECs are the most significant factors because, under acidic environments, the soil sphere will dissolve more salts. By virtue of the neutral and slight alkaline environments of the soil, pH and ECs could be the controlling factors for poultry and agricultural settlements in the analyzed area. Texture is the word expressing the size and classification of the soil particles. Individual particles, termed soil separates, may be defined, in relation to their grain size, as soil constituents (below 2 mm in diameter) or just as cobbles, pebbles, or gravel, if they are higher than this. Soils may be categorized in reference to their textures into various categories based on the ratio of sand to clay to silt [12]. A hypothetical soil constituted of equal fractions of these 3 constituents is called loam. According to the predominant constituent, a loam can be designated as sandy, clay, or silty loam.At all study sites, the soil indicated a sandy loam texture. Sandy loam substrates are usually found in oxidizing environments; nevertheless, in this instance, the water-saturation status of soils and the flooding of sediments accounted for the reducing condition.

Taking the instance of the sandy loam textures, it is reported that the sandy loam content is very moderate with values of more than 60%. This condition leads to moderate draining and low leaching of bases in the soil, and these will be reflected in the moderate CEC [12]. The occurrence of moderate sand in certain soils will speed up the process of soil structure formation, and because of that, the soil will retain a double-grain structure with remedial actions may not be needed for now. The farms, nevertheless, are exposed to a diverse set of environments. The clay content is quite moderate, with values below 20% in all the samples. At present, the structure is moderate, but in time to come the structure may form, particularly if organic matter is highly available [14]. The formation of a structure is likely in the existence of clay, silt, and sand in a satisfactory proportion. In general, the pH of these soils is moderate, with values of 6.6 or more. The moderate pH values are probably owing to the occurrence of moderate metal content in the area. Similar findings were indicated for the pH of Ogun farm settlement, Abeokuta, Ogun State, where the pH was noted to be 6.1–8.40 [15]. As indicated by [12], soil pH is one of the factors which influences the bioavailability and the mobility of heavy metals in the soil. As indicated by [13], heavy metal mobility declines with increasing soil pH by the cause of precipitation of hydroxides, carbonates or insoluble organic substances. The content of heavy metals mobilized in the soil environment is a function of pH, properties of metals, redox conditions, soil chemistry, organic matter content, clay content, cation exchange capacity and other like soil properties [12]. Moderate pH values may increase the availability of most micronutrients. The moderate soil pH values imply that heavy metal availability for plant absorption is medium in the sample soils and could satisfactorily support plant growth. This moderate pH can readily be increased by the addition of limestone and the like basic constituents. Continued addition of limestone along with other basic constituents can increase the pH to a more satisfactory level for plant growth in addition to enhancing the organic content of the soil.

Organic carbon is moderate in relation to normal soils in Nigerian environments. This is somewhat similar to the present properties of the deposits which have just been subjected to the poultry operation. Integration of organic manure (poultry manure) and/or poultry waste from the factory is viewed as important to increasing the organic matter content of the croplands. Thus, soil structure formation is encouraged and more nutrients are included. Organic matter has a high sorption capability for metals and easily forms complexes with them, reducing the rate of hydrolysis and controlling the rate and pathways of oxidation-reduction activities [7]. Elevated organic matter content implies immobilization of the metals that are associated with constituents like fulvic or humic acids. Zones with elevated organic carbon, like Zones 1, 2 and 8, are also associated with elevated metal content in the surface soil. This indicates that metals are retained in the top soil in relation to the effects of leaching and plant absorption. Other factors like clay content, organic matter content, and cation exchange capacity were simply moderate for all the study sites. The cation exchange capacity of soils is normally determined by the cation output of the soil via extraction with an ammonium acetate solution. It is also a degree of the surface negative charge, likewise the potential for cation adsorption. Cation exchange capacity is commonly reported in milliequivalents (meq) per 100 g of soil. Its value is based mostly on the organic and clay content of the soil, including the acidity and clay mineralogy of the equivalent. The CEC is moderate in these soils, even with more than 15% clay content. The value at sites 4, 8 and 12 is 0.88 C_{mol} (+)/kg of dry soil or more. This is similar to the mineralogy, where kaolinite, mica, and chlorite are present to be principal in the clay fraction [12]. By adding organic matter to the soil, it might be possible to increase the CEC of these soils in some way.

Table 2. Mean physico-chemical parameters of soil samples.

Study site	% sand	% clay	% silt	Textural class	pH	% OC	% OM	CEC(Cmol/ kg)
1	68.20	17.30	14.50	Sandy loam	7.50	1.80	3.10	1.80
2	70.30	19.40	10.30	Sandy loam	6.60	1.72	2.96	1.40
3	69.60	18.80	11.60	Sandy loam	6.70	1.50	2.58	1.60
4	67.85	16.60	15.55	Sandy loam	7.20	1.10	1.89	0.90
5	74.30	15.60	10.10	Sandy loam	7.30	1.25	2.15	1.50
6	70.40	17.90	11.70	Sandy loam	7.70	1.60	2.75	1.30
7	66.90	19.70	13.40	Sandy loam	7.10	1.55	2.67	1.20
8	65.60	18.50	15.90	Sandy loam	6.80	1.19	2.05	0.88
9	72.20	17.60	10.20	Sandy loam	7.90	1.40	2.41	1.70
10	68.80	16.90	14.30	Sandy loam	8.10	1.28	2.20	1.55
11	71.60	18.10	10.30	Sandy loam	7.60	1.36	2.34	1.68
12	70.80	17.50	11.70	Sandy loam	6.70	1.05	1.81	0.96
Overall mean±SD	69.71±2.31	17.83±1.13	12.46±1.08	Sandy loam	7.27±0.48	1.40±0.23	2.41±0.39	1.37±0.20
% CV	3	6	9		7	16		15

OC = organic carbon; OM = organic matter; CEC = cation exchange capacity (C mol/kg)

3.2. Metal speciation of soil.

Mean metal chemical speciation conducted by sequential extraction of the metals is crucial to metal mobility. The results (Tables 3 to 5) show that the levels of heavy metals extracted from each fraction vary broadly. The sequence of mobility of the metals, taking into account their abundance in the fractions, is: residual > bound to organics > exchangeable > bound to oxides > bound to carbonate. Oxides occur as nodules and cement between particles. These oxides contain trace metals and can be mobilized under reducing and acidic environments. The organic phase is fairly stable in nature but can be mobilized under high oxidizing environments by the cause of the decomposition of organic matter [15]. Arsenic is mostly common in exchangeable fractions in all the samples. The dominance of As in the exchangeable fraction is 20.32%, while in the residual fraction it is 26.79%. The dominance of As in other geochemical fractions was very moderate. This suggests that As was more mobile in this ecosystem than other metals that are mostly common in the remaining four geochemical fractions. Zinc is mostly dominant when associated with organic matter, with a dominance of 31.12%, while in the residual fraction the dominance was 29.93%. The dominance of Zn in other phases was minimal. Zinc in this ecosystem was more mobile than the metals that were mostly common in the residual phase. This is in harmony with Adewuyi and Osobamiro [15]. Because of the high formation of organic-Cu substances, copper can easily complex with organic matter.The result of sequential extraction indicates that Cu is mostly common (30.85%) in the fraction associated with organics. The dominance of Cu in the residual fraction was 24.10%.

Table 3. Mean contents ((mg/kg dry matter) of As in sequentially extracted soil fraction.

Study Site	EXC	AEX	RED	OXD	RES	TOTAL	BA	%BA
1	143	90	84	303	148	768	233	30.34
2	125	76	186	222	205	814	201	24.70
3	86	59	101	101	320	667	145	21.74
4	3.80	1.86	4.60	10.20	13.20	33.66	5.66	16.82
5	162	95	70.80	132	142	602.80	257	42.63
6	66	53	130.20	96	164	509.20	119	23.37
7	108	68	173	122	136	607	176	28.99
8	2..90	1.80	3.20	12.10	14.50	34.50	4.70	13.62
9	210	152	88	92	98	640	362	56.56
10	120	92	64	83	153	512	212	41.41
11	116	87	52	68	108	431	203	47.10
12	4.60	2.50	1.80	7.10	10.60	26.60	7.10	26.67
Overall mean±SD	95.6±12.3	64.8±10.3	79.9±12.2	104±14.3	126±16.9	470.5±27.3	160.5±18.6	31.2±6.6
%CV	13	16	15	14	13	6	12	21

Where EXC = Exchangeable phase; AEX = Acid extractable phase; RED = Reducible phase, OXD = Oxidizable phase; RES = Residual phase, BA = Bioavailable phase = EXC + AEX

Table 4. Mean contents (mg/kg dry matter) of Cu in sequentially extracted soil fraction.

Study Site	EXC	AEX	RED	OXD	RES	TOTAL	BA	% BA
1	6.8	8.1	7	16	11	48.90	14.9	30.47
2	8.2	8.6	9	19	13	57.8	16.8	29.07
3	12.10	4.8	11	17	14	58.9	16.9	28.69
4	4.80	2.2	3	10	8	28	7	25
5	9.8	10	12	22	19	72.8	19.80	27.20
6	10	12	16	26	21	85	22	25.88
7	13	14	18	25	20	90	27	30
8	4.50	3.2	4	9	6	26.70	7.7	28.84
9	9.40	13	8	23	16	69.40	22.4	32.28
10	8.60	15	12	28	22	85.60	23.20	27.57
11	16.20	18	17	30	25	106.20	34.20	32.20
12	4.30	3.80	3	8	7	26.10	8.10	31.03
Overall mean±SD	8.98±3.47	9.39±3.93	10.00±4.05	19.42±4.22	15.17±3.96	62.95±10.61	18.37±3.99	29.02±4.23
%CV	38.70	42	41	22	26	17	22	15

Where EXC = Exchangeable phase; AEX = Acid extractable phase; RED = Reducible phase, OXD = Oxidizable phase; RES = Residual phase, BA = Bioavailable phase = EXC + AEX

Table 5. Mean contents ((mg/kg dry matter) of Zn in sequentially extracted soil fraction.

Study Site	EXC	AEX	RED	OXD	RES	TOTAL	BA	%BA
1	18	23	29	48	20	138	41	29.71
2	21	22	25	53	16	137	43	31.39
3	18.40	24	28	51	68	189	42	22.22
4	4.60	8	5	6	9	32	12	37.50
5	16	20	19	85	60	200	36	18
6	17	18	18	46	48	147	35	23.80
7	13	23	20	49	61	166	36	21.68
8	7	5	4	10	9	35	12	34.29
9	15	19	21	65	23	143	34	23.78
10	19	17	23	18	40	117	36	30.77
11	11	12	22	30	85	160	23	14.38
12	6	8	9	8	12	43	14	32.38
Overall mean±SD	13.75±2.34	16.58±3.38	18.58±4.99	39.08±8.76	37.58±8.76	125.58±20.74	30.33±7.31	26.67±6.74
%CV	17	20	27	22	22	17	24	25

Where EXC = Exchangeable phase; AEX = Acid extractable phase; RED = Reducible phase, OXD = Oxidizable phase; RES = Residual phase, BA = Bioavailable phase = EXC + AEX

Heavy metals with high dominance in the fraction associated with organics are more available than heavy metals in the residual fraction. This concurs with Adewuyi and Osobamiro [15], who indicated that As, Cu, and Zn were mostly bound to the residual phase. The results of the sequential extraction indicate that most of the As, Cu, and Zn are heavily retained in the residual fraction in all soils. These heavy metals are contained in the crystal lattices of minerals with high bindings, and as a result, they will not be liberated into the ecosystem. Metals found in the residual phase are a degree of the extent of environmental contamination. The greater the metals found in this phase, the lower the level of contamination. The sum of the contents of metals in various geochemical fractions can be applied to show the potential mobility of metals. The potential mobility of a metal can be determined by adding together the results of the exchangeable fraction, carbonate fraction, oxide, and organic fraction of that metal [7].

As presented in (Table 6), the potential mobility of As in soil was 73.21%. The exchangeable fraction signifies the mobile and bioavailable heavy metal phase. In this phase, the heavy metals have more labile bounds and can be readily liberated into the ecosystem. The availability of heavy metals in this phase where they can be absorbed by plants from the soil is the most risky for the ecosystem. In our soils, just slight As, Cu, and insignificant quantities of Zn obtained in twelve soils are found in this phase. From the result of the sequential extraction in all the soil samples examined, As was mostly dominant in the residual phase and the abundance was less in the exchangeable fraction. High dominance of a metal in the residual phase relative to its dominance in other geochemical phases shows less mobility of the metal in the ecosystem. This indicates that As would not be easily liberated to the ecosystem and less toxic. The high dominance of Zn associated with organic matter explains the high potential mobility of Zn (70.07%) (Table 6). Copper has the maximum potential mobility (75.93%) of all the heavy metals because of the higher breakdown and decomposition of organic matter, resulting in the high formation of organic-Cu substances. Heavy metals with a high dominance in the residual fraction had the following potential mobility: As 26.79%, Cu 24.10%, and Zn 29.93%.These values were higher in relation to the values detected for heavy metals that were more dominant in other geochemical phases.

Table 6. Mean percentage potential mobility of metals in various geochemical phases of poultry farm soil.

Phase	As	Cu	Zn
Exchangeable	20.32	14.27	10.95
Carbonate	13.78	14.92	13.20
Fe-Mn oxide	16.98	15.89	14.80
Organic matter	22.11	30.85	31.12
Residual	26.79	24.10	29.93

Table 7 considers the total metal contents in soil with the bioavailable contents. The mean total contents of As, Cu and Zn (mg/kg) were 470.48±27.20, 62.93±10.61 and 125.58±20.74, respectively. The mean % bioavailability of As (31.166.60%) in the sampling site is more than that of Cu (29.02±4.23%) and Zn (26.67±6.74%), signifying that As is more mobile and available to the crops, which is a cause for concern. Arsenic can accumulate in soils as a result of farming practices such as the use of As-containing inorganic pesticides like lead arsenate ($PbAsO_4$), calcium arsenate ($CaAsO_4$), magnesium arsenate ($MgAsO_4$), zinc arsenate ($ZnAsO_4$), and Paris green [$Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$], and organic pesticides (mono As a result of the major role of As in animal feed, organic arsenicals perform an essential role as food additives to combat disease, increase body weight and food conversion, and amplify egg yield [5].

Table 7. Total and percentage bioavailable contents (mg/kg dry matter) of metals in soil samples based on squential fractionation.

Study Site	As			Cu			Zn		
	TOTAL	BA	%BA	TOTAL	BA	%BA	TOTAL	BA	%BA
1	768	233	30.34	48.90	14.9	30.47	138	41	29.71
2	814	201	24.70	57.8	16.8	29.07	137	43	31.39
3	667	145	21.74	58.9	16.9	28.69	189	42	22.22
4	33.66	5.66	16.82	28	7	25	32	12	37.50
5	602.80	257	42.63	72.8	19.80	27.20	200	36	18
6	509.20	119	23.37	85	22	25.88	147	35	23.80
7	607	176	28.99	90	27	30	166	36	21.68
8	34.50	4.70	13.62	26.70	7.7	28.84	35	12	34.29
9	640	362	56.56	69.40	22.4	32.28	143	34	23.78
10	512	212	41.41	85.60	23.20	27.57	117	36	30.77
11	431	203	47.10	106.20	34.20	32.20	160	23	14.38
12	26.60	7.10	26.67	26.10	8.10	31.03	43	14	32.38
Overall mean±SD	470.48± 27.27	160.46 ±18.65	31.16±6 .60	62.95±10 .61	18.37± 3.99	29.02± 4.23	125.58±2 0.74	30.33 ±7.31	26.67±6. 74

Furthermore, they are applied as desiccants and defoliants in cotton production and for weed prevention [6]. In spite of great debate, arsenic acid is still applied as a constituent of wood preservatives, whilst sodium arsenite solutions are utilized for debarking trees, in cattle, poultry, and sheep dips, and in aquatic weed prevention [6]. Due to all these uses, there is a growing concern regarding the risk of A to the ecosystem and public health [1]. The accumulated As in soils can be distributed among various soil constituents, like organic matter, Fe and Mn oxides, carbonates, and sulfides, and such distribution could have an impact on its mobility, bioavailability, and toxicity [7]. Generally, the greater the clay and/or organic matter content and pH, the more strongly bound the metals (slight mobility), and the greater their retention time in soil, and therefore, less bioavailability. Exchangeable cations are commonly available to plants and microbes. Elevated CEC, as detected in Zone 1, could increase metal mobility and bioavailability. Nevertheless, these physico-chemical properties consistently have a mutual influence [14]. Results were also determined by ANOVA employing the common linear models procedure of PAST software version 2.17. Probabilities less than 0.05 ($p < 0.05$) were considered statistically different. According to the statistical findings, we reject Ho because the pooled p-value (72.14) is greater than (p-0.05), and there is a significant difference between the physicochemical and bioavailability of metals content of poultry farm soils.As a result, at the 0.05 level of significance, we reject the null hypothesis and accept the alternate hypothesis, $F_{calculated}$ (72.14), and $F_{critical}$ (2.13) (Table 8). The amount of the indicator variable in a soil source is used to figure out what its properties are.

Table 8. Analysis of variance of total metal determination.

Source of variation	DF	Sum of Squares	Mean Sum	F_{ratio}	$F_{critical}$
Treatment	7	1672.92	2039.32	72.14	2.13
Error	88	2487.70	23.27		
Total	95				

Table 9 reveals the Pearson correlation coefficient values ($p < 0.05$) of soil properties and the bioavailability of the metals. In line with Ogunwale et al. [7], processes of metal mobilization and immobilization are governed by the status of soil parameters. To study this parameter, correlations between pH, organic carbon and clay percentages, CEC, and bioavailability of the metal contents in the five geochemical phases of the sequential extraction have been determined for all soils. As can be observed in (Table 9), aside from pH bound to the clay, % organic carbon bound to the CEC, % clay bound to the CEC, %BA (As) and %BA (Cu), there are no considerable correlations between the pH contents and the heavy metals present. Between CEC and the heavy metals, the most considerable associations are the positive correlation with Cu from the CEC and the negative one with Zn. Percentages of BA (As) formed a positive correlation with % BA (Cu) and % BA (Zn). The positive correlation suggests that % BA (Cu and Zn) has a source related to agriculture and confined animal feeding operations. Negative (inverse correlation) to weak correlations between soil parameters and bioavailability were observed. This is likely of pH, organic carbon, and clay, as their medium values are liable to increase bioavailability.

Table 9. Pearson correlation coefficient of soil properties and % bioavailability of metals.

Variable	**pH**	**% OC**	**% Clay**	**CEC**	**% BA (As)**	**% BA (Cu)**	**% BA (Zn)**
pH	1						
%OC	0.303	1					
%Clay	0.632	0.461	1				
CEC	0.432	0.740	0.803	1			
%BA(As)	-0.454	-0.362	0.581	-0.026	1		
%BA(Cu)	-0.932	-0.485	0.673	0.614	0.830	1	
%BA(Zn)	-0.106	-0.866	0.086	-0.811	0.880	0.078	1

5. Conclusion

The analysis of the soil physico-chemical parameters showed that the general moderate soil pH, organic carbon, organic matter, and CEC were useful in declining the bioavailability of the metals. The analytical results signified that As was above the natural heavy metal content of agricultural soil, which is a cause for concern as this metal can buildup to pollute the ecosystem. The contents of Cu and Zn in the soil samples were typically below FAO/WHO maximum permissive levels of 100 mg/kg and 300 mg/kg for Cu and Zn, respectively, for agricultural soils. This work also aimed to assess the distribution, retaining, and emission of As, Cu, and Zn in the chosen soils of the poultry farmland in Osun State. The finding observed from speciation analysis indicated that most of the metals studied had the highest dominance in the residual fraction. Except for Cu, this means that the metals were immobile, less reactive, and less bioavailable for liberation into the feeding level. The moderately high metal level in the poultry farmland may indicate some indirect ecological threat by way of clay distribution, and disassembled soil particles yielding heavy metals may sooner or later enter and buildup in bodies of water. The mean potential mobility of As, Cu, and Zn in the soil samples analyzed was fairly high, signifying that under favourable conditions they can be liberated to contaminate the ecosystem. The % bioavailable contents showed that As (31.16%) was more available for plant uptake than Cu (29.02%) and Zn (26.67%). In addition, the study showed that some areas of the sampling sites were more polluted by these metals than others, as a result of the prevailing man-induced activities distinctive to each area. The results of the speciation have provided the current state of metal contamination and the potential contaminants in the poultry farmland. More studies can be conducted on the speciation of heavy metals in other ecological spheres in the environs of poultry farmland. It is recommended that soils from this area under study should be well controlled to prevent the release of occluded heavy metals into bioavailable form. There is also a need for regular monitoring of Nigerian poultry farmland to determine its quality status. This will serve as a guide to the poultry farmer on action plans to be taken. Continuous testing of soil and poultry feed for metals to ensure that they are not more than safe levels. The study has provided baseline data on the bioavailable metal species and pollution status of the area under study. It has also given information on the suitability and health implications of using untreated chicken manure for farming at the evaluated center. The work has also added to the baseline data on heavy metal bioavailability studies in our environment.

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Competing Interests

The authors declare that they have no competing interests

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