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Heavy metal speciation in agricultural farmland in some selected local government areas of Benue State, Nigeria

*Odoh R.¹, Agbaji E.B.¹, Kagbu J.A.¹ and Thomas S.A.²

¹Chemistry Department, Ahmadu Bello University Zaria, Nigeria ²Sheda Science and Technology Abuja, Nigeria

ABSTRACT

This study investigates speciation of heavy metals (Cd, Co, Cu, Mn, Ni, Pb and Zn) in the cultivated farmland of three selected Local Government Areas of Benue state in Nigeria. Total of 31 selected sites and 9 controls have been sampled and five subsamples were taken in each site to create a composite sample. The seven metals have been analyzed for the sequential extraction procedure by atomic absorption spectrometry. Heavy metal speciation of soil samples from agricultural farmland indicates that the determined heavy metals are predominantly in the non-residual fractions thereby reflecting control by anthropogenic sources. The exchangeable Cd, Co, Pb, was not detected. The absence of mobile forms of Cd and Pb in all soil samples eliminates the toxic risk both in the tropic chain and from its migration downwards the soil profile.

Keywords: Speciation; Heavy Metals; Agricultural Farmland

INTRODUCTION

The accumulation of heavy metals and metalloids in soil, water and plants especially cadmium, chromium, copper, lead, nickel, and zinc poses many risks to humans and ecosystem health [1]. Risks may be expressed to humans either through the food chain (soil, water)-plant-human or soil (water) –plant-animal-human or through direct exposure by dermal contact or ingestion of soil contaminants (soil-human) or soil-water-human [2]. Environmental risks are expressed as phytotoxicity or ecotoxicity to soil flora and fauna. Risks resulting from pollution of soils by heavy metals are well recognized and several major tests have been published on this subject [3]. While many researchers have attempted to develop relationship between concentrations of contaminants in soils or plants and the effects on plants or organisms (including humans), it is important to list or characterize the major risk pathways for some of the elements of concern [4]. Cadmium is the element of most concern with regard to food-chain contamination. Compared

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with the other elements mentioned above, cadmium is unique in that it reaches concentrations of concern in crops (to human and animal consumers) at levels that are well below those at which phytotoxicity is expressed. Hence, predictive soil tests for cadmium should focus on predicting its transfer to edible crops with ecotoxicity and phytotoxicity as secondary foci. Arsenic, chromium, mercury and lead are strongly retained by the solid phase in most soils, so that accumulation of these elements from the soil poses less risk to plants and soil organisms through bioaccumulation [5]. Risks from these elements, especially arsenic and lead are more related to direct ingestion of soil by animals or humans, so that soil tests need to focus primarily on predicting bioavailability in the mammalian gut rather than on phytotoxicity or food-chain hazards. The primary concern for the remaining metals, copper, nickel, zinc and selenium are adverse effects on plant growth or microbial activity in soil, so that soil tests for risk assessment need to focus on predicting these pathways rather than food chain hazards [6].

In recent years, extensive research has been conducted on estimation of bioavailability and toxicity of metals in soils [7]. However, no methods are currently available to allow accurate prediction of plant intake or phytotoxicity, adverse effects on human health, or ecotoxicity from metal pollution of soils. Because of the relative ease of analysis, most soil quality criteria and risk assessments rely on conservation regulatory guideline values that are based solely on the total metal concentration in soil. Appropriate assessment of environmental risk of metals in soils must consider a bioavailability based rationale [8]. It is widely recognized that to assess the environmental input of soil pollution, the determination of the metal speciation will give more information about the potential for release of contaminants and further derived processes of migration and toxicity [9]. Therefore, in environmental studies of risk assessment, chemical partitioning among the various soil chemical phases is more useful than measurements of total heavy metal contents [10]. Among the procedures to determine element speciation, those based on sequential extraction are the most widely used [11]. These methods are of interest in environmental studies to inform on the interactions with other component of the biosphere as well as to outline areas of potential toxicity and to provide information on the soil micro-nutrient levels for agricultural uses [12].

No information on the speciation of metals in Agricultural farmland of Benue state despite that the state produced substantial amount of food crops (food basket of the nation) in all the local government areas of the state. The foods produced are sold in all the markets in the country and transported to the different parts of neighboring countries like Cameroon, Ghana, and Benin Republic etc.

As part of a current research program on assessment of soil contamination in the agricultural farmland, our interest focuses on chemical partitioning of heavy metals because the potential effect of soil contamination is better assessed through the knowledge of the forms in which a given metal is present rather than the use of its total concentration [13, 14].

In this work, three local government areas of the state (Otukpo, Gboko and Makurdi) where industrial, agricultural and commercial activities go on hand in hand are chosen to determine the geochemical partitioning of Cd, Co, Cu, Mn, Ni, Pb and Zn. To assess the binding of heavy metals to the main fractions in soils, a five-step sequential extraction procedure [15], based on the capacity of some extracting reagents to remove the heavy metals retained from the soil

chemical phases has been used. The seven heavy metals are selected because they are of importance in agriculture as micro-nutrients (Co, Cu, Mn, Zn) but also because of its toxicity (Cd, Ni and Pb).

SAMPLING SITES

Benue state lies in the middle of the country and shares boundaries with five others namely; Nassarawa to the North, Taraba to the East, Cross River to the South, Enugu to the South-west, and kogi to the East. The state also shares a common boundary with Republic of Cameroon on the South-East (Fig 1). Benue state has a population of over 3 million (2006, Census) and occupies a landmass of 30,955 square kilometers. It is predominantly a rural state, with about 90 percent of her population being rural resident. Indeed, only few settlements that include Otukpo, Gboko, kastina –ala and Markurdi (the state capital) qualify for urban status.

Three local government areas were selected for the study and these include Otukpo, Gboko and Markurdi (state capital) respectively (Fig. 2). These are areas where industrial activities and agricultural production go on hand in hand.



Fig 1: Map of Benue State showing the Local Government Areas



Fig 2: Map of Benue Showing Sampling Points

A total of 31 sampling sites, eleven distributed in Otukpo, ten distributed in Gboko and ten distributed in Makurdi and nine control sites, three from each of local government areas. The sampling procedure intended to obtain a representative average sample for each site made of five subsamples.

METHODOLOGY

The collected soil samples were air-dried for weeks to remove excess moisture. Large soil clods were also crushed to facilitate the drying. The dried soil-samples were crushed in a porcelain mortar with a pestle. The crushed soil-sample was sieved through a 2 mm sieve made of stainless steel, for analyzing soil _PH and particle size. Some portion of the individual sieved soil-sample was further pulverized to a fine powder and passed through a 0.5-mm sieve for analyzing organic carbon, total metal content, and speciation. The samples were then stored in labeled polyethylene bags ready for analysis.

The pH of the soil samples was determined with pH meter Hanna (Model H1991000) according to standard analytical methods. Organic matter was determined using the chromic acid oxidation method [16]. Particle size distribution was determined by the hydrometer method [17]. The exchangeable cation was determined by the method [18].

Sequential Extraction of Metals

The extraction was carried out with an initial mass of 1.0g air dried agricultural farm land soil samples in polypropylene centrifuge tube of 50 cm³ capacities. The conventional method developed by [15] was used in the extraction. However, Mg (NO₃)₂ was used instead of MgCl₂ to avoid an increase in the solubility of heavy metals within the soil solution matrix [19]. The extractions were carried out on three sub-samples from each study area as follows:

Exchangeable phase, (F1) Soil sample was extracted with 8 cm³ of 1m Mg (NO₃)₂ at pH 7.0 for 1 hour, with continuous shaking/agitation (Shuman, 1991). The carbonate bound, (F2);The residue from F1 was extracted with 8 cm³ of 1m NaOAc solution (adjusted to pH 5 with HOAc) for 5 hours at room temperature with continuous agitation [15]. Fe – Mn oxides bound (reducible) F3: The residue from F2 was extracted with 10 cm³ of 0.04m NH₂OH.HCl in 25% HOAc for 6 hours at 96⁰c with occasional agitation, [15]. Organic bound (oxidizable) F4: The residue from F3 was extracted with 8 cm³ of 30% H₂O₂ (adjusted to pH 2 with HNO₃ for 30 mins in a boiling water bath and the supernatant was filtered after centrifuging).The above step was repeated twice. The residue from the above step was washed three times with 5 cm³ of 3.2 m NH₄OAc solution (in 1:5 HNO₃), for 30 mins with continuous agitation [20]. Residual F5: The residue from F4 was quantitatively transferred into a conical beaker, evaporated to dryness, and digested with HNO₃ – H₂O₂ – HCl mixture using a water bath reflux digestion technique (USEPA SW 846 method 3050;) [21].

After each successive extraction, separation was done by centrifuging for 30 mins. The supernatants were removed with pipette and filtered. The residue was washed with 8 cm³ of deionized water followed by vigorous hand shaking and then followed by 30 min of centrifugation before the next extraction. Each filtrate of F1, F2, and F3 was individually made up to 25 cm³ in a volumetric flask, while the filtrate from F4 and F5 was made up to 50 cm³ in volumetric flask.

RESULTS

Soil Characteristics of Agricultural farmland

The pH values ranged from 6.00-7.30, 6.00-7.30 and 6.16-7.20 for Otukpo, Gboko and Makurdi Agricultural farmlands respectively (Tables 1-4). All the soils studied from the Agricultural farmlands were either weakly acid or neutral.

The soil organic carbon concentrations ranged from 0.44-0.90, 0.54-1.30 and 0.55-1.30 for Otukpo, Gboko and Makurdi respectively. The soils from the three study areas were generally low in organic carbon contents. Most of the soil samples studied from Otukpo, Gboko and Makurdi agricultural farmland have organic carbon values of less than 1.0%. The clay contents ranged from 15.60-29.60%, 9.60-22.60% and 8.60-22.60% for Otukpo, Gboko and Makurdi agricultural farmland soils respectively. The carbon exchange capacity ranged from 11.22-15.25meq/100g,11.50-18.20meq/100g and 11.70-18.20meq/100g, for Otukpo, Gboko and Makurdi respectively.

Extractable metal

The results of the sequential extraction of the metals are presented in (Tables 5-7). The exchangeable Cd level was not detected in all soils from the vicinity of the agricultural farm

land. Other Cd concentration range values are $0.309 - 0.362 \ \mu gg^{-1}$, $0.493 - 0.557 \ \mu gg^{-1}$, $0.16 - 0.19 \ \mu gg^{-1}$ and $0.12 - 0.13 \ \mu gg^{-1}$ for carbonate, oxide, organic bound and residual fractions respectively. The greatest percentage of Cd in these soils was present in oxide fraction, with about 45.69% followed by carbonate fraction with 28.45% of the total extractable fraction of the metal which indicate that this metal will be bio-available to the environment. The availability of this metal in the sequentially extracted fractions follows the order: Oxidisible > carbonate > organic > residual. Like Cd, the exchangeable Co level was not detected in all soils from the agricultural farm land. But unlike Cd, the greatest percentage of Co in these soils was present in organic fraction, with about 52.85% followed by oxidisable fraction of 26.02%. The availability of this metal in the sequentially extracted fractions follows the order: Organic > oxidesible > carbonate > carbonate > residual. The exchangeable Cu contents varied considerably from 0.50 μ gg⁻¹ to 0.65 μ gg⁻¹, the carbonate fraction ranged from 4.34 μ gg⁻¹ to 4.95 μ gg⁻¹, while the range of levels found in reducible fraction were 3.35 μ gg⁻¹ to 7.53 μ gg⁻¹. As for the organic bound copper, the concentrations ranged from 5.30 μ gg⁻¹ to 7.53 μ gg⁻¹, and the residual copper levels were 1 -13 to 1.60 μ gg⁻¹.

All the soil samples analyzed had Cu residual percentage of less than 10%. However most of the Cu in these soils was present in the organic fraction, having 39.30% Cu in soil samples of cultivated farm land studied. The carbonate bound was the next most dominant fraction for these soils 27.39%, followed by the Fe – Mn oxides bound: 21.82%, then residual: 8.09%, and exchangeable fraction with 3.40%. The predominance of the specifically sobbed Cu fraction over the reducible form found in this study may be due to sandy texture of the soils. High percentage of manganese was observed in residual fraction with about 36.23%. The order of availability of this metal in different fractions followed the pattern: Residual > oxidisable > exchangeable > organic > carbonate. About 43.76% of this metal was found to be in organic fraction while about 16.24% of the total extractable fraction contributes to the mobile phase (exchangeable). This indicates that the potential availability of this metal in the extracted fraction was: organic >> Oxidisable > exchangeable > residual.

The exchangeable Pb level was not detectable in all soils sample from agricultural farm land (Tables 9-10) other Pb concentration values are 2.37 μ gg⁻¹, 1.66 μ gg⁻¹, 0.89 μ gg⁻¹ and 0.87 μ gg⁻¹ for carbonate, oxide, organic bound and residual fractions respectively. The residual fraction constituted about 15.03% in all the studied soils. This result is consistent with 13.0% residual Pb reported, [22] in the study of heavy metals from urban soils. The greatest percentage of Pb in these soils was present in carbonate bound fraction. In these soils the sum of the carbonate and Fe – Mn oxides bound fractions accounted for the greatest portion of Pb. The exchange Zn concentration was 1.89 μ gg⁻¹. The Zn level found in the carbonate bound fraction was 7.63 μ gg⁻¹ while the Fe – Mn oxides bound had zinc content of 4.22 μ gg⁻¹. The Zn level associated with organic matter was 3.32 μ gg⁻¹, and the residual fraction had Zn concentration of 3.2 μ gg⁻¹. The most and moderately labile fractions (F1 and F2) accounted for 46.96% of Zn in all the examined soils. The Fe – Mn oxides bound was the next dominating fraction with percentage value of 20.82% and this may be partially associated with the high stability constants of Zn oxides. Unlike the Cu, the Zn in organically complexes fraction occurred in lower mean percentage value than found in oxide and carbonate fractions.

The percentages of the studied heavy metals in each fraction are in the following order: Cd: Oxide > Carbonate > Organic > Residual Co: Organic > Oxides > carbonate > Residual Cu: Organic > Carbonate > Oxide > Residual > exchangeable Mn: Residual > Oxides > Exchangeable > Organic > Carbonate Ni: Organic > Oxide > Carbonate > Exchangeable > Residual Pb: Carbonate > Oxides > Organic > Residual Zn: Carbonate > Oxides > Organic > Residual > Exchangeable.

Thus, the redistribution among the different fractions and the relative mobility of the heavy metals in cultivated farm land soil samples in this study tend to be in agreement with the observation [6], that trace elements from anthropogenic sources are potentially more mobile than those that are inherited from the parent material. Process of metal mobilization-immobilization is affected by a variety of soil properties [3, 23].

To examine this influence, correlations between pH, organic matter and clay percentages and contents of Cd,Co, Cu, Mn, Ni, Pb, and Zn in the five chemical phases of the sequential extraction have been established for all soils (Table 8). Cd associated with carbonate correlated positively with organic matter, and negatively with pH, while in the oxide fraction Cd correlated positively with pH and negatively with clay contents.Cd in organic fraction correlated positively with organic matter, while Cd in the residual fraction correlated positively with pH, organic matter but correlated negatively with clay. Co associated with carbonate fraction correlated positively with clay, and negatively with pH.Cd in the oxide fraction correlated positively with pH and negatively with clay contents. Co in organic fraction correlated positively with pH and negatively with clay contents. While Co in the residual fraction correlated positively with organic matter, but negatively with clay content. Other metals Cu, Mn, Ni, Pb, and Zn, shown positive and negative correlation with these soil properties. Although the size of data set does not allow obtaining better results, in general the main trends reported in the literature, such as positive correlations with organic matters and clays have also been observed in our soils [24, 25]. It was intended to determine similarities between soils in relation to their contents for Cd, Co, Cu, Mn, Ni, Pb and Zn in all chemical.

DISCUSSION

Fractionation of total metal contents may give indications of the origin of the metals. High levels in the exchangeable acid soluble and easily reducible fractions may indicate pollution from anthropogenic origin [24]. Even high contents in the resistant fractions, except the residual, may be significant in the long term [26]. The distribution of trace heavy metals in the soil samples allows us to predict their mobility and bioavailability and toxicity [27]. Cd, Pb, Zn and Cu seemed to be easily mobilized since the highest percentage of these metals are found in the extractable fraction (exchangeable, carbonate and oxidizable) respectively. Cd seemed to be the most mobile element even though Cd, Pb and Co was not detected in exchangeable fraction, while Co, Mn and Ni are the minimum mobilisable elements. The order of mobility of the extractable metals from soil samples is Cd>Pb>Zn>Cu>Ni>Mn>Co. Approximately 73.69% of Cd total concentration was measured in the second and third stages combined. This indicates that Cd occurs in mobile forms in soils and about 74% of its total concentration was observed in the first three extraction stages. Therefore it is the most mobilized element since it is mainly distributed among the non-residual fractions. This high amount of Cd associated with the non-residual phases shows that it may be easily transferred into the food chain through uptake by

plants growing in the soils or other mechanism [28]. The appreciable content of Cd associated with the mobile phases shows that its availability is susceptible to pH or ionic composition change in the environment. For that reason, there is much concern about the levels of Cd present in the soil, since it is a cumulative poison for mammals. Its main ways of entering the agricultural soil could be the application of manure and phosphate fertilizers since manure and fertilizer remains a primary source of nutrients added to agricultural soils. Previous studies indicate a relative case of uptake of Cd and Zn from soil [29, 30]. About 69.60% of total content associated with the extractable fraction. No exchangeable Pb was detected. The high percentage extractable fractions particularly associated with carbonate (40.93%) and oxidisable fractions (28.67%). The Pb showed high extractable fractions (69.60%) which may be a pollution indicator soils polluted by Pb to some extent. Pb mainly originated from traffic, since most of soil samples were collected from farm near highway. The other important contributions of Pb in soils are the parent geological materials from which soils are derived, smelters, coal combustion and the widespread use of lead petrol [31, 32]. Pb mainly enters soils by means of atmospheric dry and wet depositions and disposal of sewage sludge. As a consequence of Pb and materials containing Pb, substantially elevated levels of this element may be found in some local soils [32]. Zn in the soil samples is partitioned mainly in the extractable fraction; it is one of the most mobilized elements since it is mainly distributed among the non-residual fractions. It bound mainly to carbonate fraction. Cu associated mainly in the extractable fractions i.e (52.61%), the rest is distributed among the residual fraction with organic had about 39.30%. Cu was found to be high in the organic fraction; this explained its high association with organic matter. Above 60.00% of total Co, Mn and Ni content is associated with the non-extractable fractions (organic and residual). The rest of these elements is distributed among the extractable fractions, (exchangeable, carbonate and oxdisable). Co is probably present as CoS in the oxidisable fraction, but the highest percentage of Co (52.85) was found in organic fraction. Mn (51.38%) and Ni (50.66%) can be considered almost immobile because of elevated percentages of these elements are in the non-mobile fraction. These elements are strongly bounded to minerials and resistant components, and do not represent environmental risks. Mn in the soil samples is partitioned mainly in residual fraction.

pН	0. C	0. C	Sand(%)	Silt(%)	Clay(%)	C.E.C (meq/100g)
7.20 6.70	0.45 0.90	0.45 0.90	66.40 60.40	13.00 12.00	20.60 27.60	12.80 14.60
6.80	0.45	0.45	66.40	8.00	25.60	13.80
6.60	0.56	0.56	76.40	8.00	15.60	11.70
6.00	0.45	0.45	60.40	10.00	29.60	15.20
7.30	0.84	0.84	64.40	10.00	25.60	15.30
6.40	0.76	0.76	62.40	10.00	27.60	14.40
6.50	0.44	0.44	67.40	15.00	17.60	13.50
6.70	0.52	0.52	66.40	9.00	24.60	11.22
6.50	0.48	0.48	60.40	15.00	24.60	15.25
6.90	0.50	0.50	66.40	12.00	21.60	13.60
7.20	0.90	0.90	66.40	10.00	23.60	13.86
6.70	0.84	0.84	77.40	15.00	7.60	13.50
6.90	0.70	0.70	66.40	12.00	24.60	13.60

Table 1: Soil characteristics of Otukpo Agricultural farmland.

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pН	0. C	Sand (%)	Silt (%)	Clay (%)	C.E.C meq/100g
	7.30	0.78	70.40	15.00	14.60
	6.50	0.96	69.40	15.00	15.60
	6.50	0.72	76.40	13.00	10.60
	6.40	0.90	66.40	17.00	16.60
	6.50	0.50	73.40	13.00	13.60
	7.10	1.20	76.40	14.00	9.60
	7.30	1.30	62.40	15.00	22.60
	6.40	0.58	64.40	16.00	19.60
	6.00	0.64	69.40	20.00	10.60
	6.10	0.54	66.40	17.00	16.60
	7.20	0.72	76.40	13.00	10.60
	7.10	0.93	73.40	13.00	13.60
	6.90	0.85	69.40	20.00	10.60

 Table 2:Soil characteristics of Gboko Agricultural farmland

Table 3:Soil	characteristics	of Makurdi	Agricultural	farmland
			O	

		Sand	Silt	Clay	C. mE.C
pН	O.C	(%)	(%)	(%)	eq/100g
	7.20	0.66	76.40	15.00	8.60
	6.50	0.60	69.40	17.00	13.60
	6.10	0.82	70.40	13.00	16.60
	6.60	0.60	66.40	16.00	17.60
	6.40	0.92	73.40	17.00	9.60
	6.40	0.96	72.40	12.00	15.60
	6.50	1.30	64.40	15.00	20.60
	6.70	0.55	71.40	11.00	17.60
	7.10	0.60	67.40	10.00	22.60
	7.10	0.87	69.40	13.00	17.60
	7.20	0.66	76.40	12.00	11.60
	6.80	0.82	70.40	13.00	16.60
	7.10	0.87	69.40	13.00	17.60

				D	4		
				Paran	neters		
Town		pH	0. C	sand	silt	clay	C.E.C
						15.60-	
OTUKPO	Range	6.00-7.30	0.44-0.90	60.40-76.40	8.00-15.00	29.60	11.22-15.25
n=11	Mean	6.93	0.81	70107	12.33	18.6	13.65
	S.D	0.97	0.71	0.94	0.9	1.22	1.01
Gboko	Range	6.00-7.30	0.54-1.30	62.40-76.40	13.00-20.00	9.60-22.60	11.50-18.20
n=10	Mean	7.07	0.83	73.07	15.33	11.6	14.27
	S.D	0.94	0.97	0.95	1.01	1.29	1.07
Makurdi	Range	6.10-7.20	0.55-1.30	64.40-76.40	10.00-17.00	8.60-22.60	11.70-18.20
n=10	Mean	7.03	0.78	72.07	12.67	15.27	14.97
	S.D	0.95	1.01	0.97	1.1	1.05	0.99
All soil	Range	6.00-7.30	0.45-1.30	60.40-76.40	8.00-20.00	8.60-29.60	11.22-18,20
n=31	Mean	6.65	0.72	68.17	13.42	18.41	14.6
	S.D	0.38	0.24	4.7	2.92	5.68	2.04

Table 4: The ranges and mean of soil properties of Agricultural farmland in the study areas.

n=number of soil within the site

S.D= standard deviation

R= rainy season

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Sites	metals	exchangeable	Carbonate	fraction oxide	organic	residual
		F1	F2	F3	F4	F5
Otukpo	Cd	N.D	0.36	0.49	0.19	0.12
	Co	N.D	0.16	0.27	0.64	0.13
	Cu	0.50	4.73	3.35	5.30	1.42
	Mn	10.47	7.48	11.34	9.48	23.26
	Ni	1.58	1.72	1.69	5.64	0.87
	Pb	N.D	2.43	1.61	0.88	0.85
	Zn	1.75	8.66	4.31	3.41	2.49
Gboko	Cd	N.D	0.32	0.54	0.19	0.13
	Co	N.D	0.12	0.33	0.6	0.15
	Cu	0.65	4.95	3.73	7.26	1.13
	Mn	10.24	9.58	11.33	9.40	21.95
	Ni	2.92	2.71	2.53	5.31	0.89
	Pb	N.D	2.28	1.77	0.93	0.79
	Zn	1.98	6.94	4.35	3.30	3.59
Makurdi	Cd	N.D	0.31	0.55	0.16	0.11
	Co	N.D	0.14	0.35	0.65	0.11
	Cu	0.60	4.34	4.09	7.53	1.60
	Mn	9.50	9.70	11.47	9.51	22.68
	Ni	1.70	1.86	2.13	5.80	0.89
	Pb	N.D	2.40	1.61	0.86	0.98
	Zn	1.94	7.28	4.10	3.24	3.54

Table 6: Summary of the metals ($\mu g/g$) in soils fractions from Agricultural farmland

	lari	illianu			
Metal	s exchangeable	carbonate	fraction oxide	organic	Residual
	F1	F2	F3	F4	F5
Cd	N.D	0.33	0.53	0.18	0.12
Co	N.D	0.14	0.32	0.65	0.12
Cu	0.58	4.67	3.72	6.7	1.38
Mn	10.07	8.92	11.38	9.46	22.63
Ni	2.07	2.1	2.12	9.58	0.88
Pb	N.D	7.63	1.66	0.89	0.87
Zn	1.89		4.22	3.32	3.21

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area.								
Metals	exchangeable	carbonate	fraction oxide	organic	residual			
	F1	F2	F3	F4	F5			
Cd	N.D	28.45	45.69	15.52	10.34			
Co	N.D	11.38	26.02	52.85	9.76			
Cu	3.40	27.39	21.82	39.30	8.09			
Mn	16.12	14.28	18.22	15.15	36.32			
Ni	16.24	16.47	16.63	43.76	6.90			
Pb	N.D	40.93	28.67	15.37	15.03			
Zn	9.32	37.64	20.82	16.38	15.84			

Table 7: Percentage of metal associated with fractional forms in soils of Agricultural farmland in the study

Table 5.1: Correlation and Co-efficient of trace heavy metals with soil properties of cultuvated farmlands "during rainy season"

			uui	ing runny bee	ison .		
Town	metal	pН	O. C	Sand	Silt	Clay	C.E.C
Otukpo	Cd	-0.49	0.02	0.29	0.09	-0.27	0.31
	Со	-0.11	0.51*	0.46	-0.24	-0.08	-0.09
	Cu	-0.01	0.4	0.09	-0.04	-0.03	0.26
	Mn	-0.25	0.29	0.72*	-0.12	-0.37	0.67*
	Ni	0.03	0.26	0.34	-0.29	0.03	0.32
	Pb	0.21	0.16	-0.59*	-0.05	0.44	-0.39
	Zn	-0.02	-0.09	-0.06	-0.27	0.29	-0.42
Gboko	Cd	0.07	0.08	-0.06	-0.7*	0.56*	0.19
	Co	0.08	-0.38	-0.05	-0.22	0.19	0.27
	Cu	0.36	-0.24	-0.25	-0.556*	0.53*	-0.37
	Mn	0.07	-0.62	-0.55*	-0.50*	0.60*	-0.59*
	Ni	-0.14	-0.04	-0.34	0.54*	-0.29	-0.51*
	Pb	0.01	0.50*	-0.1	0.01	0.03	-0.14
	Zn	-0.42	0.26	0.12	0.06	-0.09	0.23
Makurdi	Cd	0.37	-0.38	-0.47	0.73*	-0.45	0.3
	Co	0.2	-0.37	-0.54*	0.55*	-0.09	-0.21
	Cu	-0.06	0.35	-0.36	0.38	-0.07	-0.50*
	Mn	-0.26	0.03	0.01	-0.39	0.60*	-0.29
	Ni	0.37	0.14	0.23	0.14	-0.56*	0.47
	Pb	-0.4	0.27	-0.14	-0.14	0.42	0.05
	Zn	-0.3	0.21	-0.13	-0.04	0.25	-0.80*

**indicates the significance value Correlation is significant at 0.05 level*

CONCLUSION

The study evaluate the metal distribution, retention, and release of all the Cd, Co, Cu, Mn, Ni, Pb, and Zn in selected agricultural farm of Benue State. The results obtain are a first approach to assess the environmental level of this metals in function of their availability to the ecosystem. Heavy metal speciation of selected soils samples from agricultural farmland indicated that the determined heavy metals are predominantly in the non-residual fractions there by, reflecting control by anthropogenic sources. The anthropogenic input of Cu was found mainly in the organic fraction or the associated with carbonate fraction. Zn and Pb appear to be primarily as carbonate, but both of these heavy metals were also associated with the oxide fraction. Hence, these results possibly indicate that anthropogenic heavy metals are easily mobile and potentially more phyto available than lithogenic and pedogenic heavy metals in agricultural soil.

A high mobile level of any metal may also be an indicator of which metal entered the soil recently; that is, this pattern may be relevant to anthropogenic pollution sources.

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