VERTICAL DISTRIBUTION OF CADMIUM IN SELECTED SOILS OF VARYING LITHOSEQUENCES IN A HUMID TROPICAL ENVIRONMENT

Nkwopara, U.N*., Iwuchukwu, E.E, Okoli, N.H. , Osisi, A. , Ihem, E.E., Onwudike, S.U
Department of Soil Science, Federal University of Technology, Owerri. P.M.B 1526, Imo State, Nigeria.
*Corresponding Author: ugoiken2003@yahoo.com

1.0 Abstract
The study investigated the occurrence of cadmium on soils derived from different parent materials (that is false bedded sandstone and Imo clay shale) in southeastern Nigeria. There were variations in soil properties of the two study sites. While false bedded sandstone (Mbiakpa Ibakesi) was moderately acidic (pH_{H20} = 5.6), Imo clay shale (Amuro) was slightly acidic (pH_{H20} = 6.2).Textural distribution coupled with carbon content influenced porosity of the study sites. The concentration of cadmium in both soils was below the critical value of 0.08 mg/kg. Cadmium does not pose any danger in both soils. Cadmium concentration was (0.011mg/kg) for false bedded sandstone and (0.004mg/kg) for Imo clay shale. A positive correlation (r = 0.54) was recorded between cadmium and pH for false bedded sandstone while a negative correlation (r= -0.30) was recorded for Imo clay shale. It was observed that cadmium tends to be unevenly distributed in both sites. However, cadmium concentration was higher in the second horizon in both sites.

Keywords: Pedon, distribution of Cadmium, Parent material, Tropical soil.

1.0 Introduction

Cadmium occurs naturally in soils as a result of the weathering of the parent rock (Alloway, 1995). Sedimentary rocks have the greatest range of cadmium concentrations with the highest values found in sedimentary phosphate deposits and black shales (Alloway, 1995). Although most natural soils contain less than 1 mg/kg cadmium from the weathering of parent materials, those developed on black shales and those associated with mineralised deposits can have much higher levels (Alloway, 1995). Anthropogenic sources of cadmium are much more significant than natural emissions and account for its ubiquitous presence in soil (Alloway, 1995; ECB, 2007; ATSDR, 2008). Cadmium is a trace element in phosphatic fertilizers, which have been applied extensively to arable and pasture land in the UK for decades (Alloway, 1995). ECB (2007) reported that current fertilizers contain around 79 mg of cadmium per kilogram of phosphorus. Based on the use of fertilizers in the 1980s and early 1990s, Alloway (1995) estimated that around 4.3 g of cadmium per hectare per year has been added to agricultural soils in the UK. Across the European Union, 231 tonnes of cadmium are added to agricultural soils each year from fertilizer use (ECB, 2007). Atmospheric deposition is also an important source of cadmium pollution (Alloway, 1995; ECB, 2007; ATSDR, 2008). The major sources of atmospheric emissions are non-ferrous metal production, fossil fuel combustion, waste incineration, and iron and steel production (Alloway, 1995).

Soils may become contaminated by the accumulation of heavy metals and metalloids through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition (Khan *et al*., 2008; Zhang *et al*., 2010). Heavy metals constitute an ill-defined group of inorganic chemical hazards, and those most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) (GWRTAC, 1997).

The objective of this study was to investigate the distribution of cadmium within pedons formed over false bedded sandstone and Imo clay shale

2.0 Materials and Methods

2.1 Study area

The study was conducted in two different locations namely Amuro (Okigwe LGA), which has Imo clay shale as its parent material located between latitude 5° 48'N and longitude 7° 20'E and Mbiakpa Ibakesi (Ini LGA) which has false bedded sandstone as its parent material located between latitude 5° 25' N and longitude 7° 44'E. The two study locations are in Imo State which lies between latitude 4° 40' N and longitude 6° 40'E and Akwa Ibom State which lies between latitude 5° 03' N and longitude 7° 93' E, both in Southern Nigeria (Federal Department of Agricultural Land Resources 1985). Imo state lies within the humid tropics. Temperatures are high and change slightly during the year (mean daily temperature about 27℃)(NIMET, 2014). The average annual rainfall is about 2400mm and there is a distinct dry season of about 3-month dryness. Imo State has rainforest vegetation characterized by multiple tree species (Onweremadu *et al*. 2007). Agriculture is a major socio-economic activity in the study area. Agricultural crops mostly cultivated in the study area include yam (*Dioscorea Spp*), cassava (*Manihot Spp*), oil palm (*Elaies guineensis*) and maize (*Zea mays*).

Akwa Ibom State also lies within the humid tropics with temperature of 27℃ to 31℃. Average annual rainfall is about 2500mm to 3000mm. Relative humidity of Akwa Ibom state is about 75% - 80% (NIMET, 2014).

2.2 Field study

Prior to field study, a reconnaissance visit was made at each of the study locations and sampling sites were selected using free survey sampling techniques. Two pedons were sunk, each representing soil formed over false bedded sandstone and Imo clay shale. Soil sampling was done based on the degree of horizon differentiation. A total of 10 soil samples were collected, air-dried, crushed, sieved through 2mm sized sieve and subjected to laboratory analysis.

The particle size analysis was determined using the hydrometer method (Gee and Bauder. 1986). 5% calgon (sodium hexametaphosphate) solution was used as dispersing agent. Gravimetric Moisture Content was determined by gravimetric method. This method involves weighing representative soil samples into moisture cans. Samples were oven dried and weight also obtained. Moisture calculated using formula

θ = Mw / M

:. Mc = Mw / Ms X 100 / 1

Where θ = gravimetric moisture content, Mt = total soil mass, Mw = mass of water, Ms = mass of solid particles.

Bulk density was taken in-situ using core samplers. The samples collected were oven dried after which bulk density calculated using the formula

$$\text{Bulk density } \{pB\} = \frac{\text{mass of dry soil}}{\text{Volume of soil core sampler}} = \frac{Ms}{Vt}$$

Bulk volume of soil = volume of cylinder = (πr^2h) Where r = radius, h = height of cylinder.

Soil pH was determined using a soil pH meter and this was done in both distilled water and 0.1 N KCl in a soil water ratio of 1:2:5. The pH of the resulting suspension was then read from a pH meter. Organic Carbon was determined by acid dichromate digestion and wet oxidation method (Walkley and Black. 1934). Organic matter was obtained from organic carbon by multiplying by 1.724. Total Nitrogen was determined by the regular Kjeldhal method (Bremner. 1965).Available Phosphorus was determined using Bray 2 method (Bray and Kurtz,1945).

Exchangeable bases (Ca, Mg, Na and K). Exchangeable Na and K were extracted using 1N NH4OAC and determined using flame photometer (Jackson, 1962). Exchangeable acidity was determined by extracting the soil with 0.1N KCl solution and titrating the aliquot of the extract with 1N NaOH (McClean,1965). Effective cation Exchange Capacity (CEC) was determined by the summation of exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and exchangeable acidity (H^+ and Al^{3+}). The summation of the exchangeable bases and acidity gave the effective cation exchange capacity (ECEC) value.

2.4. Heavy Metal Determination

Digestion of soil samples for cadmium concentration was carried out with mixture of concentrated HNO_3 and $HCl0_4$ at a ratio of 2:1. Cadmium was extracted using 0.5 MHCl (Lacatusu,2000). Cadmium concentration in the supernatant was determined using Atomic absorption spectrophotometer.

2.5 STATISTICAL ANALYSIS

Mean and correlation analysis were performed using SPSS computer software.

3.0 Results and Discussion

3.1. Soil properties

The result of the particle size distribution showed that for false bedded sandstone showed predominance of loamy sand and sandy clay loam, it ranges from 722.4-842.4 g/kg sand, 50.0-100.0 g/kg silt, and 77.6-217.6 g/kg clay. While Imo clay shale showed predominance of sandy loam, sandy clay and sandy clay loam, it ranges from 482.4- 702.4 g/kg sand, 155.2 -180.0g/kg silt, and 137.6 -361.6 g/kg clay (Table 1).The analytical result of these parent material shows that the soil has more of loamy sand for false bedded sandstone. The sandiness of the soil texture could attributed to the nature of the parent material. Thus, the slight difference among horizon could be the function of age that is the chronological state of the soil or the state of pedogenesis overtime. The mean values of the silt and clay for Imo clay shale were 164.2 and 273.4 g/kg. This may be due to transportation of the thiner particles by run-off. Also, this is a common trend in all humid tropics soils which are exposed to high rainfall. Akamigbo and Asadu (1983) reported that textural variabilities is as a result of diversities in the types and nature of the parent materials. The clay content and distribution in this unit increases with depth with the highest concentration occurring at horizon Bt2 and Bt3 of Imo clay shale. This may be as a result of illuviation of silicate clays in this horizon. Nkwopara et al., (2007) opined that the textures of south-eastern Nigeria are related to their parent material. Bulk density ranges from 1.43-1.71g/cm^3 with mean value of 1.55 g/cm^3 for false bedded sandstone, 0.67-0.77 g/cm^3 with mean value of 0.73 g/cm^3 for Imo clay shale. This result showed that there was slight increase in bulk density in false bedded sand stone; this could be attributed to the decrease in organic matter of the soil. The high bulk density is attributed to the high sand fraction of the parent materials which are as a result of high rainfall witnessed yearly and its consequent leaching problems. Generally in normal soil bulk density ranges from 1 – 1.60 g/cm3. Soil containing high organic matter shows lower value of bulk density. Textural variations influence the value of bulk density in soils. For example, clay. Clay loam and silt loam surface soil show low bulk density as compared to sands soils which show high bulk density value (Das, 2015).Porosity ranges from 35.5-46.1% and 70.9-74.1% for false bedded sandstone and Imo clay shale respectively. Porosity less than 50% is not desirable, so the low porosity of soil over false bedded sandstone is as a result of high bulk density of the soil. Bulk density is really a measure of pore space, the higher the bulk density for a given textural class, the smaller the amount of pore space present. High bulk density inhibit the emergence of seedlings. With bulk density 1.40 g/cm3 plants have higher concentration of anthocyanine and protein, and are low in sugar (Nagornny and Singh-Raghav , 2012). Soils containing high organic matter possess high porosity because of well aggregate formation. The decrease in porosity in false bedded sand stone may be due to reduction in organic matter content. With the increase in depth of soil, porosity will decrease because of compactness in the sub soil (Das, 2015).

The soil reaction (pH) in KCl gave mean values of 5.46 and 5.37 for false bedded sandstone and Imo clay shale. pH measured in 0.1N KCl was lower than pH measured in distilled water and pH ranges from 5.07-5.89 for false bedded sandstone and 5.17-5.89 for Imo clay shale. The soils were moderately acidic as a result of high rainfall and coarse textured soils that influences high rate of leaching which is a characteristic of humid tropics. This is in line with Brady *and Weil* (1999) who observed that acidic conditions are more conductive to reduction and solubility of heavy metals than alkaline conditions. The result of organic matter ranges from 0.64-2.64 for false bedded sandstone and 1.07-2.69 for Imo clay shale. This low organic matter content is as a result of loss by erosion and high temperature (Table 1).

3.2. Cadmium concentration

Table 2 shows the concentration of cadmium and its pattern of distribution within pedon. Cadmium was higher in false bedded sandstone (0.011 mg/kg) than in the Imo clay shale (0.004 mg/kg) The concentration of cadmium in both soils is less than the critical value as reported by Alloway et al., (1990) (Table 3). The concentration of cadmium poses no danger to the environment. Cadmium tends to be unevenly distributed in both sites. However, cadmium concentration was higher in the second horizon in both sites (Table 2).The low concentration of cadmium implies that the loads would be low. These results were consistent with the findings of Federal Environmental Protection Agency (1991), Aiyesanmi (2005) and Onweremadu et al., (2006) that concentrations of most heavy metals are generally below critical level to constitute agronomic and environmental hazards. But, critical levels of heavy metals vary geospatially. Critical values of Cadmium in a soil extracted by 0.1 m HCl corresponds to 0.5 - 1.0 mg/kg (Chen, 1991). This critical value suggests that soils of the study site are highly polluted, implying serious agronomic and environmental hazards. Crop growing on these soils absorb these metal. There was a significant relationship between the levels of cadmium and lead in roots or grain of rice and this varied with soil type (Chen, 1992). Government of Taiwan set critical levels of 10 mg/kg for Cd, 16 mg/kg for Cr, 100 mg/kg for Ni and 120 mg/kg for Pb (Onweremadu et al.,2006).

3.3. Relationship between soil properties and cadmium concentration

Relationship between Cd and some soil properties of different parent materials is shown in Table 4. The selected soil properties include bulk density, clay, pH and organic matter.

Bulk density was negatively and non- significantly correlated with cadmium (r= -0.64 ;- 0.46) for false bedded sandstone and Imo clay shale, respectively. This relationship implies that an increase in bulk density will decrease the concentration of cadmium in false bedded sandstone and Imo clay shale respectively. Clay was negatively and non-significant correlated with cadmium in false bedded sandstone and Imo clay shale (r= -0.33; r= -0.53) .This result implies that increase in clay will decrease the concentration of cadmium for false bedded sandstone and Imo clay shale. A simple correlation between cadmium and soil pH shows that a positive and non-significant correlation exist between soil pH and cadmium (r= 0.54) for false bedded sandstone and a negative and non-significant correlation between pH and cadmium (r= -0.30) for Imo clay shale. This relationship implies that as soil pH increases, the concentration of cadmium in false bedded sandstone increase and as soil pH decrease, the concentration of cadmium for Imo clay shale increases. Organic matter was positively and non-significantly correlated with cadmium (r= 0.49) for false bedded sandstone and positively and non-significantly correlated with cadmium (r=0.45) for Imo clay shale. This implies that as the organic matter increases, the concentration of cadmium increases for both soils.

Table 1: Soil properties of studied sites

Horizon	Origin of soils	Depth (cm)	Sand (gkg^{-1})	Silt (gkg^{-1})	Clay (g/kg^{-1})	Bulk density (mgm^{-3})	Total porosity (%)	pH(H_20)	Total carbon (gkg^{-1})
Ap	Falsebedded sandstone	0-20	842.4	80	77.6	1.45	45.30	6.01	15.3
AB		20-35	782.4	100	117.6	1.43	46.10	5.60	14.3
Bt1		35-69	842.4	60	97.6	1.57	40.80	5.61	13.7
Bt2		69-108	732.4	50	217.6	1.58	40.40	5.43	5.7
Bt3		108-192	722.4	60	217.6	1.71	35.50	5.41	3.7
		mean	784.4	70	145.6	1.55	41.62	5.61	10.5
		STDV	5.154	2	6.723	0.1132	4.28	0.241	0.54
		CV	6.57	28.57	40.17	7.3	10.28	4.39	51.33
	Imo clay shale								
Ap		0-15	702.4	160	137.6	0.67	74.1	6.50	16.0
A		15-25	622.4	180	177.6	0.70	73.6	6.60	13.2
Bt1		25-50	522.4	155.2	322.4	0.73	72.5	6.11	8.6
Bt2		50-69	482.4	156.0	361.6	0.77	70.9	6.05	6.4
Bt3		69-150	482.4	170	347.6	0.77	70.9	5.90	6.2
		mean	562.4	164.2	273.4	0.73	72.4	6.23	10.1
		STDV	9.70	1.06	9.98	0.04	1.487	0.30	0.44
		CV	17.23	6.45	36.50	6.05	2.10	4.85	43.12

STDV =standard deviation, CV = coefficient of variation

Table 2: Distribution of Cadmium (mg/kg) with depth of soil

Site	Origin of Soils	Depth (cm)	Cd
Mbiakpa Ibakesi	Falsebedded sandstone	0-20	0.004
		20-35	0.038
		35-69	0.007
		69-108	0.003
		108-192	0.001
		mean	0.011
		STDV	0.02
		CV	145.28
Amuro	Imo clay shale	0-15	0.003
		15-25	0.010
		25-50	0.002
		50-69	-
		69-150	0.001
		mean	0.004
		STDV	0.004
		CV	102.5

STDV =standard deviation, CV = coefficient of variation

Table 3: Critical limits of different types of heavy metals

Heavy metal	Critical limits of soil concentration (mg/kg)
Arsenic (As)	20-50
cadmium (Cd)	0.08
chromium(Cr)	75-100
colblt (Co)	25-50
lead (Pb)	100-400
manganese (Mn)	1500-3000
Mecury (Hg)	0.3-5
Nickel (Ni)	100
Selenium (SSe)	5 -10
Silver (Ag)	0-2
thallium (Ti)	1
yin (Yi)	50
Zinc (Zn)	70-100
copper (Co)	60-125

According to Alloway et al., 1990

Table 4: Correlation coefficient (r) between soil properties and cadmium (n = 5)

Site	Soil property	Cd
Mbiakpa Ibakesi	Soil pH	0.54^{NS}
	Bulk density	-0.64^{NS}
	Clay	-0.33^{NS}
	Organic carbon	0.49^{NS}
Amuro	Soil pH	-0.30^{NS}
	Bulk density	-0.46^{NS}
	Clay	-0.53^{NS}
	Organic carbon	0.45^{NS}

4.0 Conclusion

The study showed that the decreasing order of cadmium concentration in the different parent materials investigated is as follows: Imo clay shale (0.004) < false bedded sandstone (0.011). Cadmium concentration is mostly concentrated in the upper horizons and its concentration varies down the pit. Cadmium occurs in concentration considered below the critical level set by government. Cadmium correlated positively with pH and organic matter and negatively with bulk density and % clay in false bedded sandstone. While in Imo clay shale it correlated negatively with pH , % clay and bulk density and positively with organic matter. Cadmium concentration varies within and among soils of different parent materials as revealed by this research work. The study concluded that non significant relationship existed between cadmium and soil properties.

REFERENCES

Aiyesanmi, A.F. (2005). Assessment of heavy metal contamination of Robertkin oil field's soil. Nigerian journ. Of Soil Science, 15: 42 -46.

Alloway B. J, (1995). Heavy Metals in Soils.Blackie Academic & Professionals. New York. 386 pp.

Alloway B. J, Thornton I, Smart G. A, Sherlock J. C. and Quinn M. J, (1990) .Metal availability. Special issue: The Shipham Report – an investigation into cadmium contamination and its implications for human health. Science of the Total Environment, 75, 41-70.

Akamigbo, F.O.R and Asadu, C.L.A (1983). Influence of parent material on the soils of southeastern Nigeria. East Africa Agric. And For. Journal, 48:81 – 91.

ATSDR, (Agency for Toxic Substances and Disease Registry) (2008). Draft toxicological profile for cadmium. Atlanta: US Department of Health and Human Services, Available from: http://www.atsdr.cdc.gov/toxprofiles/tp5-p.pdf [Accessed June 2009].

Brady N. C, and, Weil R. R, (1999). The nature and properties of soils.12th ed. Prentice Hall.

Bray, R.H, and Kurtz, L.T, (1945). Determination of total organic and available forms of phosphorus in soils. Soil Sci. 59: 39 - 45

Bremner, J.M, (1965). Total nitrogen. In C.A Black (Ed). Methods of Soil Analysis. Agron Monogr 8. American Assoc. Agronomy Madison, WI, Part 2, Pp 1149 -1178.

Chen, Z.S, (1991). Cadmium and Lead contamination of soil near plastic stabilizing materials producing plants in Northern Taiwan. Water, Air and Soil Pollution, 57 -58: 745 -754.

Chen, Z.S, (1992). Metal contamination of flooded soils. Rice plants, and surface waters in Asia. In Adriano, D.C. (Ed) Biogeochemistry of trace elements. Lewis Publishers Inc. Florida, USA. Pp 85 – 107.

Das, K.D., (2015). Introductory Soil Science. 4th ed. Kalyani Publishers, New Delhi, India. 879 pp.

ECB, European Union Risk Assessment Report (2007).Cadmium oxide and cadmium metal, Part 1 – environment. Volume 72.EUR 22919EN. Luxembourg: Office for Official Publications of the European Communities. Available from:http://ecb.jrc.ec.europa.eu/documents/Existing-Chemicals/RISK_ASSESSMENT/REPORT/cdmetal_cdoxideENVreport302.pdf [Accessed June 2009].

Federal Department of Agricultural Land Resources. FDALR (1985). The reconnaissance soil survey of Imo state Nigeria (1: 250, 000) Soil Report 133 pp.

Federal Environmental Protection Agency, (1991) Guidelines and standard for industrial effluents, gaseous emissions and hazardous wastes management in Nigeria.

Gee, G.W and Bauder, J.W, (1986). Particle size analysis. In: Klute. A. (Ed.). Methods of soil analysis Part 1. Agronomy Monogr. No 9, ASA Madison, WI, Pp 91 -100.

GWRTAC, (1997). "Remediation of metals-contaminated soils and groundwater," Tech. Rep. TE-97 01,, GWRTAC, Pittsburgh, Pa, USA, 1997, GWRTAC-E Series.

Jackson, M.I., (1962). Soil Chemical Analysis. New York Prentice Hall Inc

Khan S, Cao Q, Zheng Y. M, Huang Y. Z, and Zhu Y. G, (2008). "Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China," EnvironmentalPollution, vol. 152, no. 3, pp. 686–692.

Lacatusu, R. {2000). Appraising levels of soil contamination and pollution with heavy metals. European Soil Bureau. Research Report No 4

Mclean, E.O, (1965) Aluminium, In: C.A Black et al (Eds) Method of Soil Analysis, Part 2. 1st ed, Amer. Soc. Of Agronomy Monogr. No 9 986-994.

Nagornny, V.D., and Singh-Raghav, J. (2012) Soil fertility management.Kalyani Publishers New Delhi, India. Pp214

NIMET (Nigerian Meteorological Agency), Nigeria, (2014). Climate Weather and Water Information, for sustainable development and safety.

Nkwopara, U.N., E.T, Eshett, E.U. Onweremadu, C.C Opara, and J.O. Omeke, (2007). Physico-chemical properties of selected soils overlying three parent materials in the humid tropics. International Journal of Agriculture and Food Systems, 1(2): 159-164.

Onweremadu, E, Nkwopara, U., Opara, E, Ihejirika, G, Onyia, V, and Ofoh, M, (2006). Vertical distribution of heavy metals in two soils in Isiukwuato, Abia State, Southeastern Nigeria. Journ. Of sustainable Tropical Agricultural Research 18:17 -21

Onweremadu, E.U., F.O.R. Akamigbo, and C.A. Igwe, 2007. Lithosequential variability and relationship between erodibility and sodium concentration in soils of a rainforest. Research Journal of Forestry, 1(2): 73- 79.

Walkley, A and Black, I.A. (1934). An examination of Degtjareff Method for determining Soil organic matter and the proposed Modification of the chromic and titration method. Soil Sci. 37: 29 – 37.

Zhang M. K, Liu Z. Y, and Wang H, (2010). "Use of single extraction methods to predict bioavailability of heavy metals in polluted soils to rice," Communications in Soil Science andPlant Analysis, vol. 41, no. 7, pp. 820–831.