

SPECIATION OF SELECTED TRACE METALS IN SOIL SAMPLES FROM DUMPSITES IN AKWANGA, NASARAWA STATE, NIGERIA

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Abstract

Speciation of lead (Pb), copper (Cu), Zinc (Zn), manganese (Mn), iron (Fe), cadmium (Cd), and chromium (Cr) were carried out on soil samples from dumpsites in Akwanga, Nasarawa State, Nigeria using Tessier, Capbell & Bisson (1997) method. The results for various fractions obtained from the Andaha road dumpsite are as follows; For samples taken from 0-5cm, the ranges of the fractions are 0.26 to 18.70%, 0.22 to 36.58%, 1.14 to 26.12%, 0.04 to 40.20%, and 0.25 to 9.85% while for the samples taken from 10-15cm, the ranges of the fractions are 0.12 to 11.86%, 0.22 to 16.78%, 0.49 to 22.14%, 0.02 to 31.30% and 0.15 to 7.81% for exchangeable, Fe- Mn oxide, organic, carbonate and residual fractions respectively. The results of the fractions obtained from Angwan Kpandon dumpsite are as follows; For samples taken from 0-5cm the ranges of the fractions are 0.15 to 5.25%, 1.68 to 6.18%, 2.20 to 18.30%, 0.05 to 32.30% and 0.80 to 27.50% while for samples taken from 10-15cm the ranges of the fractions are 0.23 to 3.40%, 0.60 to 2.50%, 1.50 to 12.27%, 6.30 to 21.52%, and 0.50 to 22.73% for exchangeable, Fe-Mn oxide, organic carbonate and residual fractions respectively. All the selected metals are available in both dumpsite which shows that dumpsite pollute the soil by releasing metals into it.

Keyword: Akwanga, Dumpsite, Speciation, soil samples, Trace Metals

In recent years, concerns over the possible health and ecological effects of accumulation of heavy metals contaminant in the soil and water have prompted numerous surveys (Tovide, Olawu, Moronkola & Ayejuyo, 2011). 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 (Amacher, 1996, Egila, Ibrahim & Mercy, 2013). One of the major challenges to human health and environmental quality is environmental pollution (Olajire, Ayodele, Oyediran & Oluyemi, 2003, Sakan, Dordevic & Manojlovic, 2010).

In particular there is very large set of health consequences due to exposure to soil contamination depending on pollutant type, pathway of attack and vulnerability of

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the exposed population. Lead is especially hazardous to young children and for whom there is a high risk of developmental damage to the brain, while to all population, kidney damage is a risk. Although many potential contaminants are required in trace amounts by plants for food production, they become hazardous when they occur in excess in the soil (Tokalioglu, Kartal & Birol, 2003).

Once there is an introduction of metals contaminants into the environment, it can exist in various chemical forms and the forms in which these metals exist in much more important as the degree of metals toxicity are closely related to their chemical form (Adekola, Inyibor & Abdul, 2012).

The occurrence of heavy metals in soil can be of geogenic in nature and anthropogenic origins. The anthropogenic sources include mining, smelting, fossil fuel combustion and various industrial activities.

Many researchers (Chandra, Kamala, Chary & Balaram, 2005, Chen, Zheng & Luo, 2005, Fayun, Zhipping, Pengferi, Kolapo, Xiping & Wei 2008, and Olajire et al, 2003) ascertained industrial activities to be the major source of soil heavy metals contamination.

Also heavy metals like iron, tin, copper, manganese and vanadium occur naturally in the environment and could serve as plant nutrient depending on their concentrations. Mercury, lead, cadmium, silver, chromium and many others that are indirectly distributed as a result of anthropogenic (human) activities could be very toxic at low concentration (Abeh, Gungshik & Adamu, 2007). Accumulation of trace metals especially heavy metals in the soil has a potential to restrict the soils function, cause toxicity to plants and contaminate food chain. In recent years it has also been found that heavy metals from point and non-point source impair water system causing lesions and deformation in fish (Henry, 2004).

The presence of toxic metals such as lead and cadmium in the environment has been a source of worry to environmentalists, government agencies and health practitioners. This is mainly due to their health implication since they are non-essential metals and of no benefit to humans (Marian and Ephraim, 2009).

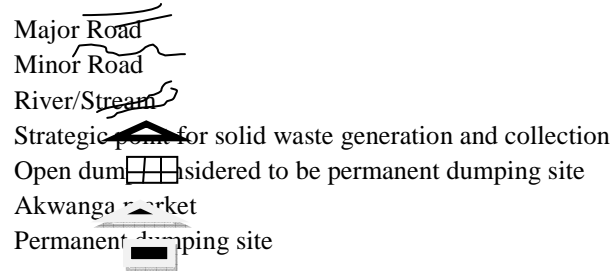
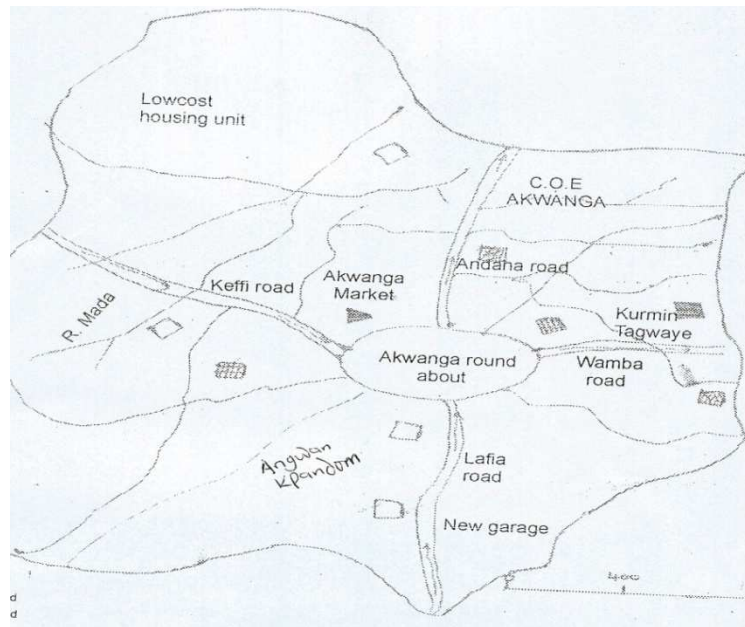
Pollution of the natural environment by heavy metals is a universal problem because these metals are indestructible and most of them have toxic effect in living organisms, when permissible concentration levels are exceeded (Mwolawa, Likuku & Gabonttoeloe, 2011). Apart from industrialization, the pollution of soil can also be from exhaust from heavy vehicles along the road. This has been proved by some researchers who found that the concentration of metals such as lead, copper, zinc and cadmium decreases rapidly within 10 to 50m from the roadside (Joshi Kumar, Bhagobaty & Thpkchon, 2010).

Material and Methods

Study Area: Akwanga is one of the Local Government Area of Nasarawa State as indicated in Fig.1. It lies between latitude 9°E of the Greenwich meridian and longitude

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8°N of the equator, at a distance some 115km from Abuja the federal Capital Territory. Nasarawa State is located centrally in the middle belt region and lies between latitude 7° 54' and 9° 25'N of equator and between longitude 7° and 9° 37'E of the Greenwich meridian. It shares boundary with Kaduna state in the north, Plateau state in the east, Taraba and Benue states in the south, while Kogi and Federal Capital Territory flank it in the west (Marcus and Binbol, 2007).



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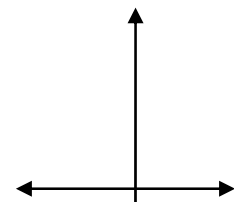


Fig. 1: Showing the Study Area



Fig. 2: Andaha Road Dumpsite

Sample Collection and Analysis

Soil samples were collected from the two dumpsite indicated in figure 2 using a plastic spoon at three different locations and mixed to form composite samples at the depth of 0-5cm and 10-15cm into polyethylene bags previously soaked in dilute nitric acid for 24hrs, rinsed with distilled water and dried. These were then transported to chemistry laboratory of College of Education, Akwanga and air dried for two weeks at room temperature and grounded with mortar and pestle. The grounded soil sample was sieved using 0.2mm sieve size and bottled in a polyethylene bottle for further treatment. Tessier, *et al* (1997) sequential method was used for extraction except for total metal and residual fraction which aqua regia was used (Maina, Egila&Shagai, 2012) to determine the fraction of the studied metals.

Determination of Total Metal

This was done using 1.00g each of the dried sieved soil sample from each of the dumpsite, digested with a mixture of 15 ml concentrated hydrochloric acid and 25ml trioxonitrate (v) acid for 2hrs at 100⁰C. The mixture was filtered and made up to 50ml volume and analyzed with AAS model 7000 series east and west analytical instrument

Sequential Extraction

1. **Exchangeable fraction;** A 1.00g triplicate dried sieved soil sample from each dumpsite was shaken with 20ml of 1m $MgCl_2$ at pH 7 for 1hr filtered and analyzed.
2. **Carbonate fraction;** The residue of the soil sample from fraction 1 was shaken with 20ml CH_3COONa at room temperature for 5hrs at pH 5, then filtered and analyzed.
3. **Fe-Mn oxide/Reducible fraction.** The residue of soil sample from fraction 2 was digested with a mixture of 10ml 0.04M $NH_2OH.HCl$ and 10ml of 25% CH_3COOH at 96^oC for 6hrs, then filtered and analyzed.
4. **Organic fraction.** The residue of the soil sample from fraction 3 was transferred into 250ml beaker and 9ml of 0.02 M HNO_3 and 15ml of 30% H_2O_2 were added, the mixture was heated for 5hrs at 85^oC on a water bath after 2hrs of heating another 15ml of 30% H_2O_2 was added. This was then filtered and analyzed.
5. **Residual Fraction;** The residue from the soil sample of fraction 4 was digested with aqua regia (7.5ml of 37% HCl and 2.5ml of HNO_3) at 85^oC for 1hr and then filtered and analyzed.

Result and Discussion

Table 1.0 The Result of Total Metal Concentration is Shown Below in $mgkg^{-1}$

Sample	Pb	Cu	Zn	Fe	Mn	Cd	Cr
Dumpsite A	1.270±	0.031±	0.910±	0.690±	0.060±	0.210±	0.330±
Dumpsite B	0.03	0.01	0.03	0.03	0.01	0.01	0.01
Dumpsite A	0.610±	0.174±	3.810±	0.280±	0.280±	ND	0.360±
Dumpsite B	0.01	0.01	0.03	0.01	0.01		0.01

Note: Dumpsite A: Andaha road dumpsite

Dumpsite B: Angwangkpondon dumpsite

ND: not detected.

Dumpsite A which is the Andaha road dumpsite has a higher value of lead (Pb). This can be attributed to exhaust from vehicle since the dumpsite is located by the roadside which is in agreement with other researchers (Godwin, O. etal, 2012). Cadmium (Cd) was not detected in AngwanKpondon dumpsite probably because the concentration is below the detection limit of the instrument.

Table 2a. Concentration (mgkg⁻¹) of Sequential Fraction of Metals in Dumpsite A

Fraction	Depth	Pb	Cu	Zn	Fe	Mn	Cd	Cr
Exchangeable	0-5cm	2.560± 0.05	0.09± 0.01	1.430± 0.03	0.022± 0.01	0.230± 0.02	0.015± 0.001	0.350± 0.12
	10-15cm	2.160±0.20	0.080± 0.01	1.150± 0.01	0.041± 0.01	0.200± 0.01	ND	ND
Fe-Mn Oxide	0-5cm	2.901±0.20	0.530± 0.02	2.320± 0.01	3.230± 0.03	3.560± 0.40	0.010± 0.01	0.120± 0.002
	0-5cm	0.98± 0.30 2.828±0.60	0.240± 0.01 0.280±	2.100± 0.30 2.630±	2.300± 0.02 3.720±	1.531± 0.45 0.650±	0.007± 0.001 0.020±	ND 0.220± 0.03
Organic	10-15cm	1.1388± 0.37	0.190± 0.01	2.300± 0.20	3.2101± 0.03	0.541± 0.20	0.010± 0.01	0.210± 0.01
Carbonate	0-5cm	1.46±0.50	0.420± 0.03	0.520± 0.02	0.004± 0.001	0.220± 0.03	1.170± 0.02	0.320± 0.03
Residual	10-15cm	0.715±0.20	0.260± 0.02	0.330± 0.02	0.002± 0.001	0.920± 0.02	1.030± 0.02	ND
	0-5a cm	0.01±0.20	0.047± 0.02	0.031± 0.01	0.035± 0.01	0.580± 0.30	0.156± 0.02	0.210± 0.01
	10-15cm	0.004±0.02	ND	0.020± 0.01	0.030± 0.01	0.370± 0.10	0.054± 0.03	0.20± 0.01

ND: Not detected**Table 2b: Percent (%) of Metal Sequential Fraction of Dumpsite A**

Fraction	Depth	Pb	Cu	Zn	Fe	Mn	Cd	Cr
Exchangeable	0-5cm	13.34	1.81	7.66	0.26	0.94	0.27	18.70
	10-15cm	11.86	2.38	7.03	0.12	1.25	ND	ND
Fe-Mn oxide	0-5cm	14.32	22.02	15.54	22.30	36.58	0.22	3.60
	10-15cm	5.57	9.71	14.75	16.68	16.78	0.20	ND
Organic	0-5cm	14.22	9.15	17.51	26.12	5.30	1.14	17.16
	10-15cm	6.06	7.12	16.25	22.14	4.03	0.49	9.10
Carbonate	0-5cm	6.61	15.72	1.19	0.04	2.47	40.20	14.20
	10-15cm	4.12	9.34	1.62	0.02	1.07	31.30	ND
Residual	0-5cm	0.48	2.20	0.29	0.25	6.28	7.40	9.85
	10-15cm	1.05	ND	0.15	0.28	3.18	3.25	7.81

ND: Not detected

Table 3a: Concentration (MgKg⁻¹) of Sequential Fraction of Metal in Dumpsite B

Fraction	Depth	Pb	Cu	Zn	Fe	Mn	Cd	Cr
Exchangeable	0-5cm	2.91± 0.05	0.13± 0.04	9.40± 0.10	0.10± 0.03	1.02± 0.01	0.63± 0.01	0.45± 0.02
	10-15cm	0.36± 0.01	0.10± 0.03	6.15± 0.04	ND	0.19± 0.02	0.32 0.02	0.45 0.02
Fe-Mn oxide	0-5cm	3.06± 0.02	1.02± 0.01	3.60± 0.20	2.79± 0.02	1.71± 0.03	0.47± 0.01	1.12± 0.20
	10-15cm	ND	1.10± 0.01	1.30± 0.10	0.85± 0.04	0.17± 0.01	ND	0.99± 0.30
Organic Fraction	0-5cm	2.60± 0.03	0.74± 0.02	29.32± 0.30	2.7± 0.20	4.43± 0.04	0.02± 0.02	0.18± 0.02
	10-15cm	ND	0.43± 0.05	21.70± 0.10	3.11± 0.03	3.07± 0.10	0.20± 0.01	0.25± 0.04
Carbonate Fraction	0-5cm	20.90± 0.01	10.45± 0.60	27.10± 0.30	0.03± 0.01	5.17± 0.02	0.92± 0.03	1.77± 0.03
	10-15cm	17.13± 0.02	8.63± 0.10	22.67± 0.03	ND	3.03± 0.30	0.30± 0.03	1.64± 0.10
Residual Fraction	0-5cm	6.06± 0.30	0.29± 0.05	1.95± 0.04	14.38± 0.10	3.32± 0.30	0.02± 0.10	0.93± 0.20
	10-15cm	3.00± 0.50	ND	1.89± 0.04	10.28± 0.13	2.26± 0.20	0.05± 0.01	0.63± 0.10

ND: Not detected

Table 3b: Percent (%) of Trace Metal Sequential Fraction of Dumpsite B

Fraction	Depth	Pb	Cu	Zn	Fe	Mn
Exchangeable	0-5cm	3.35	0.30	5.25	0.15	2.80
	10-15cm	1.10	0.23	3.40	ND	0.62
Fe-Mn oxide	0-5cm	4.15	4.40	1.68	6.18	5.30
	10-15cm	ND	2.50	1.77	1.18	0.6
Organic	0-5cm	3.19	2.20	18.30	8.30	15.80
	10-15cm	ND	1.50	12.27	6.40	7.30
Carbonate	0-5cm	26.70	32.30	15.83	0.05	15.20
	10-15cm	21.52	25.50	13.15	ND	6.30
Residual	0-5cm	8.68	1.30	0.80	27.50	8.32
	10-15cm	3.20	ND	0.50	22.73.	3.65

ND: Not detected

Speciation

The five sequential extraction methods (Tessier *et al* 1997) was used for chemical fraction (Speciation) of the selected trace metal in the two dumpsites soil

samples from Akwanga, Nasarawa State and the results are shown in table 2 to 3 which is the values and their percentages in table 2a and 3b.

One of the common trends discovered in this work that the concentration of the various metals decreases as the depth of the soil increase. This phenomenon was observed earlier by some researchers (Adekolaetal, 2012, Fagbote and Olanipekun 2010).

Exchangeable (Mg Cl₂ extractable)

From Table 2 the result of exchangeable fraction from Andaha dumpsite has a higher value of lead (2.86mgkg⁻¹), this agreed with work of other researchers (Godwin,Olapeju and Emmanuel, 2012). This concentration is also associated to the presence of dumpsite along the road which other workers reported that the concentration of metals such as Pb, Cu, Zn, and Fe increases due to exhaust from motor vehicles. The increase concentration of these Andaha road dumpsite are in order Pb>Zn>Mn>Cu>Cr>Fe>Cd. As the depth increases cadmium and chromium were not detected from table 3.

The AngwanKpandon dumpsite has the highest value of Zinc (10.50mgkg⁻¹) followed by lead (3.21mgkg⁻¹). From these result it is obvious that shallow rooted crops can easily pick up some of these metals and accumulate in these crops since their root is mostly at the surface of the soil.

Fe-Mn oxide (0.04MNH₂OH.HCL+25% CH₃COOH)

Andaha road dumpsite showed the higher value of Mn (4.134mgkg⁻¹) and Iron (3.570mgkg⁻¹), this agreed with the work of (Uba, Uzairu, Hanson &Balarabe, 2010), who attributed higher values to the precipitation of Amorphous hydrous oxides of manganese during the aging of dumpsites (Stealens,Passpian,Polprassert, 2013) for AngwanKpandon dumpsite the order is Zn>Pb>Fe>Mn>Cu>Cr>Cd which is also in agreement with the work of others (Fagbote and Olanipekun, 2013) who also discovered Zinc to be higher in the Fe-Mn oxide fraction.

Organic Fraction (H₂O₂+HNO₃ extractable)

Andaha road dumpsite showed the highest value of extractable metal to be Iron (4.101mgkg⁻¹) followed by lead and Zinc (3.128mgkg⁻¹ and 2.940mgkg⁻¹) while AngwanAkpandon dumpsite has the highest value to be Zinc (33.30mgkg⁻¹). The order is Zn>Mn>Fe>Pb>Cu>Cr>Cd. Other workers such as Fagbote and Olanipekun (2010) obtained higher levels of manganese and zinc associated with this fraction.

Carbonate Fraction (1M CH₃COONa+CH₃COOH extractable)

Andaha road dumpsite has the order of the availability of these metals as Pb>Cd>Zn>Cu>Cr>Mn>Fe and for AngwanKpandon dumpsite the order is Zn>Pb>Cu>Cr>Cd>Fe. Cadmium and Iron have a very low values in this fraction, this agreed with the work of Abdul-Salam, Ibrahim & Fatoyinbo (2014) which showed only relatively lower amount of Iron in this fraction.

Residual Fraction (Aqua Regia extractable)

For Andaha road dumpsite, majority of the trace elements are found in this fraction and in the order of Mn>Pb>Cd>Cr>Cu>Fe. For the AngwanKpandon dumpsite has the highest value of Iron (15.07mgkg⁻¹) others available along with Iron in the order Fe>Pb>Mn>Zn>Cr>Cu>Cd. Other workers such as (Effiong and Gilbert, 2012) also reported higher value of Iron and bioavailability of all other metals in this fraction. Wufem, Ibrahim, Gim, Mohammed, Ekanem and Shibdawa, (2012) also reported similar trend in the residual fraction and Iron having one of the highest content.

Conclusion

The concentration of these selected metal varied with the dumpsite. The primary objective of this study was to determine the chemical availability of metal in these soils from the dumpsites in Akwanga, Nasarawa State. The total metal concentration of Pb, Cu, Zn, Mn, Fe, Cd and Cr were determined and are all available in Andaha and AngwanKpandon dumpsites with the exception of cadmium which was not detected in AngwanKpandon dumpsite.

Five successive selective chemical fractions were used in the analysis to determine metals easily exchangeable, associated with Fe-Mn oxide, organic matter, carbonate from and residual fractions. In both dumpsites studied, the residual showed availability of all the selected metals (Pb, Cu, Zn, Fe, Mn, Cr and Cd). It was also shown that these dumpsites contaminate soil and their concentration decrease with increasing depth down that soil.

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