Research Paper

Comparison of Digestion Methods for the Determination of Metal Levels in Soils in Itakpe, Kogi State, Nigeria

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Abstract: *The analysis of agricultural soil of Itakpe, Kogi State, Nigeria to ascertain levels of concentration of total metal content of cadmium, copper, magnesium, nickel, lead and zinc and comparison of digestion methods, using % extractability was carried out by use of atomic absorption spectroscopy technique. The digestion methods used were HNO_3, HCl and different combinations of acids ($HClO_4$, HCl, HNO_3 and HF). Results show that the concentration values obtained were as follows: Cd ranged 0.17-0.36, Cu ranged 0.08-1.09, Mg ranged 0.04-0.13, Ni ranged 0.04-0.12, Pb ranged 0.05-0.42 and Zn 0.04-0.11 µg/g. The most efficient digestion methods are the combination of HNO_3 and HCl (1:3) (aquaregia) and HCl. The combination of HNO_3, $HClO_4$ and HF (3:2:1) is most efficient for Cd extraction; HNO_3, combination of HNO_3, $HClO_4$ and HF (3:2:1), HCl and combination of $HClO_4$ and HF (1:5) were most efficient for Cu extraction; HNO_3 and HCl were most efficient for Mg extraction; combination of $HClO_4$ and HF (1:5) were most efficient for Ni; combination of HNO_3, $HClO_4$ and HF (3:2:1), combination of HNO_3 and HCl (1:3), HCl and combination of $HClO_4$ and HF (1:5) were most efficient for Pb and most efficient for Zn combination of HNO_3, $HClO_4$ and HF (3:2:1), combination of HNO_3 and HCl (1:3), and combination of $HClO_4$ and HF (1:5). The possible reasons for variation in % extractability of some metals are given.*

Keywords: Acid digestion, % Extractability, Metal, Soil, Total metal content.

Introduction

Industrial revolution has resulted in soil pollution by toxic materials. Of the greatest concern are the contaminants that are due to the pollution of metals which are reported to cause many types of diseases, such as cancer, nervous diseases, and various diseases affecting different organs of the body. (Guveni and Akinci, 2011, Wilson et al., 2005) Some metals such as Cu, Fe, Ni and Zn are however

essential elements needed for the healthy growth of plants, animals and soil microbes. (Hlavay et al., 2004, Nogales et al., 1995).

Metals are found naturally throughout the earth, in rocks, soils and sediments trapped in stable form. Toxic anthropogenic imputes results in contamination of the soil. The chemical behavior of these contaminants are controlled by soil composition, soil properties such as pH and a number of processes, such as metal cation release from contamination source, cation exchange and specific adsorption onto surfaces of minerals, etc. (Guveni and Akinci, 2011, Hlavay et al., 2004) Their impact depends on the total metal concentrations in soil, speciation, mobility, and bioavailability. (Kaasalainen and Yli-Halla, 2003, Roundhill et al., 2009, Száková et al., 2010).

Several methods have been used by different researchers in the digestion of soil samples for the determination of metallic levels. Such methods have been through the use of fluxes or inorganic acids such as HCl, H_3PO_4, HNO_3, $HClO_4$, HF, H_2SO_4 or their combination. These acids (extractants) exhibit various peculiar properties which enables each acid to carry out specific functions during extraction. (Tam and Yao, 1999, Alam and Tokunaga 2006, Kislik, 2002) The choice of extractants depends on the aim of the study, type of contaminants, properties of the extractant, experimental conditions, need to readily release extracted metal and need for minimum interference from contaminants. (Kaasalainen and Yli-Halla, 2003, Roundhill et al. 2009, Guveni and Akinci, 2011, Wilson et al., 2005, Twyman, 2005) Improper selection of extractants could cause effects such as partial dissolution of soil sample resulting in decreased metal content levels in soil samples. (Hlavay et al., 2004, Twyman, 2005).

Extractants may be acidic or basic depending on their mode of action which depends on interacting mechanisms, such as the metal ion-extractant affinity, metal ion concentration, extraction temperature and acidity of the medium. (Tam and Yao, 1999, Nogales et al. 1995, Száková et al., 2010) The extent ions of extractant show affinity for metals depends on the concentration of the metal in soil and inter-metal interference in heterogeneous contaminated soils during extraction. (Tam and Yao, 1999, Nogales et al. 1995, Száková et al., 2010, Willett and Zarcinas, 1986) Extractants are soil specific. For example H_2SO_4 does not digest samples containing Ba, HCl does not digest samples containing Ag and Pb, As compounds forms volatile compounds with HCl and H_2SO_4 does not analyze some metals simultaneously especially alkaline earth metals because of the possibility of forming insoluble sulphate salts. (Twyman, 2005, Nogales et al. 1995) Their specificity can be improved by combining a series of acids during extraction. (Guveni and Akinci, 2011, Kislik, 2002, Wilson et al., 2005, Tam and Yao, 1999, Száková et al., 2010) Mixtures of HCl, HNO_3, $HClO_4$ and HF dissolve most metals in soils and this is reported to analyses with great accuracy multi-elements. (Twyman, 2005) Report is given on the use of aquaregia in the dissolution of sulfides, phosphates, and many metals and alloys including Au, Pt and Pd. (Tam and Yao, 1999) The use of use of acids in sequence has been reported to give good results. (Argon Lab Systems, 2007) The use of HNO_3 and $HClO_4$ acids premixed in a 3:1 ratio, followed by the addition of HCl and the addition of HF has been used with high extraction yield. (Twyman, 2005) Extractants have the ability of changing species of metals during extraction. Report is given of the oxidation of As (III) to As (V) during extraction of As from As contaminated soil. (Alam and Tokunaga 2006).

Levels of metals in soil have become a global concern and this has resulted in researches into methods of assessments. The aim of the present studies is to analyze and ascertains the concentration of total metal content in agricultural soil of Itakpe, Kogi State, Nigeria. The objective is to compare the various digestion methods, using % extractability to determine the best method of extracting metals from soils by use of atomic absorption spectroscopy (AAS) technique. Metals of interest are Cd, Cu, Mg, Ni, Pb, and Zn.

Materials and Methods

150 soil samples were collected during the dry and rainy season (January and July, 2010) (figure1) in nylon bags with the use of a stainless steel knife to a depth of about 15 cm, and at about 50 m interval. The collected samples were air–dried for seventy-two hours, ground in an aggregate mortar, sieved to < 0.005 mm fraction and homogenized before each weighing.

1.00 g of < 0.005 mm, air-dried soil samples were digested with 20ml each of HCl, HNO_3 and a mixture of $HClO_4$ and HF (1:5), HNO_3, $HClO_4$ and HF (3:2:1), HNO_3 and HCl (1:3) to near dryness. Each residue was dissolved in concentrated HCl and diluted to 25 ml. (Hlavay et al., 2004, Guveni and Akinci, 2011, Wilson et al. 2005, Száková et al., 2010, Willett, 1986).

The resulting solution was filtered into a plastic bottle ready for AAS. A certified reference sample, Soil Reference Material 989, Wageningen was digested for the quality assurance of analytical data using the different extractants and their mixtures.

Each extraction was carried out in three replicates. All reagents used were analytical grade (BDH, Poole, England) and were used without further purification. All glassware were washed with detergent, rinsed with distilled water, soaked in 10% HNO_3 for 24 hours and rinsed. Atomic Absorption Spectrophotometer (AAS) model 210VGP, Buck Scientific Incorporated USA was used for the determination of Metals.

Results

Precision for the determination of metals in soil ranged 8-12 % for the studied metals Cd, Cu, Mg, Ni, Pb and Zn and analysis of soil Reference Material 989 from Netherland gave Cu 144.5±11.6, Pb 253.8±13.8 and Zn 1110.9±39.4 µg/g against the standard values of 153±3.9, 282±3.6 and 1020±30 µg/g for Cu, Pb and Zn respectively. Results on Table 1 shows the mean and SEM values of total metal in soil, Table 2 the mean and SEM values of total metal in Reference soil sample, Table 3 the percentage extractability of Cd, Cu, Mg, Ni, Pb and Zn by different extractants. Total metals in soil were generally low (Table 1) and Cd levels ranged 0.17-0.36, Cu 0.08-1.09, Mg 0.04-0.13, Ni 0.04-0.12, Pb 0.05-0.42 and Zn 0.04-0.11 µg/g.

% Extractability of the studied metals by different extractant; the use of HNO3 gave a range of 82.83-111.68, the use of HNO_3/$HClO_4$/HF (3:2:1) gave a range of 66.46-136.25, the use of HNO_3/HCl(1:3) gave a range of 89.61-118.61, the use of HCl gave a range of 90.16-124.45, and the use of $HClO_4$/HF (1:5) gave a range of 67.92-135.28.

The % extractability (Table 3) of Cd, Cu, Mg, Ni, Pb and Zn were within 100 % except for a few which exceeded; Cd and Zn metallic levels for all the extractants, Ni metallic level for HNO_3/$HClO_4$/HF (3:2:1) and $HClO_4$/HF (1:5) extractant). For Mg the use of HNO_3/$HClO_4$/HF (3:2:1) and $HClO_4$/HF (1:5) gave low percentage of extractability (66.46 % and 67.92 % respectively). The result shows that HCl and aquaregia gave the best % extractability. Combination of HNO_3, $HClO_4$ and HF (3:2:1) was observed to be more efficient for Cd extraction; HNO_3, combination of HNO_3, $HClO_4$ and HF (3:2:1), HCl and combination of $HClO_4$ and HF (1:5) was more efficient for Cu extraction; HNO_3 and HCl were more efficient for Mg extraction; combination of $HClO_4$ and HF (1:5) were more efficient for Ni; combination of HNO_3, $HClO_4$ and HF (3:2:1), combination of HNO_3 and HCl (3:1), HCl and combination of $HClO_4$ and HF (1:5) were more efficient for Pb and more efficient for Zn combination of HNO_3, $HClO_4$ and HF (3:2:1), aquaregia, and combination of $HClO_4$ and HF (1:5).

Discussion

Previous studies have used different acids for metal extraction from soils with different results. According to Wilson et al. (2005) aquaregia produced the most accurate, efficient and reproducible

results while other researchers with same acid mixture also reported high % extractibility; Berrow and Stein (1983) reported 80 % of the total Cr, Cu, Pb and Mn from sewage sludges and sludge-treated soil, Abreu et al (1996) reported 90 % for Fe, Mn, Zn, Cu, Pb and Cd from soil and Kaasalainen and Yli-Halla (2003) reported 95 % of total Cu, Ni, and Zn, about 80 % of total Cd and about 60 % of total Cr and Pb in soils. Reports of the use of HNO_3 acid has also been given with low to high % extractability; Willett and Zarcinas (1986) reported the extraction of Cu, Cd, Zn, Fe, Mn and Pb in soils with 82-94%, Száková et al. extracted Cd ranging between 25-100 % and Pb between 35-80% of the total Cd and Pb in soil, Willett and Zarcinas (1986)extracted Cu, Cd, Zn, Fe, Mn and Pb in soils with 82-94 % extractibility. The use of H_3PO_4 with good % extractibility has also been reported; Alam and Tokunaga (2006) reported As(III) from soil contaminated with As(III) 99 % and Zhang et al (2010) reported Zn 79.71 %, Pb 99.1 %, Cd 87.15 %, Ni 70.57 %, Cr 78.01 %, and Cu 60.91% from soil contaminated with Zn, Pb, Cd, Ni, Cr and Cu.

% extractability in this study was within similar ranges as previous studies. The extractants had no specific pattern for the % extractability observed. The variations in % extractability observed could be due to reports that some extractants have more affinity for some contaminant metals than others due to the soft nature of such metal ions, the type, size and the geometry of the extractant ions and due to inter-metal interference in heterogeneous contaminated soils during extraction. Such reports have been given by previous researches. (Roundhill, 2009, Nogales et al. 19995, Kislik, 2002, Guveni and Akinci, 2011).

Other reasons for variation in % extractability observed in this studies could be as a result of the mineralogy of soils, soil properties, possible imputing of metals from other sources, continual deposition of heavy metal on soil surface from various sources through atmospheric transportation, sampling, sample preparation methods and soil texture which could vary on a micro scale of about 1 to 100 mm altering metal solubility and extractability concentrations. (Hlavay et al., 2004, Száková, 2010, Twyman, 2005, Kislik, 2002) Pb for example binds to soil particles and has high affinity for organic matter in soil making it less soluble in extractants. (Száková, et al, 2010) Seasonal variability and agricultural practices (fertilizing, liming, sludge application etc) could affect properties such as pH and organic matter contents of soil resulting in changes in metal solubility causing mobile metal fraction to either increase or decrease resulting in variation in the extractable metal contents in the soil. (Hlavay et al., 2004).

Soil samples can contain mixtures of organic and inorganic substances with interstitial water and water of crystallization embedded, or some adsorbed water which can affect dissolution and thus metallic levels.(Twyman, 2005) Homogenization of soil samples from different horizons could result in pH and carbonate content changes of the soil sample thereby affecting the extraction of the soil samples. (Hlavay et al., 2004) Soil sample drying method could affect % extractability. Soil sample drying has been reported to cause alterations of soil functional groups, affect organic matter content, increase extractable Mn, Fe, Cu, and Zn, and reduction in extractable Ca, Cu, Zn, Mg, and probably Co, Ni, and V. (Száková, 2010, Hlavay et al., 2004) Freeze drying is reported to result in immobilization of metals in soil and wet soils can affect microbial action causing shift of metals from oxidizing to reducing condition affecting extraction of metals. (Száková, 2010) For example the use of oxalic acid for the extraction of Cu gave result which is twice the level of the control due to the drying procedure which caused binding of the metal to organic matter. (Hlavay et al., 2004).

Sample storage, non-homogenization after sieving and nitrification could enhance the effects of air-drying and grinding through breakdown of soil micro aggregates which leads to continual mobility of metals, resulting in the exposure of fresh surfaces and cause readsorption or desorption of metals during extraction. (Hlavay et al., 2004) The destabilization of metals from their stable equilibrium and transformation of metals taking place can affect dissolution of metals. (Száková, 2010, Hlavay et al., 2004) According to Száková et al (2010) findings the differences reported in the metallic level of Cd and Pb in soil was as a result of prolonged storage of samples.

Metallic levels depend on % extractability. Thus the metallic levels observed (Table 2) are as a result of the factors affecting % extractability.

Conclusion

The results show that HCl and aquaregia gave the best % extractability. Metals with the highest concentration levels in soil did not correlate with the metals with the highest % extractability. Further studies are needed on the environmental mineralogy of soils, environmental chemistry and mineralogy of the particulate air matter. This could help to explain some of the metal concentrations levels observed.

Tables and Figures

Table 1: Mean and SEM values of Total Metal in Soil (μg/g)

	HNO$_3$	HNO$_3$/HClO$_4$/HF (3:2:1)	HNO$_3$/HCl (1:3)	HCl	HClO$_4$/HF (2:10)
Cd	0.36±0.01	0.24±0.03	0.18±0.01	0.22±0.01	0.17±0.01
Cu	0.40±0.01	1.09±0.05	0.44±0.01	0.53±0.04	0.08±0.004
Mg	0.08±0.02	0.12±0.004	0.13±0.02	0.09±0.001	0.04±0.002
Ni	0.12±0.01	0.12±0.004	0.13±0.02	0.09±0.001	0.04±0.002
Pb	0.08±0.002	0.42±0.10	0.25±0.002	0.32±0.14	0.05±0.004
Zn	0.10±0.001	0.05±0.03	0.11±0.01	0.07±0.001	0.04±0.01

SEM= Standard Error of Mean

Table 2: Mean and SEM values of Total Metal in Reference Soil sample (μg/g)

	HNO$_3$	HNO$_3$/HClO$_4$/HF (3:2:1)	HNO$_3$/HCl (3:1)	HCl	HClO$_4$/HF (1:5)
Cd	9.18±0.53	11.20±0.09	9.75±0.21	10.23±0.04	11.12±0.34
Cu	144.10±7.21	147.22±7.50	132.55±2.75	148.13±1.75	144.53±6.67
Mg	8526.08±354.80	6645.80±213.08	7495.88±106.02	8438.58±66.20	6792.25±660.11
Ni	48.73±3.59	61.15±1.06	52.72±0.22	53.50±0.59	73.10±5.21
Pb	233.58±17.10	254.28±7.27	252.27±2.61	255.58±4.37	253.82±7.94
Zn	1062.95±56.59	1118.95±63.09	1121.05±54.76	1068.55±14.80	1110.90±22.74

Table 3: % Extractability of Cd, Cu, Mg, Ni, Pb and Zn by different extractant

Extractant/Metal	Cd	Cu	Mg	Ni	Pb	Zn
HNO$_3$	111.68	94.18	91.09	90.41	82.83	104.21
HNO$_3$/HClO$_4$/HF	136.25	96.22		113.45	90.17	

(3:2:1)			66.46		109.79
HNO$_3$/HCl(1:3)					
(Aquaregia)	118.61	86.63	93.60	97.81	89.61	109.90
HCl	124.45	96.82	90.16	99.26	90.63	104.76
HClO$_4$/HF (2:10)	135.28	94.46	67.92	135.62	90.00	109.91
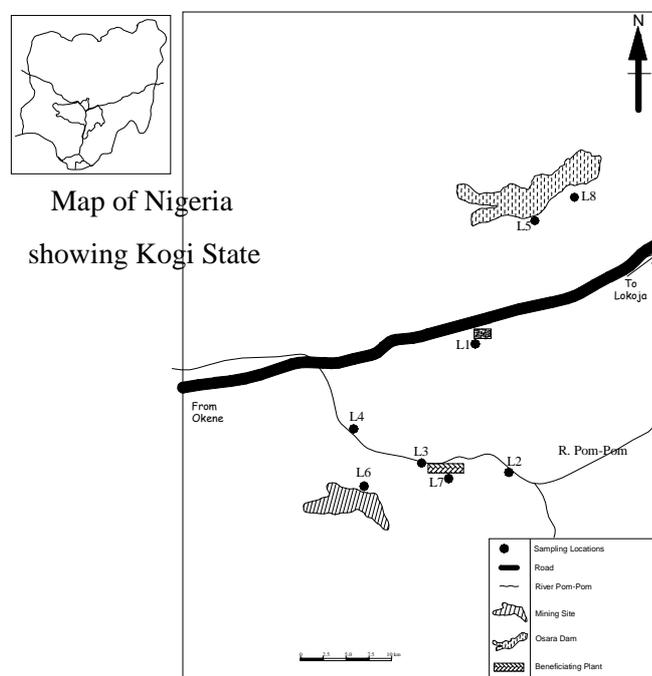
Figure 1: Map of Itakpe showing

the Locations for Sample Collection

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