Soil Environ. 40(2): 119-126, 2021
DOI:10.25252/SE/2021/222716
Online ISSN: 2075-1141
Print ISSN: 2074-9546

Assessment of potentially toxic metals and their mineral species in soils of arable farmlands in the southeastern Niger Delta basin, Nigeria

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[Received:** September 10, 2021   **Accepted:** October 15, 2021   **Published Online:** December 4, 2021**]

Abstract

Soils and sediments have the capacity to accumulate metals, and this is usually controlled by their certain properties. The concentration levels of these metals may pose a threat to the ecosystem through the food chain. This research documents concentration levels of selected potentially toxic metals and their available chemical species in arable soils within parts of the Niger Delta basin in Nigeria. The metals of interest included Cu, Pb, Zn, Ni, Co, As, Cr, Cd, Mn and V. The metal concentrations assessed were those contained in clay sized fractions of the soils which constituted 13% of total soil fractions. Cation exchange capacity (CEC) mean value indicated most metals to be bound to sesquioxides rather than soil humus. Pearson's correlation analysis indicated that Cr and Cu concentrations are significantly controlled by organic contents and pH of the soils. The metals were within average crustal concentration levels, except Pb and Cd which revealed mean value concentrations above average soil and continental rocks. Metallic pollution assessments of the soils by calculations of enrichment factors and geo-accumulation indices indicated the metals to be generally of low enrichment, with slightly-moderately polluted classifications respectively. Some metals exhibited high enrichment in some samples. The concentrations of metals were determined to be related to the underlying geology of soil formation within the Niger Delta basin. Anthropogenic influences on soil chemistry were considered minimal. Geochemical modelling of extractable metal concentrations indicated that most metals occur dominantly as free mobile ions, oxides, hydroxides and other aqueous species and these were readily bio-available in the environment.

Keywords: Metals; soils; pollution; metal species; Niger delta; Nigeria

Introduction

The concern over contamination of the natural environment by potentially toxic metals has been of interest for environmental research in recent times. The immediate concerns are usually concentration levels of these metals in rocks, soils, sediments, water and air. Also, the nature of release, transport and sorption of these metals in the environment has been assessed in most research. Some of the research has revealed total element contents in environmental media without an assay of the mode of occurrence (chemical species, mineral phases and associations) of the metals. Knowledge of the mode of occurrence of these metals is important as some may occur in forms that pose little or no hazard to the environment, while others may exist in deleterious forms. The contributions of these metals in environmental hazard may largely be related to their mode of occurrence and the series of physical and chemical processes operational in such environments.

Soils and sediments have the capacity to accumulate trace or heavy metals based on their sorption properties controlled by texture, organic matter, mineralogy, water content and other physico-chemical parameters (Pajak *et al*., 2016; Kuźniar *et al*., 2018). Soil organic matter and clay minerals are the main components of soil that possess significant sorption capacity relative to metals, through exchange sorption, complexing, or chelation (Lasota *et al*., 2020). The examination of the mode of occurrence of the metals involves knowledge of chemical, physical and mineralogical variables of the media (soils or sediments) with an attempt to interpret the possible interrelationships. These interpretations are usually defined by geochemical principles. Important also is the chemical extraction of these

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Cite This Ppaper: Ekwere, A.S., E.A. Kudamnya1 and W.E. Osung. 2021. Assessment of potentially toxic metals and their mineral species in soils of arable farmlands in the southeastern Niger Delta basin, Nigeria. *Soil Environ*. 40(2): 119-126.

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metals from sampled media, as the chemical extractants determine the availability and concentrations of the elements of interest.

The Niger Delta basin lies on the fringe of the Gulf of Guinea in southern Nigeria, representing a significant concentration of soils and sediments with varying metal geochemistry. This is presumed so, as the soils and sediments are derived from the disintegration and draining of various rock types (predominantly sandstones, shales, limestone, granites, gneisses and other rock varieties), agricultural landscapes, urban and semi-urban settlements within the region. These metals are presumed to exist as chemical species or fractions that exhibit different bioavailability with varying potential risk to humans (Ekwere *et al*., 2013; Ekwere, 2019).

Previous studies within the study area have involved measurements of concentration levels of selected metals in soils and sediments, estimation of interrelationship between the detected metals and other parameters and a diagnosis of their possible sources; (Azmathullah and Ekwere, 1989; Elueze *et al*., 2009; Ekwere and Elueze, 2012; Ekwere *et al.*, 2013; Ekwere *et al*., 2014; Ekwere, 2019).

This current research attempts to document concentration levels of selected metals in soils from arable farmlands devoid of significant anthropogenic influences; establish their distribution relative to organic contents and physicochemical factors as well as to determine the metallic species and their possible cycling in soils.

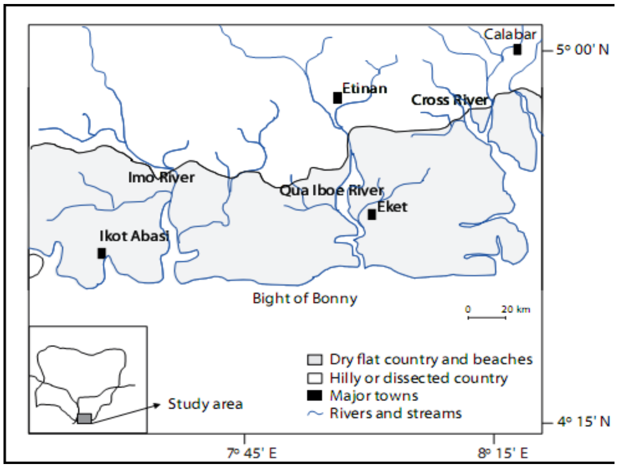

Figure 1: Map of the study area

Materials and Methods

The study area

The southeastern Niger Delta is here described as the expanse of the coastal plain physiographic provinces from Ikot-Abasi to Calabar area of south-eastern Nigeria. The area spans over 250km in length, with a width of about 65km, delimited by longitudes 7º 30 – 8º 15 E and latitudes 4º 30 - 4º 40 N (Figure 1).

Geologically the study area is composed of Tertiary and Quaternary sediments referred to as Coastal Plain Sands of the broader Niger Delta basin (Short and Stauble, 1967). The soils and sediments from the study area represent a link between fresh bedrocks, weathered profiles and soils that envelopes the landscape of the lower Niger Delta basin.

The geologic formation consists of alternating sequences of gravel, sand, silt, clay and alluvium with varying thicknesses across the basin. Soils are derivatives from three major geologic units on the hinterlands;

(1) The Precambrian Oban Massif Complex built on migmatites-gneisses, granites, schists, para-schists, pegmatites and a host of other ultra-mafic rock suites (Ekwueme, 2003).

(2) Cretaceous sedimentary fill known as the Calabar Flank, composed of limestone, sandstone, shale and marl (Reijers, 1996).

(3) The lower Benue Trough (Anambra Basin) of post-Cretaceous sediments with lodes of sulphide deposits (Zaborsky, 1998).

Another source of sediments into the study area is the Cross River Delta (Rio Del Rey Basin); Reijers (1996), Elueze *et al*., (2009) and Ekwere *et al*., (2013).

Three major rivers (Imo, Qua-Iboe and Cross River) drain the geologic units of the hinterlands with numerous distributaries.

Based on geomorphology, the area lies within the flat and low-lying terrain of the coastal region of southern Nigeria with elevations ranging from less than 10m on the coastal fringe to about 80m northwards.

The study area receives an average rainfall of about 254mm annually within two distinct seasons: dry and wet. Mean annual air temperature and relative humidity are 26.8ºC and 84.6%, respectively (Edet and Worden, 2009).

Sample collection and laboratory analysis

A total of 106 soil samples were collected from arable farmlands across the basin at a depth of 0-30cm from surface. The soils in the study area belong to the ultisol class of soil, characteristic of old landscape settings (i.e., lateritic). The surface horizons are rich in mor humus type, clay mineral groups and metal oxides with reddish coloration. The soil samples were collected from areas within the basin with minimal human influences. The samples were air dried, disaggregated and separated by an automated sieve shaker into various fractions of grain sizes. Soil pH was measured from slurries of the soil samples. Organic content percentages were estimated from loss on ignition (LOI) by oven drying method. This involved weighing 2.0 g of soil into a silica crucible with a lid and placing it into the oven at temperature of 600˚c for five hours. The samples were then removed, cooled in desiccators and reweighed and percentage loss in weight was documented as LOI.

The clay sized fraction of soils (<63µm) was packaged for metal concentration analysis. The choice of clay size fraction was to minimize possible variations in metal concentrations due to variations in grain size. 0.5 g of the clay fraction was subjected to multiple digestions and extraction routine with mild and strong extractants: ethylenediaminetetraacetic acid (EDTA) and HCl/HNO_3. These extractants were selected because they represent a broad range of kinds of chemical attack that govern availability of elements in soils or sediments to plants (McNeal *et al.*, 1985). The digested samples were then heated on a hot plate to a volume of 2.5 mL. 10 mL of deionised water was added and gently boiled to a volume of 5 mL. The resulting solution was left to cool and then filtered into 50ml measuring cylinder and deionised water was added to up to 25 mL. Metals were then measured from the aliquots by inductively coupled plasma mass spectroscopy (ICP-MS).

Results and Discussion

Physical properties of soils

Percentages of grain size distributions are presented in table 1. Results show that sand fraction of soils ranged from 72.76 – 92.10% with an average of 77.78%. Silt fraction ranged from 2.54 – 12.52% with an average of 9.46%. The clay fraction ranged from 4.30 – 19.72% with an average of 12.59%. The soils recorded a mean bulk density of 1.12 and average pore space of 58%.

Table 1: Statistical summary of physical-chemical parameters of soils

n =206	pH	LOI (%)	Sand (%)	Silt (%)	Clay (%)	BD	APS (%)	EA (cmol kg^{-1})	BS (%)	CEC (cmol kg^{-1})
Mean	5.2	7.48	77.78	9.46	12.6	1.12	58	1.80	54.2	3.28
Range	4.2-5.8	0.0-12.8	72.8-92.1	2.5-12.5	4.3-19.7	0.84-1.86	43-64	0.48-2.92	31-97	1.53–5.14
Av. Shale [a]			45	20	95	68	19	13	90	0.3
Av. Con. Val. [b]			25	20	71	20	10	1.5	35	0.1
Av. Soil [c]			26	29	60	34	12			

BD – bulk density; APS – average pore space; EA – exchange acidity; BS – base saturation; CEC – cation exchange capacity

[a] Turekean and Wedepohl, 1961; [b] McLennan and Taylor, 1999; [c] Ure and Berrow, 1982.

Table 2: Statistical summary of metal concentration levels in comparison with other soils/sediments around the world

n =206	Cu	Pb	Zn	Ni	Co	As	Cr	Cd	Mn	V
Mean[†]	10.6	33.71	49.8	10.84	7.79	1.80	35.04	1.71	156.7	54.49
Range[†]	2.5-37	4.1–130	9–60.8	2.22–27	1.0–42.9	0.1–4.2	0.1–236	1.0–3.20	9.0–470	8.0–160
Av. Shale [a]	45	20	95	68	19	13	90	0.3	900	
Av. Con. Val. [b]	25	20	71	20	10	1.5	35	0.1	600	60
Av. Soil [c]	26	29	60	34	12				760	

[a] Turekean and Wedepohl, 1961; [b] McLennan and Taylor, 1999; [c] Ure and Berrow, 1982; [d] Martin and Meybeck, 1979; [†]present study.

The soils showed pH to range from 4.2 – 5.8, indicating the soils to be acidic in nature. Exchange acidity ranged from 0.48 – 2.92 cmol kg^{-1}. Organic content of soils ranged from 0.7 – 12.8% with a mean of 7.48%. Base saturation ranged from 31 – 97% with a mean of 54.2%; while cation exchange capacity (CEC) of particulates ranged from 1.53 – 5.14 cmol kg^{-1} with a mean of 3.28 cmol kg^{-1}.

It is believed that extractable metal concentrations in particulate fractions of soils are controlled mainly by organic content, CEC and base saturation (which is the percentage of CEC occupied by exchangeable bases e.g. Ca, Mg, K, Na).

Based on mean values of the CEC which are within the 2 - 4 cmol kg^{-1} range (Tan, 1982), it is expected that most of

Table 3: Correlation coefficients of analysed metals

	pH	LOI	Cu	Pb	Zn	Ni	Co	Mn	As	V	Cr	Cd
pH	1											
LOI	**0.67**	1										
Cu	**0.32**	**0.53**	1									
Pb	**-0.52**	**0.42**	**0.40**	1								
Zn	0.13	0.04	0.14	**0.49**	1							
Ni	-0.03	0.25	**0.48**	**0.42**	**0.46**	1						
Co	**0.34**	**-0.36**	**0.67**	-0.14	**0.30**	**0.49**	1					
Mn	-0.32	-0.15	-0.05	**-0.40**	**0.70**	**0.48**	-0.02	1				
As	-0.10	-0.03	**0.65**	**0.31**	-0.05	**0.35**	**0.53**	-0.22	1			
V	-0.12	-0.06	**0.59**	-0.10	0.25	**0.40**	**0.44**	**0.67**	**0.82**	1		
Cr	**-0.51**	**0.57**	0.22	-0.23	0.18	0.21	-0.13	**0.42**	0.22	**0.59**	1	
Cd	**0.52**	**0.43**	-0.00	**-0.31**	0.05	**0.48**	0.25	-0.23	0.24	0.20	-0.29	1

the metals would be bound preferably with Fe-Mn oxides than in humus.

Metal distribution trends

Statistical summary of trace element contents in the soils are presented in table 2. Averages and ranges of measured metals are less than concentrations described from conterminous areas of similar geology. The concentration ranges are also a lot narrower than as reported from conterminous areas. The so described conterminous soils and sediments reflect estimate values of elemental concentrations with little or no alterations in their natural conditions (Pyrch *et al*, 1995). The comparison only gives a guide to background signatures and possible anthropogenic impacts, while more detailed interpretive deductions are obtained by principal component analyses.

Concentration levels in the soils indicate an enrichment of Pb and Cd in the order of 2.1 and 8.5, respectively, compared to concentration levels of average soils and continental rocks (Ure and Berrow, 1982; McLennan and Taylor, 1999). Concentrations of Zn, Ni, Mn, Cu and Co are below these reference levels though ranges for Cu and Co exceed the crustal averages in some samples.

Cu recorded an average concentration of 10.6ppm with a range of 2.5 – 37 mg kg^{-1}. Pb had a mean of 33.71 mg kg^{-1} with a range of 4.1 – 129.9 mg kg^{-1}. The other metals analyzed had average and ranges respectively as; Zn (49.80) (9.0 – 60.8), Mn (156.7) (9.0 – 470), Ni (10.84) (2.22 – 27), Cr (35.04) (0.10 - 236), Co (7.79) (1.0 – 42.9), As (1.8) (0.1 – 4.2), V (57.49) (8.0 – 160), Cd (1.71) (1.0 – 3.2) with all values in mg kg^{-1}.

Pb, Cd, Co, Cr and V show concentration ranges higher than average shale compositions though mean values for Co and Cr are lower. The high concentration of Pb is basically due to the ubiquitous nature of the element (Merian, 1991). High concentrations of Pb and Cd could be related to metallic sulphide deposits of the lower Benue Trough (Ekwere *et al*, 2013; Ekwere, 2019) as well as minimal anthropogenic sourcing within the region. Noticeable major human activities that may lead to trace metal contamination in soils and sediments include automobile repair and service workshops, urban dumpsites and other communal waste disposal practices.

Increased concentrations of Co and Cr can be attributable to ultra-mafic rocks, hornblende gneisses and gabbros (Coker, 1995) and these are common rocks in the Oban Massif and Mamfe Embayment (Ekwere *et al*, 2012). These two geologic suites are major catchments of sediments into the basin. Also, high concentrations of vanadium (V) above average shale composition could be related to sodic plagioclase, Fe-Mg silicates and Fe-Ti-V-Mn oxides which are characteristic of meta-volcanic rocks (Coker, 1995) and these rocks are also common within the catchment geology of the basin.

Geo-statistical evaluation

Correlation analysis was carried out for the measured data set to establish interrelationships between parameters and are presented in table 3, with significant coefficients in bold. Strong relations were considered for correlation coefficients > 0.6, moderate ≥ 0.3 - ≤ 0.6 and weak < 0.4.

Results of correlation analysis show strong positive correlations for Zn-Mn (0.70); As-V (0.82), Mn-V (0.67), Cu with Co and As with coefficients of 0.67 and 0.65 respectively, and pH-LOI (0.67). Moderate positive correlations exist between; Pb-Cu, Cu-Ni-V, Pb-Zn-Ni-Co-Mn-V, V-Cr. Organic content correlates positively with some metals; LOI-Cu (0.53), LOI-Pb (0.42), LOI-Cd (0.43), LOI-Cr (0.57) and LOI-Co (0.36).

The strong positive correlation between organic content (LOI) and pH indicates a mutual inclusivity of both parameters in data variation. Organic content (LOI) and pH show positive moderate correlation with Cr, while Cd indicates a positive moderate coefficient with pH. The weak and insignificant correlation between most of the metals with LOI and pH, suggests both parameters have little or no control on metal accumulation in soils of the study area.

There exists a moderate correlation between Pb and Zn and other metal sets, however the well-established and expected geochemical association between As, Pb, Zn and Cu (Levinson, 1974) wasn't noticeable for the four metals. The subtle or no correlation of Pb with other metals as expected in rock associations suggests the high contents in soils maybe anthropogenic. Also, the large size of the study area, receiving sediments from different sources with varying metal contents maybe possible influence too.

However, the relationship of metals from correlation analysis indicates soils to be reflective of the underlying geology of the basin's catchment; a mix of sediments from basement and imprints of sulphide lode deposits (Elueze *et al*., 2009; Ekwere and Elueze, 2012 and Ekwere *et al*., 2013). An assessment of the correlation of these metals in smaller areas of their localized sourcing would probably show a more intrinsic association.

Metal pollution assessment

Possible metallic pollution of soils in the study area was carried out. This involved using two assessment modules: enrichment factor (EF) and geo-accumulation index (I_{geo}).

Enrichment factor

The metal enrichment factors were calculated with metallic concentrations and concentration of aluminium (Al) using equation (1) according to Calvert and Pederson, (1993) and equation (2) Manjunatha *et al.* (2000).

$$EF = Metal/Al_{(sample)} \div Metal/Al_{(average\ shale)} \ldots (1)$$

The average shale composition (Wedepohl, 1971) was adopted as background values.

Table 4: Statistical summary of enrichment factor of metals in sediments

	Cu	Pb	Zn	Ni	Co	Mn	As	V	Cr	Cd
Mean	6.40	11.20	7.80	1.70	1.80	3.80	1.50	1.20	1.80	2.60
Max	26.00	40.40	50.80	3.50	10.40	9.40	4.30	1.80	2.33	8.20
Min	1.70	2.20	1.20	0.80	1.40	1.10	0.60	0.50	0.60	0.80

Table 5: Geo-accumulation Index classification

Item	Pollution level						
	Unpolluted	Slight	Moderate	Moderate – Strong	Strong	Strong – Very strong	Very Strong
I_{geo}	≤ 0	> 0 to ≤ 1	> 1 to ≤ 2	> 2 to ≤ 3	> 3 to ≤ 4	> 4 to ≤ 5	> 5
I_{geo} class	0	1	2	3	4	5	6
Metals		Cu, Zn, Ni, Co, Mn, As, V, Cr	Pb and Cd				

The enrichment factor was also calculated using equation (2) according to Sutherland (2000).

$$EF_M = (M_{sample} / Fe_{sample}) \div (M_{ref} / Fe_{ref}) \ldots (2)$$

where M_{sample} = concentration of considered metal M in sample, Fe_{sample} = Fe concentration in sample, while M_{ref} and Fe_{ref} represent background values of metal M and Fe, respectively.

A comparison of mean variances of results from the two approaches of calculation was assessed using T-test. At 95% confidence levels the value was 0.018, indicating no significance of variance of enrichment factor deduction from both calculations.

The enrichment factors of metals in the sediments are summarized in table 4. With respect to mean values, most of the elements are of low enrichment. Maximum EF values of Cd, Mn, Cr, Ni, As, Co and V are within the minimal to significant enrichment. Cu, Pb and Zn have values in some sediment within the very high enrichment category with up to 2-fold for Pb and Zn. This high enrichment may be from anthropogenic sources within the catchment. However, metal contents may be masked by high influx of sediments into the basin, and this has been shown by Pardue *et al.* (1988).

Geo-accumulation index

Geo-accumulation index was also used as a measure to quantify possible metal contamination in the analysed sediments. This has been widely used for deduction of metal pollution in different environments (Muller, 1979; Salomons and Förstner, 1984; Bhosale and Sahu, 1991; Manjunatha *et al*., 2001 and Adamu *et al*., 2015).

The geo-accumulation index is calculated by the mathematical expression:

$I_{geo} = log_2 (A_n / B_n \times 1.5$ ..... (3)

Where A_n is the average measured concentration of the metal of interest *n* in the sediment;

B_n is the background value i.e., average shale composition of metal *n* from Wedepohl (1971); and 1.5 is the correction factor for possible variations in the background data due to lithological effects (Taylor, 1964).

The I_{geo} may be classified into seven grades as presented in table 5. Average crustal value (McLennan and Taylor, 1999) provided background values for vanadium (V) as this was not reported in the average shale composition of Wedepohl, (1971).

From calculations, Cu, Zn, Ni, Co, Mn, As, V and Cr indicates geo-accumulation indices that classify the metals as constituting slight pollution in the soils. Pb and Cd I_{geo} values classify the soils to be moderately polluted with these metals.

Metallic speciation

Metals in sediments and soils are usually present in a number of distinct chemical forms. The speciation of these metals defines their distribution among the chemical forms and their speciation ultimately determines metal transport, retention, bioavailability and consequently their impacts on the environment. Geochemical speciation modelling of readily extractable phases of metals from the soils was carried out using the visual MINTEQ modelling program.

Results of geochemical modelling showed that all the metals and their species were under-saturated, with saturation index (SI) less than zero.

Dominant copper (Cu) species which accounted for about 82.7% of total concentration, were free mobile ions ($Cu_{(aq)}$), copper hydroxide ($Cu(OH)_2$), hydrated copper-arsenate $(Cu_3AsO_4)_2.2H_2O$ and tenorite . Lead (Pb) species were dominantly free $Pb_{(aq)}$ ions, $Pb(OH)_2$, $Pb_3(AsO_4)_2$, $PbO.3H_2O$, litharge and massicot accounting for about 93% of extractable concentrations. Cu and Pb concentrations in the sediments are basically bound to the water soluble and organic matter fractions with an average of 51.2% and 49.1% of total extractable contents, respectively. The affinity of Cu and Pb to be bound in the organic fraction of sediments and soils has also been reported by Thuy *et al.* (2000); Zeine and Brummer (1989).

Zinc (Zn) is bound in multiple hydrated phases, zincite, hydroxide (ZnOH), hydrated arsenate $(Zn3(As_2O_4)_2.5H_2O$ accounting for about 79% of total soluble concentration. Nickel (Ni) exists as aqueous Ni ions, $NiAsO_4$ and NiOH making up 89% of total species concentrations. Cobalt has $Co_{(aq)}$, $CoAsO_4^{3-}$ and CoO with 94% of total speciation concentration. Mn occurs as $Mn_3(AsO_4)_2.8H_2O$, Mn $_{(aq)}$ ions and pyrochroite accounting for 96% of total Mn species concentrations. Arsenic (As) has H_3AsO_4, H_2AsO_4 and $HAsO_4^{2-}$ as major species with 83% dominance. Vanadium is of dominantly (98%) free mobile V ions and VOH. Chromium (Cr) had $Cr_{(aq)}$, CrOH making 89% of the metal species, while cadmium (Cd) existed as free mobile Cd ions.

Generally, it was observed that Zn, Ni, Co, As, V, Cr and Cd show lower concentrations in the water soluble or organic matter fraction and exhibits levels below detection in some samples. These metals are believed to be more bound to the crystalline Fe-Mn oxides (sesquioxides).

Manganese (Mn) is also dominantly bound to the Fe-oxide crystalline fraction though water soluble fractions are present up to 18.6% of total extracted concentration.

The analysed metals, their species and complexes can be described as toxic and relatively accessible (Manjunatha *et al.*, 2001). These elements also serve as catalyst involving electron transfer in several biochemical reactions.

The metals and their species are believed to be from geogenic processes controlled by geologic and hydrogeologic features. These may include, but not limited to, mineral weathering (mainly silicates) and ion exchange reactions.

Conclusions

Interpretation of data shows that soils within the lower Niger Delta are dominantly sandy with clay fraction making up an average of about 13% of bulk soil grain size distribution. The soils are generally acidic with an average organic content of 1.48% having minimal influence on metal accumulations. Cation Exchange Capacity (CEC) indicates that most of the analysed metals are bound with Fe-Mn oxides.

Pb, Cd, Co, Cr and V show ranges of concentrations higher than average shale compositions. Metal concentrations and distributions indicate that the metal contents are related to the underlying geology of the soil development and transport within the basin. The metals represent basically inputs from a wide range of rock weathering (Precambrian basement, meta-volcanics, meta-sediments and metallic lodes deposits) with minimal localized anthropogenic influences.

The analysed metals generally exhibit low enrichment, and the soils are classed as slightly-moderately polluted by geo-accumulation indices. However, some samples are highly polluted with certain metals.

Geochemical modelling of extractable metal contents reveals most metals to occur as free mobile ions, oxides, hydroxides and other aqueous complexes which are potentially toxic and relatively bioavailable.

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