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The reactivity of soil organic fractions towards Cadmium, Calcium, Copper and Zinc

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ABSTRACT

In this project, the physico-chemical characteristics and metal binding for various soil types from a mining area were investigated. Humic substances were extracted from the soil samples using various standard procedures. The physical properties viz: pH, conductivity, particle size distribution, total nitrogen, organic matter, moisture content and exchangeable acidity were determined on the undigested soil samples and potassium, phosphorus, iron, calcium, cadmium, lead and zinc were determined after acid digestion. The mine tailings exhibited some characteristics similar to samples from Bibiani forest (cocoa plantation) e.g.: Organic Matter (New Tailings – 0.83 ± 0.05 %; Old Tailings - 0.53 ± 0.01 %; Cocoa Plantation – 1.93 ± 0.04 %); and Carbon-Nitrogen ratio (New Tailings – 12 ± 0.16 %; Old Tailings - 10.30 ± 0.35 %; Cocoa Plantation - 11.20 ± 0.12 %) were similar. The amount of humic acids extracted ranged from 0.09 ± 0.03 mg/L to 0.49 ± 0.01 mg/L, whilst the concentration of orange fulvic acid ranged from 0.11 ± 0.02 mg/L to 0.15 ± 0.09 mg/L. A study of complexation of humic acids by trace metals (Cd, Zn, Ca, and Cu) revealed that metal-humic substances association depends on the metal, the nature of the humic substance and concentration. Calcium was complexed to a higher extent than copper, followed by cadmium and zinc. Complexation of Old Tailings humic substances was stronger than that of Russel Pit humic substances. The relationship between stability constants and pH was discussed in this paper.

Keywords: Fulvic acid, Humic substances, Complexation, Stability constants, pH.

1. Introduction

In soil science in general, the study of soil organic matter has emphasised its relationship to soil productivity (Wander, 2004). Soil organic fractions are extremely important soil components because they constitute a stable fraction of carbon. They also serve to improve water holding capacity of soils. Soil organic fractions, otherwise known as humic substances (HSs) are the major and organic ubiquitous constituents of soils and sediments where they form through random reactions involved in chemical and microbial degradation of biological tissues (Hiraide, 1992). Based on their solubility properties, HSs are generally classified into the following three (3) categories: humic acids (HAs), fulvic acids (FAs) and humin. These three humic fractions are structurally similar and their properties differ, especially with respect to their molecular weight, their ultimate analysis and the number of functional groups present (Xavier et al., 2012).

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Soil organic fractions are also known to form complexes with heavy metals (Hiraide, 1992) and hence their presence in the soil enhances plant growth by providing nitrogen, phosphorous and sulphur for plants and microorganisms (Wander, 2004). Previous studies have shown that soil organic fractions increase the quality of agricultural products, increase the content of nutritious elements (Tobiašová, 2012) and cause root initiation and increased leaf growth when applied to soil (Wander, 2004).

The adsorption of humic matter unto mineral particles may influence their dissolution, speciation, distribution and mobility (Dube et al., 2001). HSs bond easily with metal ions and influence the binding of metal ions to these components (Hiraide, 1992). Data which compares the complexing abilities of HAs and FAs in mining soils with trace metal ions are scarce or inconsistent. This may be attributed to a limited number of studies in Ghana on the chelation of essential elements with HSs. The few studies conducted so far do not also take into account the amount of trace metals that form complex with compounds such as FAs and HAs.

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In this study, we compared the relativities of extracted HSs with trace elements as a function of pH and the data obtained used to predict the role of organic matter in the distribution of trace metals in the terrestrial environment. Our primary hypothesis was that the soil organic fractions would form complexes with the metals solutions prepared.

2. Material and methods

Soil samples were collected from a gold mine concession located at Bibiani latitude 6°27' N and longitude 2°17'W in the Western Region of Ghana about 80 kilometers South-West of the Ashanti capital, Kumasi. The concession has an approximate surface area of 49.0 km^2 and encompasses the town of Bibiani (Figure 1). The sampling areas were outlined as follows: Deep Drill 592 m, Russel Pit, Central Waste Damp, Old Tailings, and New Tailings. Another batch of samples was collected from a Cocoa Plantation forest which was about 20 km from the mining area. At each site, a bulk sample of 2000 g soil was collected from the area. Sampling was repeated once. The sampling areas are presented in Figure 1.

Sample preparation

All chemicals used in this study were of analytical grade, and all the experimental solutions were prepared with doubly deionized water. Each of the soil samples was air-dried by placing it in a shallow tray in a well-ventilated area for about 20 min and then placed in a forced air oven (Galenkemp, USA) at 40 °C for 24 h. Clay clods were broken and the soil lumps crushed using pestle so as to separate gravels and large organic residues. The soil samples were sieved through a 2 mm sieve leaving behind the gravels and other residues.

Physical analysis of samples

The pH was determined using a Hanna (HI 2016) pH meter in a soil to water ratio of 1:2 (Ubwa et al., 2013). Moisture content was determined according to the method described by American Society for Testing and Materials (ASTM) (Canadian Societry of Soil Science, 2008). Electrical conductivity was measured using a conductivity meter (Hanna instrument, HI917) via the aqueous extraction (1:5) method (Barrett et al., 2005). Triplicate analyses were carried out for each determination to ascertain reproducibility and for quality assurance purposes.

To determine soil texture (particle size) a 50 g portions of the air dried, meshed soil samples was placed in a 400 mL beaker and saturated with deionised water, 10 mL of 5% calgon (sodium hexameter phosphate) solution was added and allowed to stand for 10 min. The suspension was transferred to the dispersion cup and made to the mark with deionised water. It was then mixed for 2 min with a high-speed electric mixer (Shanghai ELE, China). The suspension was quantitatively transferred into a 1000 mL measuring cylinder. About 2-3 drops of pentanol was added to the soil suspension in order to remove froth and the hydrometer (Xian Prime, China) was placed gently into the column after 20 s. The hydrometer and temperature reading of the suspension were taken. The cylinder was allowed to stand undisturbed for 2 h and the hydrometer and temperature readings were determined (the necessary temperature corrections were made). The sand portion was then dried and weighed.

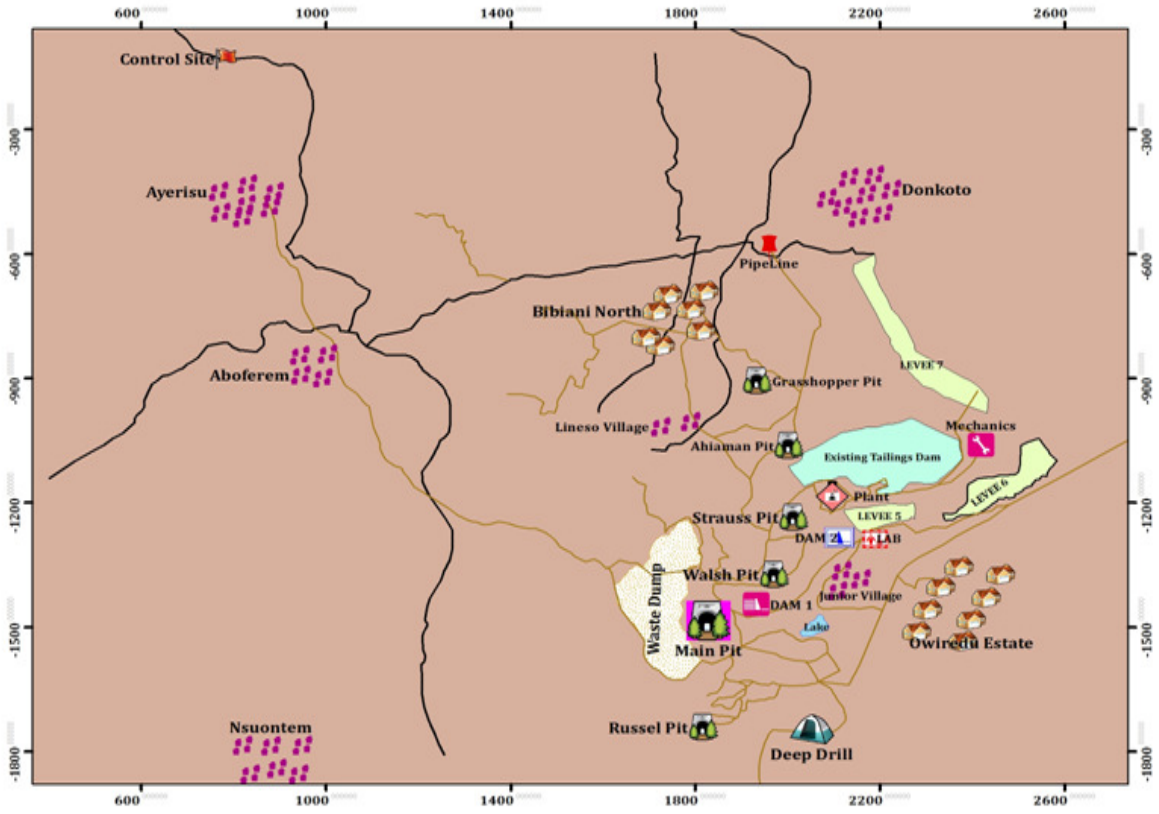


Figure 1: Sampling areas of the Noble Gold Bibiani Limited

The proportionate distribution of the different sizes of mineral particles in each of the soil samples was calculated using the formulas below:

$$\%\ Sand\ (after\ 40secs) = \frac{Sand\ content}{total\ weight\ of\ soil} \times 100 \quad (1)$$

$$\%\ Clay\ (after\ 2\ hours) = \frac{hydrometer\ reading\ after\ temperature\ correction}{total\ weight\ of\ soil} \times 100 \quad (2)$$

$$\%\ Silt = 100 - (\%\ clay + \%\ sand) \quad (3)$$

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Once the above are calculated, the soil was assigned to a texture class based on the soil textural triangle (Ubwa et al., 2013).

Chemical analysis of samples

A subsample of each soil was air-dried, ground in a ball mill, and 75 mg dry soil were analyzed on an elemental analyzer (Carlo Erba 1500) to determine total C and N content (Barrett et al., 2005). In determining the organic carbon content, an additional 75 mg subsample was acidified with 50 % HCl to remove carbonates and analyzed as above. Organic matter was determined by weight-loss-on-ignition after 2 h at 360 °C (Brye et al., 2004).

Exchangeable acidity was determined by first extracting with 1 M KCl and titrating the extract with NaOH (Robertson et al., 1999). The titration reading was corrected for blank of titration of 150 mL KCl solution. The exchangeable acidity was calculated by the formula,

$$\text{Exchangeable acidity (cmol/kg)} = (NaOH_{diff}/W) \times (0.1 \text{ mmol } H^+/\text{mmol NaOH}) \times (0.01 \text{ cmol } H^+/\text{mmol } H^+) \times (10^3 \text{ g soil /kg soil}) \quad (4)$$

where $NaOH_{diff}$ = mL of NaOH added to sample filtrate less mL of NaOH added to blank solution, W = g dry soil.

Available phosphorous was determined by a modified by the Bray and Kurtz P-1 method (Southern Cooperative Series, 2000). To determine the concentrations of K and Ca, soil samples were extracted with Mehlich-3 extractant solution (Brye et al., 2004) in a 1:10 (w/v) soil-to-extractant solution ratio and analyzed by atomic absorption spectrophotometry (Buck Scientific 210 VG).

Determination of heavy metals in soil sample

A 2.0 g portion of the each soil sample was weighed into a digestion tube and digested by the addition of 20 mL of aqua regia (mixture of HCl and HNO_3, ratio 3:1) and 10 mL of 30 % H_2O_2. Addition of H_2O_2 was done in small portions to avoid any possible overflow. The solution was heated in a fume hood until the mixture became clear. The digestion tubes were then collected, allowed to cool and the solution filtered using whatman filter paper into a volumetric flask and made up to the 100 mL mark with double distilled water. Sample blanks were prepared by digestion of acids without any samples in them. All samples and blanks were stored in plastic containers. The resulting solution was analyzed for Cd, Fe, Pb and Zn using the Buck Scientific 210 VG atomic absorption spectrophotometer (Morillo et al., 2007).

Extraction of soil organic fractions

The soil organic fractions were extracted according to the method recommended by International Humic Substances Society (Santos et al., 2004). Briefly, 100 g of each sample was weighed into a labelled beaker using the electronic balance. A volume of 150 mL aliquot of 0.1 M HCl was added to each sample and shaken for 1h. The supernatants were separated from the residue by decantation after allowing the solution to settle. The soil residues were washed thoroughly with distilled water to remove traces of acids in the sample. A 0.5 M NaOH was added and the mixtures thoroughly shaken at regular intervals for a minimum of 4 h. The alkaline suspension was allowed to settle overnight. The supernatants were then

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collected by decantation and the solid residues discarded. Immediately, the supernatant was acidified with 6.0 M HCl with constant stirring to pH of 1.0 after which it was allowed to stand for 12 h. The humic acids being the precipitate and fulvic acid being the supernatant fractions were separated using the buchner funnel.

Further treatment of the humic acid fraction for fulvic acid

To redissolve the humic acids fractions 100 mL of 0.1 M KOH was added to the precipitate. This was followed by 0.3 g of solid KCl and vigorous shaking. The resulting mixture was reprecipitated by acidifying the supernatant with 6 M HCl with constant stirring until a pH of 1.0. The mixture was allowed to stand for 12 h and separated using a buchner funnel and discarding the supernatant. The precipitated humic acids was then suspended in a 50 mL 0.1 M HCl solution and shaken overnight at room temperature. The procedure was repeated three times and the precipitate separated on a pre-weighed filter paper, followed by washing with distilled water until no Cl^- could be detected (Santos et al., 2004). The humic substances were subsequently evaporated in vacuum and dried in circulating air oven at 55 °C and reweighed. The results were recorded and the extraction process repeated for two more times. The supernatant, which is the fulvic acid was analysed using the UV-visible spectrophotometer (Cecil 8000, Japan) at 265 nm.

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Complexation study of fulvic and humic acids and metals

The complexation process involves titrating the solution with an added metal and then plotting the absorbance of the solution as a function of the wavelength (nm). After the complexating capacity of the humic substances has all been used up, all of the added metal is detected as less complexed where the titration curve becomes steeper. In evaluating the complexation efficiency of fulvic and humic acids with metals, 10 mL of fulvic acid was put in 250 mL volumetric flask and diluted to the mark with distilled water. The solutions (25 mg/L) of fulvic acid and the various metal concentrations ranging from 0.0003 to 0.0007 M of Ca, Cu, Zn and Cd salt were prepared in 10^{-3} M phosphate buffer solution (pH= 6.0 ± 0.2). The buffer solution was used as a blank. An alliquot of 25 mL of the fulvic acid was pipetted into four different plastic containers. The first container had no calcium; the second had 1ml of 0.0003 M Ca solution added. A volume of 150 mL of KOH buffer stock solution (with 1 mL of Ca) was added to each beaker containing fulvic acid. All the working pHs for the fulvic acid were close to the natural values. A rapid mix period for 5 min at 200 rpm followed by slow stirring 50 rpm for 40 min was maintained. The series was allowed to equilibrate at 22 ± 2 °C overnight (Xue and Sigg, 1999). The complexed fulvic acids were taken to the UV-Visible spectrophotometer (Cecil 8000, Japan) for analysis. This procedure was repeated for Cu, Zn and Cd metal solutions. The process described above was repeated with humic acid using 0.1 g of the humic acid extract dissolved in 100 mL KOH.

Mathematical developments

Assuming 1: 1 stoichiometry of a single ligand model, the equilibrium between metal and ligand is expressed by:

$$Me_{free} + L \longleftrightarrow Me - L \quad (5)$$

where Me_{free} = free (trace) metal and L = representative ligand

At a constant pH, the conditional stability constant, β is defined as follows:

$$\beta = [Me - L] / [Me_{free}] [L] \quad (6)$$

where $[Me_{free}]$ and $[Me - L]$ are respectively the free and bound concentration of trace metal and $[L]$ is the free concentration of ligand.

Assuming the absorbance of the complex does not overlap the absorbance of the free metal, thus the absorbance of the complex enhances that of the free metal so that there would be no perturbations, then:

$$\text{Stability constant} = \frac{\text{absorbance of complex} - \text{absorbance of free metal}}{\text{absorbance of free metals} \times \text{concentration of acid}} \quad (7)$$

Applying the formula above, the stability constants of the various complexes were calculated.

3. Results and discussions

Table 1 summarises the soil particle size distribution and soil classes (types) from the different sampling points according to the United States Department of Agriculture (USDA) classification. Soil samples from the deep drill (592m), central waste damp and old tailings (8 years old) were all loamy sand (i.e. 70 – 86 % sand, 0 – 30 % silt and 0 – 15 % clay). However, those from the Russel Pit and New Tailings were loam (relatively even mixture of sand, silt and clay), whilst that from forest (control sample) was silty clay loam (resembling clay loam in cohesive properties, but possesses more silt and less sand).

Table 1: Textural analysis of soil samples in various locations of the study area

Sample	Sand (%)	Clay (%)	Silt (%)	USDA textural class (Angel, Rey, and Taguas, 2000)
Deep drill (592 m)	84.66 ± 0.03	2.80 ± 0.01	12.54 ± 0.02	Loamy sand
Russel pit	34.12 ± 0.01	18.66 ± 0.04	47.22 ± 0.03	Loam
Central waste damp	81.40 ± 0.02	4.50 ± 0.02	14.1 ± 0.01	Loamy sand
New tailings	47.16 ± 0.03	8.63 ± 0.03	44.21 ± 0.04	Loam
Old tailings	83.84 ± 0.01	4.73 ± 0.06	11.43 ± 0.02	Loamy sand
Control/forest	2.42 ± 0.05	28.80 ± 0.01	60.14 ± 0.03	Silty clay loam

Soil samples from deep drill (592 m), central waste damp and old tailings are sandy in nature (Table 1). This makes them highly permeable and allows large quantities of leachate to pass through thereby having a potential of polluting the surrounding underground water (Ubwa et al., 2013). These soils would not support a variety of crops but russel pit and new tailings soils will do better because they are high in clay and are generally higher in soil organic matter.

Crops will do well in the control soil due the fact that soils with high silt have corresponding higher soil organic matter (Ubwa et al., 2013). Table 2 indicates that pH values of these soil samples ranged from 4.87 ± 0.03 to 9.16 ± 0.07 which is acidic to alkaline, with a mean pH value of 7.36 ± 0.24. Soil samples of central waste damp and old tailings had higher pH values. Electrical conductivity which is the index of soluble salt content, however, ranged from 0.02 ± 0.06 to 0.73 ± 0.04 µS/cm. Salt free soils exhibit up to 2 µS/cm value indicating

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0.15 % salt concentration (Asharf et al., 1999). All soil samples had relatively lower salt concentration. The difference in electrical conductivity could be attributed to treatment of tailings and also variation in organic matter contents.

Titratable exchangeable acidity varied between 0.05 ± 0.03 and 2.30 ± 0.10 meq/100 g soil (Table 2). In Russel pit with medium to very high acidity (pH = 4.87), the exchangeable acidity was higher (2.30 meq/100 g of soil) and the soil cannot be recommended for agricultural purposes. This is because soils of high acidity and high exchangeable acidity or aluminium content are associated with low fertility (Berthrong et al., 2009). High acidity and high exchangeable acidity are the main constraints for agricultural production. Although, no significant correlations were found among the variables associated with soil acidity, poor correlations were observed between Zn, Pb, Fe, K, P concentrations and exchangeable acidity. However, good correlations (R^2 = 0.5722) were observed between Ca concentration and exchangeable acidity and pH (R^2 = 0.84594).

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Moisture Content in the sample ranged from 0.48 ± 0.03 % to 25.82 ± 0.02 %. The average % moisture content in the samples were in the order cocoa plantation (control) > russel pit > old tailings > deep drill > central waste damp > new tailings (Table 2). Moisture content and temperature conditions favourable for microbial activity typically sustain nutrient release indirectly through their promoting effect on microbial mineralization of organic matter (Brye et al., 2004). For example, the % organic matter in cocoa plantation is 1.93 ± 0.04 and % moisture was 25.82 ± 0.02 whereas % organic matter was 0.72 ± 0.02 and % moisture was 19.5 ± 0.30 for russel pit sample. This trend, was not however, observed in new tailings and central waste damp. The irregularity can be due to loss of water through evaporation and microbial utilization for metabolic activities (metabolic water production).

The organic carbon, organic matter and nitrogen of the soils were significantly different in their respective locations (Table 2). The organic matter plays very important role in soil structure, water retention, cation exchange and in the formation of complexes (Ubwa et al., 2013). The % organic matter varied from a minimum of 0.10 ± 0.01 to a maximum of 1.93 ± 0.04. Good correlations were observed between % organic matter and K (R^2 = 0.5512) and Zn concentration (R^2 = 0.6555). % Organic matter increased fairly with % N and % C for the mine tailings.

Table 2: Mean physicochemical parameters, carbon/nitrogen ratio and organic substances in various locations of the study area

Sampling point	pH	Conductivity (µS/cm)	Exchangeable acidity (cmol/kg)	Moisture content (%)	Organic Carbon (%)	Total organic nitrogen (%)	C/N ratio (%)	Organic matter (%)	Humic acid (mg/L)	Fulvic acid (mg/L)
DD(592m)	7.95 ± 0.80	0.14 ± 0.02	0.15 ± 0.01	3.35 ± 0.05	0.06 ± 0.10	0.01 ± 0.04	6.00 ± 2.50	0.10 ± 0.01	0.16 ± 0.06	ND
RP	4.87 ± 0.03	0.02 ± 0.06	2.30 ± 0.10	19.5 ± 0.30	0.42 ± 0.02	0.04 ± 0.01	10.50 ± 2.00	0.72 ± 0.02	0.49 ± 0.01	0.11 ± 0.02

CWD	8.20 ± 0.03	0.73 ± 0.04	0.10 ± 0.07	1.60 ± 0.06	0.38 ± 0.01	0.03 ± 0.02	12.70 ± 0.50	0.65 ± 0.09	0.18 ± 0.02	ND
NT	7.76 ± 0.03	0.49 ± 0.02	0.05 ± 0.02	0.48 ± 0.03	0.48 ± 0.01	0.04 ± 0.05	12.00 ± 0.20	0.83 ± 0.05	0.09 ± 0.03	ND
OT	9.16 ± 0.07	0.08 ± 0.01	0.05 ± 0.03	9.99 ± 0.03	0.31 ± 0.01	0.03 ± 0.02	10.30 ± 0.50	0.53 ± 0.01	0.31 ± 0.09	0.15 ± 0.09
CP (ctrl)	6.25 ± 0.50	0.52 ± 0.04	0.10 ± 0.09	25.82 ± 0.02	1.12 ± 0.10	0.10 ± 0.06	11.20 ± 1.67	1.93 ± 0.04	0.14 ± 0.02	ND
Mean	7.36 ± 0.24	0.33 ± 0.03	0.46 ± 0.05	10.22 ± 0.08	0.46 ± 0.04	0.04 ± 0.03	10.44 ± 1.23	0.79 ± 0.04	0.23 ± 0.04	0.13 ± 0.05
Range	4.87 – 9.16	0.01 – 0.73	0.05 – 2.30	0.48 – 25.82	0.06 – 1.12	0.01 – 0.10	6.00 – 12.70	0.01 – 1.93	0.09 – 0.49	0.11 – 0.15

DD = Deep drill, RP = Russel pit, CWD = Central waste damp, NT = New tailings, OT = Old tailings, CP = Cocoa plantation/control, C/N = carbon/nitrogen ratio, ND = Not detected.

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% Organic matter also increased with all the metals (P, K, Fe, Ca, Cd, Pb and Zn) in the mine tailings. Many authors have explained the functional roles of organic matter in the release of many plant nutrients, including nitrogen (N), phosphorus (P) and sulfur (S) as it is broken down in the soil. By reducing its content soil productivity also decreases (Tobiašová, 2012). The results (Table 2) show a good organic matter horizon in the post mining tailings as well.

The C:N ratio is very important in determining the rate of decomposition of organic residues by microbes which immobilize and mineralize nitrogen (Griffith et al., 2009). Several researchers have indicated that microorganisms make use of about 30 parts of carbon for each part of nitrogen. Thus, large proportions of readily mineralizable C and N suggest that soil organic matter is potentially more active than previously thought based upon assumptions made from descriptions of soil organic matter sources (Barrett at al., 2005). All the soil samples recorded low amounts of organic carbon and nitrogen and hence there was not much an appreciable variation in organic matter content in all the soil samples (Table 2). The results for C: N ratio is presented in Table 2. The C: N ratios of soil samples ranged from 6.00 ± 2.50 % to 12.70 ± 0.50 %. The lower C:N ratio indicate less competition for nitrogen between plants and microorganisms in the soil (Griffith et al., 2009). However, the low level of nitrogen and wide ratio of C: N ratio in the post-mining soils are the main reason for their low productivity. The high and stable productivity of these soils is only possible under very high nitrogen fertilization.

Table 3: Concentration of metals in soil samples in various locations of the study area

Sampling point	Metal concentrations (mg/kg)						
	P	K	Ca	Fe	Cd	Pb	Zn

DD (592m)	7.80 ± 0.02	154.70 ± 0.80	0.85 ± 0.01	65492.78 ± 0.30	ND	35.37 ± 0.04	68.48 ± 0.02
RP	1.50 ± 0.01	65.83 ± 0.10	0.82 ± 0.01	61059.29 ± 0.10	ND	27.72 ± 0.16	58.27 ± 0.03
CWD	8.27 ± 0.10	105.32 ± 0.02	0.90 ± 0.02	27294.73 ± 0.71	ND	13.56 ± 0.70	47.10 ± 0.10
NT	3.51 ± 0.06	194.19 ± 0.04	0.76 ± 0.03	63159.03 ± 0.06	ND	29.87 ± 0.63	47.85 ± 0.14
OT	0.26 ± 0.02	92.80 ± 0.06	0.38 ± 0.01	218846.70 ± 1.20	ND	21.80 ± 0.58	32.20 ± 0.10
CP (ctrl)	1.96 ± 0.01	296.23 ± 0.04	0.40 ± 0.01	69850.88 ± 0.43	ND	35.23 ± 0.07	144.59 ± 0.75
Mean	3.88 ± 0.04	151.51 ± 0.18	0.68 ± 0.01	84283.9 ± 0.47	ND	27.26 ± 0.36	66.41 ± 0.19
Range	0.26 – 8.27	65.83 – 296.23	0.38 – 0.90	27294.73 – 218846.70	ND	13.56 – 35.37	32.20 – 144.59

DD = Deep drill, RP = Russel pit, CWD = Central waste damp, NT = New tailings, OT = Old tailings, CP = Cocoa plantation/control, ND = Not detected.

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Table 3 shows results of the levels of some metals in soil at the various sampling sites. Metals are present in the environment and most of them are essential for plants and animals and some are anthropogenic which may cause major health problems (Silveira et al., 2003). Phosphorous as phosphate is an integral component of a number of important compounds present in plant cells and acts as a limiting element in soil (Imran et al., 2010). Table 3 shows that phosphorous concentration ranged from 0.26 – 8.27 mg/kg with a mean concentration of 3.88 ± 0.04 mg/kg. The low levels of phosphorous in the soil samples as compared to other metals could be attributed to its reactive nature (Mahajan and Billore, 2014). Poor correlation was however, observed between P concentration, and pH ($R^2 = 0.1971$), % organic matter ($R^2 = 0.1853$) and % carbon ($R^2 = 0.1822$). Potassium concentration ranged between 65.83 and 296.23 mg/kg with a mean concentration of 151.51 ± 0.18 mg/kg. With the exception of Russell pit (65.83 ± 0.09 mg/kg), all soil samples recorded an appreciable concentration of potassium which is within the permissible limit of > 80 mg/kg (Table 4). Thus, all soil samples are not deficient in potassium except those from the Russell pit. Physiologically, potassium is a major nutrient which is considered essential for plant growth (Imran et al., 2010). However, good correlations were observed between potassium concentration and % carbon ($R^2 = 0.5512$) and % organic matter ($R^2 = 0.5523$). Calcium concentration in the soil samples were relatively lower. The results in table 4 reveal that during the study period, calcium concentration ranged from 0.38 – 0.90 mg/kg with a mean concentration of 0.68 ± 0.01 mg/kg. The deficiency symptoms of calcium occurs below 500 mg/kg (Table 5). This deficiency could be attributed to variables such as soil parent material, the degree of soil weathering, previous uses of the soil and leaching (Taylor and Locascio, 2004). Calcium concentration, however, increased fairly with pH ($R^2 = 0.6664$). Soil pH and organic matter content could be responsible for the variation of calcium in all the soil samples. Iron, the most abundant metal ranged between 27294.73 – 218846.70 mg/kg (Table 3) with a mean concentration of 84283.9 ± 0.47 mg/kg. This is probably because it is an element basically of natural origin i.e. it is one of the most common elements in the earth's crust (Morillo et al., 2007) and hence, has no guideline value (Table 4). The concentration of iron however, did not correlate well with % carbon ($R^2 = 0.0204$) and % organic matter ($R^2 = 0.0195$). Cadmium was below detection limit in all the soil samples. The concentration of lead in all

the soil samples was within the permissible limit of 500 mg/kg (Table 4) ranging from 13.56 – 35.37 mg/kg with a mean concentration of 27.26 ± 0.36 mg/kg, indicating no degree of lead contamination. Poor correlation was observed between lead concentration and % carbon (R^2 = 0.071) and % organic matter (R^2 = 0.0742). Zinc with a mean concentration of 66.41 ± 0.19 mg/kg was found to be in the range of 32.20 – 144.59 mg/kg (Table 3) whereas the maximum permissible limit is 250 mg/kg (Table 4). The concentrations show that the soil samples are all deficient in zinc. A good correlation was, however, observed between zinc concentration and % carbon (R^2 = 0.6517) and % organic matter (R^2 = 0.6555). The levels of lead, cadmium and zinc were low and fall below the maximum permissible limits of 500 mg/kg, 1.0 mg/kg and 250 mg/kg respectively. This then indicates no degree of contamination, meaning the soil samples are safe for re-use for agricultural purposes as far as lead, cadmium and zinc concentrations are concerned.

Table 4: Permissible limits of metal concentrations in soil

Element	Permissible limit (mg/kg)
Phosphorous	> 7
Potassium	> 80
Calcium	> 500
Iron	No guideline value set
Cadmium	1.0
Lead	500
Zinc	250

Source (Imran et al., 2010).

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Fulvic acids and humic acids

In general, the humic substances extracted were low in all the soil samples with the exception of Russel pit and Old tailings The Russel pit recorded the highest humic acid concentration of 0.49 ± 0.01 mg/L and the highest corresponding fulvic acid concentration of 0.11 ± 0.02 mg/L. The Old tailings, however, recorded a lower concentration of humic acid (0.31 ± 0.09 mg/L) and a fulvic acid concentration of 0.15 ± 0.09 mg/L (Table 2). The levels of organic matter in Russel pit (0.72 ± 0.03 %) and Old tailings (0.53 ± 0.01 %) and corresponding humic substances as compared to other soil samples is an indication that these soils consist of minimal organic matter content and humified substances.

Correlation analysis for physicochemical parameters, carbon/nitrogen ratio and organic matter

In furtherance, a correlation analysis was employed to identify the relationship among the physicochemical parameters for various soil samples from the targeted mine pits. From the correlation matrix below, generally there is there no absolute strong correlation among all the ten physicochemical parameters. This clearly confirms the differential chemical reactions among the various soil samples collected from the respective mining sites.

From Table 5, with the exception of conductivity which has a weak association with pH (i.e. r < 0.179 and p value > 0.734), the remaining parameters have absolute inverse relation with the pH (e.g. r < -0.800, -0.696, -0.439). This means that as any of these parameters (i.e. either exchangeable acidity, moisture content, organic carbon, total organic nitrogen, carbon/nitrogen ratio, organic matter, humic acid or fulvic acid) increases in reaction, the second parameter, pH decreases and vice versa. The differential pH levels for these

individual physiochemical parameters could be the contributing factor for the inverse association since each of these parameters has different pH.

However, there is a strong correlation among some of the parameters as illustrated in Table 5. For instance, moisture content, organic carbon and organic matter mutually has a strong relation (i.e. r > 0.714, 0.770, 0.712). This implies that as any of these parameters increases in reaction, the other parameter decreases.

Surprisingly, there is an extremely strong association between organic carbon and organic matter (i.e. r = 1.000, p value = 0.000). This means that as organic carbon increases in reaction organic matter on the other hand also increase and vice versa (Table 5)

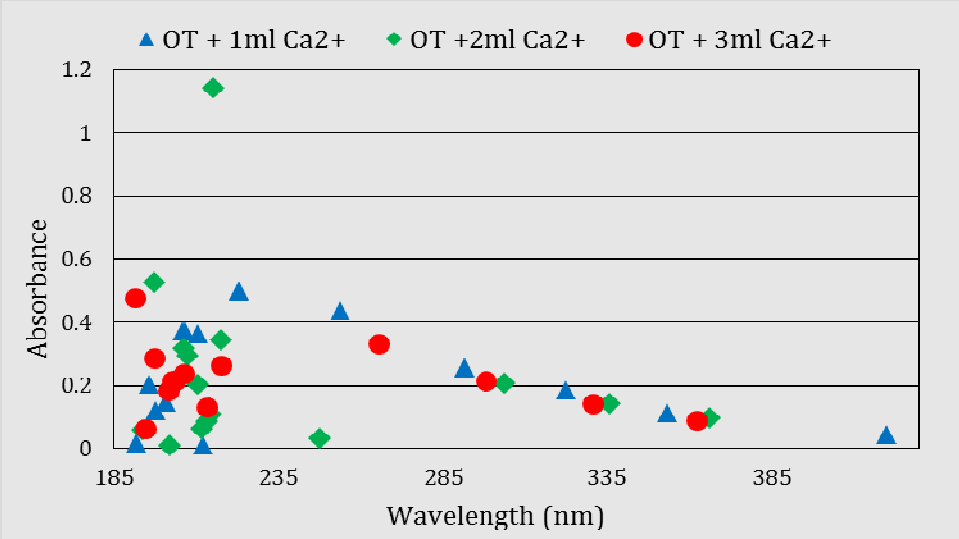
Table 5: Correlation analysis for physiochemical parameters from targeted mining sites

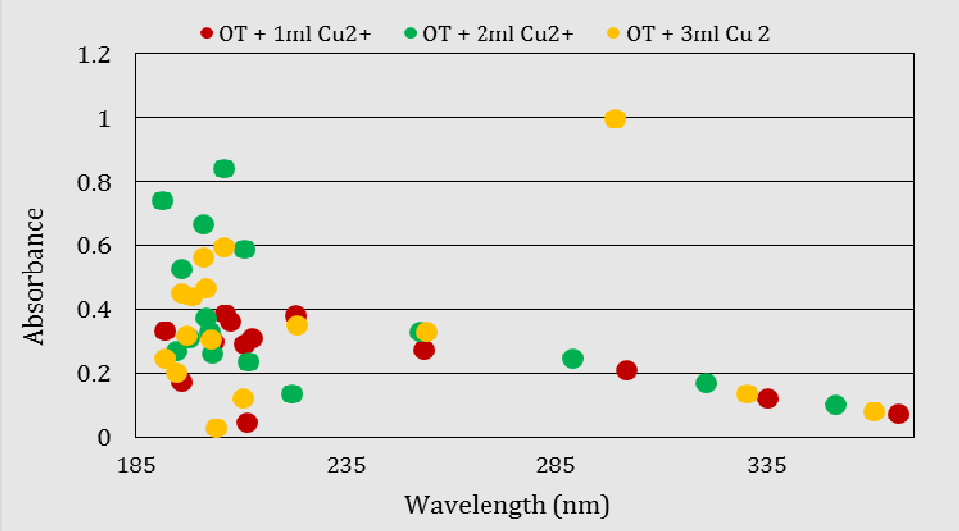
Correlations Matrix											
		pH	Conductivity	Exchange	Moisture	Organic Carbon	Organic Nitrogen	Carbon/Nitrogen Ratio	Organic Matter	Humic Acid	Acid
pH	Pearson Correlation	1	.179	-.800	-.696	-.439	-.469	-.074	-.439	-.477	-.010
	Sig. (2-tailed)		.734	.056	.125	.384	.348	.890	.384	.339	.985
	Number of Pits	6	6	6	6	6	6	6	6	6	6
Conductivity	Pearson Correlation	.179	1	-.527	-.236	.436	.353	.634	.436	-.689	-.726
	Sig. (2-tailed)	.734		.282	.653	.388	.492	.177	.387	.130	.102
	Number of Pits	6	6	6	6	6	6	6	6	6	6
Exchange	Pearson Correlation	-.800	-.527	1	.440	-.066	-.033	-.017	-.067	.882*	.458
	Sig. (2-tailed)	.056	.282		.382	.902	.950	.974	.900	.027	.361
	Number of Pits	6	6	6	6	6	6	6	6	6	6
Moisture	Pearson Correlation	-.696	-.236	.440	1	.714	.770	.067	.712	.423	.283
	Sig. (2-tailed)	.125	.653	.382		.111	.073	.899	.112	.403	.586
	Number of Pits	6	6	6	6	6	6	6	6	6	6
Organic Carbon	Pearson Correlation	-.439	.436	-.066	.714	1	.995**	.514	1.000**	-.201	-.226
	Sig. (2-tailed)	.384	.388	.902	.111		.000	.297	.000	.702	.667
	Number of Pits	6	6	6	6	6	6	6	6	6	6
Organic Nitrogen	Pearson Correlation	-.469	.353	-.033	.770	.995**	1	.436	.995**	-.159	-.185
	Sig. (2-tailed)	.348	.492	.950	.073	.000		.387	.000	.764	.726
	Number of Pits	6	6	6	6	6	6	6	6	6	6
Carbon/Nitrogen Ratio	Pearson Correlation	-.074	.634	-.017	.067	.514	.436	1	.514	-.048	-.021
	Sig. (2-tailed)	.890	.177	.974	.899	.297	.387		.297	.927	.968
	Number of Pits	6	6	6	6	6	6	6	6	6	6
Organic Matter	Pearson Correlation	-.439	.436	-.067	.712	1.000**	.995**	.514	1	-.203	-.228
	Sig. (2-tailed)	.384	.387	.900	.112	.000	.000	.297		.699	.664
	Number of Pits	6	6	6	6	6	6	6	6	6	6
Humic Acid	Pearson Correlation	-.477	-.689	.882*	.423	-.201	-.159	-.048	-.203	1	.813*
	Sig. (2-tailed)	.339	.130	.027	.403	.702	.764	.927	.699		.049
	Number of Pits	6	6	6	6	6	6	6	6	6	6
Fulvic Acid	Pearson Correlation	-.010	-.726	.458	.283	-.226	-.185	-.021	-.228	.813*	1
	Sig. (2-tailed)	.985	.102	.361	.586	.667	.726	.968	.664	.049	
	Number of Pits	6	6	6	6	6	6	6	6	6	6
*Correlation is significant at the 0.05 level (2-tailed).											
**RED (Strong Correlation among Parameters)											
***Yellow (Weak Correlation among Parameters)											
****Blue (Invers Relation among Parameters /Negative Correlation)											

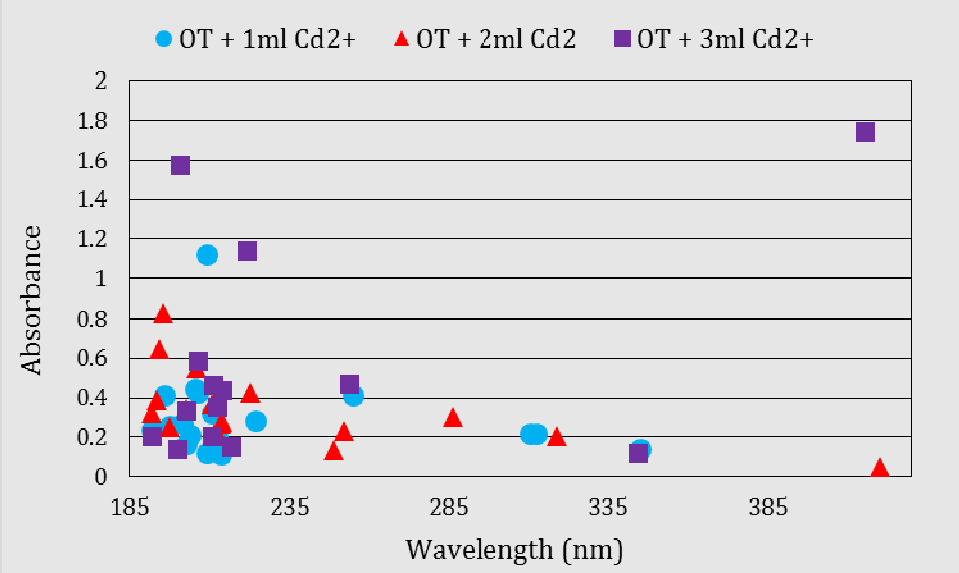
Complexation study of trace metals with humic substances

In soils, metals interact (form complexes) with both low and high weight organic molecules, including humic substances. Humic acids were not obtained for other samples except for Old tailings and Russel pit which were used in further work. Figure 2 shows the reactivity (complexation) of fulvic and humic acids with metals. For the old tailings, calcium was complexed to a higher extent than copper, followed by zinc and cadmium with fulvic acids i.e. Ca > Cu > Zn > Cd (Figure 2a).

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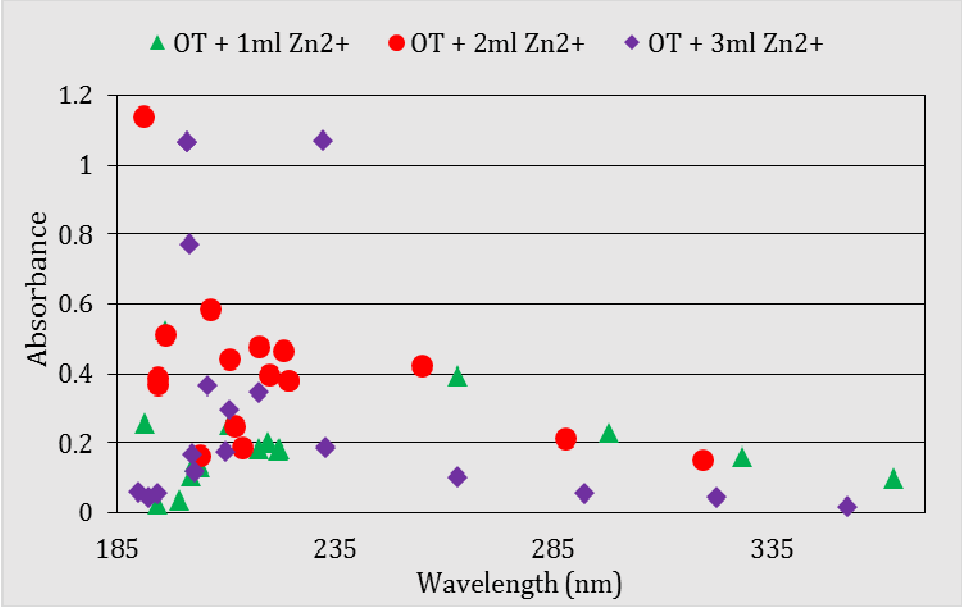
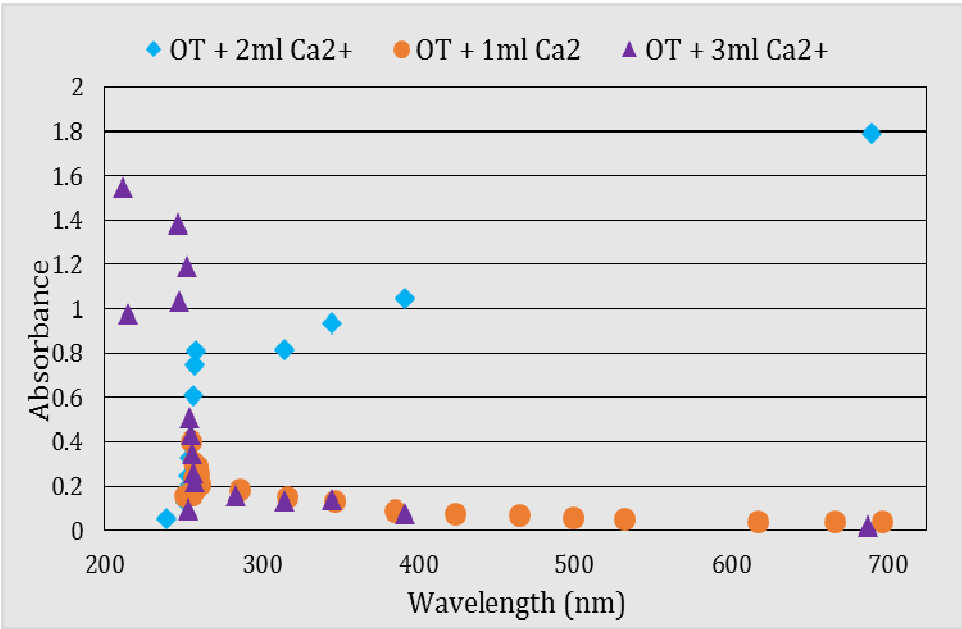
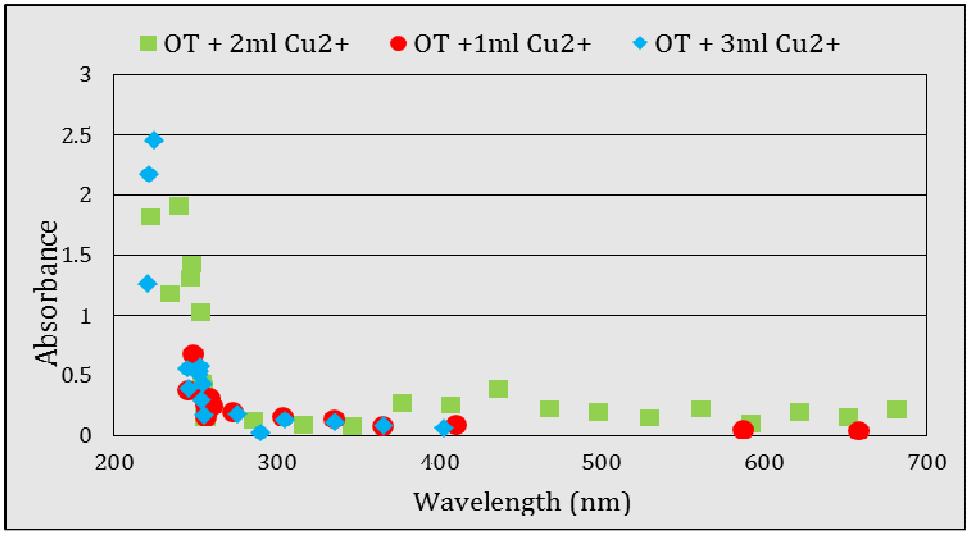


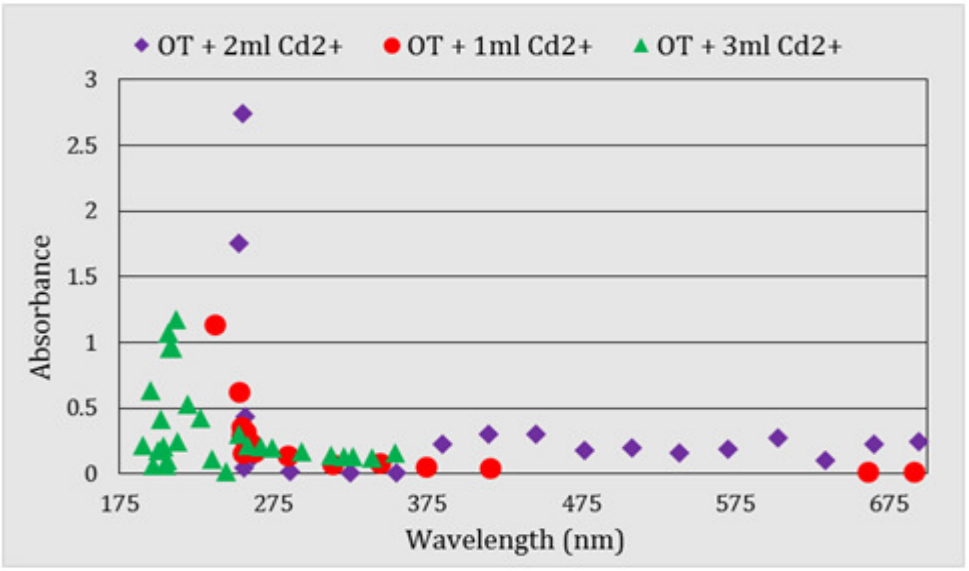
Figure 2a: Graphs showing the reactivity of calcium, copper, cadmium and zinc towards fulvic acid respectively in Old tailings.

The trend, however, changed in the reaction of the trace metals with humic acids extracted from old tailings. Thus, the order of decreasing stability constants of humic acids is Ca > Cu > Cd > Zn (Figure 2b).



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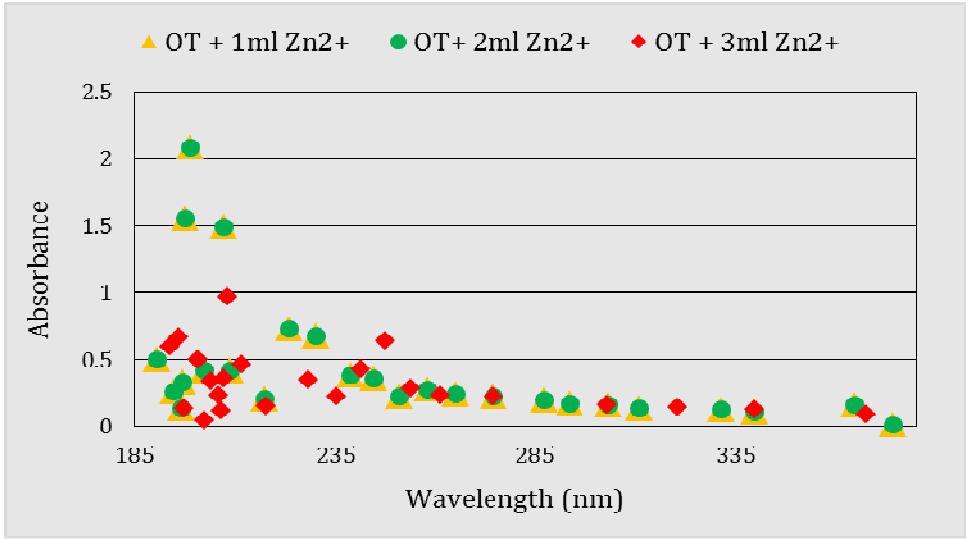
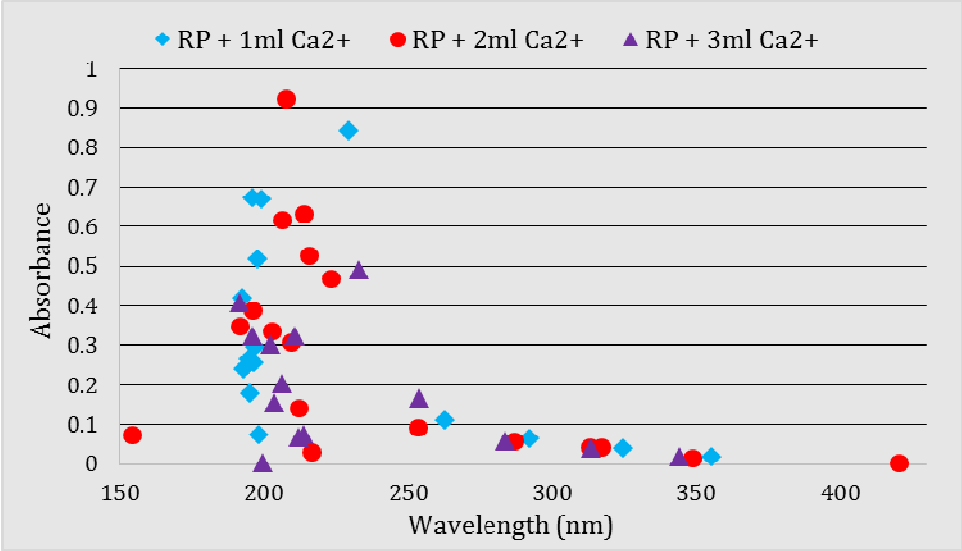
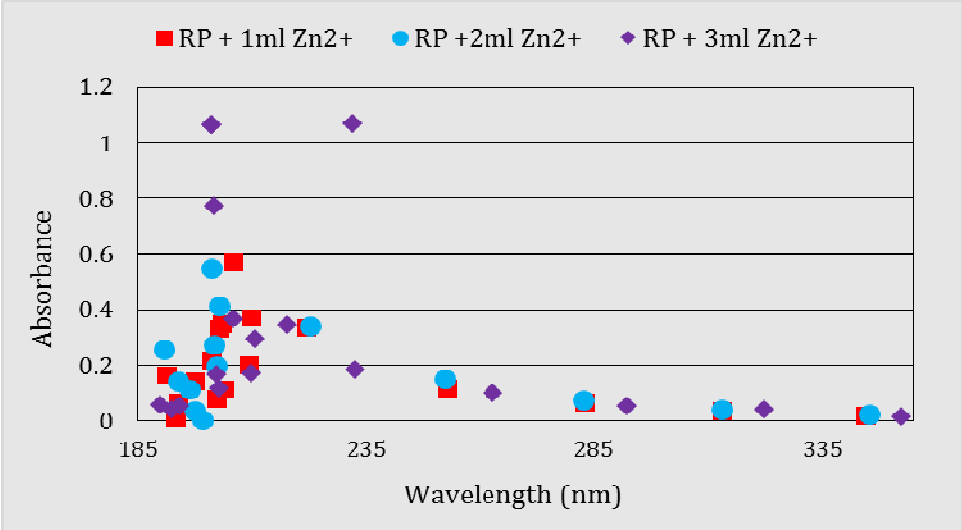


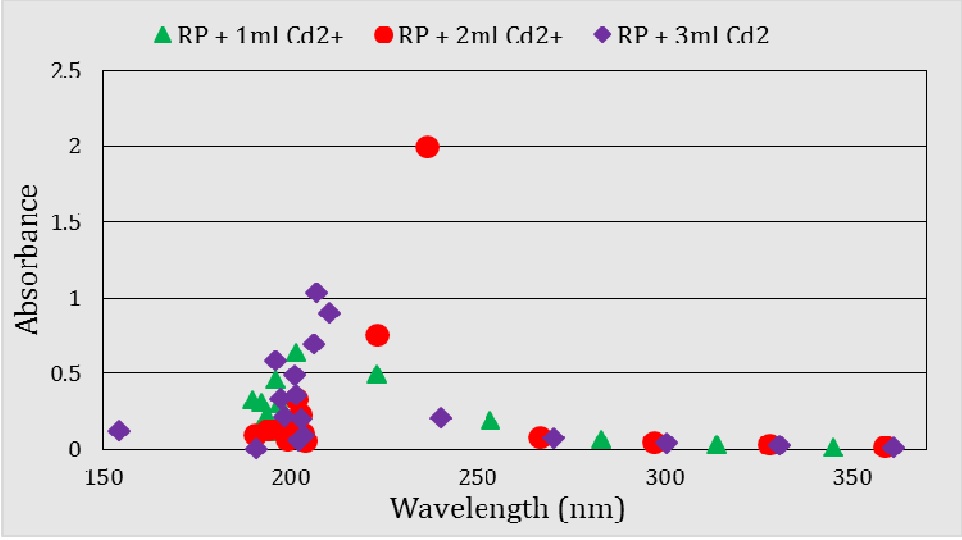
Figure 2b: Graphs showing the reactivity of calcium, copper, cadmium and zinc towards humic acid respectively in Old tailings.

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Soil samples from the Russel pit also produced fulvic and humic acids. The decreasing complexation order in fulvic acid is Ca > Cu > Cd > Zn (Figure 3a)







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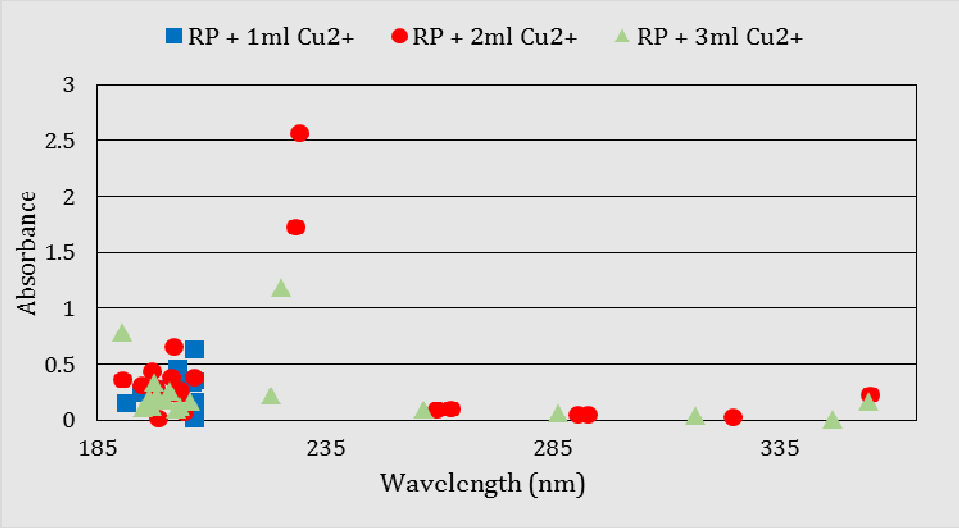
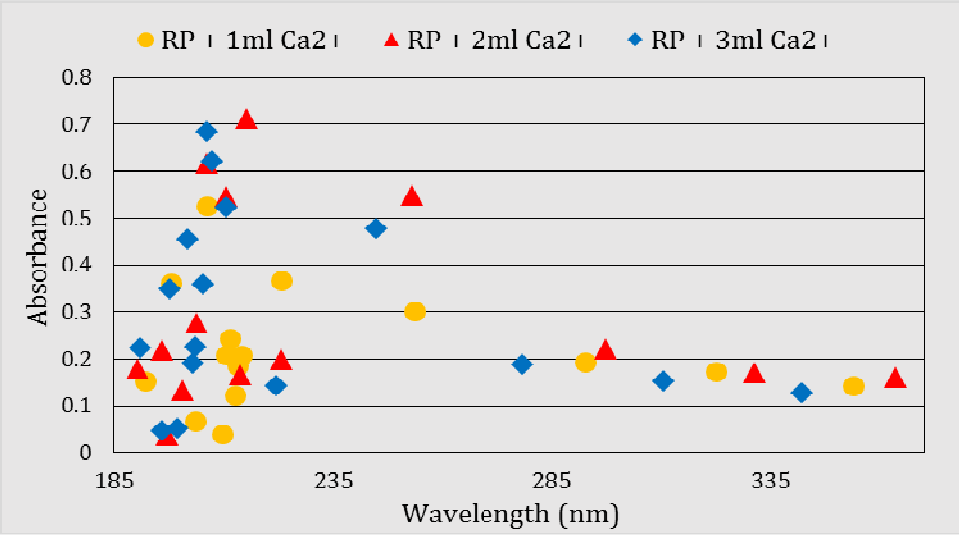
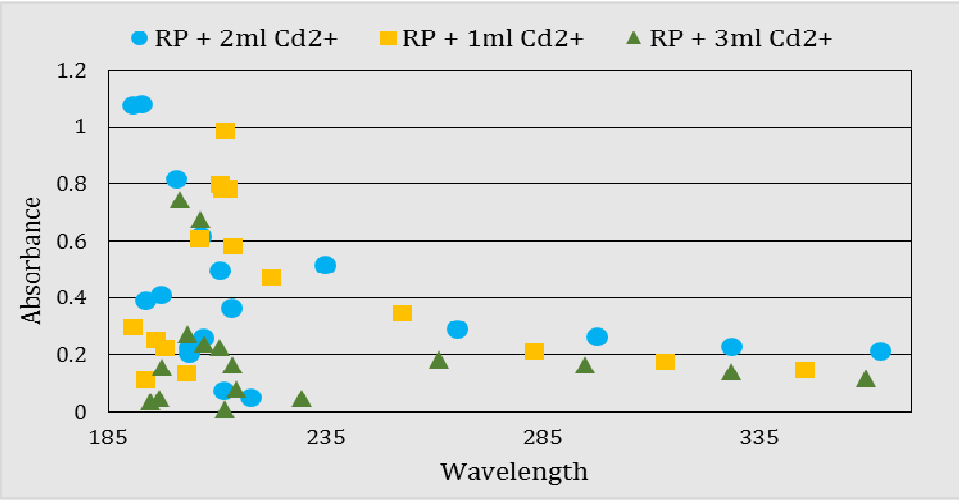


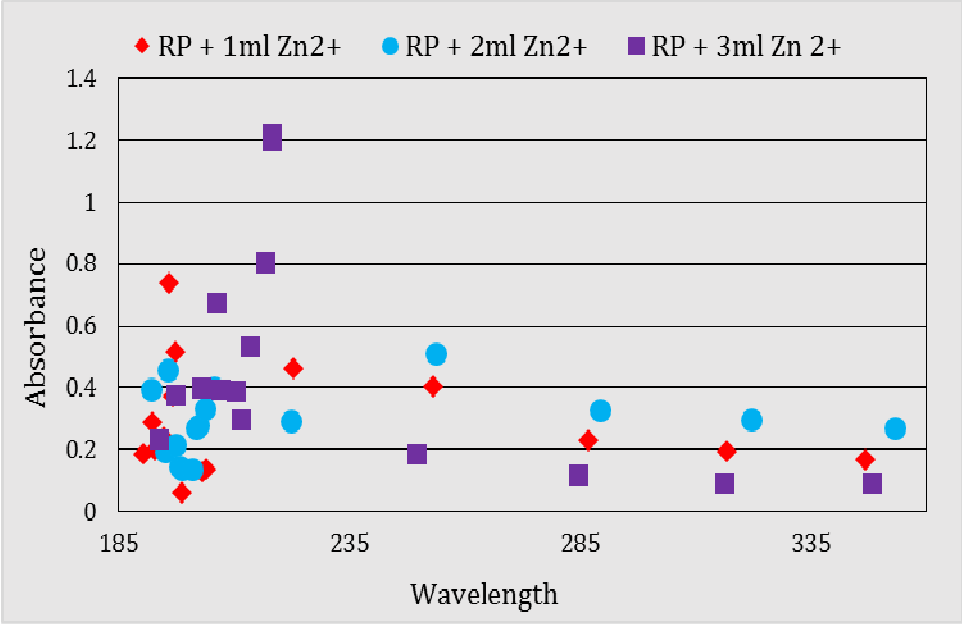
Figure 3a: Graphs showing the reactivity of calcium, copper, cadmium and zinc towards fulvic acid respectively in Russel pit.

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The trend, however, for humic acid from Russel pit was different i.e. Ca > Cd > Cu > Zn (Figure 3b).







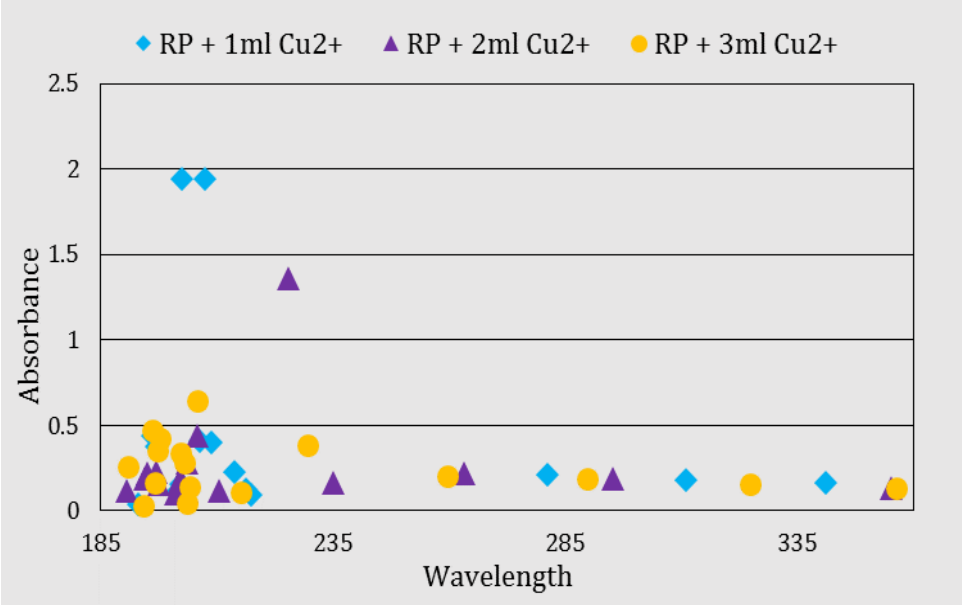


Figure 3b: Graphs showing the reactivity of calcium, copper, cadmium and zinc towards humic acid respectively in Russel pit.

Humic substances which are important ligands for most heavy metals in soils influence metal transport through soil layers. In this work, however, calcium showed a greater complexation ability in all the soil samples (Figure 3a, 3b). Thus, metal transport in soil is not only dependent on its physico-chemical properties but also on the humic substances (organic metal content) available (Dube et al., 2001). Moreover, the extent of complexation depends on the metal concentration available in the soil. For the Old Tailings, the order of decreasing complexation stability constants of the humic and fulvic acids is $Ca^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$ and $Ca^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$ respectively. For Russel Pit, the order is FA: $Ca^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$ HA: $Ca^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+}$. This implies that the mobility of humic substances in the soil will influence the impact that these metals can cause to the environment according to the order above (Mendonça et al., 2004). The summary of the results

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(complexation order) above contradicts the natural order or Irving-Williams series (Gilani et al., 2009). This means that the complexation is not entirely chemical and may be due to factors like physical adsorption accounting for the uptake of the metal.

Stability constants of humic substances

The average stability constants for the interaction of humic substances with trace metals are presented in Table 4.

Table 4: Average stability constants for the interaction of humic substances from russel pit and old tailings with trace metals

Metal-humic mixture	Average stability constant (log β) for Russel pit	Average stability constant (log β) for Old tailings
FA + Ca	6.60	8.12
HA + Ca	8.86	9.46
FA + Cd	6.78	6.58
HA + Cd	7.30	7.98
FA + Cu	6.99	6.97
HA + Cu	7.24	8.17
FA + Zn	6.06	6.96
HA + Zn	6.94	7.44

HA = Humic acid FA = Fulvic acid

The magnitude of the stability constants are high in comparison with literature data reported by Alberts and Giesy, 1983. This then indicates that the reactivity of these metals with soil organic fractions (HSs) occurs at different sites of the metal-humic mixtures. The stability of the HA species was higher than the FA species; which implies that the presence of HA did influence the toxicity of the metals, but that of FA did not significantly influence the metals. Hence with the Old Tailings, chelating with HA would result in a reduced availability of Ca^{2+} in the terrestrial environment as compared to Cu^{2+}, Cd^{2+} and Zn^{2+} thereby affecting their mobility and distribution (Table 4). The same trend is observed for the Russel pit with the order of decreasing stability constants being $Ca^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$.

Relationship between stability constants and pH

Calculated conditional stability constants (log β) versus pH (showing the variations in the presence of the metals) are presented in Figure 3 for the Old Tailings. In Figure 3, the logarithms of the stability constants are shown as functions of pH. In all cases, the stability constants apparently increased with increasing pH. This suggests that increasing the master parameter, pH enhances ionization thereby leading to an extended complexation between the metal and the ligand. This underlines the fact that pH also influences the different reactions involved in the chelating process.

It can therefore, be inferred that HA showed a significant complexing ability for the trace metals; which implies that they have a higher influence on the speciation and mobility of these metals in the terrestrial environment than FA (Figure 3).

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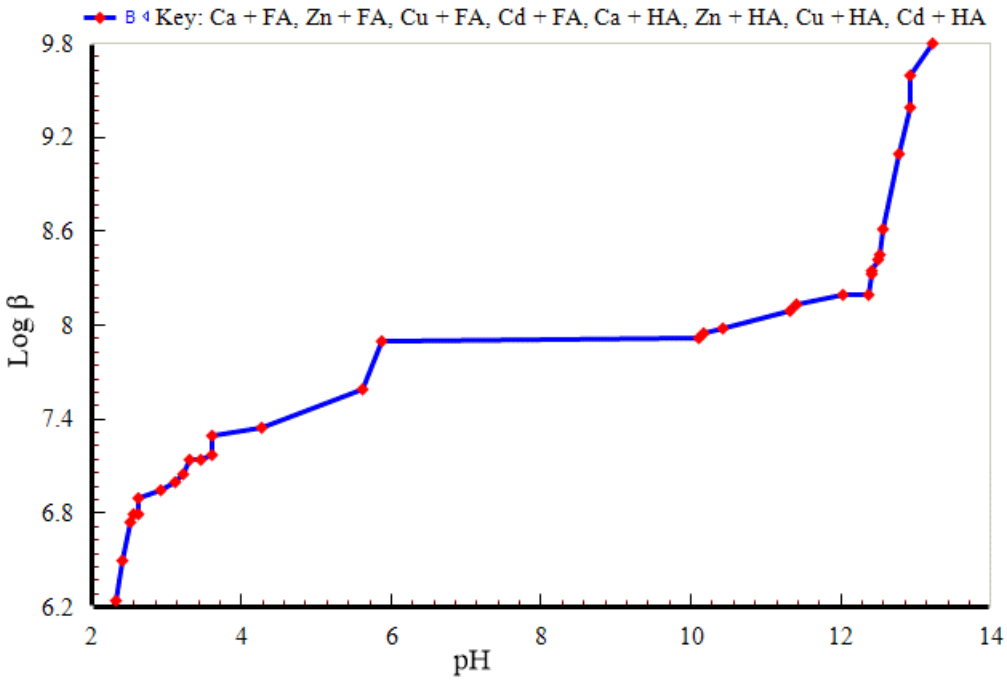


Figure 3: Variation of log β with trace metals, as a function of pH

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4. Conclusions

The results indicated that Pb, Fe and Zn concentrations varied significantly with humic acid. The low levels of Cd and Pb, compared with the World Health Organization (WHO) threshold shows that all the soil under this study are not heavily polluted and that the post-mining soil are safe for re-use for agricultural purposes so far as Cd and Pb levels are concerned. The soil samples from the forested sites had higher concentrations of organic matter and corresponding higher elemental ratios (C/N) than those from the mining areas (unforested areas). The calculated stability constants of humic substances of different soil samples with the trace metals did not differ significantly. This suggests that the analysed fractions possessed binding sites of comparable efficiency. The distribution of the metals in the various soil samples depends on the amount of humic substances in the soil. The summary of the results (complexation order) contradicted the Irving-Williams series and this might be attributed to the fact that the reaction is not entirely chemical and there could be additional physical adsorption accounting for the uptake of the metal. In all cases, the stability constants apparently increased with increasing pH. Humic acids showed greater complexing ability for the trace metals, and this implies that they have a higher influence on the speciation and mobility of these in the terrestrial environment than fulvic acid. Thus, humic acids appears to have higher complexing ability for trace metals with the highest stability constant observed for Ca^{2+} than fulvic acid. Hence, this would result in a reduced availability of Ca^{2+} in the terrestrial environment as compared to Cu^{2+}, Cd^{2+} and Zn^{2+}, thereby affecting their mobility and distribution.

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