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Full Length Research Paper

Levels of some agricultural pollutants in soil samples from Biu Local Government Area of Borno State, Nigeria

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Soil samples from four agricultural locations (Mirnga, Zira, Wangaga and Malang) in Biu Local Government Area were collected at three depths (0-10cm, 10-20cm and 20-30cm) for the determination of pH, electrical conductivity, organic matter, organic carbon, salinity, cation exchanged capacity, Ca, Na, K, heavy metals and anions using standard procedures. From the results of the study it was observed that the levels of pH and organic carbon influenced the solubility and mobility of heavy metals. Generally, the levels of heavy metals, anions, Ca, Na and K in the soil samples for the four agricultural locations increased significantly ($p < 0.05$) to a depth of 30 cm, while pH, Organic carbon, Conductivity, salinity, organic matter, Cation Exchange Capacity (CEC), decreased to a depth of 30 cm.The levels of all the metals in the soil samples were higher than those recommended by Food and Agricultural Organization (FAO) and the WHO/EU joint limits for food production.

Keywords: Agriculture, Pollutants, Soil, Heavy Metals, Solubility, Mobility, Depth Profile.

INTRODUCTION

Soils are mostly sinks for several toxic metals. Metal levels in soils are associated with complex biological and geochemical cycles and are influenced by anthropogenic factors such as agricultural activities (used of pesticides and organic fertilizers), industrial practices, effluent discharged, and vehicular emission (Kabata-Pendias 2004). These metals shows differences in soil proprieties including differences in mobility and bioavailability, also leaching lead to penetration of metals down soils profiles and plant uptake by plant with shorter tap root are usually relatively small compared with the amount of metals entering the soil from different sources. Long term accumulations of heavy metal can affect the quality of the agricultural soils, leading to phytotoxicity at high concentrations, the maintenance of soil microbial processes and the transfer of toxic metals to the human diet as a result of increased crop uptake or soil ingestion by grazing livestock (Nicholson *et al.,* 2003; Maliszewska-Kordybach and Smreczak 2003). The reduction of the levels of heavy metals in the soils is a strategic aim in soils protection policies being implemented in the European Union (EU 2008). It is necessary to know the total metals content in soils in order to be able to assess their quality and the potential risk of pollution. However, only the soluble, exchangeable, and chelated metal species in the soils are labile fractions available to plants (Nicholson *et al.,* 2003), and determination of the total

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concentrations should be complemented by measurement of the available fractions. In addition, the mobility of heavy metals, their bioavailability, and their related ecotoxicity depend strongly on their specific chemical forms, and consequently, these parameters need to be determined rather than the total concentrations in order to make a correct assessment of the environmental risks (Pueyo *et al.,* 2001). Moreover, soil conditions play an important role in the mobility and bioavailability of heavy metals, and it has been demonstrated that in well-aerated acid soils, several metals (especially cadmium and zinc) are more mobile and bioavailable, while in poorly aerated neutral or alkaline soils, metals are substantially less available (Wilson *et al.,* 2006).

Assessment of metal contents in soils and the risks due to exposures are important in environmental management decisions and overall protection of human health (Biasioli*et al.* 2007; De Miguel *et al.* 2007; Mielke*et al.* 2010). Elemental concentrations in soils arise from both natural processes and anthropogenic pollution sources. Trace elements such as zinc, chromium, copper, cobalt, and iron are beneficial for both plants and humans, but toxic effects may manifest at concentrations higher than certain threshold for each element. Other trace elements such as lead, cadmium and mercury are known to have no beneficial biological functions in humans. In particular, childhood lead poisoning remains a serious environmental health problem, affecting the central nervous system and acting as co-factor in many other illnesses (Brewster and Perazella 2004; Navas-Acien*et al.* 2007). Lead in soil is the primary causative agent of concern in addressing the population of children at risk of lead poisoning. Children are often more susceptible to chemical exposures because of their often hand-to-mouth activity and greater gastrointestinal absorptions rates than adults.

The effect of pH on heavy metal availability to plants has been reported by many researchers and it is accepted that as pH decreases, the solubility of cationic forms of metals in the soil solution increases and, therefore, they become more readily available to plants (Salam and Helmke, 1998; Oliver*et al.,* 1998). Evans (1995) explained that pH has a major effect on metal dynamics because it controls adsorption and precipitation, which are the main mechanisms of metal retention to soils. Metal solubility in the solution depends on the solubility product of the solid phase (precipitate) containing the metal. It is, thus, evident that heavy metals are influenced by the presence of humic acids, as many times heavy metals have been reported that they are organically bound (Flores *et al.,*1997). Especially for Cu and Pb, speciation depends on organic matter (Temminghoff *et al.,* 1997). Humic acids bind metals and reduce their availability to plants (Piccolo, 1989) and, thus metal retention by the soil increases when sewage sludge is applied. He and Singh (1993) found that application of sludge increased the cations exchange capacity (CEC) value of the soil (that is the ability of the soil to retain metals). The movement of heavy metals down the soil profile is often evident in high applications of heavy metals, usually in sewage sludge, in soils with low organic matter and clay contents, acidic conditions, and when high rainfall or irrigation water rates have been applied. The movement occurs through soil macropores or cracks (Dowdy and Volk, 1983).

The modern agricultural practices in this area of study employ the use of organic and inorganic fertilizers, pesticides (both herbicides and insecticides) exposes the lands of Biu Local Government of Borno State to heavy metal which bioaccumulate as a result of continuous application to the Arable lands. The quality of soils of Biu Local Government Area of Borno State has not been study for any pollutant levels. There is also no authentic information about the quality and level of pollutants in the area, hence the need for this study.

MATERIALS AND METHODS

Sample collection

Soil samples were collected from four agricultural locations (Mirnga, Zira, Wangaga and Malang) within Biu Local Government Area of Borno State, Nigeria. In the field, at each sampling sites, soil samples were collected from ten plots. In each plot, soil samples were collected at three depths (0-10cm, 10-20cm and 20-30cm), by using spiral auger of 2.5cm diameter. Soil samples from each agricultural location were randomly sampled and bulked together to form a composite sample. In all cases, soil samples were put in clean plastic bags and transported to the laboratory.

Digestion of soil samples for the determination of heavy metals

Two grammes of the soil samples were weighed into acid washed glass beaker. Soil samples were digested by the addition of 20cm^3 of aqua regia (mixture of HCl and HNO_3, ratio 3:1) and 10cm^3 of 30% H_2O_2. The H_2O_2 was added in small portions to avoid any possible overflow leading to loss of material from the beaker. The beakers were covered with watch glass, and heated over a hot plate at 90^{O}C for two hours. The beaker wall and watch glass were washed with distilled water and the samples were filtered out to separate the insoluble solid from the supernatant liquid. The volumes were adjusted to 100cm^3 with distilled water.

Table 1. Mean concentrations of heavy metals in soil samples from Mirnga agricultural location, Biu, Borno State.

Sample Depth	Conc (Mg/kg)							
	Cr	Mn	Fe	Ni	Pb	Zn	Cd	Cu
0-10 cm	15.45^{a}±0.23	26.66^{a}±2.34	33.34^{a}±0.44	12.76^{a}±2.33	8.94^{a}±1.44	34.44^{a}±1.23	3.45^{a}±0.32	1.34^{a}±0.21
10-20 cm	22.43^{b}±0.65	33.76^{b}±2.43	44.353^{b}±1.22	18.43^{b}±0.82	11.23^{b}±0.23	38.43^{b}±0.78	7.34^{b}±0.22	3.22^{b}±0.18
20-30 cm	34.54^{c}±1.23	45.87^{c}±0.98	51.34^{c}±0.66	25.65^{c}±0.33	17.23^{c}±0.44	42.34^{c}±24.85	12.45^{c}±0.21	5.34^{c}±0.34

Within columns mean with different letters are statistically different, P< 0.05

Table 2. Mean concentration of heavy metals in soil samples from Zira agricultural location, Biu, Borno State.

Sample Depth	Conc (Mg/kg)							
	Cr	Mn	Fe	Ni	Pb	Zn	Cd	Cu
0-10 cm	7.34^{a}±0.33	10.23^{a}±0.34	14.34^{a}±0.22	5.33^{a}±0.41	16.45^{a}±0.15	16.75^{a}±0.22	1.22^{a}±0.11	2.33^{a}±0.19
10-20 cm	8.34^{b}±0.23	12.65^{b}±0.33	16.77^{b}±0.32	6.34^{b}±1.32	18.32^{b}±0.55	23.44^{b}±1.43	2.54^{b}±0.31	5.34^{b}±0.12
20-30 cm	11.23^{c}±0.33	15.54^{c}±1.44	18.87^{c}±0.61	9.34^{c}±3.22	22.34^{c}±0.23	26.77^{c}±1.33	4.33^{c}±0.14	7.11^{c}±0.31

Within Columns Mean with different letters are statistically different, P< 0.05

Elemental analysis of soil samples

Determination of Pb, Fe, Cu, Zn, Cd, Ni, Mn and Cr were made directly on each final solution using Perkin-Elmer Analyst 300 Atomic Absorption Spectroscopy (AAS).

Determination of pH, Electrical Conductivity, Organic Matter, Organic Carbon, Salinity, Na, Ca, K and Cation exchanged capacity

The pH was measured using a 1:2 soil: water ratio (Mclean, 1982); electrical conductivity was determined using the aqueous extraction (1/5) method (Mathieu and Pieltain, 2003). Organic matter and organic carbon (OC) were determined using Anne method (modified Walkey-Black method) (Mathieu and Pieltain, 2003). Exchangeable cations Ca, Na and K were extracted with ammonium acetate at pH 7 and Ca, Na and K concentrations were determined by volumetric method using EDTA as the chelating agent (Afnor, 2002). Salinity was determined using method described Rhoades by (1982).
Cation exchanged capacity (CEC) was determined using standard method taken from Rowell (1994). The cation used in this method to saturate the soil solution is Na. Five gramme (5g) of soil were weighed into a 50 mL plastic centrifuge tube and 30 mL of 1 M NaOAc pH 8.2 were added. The sample was shaken at an end-to-and shaker at 21^{0}C for 5 minutes and was then centrifuged for 10 minutes at 4000 rpm. The supernatant was discarded and 30 mL of 1 M NaOAc pH 8.2 was added the sample was resuspended and the procedure was repeated for another 2 times. After the supernatant was discarded for the third time 30 mL of 95 % ethanol solution were added, the sample was resuspended and another 3 cycles were conducted. At the end of the third cycle, 30 mL of NH4OAc pH 7 were added, the sample was resuspended and a new phase of 3 cycles was commenced. This time the supernatants were filtered through a filter paper, Whatman No 42, and collected into a 100 mL volumetric flask. At the end this, the flask was taken to volume with NH4OAc pH 7 solution. The samples were kept at 4^{0}C until Na was measured on the UV-spectrophotometer according to standard

Table 3. Mean concentration of heavy metals in soil samples from Wangaga agricultural location, Biu, Borno State

Sample Depth	Conc (Mg/kg)							
	Cr	Mn	Fe	Ni	Pb	Zn	Cd	Cu
0-10 cm	26.34^{a}±2.54	18.33^{a}±2.54	32.34^{a}±1.98	4.55^{a}±1.23	2.43^{a}±1.34	12.45^{a}±1.98	6.78^{a}±0.33	6.34^{a}±1.23
10-20 cm	35.34^{b}±2.44	21.41^{b}±0.45	45.44^{b}±0.34	7.34^{b}±1.34	4.56^{b}±0.45	16.34^{b}±0.79	8.23^{b}±1.34	10.22^{b}±0.22
20-30 cm	43.54^{c}±3.22	27.33^{c}±3.23	58.34^{c}±2.78	11.41^{c}±0.76	6.45^{c}±0.67	18.34^{c}±0.34	11.23^{c}±0.44	13.24^{c}±0.22

Within Columns Mean with different letters are statistically different, P< 0.05

Table 4. Mean concentrations of heavy metals in soil samples from Malang agricultural location, Biu, Borno State.

	Conc (Mg/kg)							
	Cr	Mn	Fe	Ni	Pb	Zn	Cd	Cu
0-10 cm	13.23^{a}±0.33	17.34^{a}±1.34	22.45^{a}±1.55	2.33^{a}±0.34	4.66^{a}±0.45	9.76^{a}±0.56	10.56^{a}±1.06	15.22^{a}±1.32
10-20 cm	16.34^{b}±1.22	24.44^{b}±0.23	24.65^{b}±2.45	5.67^{b}±0.54	5.87^{b}±0.44	11.45^{b}±0.65	15.56^{b}±1.56	19.34^{b}±1.43
20-30 cm	18.23^{c}±19.12	26.23^{c}±0.43	27.45^{c}±2.45	8.45^{c}±0.44	7.45^{c}±0.21	14.55^{c}±0.32	18.43^{c}±0.56	23.65^{c}±2.13

Within Columns Mean with different letters are statistically different, P< 0.05

procedure. CEC value was then determined by the formula

$$\text{CEC, cmol}_c\ \text{kg}^{-1}\ \text{soil} = \frac{10 * \text{Na concentration in mg L}^{-1}}{\text{Mass of sample (g)}}$$

RESULTS

Concentrations of heavy metals in soil samples

The concentration of heavy metals in cultivated soil samples at different depth from the Mirnga agricultural location is as presented Table 1. The concentrations of Cr ranged between 15.45±0.23 and 34.54±1.23 mg/kg; 26.66±2.43 and 45.87±0.98 mg/kg Mn; 33.34±0.44 and 51.34-±0.66 mg/kg Fe; 12.76±2.33 and 25.65±0.33 mg/kg Ni; 8.94±1.44 to 17.23±0.44 mg/kg Pb; 34.44±1.23 and 42.34±3.22 mg/kg Zn; 3.45±0.32 and 12.45±0.21 mg/kg Cd and 1.34±0.21 and 5.34±0.34 mg/kg. the levels of heavy metals in Mirnga agricultural location are in the following order Fe > Zn >Mn> Cr > Ni >Pb> Cd >Cu. The mean concentrations for heavy metals in soils samples collected from Zira agricultural location ranged between 7.34±0.33 and 11.23±0.56 mg/kg; 10.23±0.34 and 15.54±1.44 mg/kg Mn; 14.34±0.22 and 18.87±0.61 mg/kg Fe; 5.33±0.41 and 9.34±0.41 mg/kg Ni; 16.45±0.15 to 22.34±0.23 mg/kg Pb; 16.75±0.22 and 26.77±1.33 mg/kg Zn; 1.22±0.11 and 4.33±0.14 mg/kg Cd and 2.33±0.19 and 7.11±0.31 mg/kg. The sequence of heavy metals in the soil samples in the Zira location are Zn >Pb> Fe >Mn> Cr > Ni > Cu >Cd.

Table 3 present the levels of heavy metals in Wangaga agricultural location. Cr levels ranged between 26.34±2.54 and 43.54±3.22 mg/kg; 18.33±2.54 and 27.33±3.23 mg/kg Mn; 32.34±1.98 and 58.34±2.78 mg/kg Fe; 4.55±1.23 and 11.41±0.76 mg/kg Ni; 2.43±1.34 to 6.45±0.67 mg/kg Pb; 12.45±1.98 and 18.34±0.34 mg/kg Zn; 6.78±0.33 and 11.23±0.44 mg/kg Cd and 6.34±1.23 and 1.24±0.22 mg/kg. The levels of heavy metals in the Wangaga location are in the order of Fe > Cr >Mn> Zn > Cu > Cd > Ni >Pb. From Table 4, the mean concentration of Cr in Malang agricultural location ranged between 13.23±0.33 and 18.23±1.92 mg/kg; 17.34±1.34 and 26.23±0.43 mg/kg Mn; 22.45±1.55 and27.45±2.45 mg/kg Fe; 2.33±0.34 and 8.45±0.44 mg/kg Ni; 4.66±0.45 to 7.45±0.21-

Table 5. Comparison in the concentrations of heavy metals in soil samples between the four agricultural locations at depth 0-10cm.

	Conc (Mg/kg)							
	Cr	Mn	Fe	Ni	Pb	Zn	Cd	Cu
Mirnga	15.45^{a}±0.23	26.66^{a}±2.34	33.34^{a}±0.44	12.76^{a}±2.33	8.94^{a}±1.44	34.44^{a}±1.23	3.45^{a}±0.32	1.34^{a}±0.21
Zira,	7.34^{b}±0.33	10.23^{b}±0.34	14.34^{b}±0.22	5.33^{b}±0.41	16.45^{b}±0.15	16.75^{b}±0.22	1.22^{b}±0.11	2.33^{b}±0.19
Wangaga	26.34^{c}±2.54	18.33^{c}±2.54	32.34^{c}±1.98	4.55^{c}±1.23	2.43^{c}±1.34	12.45^{c}±1.98	6.78^{c}±0.33	6.34^{c}±1.23
Malang	13.23^{d}±0.33	17.34^{d}±1.34	22.45^{d}±1.55	2.33^{d}±0.34	4.66^{d}±0.45	9.76^{d}±0.56	10.56^{d}±1.06	15.22^{d}±1.32

Within Columns Mean with different letters are statistically different, $P< 0.05$

Table 6. Comparison in the concentrations of heavy metals in soil samples between the four agricultural locations at depth 10-20cm.

	Conc (Mg/kg)							
	Cr	Mn	Fe	Ni	Pb	Zn	Cd	Cu
Mirnga	22.43^{a}±0.65	33.76^{a}±2.43	44.353^{a}±1.22	18.43^{a}±0.82	11.23^{a}±0.23	38.43^{a}±0.78	7.34^{a}±0.22	3.22^{a}±0.18
Zira,	8.34^{b}±0.23	12.65^{b}±0.33	16.77^{b}±0.32	6.34^{b}±1.32	18.32^{b}±0.55	23.44^{b}±1.43	2.54^{b}±0.31	5.34^{b}±0.12
Wangaga	35.34^{c}±2.44	21.41^{c}±0.45	45.44^{c}±0.34	7.34^{c}±1.34	4.56^{c}±0.45	16.34^{c}±0.79	8.23^{c}±1.34	10.22^{c}±0.22
Malang	16.34^{d}±1.22	24.44^{d}±0.23	24.65^{d}±2.45	5.67^{d}±0.54	5.87^{d}±0.44	11.45^{d}±0.65	15.56^{d}±1.56	19.34^{d}±1.43

Within Columns Mean with different letters are statistically different, $P< 0.05$

Table 7. Comparison in the concentrations of heavy metals in soil samples between the four agricultural locations at depth 20-30cm.

	Conc (Mg/kg)							
	Cr	Mn	Fe	Ni	Pb	Zn	Cd	Cu
Mirnga	34.54^{a}±1.23	45.87^{a}±0.98	51.34^{a}±0.66	25.65^{a}±0.33	17.23^{a}±0.44	42.34^{a}±24.85	12.45^{a}±0.21	5.34^{a}±0.34
Zira,	11.23^{b}±0.33	15.54^{b}±1.44	18.87^{b}±0.61	9.34^{b}±3.22	22.34^{b}±0.23	26.77^{b}±1.33	4.33^{b}±0.14	7.11^{b}±0.31
Wangaga	43.54^{c}±3.22	27.33^{c}±3.23	58.34^{c}±2.78	11.41^{c}±0.76	6.45^{c}±0.67	18.34^{c}±0.34	11.23^{c}±0.44	13.24^{c}±0.22
Malang	18.23^{d}±19.12	26.23^{d}±0.43	27.45^{d}±2.45	8.45^{d}±0.44	7.45^{d}±0.21	14.55^{d}±0.32	18.43^{d}±0.56	23.65^{d}±2.13

Within Columns Mean with different letters are statistically different, $P< 0.05$

mg/kg Pb; 9.76±0.56 and 14.55±0.32 mg/kg Zn; 10.56±1.06 and 18.43±0.56 mg/kg Cd and 15.22±1.32 and 23.65±2.13 mg/kg. The order of metal concentrations in the Malang agricultural location is Fe >Mn> Cu > Cr > Cd > Zn >Pb>Ni.

Table 5 shows the comparison in the concentrations of heavy metals at depth 0-10cm between locations. Cr levels ranged between 7.34±0.33 and 26.34±2.54 mg/kg; 10.23±0.34 and 14.34±0.22 mg/kg Mn; 2.33±0.34 and 12.76±2.33 mg/kg Fe; 2.43±1.34 and 16.45±0.15 mg/kg Ni; 9.76±0.56 to 34.44±1.23 mg/kg Pb; 9.76±0.56 and

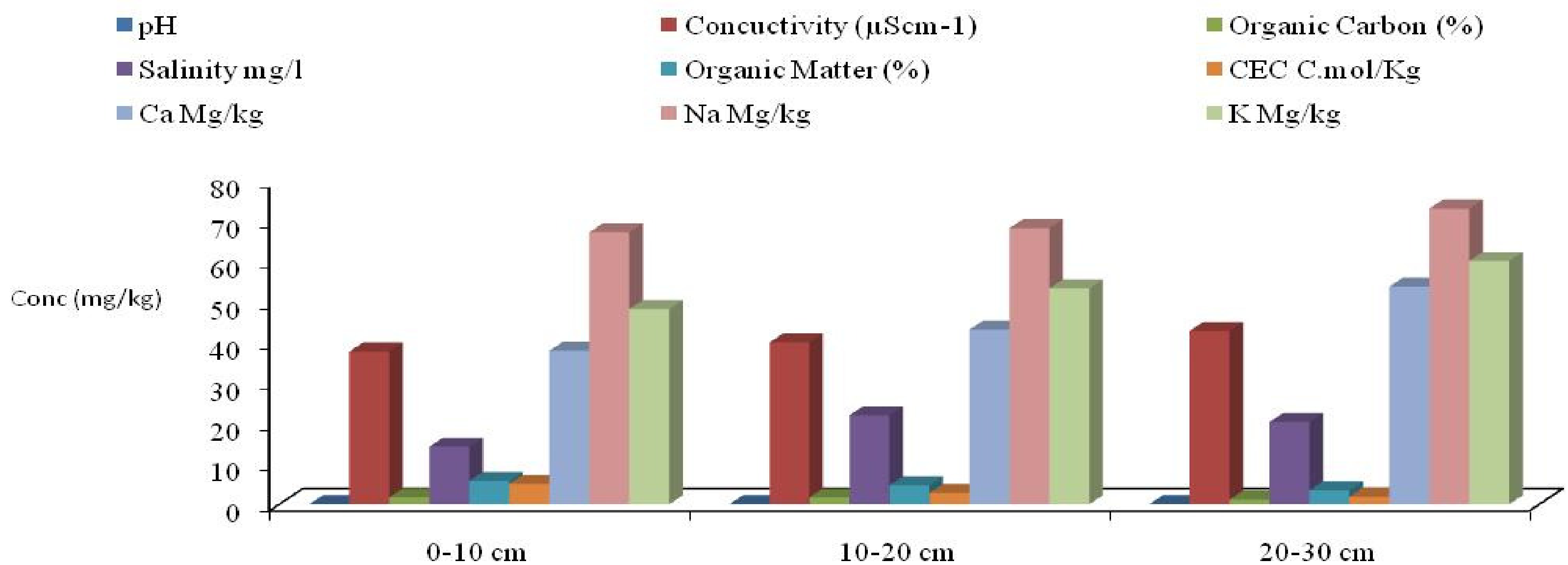

Figure 1. Mean concentrations of some physicochemical parameters in soil samples from Mirnga agricultural location, Biu, Borno State

34.44±1.23 mg/kg Zn; 1.22±0.11 and 10.56±1.06 mg/kg Cd and 1.34±0.21 and 15.22±1.32 mg/kg. Similarly, the comparison of heavy metals in the cultivated soil from different locations at depths 10-20cm are as presented in Table 6. Cr levels ranged between 8.34±0.23 and 35.34±2.44 mg/kg; 12.65±0.33 and 24.44±0.23 mg/kg Mn; 16.77±0.32 and 45.44±0.34 mg/kg Fe; 5.67±0.54 and 18.43±0.82 mg/kg Ni; 4.56±0.45 to 18.32±0.55 mg/kg Pb; 11.45±0.65 and 38.43±0.78 mg/kg Zn; 2.54±0.31 and 15.56±1.56 mg/kg Cd and 3.22±0.18 and 19.34±1.43 mg/kg. The comparison of heavy metals at depth of 20-30 cm from different locations is as presented in Table 7. Cr levels ranged between 11.23±0.33 and 43.54±3.22 mg/kg; 15.54±1.44 and 45.87±0.98 mg/kg Mn; 18.87±0.61 and 58.34±2.78 mg/kg Fe; 8.45±0.44 and 25.65±0.33 mg/kg Ni; 6.45±0.67 to 22.34±0.23 mg/kg Pb; 14.55±0.32 and 42.34±3.22 mg/kg Zn; 4.33±0.14 and 18.43±0.56 mg/kg Cd and 5.34±0.34 and 23.65±2.13 mg/kg. The levels of heavy metals in the soil samples fluctuate between locations. Wangaga agricultural location shows the highest levels of Cr, while Zira location shows the least levels. For Mn levels, Mirnga showed the highest while Zira shows the least concentrations. The maximum concentration of Fe was observed in Wangaga location, while the minimum was in Zira. Ni concentration in soil samples was highest in Mirnga, while Malang shows the least level.

Similarly for Pb concentration, the maximum was observed in Zira, while wangaga location shows the least level. The level of Zn was highest in Mirnga, while Malang shows the least concentration. Cd concentration was maximum at Malang location, while Zira showed the minimum levels. Malang agricultural location shows the highest concentrations Cu, while Mirnga showed the least concentration of Cu.

Levels of some physicochemical parameters in soil samples

The physical and chemical soil properties from Mirnga and Zira agricultural locations are as presented in Figure 1 and 2. The mean levels of

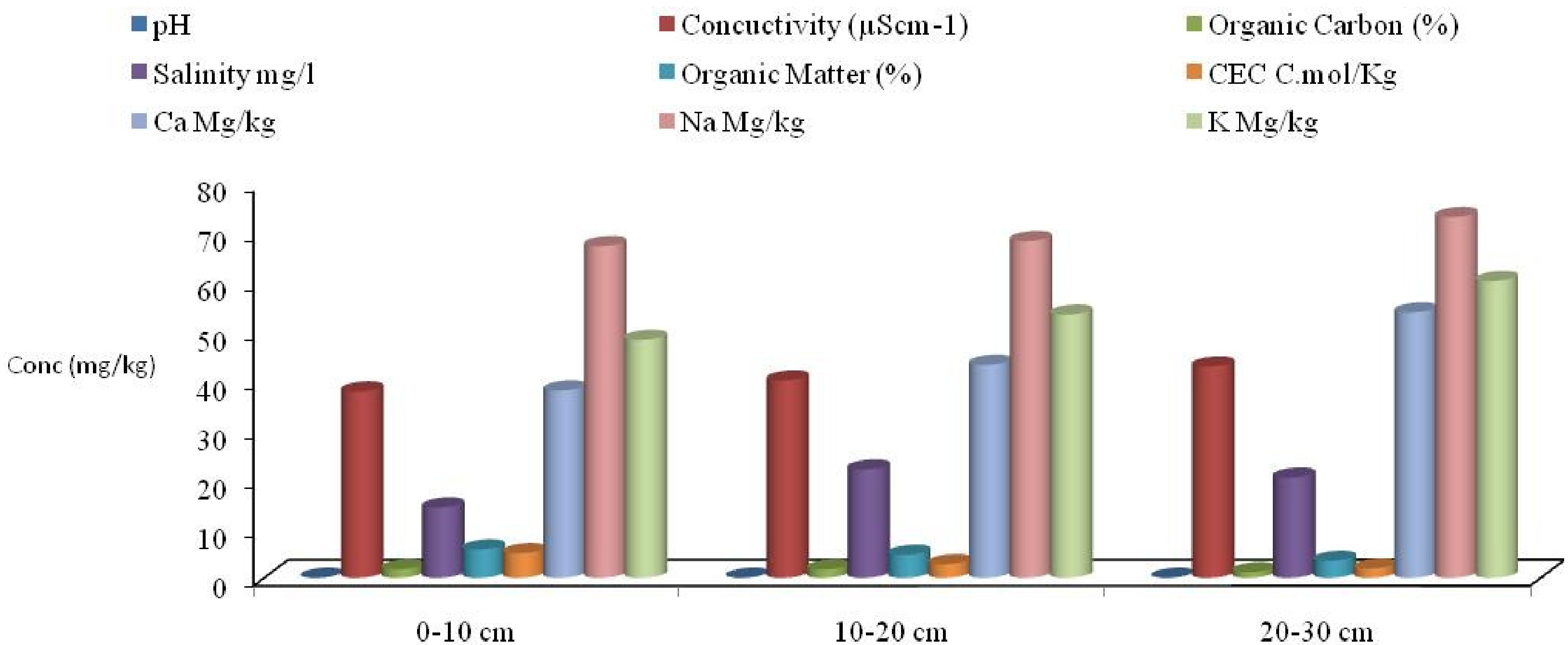

Figure 2. Mean concentrations of some physicochemical parameters in soil samples from Zira agricultural location, Biu, Borno State

pH with respect to depth ranged from 2.87 to 9.80; 22.11 to 42.87µScm^{-1} Conductivity; 1.13 to 3.45% organic carbon; 9.87 to 21.99mg/l salinity; 3.42 to 11.45% organic matter; 1.87 to 4.98 CEC C.mol/kg; 38.00 to 63.23 mg/kg Ca; 22.30 to 73.22 mg/kg Na and 7.45 to 60.23 mg/kg K. For that of Wangaga and Malang agricultural locations, the levels of pH ranged from 1.45 to 4.98; 8.75 to 62.10 µScm^{-1} Conductivity; 2.98 to 7.96% organic carbon; 6.86 to 32.14mg/l salinity; 1.86 to 8.78% organic matter; 2.43 to 32.76 CEC C.mol/kg; 32.45 to 54.67 mg/kg Ca; 18.95 to 33.96 mg/kg Na and 19.09 to 60.23 mg/kg K Figure 3 and 4. The levels of pH in the entire locations fluctuate between acidic and alkaline.

Concentrations of some anions in soil samples

Figure 5 present the levels of heavy nitrate, nitrite, sulphate and phosphate in soil samples from Mirnga and Zira agricultural locations. Nitrate concentrations ranged from 1388.00 to 1698.00 mg/kg; 20.00 to 52.00 mg/kg nitrite; 2543.00 to 5322.00 mg/kg and 456.00 to 1087.00 mg/kg. Similarly the levels of nitrate, nitrite, sulphate and phosphate in soil samples from the Wangaga and Malang agricultural locations is as presented in Figure 6. Levels of nitrate ranged from 421.00 to 1843 mg/kg; 31.00 to 68 mg/kg; 544.00 to 6342 mg/kg sulphate and 121.00 to 1234.00 mg/kg phosphate. The levels of all the anions in the soil samples were higher in Wangaga location, while Zira location shows the least values. Sulphate shows the highest level, while phosphate shows the least. They were also a significant increase in concentrations of all the anions in the soil samples with increase with depth.

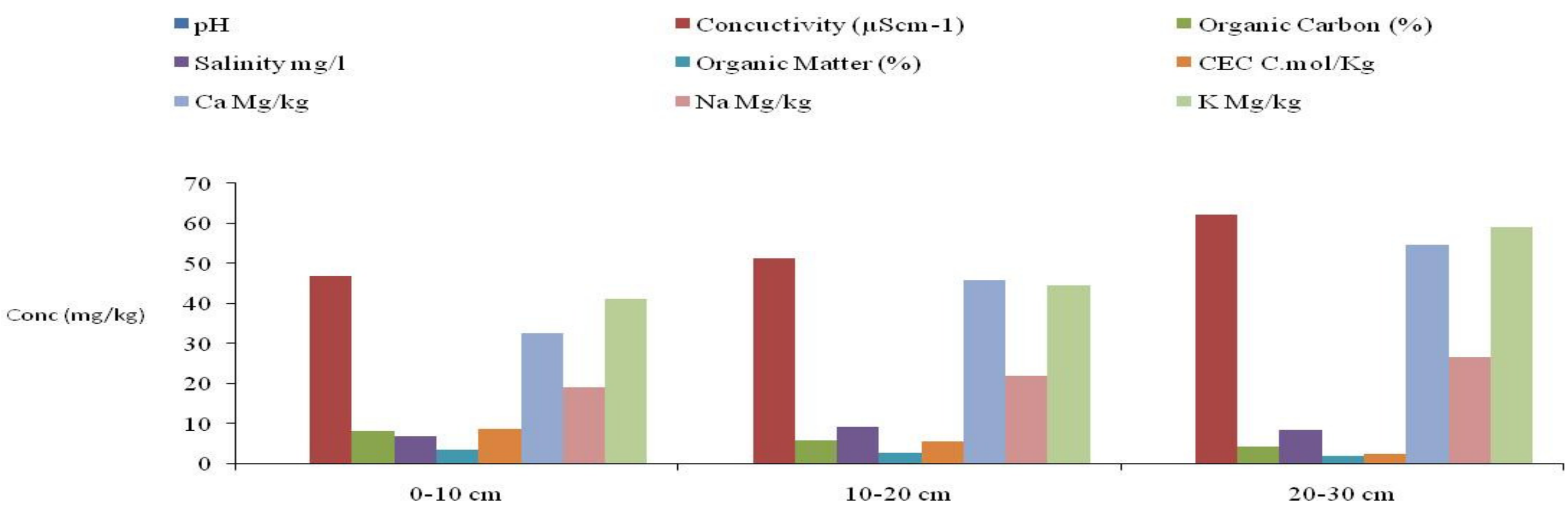

Figure 3. Mean concentrations of some physicochemical parameters in soil samples from Wangaga agricultural location, Biu, Borno State

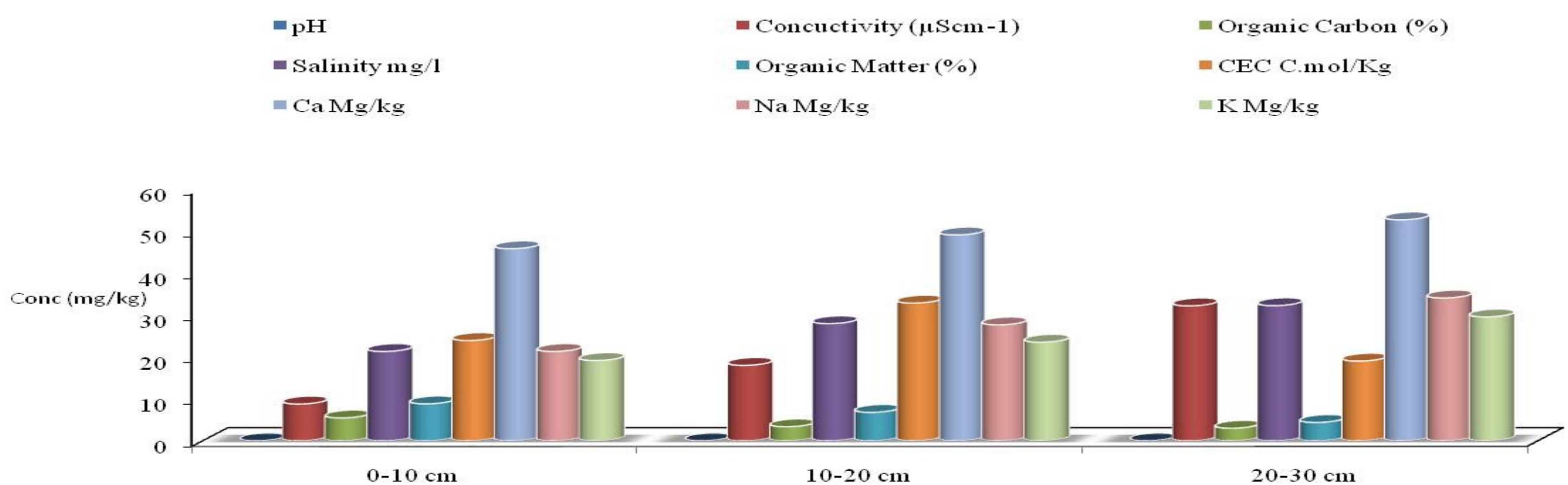

Figure 4. Mean concentrations of some physicochemical parameters in soil samples from Malang agricultural location, Biu, Borno State

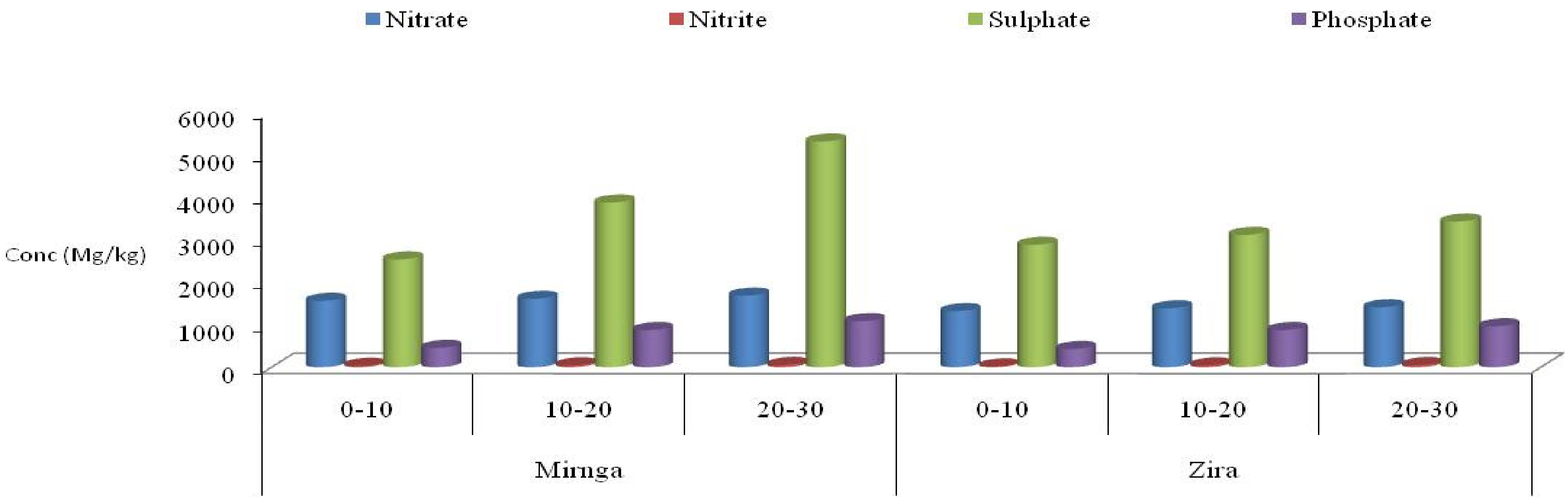

Figure 5. Mean concentrations of nitrate, nitrite, sulphate and phosphate in soil samples from Mirnga and Zira agricultural locations by depth

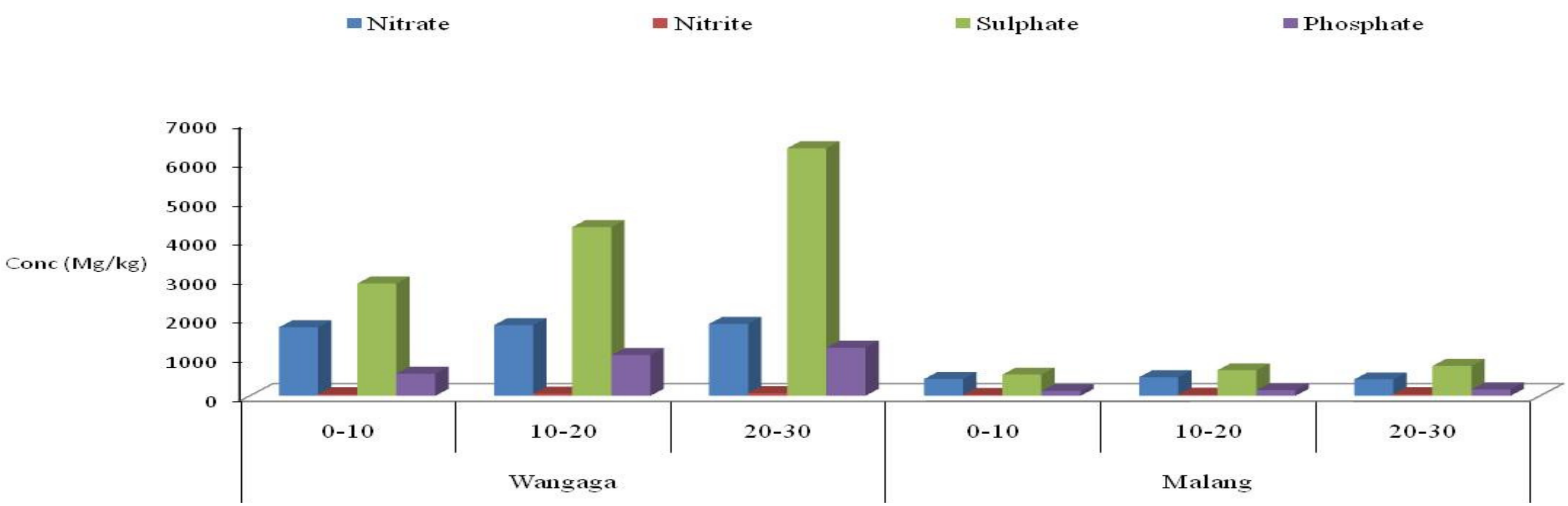

Figure 6. Mean concentrations of nitrate, nitrite sulphate and phosphate in soil samples from Mirnga and Zira agricultural locations by depth

DISCUSSION

The fluctuation of heavy metals in the four agricultural locations could be attributed to differences in agricultural activities and environmental factors in the sample areas. The higher concentrations of heavy metals in the soil samples obtained in these locations could be attributed to excessive usage of fertilizers and other agro-chemicals in the areas. The levels of organic carbon and organic matter in the four sample locations decreased significantly with depth. It was also observed that the maximum level of organic carbon was detected in the Wangaga location, while the minimum was observed in Mirnga location. For organic matter the maximum was detected at Zira location, while the minimum was observed in Malang location. Organic Carbon (OC) increased with increase in sludge application rate Willett *et al.,* 1984). In the present study, it was observed that OC increases significantly during the sampling period to a depth of 20-30cm ($p < 0.05$) Figure 1 to 4. OC also increased with the increase in the water rate Davis *et al.,* 1988). This may be of significant environmental consequences, because it was observed that higher rates of applied water may influence the amounts of OC, and this also influence the solubility and availability of heavy metals. This was in line with the present study.

The soil pH of the Wangaga location was significantly acidic compared to other location. . pH is one of the factors which influence the bioavailability and the transport of heavy metal in the soil and according to Smith and Giller (1992) heavy metal mobility decreases with increasing soil pH due to precipitation of hydroxides, carbonates or formation of insoluble organic complexes. In the present study, it was observed that heavy metals increased significantly with depths due to decreased levels of pH. The soil electrical conductivity (EC) also differed significantly among the four agricultural locations ($P < 0.05$). By comparism, Boulding (1994) classified EC of soils as: non saline <2; moderately saline 2-8; very saline 8-above; extremely saline >16. From the result of the study, the EC is classified as extremely saline. The amount of heavy metals mobilized in soil environment is a function of pH, properties of metals, redox conditions, soil chemistry, organic matter content, clay content, cation exchange capacity, and other soil properties (Arun and Mukherjee, 1998; Sauve*et al.,* 2000). Heavy metals are generally more mobile at pH < 7 than at pH > 7. The pH of the soils from the four agricultural locations ranged from 1.87 to 9.80. This is therefore hazardous for agricultural purposes since crops are known to take up and accumulate heavy metal from contaminated soils in their edible portions (Wei *et al.,* 2005).

For the four agricultural locations, the higher OC content was found higher at the Wangaga and Malang locations. This could be attributed to the decomposition of organic matter due to the agricultural activities. Moreover, the temperature in the study areas must have favored the activities of microorganisms on soil organic matter. The Ca Na and K contents were highest at Mirnga location, while Wangaga shows the least levels. This may be connected to the heterogeneous nature of agricultural activities within the study areas, which is expected to impact differently on soil properties (Oyedele*et al.,* 2008).Generally, the levels of heavy metals, Ca, Na and K in the soil samples for the four agricultural locations increased significantly ($p < 0.05$) to a depth of 30cm, while pH, Organic carbon, Conductivity, salinity, organic matter, CEC, decreased to a depth of 30 cm.

The high levels of all the anions in the soil samples compared with the vegetable samples might be attributed to possible pollution of the soils as a result of excessive usage of fertilizers, herbicides and other agro-chemicals, and as well as other environmental conditions pertinent in the areas.In general, the results revealed the soils in the sample areas to be acidic with low organic matter contents. Similarly, organic matter plays an important role in soil structure, aggregation, infiltration and retention of water, and other physical characteristics. Furthermore, the adsorption complex (clay and humus) serves the soil as a store of nutrients and is a significant contributor to the buffering capacity of soils even as cation exchange capacity can be used to determine the amount of lime that needs to be applied to reduce acidification.

CONCLUSION

The results obtained from this study clearly show that pH and organic carbon influence the solubility and mobility of heavy metals. Generally, the levels of heavy metals, anions, Ca, Na and K in the soil samples for the four agricultural locations increased significantly ($p < 0.05$) to a depth of 30 cm, while pH, Organic carbon, Conductivity, salinity, organic matter, CEC, decreased to a depth of 30 cm.

REFERENCES

Afnor (2002). Quality of the soils. Determination of exchangeable cations Ca^{2+}. Mg^{2+}KH, Na^{+} with ammonium acetate. The French Normalization Association. NF X 31-108.

Arun BM (1998). Nickel: a review of occurrence, uses, emissions, and concentration in the environment in Finland. Environ. Rev. 6: 1-15.

Biasioli M, Grcman H, Kralj T, Madrid F, Dıaz-Barrientos E,Ajmone-Marsan F (2007). Potentially toxic elements contamination in urban soils: a comparison of three European cities. J. Environ. Qual. 36:70–79

Boulding JR (1994). Description and sampling of Contaminated Soils.Afeild Guide. 2ndEdn.

Brewster UC, Perazella MA (2004). A review of chronic lead intoxication: an unrecognized cause of chronic kidney disease. Am J Med Sci 327(6):341–347

Davis RD, Charlton-Smith CH, Stark JH, Campbell JA (1988). Distribution of metals in grassland soils following surface applications of sewage sludge. *Environmental Pollution* 49, 99-115

De-Miguel E, Iribarren I, Chacon E, Ordonez A, Charlesworth S (2007). Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). Chemosphere 66:505–513

Dowdy RF, Volk VV (1983). Movement of heavy metals in soils. In: *Chemical Mobility and Reactivity in Soil Systems.* Soil Science Society of America and American Society of Agronomy, Madison, pp.229-240.

Environ 408:3965–3975

EU (2008). *European commission soil policy.*(http://ec. europa.eu/environment/soil/index_en.htm).

Evans LJ, Spiers GA, Zhao G (1995). Chemical aspects of heavy metal solubility with reference to sewage sludge-amended soils. Int. J. Environ. Anal. Chem. 59, 291-302.

Flores L, Bias G, Hernadez G, Alcala R (1997). Distribution and sequential extraction of some heavy metals from soils irrigated with waste water from Mexico city. *Water, Air and Soil Pollution* 98, 105-1 17.

He QB, Singh R (1993). Effect of organic matter on the distribution, extractability and uptake of cadmium in soils. J. Soil Sci. 44, 641-650.

Kabata-Pendias A (2001). Trace elements in soils and plants. 3rd ed, CRC Press, Boca Raton, USA.

Lewis Publishers, Boca Raton, FL, Chapter 5.

Maliszewska-Kordybach B, Smreczak B (2003). Habitat function of agricultural soils as affected by heavy metals and polycyclic aromatic hydrocarbons contamination. *Environment International, 28,* 719–728.

Mathieu C, Pieltain F (2003). Chemical analysis of soils. Selected methods. France, pp 387.

McLean EG (1982). Soil pH and lime requirement. In: A.L. Page, R.H. Miller, and D.R.Keeney (cds.), Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties. 2nd ed. American Society of Agronomy, Madison, WI, pp. 199-224.

Mielke HW, Laidlaw MAS, Gonzales C (2010). Lead (Pb) legacy from vehicle traffic in eight California urbanized areas: continuing influence of lead dust on children's health. Sci Total

Navas-Acien A, Guallar E, Silbergeld EK, Rothenberg SJ (2007). Lead exposure and cardiovascular disease—a systematic review. Environ Health Perspect 115(3):472–482

Nicholson FA, Smith SR, Alloway BJ, Carlton- Smith C, Chambers BJ (2003). An inventory of heavy metals inputs to agricultural soils in England and Wales. *The Science of the Total Environment, 311,* 205–219.

Oliver DP, Tiller KG, Alston AM, Cozens GD, Merry RH (1998). Effect of soil pH and applied cadmium on cadmium concentration in wheat grain. Aus. J. Soil Res. 36, 57 1-583.

Oyedele DJ, Gasu MB, Awotoye OO (2008). Changes in soil properties and plant uptake of heavy metals on selected municipal solid waste dump sites in Ile-Ife, Nigeria. Afr. J. Environ. Sci. Technol. Vol. 3 (5): 107-115

Piccolo A (1989). Reactivity of added humic substances towards plant available heavy metals in soils. *The Science of the Total Environment* 81 /82, 607-614.

Pueyo M, Rauret G, Luck D, Yli-Halla M, Muntau H, Quevauville P (2001). Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. J. Environ. Monitor. *3,* 243–250.

Rhoades JD (1982). Cation exchange capacity. In: A.L. Page, R.H. Miller, and D.R.Keeney (eds.), Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties. 2nd ed. American Society of Agronomy, Madison, WI, pp. 149-158.

Rowell DL (1994), *Soil Science: Methods and Applications.* Longman, Harlow.

Salam AK, Helmke PA (1998). The pH dependence of free ionic activities and total dissolved concentrations of copper and cadmium in soil solution. *Geoderma*83, 281-291.

Sauve S, Henderson W, Allen HE (2000). Solid-solution portioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. Environ. Sci. Technol. 34: 1125- 1131.

Smith SR, Giller KE (1992). Effective *Rhizombiumlegumino-sarum*biovar*Trifolii* present in five soils contaminated with heavy metals from long-term applications of sewage sludge or metal mine spoil. *Soil Biology and Biochemistry* 24, 781-788

Temminghoff EJM, vanderZee TM, De Haan HAM (1997). Copper mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved organic matter. *Environmental Science and Technolgy*3 1 , 1 1 0 9 -1115.

Wei S, Zhou Q, Xin W (2005). Identification of weed plants excluding the uptake of heavy metals. Environment International. p. 31, pp. 829-834.

Willett IR, Jakobsen P, Malafant KWJ, Bond WJ (1984). Effect of land disposal of lime treated sewage sludge on soil properties and plant growth. Division of Water and Land Resource. CSIRO. Canberra. Div. Rep., 84/3:56.

Wilson CA, Cresser MS Davidson DA (2006). Sequential element extraction of soils from abandoned farms: An investigation of the partitioning of anthropogenic element inputs from historic land use. J. Environ. Monitor. *8,* 439–444.