academicJournals

Vol. 8(44), pp. 5429-5439, 14 November, 2013
DOI: 10.5897/AJAR09.188
ISSN 1991-637X ©2013 Academic Journals
http://www.academicjournals.org/AJAR

African Journal of Agricultural Research

Full Length Research Paper

Pedogenic impacts on the distribution of total and available Fe, Mn, Cu, Zn, Cd, Pb and Co contents of vertisols and vertic inceptisols of the Bale Mountain area of Ethiopia

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Accepted 26 June, 2010

Total and DTPA-extractable micronutrient cations and heavy metals were determined for some 'vertisols and vertic inceptisols' of the Bale Mountain area of Ethiopia. Total micronutrients and heavy metal contents in these soils were 4.8 to 11.9% Fe, 774 to 2947 ug/g Mn, 55 to 143 ug/g Zn, 5 to 65 ug/g Cu, 19 to 119 ug/g Co, 6 to 35 ug/g Pb and 0 to 4 ug/g Cd, and are generally within the ranges reported worldwide for similar soils. DTPA-extractable Fe, Mn, Zn, Cu, Co, Pb and Cd ranged from 1.81 to 17.4, 5.9 to 41.5, 0.07 to 0.37, 0.70 to 1.73, 0.07 to 0.83, 0.04 to 1.31 and 0.0 to 0.02 ug/g, respectively. Available indices of the micronutrients studied are believed to be sufficient for plant growth except Zn, which is inadequate. Available heavy metal contents are below tolerable levels that can pose danger to man and livestock. Extractable micronutrients and heavy metals generally showed a decrease in concentration with depth associated with decreasing organic carbon contents and increasing pH and $CaCO_3$ contents that exert a major influence on the availability of the micronutrients and heavy metals. Multiple linear and quadratic regression equations generally improved the predictive abilities for available Fe, Mn, Cu, Zn and Co over simple linear relationships when pH, EC, OC and $CaCO_3$ were used as independent variables. Regression relationships developed constitute useful predictive indices for estimating micronutrients and heavy metals from existing soil survey reports of the Bale Mountain area.

Key words: Ethiopia, Bale Mountain, micronutrients, heavy metals, soils, vertisols, regression relationship.

INTRODUCTION

The Bale Mountain area of Ethiopia is coming under increased pressure for the production of food and fuel to meet the needs of the increasing population. This has resulted in increased deforestation of the adjoining Bale National Park for the production of fuel wood, land preparation for crop cultivation and cattle grazing. The result is that at the present rate of exploitation the survival of this tourist resort is at stake. Most of the

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cultivated area is put to barley (*Hordeum vulgare*) and wheat (*Triticum aestivum*) and the grasslands to sheep, goats and cattle grazing. Soil survey and other socio-economic studies had earlier been carried out by the Land Use Service to enable conception of judicious management strategies necessary for proper management for sustainability. The implementation of some of the findings of these studies are believed to result in increased food production per unit area and having a direct impact on the Bale Mountain National Park through reduction in pressures for additional agricultural land and fuel wood. In the future, increased and sustained food production will need fertilizer amendments. Under heavy or continuous fertilization, micronutrients and other heavy metals could also be introduced into the soil. Also, important changes in the forms and amounts of these elements can occur in the soils and affect their uptake by plants.

Micronutrient and heavy metal data for the soils of the Bale Mountain area of Ethiopia, like most tropical environments, are sparse to nonexistent. Because of the important role of micronutrients in plant growth and the delicate balance between adequacy and deficiency, their determination is important as a guide to fertilization. Cattle rearing are also a predominant occupation in the Bale Mountain area of Ethiopia. Low concentrations of available micronutrients are not only a deterrent to pasture growth, but can also cause physiological disorders in cattle or livestock (Reid and Horvath, 1980; Haynes and Swift, 1984). Though, risk of contamination from heavy metals is minimal, acquisition of base line data on their concentrations would be useful in future in decision making about the type of organic and/or inorganic fertilizers that could be applied. Given the important role of micronutrients in plant growth and animal nutrition and the deleterious effects of heavy metal contamination in the environment, the determination of background levels of these elements is therefore an important guide to obviate physiological disorders in grazing animals as well as serve as initial threshold levels for studying micronutrient concentrations and heavy metal pollution in future. While the total micronutrients and heavy metals determine the elemental reserves, the available micronutrients and heavy metals are of more importance since they constitute the labile pool taken up by the plants.

Ranges of concentrations of total micronutrients and heavy metals in some vertisols and clay soils worldwide are presented on Table 1. Heavy metal content and distribution in soils are influenced by several factors including organic matter content, particle-size distribution, parent material, drainage, soil age, vegetation and aerosol input (Esser et al., 1991; Lee et al., 1997). Karathanasis and Seta (1993) have pointed out that naturally occurring background levels of heavy metals in uncontaminated soils usually occur in trace amounts related to the biogeochemistry of the parent materials.

Alloway (1995) also reported that mafic and ultramafic parent materials contain more heavy metals than siliceous rocks. Tiller (1958) observed that feldspars, micas, Fe oxides and hydroxides, clay minerals and humus are the main carriers of heavy metals with each of these groups selective for several metals. Secondary Fe and Al hydroxides have been reported to be important in sorption of heavy metals released by weathering (Koons et al., 1980). 'vertisols and vertic inceptisols' in the Bale Mountain area occur on undulating foot slopes and flat inter mountain plains; they have developed from basaltic, alluvial and colluvial materials on 1 to 10% slopes. The climate of the Bale Mountain area is semi-arid with a marked wet and dry season. Mean annual rainfall and temperatures average is 800 to 1200 mm and 8 to 14°C, respectively. Soils are in the mesic temperature regimes.

Vegetation on mountain slopes is Juniperus woodland savanna; it is dominantly acacia on the plains. Man's influence, overgrazing and wild fires have eliminated most tree species within the lowlands and the mountain areas. Thus, given the potential toxicity to living systems, understanding biogeochemical cycling and accumulation of Fe, Mn, Cu, Zn, Co, Cd and Pb in these vertisols is important. The objectives of this study were to index the total and DTPA extractable levels of Fe, Mn, Cu, Zn, Co, Cd and Pb and investigate the influence of physical and chemical properties on the availability and total concentrations of these elements for better management and sustainable productivity of these soils.

MATERIALS AND METHODS

The soils of the study area (Figure 1) are composed of mostly moderately to poorly drained 'vertisols and vertic inceptisols', derived from varied parent materials, on 0 to 3% slopes at elevations exceeding 2350 m above sea level (Table 2). Samples were collected by genetic horizons from pits excavated to 1.5 to 2 m deep. They were described following standard terminology (FAO, 1990; FAO/UNESCO/ISRIC, 1989; Soil Survey Staff, 1975). Bulk samples were collected from each horizon. The soil samples were air-dried and the fine earth fraction screened through a 2-mm sieve. Particle size distribution, cation exchange capacity (CEC), exchangeable bases, EC, $CaCO_3$ percent and pH were determined on the fine earth fraction by standard procedures (Soil Conservation Service, 1984). Organic carbon was determined by the wet oxidation potassium dichromate method of Walkley and Black. Total N was determined by the Kjeldahl method. Total Fe, Mn, Cu, Zn, Co, Cd and Pb were determined by wet digestion in aqua regia; the available indices of these elements were extracted with DTPA solution and determined by an atomic absorption spectrophotometer. The relationships among physical and chemical properties were investigated using correlation and regression analysis (Gomez and Gomez, 1984). Statistical analysis was done using Microsoft Programme (Ecosoft Inc., 1984).

RESULTS AND DISCUSSION

Morphological properties

Munsell color values of surface horizons of these 'vertisols and vertic inceptisols' are generally around 3.1

Table 1. Ranges of concentrations of some total micronutrients and heavy metals in soils worldwide.

Element	Parent material	Soil type and area	Total concentration	Source
Fe	Earth’s crust	-	0.1 – 10%	Sillanpaa (1972), Bernard and Ellis (1980)
	Igneous and metamorphic rocks	Gezira Vertisols, Sudan	2 – 6.9%	Adam (1982)
	Lacustrine sediments and precambrian biotite schist	Vertisols and Alfisols of North Cameroon	2.01-6.54%	Yerima (1986), Yerima et al. (2003)
Mn	Earth’s crust and mineral soils	Mineral soils worldwide	<100 > 6000 (ug/g)	Sillanpaa (FAO Soil Bull. NO 17, 1972).
	Igneous and metamorphic rocks	Gezira vertisols, Sudan	534-941 (ug/g)	Adam (1982)
	Lacustrine sediments and precambrian biotite schist	Clayez sediments Chad and Vertisols in Indian	100-1000 (ug/g)	Aubert and Pinta (1977)
		Vertisols and Alfisols of North Cameroon	343-1230 (ug/g)	Yerima (1986), Yerima et al. (2003)
Cu	Earth’s crust	Australian black earths	2-100 (ug/g)	Sillanpaa (FAO Bull. NO. 17, 1972)
	Basic igneous and metamorphic rocks	Indian Vertisols	28-110 (ug/g)	Tiller (1983)
	Lacustrine sediments and precambrian biotite schist	Gezira Vertisols	200-250 (ug/g)	Aubert and Pinta (1977)
		Sudan	22-41 (ug/g)	Adam (1982)
		Vertisols and Alfisols of North Cameroon	33-101 (ug/g)	Yerima (1986); Yerima et al. (2003).
Zn	Earth’s crust	-	10-300 (ug/g)	Sillanpaa (FAO Soil Bull. NO. 17, 1972)
	Igneous and metamorphic rocks	Gezira Vertisols, Sudan	48-78 (ug/g)	Adam (1982)
	Sandy sediments	Ferruginous pseudogley soils in Chad	300 (ug/g)	Aubert and Pinta (1977)
	Lacustrine sediments and Precambrian biotite schist	Vertisols and Alfisols of North Cameroon	132-262 (ug/g)	Yerima (1986), Yerima et al. (2003)
Co	Earth’s crust	Mineral soils	1-70 (ug/g)	Sillanpaa (FAO, Soil Bull. NO. 17, 1972)
Pb	Earth’s crust	-	2-300 (16*)	Sillanpaa (FAO Soil Bull. NO. 17, 1972)
		Soil	< 15-25 (ug/g)	Burau (1982)
Cd		Surface soil in Russia near Ni deposit.	45 (ug/g)	Swaine (1969)
		Finland, from peat bogs	< 3-30 (ug/g)	Salmi (1950)
			Normal soil conc. 1 ppm	Swaine (1969)

* Value typical for soils

to 3.2, but these values increase with depth to about 4.1 to 4.4 in the lower sola. The structure of the soil in the surface horizons is dominantly angular blocky parting to fine angular blocky. Coarse granular structures and slickensides are observed in the lower sola of the vertisols. The vertic inceptisols demonstrated surficial cracking and minimal development of slickensides which do not meet the vertisol criteria. Consistence, when moist, generally varies from friable through firm to very firm and is sticky and plastic when wet.

Physical and chemical properties

Studies were conducted on seven profiles, but physical, chemical, and micronutrient and heavy metal contents of only 5 representative profiles are presented (Table 3). Clay contents of these

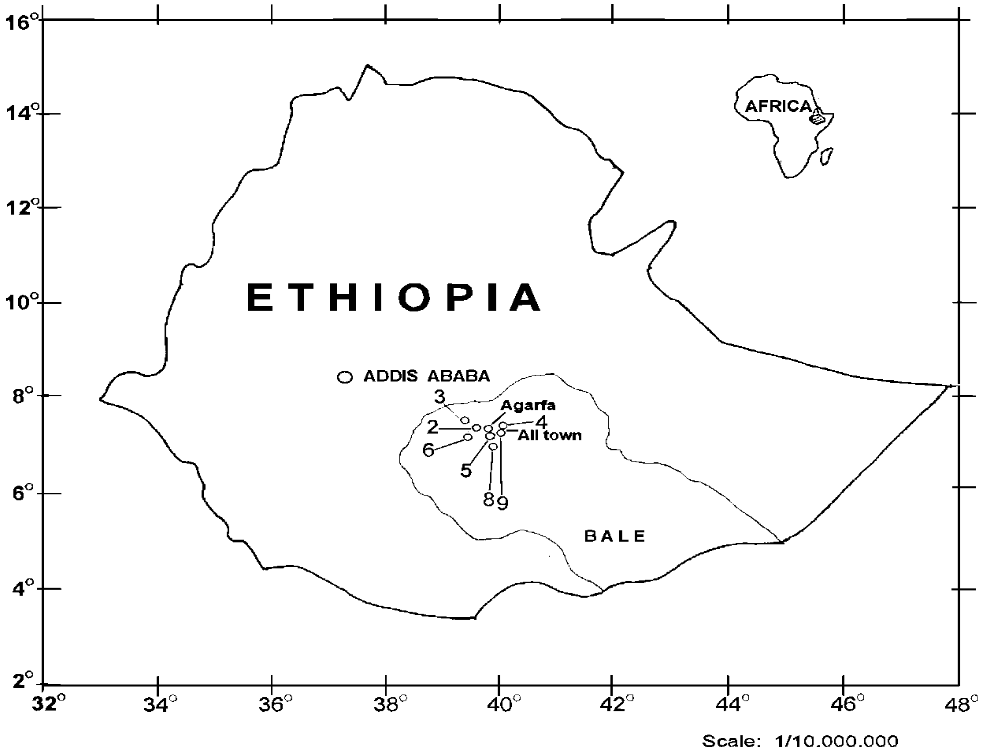

Figure 1. Map of the Bale Mountain area in Ethiopia showing study sites. Where: 4= Ali Town NE; 5= Ali Michael; 6=Agarfa West; 8=Amigna Haro; 9= Ali Town West.

soils are usually high and range from a low value of 42% in the Ap horizon of the Ali Town Vertic Haplustepts (vertic cambisol) to a high of 86% in the Bw horizon of Ali Michael Haplusterts (eutric vertisol), with lowest values observed in surface horizons. The A horizons of these soils have dark colors attributed to high organic matter contents (Table 3), which gradually decrease with depth. Total nitrogen is strongly associated with organic matter contents and also decreases with depth. Similar observations have been made for El Salvador Vertisols (Yerima et al., 1987), North Cameroon Vertisols (Yerima, 1986; Yerima et al., 2003), vertisols developed under Mediterranean climate in Turkey (Aydinalp, 2010) and oxisols (ferralsols) of the Central African Republic (Yerima et al., 2009). The pH (2:5 soil:water) of these soils range from very acidic (5.15) to alkaline (8.27). Also, for all soils, pH, EC, base saturation percent and $CaCO_3$ contents generally increased with depth while organic carbon and total N had an opposite trend. This is consistent with findings for some Vertisols of Turkey (Aydinalp, 2010). Calcium and magnesium dominate the exchange complex.

The CEC values of these soils are generally high and range from 49 to 128 cmol (+)/kg clay (Yerima et al., 2009). This indicates a varying mineralogical suite probably dominated by 2:1 clay minerals of the smectitic or vermiculitic group. The presence of mica was optically confirmed in the silt and fine sand fractions. Also, the high exchangeable K contents of 1.45 to 3.99 cmol (+)/kg (Yerima et al., 2009), indicates the presence of micaceous minerals. Since mica is a precursor to vermiculite; it is probable that the vermiculite would be forming through transformation from mica.

Total micronutrients and heavy metals

The Bale Mountain area soils have developed largely from basaltic and colluvial material under a semi-arid environment (Table 2). These soils are developed on relatively young geomorphic surfaces where slight to moderate weathering has occurred. Hence, they are generally regarded as containing adequate levels of total mineral reserves and essential plant micronutrients (Table 3). Total Fe contents in these soils range from 4.8 to 11.9% (Table 3). These values are slightly higher than those reported for Gezira soils developed from basic igneous and metamorphic rocks (Adam, 1982) and Northern Cameroon Vertisols and associated alfisols (luvisols) (Yerima, 1986) (Table 1). Total Mn concentrations for the Bale Mountain area soils developed from basalt range from 774 to 2947 ug/g. These values are within the range reported by Sillanpaa (1972) for mineral soils but higher than the values reported by Adam (1982), Aubert and Pinta (1977), Yerima (1986) and Yerima et al. (2003) for vertisols in the

Table 2. Site Characteristics and Classification of Selected Vertisols and Vertic Inceptisols of the Bale Mountain area of Ethiopia.

Soil series and pedon no.	Parent material	Landform position	Vegetation or land use	Slope (%)	Drainage	Classification: Soil taxonomy, 2003; WRB, 1998
Ali Town (4) (12.5 Km-NE of Town)	Basalt + Colluvium and alluvium	Middle part of plain (2360 masl)	Grassland/Grazing	0-2	Moderately well-drained	Vertic Haplustept (Vertic Cambisols)
Ali Michael (5)	Basalt + Colluvium and alluvium	Middle part of flat plain (2410 masl)	Grassland/ Cultivation and grazing	0-2	Moderately well-drained	Haplusterts (Eutric Vertisols)
Agarfa (6) about 2 km SW of Agarfa	Basalt + Colluvium and alluvium	Middle part of flat plain (2410 masl)	Acasia woodland, browsing and grazing	0-2	Moderately well-drained	Haplusterts (Eutric Vertisols)
Amigna Haro (8)	Basalt + alluvium	Middle part of undulating plain (2380 masl)	Grassland and acasia	2-3	Imperfectly drained	Haplusterts (Eutric Vertisols)
Ali Town (9) 3 Km west of Ali Town	Basalt + alluvium	Middle part of plain (2490 masl)	Cultivated to barley and wheat	1-3	Imperfectly drained	Haplusterts (Eutric Vertisols)

Table 3. Selected Site Characteristics and Micronutrients and Heavy Metal Distribution in some Vertisols and Vertic Inceptisols of the Bale Mountain Area of Ethiopia.

Horizon	Depth (cm)	Clay <2 um	OC	$CaCO_3$	pH (2:5) H_2O	EC dS/m	Total							DTPA-extractable						
							Co	Cd	Pb	Fe	Mn	Cu	Zn	Co	Cd	Pb	Fe	Mn	Cu	Zn
			(%)					ug/g		(%)						ug/g				
Site 4: Ali Town 1 - Vertic Haplustepts (Vertic Cambisol)																				
Ap	0-30	56	2.04	2.3	6.48	0.28	66	0.00	24	8.06	1197	28	48	0.39	0.00	0.98	9.86	41.46	1.75	0.37
AB	30-75	47	0.84	3.4	6.95	0.41	37	0.00	27	5.56	957	20	117	0.16	0.00	1.36	1.81	12.16	1.08	0.23
Bk	75-100	48	0.72	3.8	8.27	0.65	41	0.00	24	5.78	1052	23	68	0.07	0.00	0.90	3.09	7.83	1.38	0.26
BCk	100-155	57	0.34	4.2	8.24	0.75	35	1.00	19	6.18	1044	19	63	0.09	0.02	0.86	4.02	3.59	0.98	0.19
Site 5: Ali Michael - Haplusterts (Eutric Vertisol)																				
Ap	0-34	45	2.20	0.0	5.88	0.19	63	2	17	Nd	2947	29	87	0.50	0.0	0.30	8.44	32.02	1.37	0.33
Bw	34-95	86	0.74	0.0	6.25	0.33	58	2	6	Nd	2257	32	112	0.26	0.0	0.04	14.3	10.25	0.77	0.12
Bk	95-170	85	0.42	5.9	7.26	0.36	34	2	8	Nd	1541	41	109	0.43	0.0	0.21	8.72	25.11	1.42	0.16
Site 6: Agarfa – Haplusterts (Eutric Vertisol)																				
Ap	0-25	45	2.23	0.0	5.97	0.23	51	0	37	6.04	1180	26	99	0.40	0.00	0.13	11.7	32.19	1.15	0.37
B	25-50	70	1.16	0.0	6.14	0.29	47	0	32	4.80	1245	5	94	0.28	0.00	0.50	14.0	21.22	1.48	0.16
Bk1	50-86	83	0.78	3.8	6.98	0.42	43	0	23	6.12	889	25	98	0.43	0.00	0.55	13.8	24.31	1.18	0.21
Bk2	86-160	57	0.48	3.0	7.18	0.39	24	0	7	Nd	1174	27	133	0.34	0.00	0.65	8.39	20.08	1.19	0.12

Table 3. Contd.

Site 8: Amigna Haro – Haplusterts (Eutric Vertisol)																				
Ap	0-20	59	1.46	0.0	5.59	0.32	24	1	12	Nd	1745	26	103	0.36	0.00	1.31	12.3	18.34	1.31	0.27
Bk1	20-85	83	1.00	2.8	7.01	0.45	29	3	21	Nd	1556	29	115	0.26	0.02	0.72	12.2	13.64	1.73	0.19
Bk2	85-165	66	0.32	3.8	7.77	0.30	19	4	30	Nd	973	31	114	0.24	0.02	1.31	3.95	6.70	1.65	0.19
Site 9: Ali Town 2 - Haplusterts (Eutric Vertisol)																				
Ap	0-30	42	2.02	0.0	5.94	0.18	37	1	34	6.14	999	20	93	0.56	0.00	0.00	7.70	37.17	0.91	0.21
Bw	30-95	72	0.70	0.0	6.36	0.32	55	1	32	4.52	1280	9	56	0.35	0.02	0.26	16.4	15.55	1.42	0.16
Bk	95-165	73	0.12	4.2	6.97	0.40	66	0	34	6.44	1133	25	105	0.26	0.00	0.93	10.4	19.37	1.32	0.19

Table 4. Ranges of the soil properties in the soils studied used for the regression equations.

Range	OC	Clay	$CaCO_3$	BS	pH H_2O (2:5)	EC dS/m	Total							DTPA extractable						
							Co	Cd	Pb	Zn	Mn	Cu	Fe	Co	Cd	Pb	Fe	Mn	Cu	Zn
	%						mg/kg						(%)	mg/kg						
From	0.12	25	0.0	44	5.59	0.05	19	0	6	55	774	5	4.8	0.07	0.00	0.04	1.81	5.9	0.70	0.07
To	2.25	86	4.2	100	8.27	0.75	119	4	35	143	2947	65	11.9	0.83	0.02	1.31	17.4	41.5	1.73	0.37

Sudan, India and North Cameroon, respectively. The Zn contents range from 55 to 143 ug/g. These values are within the range observed for most vertisols worldwide (Table 1). The range of copper values observed for these soils (5 to 65 ug/g) is lower than the range reported for Australian Black earths (Tiller, 1983), Indian Vertisols (Aubert and Pinta, 1977) and North Cameroon Vertisols (Yerima, 1986; Yerima et al., 2003), but higher than those reported for Gezira Vertisols in the Sudan (Table 1).

Literature on the distribution of the elements Co, Pb and Cd in vertisols is very sparse to non-existent. Total Co concentration for these soils range from 19 to 119 ug/g. Except for few horizons, most of these values (Table 3) are within the range of 1 to 70 ug/g reported for mineral soils (Sillanpaa, 1972). The range of lead values observed for these soils (6 to 35 ug/g) are within the range of 2 to 300 ug/g reported for the Earth's crust (Sillanpaa, 1972) and for some soils from Korea (Jo and Koh, 2004), but slightly higher than the range (15 to 25 ug/g) reported for soils (Burau, 1982).

Total cadmium values for these soils range from 0 to 4 ug/g with more than 50% of the soils showing no trace of Cd. Jo and Koh (2004) reported values for soils of Korea of 0.11 ug/g Cd. Though, Swaine (1969) and Salmi (1950) have reported Cd concentrations of 45 ug/g for surface soils in Russia close to Nickel deposits and < 3 to 30 ug/g for Finland peat bog soils, the former investigators also noted that the normal Cd concentration in soil was 1 ug/g. Concentrations of most of the elements studied are very uniform within the profiles confirming their origin from a common parent material. Further, pedoturbation in these soils, due to the high shrink-swell processes, associated with the smectitic mineralogy may also be responsible for the near uniformity in elemental distribution within the profiles.

Correlation and regression relationships of total micronutrients and heavy metals

For development of regression equations, a given range of soil parameters were used (Table 4). In the present study, the total concentrations of micronutrients (Fe, Mn, Cu and Zn) and heavy metals (Co, Pb, Cd) conformed more to normality when log-transformed (plots not shown). This is consistent with studies by Ahrens (1954), Bradley

Table 5. Simple and multiple linear and quadratic equations between total Fe, Mn, Cu, Zn, Co, Cd, and Pb and selected independent soil properties of Vertisols and Vertic Inceptisols of the Bale Mountain area of Ethiopia.

Dependent variable	Intercept	Coefficient	Variable	Standard error	n	r^2
			Linear (a)			
Log T-Fe	0.7668	-1.6185	Log T-Cd	0.2320	23	0.6768**
Log T-Zn	1.8980	-0.3342	Log (T-Cd)^2	0.1166	23	0.2611*
Log T-Cu	1.0709	0.1223	Log (T-Co)^2	0.2202	23	0.1788*
Log T-Co	1.4674	0.4876	Log (T-Fe)^2	0.1559	23	0.5778**
Log T-Cd	0.3555	-0.4181	Log T-Fe	0.1179	23	0.6768**
Log T-Pb	1.1071	0.3666	Log T-Fe	0.2037	23	0.3504**

Dependent var.	Intercept	Coeff. (XI)	Var. (XI)	Coeff. (X2)	Var. (X2)	Std. Error	n	R^2
				Multiple linear (b)				
Log T-Mn	2.3722	55.84	Log T-Co	-0.3613	Log T-Fe	0.0521	23	0.8339**
				Quadratic (c)				
Log T-Fe	0.7896	-4.2691	Log T-Cd	-3.8522	Log (T-Cd)^2	0.2024	23	0.7650**
Log T-Cu	0.8206	0.5134	Log T-Cd	0.1874	Log (T-Co)^2	0.2025	23	0.3238
Log T-Co	2.1352	0.2613	Log Sand	-0.3943	Log (Silt)^2	0.1973	23	0.3549
	-2.3167	1.1923	Log T-Mn	0.6280	Log (T-Fe)^2	0.0717	23	0.9179**
Log T-Pb	1.1001	0.5067	Log T-Fe	-0.4344	Log (T-Hg)^2	0.1825	23	0.5021**

Dependent var.	Intercept	Coeff. (X1)	Var.(X1)	Coeff. (X2)	Var. (X2)	Coeff. (X3)	Var. (X3)	n	R^2
Log T-Fe	-0.4859	0.7196	Log T-Co	-3.9916	Log T-Cd	5.4006	Log (T-Cd)^2	23	0.8850**
Log T-Mn	2.4944	0.5258	Log T-Co	-0.4355	Log T-Fe	-0.4399	Log (T-Cd)^2	23	0.9068**

Log T-Fe = Log total Fe; Std error = Standard Error of the estimate; Var. = Variable; Coeff. = Coefficient; * and ** significant at the 0.05 and 0.01 levels.

(1980), Berrow and Reaves (1981) and Reaves and Berrow (1984) who showed that the frequency distribution of trace element concentration levels in soils is highly asymmetric (positively skewed). The aforementioned investigators observed that log-transformation made the distribution approximately normal. Similar observations have been reported for North Cameroon Vertisols (Yerima, 1986; Yerima et al., 2003) for Fe, Cu, Zn and Mn distribution. Predictive simple, multiple linear and quadratic models between Fe, Mn, Zn, Cu, Co, Cd, and Pb and selected soil properties of the Bale Mountain area in Ethiopia (Table 5), indicate that the best models could be obtained from the mutual relationships that exist among the heavy metals and the micronutrients and is consistent with findings by Zarcinas et al. (2004); parameters such as percent sand, silt and clay and organic carbon gave very low correlation coefficients and are not shown here.

Lee et al. (1997) reported that where the clay content was high in soils, prediction equations are not significant and cannot be used for Zn, Pb, Cu and Co versus organic matter content and extractable Fe for the soils (ustolls, udults and ustalfs) he studied, because the predominant influence on heavy metal concentration by clay content compared with organic carbon content and extractable Fe limited the use of simple linear equations for predicting heavy metal concentrations by organic carbon content and extractable Fe.

DTPA - extractable micronutrients and heavy metals

The DTPA-extractable micronutrients for these soils (Table 4) ranged from 1.81 to 17.4 ug/g for Fe, 5.9 to 41.5 ug/g for Mn, 0.07 to 1.73 ug/g for Cu and 0.07 to 0.37 ug/g for Zn. The distribution of the extractable micronutrients generally shows a decrease in concentration with depth except for Fe and Cu, which did not show a definite trend (Table 3). Decreases with depth are associated with decreases in organic carbon contents and increasing pH that causes reduced metal solubility. This is consistent with findings by Sharma et al. (2006) for Indian Vertisols. Willet (1983), Yerima (1986), Sillanpaa (1982) and Yerima et al. (2003) reported that increases in soil pH and $CaCO_3$ equivalent values were accompanied by decreases in the extractable Fe and Mn while decreases in soil pH had an opposite effect. The lower sola of these soils also had increasing amounts of $CaCO_3$ (Table 3) and would reduce the amount of extractable Fe and Mn. Studies by Yerima (1986) and Yerima et al. (2003) showed that Fe-Mn oxides frequently coat the carbonate nodules and concretions, forming Fe-Mn-carbonate precipitates. Adam (1982) analyzed carbonate nodules larger than 2 mm and found that the nodules contained less or comparable amounts of Zn, Fe and Cu than the soil, but they contained 10 to 20 times more of Mn. The optical evidence (Yerima, 1986) which indicates a chemisorption of Fe and Mn by carbonates, in light of findings by Adam (1982) probably explains in part the generally lower values, especially for Mn, in the $CaCO_3$-rich lower sola of these soils. This is consistent with observations by McBridge (1979), that carbonate surfaces are very reactive and retain heavy metals by chemisorption and hence, lowers the solubility of these metals. Since an alkaline extractant (DTPA buffered at pH 7.3) was used, it is apparent that micronutrients in the carbonate nodules were not readily released.

Zinc contents in these soils decreased with decreasing organic matter content, and increasing pH and $CaCO_3$ equivalent. These findings are also consistent with observations by Sillanpaa (1982) for studies on representative soils worldwide, and Yerima (1986) and Yerima et al. (2003) for North Cameroon Vertisols. Soil copper in these soils tends to be high at the surface, slightly decrease with depth and then increase with increase in pH. Since electrical conductivity and $CaCO_3$ equivalent of soils are highly correlated with each other as well as with pH (Sahlemedhin et al., 1994), the relations between soil Cu to these factors would not differ substantially from the Cu-pH relations. These observations are consistent with findings by Sillanpaa (1982) in a global study of soil micronutrients. DTPA extractable critical concentrations for plant growth were 0.12 to 0.25 mg/kg for copper, 2.5 to 5.0 mg/kg for iron, 1.0 to 5.0 mg/kg for manganese and 0.5 to 1.0 mg/kg zinc (Sims and Johnson, 1991). Except for zinc, the available micronutrient concentrations for the Bale Mountain area soils are believed to be adequate for plant growth. The DTPA -extractable heavy metals concentrations were 0.07 to 0.83 ug/g for Co, 0.0 to 0.02 ug/g for Cd, and 0.04 to 1.31 ug/g for Pb. Cobalt concentrations generally decreased with depth. Lead did not show a definite pattern in surface horizons but generally increased with depth in the lower sola. Cadmium concentrations in all the horizons are <0.02 ug/g. Trace amounts of Cd and decreasing concentrations of Co with depth may be attributable to the increasing pH and $CaCO_3$ content which has been observed to reduce the solubility of heavy metals (McBride, 1979).

Generally, the decreasing micronutrient and heavy metal content trend with depth can be attributed to the recycling of essential nutrients to the surface horizons by plants. Organic matter is concentrated in the surface A-horizons by the process of melanization (Lee et al., 1997). As organic matter (roots and other plant and animal tissue) decompose, plant-essential heavy metals are released into the soil (A –horizon) and subsequently sorbed onto clay minerals. Generally, there is a decrease in DTPA-extractable heavy metals with depth (except Fe, Pb and Cd). However, the high and near uniform distribution of these elements (except Cd) in the B horizons is associated with sorption and pedoturbation resulting from the high clay contents (clay contents exceed 70% in most of the B horizons) with shrink-swell properties. Lead and Cd are not concentrated by melanization in the organic matter-rich A horizons of these soils. Lead and Cd are not essential elements. Zinc, Mn and Cu accumulation in surface soil is associated with plant uptake (Adriano, 1986; Lee et al., 1997) and is consistent with findings in this study. Based on the suggested tolerance levels proposed by Risser and Baker (1990), plant concentrations of Cd and Pb of 1 and 10 ug/g, respectively would be considered above tolerance levels, while for animal feed, Cd and Pb concentrations of 0.5 and 30 ug/g, respectively would be considered to be above tolerance levels.

The Bale Mountain area soils studied generally have available Cd and Pb values below the indicated tolerance levels.

Correlation and regression relationships of DTPA extractable micronutrients and heavy metals

For DTPA extractable indices statistical correlations were made between soil properties, which have been observed to influence micronutrient availability in soils (Sillanpaa, 1982; Alloway, 1995; Lee et al., 1997) such as pH, EC, $CaCO_3$ equivalent, organic carbon and percent heavy metals. Moreover, the different elements were also introduced as independent variables. Simple linear regression equations (Table 6) indicate that except for pH-H_2O and EC, which give high r^2 values and can be used to predict available Fe and Co, respectively, the other micronutrients, Mn, Cu, Zn and Pb could better be predicted by the mutual relationships that exist among

Table 6. Simple and multiple linear and quadratic equations between DTPA extractable Fe, Mn, Cu, Zn, Co, Cd, and Pb and selected independent soil properties of Vertisols and Vertic Inceptisols of the Bale Mountain area of Ethiopia.

Dependent variable	Linear (a)					
	Intercept	Coefficient	Variable	Std. error	n	r^2
Available Fe	32.2050	-46.3889	Log $(pH\text{-}H_2O)^2$	3.3834	23	0.4823**
Log A-Fe	1.0369	-0.5366	Log $(A\text{-}Co)^2$	0.1896	23	0.5441**
Log A-Mn	1.5248	0.5950	Log A-Co	0.1939	23	0.4246**
Available Cu	1.5699	-0.5583	Log $(A\text{-}Zn)^2$	0.2491	23	0.4181**
Available Zn	0.0891	0.0684	Log $(A\text{-}Mn)^2$	0.0787	23	0.2100*
Available Co	-0.0576	-0.8096	Log EC	0.1260	23	0.5626**
Log A-Co	-1.1851	-1.3055	Log EC	0.1714	23	0.6439**
Log A-Pb	5.3715	-1.8245	Log T-Mn	0.3575	23	0.2888

Multiple linear (b)								
Dependent var	Intercept	Coeff. (X1)	Var. (X1)	Coeff. (X2)	Var. (X2)	Std. error	n	R^2
Available Mn	43.7911	19.9416	Log A-Co	19.0224	Log A-Zn	0.9393	23	0.5280**
Log A-Mn	1.5400	0.5350	Log A-Co	0.1331	Log A-Cd	0.1792	23	0.5540**
Quadratic (c)								
Available Fe	44.9028	-11.8541	Log (EC)2	-65.3257	Log $(pH\text{-}KCl)^2$	3.0711	23	0.5928**
Log A-Mn	-34.2169	87.8038	Log $pH\text{-}H_2O$	54.2258	Log $(pH\text{-}H_2O)^2$	0.2007	23	0.4407*
Available Zn	0.1880	0.2691	Log OC	0.3248	Log $(OC)^2$	0.0637	23	0.5062**
Available Co	-0.0023	-0.5457	Log EC	0.2756	Log $(EC)^2$	0.1285	23	0.5657**
Log A-Co	0.3158	-0.9660	Log EC	-1.3503	Log $(pH\text{-}KCl)^2$	0.1628	23	0.6935**
	-0.4726	-2.6802	Log EC	-1.4351	Log $(EC)^2$	0.1663	23	0.6799**

Dependent variable	Intercept	Coeff. (X1)	Var. (X1)	Coeff. (X2)	Var. (X2)	Coeff. (X3)	Var. (X3)	n	R^2
Log A-Mn	3.8860	1.0204	Log $CaCO_3$	0.2712	Log OC	-4.3005	Log $(pH\text{-}H_2O)^2$	23	0.5537**
Log A-Co	0.2046	-0.9981	Log EC	0.8558	Log $(CaCO_3)^2$	-2.7581	Log$(pH\text{-}KCl)^2$	23	0.8209**
Log A-Zn	-0.5339	0.8440	Log OC	0.9294	Log $(OC)^2$	-0.8359	Log $(EC)^2$	23	0.6570**

these different elements. When quadratic models were used, the results indicate that the prediction of available Fe, Mn, Zn and Co, could better be effected through the use of independent parameters such as EC, pH-KCl, $pH\text{-}H_2O$, organic carbon, and $CaCO_3$ equivalent either alone or in combination. These findings are consistent with observations by Sillanpaa (1982) obtained in a global study of different soils, and that of Smith (2009) who reported that composting processes overall are likely to contribute to lowering the availability of metals in amended soils.

The heavy metals, Cd and Pb had very low correlation coefficients, which would not be very useful for predictive purposes and hence are not presented here.

Conclusions

The ‘vertisols and vertic inceptisols’ of the Bale Mountain area of Ethiopia have adequate nutrient reserves. The total micronutrient and heavy metal concentrations of these soils are generally within the ranges reported for most soils worldwide, which have not received fertilizer amendments. Extractable micronutrients levels are adequate (except for Zn) for all soils. Apparently, soil pH and $CaCO_3$ concentration exert a major influence on the extractable Fe, Mn and Zn lowering the concentrations of these elements. The concentrations of Cd and Pb are below tolerance levels both for plant and animal feed and hence pose little concern to human and livestock health. The distribution of Fe, Mn, Cu, Zn, Pb, Cd and Co depends on soil horizonation. Generally, higher levels of total heavy metals of the profiles studied are found in the A-horizons (70% of the A horizons have greater concentrations than the B horizons). This is associated with limited leaching, near-uniformity and distribution in parent material type, considerable high clay contents in the surface horizons and biogeochemical cycling. Biogeochemical cycling is apparently a very important determinant of heavy metal content in the soil. This process increases the heavy metal content of plant essential elements (Zn, Mn, Cu, and Co) compared with non-essential elements (Pb and Cd) in the soil surface horizons. However, biogeochemical cycling is not great enough to increase the total heavy metal content of the A-horizons.

Parent material uniformity and pedoturbation are responsible for the near uniform distribution of total heavy metal contents in the B-horizons of the soils studied. Pedoturbation and biogeochemical cycling are factors that determine the distribution of total heavy metals in the soils studied. The total concentrations of micronutrients and heavy metals can best be predicted using the mutual interrelationships that exist among them. Parameters such as pH, EC and organic carbon and the mutual interrelationships among these metals are important for development of predictive models for available indices of micronutrients and some heavy metals as demonstrated in this study. Because the parameters pH, EC, organic carbon and $CaCO_3$ equivalent are generally available from most soil survey data or can be determined at minimal cost, they can be used for prediction of the available micronutrients Fe, Mn, Zn and Co with a fair degree of accuracy at little cost.

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