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Fractioning of Cu, Mn, Zn, and Pb in Mineral Soils Along an Oak Forest Vegetation Gradient in Mexico City

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Different studies throughout the world demonstrate that the forest ecosystems associated with urban and suburban areas are potentially contaminated by airborne particles (Pouyat and McDonnell, 1991), and the airborne particles containing heavy metals are of particular interest because metal cations accumulate in forest soils (Smith, 1990).

In Mexico City metropolitan area circulate over 3 millions of automobiles and approximately 25% of the heavy industries of the country are located in the northern metropolitan area (Bravo, 19889). Both of the anthropogenic sources introduce Pb in to the atmosphere of Mexico City. In 1988, the mean annual levels of lead reached 2.4 $\mu g/m^3$ (Legorreta, 1995).

Efforts by city authorities to reduce toxic air pollutants like lead has met with mixed success. While the introduction of a new low lead-content gasoline has abated atmospheric lead levels in the capital city, it seems that this measure has given raise to higher concentrations of ozone precursors (Rosas, 1995) and the change in the acidity of air and precipitation.

For many years, in the surrounding mountains of Mexico City, the exploitation of the oak forests for tire-wood was the only use by local peasants but 30 years ago the accelerated growth of the metropolitan area has contributed to the deforestation of almost all mountainous region. At present in the suburban area there are two undistributed oak forest National Parks, namely the “Ajusco Crest” with 920 ha and the “Lion’s Desert” with 1866 ha., (Soberon, 1989). Unfortunately, furtive logging and pasturing have been decreasing both of the areas continuously. This zone is one of the principal areas for capture of wind-driven cloud water and thus contribute, in great manner, to the hydrological cycle.

The purpose of this study was to characterize the distribution and pattern of heavy metals selected along different plant species composition over the same soil type of the Ajusco Crest. Specifically, the study investigates the concentration and the distribution of Cu, Mn, Zn, and Pb among certain soil fractions below the different types of vegetation.

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MATERIALS AND METHODS

Study Area: The study area is about 720 ha. In a reservation of the Ajusco Sierra, 23 km. Southwes of Mexico City, at an altitude od 2500 m above sea level. The rainy season s summer, with mean annual rainfall between 1000 - 1100 mm. The study area is dominated by oak trees with *Quercus rugosa, Quercus laurina,* and *Quercus crassipes* on sand soil. Xerophytic bushes with *Sedum oxypetalum* and *Senecio praecox* dominate on rocky substrate. The oak forests have been substitutedin 3 hectares by mountain grasses like *Muhlenbergia mucroura* and *Festuca tolucensis,* as a result of human induced disturbance. *Buddleia cordata* and *B. parviflora* dominate between the limits of the oak forsests and mountain grasses.

Soil Samples: Within the forest study area 3 plots (10 x 100 m) for each vegetation type were established. Horizons and subhorizons of soils under the *Quercus rugosa, Buddleia cordata,* and *Muhlenbergia macroura* were randomly sampled. Physico chemical properties of the soil investigated, were determined by standard methods (Black, 1965) and are listed in Table 1. Detailed field observations indicated that soil properties were rather uniform across each experimental plot. The soil was tentatively identified as Eutric Regosol.

Table1. Physico chemical properties of the soil.

Horizon	Soil Depth (cm)	B.D. g/cc	Texture	PH 1:25 water	PH $CaCl_2$ 0.01 M	O.M. %	E. C.				C.E.C. cmol/kg
							Ca cmol/kg	Mg cmol/kg	K cmol/kg	Na cmol/kg	
Ah	0-20	1.12	Sandy clay loam	5.13	5.74	3.83	5.3	3.03	0.65	0.08	11.74
C1	20-90	1.16	Sandy loam	5.92	6.11	2.48	6.36	3.68	0.24	0.1	13.27
C2	>90	1.28	Sandy loam	6.25	6.35	1.55	4.39	2.92	0.15	0.15	9.69

B.D. = Bulk Density, O.M = Organic Matter, Ah = Organic Layer of soil, C1 and C2 = Mineral layer of soil, E.C. = Exchangeable cations

Trace Metal Fractionation: The total content of Cu, Mn, Zn, and Pb in the soil samples were determined on filtered extracts obtained from 2g samples which were calcinated for 8 hours at 450 °C. Ashes were digested with 8N HNO_3 at 80 °C overnight. The four heavy metals were fractionated in duplicate 2g soil samples by a sequential extraction procedure following the method of Zeien and Brümmer (1989). This extraction procedure is believed to give data concerning the fraction of trace metals in water soluble, adsorbed, exchangeable organic, amorphous iron oxide, crystalline iron oxide and residual phase. These solid phase chemical forms were determined by sequential extraction using the following reagents with 2g of soil: 1M NH_4NO_3, 24 hours; 1M CH_3COONH_4, 24 hours; 0.1M NH_2OH-HCL + 1M CH_3COONH_4(pH 6.0), 30 minutes; 0.025M NH_4EDTA (pH 4.6) 90 minutes; 0.2M $NH_4OOCCOONH_4$ (pH 3.25) 4 hours; 0.1M absorbic acid + 0.2M $NH_4OOCCOONH_4$(pH 3.25), 30 minutes. During each extraction, a soil suspension was taken. After extraction the suspension was centrifuged and the resulting supernatant solution was decanted and filtered. The contents of the four trace metals in the filtered solution were determined by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

The total contents of Cu, Mn, Zn, and Pb in the soil samples are shown in Tables 2, 3, and 4. Metal contents in the Ah horizon unde *Quercus rugosa* and *Buddleia sordata* are Mn > Zn > Pb > Cu and for *Muhlenbergia macroura* in the same horizon soil es Mn > Zn >Cu > Pb. Patterns of total trace metal content levels can be explained by geochemical properties of the soil, plant species composition, and fluxes of atmospheric deposition.

Table 2. Sequential Extraction of Heavy Metals in the Horizon Ah (0-20 cm)

	Q. rugosa				*B. cordata*				*M. macroura*			
Fraction	Pb	Zn	Cu	Mn	Pb	Zn	Cu	Mn	Pb	Zn	Cu	Mn
		(µg/g)				(µg/g)				(µg/g)		
Water Soluble	0.3 <(0.1)	0.8 (0.1)	n.d	9.3 (1.4)	0.4 (0.1)	0.9 (0.1)	n.d	9.3 (0.3)	n.d	1.8 (0.1)	n.d	3.2 (0.4)
Exchangeable	0.1 <(0.1)	1.0 (0.1)	n.d	14.6 (0.4)	0.4 (0.1)	2.3 (0.3)	n.d	16.8 (2.3)	n.d	0.4 <(0.1)	n.d	1.9 (0.9)
Manganese Oxide Bounde	0.2 <(0.1)	0.9 (0.1)	n.d	53.7 (3.6)	0.2 (0.1)	2.4 (0.2)	n.d	34.5 (2.3)	0.2 <(0.1)	0.8 <(0.1)	n.d	27.2 (0.9)
Organically Complexed	10.1 (1)	10.5 (1.6)	3.3 <(0.1)	125.0 (9.2)	16.2 (2.8)	26.7 (7.4)	4.0 (0.6)	96.1 (18.7)	2.9 (0.6)	3.2 (0.3)	2.6 (0.1)	43.1 (1.7)
Amorphous Iron Oxide	9.5 (1.6)	9.6 (0.7)	4.6 (0.3)	44.1 (1.7)	9.2 (2.1)	14.1 (3)	4.8 (0.6)	46.6 (2)	5.5 (1.1)	12.3 (0.4)	3.9 <(0.1)	62.8 (1.5)
Crystalline Iron Oxide Bound	7.6 (0.2)	12.3 (0.3)	2.1 (0.2)	54.3 (0.3)	5.8 (1.7)	18.7 (0.3)	2.3 <(0.1)	53.8 (0.8)	2.7 (0.5)	7.9 (0.1)	1.6 <(0.1)	29.9 (1.5)
Residual	5.0 (0.6)	27.6 (2.1)	7.9 (1)	99.3 (5.3)	5.3 (1)	27.3 (4.4)	8.4 (1.4)	100.3 (13)	1.8 (0.3)	36.1 (0.5)	7.4 <(0.1)	159.3 (5.2)
Total	33.0 (0.6)	65.6 (4.6)	18.5 (1.1)	405.2 (8.7)	38.0 (7.8)	95.2 (15.1)	20.0 (1.4)	362.3 (35.5)	15.1 (2.5)	64.5 (1.5)	16.1 (0.2)	332.4 (11.3)

Average of nine samples with standard errors in parenthesis n.d = not detectable

Specially for lead there is a gradient between the plant species and horizons. As a complement to understand the trend of Pb we analyzed in a previous study (unpublished data) the litter of *Quercus* Sp., and *Buddleia* Sp. (leaves, twigs barks) contained 43 mg/kg of Pb in leaves 54 mg/kg in twigs and 61 mg/kg in the bark. If we compare our data with the literature, lead concentrations appear to be higher in the study of the National Park than in the rural stands. Some of this lead moves into the soil mineral layers and consequently there is an enrichment of the superficial horizon. For Cu and Zn, there is no significant difference between *Muhlenbergia macroura* and the other vegetation types because the soil with *M. macroura* has a lower content of organic matter and vegetation cover and thus some of the soluble and exchangeable manganese could get lost by runoffs.

Table 3. Sequential Extraction of Heavy Metals in the Horizon C1 (20-90cm)

	Q. rugosa				*B. cordata*				*M. macroura*			
Fraction	Pb	Zn	Cu	Mn	Pb	Zn	Cu	Mn	Pb	Zn	Cu	Mn
		(µg/g)				(µg/g)				(µg/g)		
Water Soluble	0.1	0.2	n.d.	3.4	0.4	0.3	n.d.	4.3	1	0	n.d.	1.7
	<(0.1)	<(0.1)		(0.5)	(0.2)	<(0.1)		(0.6)	(0.1)	(0)		<(0.1)
Exchangeable	0.04	0.2	n.d.	4.7	0	0.6	n.d.	6.3	0	0.4	n.d.	1.3
	<(0.1)	(0)		(0.3)	(0)	(0.1)		(1.3)	(0)	<(0.1)		<(0.1)
Manganese Oxide Bounde	0.1	0.3	n.d.	78	0.1	0.8	n.d.	46.4	0	0.6	n.d.	35
	<(0.1)	(0)		(4.1)	<(0.1)	(0.1)		(5.6)	(0)	<(0.1)		(0.6)
Organically Complexed	1.1	1.9	2.7	90.1	3.2	4.8	2.3	73.4	0.8	2.2	1.1	24.4
	<(0.1)	(0.1)	(0.6)	(2)	(0.5)	(0.1)	(0.2)	(10.5)	<(0.1)	(0.5)	(0.1)	(0.6)
Amorphous Iron Oxide	4.4	5.3	4.7	45.7	2.5	7	5.2	48.1	4.7	4.3	4	39.5
	(0.7)	(0.1)	(0.3)	(0.3)	(0.1)	(1)	(0.1)	(1.8)	(0.6)	(0.5)	(0.1)	(0.3)
Crystalline Iron Oxide Bound	3.7	8.3	3	34.2	3.2	10.2	1.8	48.4	1.8	14.7	2.1	40.8
	(0.3)	(0.3)	(0.5)	(2.2)	(1.2)	(0.4)	(0.3)	(1.6)	(0.2)	(0.9)	(0.1)	(0.8)
Residual	3.1	29.9	8.6	129.1	3.3	25.3	6.4	117.4	2.7	21.3	5.9	111.5
	(0.4)	(1)	(0.4)	(7.1)	<(0.1)	(3.3)	(0.8)	(14.8)	(0.2)	(0.9)	(0.1)	(0.9)
Total	13.5	49.1	18.8	390.1	13.8	52	15.5	349.3	12	44.4	12.8	259.2
	(0.6)	(0.7)	(1.4)	(4)	(0.5)	(4.5)	(1.1)	(32.3)	(1.2)	(2.9)	(0.3)	(3.1)

Average of nine samples with standard errors in parenthesis **n.d = not detectable**

The distribution of trace metals among the fractions of the soils studied are summarized in Tables 2, 3, and 4. The sequential extraction procedure used tended to produce sums of extracted contents of Cu, Mn, Zn, and Pb which always were below the total metal contents. These differences may have been the result of the HNO_3 extraction in the sequential procedure being less effective than the ignition and digestion the HNO_3 to obtain the total metal content. The amounts of trace metals extracted with NH_4NO_3, CH_3COONH_4 and NH_2OH-HCL + CH_3COONH_4 were very small, except for lead in the horizon with *M. macroura* in the soluble phase, and for zinc in the Ah horizon with *M. macroura* in the soluble phase. It appears that Pb cation are moving into deeper mineral layers due to the combination of coarse textures and high precipitation with a low vegetation cover.

Table 4. Sequential Extraction of Heavy Metals in the Horizon C2 (<90 cm)

		Q. rugosa				*B. cordata*				*M. macroura*		
Fraction	Pb	Zn	Cu	Mn	Pb	Zn	Cu	Mn	Pb	Zn	Cu	Mn
		(µg/g)				(µg/g)				(µg/g)		
Water Soluble	0	0.1	n.d.	2.3	0.4	0	n.d.	1.5	0.5	0	n.d.	0.5
	(0)	<(0.1)		<(0.1)	(0.2)	(0)		(0.1)	(0)	(0)		<(0.1)
Exchangeable	0	0.1	n.d.	2.9	0.2	0.1	n.d.	2.5	0	0.1	n.d.	0.9
	(0)	<(0.1)		(0.1)	<(0.1)	<(0.1)		(0.2)	(0)	<(0.1)		<(0.1)
Manganese Oxide Bounde	0.3	0.3	n.d.	78.9	0.1	0.3	n.d.	64	0.9	0.5	n.d.	44.4
	(0.1)	<(0.1)		(0.8)	<(0.1)	<(0.1)		(0.5)	<(0.1)	<(0.1)		(0.3)
Organically Complexed	0.3	1.1	2.6	85.2	0.5	1.3	2.6	72	0.4	1.2	1.1	13.9
	<(0.1)	<(0.1)	(0.5)	(1.4)	<(0.1)	<(0.1)	(0.3)	(10.2)	<(0.1)	<(0.1)	(0.1)	(0.2)
Amorphous Iron Oxide	1.7	6.2	5.2	52.8	2.7	3.6	4.3	14.7	0.4	5.8	3.9	34.6
	(0.4)	(0.7)	(0.1)	(1.7)	(0.9)	(0.7)	(0.7)	(3.7)	<(0.1)	(0.1)	(0.2)	(0.6)
Crystalline Iron Oxide Bound	3.8	9.6	3.1	49.7	2.4	5	1.4	35.2	0.4	11.5	2	31.1
	(0.7)	(0.8)	(0.1)	(4.6)	(1.3)	(0.4)	(0.4)	(2.6)	<(0.1)	(0.3)	(0.1)	(0.5)
Residual	2.6	29.3	8.0	145.3	3.7	27.3	9	129.2	3.1	15	6.2	102.8
	(0.5)	(2)	(0.4)	(6.5)	<(0.1)	(3.6)	(0.1)	(14.9)	(0.6)	(0.3)	(0.6)	(1)
Total	9.8	49.8	18.7	422.0	10.9	40.5	17.1	351.0	6.7	35.1	13	233.1
	(0.7)	(0.6)	(0.9)	(2)	(0.1)	(4.6)	<(0.1)	(25.4)	(0.8)	(0.5)	(1.1)	(2.1)

Average of nine samples with standard errors in parenthesis n.d = not detectable

The organic fraction in the Ah horizon conatins the highest proportion of lead, manganese and zinc for soils with *Q. rugosa* and *B. cordata*. For lead, these results may reflect indirectly the anthropogenic nature of the metals because if we compare the data for *M. macroura* with low vegetation cover the soil's organic matter content, the highest proportion of lead is on the amorphous Fe-oxide fraction, and there is no lead in the soluble and exchangeable fractions. The copper and manganese contents were similar to those soils reported in the literature for rural stands (Pouyat and McDonell, 1991). Finally, in deeper layers the major proportion of trace metals is basically on amorphous Fe-oxide and crystalline Fe-oxide bounds.

The accumulation amd mobilization of lead and zinc in the soil studied is governed principally by the vegetation type and cover. The complexity of trace metals with organic matter fraction diminish the transport of metals into deeper layers of soil. The level of metals in the soil solution could affect the rate of % carbon mineralization (Gupta, 1991), and thus restrain the mineral cycling because the levels of soluble zinc and lead are above the toxicological threshold limits of nitrifying bacteria. The oak forest is acting like cover protection against the infiltration of anthropogenic lead into deeper layers and runoff. For the area studied deforestation by tire, furtive logging, and urbanization could limit the turnover of lead to the atmosphere, stream channels and probably entry into the ground water.

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