Mobility of Some Heavy Metals in Soils Used for Market Gardening in the Urban Zone of Ngaoundere (Cameroon)

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Abstract: The mobility of six heavy metals (Zn, Ni, Pb, Cr, Cu and Cd) in soils from market gardening lands in Ngaoundere urban area was studied. To this effect, ten samples were collected at different depths (5 samples were taken between 0 and 20 cm and 5 samples between 20-40 cm) in two different lay outs. Total, sequential and simple extractions were realized on these samples using standardized methods with Distilled Water (DW), Calcium Chloride ($CaCl_2$) and Ethylene Diamine Tetraacetic Acid (EDTA) as solvents. Heavy metals were quantified by Atomic Absorption Spectrophotometry (AAS). Results showed that soils from the two lay outs were highly contaminated by Zn, Ni, Pb, Cr, Cu and Cd. Sequential extractions revealed that only 17% of these heavy metals (especially Zn, Ni, Pb, Cr and Cu) could be exchanged or were linked to carbonates while 42% were in the residual forms and 29% were adsorbed to soil organic matter. With the exception of Cd which was mainly residual in the studied soils, >50% of the five other heavy metals were strongly linked to iron, manganese and aluminum oxides. Furthermore, simple extractions revealed that >60% of these heavy metals could be exchanged and are therefore bioavailable. This study revealed that market gardening in urban areas of Ngaoundere could be associated with environment and health hazards.

Key words: Soil pollution, market gardening, heavy metals, mobility, environment, hazards

INTRODUCTION

Developing countries like South Saharan Africa countries have witnessed very important socio-cultural changes in the last two decades. The most visible face of these changes is the rapid urban growth in most countries with new food habits and practices to fulfill the city dwellers'needs. It is the case for Cameroon were towns like Ngaoundere are hosting important urban market gardening activities. To satisfy the increasing demand, market-gardeners make an uncontrolled use of pesticides and other chemical inputs. Moreover, urban agriculture is carried out essentially with waste water and sometimes with the help of different wastes as fertilizers: crop residues, animal feces and bones. This might have dramatic consequences in the concentration of various minerals including heavy metals in soils used for this activity. It is believed that the reuse of waste can reduce the cost of waste management but also increase the amount of minerals found in the soil which constitutes a major environmental problem (Barber, 1995).

The origin of heavy metals in soils has been well documented. Previous studies showed that metals like Pb, Zn and Cu are easily released during car traffic (Sanka et al., 1995), Cd during the incineration of household wastes, Sr, Ba, F, Zn and Cd during gas emissions of contaminated sites (Cambier, 1994) and the use of fertilizers in agriculture.

One of the pathways through which these metals contaminate the environment is their horizontal (by streaming water) and vertical (migration into the depths by scrubbing) mobility.

The movement of these metals can be made in association with solid particles such as clays, dissolved organic matter and biomass (Mills et al., 1991) and is accelerated by the macroporosity of soils.

These heavy metals can also be adsorbed or absorbed by plants' roots, diffuse inside the plant, accumulate in the leaves and the stalk and contaminate the food chain (Morel et al., 1997; Baker et al., 1994; Barbarick et al., 1998; Baveye et al., 1999; Jarausch-Wehrheim et al., 1999).

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Given the possible contamination of the environment and the food chain, it is necessary to access the potential risk through bioavailability of heavy metals in contaminated soils. To this effect, speciation is generally used because trace elements in soils are present in various forms which influence their ability to react thus, their mobility.

The aim of this research is therefore to determine the speciation of some heavy metals (Zn, Ni, Pb, Cr, Cu and Cd) of urban culture soils near the Soum-Soum river in Ngaoundere to evaluate the environmental and health hazards.

MATERIALS AND METHODS

Soil sampling: Soil samples were collected in two market gardening areas situated in Ngaoundere, Adamawa region of Cameroon. The site 1 with geographic coordinates (1114 Alt; 07°32'N N; 13°33'E E) is located behind the central prison along the River Soum-Soum were solid and liquid waste from the prison are generally disposed. The second site (1103 Alt; 07°33'N N; 13°60'E E) was at Sabongari park also near the same river. The distance between the two sites is about 5 km with the first site been situated upstream and the second downstream. Five cultivated plots of 5 m length and 2 m width were chosen on each site and ten samples of cultivated soils were taken on each site. The sampling was done on a surface area of 100 cm² at various soil depths (0-20 and 20-40 cm). The choice of the plots was function of the duration of exploitation, their position with regard to the river and the former common dumps and with regard to the presence of cultures in gardens. Samples were respectively dried (105°C, 12 h), crushed and sieved (<2mm).

Soils characteristics: The pH and electric conductivity of the soil were determined respectively with a pH meter and a conductivimeter according to the NF ISO 10390 and NF ISO 11265. The mass of humid soil and dry soil (after drying at 105°C for 12 h) were measured with a balance. The Residual humidity (Rh) of the soil were obtained suing the mathematical formula below, according to NF ISO 11465 norms.

$$Rh = \frac{\text{Humid soil mass} - \text{Dry soil mass}}{\text{Humid soil mass}} \times 100$$

Organic Matter (OM) was obtained by potassium dichromate oxidation (K_2CrO_7) in acid medium according to the norms NF ISO 14235.

Total and sequential extractions: Total extractions were realized as defined by the NF standard X31-415 (NF AFNOR X31-415, 1995) while sequential extractions were realized according to the protocol of the Community Reference office (BRC) (Quevauviller *et al.*, 1997).

Simple extractions with Distilled Water (DW), $CaCl_2$ and EDTA: For simple extractions, the soils samples were dissolved under agitation (1 g/10 mL) in distilled water during 24 h and in a solution of $CaCl_2$ (0.01 mol L^{-1}) during 24 h. Extractions in EDTA (0.05 mol L^{-1}) were carried out in the ratio of 100 mL g^{-1} of soil and pH 7.5±0.5. These techniques were efficiently used to extract cationic species such as Zn, Pb, Cu and Cd present in contaminated soils by Elliot and Shasteri (1999), Garrabrants and Kosson (2000), Sun *et al.* (2001) and Tandy *et al.* (2004).

RESULTS AND DISCUSSION

Physico-chemical parameters: The main physico-chemical parameters analysed are shown in Table 1. These results show the values obtained for some parameters varied significantly either with the soil depth or with the site. Hence, OM seemed to be influenced only by the soil depth since for both sites, different values were obtained at 20 and at 40 cm. However for the same depth, quite similar amount of OM was measured. This may be due to the fact that the two sites belonged to the same agro-climatic zone with the same vegetation. Given that organic matter consists essentially in plant and animal materials, it could be assumed that comparable amounts of these organic materials are deposited in both sites. Generally, organic matters are disposed in special containers and are collected by a company in charge of waste management.

The fact that the first 20 cm soil depths are generally more affected than others (>20 cm) could be explained by deposits of garbage (household and urban) and debris of all kinds at the surface of the soil.

The residual humidity increased with the soil depth and was not influenced by the site. The two sites are situated in swampy areas and probably receive comparable amounts of water.

The pH varied significantly from one site to another and from one depth to another. The increase in pH with depth could be correlated to the variation in relative

Table 1: Physico-chemical parameters of soil samples from the two sites

	OM (%)		Rh (%)		pH		Ω (μS cm^{-1})	
Depth	20 cm	40 cm	20 cm	40 cm	20 cm	40 cm	20 cm	40 cm
Site 1	3.5[Ba]	2.62[Aa]	46.17[Ab]	47.73[Ba]	6.18[Aa]	6.40[Ba]	286.00[Bb]	264.00[Ab]
Site 2	3.3[Ba]	2.90[Aa]	45.63[Aa]	47.07[Bb]	6.67[Ab]	6.88[Bb]	259.95[Ba]	136.96[Aa]

A and B: for each column, values with the same capital letter are not significantly different (p<0.05), a and b for each line, values with the same small letter are not significantly different (p<0.05)

Table 2: Average concentrations of heavy metals found on Sites 1 and 2 at 0-20 and 20-40 cm depth

Heavy metal (mg kg^{-1})	Site 1 depth		Site 2 depth		Standards
	0-20 cm	20-40 cm	0-20 cm	20-40 cm	
Zn	102.68±3.950^{Ab}	75.29±13.19^{Aa}	110.58±6.58^{Bb}	95.57±3.95^{Ba}	200.0
Ni	914.96±1.850^{Bb}	840.49±16.99^{Ba}	776.64±8.73^{Ab}	421.39±7.73^{Aa}	70.0
Pb	936.59±15.02^{Bb}	718.61±2.120^{Ba}	577.26±2.45^{Ab}	406.47±2.12^{Aa}	100.0
Cr	389.42±14.15^{Aa}	433.74±7.130^{Ab}	503.18±9.44^{Bb}	317.32±2.21^{Ba}	70.0
Cu	240.69±7.810^{Ba}	250.07±3.120^{Ba}	134.42±5.65^{Aa}	133.38±3.05^{Aa}	100.0
Cd	218.29±4.530^{Bb}	118.39±7.270^{Ba}	144.67±1.78^{Ab}	81.71±7.27^{Aa}	1.5

A and B (S), a and b (D) for each line, values with the same capital letter or small letter are not significantly different (p<0.05); S: Site; D: Depth

humidity and in organic matter. Hence, the pH increased with the reduction of OM and the increase of Rh. The higher the pH, the lower the OM and the lower the Rh. Variable chemical reactions including hydrolysis in humid milieu could explain the increase in pH. The probable action of soil microorganisms on the organic matter could also be reasonably hypothesized.

Total heavy metals: Heavy metal concentrations of each Site (1 and 2) and at different depths are shown in Table 2. The concentrations of all metals for Site 1 were greater than those for Site 2. The average concentrations varied on both sites from 75.30-110.58 mg kg^{-1} for Zn; 421.40-914.97 mg kg^{-1} for Ni; 406.48-936.60 mg kg^{-1} for Pb; 317.33-503.19 mg kg^{-1} for Cr; 133.39-250.07 mg kg^{-1} for Cu and 81.71-218.294 mg kg^{-1} for Cd. Apart from the concentration of Zn, the other heavy metals analyzed were detected at values very largely above the admitted standards.

The high concentrations in Ni, Pb, Cr, Cu and Cd could be due to different environmental and human reasons. The two sites were former dumps before being cultivated. Moreover, Adjia *et al.* (2008) have shown that River Soum-Soum water used for irrigation was highly polluted with heavy metals. The final amounts of heavy metals are the consequence of the accumulation of minerals from different sources and the efficiency of plants grown on these soils to fix these metals.

Soil distribution of heavy metals: Table 3 shows the ratio of heavy metals at different depths on Site 1 and 2. These ratio compare the importance of heavy metals in upper layers of soils with that of the lower layers. Values <1 indicate that the metal is most concentrated in the lower soil layer while values >1 traduce greater concentrations in the upper soil layer. Therefore, almost all the heavy metals analyzed are mostly concentrated in the upper soil layers in both sites. Only Cr for the soil sample from Site 1 was found at greater amounts in deeper layer than at the surface.

The sequential extractions: Heavy metals (Zn, Ni, Pb, Cr, Cu and Cd) are mainly present in the reducible fraction (B2) as shown in Table 4. They have a strong affinity with

Table 3: Ratio of heavy metal concentrations at different layers 0-20 and 20-40 cm depth

Sites	Zn	Ni	Pb	Cr	Cu	Cd
Site 1	1.44	1.14	1.31	0.99	1.03	2.04
Site 2	1.20	1.48	1.42	1.72	1.09	2.09

oxy-hydroxides of iron, manganese and/or aluminum. They are generally present in abundance under amorphous or crystalline form in most soils where they play a predominant role in the sorption of the metallic ions. This is due to their low solubility in common conditions of pH (Sposito, 1989). It has been shown that most soils of Ngaoundere are ferralitic and ferruginous thus very rich in iron, manganese and aluminum. This implies that metallic ions (Zn, Ni, Pb, Cr, Cu and Cd) bind strongly in the matrix of iron, manganese and aluminium (hydro) oxides. Indeed, zinc, nickel, lead, chromium, copper and cadmium ions are sorbed chemically on the surface of (hydro) oxides of Fe, Mn and Al. According to Buffle, the acidity of the environment could control the quantity of adsorbed ions and the value of the pH allows an estimation of the oxides domain of activity. According to the same author, the adsorption is maximal for pH values of 2.3, 7.9 and 8.1 for amorphous oxides of iron and manganese and pH >9 for aluminum oxides. It can therefore be deduced that Zn, Ni, Pb, Cr, Cu and Cd are more adsorbed by iron and manganese oxides than they are with aluminum oxides, given that the pH of the soils sample are between 2.3 and 7.9.

Table 4 shows that the quantities of Zn, Ni, Pb, Cr, Cu and Cd in the residual phase (B4) are greater than standard values. This could be explain by the stabilization of these metals with time that is their evolution towards non extractible forms in soils amended by muds and thus by contaminated manure from urban dumps (Emmerich *et al.*, 1982).

It could also be due to reabsorption of part of the metals in the previous stages (fractions B1-B3) on the remaining phases and/or the incomplete destruction of the metal phases in the previous stages (Nirel and Morel, 1990). Indeed, the absence of these metals in the fractions B1-B3 shows well that they are under non-extractibles or residual forms.

Table 4: Sequential extractions of the six heavy metals at 20 and 40 cm depth of soil

Heavy metal (mg kg^{-1})	Fractions	Site 1 depth		Site 2 depth	
		0-20 cm	20-40 cm	0-20 cm	20-40 cm
Zn					
	B1	4.48±0.100^{Ba}	6.946±0.08^{Bb}	3.58±0.810^{Aa}	3.09±0.08^{Aa}
	B2	36.49±3.120^{Aa}	40.83±1.870^{Aa}	44.79±7.700^{Aa}	47.49±2.76^{Aa}
	B3	24.528±3.38^{Ab}	7.39±0.930^{Aa}	35.21±1.130^{Bb}	8.07±0.34^{Ba}
	B4	38.25±1.950^{Ab}	21.13±0.230^{Aa}	27.00±2.560^{Aa}	36.91±3.77^{Ab}
Ni	B1	130.19±4.410^{Ba}	123.90±2.410^{Ba}	104.3±3.2100^{Ab}	67.83±2.91^{Aa}
	B2	327.82±8.610^{Ba}	388.22±4.450^{Bb}	243.53±2.990^{Ab}	190.13±8.90^{Aa}
	B3	188.28±8.090^{Bb}	159.24±2.210^{Ba}	120.354±6.07^{Ab}	62.56±2.54^{Aa}
	B4	266.38±2.230^{Ab}	169.01±1.230^{Aa}	308.31±1.240^{Bb}	201.13±4.02^{Ba}
Pb	B1	126.72±1.950^{Bb}	72.49±1.570^{Ba}	71.36±1.570^{Aa}	73.63±0.52^{Aa}
	B2	298.58±3.180^{Ba}	356.64±3.680^{Bb}	244.52±0.210^{Aa}	230.51±2.14^{Aa}
	B3	192.89±7.570^{Bb}	108.41±1.930^{Ba}	71.44±1.240^{Ab}	38.91±2.47^{Aa}
	B4	318.32±5.870^{Bb}	181.08±3.210^{Ba}	189.95±1.580^{Ab}	63.44±5.46^{Aa}
Cr	B1	12.93±1.620^{Bb}	1.69±0.140^{Ba}	0.00^{Aa}	0.00^{Aa}
	B2	236.96±2.890^{Bb}	198.70±7.090^{Ba}	297.39±4.350^{Ab}	150.00±4.35^{Aa}
	B3	69.21±6.500^{Bb}	49.27±1.830^{Ba}	79.75±0.260^{Ab}	29.19±0.01^{Aa}
	B4	70.25±2.040^{Ba}	184.09±2.930^{Bb}	126.05±4.020^{Aa}	138.43±5.41^{Aa}
Cu	B1	10.71±7.550^{Ab}	5.28±0.540^{Aa}	11.32±3.770^{Ab}	6.41±0.71^{Aa}
	B2	118.99±2.140^{Ba}	138.86±2.470^{Bb}	64.85±6.550^{Aa}	67.85±2.47^{Aa}
	B3	18.81±4.710^{Ba}	24.47±2.720^{Bb}	17.87±2.720^{Ab}	11.98±2.36^{Aa}
	B4	92.16±4.540^{Bb}	81.46±4.890^{Ba}	40.98±2.540^{Aa}	47.13±6.33^{Ab}
Cd	B1	0.00^{Aa}	0.00^{Aa}	0.00^{Aa}	0.00^{Aa}
	B2	60.724±5.13^{Bb}	33.754±8.89^{Ba}	24.57±7.700^{Aa}	33.53±2.57^{Ab}
	B3	24.24±3.010^{Ba}	20.77±0.500^{Ba}	19.47±3.010^{Ab}	12.79±0.51^{Aa}
	B4	133.33±5.780^{Bb}	56.24±4.780^{Ba}	100.34±8.120^{Ab}	35.38±1.54^{Aa}

A and B (S), a and b (D): for each line, values with the same capital letter or small letter are not significantly different (p<0.05), B1: Exchangeable soluble acid fraction; B2: Reducible fraction; S: Site; B3: Oxidizible fraction; B4: residual fraction; D: Depth

The extracted metals (Zn, Ni, Pb, Cr, Cu and Cd) are found in the oxidizible fraction (B3). This means that they are fixed to the soil organic matter due to the specific link their can have with humic substances (Choudhry, 1984) through reactions with carboxylic functions (-COOH) and phenolic functions (in particular-OH) by complexation. It was earlier demonstrated that there exist a high selectivity between organic matter and some metals (McBride, 1989). It is the case for example of a soil contaminated by Pb from alkyl products (compounds added to the fuel) which can form complexes with many carboxylic groups found in the organic matter (Manceau *et al.*, 1996). The complexes formed directly between the lead and humic substances are very stable thus reducing their mobility.

Results from Fig. 1a-d show that heavy metals are found in the fraction B1 except Cd. They are present specifically in exchangeable forms in the soil and/or acido-soluble. Metals in exchangeable forms are fixed to the solid soil particles like clay, silica and organic matter. This may be due to the compensation of negative charges at the surface of clay by the cations at the surface of minerals. A variable charge due to the presence of hydroxyl groups on clay borders can also be found leading to the fixation of these heavy metals (Zn^{2+}, Ni^{2+}, Pb^{2+}, Cr^{2+} and Cu^{2+}) either by ion exchange or by chemical sorption/physical sorption (Manceau *et al.*, 1996; Mancean *et al.*, 2000). Also, acid-soluble heavy metals

precipitate with the carbonate present in the soil (Miller *et al.*, 1983) due to their ability to react by hydration of their surface which leads to the formation of -CaOH, -POH groups. The dissociation of these compounds enhances the adsorption of heavy metals on their surface. The precipitation or co-precipitation of Zn, Ni, Pb, Cr and Cu with these compounds is also responsible for their retention in soils (Cotter-Howells, 1996).

Simple extractions: Soil fraction distributions (soluble, mobile and mobilizable) for each metal with regard to the total concentration varied from a site to another as shown by Fig. 2a-d. These variations are coherent with the physico-chemical characteristics of the soils at different depth of the sampling sites. The average humidity of soil from Site 2 is higher than that of Site 1, the solubility, the mobility and even the bioavailability of the zinc in Site 1 would be greater than what is observed in Site 2.

Figure 2 shows that the studied heavy metals are all weakly soluble in soil. This low solubility could be due to the acid and neutral pH (5.81 and 7.66) of the soils and to the strong interactions between the soil and the metal. Indeed, the solubility of an element in solution is a function of the volume of the solvent, the concentration of the solution (metal) and the other physical parameters including the environment's pH. This solubility increased slightly with depth for certain metals (Ni, Cu and Cd),
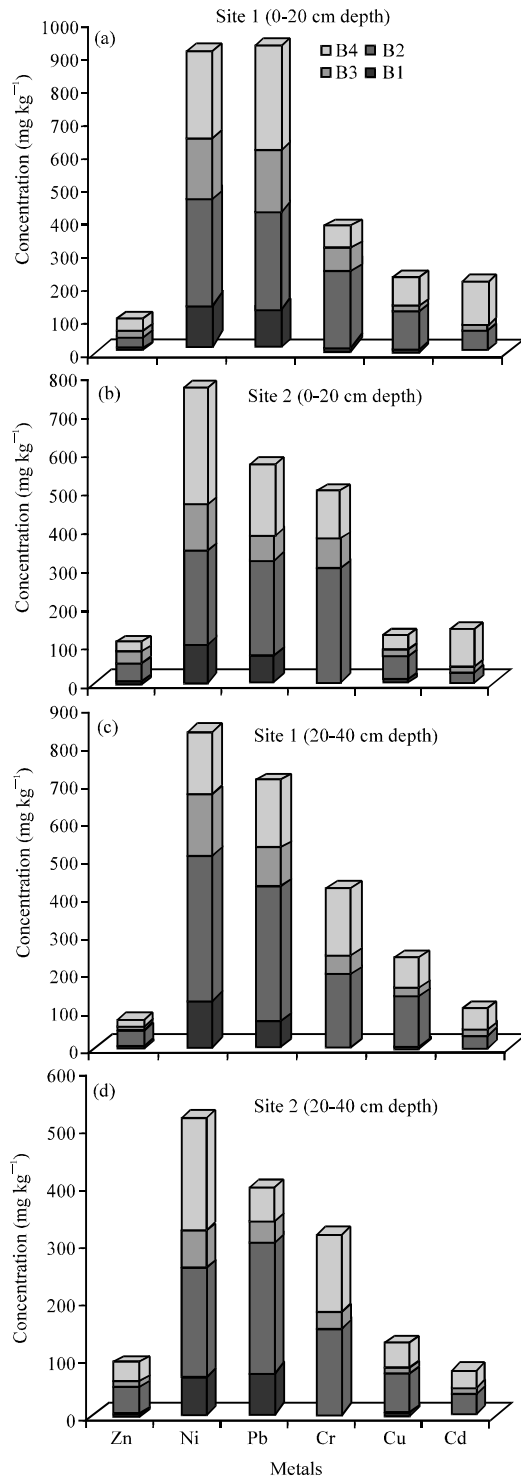
Fig. 1: Distribution of total concentration of Zn, Ni, Pb, Cr, Cu and Cd in different reactional fractions in the soils of Sites 1a-b and 2c-d in 20 cm and 40 cm depth; B1: Exchangeable soluble acid fraction; B2: Reducible fraction; B3: Oxidizible fraction; B4: residual fraction
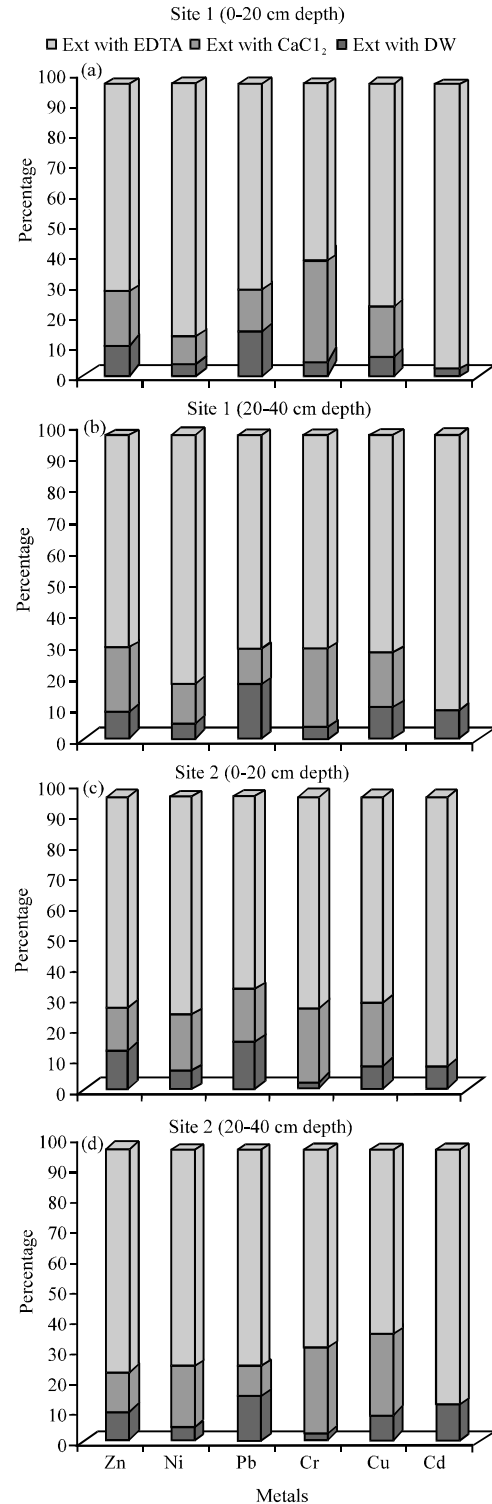
Fig. 2: Distribution of total concentration of Zn, Ni, Pb, Cr Cu and Cd to soluble (Ext. with DW), mobile (Ext with $CaCl_2$) and mobilizable (Ext with EDTA) fraction in the soil of Sites 1a-b and 2c-d of 20 and 40 cm depth

probably as the consequence of the increase in residual humidity with the depth. Indeed, the relative humidity is higher between 20-40 cm than between 0-20 cm depth. This means that the higher quantity of water at this depth is responsible of lixiviation of the soil and consequently of the solubilization of minerals.

The CaCl$_2$ solution (0.01 M) reproduces the composition of soil solution in terms of ionic strength and pH in natural conditions. Except for elements such as Cu, Cr and in a lesser extend Zn, studied heavy metals are slightly soluble and weakly mobile in the studied soils. The observed difference between the extraction with DW and with CaCl$_2$ for all heavy metals could be explained firstly by the ionic strength of the solutions, then by the difference in pH of the solutions after treatment of the DW and CaCl$_2$.

The ionic strength of distilled water is lower than that of natural soil and result in the destabilization of colloids which are more stable when using CaCl$_2$. The destabilization of these colloids increases their transport by lixiviation and thus those of the minerals (Zn, Ni, Pb, Cr and Cu) fixed on them. On the other hand while the pH obtained at the end of the tests with CaCl$_2$ varied between 5 and 5.7; it varied between 5.81 and 7.56 (almost neutral) during the tests with DW. This is responsible for the lesser solubilization of the metallic ions including Cd^{2+}.

The mobility of Zn, Ni and Cu increased with soil depth as shown in Table 5. This trend could be attributed to the humidity of the soils which also increased with depth. Such a high mobility seemed paradoxical because the physical environment of the soil at depth is less porous and less permeable due to its structure which is mainly made up of clay and silt. However, it is this later reason that accounts for the reverse phenomenon observed in Pd and Cr where their mobility rather decreased with the increase in soil depth.

The extraction with EDTA helped in determining the mobilizable or bioavailable fractions of heavy metals in the soils of both sites. The amount of extract using EDTA varied from 51-70% with regard to the total contents. This greater mobilization could be attributed to the chelating power of EDTA which can extract metals in the phases not bound to silica and those bound to organic complexes (Garrabrants and Kosson, 2000). When extracting with EDTA (0.05 M, buffer pH 7.5), final soils' pH were within 7 and 8. These pH could solubilize anions in an acid environment or increase chelation of different cations in a basic environment (Garrabrants and Kosson, 2000). For Zn, Cu and Ni the percentages of extraction of these metals with EDTA were respectively 60.16, 61.57 and 70.24% showing that they are mobilizable and consequently available for plants. The bioavailability of some heavy metals (Zn, Ni, Pb and Cr) has been found to vary with soil depth. This is as a result of the intense activity of plant roots in the 1st 30 cm soil depth. As the cultivated plant will adsorb or absorb the metals, their concentration will vary. The more the roots reach 30 cm depth, the less the amount of metals found. Cu appears to be one of the metals with great importance for plants. It is not the case for Cd. Paradoxically the bioavailability of Cu decreased with soil depth while a reverse trend was noted for Zn and Ni.

CONCLUSION

The present study brought evidence that soils used to produce food for Ngaoundere dwellers are highly contaminated by heavy metals (Zn, Ni, Pb, Cr, Cu and Cd). The contamination levels were greater at the upper soil layers. The heavy metals were of exogenous (for Zn, Ni, Pb and Cd) and endogenous (for Cr and Cu) origins. The reducible and residual forms of these metals were more important at 20-40 cm depth while oxidizible forms dominated at 0-20 cm depth. All the heavy metals studied were bioavailable in soils and higher concentrations were found for Zn, Cu and Ni. These findings raised serious environmental and health questions. Consequently, the consumption of the plant grown on such soils may tremendously increase cases of food poisoning of the consumers. Necessary measures most therefore be taken to decontaminate these soils. The use of comprehensive methods like phyto-remediation or phyto-stabilization appears to be reasonable and accessible solution.

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