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CONCENTRATION AND SPECIATION OF Cu, Ni, Pb and Zn IN CULTIVATED AND UNCULTIVATED SOILS

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Abstract

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This research was carried out to determine the concentration and speciation of some heavy metals in cultivated and uncultivated soils of northwestern Turkey. The total of 50 cultivated soil samples (25 Ultisols and 25 Inceptisols) were collected from some major vegetable growing areas developed over granite (Ultisols) and riverine alluvium (Inceptisols) from Bursa province, Turkey. The Cu, Ni, Pb and Zn were determined by the aqua regia method. The mean values of total heavy metals for the cultivated Ultisols are Cu (21.2 mg kg^{-1}), Ni (15.1 mg kg^{-1}), Pb (19.2 mg kg^{-1}) and Zn (59.7 mg kg^{-1}) while those of the cultivated Inceptisols show higher values of Cu (43.6 mg kg^{-1}), Zn (79.9 mg kg^{-1}) while Pb (13.0 mg kg^{-1}) and Ni (7.7 mg kg^{-1}) in Inceptisols are lower. The general trend in the Ultisols for Pb and Ni is residual > oxalate >exchangeable>organic. The oxalate extractable phase is highest followed by the residual phase for Zn and Cu. However, all the metals are highest in the residual phase for the Inceptisols. Zinc and lead contents in the Ultisols are also positively correlated to pH of the soil.

Key words: heavy metals, vegetable soils, metal speciation

Introduction

Metals present in soils can be associated with several reactive components. Although total metal concentrations may indicate the overall level of metals in soils, they provide no information regarding the chemical nature or potential mobility and bioavailability of a particular element (Vijver et al., 2004; Jin et al., 2005; Powell et al., 2005). Sequential fractionation is a frequently used approach to evaluate metal distribution into different chemical forms present in a solid phase. Conceptually, sequential fractionation categorizes metals associated with chemically homogeneous fractions that, ultimately, affect metal availability. Although often criticized due to lack of specificity of extractants and possible readsorption of metals during extraction (Beckett, 1989), sequential fractionation can provide useful information to predict the fate of heavy metal in the environment. Ideally, sequential extraction procedures selectively extract metals bound by specific soil fractions with minimal effect on the other soil components. In practice, sequential fractionation schemes have been suggested to identify element distribution with "operationally" defined soil pools. These chemical pools range from water soluble to recalcitrant forms immobilized in mineral lattices. Several single and sequential extraction methods have been proposed (Tessier et al., 1979; Ahnstrom and Parker, 1999;

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Qiao et al., 2003). Fractionation schemes have not been standardized and the results of different procedures are not always comparable due to the lack of uniformity in the experiment conditions (i.e., number of extractions, reagents, shaking time).

Different sequential extraction techniques such as the five-step procedure of Tessier et al. (1979) are commonly applied to evaluate both the actual and potential mobility of metals in the environment. This extraction scheme allows the division of the total metal content into five fractions: exchangeable, carbonate bound iron/manganese oxide bound and residual fraction. The scheme was developed for sediments but many studies have used these procedures for soils (Abollino et al., 2002; Lu et al., 2003; Lu et al., 2004). However, this scheme may not be suitable for soils which do not contain carbonate. Rauret (1998) also elaborated that the extractants used for the fraction of metals bound to carbonates (ie acetic acid and sodium acetate) and the iron and manganese oxides (ie. hydroxylamine in acid solution) were not completely suitable. Both carbonates and oxides may not be completely attacked. Shuman (1979) proposed a scheme to study microelements in acid soils that do not contain carbonates or sulphides. This scheme included exchangeable, organic matter, Fe oxide, sand, silt and clay. Another speciation scheme was developed by the EC Standards, Measurement and Testing Programme., formerly BCR (Bureau Community of Reference). This scheme proposed only four fractions: ie: exchangeable; (acetic acid), reducible (hydroxylamine hydrochloride), oxidisable species (hydrogen peroxide and nitric acid) and residual (aqua regia), (Rauret, 1998). The BCR procedure had been tested for sediments (Thomas et al., 1994) and soils (Davidson et al., 1998). In Turkey, studies on heavy metal concentrations in the common agriculture soils have only started in the last decade or so and speciation studies are still lacking. An earlier study on the assessment of contamination of agricultural soils and crops in northwestern Turkey (Aydinalp, 1996) showed that some of our soils already contain observed values of Cd and Zn. Ultisols and Inceptisols were chosen for this study. These soils are all located in vegetable farms. The main objectives of this study were to determine the concentration ranges of total heavy metals (Cu, Pb, Zn and Ni) and the chemical speciation in four soil phases (i.e exchangeable, amorphous Fe oxides, organic matter and residual).

Methods

The soil samples (0-20 cm) were collected using a stainless steel auger. The bulk samples were air dried, crushed with mortar and pestle, and sieved to remove coarse fragments. Soil samples were analysed for pH (Mclean, 1982), organic carbon (Nelson et al., 1982) and CEC (Rhoades, 1982). The total heavy metal concentrations (Cu, Ni, Pb and Zn) were determined by the aqua regia method (Van Ranst, 1999).

Twenty five soil samples developed over granite (Ultisols) and riverine alluvium (Inceptisols) were collected from some major vegetable growing areas in the Bursa province of Turkey. Twenty five soils from uncultivated areas developed over granite were also sampled for background values.

The used sequential extraction procedures are modified from the schemes developed by Tessier et al. (1979) and Shuman (1979). The extraction was modified for soils because of these soils do not contain carbonates and appreciable sulphides and manganese. The first two steps are those from Tessier's scheme for exchangeable and organic bound fractions while the third step for amorphous iron oxides followed that of Shuman (1979). Step four is the heavy metals in the residual fraction using aqua regia instead of nitric, hydrofluoric and perchloric acid. The extractions were carried out on 1.0 g of soil and involved the following steps:

F1: Eight ml of 1 M $MgCl_2$ were added to the sample and suspension was shaken for 1 h and then centrifuged (20 min, 4000 rpm).

F2: Six ml of 0.02 M HNO_3 and 10 ml of 30% H_2O_2 were added to the residue obtained from the first extraction, and the suspension was shaken for 5h at the temperature of 85±2 °C. After cooling, 10 ml of 3.2 M CH_3COONH_4 were added and shaken for 30 min and centrifuged.

F3: The soil samples were extracted with 20 ml of solution 0.2 M ammonium oxalate and 0.2 M oxalic acid, shaken in the dark for 4 h and centrifuged.

F4: The heavy metals contents in the residual fractions were determined by aqua regia method. Cu, Ni, Zn and Pb were determined by atomic absorption spectroscopy (AAS).

Results

Chemical properties and total heavy metal concentrations

Some selected chemical results of the soil samples were presented in Table 1.

The soil pH, organic carbon and CEC in the cultivated soils are higher than the uncultivated soils. These values showed that chemical properties have increased due to the soil amendments such as addition of chicken dung and liming as seen in Table 3. The zinc values are the highest in both soil orders, followed by Cu, Pb and Ni. Comparing these heavy metals between the cultivated and uncultivated Ultisols using T test, Cu and Zinc contents have shown significant increase ($p<0.001$) in the cultivated soils. The potential source of these metals may be the chicken dung which is added in large quantities to the soils for the production of vegetables in the study area. The total Cu and Zn in the Inceptisols showed much higher values than those in the Ultisols. This may be due to the length of time that these soils have been used. The farmers in the Inceptisols area have been operating for more that 30 years while those in the Ultisols have only been recently developed. In general, all the heavy metal values are lower than established in an earlier study by Aydinalp (1996), thus indicating that these soils are still not considered contaminated. However, Cu and Zn in the Inceptisols show that they are close to being in the contaminated zone. Correlation studies of total heavy metal concentrations and soil chemical properties show that only total Zn and Pb is positively correlated to pH, Zn with organic carbon, while Cu is negatively correlated with CEC (Table 2).

Speciation of Heavy Metals

The mean values of Cu, Pb, Ni and Zn fractions of soils are presented in Tables 3 and 4. The Cu and Zn show the highest concentration in the amorphous iron oxides fraction, while Ni and Pb are highest in the residual fraction of the cultivated Ultisols. The Cu fractions follow the order: amorphous iron oxides > residual > organic > exchangeable. For Pb, the order: residual > amorphous iron oxides > exchangeable > organic. The Zn fractions follow the order: amorphous iron oxides > residual > exchangeable > organic. For Ni fractions follow the order: residual > amorphous iron oxides > exchangeable > organic. The amounts of non-residual fractions (F1, F2 and F3) represents the amounts of active heavy metals while those of the residual fractions may be considered to be the stable form and thus not available to plants for a reasonable period.

In this research, the non-residual fractions of Cu, Ni, Pb and Zn in the Ultisols average 60.8%, 51.1%, 67.7% and 25.4% which suggests that the mobility and bioavailability of the four metals are in the order: Zn > Cu > Pb > Ni. This trend is not similar in the cultivated Inceptisols (Table 4). The highest amounts of all the heavy metals were found to be in the residual fractions.

This trend was also found by Adamo et al. (2003) in southern Italy for volcanic soils which was irrigated for a long time with contaminated river water. More

Table 1

Mean values for total heavy metal concentrations and chemical properties of soils

Soil Type	pH	O.C, %	C.E.C. mmol kg^{-1}	Cu	Ni, mg kg^{-1}	Pb, mg kg^{-1}	Zn, mg kg^{-1}
Cultivated Ultisols	6.04	1.74	179	21.2	15.1	19.2	59.7
Uncultivated Ultisols	5.6	0.7	627	7.2	5.5	17.5	5.5
Cultivated Inceptisols	6.16	2.6	193	43.6	7.7	13	79.9

Table 2

Correlation coefficients between total heavy metal contents and chemical properties of cultivated Ultisols

	Cu	Ni	Pb	Zn
	mg kg^{-1}			
C.E.C	-0.35**	ns	ns	ns
pH	ns	ns	0.41**	0.27**
Organic Carbon	ns	ns	ns	0.30**

ns. not significant

** significant at the 0.01 probably level

Table 3

The mean values of Cu, Pb, Zn and Ni fractions expressed as percentage of sum of fraction (%) for the cultivated Ultisols

	F1 Exchangeable	F2 Organic	F3 Amorphous Fe oxides	F4 Residual
Cu	1.1	2.3	56.8	39
Ni	8.8	1.1	15	74.4
Pb	7.7	6.2	36.7	48.7
Zn	2.2	1.1	15	32.1

Table 4

The mean values of Cu, Pb, Zn and Ni fractions expressed as percentage of sum of fraction (%) for the cultivated Inceptisols

	F1 Exchangeable	F2 Organic	F3 Amorphous Fe oxides	F4 Residual
Cu	4.7	8.6	18.2	67.7
Ni	1.4	1.7	5.6	90.5
Pb	5.5	2	3.1	88.6
Zn	0.6	2.1	4.4	92.1

than 50% of Ni, Pb and Zn in these soils were held in the residual fraction. This trend may be explained by residence time effect which may reduce metal mobility and bioavailability due to complexation, adsorption and precipitation of metal ions in the soil particle surface. Lu et al. (2004) studied the time effect on the fractionation of heavy metals in soils and found that soluble metals added were transformed from easily extractable fractions to more stable fractions. The non-residual Cu, Ni, Pb and Zn fractions in the cultivated Inceptisols average 32.1%, 11.2%, 7.7 % and 9.3 %. This trend suggests that the mobility and bioavailability of the four metals are in the order Cu> Pb > Ni > Zn. These soil results indicated the order of mobility of metals differ in these two types of cultivated soils which are both amended with chicken dung and also the amount in the residual fractions. The Cu fractionation and extractability in two contaminated soils found that most of the anthropogenic Cu was associated with the mobile fractions in Inceptisols af-

ter six weeks incubation whereas in the Ultisols, the mobile became dominant only at the higher rate of Cu amendments by Yu et al. (2004). The chicken dung types and other soil amendments may also be responsible for these differences. Stacy et al. (2001) studied the effect of aging biosolids on the availability of cadmium and zinc in soil found that the release of both these metals depended on the biosolid composition. While two sludges showed no change in plant available metal pools, the third sludge showed an increase.

Conclusion

Total heavy metal concentrations in cultivated both soil types fall within the typical range for unpolluted soils. The modified Tessier's sequential extraction procedure showed that all the metals in the Inceptisols are dominantly in the residual fraction. The general trend is residual > amorphous iron oxides > exchangeable > organic for Pb and Ni in the Ultisols. The amorphous iron oxide extractable phase is highest followed by the residual phase for Zn and Cu. The contents of Pb and Zn in the Ultisols are also positively correlated to the soil pH.

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