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Influence of Some Soil Parameters on Heavy Metals Accumulation by Vegetables Grown in Agricultural Soils of Different Soil Orders

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Abstract The main purpose of this research was to determine the levels of heavy metals in tomato, potato and lettuce, grown in agricultural soils of different soil orders (Alfisols, Endisols and Vertisols), located at Central Greece. Soil samples were analysed for available forms (after extraction with DTPA) and for total concentrations (after digestion with Aqua Regia) of metals. Zn, Cu, Cr and Ni were the common metals detected in the vegetables studied. Pb and Cd concentrations were low and in some cases not detectable. Significant correlations among metals concentrations and soil physicochemical parameters were obtained and discussed. The pH value and the percentage of clay content were found to determine the solubility of metals in the soil and their availability for uptake by plants.

Keywords Metals · Vegetables · Agricultural soils · Greece

Contamination from heavy metals is a serious problem recognized in most countries of the world. The main sources of trace elements to plants are their grown media (soil, air, nutrient solutions) from which trace elements are taken up by the root of the foliage. The bioavailability of elements to plants is controlled by many factors associated with physicochemical characteristics of soils, the climatic conditions, plant genotype and agronomic management (Kabata-Pendias and Pendias 1992; Van Lune and Zwart 1997; Chojnacka et al. 2005; Tokalıoğlu and Kartal 2006).

The solubility and therefore the bioavailability of heavy-metal ions vary widely because many factors influence their concentration in soil solution. The most important factors affecting metal availability are soil pH, clay content and organic matter content (Anderson and Christensen 1988; McGrath et al. 1988; Davies 1989; Alloway 1990; Kabata-Pendias and Pendias 1992).

As plants acquire necessary nutrients, such as nitrogen, phosphorus and potassium, they also accumulate metals such as lead, cadmium (Ismail et al. 2005). Heavy metals are not biodegradable and can accumulate in human organs, producing progressive toxicity. Ingestion of vegetables grown in soils contaminated with heavy metals poses a possible risk to human health (Intawongse and Dean 2006). The main route of exposure to these toxic heavy metals is through the diet (Liu et al. 2006).

Knowledge on the contamination of vegetables with heavy metals from different soil types (orders) is not well established in Greece. The purpose of this study was to determine the level of heavy metals in selected vegetables namely tomato, potato and lettuce, grown in different agricultural soils of different soil orders (Alfisols, Endisols and Vertisols), located at Central Greece.

Alfisols have an argillic horizon and in Karditsa location they appear to have low pH values (<5.5). Endisols were found in Trikala region, they have pH values that range from 6.5 to 7.5, and they are mostly sandy soils. Vertisols were in Larissa region. They are calcareous with high clay content (Soil Survey Staff 1999).

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Materials and Methods

The sampling area is located in central Greece. It has a warm spring continental weather with an annual average temperature and rainfall of 15.2°C and 245.5 mm, respectively. Three locations were chosen: Trikala (Tr), Larissa (La) and Karditsa (Ka) and they represent three different soil orders: Endisols, Vertisols and Alfisols, respectively.

Surface (0–30 cm) soil samples were collected randomly from the sampling area. They were air dried at room temperature and then ground with a mortar and a pestle, sieved through a 2-mm sieve and analyzed for soil pH and electrical conductivity (soil–H_2O, 1:1), clay content (%) and organic matter. Available metals were determined using diethylene-triamine-pentacetic acid (DTPA) buffered at pH 7.3 (Lindsay and Norvell 1978). Total concentration of heavy metals in soil samples was determined using Aqua Regia (HCl–HNO_3, 3:1) extraction method (ISO/DIS 11466 1994). Three grams of soil sample had been digested for 2 h at 180°C. Then they were filtered through Whatman[R] No. 42 filter paper and analyzed for metals concentration. All reagents were of analytical grade (Merck, Germany).

Three types of vegetable comprising fruit, storage roots and leafy vegetables were collected from the same sampling area. The vegetables studied were tomato (*Lycopersicon esculentum* L.) for the fruit vegetable, potato (*solanum tuberosum* L.) for the storage roots and lettuce (*Lactuca sativa* L.) for the leafy vegetable. Sampling was done randomly with five replicates.

The freshly harvest vegetables were washed initially with running water to remove the soil particles. Samples were cut into small pieces before being oven dried at 75°C to constant weight. The samples were then pulverized with a mortar and pestle and were subjected to wet digestion in a conical flask with HNO_3:$HClO_4$ (2:1) for 3 h on sand bath (AOAC 1984). 10 mL of HCl was added to dissolve inorganic salts and oxides. Digested samples were filtered through Whatman[R] No. 42 filter paper and analyzed for heavy metals concentration.

Cadmium and Lead were determined by atomic absorption spectrophotometry (AAS) using the Graphite Furnace (GF) technique. Zn, Cu, Cr and Ni were determined by flame (F) AAS. Deuterium background corrections were used in the analysis of Cd and Pb followed the standard Methods of AOAC (1984). Certified Reference Material (CRM) (No. 141R, calcareous loam soil) by BCR (Community Bureau of Reference) was also analyzed for the verification of the accuracy of trace element determination in soils. Recovery values were calculated as the ratio of the BCR results to those of the Aqua Regia digestion and ranged from 94% to 102%. The detection limits based on three times the standard deviation of the blank (n = 10), were found between 0.08 μg L^{-1} (Cd—GFAAS) and 0.3 mg L^{-1} (Cu—FAAS).

All data are the mean values of five replicates. Data were subjected to an analysis of variance and means were compared by the Tukey test at the 5% level of significance. Correlation analysis (Pearson Correlation, 2-tailed) was conducted to determine the correlations between heavy metals concentration in soil and vegetable samples.

Results and Discussion

Heavy metals concentration in tomato, potato and lettuce samples from the three sampling locations, are shown in Table 1.

Concentration levels of Cd and Pb metals in the study area were comparable to those previously reported (Alama et al. 2003; Ismail et al. 2005). Zn and Cu concentrations both in tomato and lettuce samples were lower than those found in vegetables from mostly industrial and agricultural areas in Greece (Stalikas et al. 1997; Fytianos et al. 2001; Karavoltsos et al. 2002; Narin et al. 2005; Vavoulidou et al. 2005).

Table 1 Concentration[a] of heavy metals (μg g^{-1}) in tomato, potato and lettuce samples from Trikala (Tr), Larissa (La) and Karditsa (Ka) regions

	Tomato			Potato			Lettuce		
	Tr	La	Ka	Tr	La	Ka	Tr	La	Ka
Cd	0.004d	0.001e	0.008c	0.008c	0.003d	0.013b	0.013b	0.009c	0.029a
Pb	0.092b	0.090b	0.119a	0.077c	0.051d	0.077c	0.091b	0.010e	0.122a
Ni	0.120a	0.101b	0.121a	0.057d	0.081c	0.100b	0.058d	0.009f	0.080c
Cr	0.132c	0.116d	0.155b	0.089f	0.101e	0.115d	0.181a	0.090f	0.188a
Cu	0.160c	0.145d	0.175b	0.101f	0.122e	0.144d	0.177b	0.176b	0.191a
Zn	0.184c	0.169d	0.200b	0.201b	0.185c	0.222a	0.185c	0.150e	0.199b

[a] Means within a row followed of each fraction by the same letter are not significantly different at $p > 0.05$

Higher Cd concentrations were found in lettuce samples mostly in Alfisols where the soil samples were acid ($pH < 5.5$), followed by Cd concentration in Endisols where soil pH values ranged from 6.5 to 7.5. In Endisols also the increased availability of Cd is due to the high amount of sand. Lower Cd concentrations were found in lettuce samples grown in Vertisols where the soils were alkaline ($pH > 8.2$) and also they have high clay content. Lower Cd concentrations were found in tomato and even lower in potato samples. Root and leafy vegetables were found to accumulate Cd from soil much more efficiently than fruit vegetables.

Highest lead concentrations were observed in lettuce in Vertisols (Larissa) despite the fact that the soil sampling area appears higher pH values than in Karditsa or in Trikala region. Probably lead contents in vegetables were because of the increased air pollution and traffic in this area.

Ni concentrations were higher in tomato and lower in lettuce samples, while Cr concentrations in tomato and potato samples were almost equal. Zn and Cu were found in higher concentration in the vegetables studied as compared to the other metals. The highest Cu concentration was found to lettuce samples, while the highest Zn concentration observed to potato samples, with mean values of 0.191 and 0.222 $\mu g\ g^{-1}$ dry matter, respectively. In general Zn, Cu, Cr and Ni were the common metals detected in tomato, potato and lettuce samples. Pb and Cd concentrations were low and in some cases not detectable. In all cases the higher metal concentrations were observed in Alfisols probably due to the low pH value.

Table 2 Concentration[a] of heavy metals ($\mu g\ g^{-1}$) in soil grown with the three vegetables from Trikala (Tr), Larissa (La) and Karditsa (Ka) regions

		Cd	Pb	Ni	Cr	Cu	Zn
$Dtpa_{To}$	Tr	0.022f	0.057d	0.038e	0.026f	0.999b	1.123a
	La	0.014g	0.045e	0.029f	0.029f	0.810b	0.986a
	Ka	0.031g	0.061e	0.049f	0.037g	1.112c	2.369a
$AqRe_{To}$	Tr	0.078g	0.101f	0.077g	0.078g	2.133d	9.867a
	La	0.050g	0.095e	0.052g	0.077f	1.968d	7.563a
	Ka	0.091g	0.110f	0.055h	0.099g	2.566d	13.23a
$Dtpa_{Po}$	Tr	0.015g	0.051e	0.024f	0.018g	0.925c	4.036a
	La	0.009i	0.048f	0.018g	0.014g	0.859c	3.765a
	Ka	0.025f	0.070e	0.029f	0.031f	0.969c	4.258a
$AqRe_{Po}$	Tr	0.081f	0.099f	0.062g	0.055g	2.089d	12.36a
	La	0.052g	0.082f	0.060g	0.056g	1.123d	10.29a
	Ka	0.099h	0.111g	0.063i	0.081h	2.236e	15.89a
$Dtpa_{Le}$	Tr	0.032e	0.055d	0.022f	0.019f	0.956b	1.859a
	La	0.029f	0.040e	0.011g	0.012g	0.888b	1.336a
	Ka	0.041f	0.065e	0.029g	0.025g	1.236c	2.969a
$AqRe_{Le}$	Tr	0.091h	0.103g	0.041j	0.065i	1.892d	8.967a
	La	0.077g	0.099f	0.033i	0.052h	2.997c	8.236a
	Ka	0.101f	0.115f	0.039i	0.088g	4.522d	10.23a

[a] Means within a row followed of each fraction by the same letter are not significantly different at $p > 0.05$

Table 2 shows the concentration of heavy metals in soils grown with tomato (To), potato (Po) and lettuce (Le) from the three soil sampling areas studied. Total metal concentrations appear to be higher than the available metal concentration in all cases of heavy metals studied.

The ratio $DTPA_{metal}$/Aqua $Regia_{metal}$, was calculated in all metals and ranged as follows: Cd: 0.173 in Vertisols and 0.406 in Alfisols, Pb: 0.404 in Vertisols and 0.631 in Alfisols, Ni: 0.300 in Vertisols and 0.891 in Alfisols, Cr: 0.231 in Vertisols and 0.383 in Alfisols, Cu: 0.273 in Alfisols and 0.765 in Vertisols and finally Zn: 0.114 in Endisols and 0.366 in Vertisols. Thus, the availability of the heavy metals studied as expressed by the ratio $DTPA_{metal}/AqRe_{metal}$ was higher in acid soils as far is concerned the more dangerous and hazardous metals (Cd, Pb, Ni and Cr). These results agree with previous investigation (Mitsios et al. 2005).

Table 3 shows the correlation coefficients among soil parameters and heavy metals concentration in the three types of vegetable.

In Table 3 they are presented only the correlation coefficients that they are higher than 0.500 both in 0.01 level and 0.05 level. There was no significant correlation among soil total concentration (Aqua Regia method) of the metals studied and metals in tomato, potato or lettuce samples. On the other hand, there was a strong correlation among heavy metal concentrations in all types of vegetable studied and the available metal concentrations (DTPA method) in their respective soils.

The concentration of heavy metals in vegetable samples was negatively correlated with soil pH. Soil pH is the dominant factor controlling heavy metal uptake by plants. That generally agrees with other investigators (Sanders et al. 1986; Alloway 1990; Kabata-Pendias and Pendias 1992; Ismail et al. 2005). According to Table 3 it is obvious that there is a strong correlation among soil pH and concentrations of Cd, Pb, Ni and Cr in all vegetables. There is also a strong correlation among soil pH and concentrations of Cu and Zn, but only in potato and lettuce samples.

The correlation coefficients between all metals in vegetables and soil clay content were negative but not significant neither at the 0,01 level nor at the 0,05 level (Pearson Correlation, 2- tailed). Significant negative correlation was also found between soil organic matter and heavy metal concentrations in tomato samples, apart from Zn and Pb concentration where the concentration was positive.

Significant positive correlations were observed between total and DTPA extractable metals in all cases, with Cu

Table 3 Correlation coefficienst among soil parameters, available heavy metals concentration in soils (DTPA method) and heavy metals concentration tomato, potato and lettuce samples from the three regions studied

	pH	Cd_{DTPA}	Pb_{DTPA}	Ni_{DTPA}	Cr_{DTPA}	Cu_{DTPA}	Zn_{DTPA}
Cd_{ToKa}	−0.821**	0.752**	0.614*	0.742**	0.633**	0.659**	0.748**
Cd_{PoKa}	−0.886**	0.816**	0.602*	0.633**	0.618**	0.558*	0.519*
Cd_{LeKa}	−0.799**	0.612**	0.666*	0.599*	0.506*	0.612*	0.672**
Cd_{PoTr}	−0.723*	0.589*	0.526*	0.648*	0.639*	0.57**	0.639**
Pb_{ToKa}	−0.678**	0.692**	0.824**	0.588*	0.772**	0.593**	0.518**
Pb_{PoKa}	−0.633**	0.698*	0.892**	0.588*	0.589*	0.613*	0.578*
Pb_{LeTr}	−0.512**	0.672**	0.716**	0.566*	0.582**	0.668*	0.553**
Pb_{PoLa}	−0.699**	0.599*	0.672**	0.577*	0.577*	0.772**	0.599*
Ni_{ToKa}	−0.758**	0.623**	0.656**	0.772**	0.589**	0.639*	0.633*
Ni_{LeKa}	−0.695**	0.623*	0.658**	0.859**	0.596*	0.672**	0.588*
Ni_{PoTr}	−0.677**	0.658*	0.618*	0.642**	0.523*	0.578*	0.918*
Ni_{LeTr}	−0.612**	0.612*	0.584*	0.619**	0.588*	0.639*	0.523*
Cr_{ToKa}	−0.799**	0.563*	0.643*	0.788*	0.872**	0.569*	0.588*
Cr_{LeKa}	−0.725**	0.589*	0.689*	0.527*	0.878**	0.599*	0.569*
Cr_{PoTr}	−0.612**	0.512*	0.547*	0.623*	0.619**	0.587*	0.578*
Cr_{LeTr}	−0.623**	0.545*	0.563*	0.581*	0.745**	0.566*	0.523*
Cu_{PoKa}	−0.788**	0.658*	0.563*	0.632*	0.654*	0.852**	0.587*
Cu_{LeKa}	−0.759**	0.548*	0.578*	0.648*	0.688*	0.876**	0.695*
Cu_{PoTr}	−0.691**	0.536*	0.598*	0.589*	0.699*	0.733**	0.659*
Cu_{PoLa}	−0.578**	0.588*	0.577*	0.668*	0.647*	0.745**	0.661*
Zn_{PoKa}	−0.733**	0.589*	0.633*	0.635*	0.589*	0.777*	0.814**
Zn_{PoKa}	−0.829**	0.788*	0.645*	0.655*	0.548*	0.745*	0.856**
Zn_{LeKa}	−0.699**	0.698*	0.588*	0.678*	0.533*	0.755*	0.772**
Zn_{PoTr}	−0.688**	0.526*	0.623*	0.589*	0.569*	0.788*	0.793**

** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

exhibiting the highest correlation coefficients (0.49** and 0.48**) in acid soils cultivated with lettuce and tomato plants, respectively.

There was a significant interaction between the metals studied, as the metals concentration in the vegetables samples were highly correlated with all the metals extracted with the DTPA solution. The higher correlation coefficients were found in the vegetables (particularly in potato and lettuce) grown in Alfisols (Karditsa).

Differences in metal concentration in the vegetables examined seem to imply that different types of vegetables have different response to metal accumulation. In spite of the mechanisms involved in the elemental uptake by roots (mon-metabolic or metabolic), plants are known to respond to the amounts of readily mobile type of metals in soils (Liu et al. 2006; Tokalıoğlu and Kartal 2006).

It should be noted that the pH value, as well as the percentage of clay content determines the solubility of metals in the soil and their availability for uptake by plants. Low soil pH may induce metals to be easily soluble and have ion exchange comparable to high soil pH. Acid soils were found to be in Karditsa area where also the clay content was higher than in Endisols (Trikala) or in Vertisols (Larissa). The three types of vegetables grown in this area appear to have higher concentration of Cd than those cultivated in Endisols and Vertisols with soils almost neutral and alkaline, respectively.

In all cases the metal concentrations found in the vegetables studied are lower than the maximum limit as permitted in the EC regulation (EU Commission Regulation 2002).

Therefore lettuce, tomato and potato grown in these areas are safe as they are less contaminated than the allowed limit. Heavy metal concentration of the vegetables examined showed large variations even at the same sample location in the field. This is probably due to the different plant uptake. Agricultural soils from the areas of central Greece studied were also less polluted as most of the metals were present at concentrations lower than the critical limits (Alloway 1990; Kabata-Pendias and Pendias 1992).

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