

Letter to Editor

Distribution and Forms of Heavy Metals in Some Agricultural Soils

C. Aydinalp^{1*}, S. Marinova²

¹Uludag University, Faculty of Agriculture, Department of Soil Science, 16059 Bursa, Turkey

²Nicola Poushkarov Institute of Soil Science and Agroecology, Sofia, Bulgaria

Received: 23 January, 2003

Accepted: 21 March, 2003

Abstract

Distribution and availability of heavy metals to plants is important when assessing the environmental quality of an area. The objectives of this study conducted in 2002 were: a) determine the levels of the heavy metals cadmium (Cd), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn) in the agricultural soils of the Bursa plain so that the degree of pollution could be ascertained, b) identify the various heavy metal forms present in soils using a fractionation scheme based on sequential extraction, and c) to find possible dependence on soil physicochemical properties. Total heavy metal content of the soils studied was generally higher than the levels reported in literature for similar soils, suggesting some degree of pollution with heavy metals. The exchangeable forms of the heavy metals, however, were very low, indicating that under present conditions, the availability of heavy metals to plants is at a minimum.

Keywords: heavy metals, agricultural soil, pollution, extraction methods

Introduction

The loading of ecosystems with heavy metals can be due to excessive fertilizer and pesticide use, irrigation, atmospheric deposition, and pollution by waste materials. In natural ecosystems, and especially in wetlands, watershed management plays an important role, determining not only the degree of plant uptake and soil retention of the heavy metals but also the extent to which they are leached into aquifers. A precise knowledge of heavy metals concentrations, the forms in which they are found, their dependence on soil physicochemical properties provide a basis for careful soil management which will limit, as far as possible, the negative impact of heavy metals on the ecosystem. A knowledge of present heavy metal pollution levels within the watershed would be a starting point in estimating the consequences of poor watershed management regimes

which may mobilize previously unavailable forms of the heavy metals and lead to their incorporation into the food chain.

Heavy metals in soil may be found in one or more of the following forms:

- a) dissolved (in soil solution),
- b) exchangeable (in organic and inorganic components),
- c) as structural components of the lattices of soil minerals,
- d) as insoluble precipitates with other soil components.

The first two forms are available to the plants while the other two are potentially available in the longer term.

Understanding the mechanisms by which a heavy metal element changes from one form to another and the speed at which it does so, is imperfect but improving. In general, the concentration of an element in the soil solution is believed to depend on the equilibrium between the soil solution and solid phase, with pH playing the decisive role [1]. The soil's ability to immobilize heavy metals increases with rising pH and peaks under mildly alkaline conditions. Heavy metal mobility is related to their im-

*Corresponding author; e-mail: cumhur@uludag.edu.tr

mobilization in the solid phase. Fuller [2], in discussing the relatively high mobility of heavy metals with regard to pH, considered that in acid soils (pH 4.2-6.6) the elements Cd, Ni, and Zn are highly mobile, Cr is moderately mobile, and Cu and Pb practically immobile, and in neutral to alkaline (pH 6.7-7.8), Cr is highly mobile, Cd and Zn are moderately mobile and Ni is immobile.

Apart from pH, other soil properties, such as cation exchange capacity (CEC), organic matter content, quantity and type of clay minerals, the content of the oxides of iron (Fe), aluminum (Al), and manganese (Mn), and the redox potential determine the soil's ability to retain and immobilize heavy metals. When this ability is exceeded, the quantities of heavy metals available to plants increase, resulting in the appearance of toxicity phenomena.

Heavy metals tend to form complexes with organic matter in the soil (humic and fulvic acids), which are different for each metal [3]. Organic matter plays an important role not only in forming complexes, but also in retaining heavy metals in an exchangeable form. These two properties affect each heavy metal differently. For example, Cu is bound and rendered unavailable chiefly through the formation of complexes [4], while Cd is retained in an exchangeable form and is more readily available [5].

The CEC of a soil depends upon its organic matter content and clay type and content. In general, the higher the CEC the greater the ability to retain heavy metals. The type and quantity of clay determines the CEC, which increases with clay content, particularly when it contains a high proportion of 2:1 lattice-type minerals (e.g., montmorillonite). The specific soil surface is also closely related to clay content and type. Korte et al. [6] reported that the soil's ability to retain heavy metals is more closely tied to the specific surface than to the soil CEC.

In cases of soil pollution by heavy metals, it is important to identify the available and unavailable forms of the heavy metals to ensure that the soil is managed in such a way as to prevent the unavailable forms from becoming available. The most common and simple way to identify the forms in which heavy metals are found in soils is to use sequential extraction in which components loosely held by the soil are extracted first, followed by those more tightly bonded.

The various forms of the heavy metals thus sequentially extracted can be classified as dissolved, exchangeable, organically-bound, or bound to oxides. As Beckett [7] pointed out, the fractionation of heavy metals into various forms on the basis of sequential extraction is only operational and cannot indicate a specific mechanism, since it is by no means certain that a given extract does not contain smaller quantities of another form, nor that the extractant would dissolve similar forms (e.g., carbonates) of different metals. Nevertheless, it is useful to attribute a specific fraction to each extractant. Thus, neutral salts like potassium nitrate (KNO_3) are assumed to take up exchangeable forms of heavy metals, sodium hydroxide (NaOH) organically-bound forms, Na_2EDTA forms associated with carbonate salts, while strong acids like nitric

acid (HNO_3) take up chiefly that fraction which is structural component of mineral lattices and surfaces.

Beckett [7] in his extensive review suggested that is preferable to classify the metal by its extract, e.g., EDTA extract, and to describe the experimental method exactly. However, this approach would ignore the purpose of sequential extraction, which is to investigate the chemistry of various forms of heavy metals in the soil. It would be preferable to find extractants that will actually distinguish between the various metal forms on the basis of their chemistry. Earlier studies in the wider area of the Bursa plain have shown by sequential extraction that heavy metals exist in the soils at various sites [8, 9].

The objectives of this research are to conduct a survey based on the total heavy metal content required for monitoring future pollution trends, and then identify what common forms exist in order to assess the availability of the heavy metals to plant in the agricultural soils of the Bursa plain. An attempt was also made to correlate heavy metal concentrations with other easily measurable physical and chemical properties of the soils.

Experimental Procedure

The study area (Figure 1) is located 10 km east of Bursa city between $40^{\circ}13'$ - $40^{\circ}14'$ N latitudes and $29^{\circ}10'$ - $29^{\circ}20'$ E longitudes in Turkey, and is a very recent alluvium.

Soil sampling was done on a grid basis with each square approximately 250x250 m. At each junction point of the grid, five surface subsamples (0-25 cm) were taken with an auger-type sampler within a radius of 5 m and

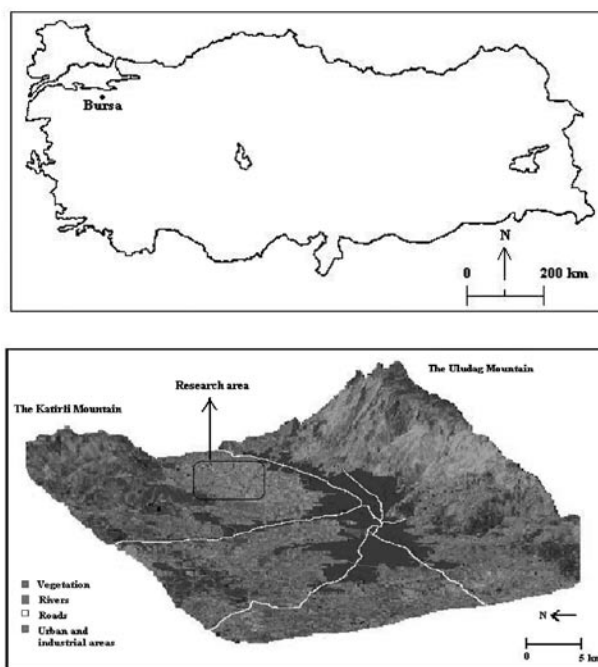


Fig. 1. The location of the research area in the Bursa province, Turkey.

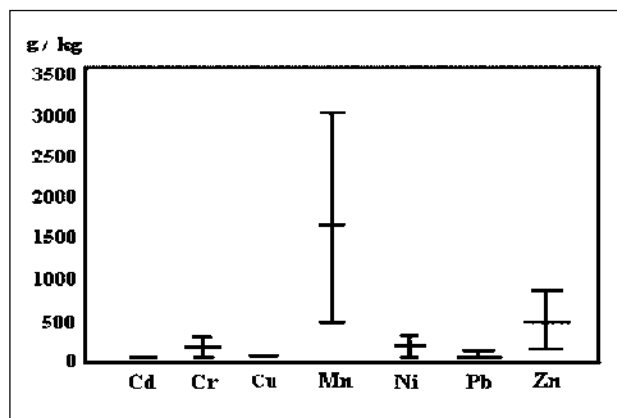


Fig. 2. Range and mean value of total heavy metal concentration for studied soils.

mixed to a composite sample. The composite samples were air dried, crushed lightly, and then passed through a 2-mm sieve. All subsequent analyses were performed on the <2-mm fraction using standard methods. Particle size distribution determined by the hydrometer method [10], pH in a 1:2 soil:water ratio [11], organic matter with the wet oxidation method [12], and equivalent calcium carbonate volumetrically [13]. Electrical conductivity was measured in a saturation extract. The analyses were performed on 25 soil samples from this area, resulting in the measurement of some soil properties. Thus, soil pH ranged from 7.6 to 8.6, CaCO_3 from 3.0 to 65%, EC from 1 to 120 mS cm^{-1} , organic matter content from 0.5 to 5.0%, and clay content ranged between 3.8-5.7%. X-ray analyses showed that the predominant clay minerals were micas and chlorites.

Sequential extraction was carried out according to Emmerich et al. [14]. After removing the saturation extract using a vacuum and a Buchner funnel, the soil sample was leached two to three times with 15-20 ml of deionized water to remove the soluble salts. Two grams of dry soil (on a 105°C basis) were placed in preweighed centrifuge tube (three replicates) and the following sequence was used.

1. Add 25 ml 0.5M KNO_3 , shake for 16 h, centrifuge and filter the supernatant liquid.
2. Add 25 ml of deionized water, shake for 21 h, centrifuge and filter the supernatant liquid. Extraction with water on a number of samples showed that the concentration of heavy metals in the extract was below the sensitivity limit of the atomic absorption spectrometer, and therefore this step was omitted in the rest of the samples.
3. Add 25 ml 0.5M NaOH, shake for 16 h, centrifuge and filter.
4. Add 25 ml 0.05N Na_2EDTA , shake 6 h, centrifuge and filter.
5. Add 23 ml 4M HNO_3 and heat for 16 h in a water bath at 70-80 °C. After cooling, the solution was filtered. After each step, the centrifuge tube was weighed to

estimate the quantity of the remaining extractant and to calculate the amount of heavy metal carried over to the next step. Heavy metal concentrations in all extracts were determined by atomic absorption spectrometry. Statistical analyses were performed using the correlation procedure (Pearson test) and the generalized linear model procedure.

Results and Discussion

The range and mean values of the total quantity of each heavy metals extracted, calculated as sum of all fractions for all sampling sites are given in Figure 2.

In this figure, it is apparent that while the concentration for some metals (Cd) is very low, for some others (Mn and Zn), they are quite high. This can be attributed to pollution sources existing in the surrounding area. Overall, the range of values indicates uniform spatial distribution for most of the heavy metals. For Mn, the presence of very high values can be attributed in the presence of Mn-oxides concentrations (field observations) due to locally reduced conditions.

The range and mean values of total heavy metal content obtained from all sampling sites along with comparative values from several sources found in the literature [15, 16, 17, 18, 19] for non-polluted soils are shown in Table 1. The mean and the lower limit values are higher while the upper limit values are lower than the comparable values given by the above identified author, indicating some degree of pollution, probably due to the effects of industrial activities in this area [9]. Also, Adriano [20] reported that alluvial soils showed a mean Cd content of 1.5 mg kg^{-1} (range 0.1-6.0 mg kg^{-1}) and it is known that chlorite minerals sometimes contain Cr and Ni.

The absolute quantities of each heavy metal extracted with different extractants are given in Figure 3, with each heavy metal fraction expressed as a percentage of the total heavy metal quantity. As expected, in agreement with the findings of Emmerich et al. [14] and McGrath and Ce-

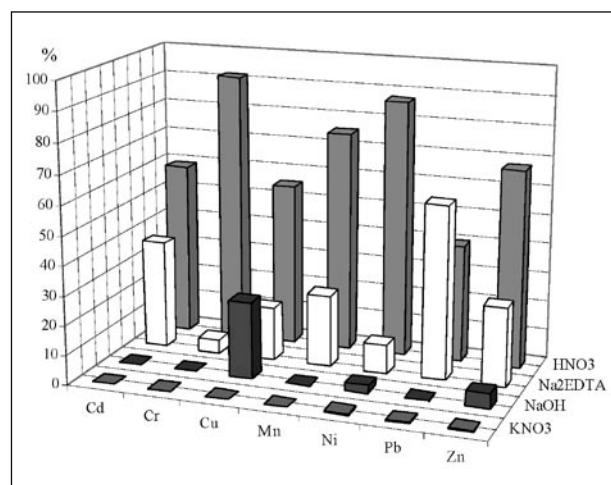


Fig. 3. Percentage of extracted metals in using sequential extraction.

Table 1. Average and range values of total heavy metal content (g kg⁻¹) of all sampling sites and related background values from different sources.

Metal	Values of sites		Background values from different sources				
			Bowen, [15]	Shacklette & Boerngen, [16]	Vinogradov, [17]	Rose et al. [18]	Mitchell, [19]
Cd	Min.	0.1	0.01	---	---	---	---
	Max.	8.7	2.00	---	---	---	---
	Aver.	2	0.35	---	---	---	---
Cr	Min.	42.0	5	1	---	---	5
	Max.	329.2	1500	2000	---	---	3000
	Aver.	124.5	70	54	200	6.3	---
Cu	Min.	14.2	2	1	---	---	10
	Max.	68.9	250	700	---	---	100
	Aver.	40	30	25	20	15	---
Mn	Min.	587.9	20	2	---	---	200
	Max.	3112	10000	7000	---	---	5000
	Aver.	1667.1	1000	550	850	320	---
Ni	Min.	54.6	2	5	---	---	10
	Max.	378.0	750	700	---	---	800
	Aver.	157.8	50	19	40	17	---
Pb	Min.	33.4	2	10	---	---	20
	Max.	163.3	300	700	---	---	8
	Aver.	80.9	35	19	---	17	---
Zn	Min.	187.9	1	5	---	---	---
	Max.	1087.0	900	2900	---	---	---
	Aver.	476.7	90	60	50	36	---

garra [21] who used the same extraction procedures, the quantity of heavy metals extracted with KNO₃, except for Mn was less than 0.1% of the total extracted. Manganese extracted with KNO₃ ranged between 0.01 to 12.5 mg kg⁻¹ with a mean value of 1.8 mg kg⁻¹ and its presence can be attributed to the Mn-oxides (field observations) that exist in these soils, which are dissolved during periodic flooding of the soils.

Sodium hydroxide extracted the highest quantity of Cu, 26% of the total, with a mean value of 1.08 mg kg⁻¹ (range 2.8-26.0 mg kg⁻¹). A statistically significant relationship ($r=0.7$, $p<0.001$) between NaOH-Cu and soil organic matter content suggests that NaOH-extracted Cu is associated with organic matter. This is in agreement with the findings of Stevenson [3], who reported that 20-50% of the Cu in soils occurs in the form of complexes with organic matter.

Sodium hydroxide-extractable Zn accounted for 5.2% of the total with a mean value of 29.4 mg kg⁻¹ and a range from 1.3 to 189 mg kg⁻¹. McGrath and Cegarra [21] re-

ported an average of 2.5% for NaOH-extracted Zn. Pb, Cr and Cd were <0.1% while Mn was in the same order with KNO₃-Mn (0.1% of the total) and Ni averaged 2.8% of the total.

Pb showed the highest (59% of the total) quantities extracted with Na₂EDTA with a mean value of 49 mg kg⁻¹ and range 7.7 to 128 mg kg⁻¹. Archer and Hodgson [22] reported a similar percentage of Na₂EDTA-Pb when Na₂EDTA was used as a single extractant for soil Pb. Zn and Mn extracted with Na₂EDTA were 27.0% and 24.5 % of the total, while Cu, Ni, and Cr were 18.1%, 9.6%, and 4.6% respectively. Cd showed very large spatial variability with values ranging from 0.01 to 3.7 mg kg⁻¹.

Nitric acid extracted the major fractions of all the heavy metals except for Pb. For example, HNO₃-extractable Cr was 92%, Ni 87.4%, Mn 75.2%, Zn 67.5%, Cd 59.2%, Cu 55.5% and Pb 40% of the total. The results were expected since HNO₃ is the strongest of the reagents used, which dissolves the finer soil particles, and there-

fore, heavy metals that exist as structural components of the soil minerals are dissolved and measured.

Statistically significant relationships were found between the structural components of the various heavy metals (HNO₃ extracted) and HNO₃-extracted Mn. For example, Mn-Cu: $r=0.893$, $p<0.001$, Mn-Zn: $r=0.677$, $p<0.001$; Mn-Cr: $r=0.598$, $p<0.001$, and Mn-Pb: $r=0.89$, $p<0.001$. The close relationships indicate retention of Cu, Zn, Cr, and Pb on Mn-oxides.

Conclusion

The total heavy metal contents of the investigated soils were generally higher than the comparative levels reported in the literature for similar soils. The exchangeable forms of these metals were very low, indicating that under the present conditions, the availability of these metals to plants would be minimal. The largest proportion of the metals occurred in forms that are considered immobile, being structural constituents of inorganic minerals or carbonate compounds. Cu and Zn were present in appreciable quantities as organically-based forms. The spatial distribution of Cu and Zn correlated to the soil organic matter distribution. There were indications that the immobile fraction of the heavy metals was adsorbed onto Mn-oxides.

References

- LINDSAY W.L. Chemical equilibria in soils. John Wiley & Sons, New York, NY, **1979**.
- FULLER W.H. Movement of selected metals, asbestos and cyanide in soil: Application to waste disposal problem. EPA-600/2-77-020. Solid and hazardous waste research division, U.S. Environmental protection agency, Cincinnati, OH, **1977**.
- STEVENSON F.J. Humus chemistry. John Wiley & Sons, New York, NY, **1982**.
- KIRKHAM M.B. Trace elements sludge on land: Effect on plants, soils, and ground water. pp. 209-247. In: R.C. Laehr (ed.) Land as a waste management alternative. Ann Arbor Science Publishers, Ann Arbor, MI, **1977**.
- HAGHIRI F. Plant uptake of cadmium as influenced by cation exchange capacity, organic matter, zinc and soil temperature. J Environ. Qual. **3**, 180, **1974**.
- KORTE N.E., SKOPP J., FULLER W.H., NIEBLA E.E., ALESII B.A. Trace elements movements in soils. Influence of soil physical and chemical properties. Soil Sci. **122**, 350, **1976**.
- BECKETT P.H.T. The use of extractants in studies on trace metals, in soils, sewage sludge and sludge-treated soils. Adv. Soil Sci. **9**, 142, **1989**.
- AYDINALP C. Characterization of the main soil types in the Bursa province, Turkey, PhD Thesis, University of Aberdeen, Aberdeen, UK, **1996**.
- AYDINALP C., MARINOVA S. Distribution of some heavy metals in the alluvial soils of the Bursa plain, Turkey. J. of Agricultural Science and Forest Science. **I (2-4)**, 84, Sofia, Bulgaria, **2002**.
- GEE G.W., BAUDER J.W. Particle-size analyses. pp. 383-412. In: A. Klute (ed.), Method of soil analyses. Part 1: Physical and mineralogical methods. 2nd ed. American Society of Agronomy, Madison, WI, **1982**.
- MC LEAN E.O. Soil pH and lime requirement. pp. 199-224. In: A.L. Page, R.H. Miller and D.R. Keeney (eds.), Methods of soil analyses. Part 2: Chemical and microbiological properties. 2nd ed. American Society of Agronomy, Madison, WI, **1982**.
- NELSON D.W., SOMMERS L.E. Total carbon, organic carbon, and organic matter. pp. 538-580. In: A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2: Chemical and microbiological properties. 2nd ed. American Society of Agronomy, Madison, WI, **1982**.
- NELSON R.E. Carbonate and gypsum. pp. 181-198. In: A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2: Chemical and microbiological properties. 2nd ed. American Society of Agronomy, Madison, WI, **1982**.
- EMMERICH W.E., LUND L.J., PAGE A.L., CHANGE A.E. Solid phase form of heavy metals in sewage sludge-treated soils. J Environ. Qual. **11**, 178, **1977**.
- BOWEN H.J.M. Environmental chemistry of the elements. Academic press, New York, NY, **1979**.
- SHACKLETTE H.T., BOERNGEN J.G. Element concentrations in soils and other surface materials of the contiguous United States. USGS professional paper 1270. U.S. Government Printing Office, Washington, DC, **1984**.
- VINOGRADOV A.P. The geochemistry of rare and dispersed chemical elements in soils. Consultants Bureau, Inc., New York, NY, **1959**.
- ROSE A.W., HAWKES F.E., WEBB J.S. Geochemistry in mineral exploration. Academic press, London, England, **1979**.
- MITCHELL R.L. Trace elements in soils. pp. 320-368. In: F.E. Bear (ed.), Chemistry of the soil. Reinhold Publisher Corporation, New York, NY, **1964**.
- ADRIANO D.E. Trace elements in the terrestrial environment, Springer-Verlag, New York, N.Y, **1986**.
- MC GRATH S.P., CEGARRA J. Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soil. J Soil Sci. **43**, 313, **1992**.
- ARCHER F.E., HODGSON I.H. Total and extractable trace element contents of soils in England and Wales. J. Soil Science. **38**, 421, **1987**.