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# Heavy metal content of agricultural soils in a Mediterranean semiarid area: the Segura River Valley (Alicante, Spain)

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## Abstract

Assessment of the content and sources of heavy metals in soils is required to identify agricultural areas affected by contamination on a regional level, according to the European Thematic Strategy for Soil Protection. The total content of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn of 29 agricultural soils used to grow vegetable crops such as artichoke, broccoli, and potato, in the Segura River Valley, Alicante, Spain, as a representative area of the semiarid Mediterranean region, was determined to assess the current state of heavy metal contamination of agricultural soils. The mean values (mg $kg^{-1}$) were: Cd, 0.38; Co, 7.9; Cr, 28.3; Cu, 21.6; Fe, 15,274; Mn, 320; Ni, 23.7; Pb, 19.6; and Zn, 57.8. These values followed the sequence: Fe > Mn > Zn > Cr > Ni > Cu > Pb > Co > Cd. Despite intensive production, the soil heavy metal concentrations were equal to, or lower than concentrations determined by others working on Spanish agricultural soils. Nevertheless, some plots had high Cd and Pb concentrations. Based on these results and others from the Spanish Mediterranean region, further studies under semiarid conditions are required to obtain a better knowledge of the pollution levels, especially in the case of anthropogenic metals such as Cd and Pb. This is critical to safeguard the environmental and production functions of these soils and, therefore, their quality. Further, given the importance of vegetables in the Mediterranean diet, it is important to extend the work to other areas of the European Mediterranean region.

**Additional key words:** agriculture, Alicante province, contamination, vegetable crops.

## Resumen

**Contenido de metales pesados en suelos agrícolas de un área del Mediterráneo semiárido: el valle del río Segura (Alicante, España)**

La evaluación del contenido y origen de los metales pesados en suelos a escala regional es relevante para la identificación de zonas agrícolas afectadas por contaminación, de acuerdo con la Estrategia Temática Europea para la Protección del Suelo. Los contenidos totales de Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb y Zn en 29 suelos agrícolas dedicados a cultivos vegetales (ej. alcachofa, bróculi, patata) de la comarca del Bajo Segura (Alicante, España), área representativa del ámbito mediterráneo semiárido, fueron analizados con el objeto de evaluar el estado actual de estos suelos agrícolas, en referencia a procesos de contaminación por metales pesados. Los valores medios fueron (en mg $kg^{-1}$): Cd 0,38; Co 7,9; Cr 28,3; Cu 21,6; Fe 15.274; Mn 320; Ni 23,7; Pb 19,6; y Zn 57,8. Estos valores medios siguieron la siguiente secuencia: Fe > Mn > Zn > Cr > Ni > Cu > Pb > Co > Cd. A pesar de las prácticas agrícolas intensivas en estos suelos, los contenidos de metales pesados fueron iguales o incluso menores a las concentraciones analizadas por otros autores en suelos agrícolas españoles. No obstante, algunas parcelas presentaron mayores concentraciones de Cd y Pb, desde un punto de vista comparativo. Teniendo en cuenta estos resultados y otros alcanzados en la región mediterránea española, se requieren mayores estudios en condiciones semiáridas para obtener un mejor conocimiento sobre los niveles de contaminación, especialmente en el caso de metales de origen antrópico como el Cd y Pb. Esto resulta crítico para preservar las funciones productivas y ambientales de estos suelos y, por tanto, su calidad. Además, dada la importancia de los cultivos vegetales en la dieta mediterránea, sería relevante extender esta investigación a otras zonas semiáridas de la región mediterránea europea.

**Palabras clave adicionales:** agricultura, contaminación, cultivos vegetales, provincia de Alicante.

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## Introduction

Knowledge of the heavy metal content of soils, and the origin of these metals, are priority objectives of the European Union (EU). The European Commission in 2002 published «Towards a thematic strategy for soil protection» (EC, 2002) that established the basis and guidelines for maintaining or improving soil quality. Recently, different groups have produced reports addressing the state of the soils, impacts and pressures and recommendations for soil protection policy making at the EU level. The report of van-Camp *et al*. (2004) as part of the technical group working on «Contamination and Land Management» established the need to measure soil heavy metal concentrations and to identify contamination processes. Moreover, the intensification of agriculture in Europe encouraged by the Common Agricultural Policy (CAP) has resulted in the incorporation of several types of pollutants to soil, such as heavy metals, due to excess use of agrochemicals (Groom *et al*., 1995). The analysis of heavy metal concentrations in agricultural soils is, therefore, critical for policy making orientated toward reducing heavy metal inputs to soil and guaranteeing the maintenance or even the improvement in soil quality.

The Valencian Region is an important agricultural area of irrigated land in the Mediterranean region. Alicante is the smallest province (581,901 ha) but is important for growing irrigated vegetable crops (11,858 ha) and is ahead of Valencia (11,338 ha) and Castellón (5,268 ha) provinces (CAPA, 2002). Consequently, Alicante plays an important role in the economy of the Valencian Region and of Spain, because of the production of vegetable crops destined for local markets and for export to national and international markets. Agricultural practices used on these soils, such as the intensive use of agrochemical products and wastewater, for soil irrigation, result in contamination that requires in-depth investigation. In addition, the concentration of industrial areas near villages and the presence of small industries in the agricultural zones could increase the concentration of pollutants, which should be assessed. In Alicante, the Segura River valley is characterised by intensive agricultural and industrial activity, a high population density (279 inhabitants $km^{-2}$) and urban expansion resulting from tourism. These factors exert a high pressure on the soils and could result in contamination. This land use pattern is typical and representative of Mediterranean semiarid areas, where, in recent decades, agricultural intensification has occurred in parallel with industrial and urban expansion (Coccossis, 1991).

Despite the importance of agriculture in the Mediterranean region, there is little information on the present state of agricultural soils, as heavy metal studies have mainly referred to northern European countries (e.g. Reimann *et al*., 2001) and there are few works on Southern Europe, particularly on the semiarid Mediterranean region (Groom *et al*., 1995). At a national level López and Grau (2004) reported on heavy metal levels in provincial Spanish agricultural soils. The heavy metal content was analysed in 56 agricultural plots, including dry-land crops (e.g. vineyards, olives), irrigated tree crops (e.g. oranges, cherries) and irrigated horticultural crops (e.g. artichokes, cabbages) in Alicante. Locally different scientists in Valencia have studied the heavy metal content and dynamics after the addition of different soil amendments, i.e. sewage sludge, compost, or doses of contaminants (e.g. Moral *et al*., 1998; Ramos, 2000).

The aim of this work was to analyse the heavy metal content (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in agricultural soils used to grow vegetable crops in the Segura River valley (Alicante, SE Spain), as a representative of a semiarid Mediterranean region. Comparison of these results with those of other authors from soils with similar properties (e.g. basic soils, high carbonates) will provide an insight into possible heavy metal contamination that may be occurring in the study area. Moreover, these crops can accumulate heavy metals and introduce them into the food chain, giving a potential risk to human health. Given the importance of these crops in the Mediterranean diet (Cuadrado *et al*., 1995) and the toxicity of some elements (e.g. Cd and Pb), a knowledge of soil heavy metal concentration of the region is critical.

## Material and Methods

### Characteristics of the study area

The study was carried out on agricultural soils under vegetable crops of the Segura River valley in the South of Alicante province, Southeast Spain (Fig. 1). These soils occupy a discontinuous area across the fertile Segura River valley, which crosses the centre of the lower Segura region. The Segura River does not have any tributaries in the region and its waters irrigate land of the Segura River valley and part of the lower Vinalopó River valley. At Orihuela, the main city of the study area,

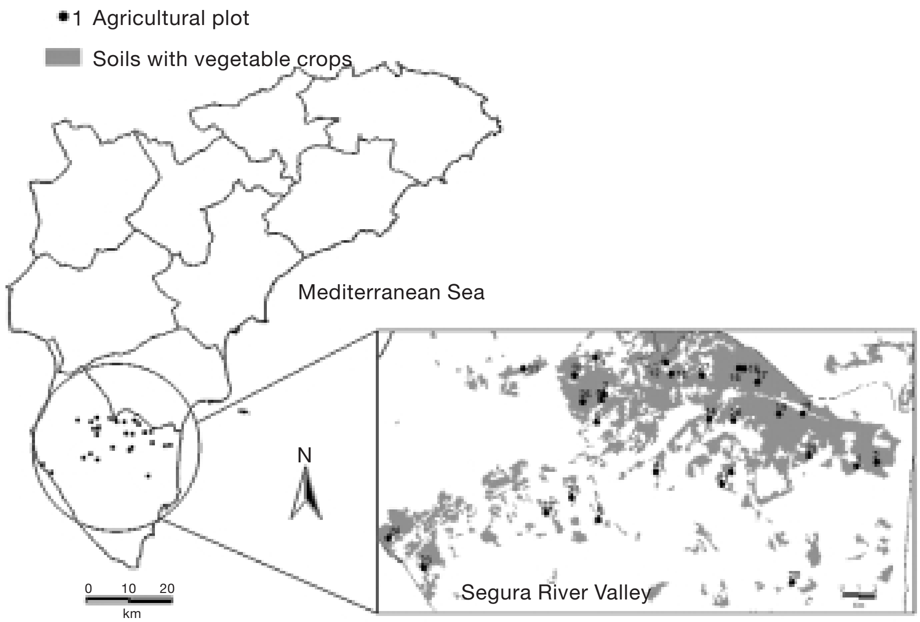


**Figure 1.** The location of the study area and distribution of the plots sampled.

the mean annual rainfall is 300 mm and mean annual temperature is 18ºC (Pérez-Cueva, 1994). This annual rainfall is insufficient for agricultural production because of the high evapotranspiration rate and the water loss by infiltration. Irrigation is therefore critical to ensure productivity in the region (Bru, 1993).

Around the middle of the last century, half of the study area was irrigated and the other half was dry land (Hernández, 1997). Over the last few decades, the irrigated area has increased rapidly. In 2001, the Segura River valley had 50,111 ha of irrigated land, of which 11,858 ha were devoted to crops such as cereals, vegetables and tubers. In this area 6,694 ha were devoted to vegetable crops (e.g. artichoke, broccoli) and 594 ha to tubers (e.g. potato) (CAPA, 2002). The fertile valley of the Segura River is formed by quaternary alluvial materials that accumulated in the Intrabetic depression as a result of different flooding events. The main agricultural soils in the irrigated agricultural area are calcaric Regosols and calcaric Fluvisols (FAO-UNESCO, 1988), which are classified as salic Fluvisols in high salinity areas (Ortiz and Caselles, 1982).

## Soil sampling and preparation

Due to the lack of previous information on the soil heavy metal content in the study area, which was mainly soils formed of alluvial and alluvial-colluvial materials, a simple random procedure was used for soil sampling. The procedure was selected to avoid deliberate sampling bias and to randomly determine the present state of these agricultural soils in relation to their contamination by heavy metals. The selection of sampling points was by means of a random point generator incorporated into a GIS (Arcview® version 3.2), into which a land use map of the Alicante province had been programmed. A total of 29 agricultural plots were located in the study area, from Orihuela (5), Dolores (5), Almoradí (4), Callosa de Segura (4), Catral (3), Cox (2), Guardamar del Segura (2), Rojales (2), San Fulgencio (1) and Granja de Rocamora (1). Figure 1 shows the spatial distribution of the plots sampled.

Soil samples were taken in 2001. Composite samples were 16 soil cores from the surface horizon (25 cm depth topsoil). Cores were mixed into a composite sample for each plot and analysed in triplicate. Samples were air dried for several days at room temperature, in the laboratory and sieved to 2 mm for soil analysis. A representative sample of each soil was finely ground, in an agate mortar, and stored in sealed bottles for the determination of heavy metal content.

## Chemical analysis

Selected physical and chemical soil properties were analysed according to the official methods of the Spanish Ministry of Agriculture, Fisheries and Food (MAPA, 1994): pH (1:2.5 soil:water suspension), electrical conductivity (EC, saturation paste extract), organic matter content (OM, Walkley-Black method), total carbonates (TC, Bernard calcimeter), cation exchange capacity (CEC, Peech method which consists in saturation with sodium acetate solution, replacement of the adsorbed sodium with ammonium and determination of displaced sodium by flame atomic absorption spectrometry-FAAS) and particle-size distribution (pipette method).

Analysis of the total heavy metal content was carried out using method 3051A of the United States Environmental Protection Agency (USEPA, 1998), consisting of a soil sample digestion with $HNO_3$ and HCl in a microwave oven (Milestone Ethos D). Heavy metal content was then determined in the final solutions by FAAS in a Varian SpectrAA-220FS spectrometer with the exception of some samples for Cd, which were analysed by graphite furnace atomic absorption spectrometry-GFAAS. Results were expressed in mg $kg^{-1}$ dry weight on the basis of soil dried at 105ºC.

The accuracy of the digestion method was checked by analysing a certified reference material (CRM) supplied by the Community Bureau of Reference Sample (CRM 141R, calcareous loam soil). Accuracy was evaluated by calculating the recovery of each metal, based on the mean certified value for CRM 141R [measured concentration (mg $kg^{-1}$)/mean certified values to aqua regia soluble contents for the CRM 141R (mg $kg^{-1}$) × 100]. Eight replicates were made of the CRM 141R by microwave-assisted digestion for several days. Recoveries were acceptable for most elements, at 85% to 103%. However, there was a low recovery of Zn (76%), due to Zn retention by some soil components (e.g. silicates) which are moderately resistant to dissolution with $HNO_3$ and HCl.

# Results

## Soil properties

The main soil properties of the soils tested are shown in Table 1. The results indicated the presence of basic soils as a consequence of the presence of calcareous parent material. The EC was higher than 4 dS $m^{-1}$ in some samples, reflecting soil salinity problems according to USDA criteria. The OM content was low as a result of intensive use of these soils and the rapid mineralization of OM under semiarid conditions. Carbonate content was also high and in 90% of the plots it was higher than 40%. All soils had an adequate CEC for agricultural use and none displayed a low capacity for nutrient storage (CEC < 10 $cmol_{(+)}$ $kg^{-1}$). The soils were generally silty clays or silty clay loams. Therefore, 89% of the soils were fine textures.

## Total heavy metal content

Descriptive statistics for the heavy metal content of soils from the study area are shown in Table 2. The mean values of the elements followed the sequence: Fe > Mn > Zn > Cr > Ni > Cu > Pb > Co > Cd. The maximum values followed the same order except for Pb which had a higher maximum value than Ni.

The elements Fe, Mn and Zn are considered essential for living organisms. Mean values were 15,274 mg $kg^{-1}$ for Fe, 320 mg $kg^{-1}$ for Mn and 57.8 mg $kg^{-1}$ for Zn. Nickel and Cu are also essential elements and their mean values were 21.6 and 23.7 mg $kg^{-1}$, respectively. Chromium and Pb are not essential elements for plants and are toxic. Their mean values were 28.3 and 19.6 mg $kg^{-1}$, respectively. Cobalt is a micronutrient with

**Table 1.** Physical and chemical properties of the Segura River valley soils

| Properties | Mean | Minimum | Maximum | Median | SD | CV (%) |
|---|---|---|---|---|---|---|
| pH | 8.2 | 7.8 | 8.5 | 8.2 | 0.2 | 2 |
| EC (dS $m^{-1}$) | 7.7 | 2.3 | 19.6 | 6.4 | 4.7 | 61 |
| OM (%) | 2.2 | 1.4 | 3.3 | 2.2 | 0.5 | 22 |
| TC (%) | 43.7 | 38.1 | 51.1 | 43.9 | 3.3 | 8 |
| CEC ($cmol_{(+)}$ $kg^{-1}$) | 18.1 | 10.1 | 25.1 | 18.6 | 3.2 | 18 |
| Sand (%) | 12 | 2 | 33 | 11 | 8 | 68 |
| Silt (%) | 49 | 40 | 63 | 48 | 6 | 12 |
| Clay (%) | 38 | 14 | 56 | 40 | 10 | 27 |

SD: standard deviation. CV: coefficient of variation. EC: electrical conductivity. OM: organic matter. TC: total carbonate. CEC: cation exchange capacity.

**Table 2.** Total soil heavy metal content in the Segura River valley (mg $kg^{-1}$)

| Heavy metal | Mean | Minimum | Maximum | Median | SD | CV (%) |
|---|---|---|---|---|---|---|
| Cd | 0.38 | 0.15 | 0.88 | 0.33 | 0.20 | 51 |
| Co | 7.9 | 5.8 | 10.1 | 7.7 | 1.2 | 16 |
| Cr | 28.3 | 21.1 | 42.5 | 27.2 | 5.4 | 19 |
| Cu | 21.6 | 16.1 | 30.6 | 21.1 | 3.1 | 15 |
| Fe | 15,274 | 10,979 | 19,807 | 15,365 | 2,181 | 14 |
| Mn | 320 | 213 | 406 | 318 | 41 | 13 |
| Ni | 23.7 | 16.4 | 32.0 | 24.1 | 3.7 | 16 |
| Pb | 19.6 | 8.9 | 34.5 | 19.3 | 5.2 | 27 |
| Zn | 57.8 | 33.4 | 80.7 | 59.1 | 10.6 | 18 |

SD: standard deviation. CV: coefficient of variation.

low concentrations in the study area, with a mean value of 7.9 mg $kg^{-1}$. Finally, Cd is generally related to human activities and, in spite of its low soil content, Cd is toxic at much lower concentrations than the other elements analysed in this study. The mean Cd value was 0.38 mg $kg^{-1}$. However, the coefficient of variation was 51%. This last value may be due to the measurement of some samples by GFAAS because the Cd values were below the detection limit of FAAS. This biased the population in the low value zone and gave a high coefficient of variation.

# Discussion

## Soil properties

Based on the results, 45% of the plots tested were slightly saline (EC > 4 dS $m^{-1}$) and 34% were saline (EC > 8 dS $m^{-1}$). This has been reported by other authors working in Alicante (Ortiz and Caselles, 1982; Aragón *et al.*, 1998) and is probably due to poor quality wastewater being used for irrigation combined with the semiarid conditions in the South of Alicante. These results suggest the need for rational, efficient management of wastewater and desalted water to avoid increasing salt concentrations in the soil profile, especially in agricultural soils for vegetable crops which are highly sensitive to salinity.

The presence of basic soils is a consequence of elevated carbonate levels in all the plots tested and the predominance of fine soil texture. A low bioavailability of heavy metals can be expected due to a direct effect of soil pH on metal solubility and the adsorption of these elements onto negatively-charged surfaces of clay minerals and soil organic matter. However, point contamination from industries and the intensive use of agrochemicals can introduce these elements in soluble forms, which can be assimilated by crops or can be transferred from soil to other agroecosystem components such as surface or underground water. Further, some soil properties, such as salinity, could facilitate mobility of some trace elements (e.g. Cd, Cu). Doner (1978) found increased Cu(II) mobility in the soil profile as a consequence of chlorocomplex formation. The substitution of Na in exchange positions can also produce desorption of some elements such as Cd or Cu and give them a higher mobility. The results suggest a higher Cd and Cu bioavailability in soils with salinity problems.

## Total heavy metal content

Due to a lack of soil quality standards for agricultural soils in Alicante and studies in the Segura River valley on soil heavy metal content, a comparative study between the results obtained and of other works on agricultural soils in the Spanish Mediterranean region was carried out (Table 3). The other works were selected according to soil properties to give a comparative study among soils with similar properties (e.g. basic soils, high carbonate soils, etc.). Moreover, Table 4 gives reference values of heavy metals determined by Pérez *et al.* (2002) for horticultural soils in the region of Murcia, the maximum permissible heavy metal concentration (Kabata-Pendias and Pendias, 2001) for some European countries and the guidelines values from the 86/278/EEC Directive (CEC, 1986) for agricultural soils with a pH > 7, which were taken into account in this study.

### *Cadmium*

In the Spanish Mediterranean region, the lowest mean soil Cd was reported by Moreno *et al.* (1992) in

**Table 3.** Comparative study of these results and different works on agricultural soils of the Spanish Mediterranean region (mg kg$^{-1}$)

| Source | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| This work | 0.38 | 7.9 | 28.3 | 21.6 | 15,274 | 320 | 23.7 | 19.6 | 57.8 |
| Aller and Deban (1989) | 0.7 | 7 | 42 | 18 | — | — | 28 | 13 | 39 |
| Andreu (1991) | 0.4 | 10 | 13 | 19 | — | — | 24 | 41 | 52 |
| Andreu and Gimeno-García (1996) | 0.6 | 7 | — | 26 | — | — | 16 | 47 | 81 |
| Boluda *et al.* (1988) | — | 16 | 49 | — | — | — | 37 | 42 | 62 |
| Cala *et al.* (1985) | 1.4 | — | 17 | 17 | — | — | 16 | 36 | 65 |
| Campos (1997) | 2.3 | 22 | — | 29 | 34,000 | 533 | 41 | 64 | 90 |
| Errecalde *et al.* (1991) | 0.5 | 4 | — | 25 | — | — | 13 | 38 | 71 |
| López and Grau (2004)[a] | 0.25 | — | 34.2 | 19.8 | — | — | 13.6 | 17.8 | 57.5 |
| Marín *et al.* (2000) | 0.3 | — | — | 29 | — | 263 | 29 | 22 | 48 |
| Millán *et al.* (1983) | — | — | — | 39 | 20,787 | 382 | — | — | 57 |
| Moreno *et al.* (1992) | 0.07 | — | — | 16 | — | — | — | 50 | 46 |
| Pérez *et al.* (1995) | 0.1 | — | — | 16 | — | — | — | 52 | 51 |
| Pérez *et al.* (2000) | 0.09 | — | — | 12 | — | — | — | 31 | 34 |

[a] Data for Alicante. —: not determined.

agricultural soils of the Madrid region. The maximum mean values were reported by Campos (1997) from the fertile valley of Granada and by Cala *et al.* (1985) from the fertile Aranjuez valley. Similar results to those found in this study were obtained by Marín *et al.* (2000) in vineyard soils of La Rioja and Andreu (1991) and by Errecalde *et al*. (1991) in soils cropped with vegetables in Valencia.

Human activity can contribute to increased Cd levels as a result of urban-industrial activity and/or agricultural practices (Adriano, 2001). In Alicante, fertilizers used to increase productivity could be the Cd source. In Valencia, Gimeno-García (1993) reported that Cd content was increased due to the use of phosphatic fertilizers and other agrochemicals used on vegetable crops, which have a Cd content of 2-156 mg kg$^{-1}$. Wastewater insufficiently treated for soil irrigation (Bru, 1993) can also be a source of Cd contamination in the study area. Urban-industrial wastewater could be affecting the Segura River due to a deficient cleaning and, in some cases, uncontrolled spills as suggested by Bru (1993). Different international authors fix a normal Cd range of 0.07 and 1.1 mg kg$^{-1}$ (Alloway, 1990; Kabata-Pendias and Pendias, 2001). Concentrations above 0.5 mg kg$^{-1}$ could reflect the influence of human activity (McBride, 1994). In the study area, six plots exceeded this value, indicating a slight increase in this heavy metal in relation to the normal level. However 15 plots exceeded the value established by Pérez *et al.* (2002) for vegetable crop soils in Murcia. None of the plots exceeded the maximum permissible concentration established by Kabata-Pendias and Pendias (2001). Therefore, the Cd contents of agricultural soils of the Segura River valley did not reach toxic levels. However, further studies are required to identify possible increase in the content due to the presence of contamination sources.

### *Cobalt*

The mean Co value in the study area was close to the values of Andreu and Gimeno-García (1996) in Valencia and of Aller and Deban (1989) in cultivated

**Table 4.** Reference values for soil heavy metals (mg kg$^{-1}$)

| | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| Pérez *et al.* (2002)[a] | 0.3 | — | 73 | 41 | — | — | 43 | 30 | 192 |
| Kabata-Pendias and Pendias (2001)[b] | 5 | 50 | 100 | 100 | — | — | 100 | 100 | 300 |
| 86/278/EEC Directive (CEC, 1986)[c] | 3 | — | — | 140 | — | — | 75 | 300 | 300 |

[a] Reference values for horticultural soils in murcia. [b] Maximum permissible agricultural soil concentration in some European countries. [c] Guidelines values for agricultural soils with a pH > 7. —: not determined.

soils in León. Other studies reported higher levels (Boluda *et al.,* 1988) in dry land of Valencia province, and in the fertile Granada Valley (Campos, 1997).

Generally, the Co content of basic and sedimentary rocks is low and subsequently soil Co concentrations in soils formed from these rocks are usually low, which is the case in the Segura River valley. The Co levels in the study area were similar to, or lower than the mean value in other agricultural soils in the Spanish Mediterranean region. Thus, a significant increase in soil Co content as a result of human activity has not occurred.

*Chromium*

The Cr mean value was lower than those reported by Aller and Deban (1989) in León or by Boluda *et al.* (1988) in Valencia. In this study, two plots with 41 and 43 mg $kg^{-1}$, respectively, were identified in the municipality of Orihuela. These values were not high enough to indicate contamination, although a slight increase in Cr content is occurring. Both plots contained soil with a high clay content (54 and 56%, respectively), which seems to suggest high Cr adsorption by this soil component.

The normal Cr range in calcareous soils is 5 to 16 mg $kg^{-1}$ (Adriano, 2001; Kabata-Pendias and Pendias, 2001). However, the presence of high clay content and intensive human activities can increase the normal contents of Cr in soils (Boluda *et al.*, 1988). In the study area, urban and industrial waste water has affected the Segura river due to a poor cleaning and, in some cases, uncontrolled spills (Bru, 1993), which could be due to human activity. Vegetable crop plots in Alicante did not reach the Cr reference value of Pérez *et al.* (2002) for agricultural soils in Murcia or the maximum permissible concentration established by Kabata-Pendias and Pendias (2001).

*Copper*

Some studies have reported higher mean Cu values, such as that of Campos (1997) in the fertile Granada Valley, Marín *et al.* (2000) in vineyard soils of La Rioja and Millán *et al.* (1983) in the Ebro Valley. The mean value in the study area was close to that of López and Grau (2004) from agricultural soils in Alicante.

The normal Cu content of agricultural soils is 5 to 50 mg $kg^{-1}$. Concentrations below 8 mg $kg^{-1}$ could indicate a deficiency for some crops as Cu is an essential micronutrient (McBride, 1994; Kabata-Pendias and Pendias, 2001). In this study, all sampled plots were in the normal range and none exceeded the reference value of Pérez *et al.* (2002) for agricultural soils in Murcia.

*Iron and manganese*

In general, the soil Fe and Mn concentrations are not reported in studies focussing on soil heavy metal content because they are not contaminant elements. Both metals are important in plant nutrition as they are essential crop micronutrients. These elements can be in insoluble forms in calcareous soils causing deficiencies (e.g. ferric chlorosis). The mean Fe value in the study area was lower than the mean obtained by Millán *et al.* (1983) from agricultural soils of the Ebro Valley and Campos (1997) in the Granada Valley. In spite of an elevated soil content, total Fe or Mn are not a good indicator of their plant availability. For example, Fe is mainly present in precipitated forms, such as oxides and hydroxides, in these soils. Therefore, Fe deficiency does not seem to be due to an insufficient total soil Fe content but to the formation of insoluble compounds. However, further study would be necessary to properly assess deficiency processes of these metals in the study area.

*Nickel*

The mean Ni value in the study area was similar to that reported by Andreu (1991). However, other studies report higher mean values, Boluda *et al.* (1988) in soils of Valencia and Campos (1997) in the fertile Granada Valley. The normal soil Ni content varies from 1 to 100 mg $kg^{-1}$ (Kabata-Pendias and Pendias, 2001). In this study all sampled plots were in this range. None of agricultural plots exceeded the reference value of Pérez *et al.* (2002) for agricultural soils in Murcia and all of them were below the maximum permissible concentration (Kabata-Pendias and Pendias, 2001).

*Lead*

The mean Pb value in the Segura River valley was lower than those reported in most studies of soil heavy metal content in Spain (e.g. Cala *et al.*, 1985; Boluda *et al.*, 1988; Andreu, 1991; Errecalde *et al.*, 1991; Moreno *et al.*, 1992; Pérez *et al.*, 1995; Andreu and Gimeno-García, 1996; Campos, 1997; Pérez *et al.*, 2000), with the exception of Aller and Deban (1989) and López and Grau (2004). However, one plot exceeded the reference value of Pérez *et al.* (2002) for soils of Murcia but did not reach the maximum permissible concentration of Kabata-Pendias and Pendias (2001). This high value was from a plot with high soil organic matter content (2.5%). This soil component could possibly be responsible for the higher soil Pb retention.

It is difficult to establish human sources of Pb in some soils from the study area. Aucejo *et al.* (1997) reported the use of industrial wastewater for irrigation as the source of high Pb content in cultivated citrus growing soils of Castellón. Bru (1993) reported the reduced number of sewage plants in Alicante over the last decade. In agricultural soils, Pb could also be from the application of agrochemicals. Gimeno-García (1993) reported a slight increase in soil Pb content as a result of fertilizer use (e.g. urea and superphosphate) in cultivated soils of Valencia. Concentrations over 100 mg $kg^{-1}$ (Kabata-Pendias and Pendias, 2001) would represent potentially contaminated soils. These levels were not reached in the Segura River valley. Although current Pb levels are not high, further studies are recommended to identify possible increases in soil Pb concentrations in these soils, given the human origin of Pb in some soils in the study area.

### *Zinc*

The mean Zn value was close to that of Millán *et al.* (1983). However, Andreu and Gimeno-García (1996) and Campos (1997) reported highest mean values in agricultural soils of the Spanish Mediterranean region. The Zn concentration in agricultural soils varies from 10 to 300 mg $kg^{-1}$. It is abundant in sedimentary materials and clayey soils (Kabata-Pendias and Pendias, 2001), such as alluvial and alluvial-colluvial soils. In this work, no plots exceeded the reference value of Pérez *et al.* (2002) for agricultural soils and plots contained less Zn than the maximum permissible concentration (Kabata-Pendias and Pendias, 2001).

## Conclusions

Over the last few decades the agricultural soils of the Segura River valley have experienced a transition from traditional to intense agriculture that has been consistent with the whole of the European Mediterranean region (Groom *et al*., 1995). This intensification, which started in Europe in the 1950s, was promoted by the Common Agricultural Policy (CAP) and has resulted in the increased use of fertilizers and pesticides. Consequently, the soil content of some contaminants such as heavy metals, has increased over their background values. Mean soil values of Cd, Cu, Ni and Pb in this work were slightly higher than the values reported by López and Grau (2004) in agricultural soils of Alicante (Table 3). Soil from some of the plots had a higher heavy metal content than reference values established for Cd (15 samples) and Pb (one sample) by Pérez *et al*. (2002) in Murcia, where edaphic and environmental conditions are similar to the study area. This could indicate an effect of human activity on the origin of both these elements in some agricultural soils. However, the heavy metal levels in all of the soil samples were below the maximum permissible concentration (Kabata-Pendias and Pendias, 2001) and did not exceed guidelines in the 86/278/EEC Directive (CEC, 1986) for agricultural soils with a pH > 7 (Table 4).

Given the presence of human sources of heavy metals in the study area (e.g. urban-industrial uses, agricultural practices) and the identification of some contaminated agricultural plots in other areas of Alicante (e.g. the Lower Vinalopó region) (Micó, 2005), further studies under semiarid conditions are required to identify a possible increase in the total soil heavy metal content to preserve the environment and the production from these soils. It therefore may be necessary to reduce the use of agrochemicals. Since the 1990s this has been encouraged by the new CAP (OECD, 2004). However, this reduction may not be enough to guarantee non-contamination of soils and crops with heavy metals. Industrial activity and increased population near these soils have generated contaminant emissions and a large volume of wastewater, which are not sufficiently purified for soil irrigation (Bru, 1993). These could also be partly responsible for the increased heavy metal content (i.e. Cd and Pb) of some agricultural soils over normal levels. Gisbert *et al*. (2006) working in the Mediterranean region, showed that heavy metal accumulation in agricultural soils and vegetable crops is already occurring in agricultural areas affected by industrial activity, with a consequent risk to human health. They reported Cd and Pb accumulation in *Brassica* species grown in soils contaminated by air-borne metals in Murcia and Valencia

(Spain). Therefore, in addition to reduced use of agrochemicals, the careful planning and location of industries is required so soils and crops are not affected by wastewater and air emissions which contain heavy metals.

Although contamination is taking place locally in plots affected by human activity in the study area, the quality of agricultural soils in the Segura River valley is still generally acceptable. A better indication of potential risk would be achieved by measuring the bioavailable metal concentrations, extractable with solutions of neutral salts or synthetic chelates such as DTPA. This would be especially relevant for Cd in areas of saline soils as some authors have reported increased Cd mobility in saline soils (e.g. Doner, 1978). Given that the land use pattern in the study area, over the past few decades, has been similar to that in other parts of the semiarid European Mediterranean region, the results obtained here could be extrapolated to the whole region sharing similar conditions. Reductions in the use of agrochemicals combined with adequate planning of urban-industrial land use are critical to guarantee soil quality in this region, according to the European strategy for soil protection. These actions would also improve the quality of the vegetable crops produced on these soils, vegetables being an important part of the Mediterranean diet.

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