Study of heavy metal and arsenic concentrations in olive farm soils, Sierra Mágina, Jaen, Spain.

Estudio de metales pesados y arsénico en los suelos de olivar de Sierra Mágina, Jaén (España)

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Abstract

The content of heavy metals and arsenic was studied in 35 soils under olive cultivation in the Sierra Mágina, Jaen, Spain. The concentrations of chromium (Cr), nickel (Ni), copper (Cu), lead (Pb), zinc (Zn) and arsenic (As) were determined at depths between 0 - 20 and 20- 40 cm. These soils developed on carbonate materials, predominantly Petric Calcisols and Calcaric Regosols (FAO, 1999). The homogeneity of parental material was responsible for the lack of significant variation seen in soil properties, and also heavy metal and arsenic content at the depths studied. Copper was the only element that varied over depth (p<0.01), with a higher mean value between 0 - 20 cm; a consequence of agrochemical applications in the region. Soils with a clay and silt texture had higher concentrations of Cr and Ni, while the rest of the metals and As did not present significant variation with the main physical chemical properties of the soil. The studied elements did not exceed the reference levels established by the Andalucia Authorities, presenting similar concentrations to those found in equivalent rocks and in non-contaminated soils. The mean values for As, Cr, Cu, Ni, Pb and Zn were related to the concentrations inherited from the lithological material from which the soils are derived.

Resumen

En Sierra Mágina, Jaén (España) fueron seleccionados 35 suelos dedicados al cultivo del olivar en los que se estudió la concentración de cromo (Cr), níquel (Ni), cobre (Cu), plomo (Pb), Zinc (Zn) y arsénico (As) a profundidades entre 0 - 20 y 20 - 40 cm. Estos suelos se desarrollan sobre materiales carbonatados,

predominando Calcisoles pétricos y Regosoles calcáricos (FAO, 1999). La homogeneidad del material parental es responsable de la ausencia de variaciones significativas en las propiedades de los suelos a las profundidades estudiadas, así como en el contenido de metales pesados y arsénico. El Cu es el único elemento que varía con la profundidad (p < 0.01), presentando un valor promedio más elevado entre 0 y 20 cm debido a la aplicación de controles fitosanitarios en los cultivos de la región. En los suelos con texturas arcillosa y limosa se presentan concentraciones más altas de Cr y Ni, mientras que el resto de metales analizados y el As no presentan variaciones significativas con las principales propiedades físicas y químicas de los suelos. Los elementos estudiados no exceden el nivel de referencia establecido para suelos por la Junta de Andalucía y presentan concentraciones similares a las encontradas en rocas equivalentes y en suelos no contaminados. Los valores promedio en As, Cr, Cu, Ni, Pb y Zn están relacionados con las concentraciones heredadas del material litológico del que se derivan.

Introduction

The heavy metals present in the soil have diverse origins, being either naturally derived from the original lithological material, or originating through human (anthropogenic) activity. The heavy metals may be distributed across the soil horizons or in soil particles as a result of mineral transformations or edaphological processes. Agricultural practices may frequently be a source of heavy metal contamination (Kabata-Pendias, 1995) as a result of impurities in the fertilizers used. Other sources include the use of sludge as organic fertilizers, the application of urban solid residues and the transportation of atmospheric particles (Alloway, 1995; Föstner, 1995).

The evaluation and knowledge of heavy metal contamination in the soil is of interest because of its possible effects in the trophic chain. In the province of Jaen, Andalucia, Spain, there exists an olive monoculture of the variety picual. In the province several varieties of oils are produced of certified origin ('denominación de origen'), with one of these being Sierra Mágina, located in the region with the same name, where two types of virgin olive oil are produced, one organic and the other derived from an integrated production process. The soils within a single region have the advantage that they receive the same treatment, except that the organic crop has no phytosanitary products applied, while for the integrated production equal quantities of agrochemicals are applied in each period.

The aim of the present study was to determine the total content of As, Cr, Cu, Ni, Pb and Zn in soils in the olive groves of Sierra Mágina, and compare them with

reference levels in other zones, identifying possible anomalies and their relationships with the variations in soil use, or the soil properties.

Materials and methods

For this study 35 soils were sampled in the olive groves of Sierra Mágina between 0 - 20 and 20 - 40 cm depth, with a total of 70 samples. All soils sampled had developed on carbonate material (limestone, marlaceous lime, marl, dolomite, alluvial material and Triassic material). The samples corresponded to all types of soil present in the study zone, and varied from those least developed such as calcaric leptosols (n = 3) and calcaric and fluvial-calcaric regosols (n = 22), to more evolved soils such as chromic luvisols (n = 2), passing through vertic calcareous cambisols (n = 14) and petric, hypercalcic and haplic calcisols (n = 24) (Menjivar, 2001).

For the soil sampling, the distinct factors through which they originated was taken into account, and particular attention was paid to the zones with and without irrigation, and to the type of management: traditional, and that of minimal labor.

To determine the elements present, the following analytical methods were used: organic carbon, according to Tyurin (1951); carbonates using the methods of Barahona et al. (1984); texture by pipette following Robinson (Soil Conservation Service, 1972); bases and exchange capacity with ammonium acetate (1N, pH = 7) and sodium acetate (1N, pH = 8,2); pH in soil-water suspension 1:2.5. The heavy metals (Cr, Cu, Ni, Pb y Zn) and As were determined after an acid digestion (HF, HNO $_3$ y HCl) using ICP-MS in a spectrophotometer Pe Sciex Elan-5000A. For the statistical study of the data obtain the program SPSS v.11.0 was used.

Results and discussion

In Box 1 mean values are given with standard deviation (SD), and the minimum and maximum values for the principle properties of the soil and the total content (mg/kg) of Cr, Cu, Ni, Pb, Zn and As of the soil groups in the study.

Box 1. Principle properties, metal and As content of the groups of soils in the study, olive groves of Sierra Mágina, Jaen, Spain.

Cuadro 1. Principales propiedades, contenidos de metales y As de los grupos de suelos en el estudio. Olivar de Sierra

	Mágin	a, Jaen (España).									
Suelo		pH	CaCO ₃	CO	Arcilla.	CIC	As	Cr	Cu	Ni	Pb	Zn
		(%)	(%)	(%)	(cmol _c /kg)			(mg/kg)				
Leptosol	Media	8.42	58.77	0.63	25.97	12.81	4.23	3.433	25.33	19.33	27.00	38.33
	D.E.	0.29	9.76	0.21	9.53	3.72	2.22	11.01	9.71	8.74	3.61	9.61
	Min.	8.08	52.30	0.46	15.00	8.77	2.40	23.00	17.00	12.00	24.00	28.00
	Max.	8.60	70.00	0.86	32.20	16.09	6.70	45.00	36.00	29.00	31.00	47.00
	Media	8.07	39.75	0.78	33.06	14.33	5.92	45.37	18.96	20.58	25.96	37.29
Calcisol	D.E.	0.46	17.41	0.46	8.16	3.62	2.35	23.53	7.53	10.25	17.10	15.82
	Min.	7.20	7.24	0.17	18.70	6.57	2.70	9.00	5.00	4.00	7.00	2.00
	Max.	9.10	82.00	2.04	49.50	20.73	12.0	109.00	33.00	46.00	83.00	65.00
	Media	7.44	11.75	1.20	41.30	17.37	4.10	47.50	18.00	20.00	21.50	43.00
75	D.E.	0.18	7.60	0.16	17.39	2.55	0.28	12.02	1.41	1.41	0.71	C
Visc	Min.	7.32	6.38	1.09	29.00	15.57	3.90	39.00	17.00	19.00	21.00	43.00
Luvisol	Max.	7.57	17.13	1.31	53.60	19.17	4.30	56.00	19.00	21.00	22.00	43.00
Regosol Cambisol	Media	8.17	48.95	0.85	38.40	18.67	7.86	55.93	21.71	24.21	22.93	42.36
	D.E.	0.34	22.03	0.32	9.61	7.60	1.53	17.25	5.31	6.34	9.73	14.58
	Min.	7.34	13.56	0.43	19.50	7.10	5.90	29.00	15.00	13.00	12.00	24.00
	Max.	8.70	76.25	1.56	51.90	32.08	10.2	86.00	32.00	32.00	43.00	63.00
	Media	8.30	46.96	0.65	34.96	14.96	4.61	40.36	20.27	19.18	20.23	32.95
	DE	0.50	17.96	0.36	10.01	5.13	2.61	20.96	11.78	9.01	7.91	17.13
	Min.	7.00	24.80	0.14	14.40	8.47	0.60	11.00	2.00	4.00	7.00	7.00
	Max.	8.87	82.00	1.30	58.10	29.13	11.8	75.00	53.00	33.00	36.00	64.00

DE desviación estándar ; CO: carbono orgánico, CIC: capacidad de intercambio catiónico

The soils have in common an elevated content of calcium carbonate equivalent (> 40%), due to the predominance of Calcisols and the calcareous forms of many of the types. This excess of calcium carbonate causes many plantations to present iron chlorosis due to the lack of iron uptake.

The pH of the soils varied from lightly to moderately basic, and the percentage of organic carbon was low in all the soils studied. The different groups of soils did not show significant differences in their properties (P < 0.05), however, at the level of individual soils some variations were seen. The chromic luvisols have a lower pH (P < 0.05), less $CaCO_3$ and a clay texture; the vertic cambisols have a high clay content and exchange capacity; the fluvial-calcaric regosols have a clearly different sandy texture (P < 0.05). The parental material is very homogenous in the majority of cases and is dominated by carbonate material. The influence of this material could be responsible for the lack of significant variation in the soil properties down to 40 cm depth, despite the fact that the study included relatively evolved luvisols and cambisols.

The pH is a property that has apparently not been affected (P < 0.01) by the soil use. Soils under traditional labor present lower values of pH (7.98 \pm 0.45) compared to those soils managed with minimal labor (pH 8.38 \pm 0.38).

The values found for heavy metals and As indicate that, similarly to other soil properties, there is a degree of homogeneity between the different soil types as well as across their depths. The only variations found were in the content of Cu, which presented differences (P < 0,01) in depth, showing higher means between 0 and 20 cm (23.09 \pm 9 mg/kg) and lower between 20 and 40 cm (17.16 \pm 7.51 mg/kg). The greatest superficial content of Cu in these soils may be explained by the application of this element in phytosanitary compounds, a common practice in the region.

The influence of parental material and weathering processes are revealed in the values of Cr and Ni (Box 2), which reached greater concentrations in soils with a finer texture (clay and lime), agreeing with that observed by McGrath and Loveland (1992) in soils in England and Wales.

Box 2. Concentrations of Cr and Ni as a function of the soil texture. Olive groves in Sierrra Mágina, Jaén, Spain.

Cuadro 2. Concentraciones de Cr y Ni en función de la textura del suelo. Olivar de Sierra Mágina, Jaén (España)

	(Espan	aj.						
Textura		Cr		Ni				
		(mg/kg)	Ì	(mg/kg)				
, i	Prom.		DE	Prom.		DE		
Arcillosa	54.75	_	12.85	24.10	-	4.86		
Limosa	58.20	-	32.03	26.70	-	11.89		
Franca	33.5	37.25	16.59	10 00	17.32	7.61		
Arenosa	2	28	21.37	<u></u>	11.07			
	34.	.00						
	P =		-	P =		1		
	0.002		0.003					

The concentrations of the other metals and As did not show significant variations related to the main soil properties. Similarly, variation was not observed between the main groups of soils studied (see Box 1). The influence of the parental material on concentrations of the analyzed elements in these soils is evident; as mentioned previously, a high similarity exists between the different lithological types on which these soils develop, which is reflected in the absence of significant variation in the concentration of metals and As. Additionally, the few soils developed on non-carbonate material (sandy) are those that present differences (P < 0.01) in elements such as Cu, reaching concentrations between three or four times lower than those soils developed on carbonate material.

The study of metal and As concentrations, compared with reference levels for the soils of Andalucia (Aguilar et al., 1999) shows that the analyzed elements are generally found at lower levels than the reference soils (Figure 1) and have similar concentrations to those found in rock equivalents, and in non-contaminated soils y (Alloway, 1995). Thus, the values found in the present study could be considered normal, and related to concentrations inherited from the original lithological material.

Conclusions

The heavy metal and arsenic content of the soils under olive cultivation in the Sierra Mágina are related to the original material from which these soils have developed. The use or management of the soil, such as the irrigation type or other cultural practices influence the total metal concentrations, but the levels do not, in any case, exceed the reference levels established by the Andalusia authorities.

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