

## Trace elements contamination of agricultural soils affected by sulphide exploitation (Iberian Pyrite Belt, Sw Spain)

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**Abstract** Agricultural soils of the Riotinto mining area (Iberian Pyrite Belt) have been studied to assess the degree of pollution by trace elements as a consequence of the extraction and treatment of sulphides. Fifteen soil samples were collected and analysed by ICP-OES and INAA for 51 elements. Chemical analyses showed an As–Cu–Pb–Zn association related with the mineralisation of the Iberian Pyrite Belt. Concentrations were 19–994 mg kg<sup>-1</sup> for As, 41–4,890 mg kg<sup>-1</sup> for Pb, 95–897 mg kg<sup>-1</sup> for Zn and of 27–1,160 mg kg<sup>-1</sup> for Cu. Most of the samples displayed concentrations of these elements higher than the 90th percentile of the corresponding geological dominium, which suggests an anthropogenic input besides the bedrock influence. Samples collected from sediments were more contaminated than leptosols because they were polluted by leachates or by mining spills coming from the waste rock piles. The weathering of the bedrock is responsible for high concentrations in Co, Cr and Ni, but an anthropogenic input, such as wind-blown dust, seems to be indicative of the high content of As, Cu, Pb and Zn in leptosols. The metal partitioning patterns show that most trace elements are associated with Fe amorphous oxy-hydroxides, or take part of the residual fraction. According to the results obtained, the following mobility sequence is proposed for major and minor elements: Mn, Pb, Cd, > Zn, Cu > Ni > As > Fe > Cr. The high mobility of Pb, Cu and Zn involve an environmental risk in this area, even in soils where the concentrations are not so high.

**Keywords** Trace elements · Agricultural soils · Sulphide exploitation · Iberian Pyrite Belt · Spain

### Introduction

The extraction of mineral resources brings with it a series of environmental alterations that can at times have very negative consequences (Merefield 1995; Salomons 1995; Gäbler and Schneider 2000; González 2003; Lee 2003). In Spain, the exploitation of metallic mineral deposits and its subsequent abandonment in recent years, particularly in the Iberian Pyrite Belt (in the southwest of the Iberian Peninsula), has had some broad repercussions. The intensive mining activity in the Riotinto area since prehistoric times (Blanco and Rothenberg 1981) has generated large amounts of scoria, pyrite ashes and other leachable materials which continue to cause acidic waters and contaminating elements to enter the Tinto and Odiel River basins (Fernández Caliani and Galán 1996; González et al. 2004; Romero et al. 2006). The abandoned mine spoils not only affects the quality of the water, but also may cause the pollution of soils by wind-blown dust (Chopin et al. 2003) or by water as a consequence of leachates or spills (Gäbler and Schneider 2000; Galán et al. 2002).

In addition to the problems of air, water and soil pollution, the abandoning of the mines in the Pyrite Belt (South Portuguese Zone) has had an important socio-economic impact; resulting in a great loss of employment. This has led to the growth of agriculture as the new base for social development, with large planting of citrus and other fruit-bearing trees around the old waste rock piles. Correspondingly, the traditional subsistence agriculture is usually developed on floodplains near the mining sites. The level of soil pollution has not been taken into account in

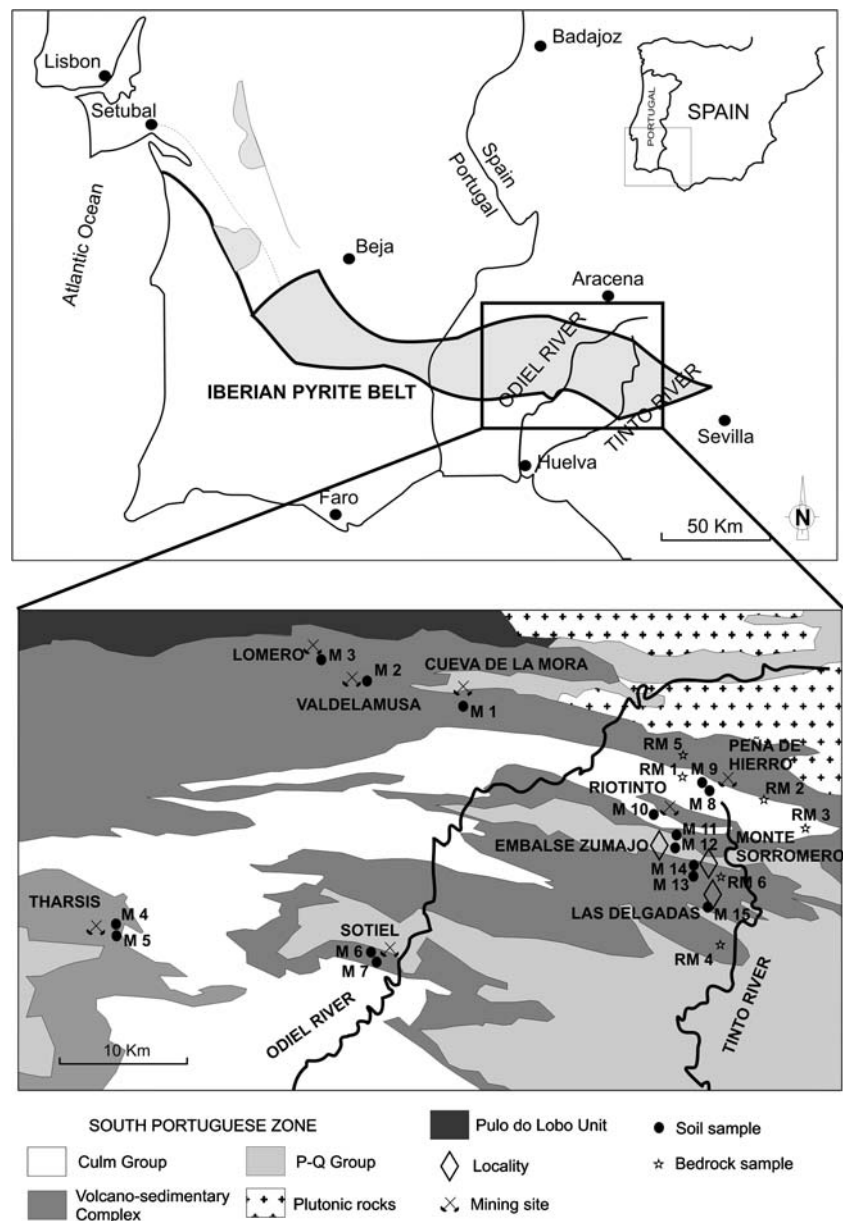
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these cases, nor has its impact on the health of the inhabitants of these areas. At present, the only works related to this subject are those by Chopin et al. (2003) and Barba Brioso et al. (2006). Therefore, in agricultural areas close to the abandoned mines, it is of great interest to know the current state of the soils and the sources and types of contaminants derived from mining activity in order to programme its decontamination, where appropriate, according to legislation.

In this work, potentially contaminated soils surrounding several mines of the Iberian Pyrite Belt have been studied (Fig. 1). The trace element content has been assessed and the maximum values allowed (contamination threshold) have been compared, taking into account the results

obtained by authors of other countries (Finnecey and Pearce 1986; Barth and L'Hermite 1987; Kabata Pendias and Pendias 1992; Azcue 1993; Cambier 1994; Alloway 1995; Kabata Pendias 1995; Adriano 1997; Baize 1997; Cano Parrilla et al. 1997; Llamas et al. 2000; Martín 2000; Chen et al. 2001; Navas and Machín 2002; Tarvainen and Kallio 2002) and also the regional geochemical baseline of Andalusia (<http://www.juntadeandalucia.es/medioambiente/site/web/>). The background levels for the geological setting (South Portuguese Zone) have also been taken into account owing to the great influence that lithology, mineralogy and granulometry have on these levels (Gregorauskiene and Kadunas 1997; Salminen and Tarvainen 1997; Salminen and Gregorauskiene 2000).

**Fig. 1** Geological setting and location of soil and bedrock samples



In order to know the present and future hazard posed by the soils, chemical and mineralogical speciation has been carried out, given that the availability of a metal depends on the phase in which it is found (McLean and Bledsoe 1992; Pérez et al. 2000; Galán 2003a). Bioavailability has also been assessed. This will permit the degree of actual contamination to be evaluated for contaminated soils and sediments (Lindsay 1979; Plant and Raiswell 1983; Chao 1984; Bohn et al. 1985; Kloke and Einkmann 1991; Kabata-Pendias and Pendias 1992; Van der Berg et al. 1993; O'Neill 1995; López Julián and Mandado Collado 2002).

The aim of this work is to determine the content of potentially toxic elements in the soils studied and to evaluate the consequential environmental problems. The following specific objectives have been covered: (a) chemical and mineralogical characterisation of the soils, (b) determination of potentially toxic trace element content, and (c) chemical and mineralogical speciation of the trace elements and their bioavailability. With the results obtained the potential risk incurred in the agricultural use of the studied soils has been assessed.

## Materials and methods

Fifteen surface samples (0–20 cm deep) of agricultural soils were taken in the Iberian Pyrite Belt. In this area, the bedrock is composed of shales and volcanic rocks, as these are the lithological characteristics of the South Portuguese Zone (Iberian Massif) (Leistel et al. 1998), and the soils developed are usually leptosols, cambisols and luvisols. The samples were taken at random in areas close to the mines or which might have been affected by them. Some of them were taken from small-scale orchards located over quaternary sediments and with a well-developed soil cover. Those locations were Cueva de la Mora, Valdelamusa, El Lomero, Tharsis, Sotiel, and Las Delgadas (Fig. 1). Other samples come from large plantations of citrus usually located on leptosols developed over shales such as Peña de Hierro, Riotinto and Monte Sorromero. Sometimes, this intensive agriculture also covers the valleys, such as the samples taken in Embalse Zumajo. In order to assess the bedrock's influence on the chemical characteristics of the soils, several samples of shales and volcanic rocks were collected for to be analysed. Given that the mobility of trace elements depends directly on the characteristics of the soil in which they are found (Cambier 1994; Galán 2003b), the following edaphic parameters were determined: pH, texture and mineralogy of clays.

Determination of pH was performed using a Microph 2002 (Crisson) pH-meter, previously calibrated with two buffer solutions of pH = 4 and pH = 7. In order to perform

measurements, 10 g of sample was mixed with 25 ml distilled water in a mechanical shaker for 10 min, and the pH was read after 30 min of the solution at rest.

*Major, minor and trace elements analyses* were performed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Instrumental Neutron Activation Analysis (INAA) at Activation Laboratories Ltd. (1428 Sandhill Drive, Ancaster, Ontario, Canada, <http://www.actlabs.com>).

*Mineralogical analysis* was performed by X-Ray Diffraction (XRD), using a Bruker D8 Advance powder device with Cu anticathode and standard conditions of speed  $2^\circ$   $2\theta$ /min between  $3^\circ$  and  $70^\circ$  at 30 mA and 40 KV. The study of the total sample was made by crystalline powder diffraction (non-oriented powder) on a side-loading sample holder. Bulk quantitative analyses were based on the Schultz (1964) method after correcting intensities for the automatic slit. Clay-minerals were studied in oriented aggregates using standard methods involving drying at room temperature, solvation with ethylene glycol and heating to  $550^\circ\text{C}$  for 2 h. Phase abundances were semi-quantitatively estimated according to mineral intensity factor proposed by Martín-Pozas et al. (1969).

*Chemical speciation* was carried out according to the methodological scheme given by Tessier et al. (1979). Sequential extraction involves several stages of chemical extraction in which reagents of different strength are used to separate the metallic species into the different fractions (Table 1).

In the *mineralogical speciation*, seven samples were selected for their content in trace metal, iron oxide and phyllosilicate, and type of interstratified minerals, so as to observe their behaviour and the mineralogical evolution, once the sequential extraction had been performed. The existing mineral phases were identified in the solid residues obtained from the different extractions carried out following Tessier's protocol.

In order to obtain the *bioavailability of trace elements* the samples were treated with a solution of EDTA 0.05 M in the form of sodium salt and at pH = 7 with continuous shaking for 1 h. The resulting extract was analysed with spectrophotometric techniques (in the same way as Tessier's different fractions).

In order to obtain *metals extractable in acidic water*, the samples were treated with water at pH = 1 (acidified with  $\text{HNO}_3$ ), with continuous shaking for one hour. The extract, in the same way as the previous case, was analysed using spectrophotometric techniques.

A statistical processing was performed on the data from the surface samples with the aim of corroborating interelement links observed between elements with similar geochemical behaviour. Specifically, correlation and principal component-analyses were accomplished.

**Table 1** Analytical procedure of sequential extractions

Fraction	Solution	MI	Conditions
Interchangeable	MgCl <sub>2</sub> 1 M at pH = 7	8	Shaking 1 h Room temperature
Associated to carbonates	NaOAc/HOAc at pH = 5	8	Shaking 5 h Room temperature
Associated to Fe and Mn oxides	NH <sub>2</sub> OH.HCl 0.04 M in HOAc 25% HNO <sub>3</sub> 0.02M + H <sub>2</sub> O <sub>2</sub> 30% at pH = 2	20 38,840	Shaking 96°C. 6 h Shaking 85°C. 2 h
Associated to organic matter	H <sub>2</sub> O <sub>2</sub> 30% at pH = 2 NH <sub>4</sub> OAc 3.2M in HNO <sub>3</sub> 20% + H <sub>2</sub> O	3 38,812	Shaking 85°C. 3 h Shaking 30 min. Room temperature
Residual	HF + HNO <sub>3</sub> /HCl + HClO <sub>4</sub>	38,482	Sand bath 80°C. 16 h

## Results and discussion

### Physico-chemical characterisation

The pH values of the soil samples range from 7.6 to 3.6 (Table 2). The most acidic values correspond to samples collected in the immediate vicinity of the Peña de Hierro mine (pH = 3.6, 4.2). Also showing important acidity are those samples collected at Monte Sorromero (pH = 4.9, 5.5). Those acidic pH values seem to originate from the bedrock, as those soils are leptosols and no other source of acidity has been found. Samples collected at Tharsis (pH

5–6) are well-developed soils, and the pH does not seem to be influenced by the bedrock. In this case, the source seems to be the leachates or the erosion of the adjacent waste mining piles. The rest of pH values were above 6. The values for pH are of great significance given that the concentration of hydrogen ions modifies the availability of trace elements and of nutrients, and in addition, can indicate deficiencies or alterations in the soil (Wen and Allen 1999; Galán 2003a). Most of the studied metals tend to be more available at acidic pH, with the exception of As, Mo and Cr, which are more mobile at alkaline pH. In general, the content in divalent metals such as Cu, Zn, Ni, Co, Cd

**Table 2** Major element chemical analyses and pH values of the soil samples

Location	DL	SiO <sub>2</sub> 0.01	Al <sub>2</sub> O <sub>3</sub> 0.01	Fe <sub>2</sub> O <sub>3</sub> 0.01	MnO 0.001	MgO 0.01	CaO 0.01	Na <sub>2</sub> O 0.01	K <sub>2</sub> O 0.01	TiO <sub>2</sub> 0.001	P <sub>2</sub> O <sub>5</sub> 0.01	LOI	pH
	sample												
Cueva de la Mora	M1	57.13	14.89	7.84	0.24	1.84	1.19	1.50	2.15	1.15	0.39	11.08	6.7
Valdelamusa	M2	67.26	10.07	5.02	0.10	1.12	1.47	1.08	2.33	0.49	0.42	10.60	7.2
El Lomero	M3	58.00	14.98	6.66	0.12	1.66	3.36	2.12	1.23	0.88	0.18	10.55	7.1
Tharsis	M4	55.50	16.06	<b>9.39</b>	0.29	0.78	0.71	0.53	2.93	0.85	0.51	12.41	5.9
Tharsis	M5	54.75	13.11	<b>12.61</b>	0.42	0.66	0.47	0.51	2.29	0.79	0.68	12.80	5.3
Sotiel	M6	55.35	16.38	<b>8.97</b>	0.19	1.53	1.46	0.85	2.48	1.03	0.42	11.24	7.0
Sotiel	M7	52.09	13.91	<b>10.15</b>	0.18	0.96	2.61	0.60	2.49	0.76	0.70	14.18	7.6
Peña de Hierro	M8*	62.13	18.15	6.49	0.02	0.92	0.07	0.39	3.07	0.87	0.15	7.59	3.6
Peña de Hierro	M9*	63.83	17.00	6.50	0.02	0.83	0.03	0.39	2.71	0.81	0.11	7.34	4.2
Riotinto	M10*	58.12	15.66	7.43	0.11	2.35	2.61	1.59	1.27	0.93	0.11	9.64	6.0
Embalse Zumajo	M11	57.43	14.48	<b>8.81</b>	0.17	2.20	2.10	2.30	1.20	1.24	0.34	9.73	6.6
Embalse Zumajo	M12	55.53	14.52	<b>8.52</b>	0.15	2.04	2.40	2.53	1.14	1.39	0.41	11.27	6.6
Monte Sorromero	M13*	66.40	13.80	5.27	0.10	1.87	1.78	0.84	1.91	0.57	0.07	6.76	4.9
Monte Sorromero	M14*	51.10	18.40	<b>10.12</b>	0.20	1.78	4.43	2.41	0.21	1.63	0.14	9.23	5.5
Las Delgadas	M15	54.40	13.80	6.75	0.17	2.38	4.22	2.06	1.44	1.45	0.51	11.89	6.7

Values in %. DL detection limit

In bold: iron concentration > mean value (8.0)

\*: Leptosols

and Mn decreases when pH increases (Cama et al. 2005). For this reason, the samples that may have greater availability are those which have lower pH.

*Chemical analyses* show values for silica ranging between 50 and 70% and for alumina between 10 and 19% (Table 2). The iron and manganese content of these soils is important owing to the fact that oxides and hydroxides of these elements, if found dispersed in the soil mass, can be very active and have a great sorption capacity for some metals (Cu, Pb) and As (Galán et al. 2003). Iron content in the studied samples ranges from 5 to 13%. The samples from Tharsis, Sotiel, Embalse Zumajo and the sample M14 in Monte Sorromero show Fe<sub>2</sub>O<sub>3</sub> concentrations higher than the mean (8.0%). Other oxides such as CaO, K<sub>2</sub>O, MgO and Na<sub>2</sub>O are under 5%. The loss on ignition (LOI) ranges from 7 to 15%.

There were 50 minor and trace elements analysed, although only 7 were chosen for study (As, Cd, Co, Ni, Cu, Pb and Zn) owing to their abundance in soils (Bowen 1979), because they are easily mobilised (Novotny 1995), and also because they are included in the U.S. Environmental Protection Agency (EPA) priority contaminant list. Content of As ranged between 19 and 994 ppm (Table 3). The highest values appear in the samples from Tharsis (994 ppm) and Sotiel (882 ppm), which are well over the

mean (227 ppm, Table 4). Lead-content oscillates between 40 and 4,900 ppm. The highest values correspond to samples from Tharsis (2,650 ppm) and Sotiel (4,890 ppm), which are also well over the mean (810 ppm). Relating to Zn, values are between 95 and 900 ppm, and of Cu between 27 and 1,160 ppm. The highest concentration of those elements also appeared in samples from Tharsis and Sotiel. Regarding Chromium, its values range between 35 and 236 ppm. Values over 200 ppm appeared in samples from Embalse Zumajo. Cadmium, a highly toxic element, is always below 2 ppm, except in Cueva de la Mora (2.3 ppm). These values are higher than those found in New Zealand (Sheppard et al. 2000) and similar to the values found in soils in Korea for Pb, Zn and Cd (Song et al. 1999) and in soils in the Iberian Pyrite Belt (Chopin et al. 2003; Barba Brioso et al 2006).

Chemical analyses of bedrock samples show that shales are poorer in MgO, CaO and Na<sub>2</sub>O (<0.1%) than volcanic rocks, but K<sub>2</sub>O is richer (3–5% in shales versus <1% in volcanic rocks) (Table 5). Iron is usually higher in volcanic rocks (up to 14.65%) as well as manganese. According to trace elements (Table 6), As and Pb (up to 58 and 69 ppm, respectively) seem to be more concentrated in shales than in volcanic rocks but the values are much lower than those noticed in the soil samples. Cadmium and S are below the

**Table 3** Minor and trace element chemical analyses of the soil samples

Location	DL	As	Cd	Co	Cr	Ni	Cu	Pb	Zn	S
	sample	0.5	0.3	1	2	1	1	3	1	0.01
Cueva de la Mora	M1	<b>115</b>	2.3	23	126	60	<b>159</b>	<b>169</b>	<b>227</b>	0.02
Valdelamusa	M2	30.2	1.2	10	35	19	<b>90</b>	<b>171</b>	<b>285</b>	0.07
El Lomero	M3	22.5	1	18	67	20	<b>67</b>	93	<b>171</b>	0.02
Tharsis	M4	<b>444</b>	1	<b>41</b>	105	51	<b>198</b>	<b>1,270</b>	<b>667</b>	0.05
Tharsis	M5	<b>994</b>	1.3	<b>70</b>	105	54	<b>443</b>	<b>2,650</b>	<b>897</b>	0.08
Sotiel	M6	<b>361</b>	0.8	26	140	<b>70</b>	<b>648</b>	<b>1,410</b>	<b>356</b>	0.07
Sotiel	M7	<b>882</b>	1.4	19	98	48	<b>1160</b>	<b>4,890</b>	<b>585</b>	0.16
Peña de Hierro	M8*	38.6	0.5	18	118	53	<b>100</b>	50	119	0.03
Peña de Hierro	M9*	<b>60.2</b>	0.4	17	108	55	<b>111</b>	66	106	0.02
Riotinto	M10*	<b>78.7</b>	0.5	28	111	26	<b>212</b>	<b>174</b>	<b>147</b>	0.02
Embalse Zumajo	M11	<b>189</b>	1.2	<b>32</b>	<b>236</b>	<b>75</b>	<b>253</b>	<b>483</b>	<b>183</b>	0.04
Embalse Zumajo	M12	<b>96.8</b>	0.8	<b>32</b>	<b>234</b>	<b>73</b>	<b>217</b>	<b>218</b>	<b>206</b>	0.05
Monte Sorromero	M13*	21.7	0.7	16	93	28	57	<b>197</b>	<b>201</b>	<0.01
Monte Sorromero	M14*	18.8	<0.3	<b>34</b>	<b>190</b>	14	27	41	95	0.02
Las Delgadas	M15	49.5	0.5	28	<b>173</b>	43	<b>153</b>	<b>268</b>	<b>302</b>	0.06
Andalucía 95th percentile		<i>54</i>	<i>3</i>	<i>32</i>	<i>144</i>	<i>69</i>	<i>62</i>	<i>109</i>	<i>145</i>	<i>NC</i>
South Portuguese Zone 90th percentile		<i>157</i>	<i>NC</i>	<i>34</i>	<i>209</i>	<i>62</i>	<i>108</i>	<i>117</i>	<i>134</i>	<i>NC</i>

Values in ppm except for S (in %). DL detection limit. N.C.: not calculated

**Bold:** values above the 95th percentile of regional soils (Andalusia soils)

**Bold italics:** Values above the 90th percentile of the corresponding geological dominium (South Portuguese Zone)

\*: Leptosols

**Table 4** Maximum and minimum values, median and mean for trace elements and for iron and aluminium oxides

	Valid <i>N</i>	Mean	Median	Minimum	Maximum	Std. Dev.
As	15	227	79	19	994	316
Cd	15	0.9	0.8	0.0	2.3	0.5
Co	15	27	26	10	70	14
Cr	15	129	111	35	236	57
Ni	15	46	51	14	75	20
Cu	15	260	159	27	1,160	297
Pb	15	810	197	41	4,890	1,341
Zn	15	303	206	95	897	234
Al <sub>2</sub> O <sub>3</sub>	15	15.0	14.9	10.1	18.4	2.1
Fe <sub>2</sub> O <sub>3</sub>	15	8.0	7.8	5.0	12.6	2.0

**Table 5** Major element chemical analyses of the bedrock samples

Sample	Location	DL	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>
		description	0.01	0.01	0.01	0.001	0.01	0.01	0.01	0.01	0.001
RM1	Peña de Hierro	Shale	62.77	21.02	3.76	0.003	0.47	0.04	0.69	4.58	1.054
RM2	East of P. de Hierro	Shale	62.12	19.22	5.38	0.014	0.75	0.05	0.70	3.50	0.957
RM3	Northeast of Nerva	Shale	62.92	17.82	7.27	0.007	0.47	0.05	0.73	3.59	0.890
RM4	Marigenta	Basic volcanic rock	44.53	18.42	12.41	0.219	5.27	6.32	4.05	0.12	2.052
RM5	Gossan dam	Basic volcanic rock	60.44	17.47	6.44	0.127	2.55	3.23	5.33	0.45	1.098
RM6	Monte Sorromero	Altered volcanic rock	40.65	8.49	14.65	0.216	14.86	4.49	0.21	0.26	0.944

Values in %. *DL* detection limit

**Table 6** Minor and trace element chemical analyses of the bedrock samples

Sample	Location	DL	As	Cd	Co	Cr	Ni	Cu	Pb	Zn	S
		description	0.5	0.3	1	2	1	1	3	1	0.01
RM1	Peña de Hierro	Shale	58.5	0.9	5	111	18	41	32	20	0.01
RM2	East of P. de Hierro	Shale	35.6	0.5	9	100	463	89	43	112	0.03
RM3	Northeast of Nerva	Shale	24.5	0.4	<1	95	18	69	69	74	0.01
RM4	Marigenta	Basic volcanic rock	<0.5	<0.3	41	529	91	30	9	62	<0.01
RM5	Gossan dam	Basic volcanic rock	19.3	<0.3	14	84	23	38	38	62	<0.01
RM6	Monte Sorromero	Altered volcanic rock	<0.5	<0.3	86	702	533	81	8	133	<0.01

Values in ppm except for S (in %). *DL* detection limit

detection limit in volcanic rocks, but both appear in shales. Cobalt (up to 86 ppm), Cr (up to 7.2 ppm) and Ni (up to 533) usually display higher concentrations in volcanic rocks, which are similar to or higher than those observed in soils. Copper (30–89 ppm) and Zn (20–133 ppm) show similar values in shales and volcanic rocks, but are lower than those that occur in soil samples.

Most of the soil samples displayed concentrations of Cu, Pb, Zn and As exceeding the values defined for the 95th percentile of regional soils (values referred to Andalusia) (Table 3), which is indicative of an enrichment of trace

elements in the soils at the studied area. In fact, the statistical processing shows a clear Pb–Zn–As–Cu association (Table 7), which is quite logical in the South Portuguese Zone where massive sulphide mineralisations exist associated to the Volcano-sedimentary Complex. Moreover, most of those values also were over the 90th percentile of the soils of South Portuguese Zone (Table 3), which suggests that the mining activity could have increased the concentration of trace elements besides the geological setting influence (Moon et al. 2000; Peng et al. 2004). On the other hand, the soils developed on sediments are more



**Table 7** Correlation coefficients obtained from the chemical data

	As	Cd	Co	Cr	Ni	Cu	Pb	Zn	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
As	1.00									
Cd	0.38	1.00								
Co	0.62	0.07	1.00							
Cr	-0.13	-0.20	0.28	1.00						
Ni	0.30	0.33	0.27	0.53	1.00					
Cu	<b>0.78</b>	0.32	0.13	-0.04	0.35	1.00				
Pb	<b>0.92</b>	0.34	0.30	-0.17	0.21	<b>0.93</b>	1.00			
Zn	<b>0.91</b>	0.39	0.68	-0.24	0.21	0.55	<b>0.75</b>	1.00		
Al <sub>2</sub> O <sub>3</sub>	-0.21	-0.50	0.02	0.32	0.12	-0.14	-0.21	-0.35	1.00	
Fe <sub>2</sub> O <sub>3</sub>	<b>0.79</b>	0.17	<b>0.83</b>	0.33	0.34	0.53	0.63	0.67	0.16	1.00

Bold values higher than  $r > 0.70$

contaminated than leptosols (Table 3), which is also consistent with the theory of an anthropogenic influence. Chemical analyses of bedrock samples (Table 6), show that even their contribution may be not enough to enrich the leptosols, especially in the sample M10, which was taken close to the Riotinto Mines and could have been affected by wind-blown dust. Only the high concentration of Cr and Ni in samples from Embalse Zumajo may be influenced by the weathering of volcanic rocks (Moon et al. 2000; Zhai et al. 2003), which are rich in those elements, but an anthropogenic contribution seems to be a likely explanation for the high concentration in elements such as As, Cu or Pb.

The *magnitude of anomalies* can be also evaluated on the basis of the enrichment factor, defined as the relation between the total concentration and the geochemical background for the corresponding geological domain, determined as the median of the soils, in this case, of the South Portuguese Zone. The samples corresponding to the

Tharsis and Sotiel mining areas are those which show the greatest degree of enrichment for As, Cu, Pb and Zn (Table 8), especially that from Sotiel which exceeds the background value of Pb by almost 200 times, and As by 50 times. The nearness of the sample location to the waste rock piles in these cases suggests that the soils might have been developed over mining spills, or they are polluted by leachates or erosion coming from the mining spoils (Fig. 2). This is consistent with the acidic pH found in samples from Tharsis. Other authors found polluted soils close to mining dumps (Lottermoser et al. 1999; Lee 2003)

Mineralogy

The *mineralogy* of the soil samples is made principally of quartz, phyllosilicates and feldspars (Table 9). Feldspars are Ca-plagioclase, which explains the high calcium content readings obtained in the chemical analysis for some

**Table 8** Enrichment factor for the soil samples calculated as the relation between the concentration in the soil and the background

The value of the background represents the median of the soils of the corresponding geological dominium (South Portuguese Zone)

Element	As	Co	Cr	Cu	Ni	Pb	Zn
Background	20	16	85	31	27	31	72
Cueva de la Mora	6.76	1.35	1.59	7.23	1.33	7.04	3.98
Valdelamusa	1.78	0.59	0.44	4.09	0.42	7.13	5.00
El Lomero	1.32	1.06	0.85	3.05	0.44	3.88	3.00
Tharsis	26.12	2.41	1.33	9.00	1.13	52.92	11.70
Tharsis	58.47	4.12	1.33	20.14	1.20	110.42	15.74
Sotiel	21.24	1.53	1.77	29.45	1.56	58.75	6.25
Sotiel	51.88	1.12	1.24	52.73	1.07	203.75	10.26
Peña de Hierro	2.27	1.06	1.49	4.55	1.18	2.08	2.09
Peña de Hierro	3.54	1.00	1.37	5.05	1.22	2.75	1.86
Riotinto	4.63	1.65	1.41	9.64	0.58	7.25	2.58
Embalse Zumajo	11.12	1.88	2.99	11.50	1.67	20.13	3.21
Embalse Zumajo	5.69	1.88	2.96	9.86	1.62	9.08	3.61
Monte Sorromero	1.28	0.94	1.18	2.59	0.62	8.21	3.53
Monte Sorromero	1.11	2.00	2.41	1.23	0.31	1.71	1.67
Las Delgadas	2.91	1.65	2.19	6.95	0.96	11.17	5.30



**Fig. 2** Location of soil sample in Tharsis area with regard to the waste dumps. The leachates of mining spoils and their erosion can feed the sediments causing extreme values of trace elements

samples despite not finding any carbonates in them. The phyllosilicate content is usually low. Only the samples from Peña de Hierro and Montesorromero have concentrations higher than 30%, but they are samples of leptosols (shales) with poor content of clay grain size, which involves a low capacity for metal adsorption. Mention should also be made of the presence of hematite in the Cuevas de la Mora, El Lomero, Tharsis, Riotinto, Embalse Zumajo and Monte Sorromero samples. The high iron oxide values (Table 2) found in the samples M5 and M7, where the presence of hematite was not detected, leads one to consider the existence of amorphous iron oxides in these samples. With regard to the fraction under 2  $\mu\text{m}$ , we would highlight the fact that the samples were found to be com-

posed of illite and of kaolinite and chlorite. Smectites, which have a high ability for metal retention, are not present generally. Only those samples corresponding to the Embalse Zumajo area show a slight content in smectite and illite-smectite interstratified minerals, but their phyllosilicate content is low and their retention ability must be limited. In some samples of shales (Peña de Hierro, Riotinto and Monte Sorromero), chlorite–vermiculite interstratified has been also identified. On the other hand, the content of gravel shows high values, over 50% in some cases, and therefore is indicative of sandy soils (Table 9). This type of soil jointed to the shortage of clay minerals lacks the ability to fix trace elements.

The correlation between  $\text{Fe}_2\text{O}_3$  and the Pb–Zn–As–Cu association suggest that iron oxy-hydroxides are the main phases to store most of the trace elements (Table 7). The high content in  $\text{Fe}_2\text{O}_3$  of the most contaminated samples, such as those from Sotiel, Tharsis and Embalse Zumajo, is consistent with this idea. It should also be pointed out that they are not associated with the phyllosilicates as it has been proposed by some authors (Brigatti et al. 1994; Galán 2000). The low phyllosilicate contents and, especially, the absence of clay minerals with sorption capacity support that idea. Other authors such as Rasmussen et al. (1998), Gobeil (1999) and Bilali et al. (2002) found similar results for lacustrine sediments.

#### Chemical speciation

The sequential extraction confirms the low significance of phyllosilicates in the retention of metals in this study, and

**Table 9** Mineralogical composition of total sample, mineralogy of fraction <2  $\mu\text{m}$  and content of the fraction <2 mm (all the data in %)

Location	Sample	Phyllo	Q	Fds	Hem	I	K	Ch	Sm	Int Ch-V	Int I-Sm	<2mm
Cueva de la Mora	M1	21	60	14	Traces	80	20	0	0	0	0	35
Valdelamusa	M2	10	80	10	0	85	0	15	0	0	0	49
El Lomero	M3	18	60	17	Traces	45	55	0	0	0	0	41
Tharsis	M4	34	56	5	Traces	79	21	0	0	0	0	32
Tharsis	M5	24	76	5	0	70	30	0	0	0	0	46
Sotiel	M6	15	80	5	0	86	7	7	0	0	0	39
Sotiel	M7	16	80	4	0	85	15	0	0	0	0	59
Peña de Hierro	M8	30	60	5	0	66	0	20	0	14	0	61
Peña de Hierro	M9	35	55	5	0	68	0	32	0	0	0	65
Riotinto	M10	15	75	15	Traces	24	0	52	0	24	0	59
Embalse Zumajo	M11	10	59	30	0	27	20	10	15	0	28	47
Embalse Zumajo	M12	19	50	26	Traces	30	24	12	14	0	20	54
Monte Sorromero	M13	29	54	27	Traces	41	0	43	0	16	0	55
Monte Sorromero	M14	22	45	28	Traces	0	0	79	0	21	0	47
Las Delgadas	M15	10	80	10	0	95	5	0	0	0	0	54

*Phyllo* Phyllosilicates, *Q* Quartz, *Fds* Feldspars, *Hem* Hematite, *I* illite, *K* Kaolinite, *Ch* Chlorite, *Sm* Smectite, *Int Ch-V* Interstratified chlorite-vermiculite, *Int I-Sm* Interstratified Illite-smectite



shows that most of the trace elements were associated significantly with the iron and manganese oxides fraction. Arsenic was extracted with the iron and manganese oxides fraction, with the rest practically remaining in the residual fraction (Fig. 3). Therefore, the amounts united to fractions of greater mobility are very discrete. Cadmium is distributed homogeneously in the different extractions but it should be mentioned that in some samples it is in greater proportion in the interchangeable fraction, although in general it is found in scant proportions in the studied samples. Chromium is distributed only into three fractions: iron and manganese oxides, organic matter and insoluble residue. Copper is present in all of the fractions, but is found mostly associated with iron and manganese oxides. In samples M11 and M12 from Embalse Zumajo Cu is also extracted with the interchangeable, carbonate and organic matter fractions. Nickel appears in all of the fractions but it is associated mainly with iron and manganese oxides and to the residual fraction. Lead appears associated to iron and manganese oxides, but also it is associated with carbonates and with the insoluble residue; a small proportion may be also interchangeable. Zinc, as in the case of Pb, was essentially found in the fraction joined to iron and manganese oxides. A small proportion can be found in the insoluble residue or in the fraction bound to the organic matter, depending on the sample type. For all the extractions, the total of the trace elements in the different fractions did not exceed  $\pm 10\%$  of the bulk sample which is

accepted as satisfactory (Tessier et al. 1980; Pickering 1986; Yan et al. 1999), except the values obtained for Pb and Zn, which exceeded those detected with ICP-OES. In these cases only the relative percentages have been considered.

Iron, as expected owing to the mineralogical composition (iron amorphous oxides and hematite), is basically found distributed into two fractions: iron and manganese oxides and insoluble residue (Fig. 3). This distribution is very similar to that obtained for As. Manganese is associated with the iron and manganese oxides fraction. It is also found in a small proportion in the fraction associated with carbonates and in the interchangeable fraction.

In general, the partitioning data obtained shows that most of the elements are found in the residual fraction or are linked to the iron and manganese oxide fraction, affirmations which are in agreement with the results obtained by Howari and Banat (2001) and by Galán et al. (2003).

### Mineralogical speciation

The characterisation of the mineralogy of the different fractions does not seem to be a good tool in these types of samples, since the results are very similar for every fraction (Table 10). This is due to the fact that the mineralogical composition of the samples is mostly made up of quartz, feldspars and traces of hematite, which are resistant to different attacks. Moreover, the mineralogical characteri-

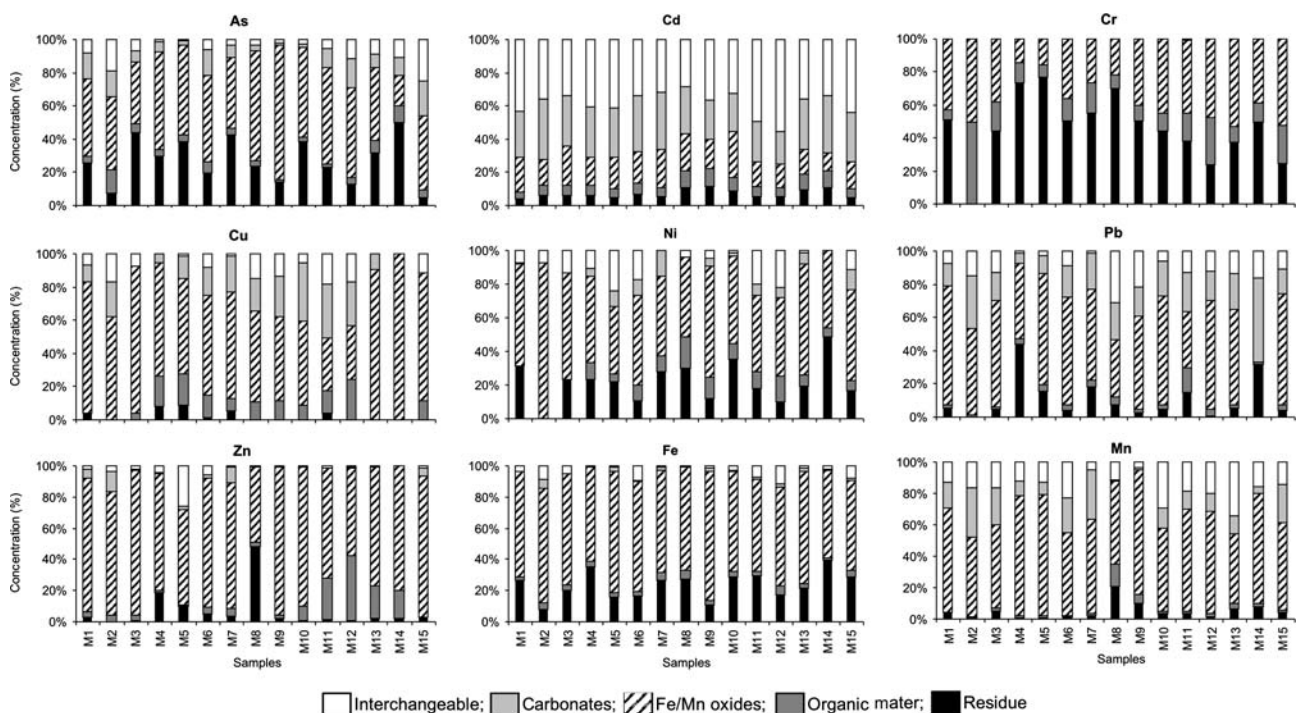


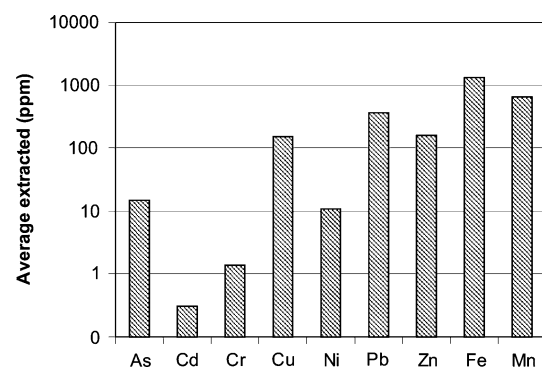
Fig. 3 Sequential extraction of analysed trace elements

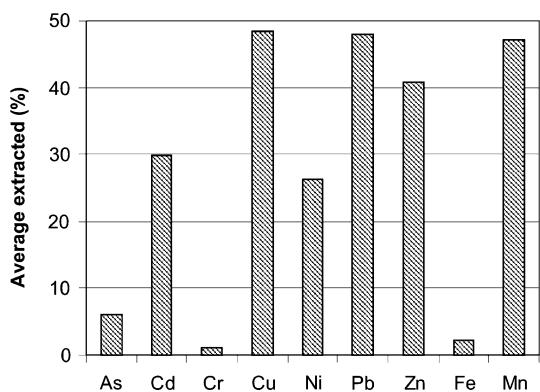
**Table 10** Mineralogical composition of the extractable fractions

Sample	Fractions	Phyllo (%)	Q (%)	Fds (%)	Hem (%)
Cueva de la Mora (M1)	Total – Int.	19	60	16	Traces
	Total – Int. – Carb.	23	58	14	Traces
	Total – Int. – Carb. – Ox.	25	56	14	Traces
	Residual	25	51	19	Traces
Tharsis (M4)	Total – Int.	30	65	Traces	Traces
	Total – Int. – Carb.	28	67	Traces	Traces
	Total – Int. – Carb. – Ox.	33	62	Traces	0
	Residual	35	60	Traces	0
Tharsis (M5)	Total – Int.	25	70	Traces	0
	Total – Int. – Carb.	30	65	Traces	0
	Total – Int. – Carb. – Ox.	28	67	Traces	0
	Residual	29	66	Traces	0
Sotiel (M6)	Total – Int.	16	79	5	0
	Total – Int. – Carb.	17	78	Traces	0
	Total – Int. – Carb. – Ox.	28	66	6	0
	Residual	27	65	8	0
Sotiel (M7)	Total – Int.	20	78	Traces	0
	Total – Int. – Carb.	20	75	Traces	0
	Total – Int. – Carb. – Ox.	22	73	Traces	0
	Residual	25	70	Traces	0
Embalse Zumajo (M11)	Total – Int.	15	60	25	0
	Total – Int. – Carb.	23	50	27	0
	Total – Int. – Carb. – Ox.	22	53	25	0
	Residual	18	55	27	0
Embalse Zumajo (12)	Total – Int.	10	60	25	Traces
	Total – Int. – Carb.	18	50	27	Traces
	Total – Int. – Carb. – Ox.	19	53	23	0
	Residual	20	55	25	0
Las Delgadas (M15)	Total – Int.	15	60	20	0
	Total – Int. – Carb.	12	63	20	0
	Total – Int. – Carb. – Ox.	12	60	23	0
	Residual	12	68	20	0

*Phyllo* phyllosilicate, *Q* quartz, *Fds* feldspars, *Hem* hematite, *Int* interchangeable, *Carb* carbonates, *Ox* oxides

sation method of XRD with an error of ( $\pm 5\%$ ) does not allow the detection of mineral phases present in small proportions, which could be of interest owing to the ease with which they may capture trace elements (e.g. jarosite). The most relevant feature is the decrease of the diffractogram background after the extraction of Mn and Fe oxides, which may be related with the dissolution of amorphous iron oxy-hydroxides. The hematite content may disappear with this step, but may sometimes also remain in the residual fraction. The mineralogy of the interchangeable fraction shows a slight decrease in the phyllosilicate content, particularly in those samples containing smectite and interstratified illite–smectite (M11, M12).

**Fig. 4** Average concentration of trace elements extracted with acidic water

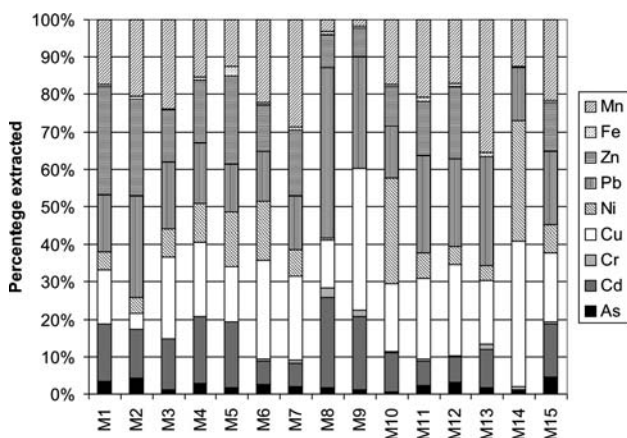


**Fig. 5** Average percentage of trace elements extracted with acidic water. The percentage was calculated as the rate between the extracted and the total concentration of the element in every sample

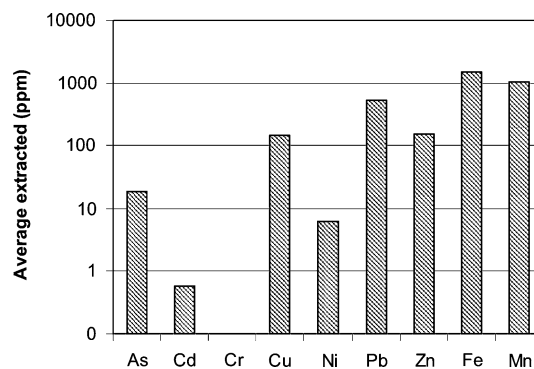
Availability and bioavailability

*Extractions with acidic water* have given positive readings for all cations. The highest concentrations extracted corresponded to Cu, Pb and Zn, which reached values over 100 ppm on average (Fig. 4). They were followed by As and Ni which were around 10 ppm and Cd and Cr showed values usually lower than 1 ppm. The mobility of the trace elements was assessed comparing the amounts extracted with total concentration of the samples (Fig. 5). Copper, Pb, Zn and Mn were the most mobile elements (average extraction higher than 40%, Figs. 5, 6), followed by Cd, which is also available although its concentration is very low. The most immobile elements are As, Cr and Fe.

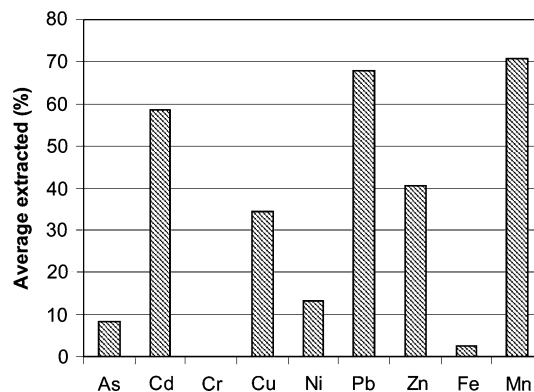
*Extractions performed with EDTA* have also given a positive reading for all cations (Fig. 6). The amounts extracted are above 100 ppm for Cu, Pb and Zn, around 10 ppm for As and Ni and lower than 1 ppm for Cd (Fig. 7). The most available metals were Cd, Pb and Mn (average



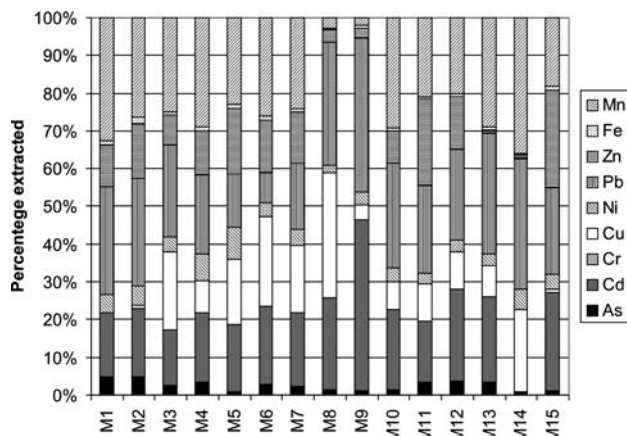
**Fig. 6** Relative percentages of trace elements extracted with acidic water in every sample. The amount of every element was normalised with its total concentration



**Fig. 7** Average concentration of trace elements extracted with EDTA



**Fig. 8** Average percentage of trace elements extracted with EDTA. The percentage was calculated as the rate between the extracted and the total concentration of the element in every sample



**Fig. 9** Relative percentages of trace elements extracted with EDTA in every sample. The amount of every element was normalised with its total concentration

extraction 60–70%), followed by Cu and Zn (30–40% extraction) and As, Cr, Ni and Fe as the most immobile phases (Figs. 8, 9). According to the results obtained, the

mobility sequence proposed is the following: Mn, Pb, Cd, > Zn, Cu > Ni > As > Fe > Cr.

## Conclusions

Most of the samples studied were contaminated in Cu, Pb, Zn and As, especially those taken in small-scale orchards positioned over sediments close to the mining area or next to waste rock piles. Samples collected from leptosols show lower levels of pollution, but some of them surpass the 90th percentile of the corresponding geological dominium (South Portuguese Zone). This may suggest an antropogenic input of metals through a vector such us wind-blown dust. The bedrock influence may explain high values in Co, Cr and Ni, but it does not seem to be the source of As, Cu, Pb and Zn, which are associated with the ore deposits. Samples from El Lomero, Peña de Hierro and M14 in Monte Sorromero displayed concentrations of trace elements lower than the contamination threshold, but the high mobility of Cu, Pb and Zn may cause their availability and their entrance in the trophic chain. When elements such us Cr and Ni, and even As occurs in not so high concentrations, they have a low risk owing to their low mobility. Extra studies concerning the effects on plants may be required to ensure that these metals are not being assimilated.

A methodology similar to that proposed in this paper is necessary to assess the degree and origin of pollution in soils. Values of local or geological dominium background rather than regional background allow us to assess the degree of pollution in soils, and comparisons with the bedrock show the anthropogenic contribution. The mineralogical characterisation and mineralogical speciation have not been very useful tools to find phases hosting metals, as they can be stored by accessories or amorphous matter, which are difficult to identify and quantify. The chemical speciation allows quantifying the percentages of trace elements associated with the different extractions, but does not supply information about the total mobility. Availability and bioavailability studies are necessary to assess real risk of the trace elements' contamination in soils. A high mobility may involve that elements below the contamination threshold are dangerous, or a low mobility may allow the agricultural usage of a soil with high values in several elements. Although the bioavailability shows the amount of metals that plants may assimilate, other studies about the concentration in leaves or fruits may be necessary to carry out a more accurate evaluation.

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