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Short communication

Potential use in phytoremediation of three plant species growing on contaminated mine-tailing soils in Sardinia

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ABSTRACT

We have analyzed the relationship between total Zn, Pb and Cu concentrations in the soil and the capacity of three plant species to accumulate these elements in their leaves. The study was carried out in a highly contaminated area at Sulcis-Iglesiente (SW-Sardinia, Italy). We took samples of the leaves of *Dittrichia viscosa*, *Cistus salviifolius* and *Euphorbia pithyusa* subsp. *cupanii* and samples of the soil beneath each of them at depths of 0–30 and 30–60 cm, both in contaminated mine tailings and surrounding areas. Due to the anthropic origin of the soil materials the results varied considerably. Bioavailability of trace elements was mainly related to the calcium-carbonate content and the crystalline and amorphous forms of iron in the soil. The concentration of Zn in the leaves of the three plant species studied was highest, followed by Pb and finally Cu. The leaves of *Dittrichia viscosa* contained the highest concentrations of trace elements and this species may be considered as being a "phytoextractor" in soils where the trace-element concentrations are not too high. *Euphorbia pithyusa* subsp. *cupanii* had low trace-element concentrations in its leaves despite growing in highly contaminated soils, and so might be used as a "phytostabilizer". Although *Cistus salviifolius* does not grow in the most contaminated soils, could be considered as a contamination indicator up to a given level.

1. Introduction

The accumulation of trace elements in the above-ground parts of plants was described by Baker (1981) as being a strategy to allow them to tolerate large quantities of these elements present in their environment. Plant species which are capable of accumulating very large quantities of trace elements that are toxic for other species are known as hyperaccumulators (Baker and Whiting, 2002) and their use in phytoremediation is of considerable interest (Nanda Kumar et al., 1995; Rai, 2008).

Phytostabilization and phytoextraction are two common phytoremediation techniques for treating metal-contaminated soils (Brennam and Shelley, 1999; Susarla et al., 2002; Wong, 2003). Phytoextraction entails removing metals from the soil through hyperaccumulators and phytostabilization immobilizes and/or detoxifies metals in the soil (Salt et al., 1995). Baker and Brooks (1989) established concentrations of 10 000 mg kg^{-1} of Zn and 1000 mg kg^{-1} of Cu or Pb in plants as constituting hyperaccumulators. Other studies (Dowdy and McKone, 1997; Fellet et al., 2007). Felle have taken the ratio between the total metal concentration in the plant and that in the soil, known as the bioconcentration factor (BCF) to be the reference indicator. A BCF value higher than 1 may be taken to indicate that the plant could act as a phytohyperaccumulator of trace elements (Zhang et al., 2002). Whichever of these indicators is most valid, the success of phytoremediation depends upon three basic factors: the quantity of metals in the soil, their degree of bioavailability and the plant capacity to accumulate them (Ernst, 1996).

Phytoextraction is not a technique to be recommended in very contaminated mine tailings because of the high quantities of trace elements present, but phytostabilization, on the other hand, could be useful to immobilize the metals, stabilize the spoil heaps themselves and at the same time diminish their visual impact (Wong, 2003; Remon et al., 2005). The bioavailability of heavy metals in soil depends upon the physical and chemical characteristics of the soil, especially the pH, clay content, organic matter, the presence of

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Mn, Fe and Al oxides and hydroxides and the $CaCO_3$ content (Jung and Thornton, 1996).

Various species of metal-accumulating plants have been described in recent years (Bert et al., 2000; Rosselli et al., 2003). Nevertheless, replanting a highly contaminated area demands the use of species that are not only tolerant to high concentrations of trace elements but also adapted to the specific ecological conditions of this area (Bidar et al., 2007). Thus research is required at a local level on both the plant species and the soils.

Sardinia is one of the few regions in Italy with a history of mining going back more than 2000 years (Bechstädt and Boni, 1994). In the Sulcis-Iglesiente region, the most important metals mined were lead, zinc, silver and barium. From the 1970s, however, the mines began to close, leaving large quantities of tailings and numerous spoil heaps of various types of material deriving from the mining process itself, the separation of the minerals and their chemical and electrolytic treatments. All these materials have a highly contaminating potential due to the presence of Zn, Cu and Pb, among other metals (Boni et al., 1999). Nowadays numerous species of pioneering plants capable of withstanding high concentrations of metals and living in nutrient-starved environments can be seen colonising these materials.

Our aim was to study the characteristics of the soils in old mine tailings and other soils in the neighbourhood as well as the concentrations of Zn, Pb and Cu they contained and to analyze their relation with the metal contents in various plant species growing in these soils. In this work, we have focused on three species which stand out because of their abundance in the sites studied: *Dittrichia viscosa* (L.) Greuter, *Cistus salviifolius* L. and *Euphorbia pithyusa* L. subsp. *cupanii* (Guss. ex Bertol.) Radcl.-Sm. Specifically, we have determined the capacity of the three chosen plant species for the phytostabilisation and/or phytoextraction of such metals.

2. Material and methods

The sites are located in SW Sardinia and more precisely in the area of Sulcis-Iglesiente, a biogeographic sector separated from the rest of the island by the Graben of Campidano (Bacchetta and Pontecorvo, 2005). The most important lithologies, from the point of view of the mineral richness, belong to the pre/mid-Ordovician Iglesiente sequence. One of the most important formations is that of Gonnesa, which comprises metalliferous veins within a carbonate host rock. The most abundant minerals in this formation are barite and, above all, the sulphydes: pyrite, galena and blende (Stara et al., 1996).

The exploitation of these materials over the centuries has generated different types of waste mixed up together, with considerable differences being found between the metalliferous compounds in the spoil heaps and/or the tailings, depending upon the year in which they were produced. Furthermore, all around Monteponi, there are red tailing muds deriving from the electrolysis of oxidized and roasted ores (Boni et al., 1999), which give rise to highly contaminated run-off water.

The temperature in the area under study shows monthly averages ranging from 9.7 to 29.6 °C. A mean annual rainfall of 791 mm was measured. Bacchetta (2006) classified this area by a Mediterranean pluviseasonal bioclimate.

Among the metal tolerant species occurring in SW-Sardinia, we selected three scrubs: *Dittrichia viscosa* (Compositae), a ruderal species with a wide distribution in the Mediterranean region, *Euphorbia pithyusa* subsp. *cupanii* (Euphorbiaceae), endemic from Sardinia, Corsica and Sicily, and *Cistus salviifolius* (Cistaceae), which can be found widely in the Mediterranean basin. The three species exceed normally 1 m of height. We collected, in spring, the leaves of three individuals of each species growing both in mine tailings (MT) and in soils outside mine tailings (OMT).

At the same time we took soil samples from depths of 0–30 cm and 30–60 cm around the root systems of the plants, for each individual. *Dittrichia viscosa* (Dv) and *Euphorbia pithyusa* subsp. *cupanii* (Ec) grew very close to each other in MT and so the soil samples were the same for these species. *Cistus salviifolius* (Cs) was not found at the same sites where we sampled the other two species.

The total concentrations of metals in soils were determined in finely ground samples (0.2 mm) in the IGEA laboratory of Monteponi, according to the protocol of the Società Italiana della Scienza del Suolo. We labelled these concentrations with $t^{\alpha}_{i,j;k}$, where α indicates the metal (Zn, Pb and Cu), i corresponds to the soil situation ($i = 1$ are the MT soils common to Dv and Ec species, $i = 2$ labels the MT soil under Cs plant and $i = 3, 4, 5$ are OMT soils under Dv, Cs and Ec plants, respectively), j labels the repetition ($j = 1, 2, 3$ for each soil sample) and, finally, k refers to the two depths studied ($k = 1$ for 0–30 cm and $k = 2$ for 30–60 cm).

The remaining analyses were carried out in the Departamento de Edafología y Química Agrícola at the Universidad de Granada. Soil texture, pH, electrical conductivity (EC), organic carbon (OC), P and $CaCO_3$, in soils, and foliar Zn, Cu and Pb content were analyzed according to Ministerio de Agricultura and Pesca y Alimentación, 1994. The crystalline forms of Al and Fe were extracted with the sodium-dithionite citrate–carbonate system (Fe_{dc}, Al_{dc}) and amorphous forms (Fe_{ox}, Al_{ox}) were extracted with 1 M ammonium oxalate (Schwertmann and Taylor, 1977).

Correlations between different quantities have been calculated using the Pearson's linear correlation coefficient, r (Press et al., 1992). The uncertainty of this coefficient was estimated using a Monte Carlo methodology, generating 1000 values of the correlation coefficient according to the experimental uncertainties of the correlated data (Jiménez et al., 2007).

We studied the correlations between the total concentrations of the three metals in the plants and in the soils. We considered each of the depths independently, what gives $r^{\alpha}_{k}(t, Pl)$, and, also, the corresponding average values, obtaining the coefficients $r^{\alpha}_{av}(t, Pl)$. Here Pl stands for the plant species.

The correlations between the total concentration in the plants, for the three metals, and the edaphic properties of the soil samples were also calculated. We have considered the two depths independently, obtaining $r^{\alpha}_{k}(p, Pl)$, and the corresponding average values, what produces $r^{\alpha}_{av}(p, Pl)$. Here p indicates the edaphic property involved.

3. Results and discussion

3.1. Soil characteristics

Soil textures (see Table 1) are typical of soils in dumps and are very different in their maximum and minimum values. The textures are predominantly loam or clayey loam, except soils 2 and 3, in which sandy clayey loam textures are found. In both MT and OMT soils, the gravel content is quite high and the proportion of silt is higher than that of clay.

The metals mined in the study area formed veins within host carbonate rocks. The extraction process generated carbonate residues mixed with others that contain no carbonates because of the chemical processes to which they have been subjected. This resulted in a great variability in $CaCO_3$ content in the soil samples taken. Thus, the calcium-carbonate contents in the MT soils taken from beneath Dv and Ec ($i = 1$) range from 1% to more than 60%. The OMT soils related to these two species ($i = 3$ and 5) contain no carbonates. The MT soils sampled from below Cs ($i = 2$) are lower

Table 1
Soil characteristics of the various samples studied in this work. The plants in each of these samples are given for completeness. For each soil, the values defining the interval correspond to the minimum and maximum values found for the three samples and the two depths analyzed. The uncertainties are 5% for gravel, sand, silt and clay, 3% for P, Fe and Al, 2% for $CaCO_3$, OC and EC and 0.2% for pH. Note that the type 1 soil samples are the same for both Dv and Ec plants.

	MT		OMT		
	$i=1$ (Dv/Ec)	$i=2$ (Cs)	$i=3$ (Dv)	$i=4$ (Cs)	$i=5$ (Ec)
Gravel [%]	30.49–73.39	26.78–41.0034.70–8	26.78–41.00	34.70–86.46	50.08–85.30
Sand [%]	38.06–57.62	30.66–63.00	26.11–63.42	48.08–54.51	38.70–52.95
Coarse silt [%]	0.87–13.23	6.38–21.32	10.81–29.84	7.74–12.82	6.39–10.16
Fine silt [%]	9.68–29.69	14.95–38.61	15.10–36.00	14.66–18.46	12.55–24.63
Clay [%]	17.74–31.83	13.02–23.50	7.26–13.92	21.11–25.42	24.33–36.99
$CaCO_3$ [%]	0.30–62.40	3.10–21.60	0.00–5.50	41.70–98.40	0.00–0.20
pH	7.30–8.20	7.40–8.307.10	7.10–7.70	7.10–7.70	7.60–8.40
OC [%]	0.30–2.20	0.80–1.80	0.60–1.70	0.60–3.70	1.40–3.40
EC [$dS\,m^{-1}$]	265.00–988.00	196.00–315.00	104.00–208.00	143.00–336.00	89.00–178.00
P [ppm]	0.60–18.65	1.60–11.83	2.21–27.08	3.01–29.29	2.61–52.35
Fe_{dc} [ppm]	6390.60–21290.60	11700.00–26765.60	6125.00–13575.00	4475.00–7296.90	8859.40–13643.80
Fe_{ox} [ppm]	2075.00–15062.50	1725.00–4146.90	2121.90–3043.80	681.30–1087.50	2265.60–3493.80
Al_{dc} [ppm]	327.13–947.25	426.88–1646.88	590.88–957.00	302.75–634.75	571.88–1171.88
Al_{ox} [ppm]	385.75–1040.13	811.63–2050.63	424.88–776.38	361.38–922.88	669.00–1225.63

in carbonate content than the OMT soils ($i=4$), which contain up to 90%. Despite the low $CaCO_3$ content of some of the soils studied, pH varies between 7.1 and 8.4. The bioavailability of all three metals studied changes according to the pH and $CaCO_3$ content of the soil. Thus, the solubility of Cu diminishes at pH values between 7 and 8, whilst the mobility of Zn is greater in acidic soils and Pb precipitates as a hydroxide, phosphate or carbonate in basic soils. The presence of high quantities of $CaCO_3$ also favours precipitation, especially that of Pb and Cu (Kabata-Pendias, 2001).

The reduced capacity of MT soils ($i=1$ and 2) to encourage the establishment of vegetation leads to generally lower OC and phosphorous contents than in OMT soils, especially those related to Cs and Ec ($i=4$ and 5), which were sampled in scrublands and woodlands, respectively. Electrical conductivity was higher in MT than in OMT in all the studied sites. The MT soils generally contain higher concentrations of the two forms of iron studied (Fe_{dc} and Fe_{ox}) than the OMT soils. The forms of aluminium, at much lower concentrations than iron, are not associated in any clear way with the tailings beneath the three species studied. Thus the MT soil samples associated with Cs contain more Al_{ox} and Al_{dc} than the OMT soils collected from beneath the same species. On the other hand, the minimum values of both Al_{ox} and Al_{dc} in OMT soils related to Ec are higher than those found in MT soils. Both types of soil beneath Dv contain practically the same levels of Al.

3.2. *Trace-element soil concentrations*

As shown in Table 2, $t^{Zn}_{i,j;k} > t^{Pb}_{i,j;k} > t^{Cu}_{i,j;k}$. The highest levels of all three trace elements are found in MT associated with Dv and Ec ($i=1$, $j=1$, 2 and 3). The highest concentrations of Zn and Pb in OMT soils are associated with Cs ($i=4$, $j=1$, 2 and 3). In MT there are great differences, especially for Zn and Pb, between soils sampled from beneath the same species and also at the two different depths ($k=1$ and 2). On the whole, the OMT soils ($i=3$, 4 and 5) show more homogeneous values between the soils taken from beneath plants of the same species and the two depths studied, except in the case of Pb beneath Cs, where the concentrations found in all three samples are very different.

The values for all three metals both in MT and OMT fell within the range established by other authors working in Sardinia (De Vivo et al., 1997; Boni et al., 1999). However, the $t^{Zn}_{i,j;k}$ and $t^{Pb}_{i,j;k}$ contents of MT soils ($i=1$ and 2) are higher than those found by other authors in Zn smelting and mining centres in other regions (Verner and Ramsey, 1996; Mattina et al., 2003). $t^{Zn}_{i,j;k}$ in OMT ($i=3$, 4 and 5) is also sometimes higher than the values recorded by these latter authors.

We have only found a few significant correlations (above 0.8 in absolute value) between the $t^{\alpha}_{i,j;k}$ concentrations and the soil characteristics, when all the data obtained are considered: $t^{Zn}_{i,j;k}$ is correlated with the electrical conductivity and $t^{Cu}_{i,j;k}$ is correlated with Fe_{ox}. This coincides with the observations of other authors (Kabata-Pendias, 2001; Covelo et al., 2008).

The positive and negative correlations between the total concentrations in soils and their edaphic characteristics below the three plant species at both depths studied are set out in Fig. 1. The soils associated with Dv and Ec with the highest $t^{Pb}_{i,j;k}$, $t^{Zn}_{i,j;k}$ and $t^{Cu}_{i,j;k}$ contents are those which also present the highest calcium-carbonate content (positive correlations). Contrary to what one should expect, $t^{Pb}_{i,j;k}$ and $t^{Zn}_{i,j;k}$ correlate negatively with the pH content in these soils. In the soils associated with Cs, these two concentrations show negative correlations with the $CaCO_3$ contents and no correlation was found with pH. The amounts of Fe_{dc}, Al_{dc}, Fe_{ox} and Al_{ox} are positively correlated with the total concentrations of the three trace elements in the soils associated with Cs, whilst in

Table 2
Total soil concentrations $t^{\alpha}_{i,j;k}$, in ppm, for the three elements (Zn, Pb, Cu) corresponding to each one of the five soils studied in this work and for the two depths analyzed. The plants in each of these samples are given for completeness. The uncertainties are 5% for Pb and 1% for Zn and Cu. Note that the first three soils are the same for both Dv and Ec plants.

	i, j	α = Pb		α = Zn		α = Cu	
		$k=1$	$k=2$	$k=1$	$k=2$	$k=1$	$k=2$
MT	1,1 (Dv/Ec)	9166	3618	43300	17100	139	62
	1,2 (Dv/Ec)	3508	3743	15000	31100	79	417
	1,3 (Dv/Ec)	577	6675	4900	50200	41	122
	2,1 (Cs)	5772	3628	14400	6386	44	42
	2,2 (Cs)	4444	2023	20480	4931	31	22
	2,3 (Cs)	2481	1392	9253	4460	15	13
OMT	3,1 (Dv)	307	273	394	362	22	21
	3,2 (Dv)	269	261	342	338	18	17
	3,3 (Dv)	300	205	379	298	21	28
	4,1 (Cs)	1495	2069	3263	3502	15	16
	4,2 (Cs)	870	1267	2446	3342	14	13
	4,3 (Cs)	397	463	3684	3977	7	12
	5,1 (Ec)	363	315	550	410	16	14
	5,2 (Ec)	408	236	512	220	24	17
	5,3 (Ec)	355	193	560	250	16	16

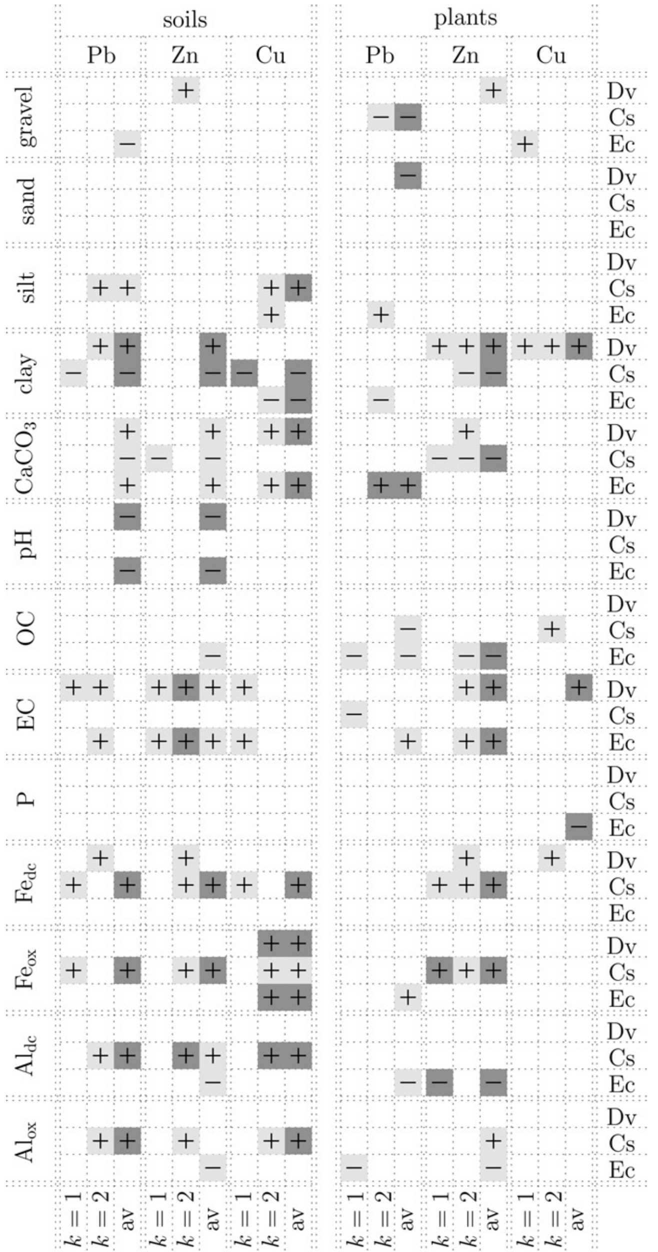

Fig. 1. Correlations between the total concentrations in soils and plants and the edaphic characteristics of the soils. Only the cases for which the value 0.8 (0.95) is inside the interval of uncertainty of the coefficient calculated are indicated by a clear (dark) gray cell. The symbols plus or minus indicate a positive or negative correlation. In addition to the two depths, also the average value between them has been considered.

the soils associated with Dv and Ec the significant correlations are positive or negative randomly. The soils with the greatest proportion of clay are the least contaminated in the samples associated with Cs and, as far as Cu is concerned, also in those beneath Ec. The soils associated with Dv are the most clayey and also have the highest total concentrations of Pb and Zn.

The fact that the expected negative correlations between the concentration of trace elements and the pH of the soil only appear in a few cases, might be due to the markedly basic character of most of the soil samples. Furthermore, in accordance with the observations of Kuo et al. (1985), apart from pH, another series of factors, such as the amorphous Fe oxide content and the total metal content in the soil, needs to be taken into account.

3.3. Trace element concentrations in plants

The total concentrations in plants as a function of the total concentration in the corresponding soils are shown in Fig. 2. The highest concentrations for all the metals studied are found in Dv, when growing both in MT and OMT soils. The lowest concentrations occur practically always in Ec. Plants growing in MT soils contain in general higher quantities of trace elements than those of the same species growing in OMT soils. In all three species studied, accumulations of Zn are highest, followed by Pb and then Cu. This tendency does not coincide completely with that observed by other authors (Doumett et al., 2008), who have found higher quantities of Zn and Cu, which are micronutrients in plants, compared to Pb, an element toxic to several vegetable species (Lasat, 2000). Nevertheless, we always found lower concentrations of Cu than Pb in the soils we sampled, which may explain our results because, as Jung and Thornton (1996) pointed out, the concentrations of metals in plants tends to increase concomitantly with the concentrations in the soil.

As can be seen in Fig. 2, in most cases the concentrations in our plants tend to increase with those in the soil. However, the increasing rates depend upon the plant species and the trace element, which would seem to indicate different adaptation mechanisms. According to Li et al. (2007), accumulator species contain higher quantities of metals when found growing in contaminated areas. Thus, Dv, because it always presents the highest concentrations, can be considered as an accumulator, at least until the soil concentrations become so high that they possibly saturate the plant capacity to store trace-metals.

Ec is capable of growing in places as contaminated as those beneath Dv, but the concentrations of metals in its leaves, including that of Cu, remain almost constant whatever the concentrations in the soil. This, together with the fact that Ec presents the lowest concentrations, would indicate that this species has mechanisms that adapt in such a way as to impede the accumulation of metals in the above-ground parts of the plant at least. In this way the plants would be able to adapt and develop in highly polluted environments. Similar mechanisms for excluding metals have been described by other authors (Fischerová et al., 2006).

Cs does not grow in soils containing concentrations of metals as high as those found in the soils beneath the other species. The trace element concentrations in the MT soils beneath Cs were always much smaller than those in the MT soils where Dv and Ec were sampled. This could indicate that when the soil metal concentrations rise above a certain threshold they become toxic for Cs.

None of the plants studied surpass the contents proposed by Baker and Brooks (1989) to be accepted as hyperaccumulators. Furthermore, on only one occasion does the bioconcentration factor (BCF) reach a value higher than 1 and this is with Zn in Dv growing on OMT soils.

Another way of comparing the different strategies developed by the three species in order to survive in such contaminated environments was that of finding places where individuals belonging to different species grew together. The different strategies of the chosen species only allowed us to collect samples of Dv and Ec from the same MT sites. The ratio of the total concentrations in Dv and Ec plants as a function of the total concentration in the common MT soil appears in Fig. 3, where it can be seen that the ratio $t^{\alpha}_{\mathrm{Dv}}/t^{\alpha}_{\mathrm{Ec}}$ is often higher than 5 and even reaches values of 15 for Pb. The tendency is similar in the ratio of the data for the two depths studied, all of which seems to indicate that Dv has a greater disposition to accumulate trace metals than Ec does.

Pearson's correlation coefficients for the total concentration in plants and soils were also calculated. The concentrations of Zn

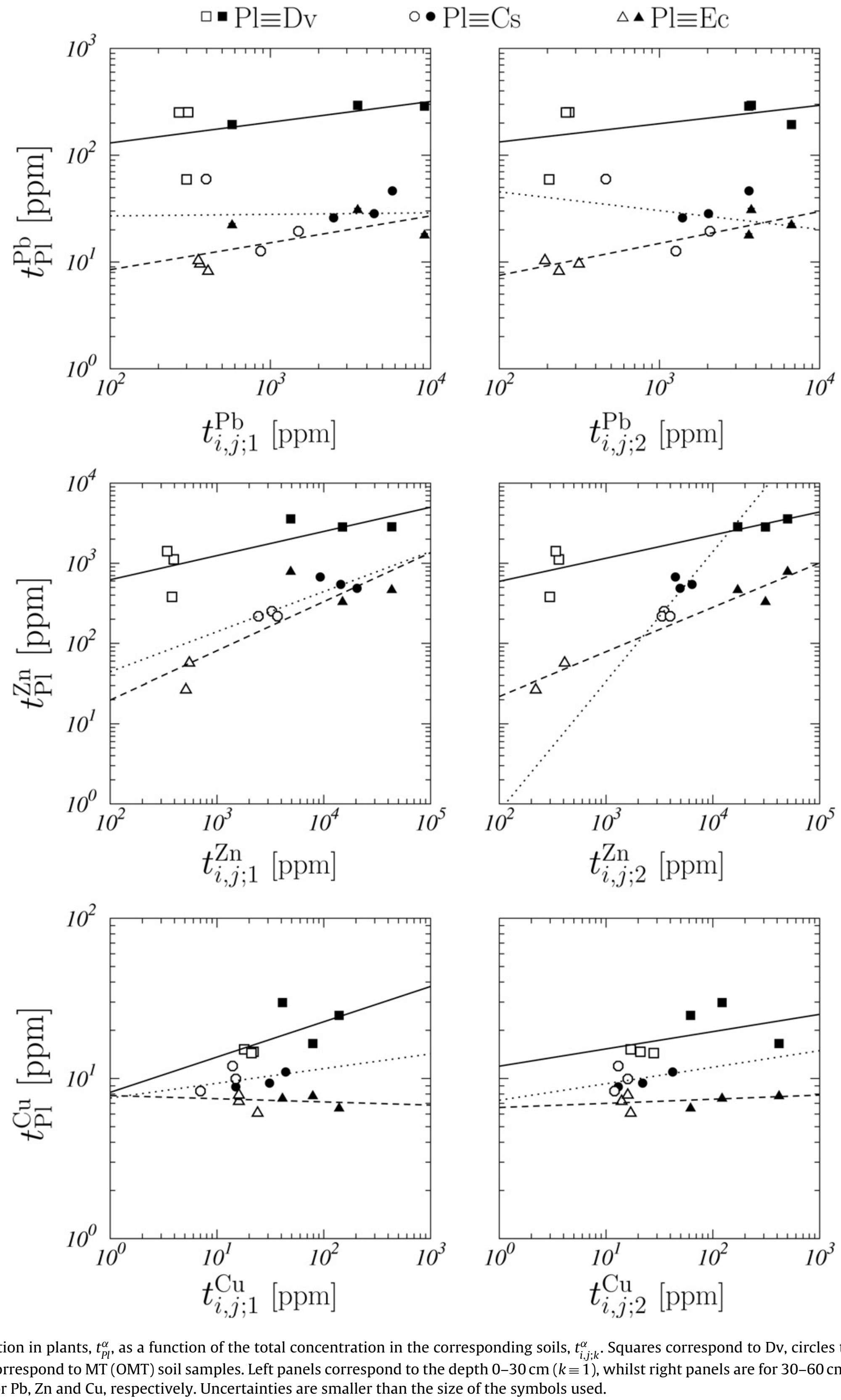

Fig. 2. Total concentration in plants, t_{Pl}^{α}, as a function of the total concentration in the corresponding soils, $t_{i,j;k}^{\alpha}$. Squares correspond to Dv, circles to Cs and triangles to Ec. Solid (open) symbols correspond to MT (OMT) soil samples. Left panels correspond to the depth 0–30 cm ($k \equiv 1$), whilst right panels are for 30–60 cm ($k \equiv 2$). Upper, medium and lower panels are for Pb, Zn and Cu, respectively. Uncertainties are smaller than the size of the symbols used.

found in Dv and Ec correlate positively ($r > 0.9$) with the total soil concentration, for either the lower depth assayed or the average of both depths. With Cs, however, this correlation is 0.7. In the case of Pb, we only obtained significant correlations with the concentrations in Ec and for the average values of the two soil depths analyzed ($r = 0.7$).

Fischerová et al. (2006) pointed out the scarce mobility of lead in plants and its tendency to accumulate in the roots rather than

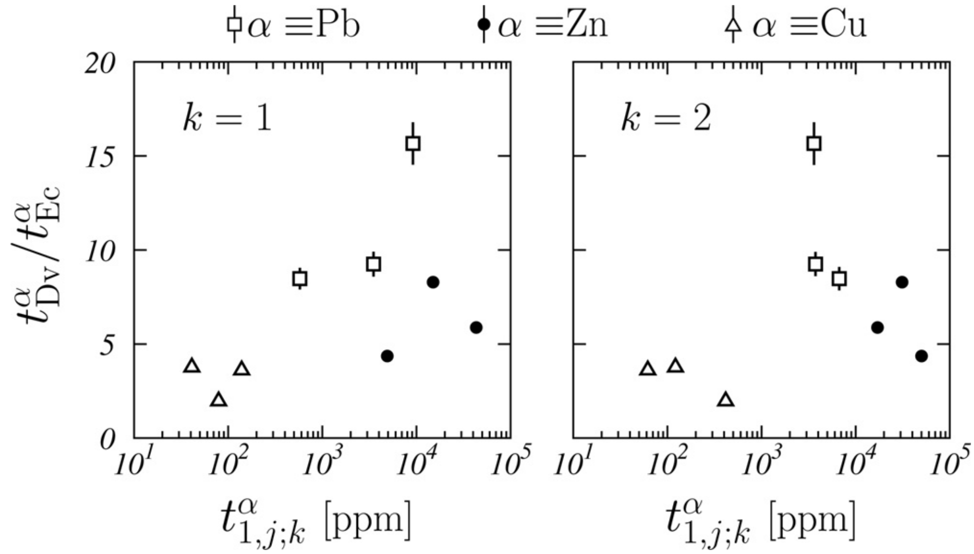

Fig. 3. Ratio of the total concentrations in Dv and Ec plants, $t^{\alpha}_{\mathrm{Dv}}/t^{\alpha}_{\mathrm{Ec}}$, as a function of the total concentration in the common MT soil, $t^{\alpha}_{1,j;k}$. Results for the three metals ($\alpha \equiv$ Pb, Zn, Cu) and the two depths ($k \equiv 1, 2$) studied in this work are shown.

the leaves. Besides, it has been reported that concentrations of lead found in the above-ground parts of plants are often more the result of wind contamination than soil concentrations (Dalenberg and van Driel, 1990). Ec, collected in our study from OMT soil in a woodland, may have been sheltered from wind contamination and so presents some positive correlation with the concentration in the soil. Whatever the case, it would be necessary to check the lead concentrations throughout the plant, including the roots, to confirm this hypothesis.

Pearson's correlation coefficients for the trace element concentration in plants and the edaphic properties of the soils are set out in Fig. 1. The lead concentration in Ec shows the highest number of correlations with the characteristics of the soil, positive compared to $CaCO_3$, EC and Fe_{ox}, and negative compared to clay content, Al_{dc} and Al_{ox}. This coincides with the results described above concerning the correlations between the Pb content in Ec and total Pb in the soil. Chlopeacka (1996) reported that lead and other heavy metals in plants is related to the values of exchangeable and carbon-associated fractions in the soil. Nevertheless, other factors such as the relationship between $CaCO_3$, P and the total concentration of metals in the soil have also to be taken into account (Hashimoto et al., 2008). The negative correlation with OC and clay seem to indicate that iron oxides are changing elements. This agrees with the observations of Sipos et al. (2008), who state that iron-oxide phases prefer mostly to immobilize lead in soil.

Zinc in plants is the metal that presents the highest number of correlations with the characteristics of the soil (Fig. 1). In Dv its content correlates positively with the percentage in gravel, clay, Fe_{dc}, $CaCO_3$ and EC. In Cs, it correlates negatively with clay and $CaCO_3$ and positively with Fe_{dc}, Fe_{ox} and Al_{ox}. Correlations between Cu in the plants and the characteristics of the soil are scarce, only occurring between Cu in Dv and the clay, EC and Fe_{dc} contents. There is a noteworthy negative correlation between Cu and P in Ec and a positive one between Cu and OC in Cs.

In our opinion all three species may be useful in metal-polluted environments. At moderate concentrations Dv could act as a phytoextractor. When metal concentrations are as high as those found in some of the soils in this study, it becomes inviable to use plants to extract them (Salt et al., 1995) but it is still essential to plant vegetation capable of developing in these environments in order to stabilize the spoil heaps and prevent the spreading of contaminants by leaching or wind dispersion (Hashimoto et al., 2008). Both Dv and Ec could be used as phytostabilizers, with the caveat that whilst Dv is a generic species that can be planted in a variety of environments, Ec is endemic to Corsica, Sicily and Sardinia and is thus adapted specifically to the climate of this Mediterranean area. In environments that have been subject to mining over a long period of time or those in which attempts to clean up the results of mining pollution have been attempted, it is quite common to find that the offending metals are distributed fairly heterogeneously over the area, in which highly contaminated zones can be found alternating with quite unpolluted ones (Aguilar et al., 2004; Domnguez et al., 2008). In cases such as these, it is important to be able to resort to indicator species, which mark the most contaminated sites, either for their possible use or to be able to apply more localised cleaning techniques. Cs, a species found in very varied climatic conditions, could indicate an upper level of contamination in the soil, because it does not appear in soils with very high concentrations of trace-element.

4. Conclusions

The soils beneath the three plant species chosen for this study have very different properties and components, which control the form in which the metals are found and their availability to the plants. Beneath Cs, Pb, Zn and Cu are found associated with amorphous, poorly crystallized Fe and Al. Below Dv and Ec they are associated with $CaCO_3$.

The Zn content in Dv and Ec is closely related its total concentration in the soil, but below Cs, it is associated to Fe and Al oxides. The concentrations of trace metals in plants are most closely related to the soil contents of $CaCO_3$, EC, Fe_{ox} and Fe_{dc}.

Dittrichia viscosa and *Euphorbia pithyusa* subsp. *cupanii*, both species capable of growing in soils highly contaminated with Pb, Zn and Cu, have the potential to be used as phytostabilizers in such environments. In moderately contaminated environments, especially those containing Zn, *Dittrichia viscosa* could be used as a phytoextractor. In areas such as those studied here, where a long history of mining has left a very heterogeneous distribution of contaminated and relatively uncontaminated sites, a species such as *Cistus salviifolius*, which does not grow on very polluted soils, could be valuable as a marker species of a upper level of contamination.

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