

**STUDY OF CHEMICAL AND MINERALOGICAL FORMS AND
MOBILITY/BIOAVAILABILITY OF HEAVY METALS IN SOILS, PLANTS
(*Pistacia Lentiscus* L.) AND SOIL PORE WATERS OF THE RIO SAN GIORGIO
BASIN (IGLESIAS – GONNESA, SOUTHWESTERN SARDINIA, ITALY), AIMED
TO DEVELOPMENT OF SOIL REMEDIATION STRATEGIES**

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This study was addressed to the environmental consequences that the intense extractive activity of lead and zinc has produced around the towns of Iglesias and Gonnese (southwestern Sardinia, Italy), with particular reference to soil contamination and possible actions of phytoremediation (Barbafieri *et al.*, 2011; Bacchetta *et al.*, 2012). The research project, performed in cooperation with various national and international institutions, including ENEA, CNR and NTU (Nottingham Trent University), focused the investigation on different aspects related to environmental pollution by elements such as Zn, Pb, and Hg associated with the mines of the district.

The study area is the Rio San Giorgio basin, where the following representative sites were chosen: *i*) one of the ‘hazard centres’ of the district, consisting of mining flotation wastes at Campo Pisano, close to the town of Iglesias; *ii*) three natural sites, not directly affected by morphological alterations due to mineral extraction, located along the ‘metalliferous ring’, that is the Cambrian limestones-dolomites that host the Pb-Zn mineralisation (Bechstädt *et al.*, 1994); *iii*) the Sa Masa swamp, that is the final collector of drainage waters of the river basin, closed by the Iglesias valley to the north and by the Sulcis coal district to the south.

The aims of this work are: *i*) to quantify the total content of ‘heavy metals’ in the various abiotic sectors (soils and soil pore waters), and in the biotic sector, specifically *Pistacia lentiscus* L., a spontaneous vegetal species; *ii*) to identify the chemical and mineralogical forms of heavy metals, and to define their mobility and bioavailability in the interactive environmental system soil - plant - soil pore water; *iii*) to study the relationship between the different concentrations of heavy metals in the various environmental media considered, to understand the mobility mechanisms; *iv*) to establish how much *Pistacia lentiscus* L. takes up and translocates each metal from roots to leaves; *v*) to provide an *in situ* full description of the spontaneous system of the selected vegetal species, which is characteristic of these contaminated zones, as an example of phytostabilization and soil remediation techniques, aimed to reclamation and stabilization of the abandoned mining areas.

In the sampling points, soil profiles were opened, making a distinction of pedological horizons according to the standard procedures of soil investigation; samples were collected for each horizon for subsequent laboratory analysis. These included the determination of standard chemical and physical properties according to the official Italian soil study methods (D.M. 13/09/1999). In general, *i*) the soils occurring in the mining wastes are not pedogenised; *ii*) the soils on dolomitic limestones are sparsely and moderately deep, in lithic contact with the underlying rock; *iii*) the soils in the marshy deposits are characterized by a sequence of different sedimentary cycles (marked by textural differences). The pH reaction is generally from neutral to weakly alkaline (from 7.1 to 8.1), with variations and exceptions attributable to different parent materials from which the studied soils originate. The mineralogical and chemical analyses point out a great abundance of calcite and dolomite, in agreement with the geological substrate of the area. The organic carbon contents are generally higher in the surface horizons, with a minimum value of 11 g/kg and a maximum of 202 g/kg, and they decrease at increasing depths. The study of thin sections allowed refining the attribution of acronyms to the horizons, according to the international soil classification systems of the Soil Taxonomy (Soil Survey Staff, 2010) and IUSS Working Group WRB (2007).

On the same soil samples, further mineralogical determinations (X-ray powder diffraction), loss on ignition (LOI), and chemical composition (major elements with X fluorescence; trace metals with acid digestion

followed by ICP-OES analysis) were carried out. In agreement with thin sections, calcite, dolomite, and quartz resulted abundant; in some samples the presence of barite, pyrite, and gypsum was detected, as well as trace heavy metals-bearing minerals (hemimorphite, cerussite, hydrozincite, anglesite). Consistent with mineralogy, the chemical composition was dominated by CaO-MgO-SiO₂.

Among the analysed heavy metals, Zn, Pb, As, Cd, and Hg almost always occurred in higher concentrations than Italian law limits (D. Lgs 152/2006) for the metal contents in soils for industrial use; as shown in Table 1, the contents of Zn (1655-220946 mg/kg), and Pb (1360-54914 mg/kg) are particularly high. These values were found also in the soils developed on natural substrates, presumably not much interested by anthropic impacts, reflecting therefore a natural geochemical anomaly; however, in the sites impacted by the mining activity all values are higher, demonstrating the influence of anthropic action.

Table 1 - Total HM contents in soils for each horizon and weighted average for each site.

Profile	Horizon	Depth (cm)	Zn (mg/kg)	Zn (weighted average)	Pb (mg/kg)	Pb (weighted average)	Hg (mg/kg)	Hg (weighted average)
P3 Mining wastes			8843		1663		9	
P6 Natural site	A	0-10	4680		1360		2	
	Bw	10-37/50	5244	5131	1453	1434	3	3
P7 Natural site	A1	0-4	9225		4054		6	
	A2	4-20/25	8659	8750	4050	4051	5	5
p9 Sa Masa swamp	A	0-8	220946		37616		16	
	2C1	8-12	22400		4300		24	
	3C2	12-25	18805	446941	3401	7757	21	20
	4C3	25-40	13792		3398		21	
	5C4	40-59	17122		2335		18	
Limits*			1500		1000		5	

*as imposed by Italian laws (D.L. 152/2006) for soils of commercial and industrial use.

The mobility of metals was estimated through two different single extraction chemical methods: with DTPA solution (Lindsay & Norvell, 1978; Barbaferi *et al.*, 1996; GURI, 1999), followed by analysis of the extracted metals by ICP-OES, and with sodium citrate/hydroxylamine hydrochloride/TEA followed by colorimetric titration with Dithizone (DZ) solution (Pinto *et al.*, 2010). The data comparison showed a good correlation between these two methods (Fig. 1), with values obtained from the DZ method roughly double with respect to those from the DTPA method. The mobile fraction extracted with both methods reveals also a good correlation with the total metal contents in soils (Fig. 2). From a practical point of view, the fast test with DZ titration can be reliably used in the field for a quick screening of soil samples, to be characterised in the laboratory.

As mentioned previously, a particularly innovative aspect of this study was the sampling and analysis of soil pore waters. This is a very useful alternative to estimate the mobility of metals and their transferral from geosphere to the biosphere, because it represents the real mobility of metals, and a close approximation to bioavailability (Di Bonito *et al.*, 2008). Soil water sampling may be carried out in the field, or in laboratory; in this case, the field-based approach was deemed more adequate, and was applied using the tension vacuum

samplers that simulate the suction action of plant roots, namely the ‘rhizon samplers’ or ‘rhizometers’ (Tye *et al.*, 2003; Di Bonito *et al.*, 2008).

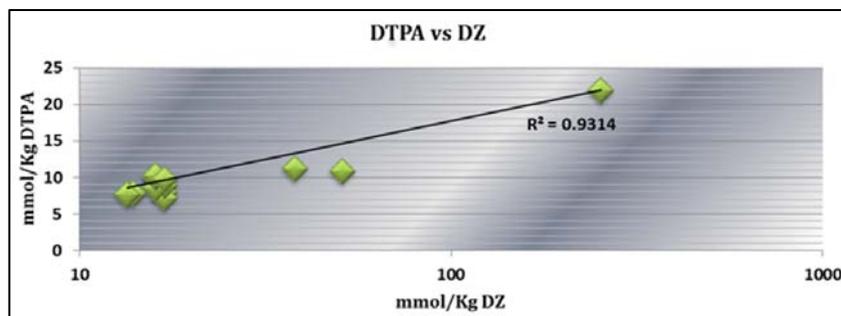


Fig. 1 - Correlation of DTPA and DZ mobile fractions.

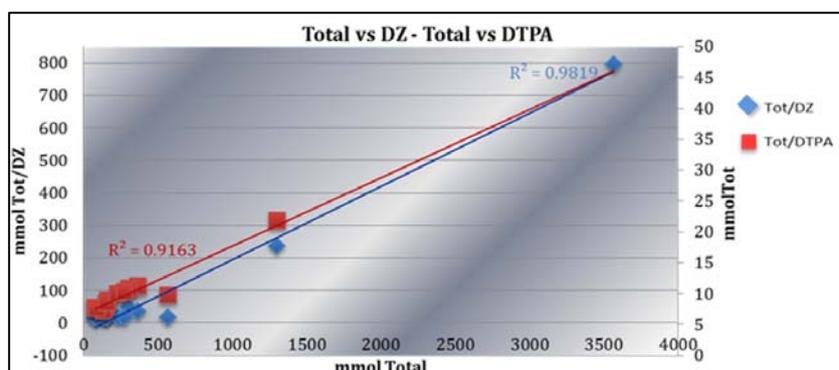


Fig. 2 - Correlation of DZ and DTPA mobile contents vs. Total contents in the soil.

This is a field practice that does not require invasive or destructive procedures, and allows repeated samplings from the same location over an extended time, to monitor environmental mobility of trace elements (in both soils and plants). In the following graphs (Fig. 3 and 4), the contents of Zn and Pb is compared in all different compartments of the interactive environmental systems studied: soil (total and mobile), soil pore waters and plants (roots, stems and leaves).

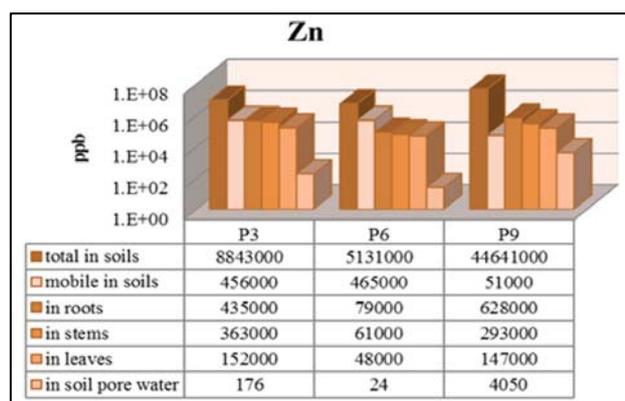


Fig. 3 - Comparison of total and mobile Zn contents in soils and in each part of plants.

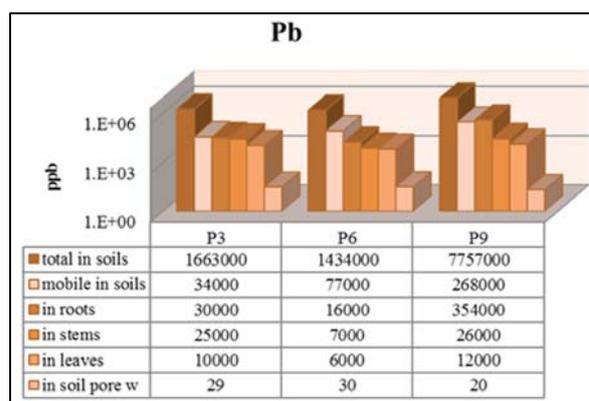


Fig. 4 - Comparison of total and mobile Pb contents in soils and in each part of plants.

The chemical composition of soil pore waters is variable among the various sites, and one can identify at least two principal compositional types (Fig. 5): Ca-SO₄ and Ca-Mg-HCO₃; to this last type, a Na-Cl-SO₄

component of possible seawater origin is locally associated (Sa Masa). Regarding the trace elements, the metals more abundant are Ba in some sites, and Zn in others; this last is usually the more abundant trace metal, particularly if compared to Pb. The modelisation with the speciation programs PHREEQC and WHAM shows in general an approach to equilibrium of the solutions with the minerals occurring in soils; specifically, the concentrations of Ba, Zn, and Pb appear substantially controlled by barite, hydrozincite, and cerussite, respectively.

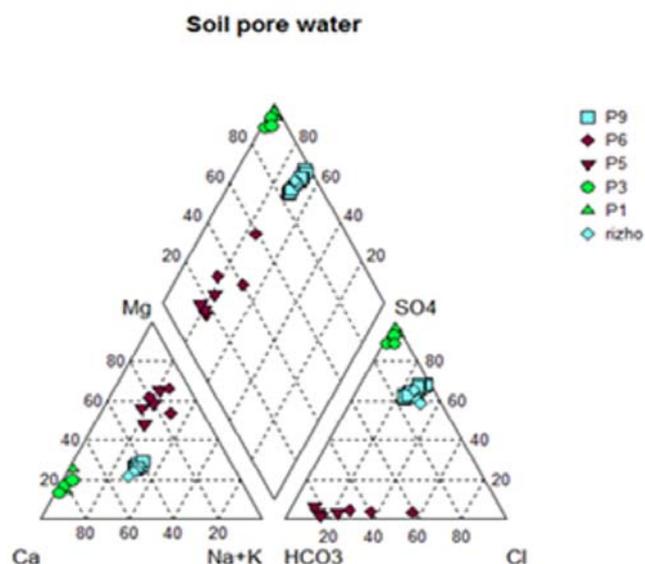


Fig. 5 - Piper diagram showing composition of the sampled soil pore waters.

As it concerns the actual transfer of metals to the biosphere, the contents of Zn, Pb and Hg were determined on individuals of *P. lentiscus*, for roots, stems, and leaves separately. In general, the metal concentrations decrease according to the order roots > stems > leaves, with the partial exception of Hg, for which there is locally an enrichment in leaves ($TF > 1$), perhaps due to foliar absorption of Hg volatilised from soils. The metal contents in plants are considerably lower than those in soils ($BAC \ll 1$), and nevertheless roughly proportional to them. The *P. lentiscus* seems in fact to behave as a tolerant species with strategies of exclusion, and with character of *indicator*. It is confirmed therefore that this species is particularly apt to revegetation actions aimed at the phytostabilisation of soils.

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