

USE OF NATIVE SPECIES AND BIODEGRADABLE CHELATING AGENTS IN THE PHYTOREMEDIATION OF ABANDONED MINING AREAS

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ABSTRACT

The application of assisted phytoextraction to the remediation of abandoned mining areas can be a valuable method to reclaim these areas without modifying soil and landscape characteristics. An *in situ* application of continuous phytoextraction technique was carried out in the area of Campo Pisano, near Iglesias (Sardinia, Italy) followed by a laboratory assisted phytoextraction test using the biodegradable chelating agents MGDA and IDS. The plants used were *Scrophularia canina* L. subsp. *bicolor*, *Cistus salviifolius* L. and *Teucrium flavum* L. subsp. *glaucum*. The plant that demonstrated the better ability to accumulate heavy metals was *C. salviifolius* while *S. canina* demonstrated the better tolerance to metals. The low soil cation exchange capacity determined a high accumulation of metals immediately after chelant treatment up to 300 mg/kg of Pb and 3,000 mg/kg of Zn which did not further increase during the assisted phytoextraction experiment.

1. INTRODUCTION

Abandoned mining areas constitute a relevant problem all over Europe. In Sardinia (Italy) the closure of mining activities caused serious threats as a result of the insufficient attention on the possible environmental impacts and of the inadequate definition of pollution containment plans. In particular the area of Sulcis-Iglesiente is the most important metalliferous region in Italy, in which hundreds of mining dumps exist and the volume of abandoned and contaminated materials is more than 70 millions of m³.

Phytoremediation can be considered a good solution for soil remediation in these areas because it can be used as an *in situ* low cost technique but requires a long remediation time. Assisted phytoextraction is an optimization that, by increasing the metal bioavailable fraction in soil, enables to enhance metal transport into the aerial part of the plants reducing soil remediation times. Recent research has been focused on the study of easily biodegradable chelating agents with low impact due to their short persistence in the environment. Cao *et al.* [1] demonstrated the capacity of MGDA to mobilize both Pb and Zn in soil: in the days immediately after chelate addition Pb concentration in soil solution reached 5,700 and 2,000 mg/l in reactors treated with 8 mmol and 4 mmol per kg of soil respectively.

This study aims at investigating the possibility to identify Mediterranean native plant species for the application of assisted phytoextraction in abandoned mines remediation projects.

2. MATERIALS AND METHODS

2.1 Plant selection

The plant selection was based on previous field studies related to geobotanical aspects of SW-Sardinia mining areas [2,3,4] and was directed to choose metal tolerant plants which develop enough biomass to decontaminate the soil in acceptable times. Three little shrub species that often occur on contaminated substrata were selected. *Cistus salviifolius* L. is a shrub up to 2 meters tall that usually develops on poor and rocky soils or forms secondary communities as a result of destruction of Mediterranean maquis or evergreen forests. *Teucrium flavum* L. subsp. *glaucum* (Jordan & Fourr.) Ronn. and *Scrophularia canina* L. subsp. *bicolor* (Sibth. & Sm.) Greuter are chamephytic species, the first developing in the glades of sclerophyllous formations, the second is a typical pioneer plant on moving and gravelly ground such as the mine dumps.

2.2 Plant and soil analyses

Soil was characterized chemically using Italian official analytical methods [5]. Metals concentration in soil was determined using the *aqua regia* extraction method [5]. Carbon and nitrogen total contents were determined with an elemental analyser CHN, while cation exchange capacity (C.E.C.) was measured using the BaCl₂ method [5]. The bioavailable metal content was evaluated through the sequential extraction procedure [6]. This method divides the metal mobile fraction into three different pools: H₂O extractable (immediately soluble metals), KNO₃ extractable (exchangeable metal form), and EDTA extractable (complexed or adsorbed metal forms), whose sum represents the metal bioavailable fraction. The heavy metals accumulation capability was determined by measuring the concentration

of Pb and Zn in leaves. Plants samples were washed with tap water and dried at 105 °C before analysis. The dried material was digested with *aqua regia*. All determinations were performed in triplicate.

2.3 Site description and soil characterization

The Iglesias district (South-Western Sardinia, Italy) has been a very important mining area for centuries. The Gonnese Group, known as the “Metalliferous Ring”, was one of the richest deposits of argentiferous lead-zinc. In this area about 40 mines were distributed over approximately 150 km², where exploitation is documented since the Punic and Roman period [7]. The area object of study is a tailing dam of the mine called Monteponi. The characterization of a representative sample of soil is presented in Table 1.

Table 1. Campo Pisano soil characterization.

C.E.C. [cmol kg ⁻¹]	pH		N [%]	C [%]	Total [mg/kg]		H ₂ O [mg/kg]		KNO ₃ [mg/kg]		EDTA [mg/kg]	
	H ₂ O	KCl			Pb	Zn	Pb	Zn	Pb	Zn	Pb	Zn
0	7.3	7.2	0.01	6.28	3258	12038	DL*	776	DL*	50	612	3504

* value lower than instrument detection limit (Inductively Coupled Plasma-Optical Emission Spectrometer- ICP-OES), which is equal to 0.0015 mg/l and 0.0002 for Pb and Zn respectively.

2.4 Organization of the experiments

The experiment was divided into two phases. During the first phase a continuous phytoextraction field test was performed in Monteponi mining area. In the second phase the plants that demonstrated to have a better tolerance to high heavy metals concentration, specifically *Scrophularia canina*, were extracted from the site and assisted phytoextraction tests were made in laboratory under controlled conditions using easily biodegradable chelants.

2.4.1 The continuous phytoextraction experiment

In the continuous phytoextraction experiment in field scale the species *T. flavum*, *S.canina*, *C. salvifolius* were used. The total number of seedlings was 71 for *S. canina*, 31 for *C. salvifolius* species and 9 for *T. flavum* plant species; the number of seedlings was limited by the number of seeds that grew from germination tests. The plants were placed in field after six months from germination; all seedlings had a height from 5 to 8 cm and were planted at a distance of 60 cm from each other covering a total area of about 28 m². The experiment lasted 11 months. During the field test the plants tolerance to high concentrations of metals was evaluated by regular counting of the vital plants.

2.4.2 The assisted phytoextraction experiments

S. canina plants, drawn from the contaminated site with their clods, were placed in 5 litres pots and were transported in laboratory where they were maintained under controlled conditions.

Two types of easily biodegradable chelating agents were used: IDS (iminodisuccinate acid, Bayer) and MGDA (methylglycinediacetic acid, BASF). They were selected valuating both the biodegradability and the capacity to mobilize metals in soil. MGDA has a far higher biodegradability with respect to EDTA (Ethylenediaminetetraacetic acid): 89-100% of MGDA can be degraded in 14 days (Data sheet, BASF) while no EDTA was degraded in 30 days. OECD 301 E test made on IDS showed a 79% decrease in DOC after 28 days (Data sheet, Bayer). Chelants were applied by adding 100 ml of water, with a dose of 4 mmol/kg of soil. Untreated reactors were used as control. The experiment was performed in triple and lasted two months.

In order to evaluate the potential bioavailable metal fraction and the potential risks of chelant application, metals concentrations in soil solution and leachate were measured during the experiment. In each pot a Rhizon soil moisture sampler was installed (Eijkellkamp, Agrisearch equipment, the Netherlands). Every pot was equipped with a leachate sampling device. Soil solution, leachate and plants were sampled one day before and after chelant treatment, and monthly until the end of the experiment. At the end of the experiment the plants were extracted from the growing media, washed carefully and roots and shoots were separated to be analysed.

3. RESULTS AND DISCUSSION

3.1 The continuous phytoextraction experiment

During the continuous phytoextraction test both plants tolerance to metals and metal accumulation capacity were evaluated and the performances of the different plants species were compared.

3.1.1 Plant growth

During the first thirty days the plant species have shown signs of suffering due to the extreme environmental conditions and the high heavy metals concentrations in soil.

T. flavum showed a high tolerance in the early months of observation, but only a small percentage of plants (11%) was vital at the end of the experiment. The biomass production and the plant growth was low (maximum height of 11 cm). *C. salviifolius* was the most suffering in field conditions and after thirty days the vital plants were reduced to 52% reaching

10% at the end of the observation period. The vital plants at the end of the experiment reached a maximum height of 30 cm but did not show a high biomass production.

The plant species that has better tolerated field extreme conditions (maximum height measured of 24 cm and the highest biomass production) was *S. canina*. The percentage of vital plants at the end of the test was 68%.

3.1.2 Metal accumulation in plants

During the experiment the capability of the plant species to accumulate lead and zinc in the aerial part was evaluated. At the end of the observation period plant species showing a greater ability to accumulate lead in the aerial part were *T. flavum* (346 mg/kg) and *C. salviifolius* (185 mg/kg). The accumulation of lead in the aerial part for *S. canina* was 119 mg/kg. The concentration of zinc was high for all species: 1560 mg/kg for *C. salviifolius*, 1190 mg/kg for *S. canina* and 1130 mg/kg for *T. flavum*.

3.2 The assisted phytoextraction experiments

During the assisted phytoextraction test the chelating agents capacity to mobilize heavy metals and to enhance metal accumulation in plants was evaluated.

3.2.1 Metal mobilization

Chelant capacity to mobilize heavy metals was evaluated through the determination of heavy metal concentration in soil solution. Both chelants demonstrated to enhance mobilization of Zn in soil solution and to a less extent that of Pb. Zn concentration in soil solution reached a maximum value of 600 mg/l in the presence of MGDA and 220 mg/l in the presence of IDS, while Pb concentration reached 1.6 mg/l using MGDA and 0.4 mg/l using IDS. The low heavy metals mobilization can be a consequence of soil characteristics and in particular of its low cation exchange capacity.

3.2.2 Metal accumulation in plants

Pb accumulation in plants was increased by chelant treatment and reached 300 mg/kg in the pots treated with IDS and 200 mg/kg in those treated with MGDA. Zn concentration increased reaching a maximum value of 3,000 mg/kg in pots treated with IDS and 2,200 mg/kg in pots treated with MGDA (Figure 1). On the contrary metal concentration in roots decreased considerably in the treated reactors. Pb concentration in control reactors was around 250 mg/kg while its concentration was 25 and 70 mg/kg in reactors treated with IDS and MGDA respectively. This difference demonstrates the modification of plant reaction to metals consequent to chelating agents application [8].

Previous experiments [9] performed using the same plant species and MGDA but in a soil characterized by a higher cation exchange capacity showed a higher mobilization capacity (183 mg/l of Pb and 960 mg/l of Zn) of MGDA and metal accumulation in plant (1800 mg/kg of Pb and 10900 mg/kg of Zn). We can consequently hypothesize that the low soil cation exchange capacity may have determined an increased chelant transport in leachate and its low retention in soil.

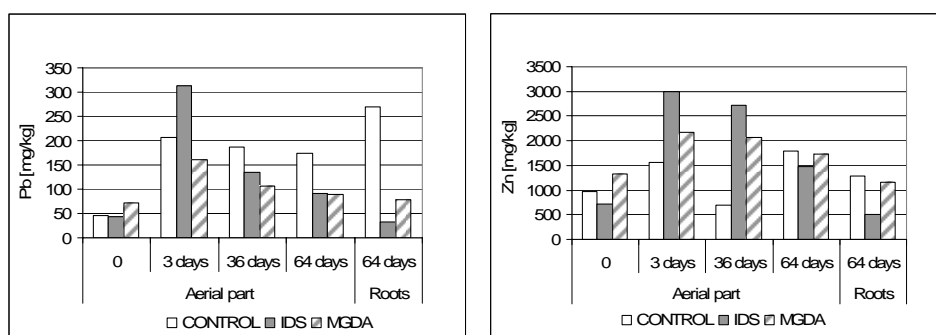


Figure 1. Pb and Zn accumulation in the aerial part of the plants during the experiment and in roots at the end of the experiment

CONCLUSIONS

The results of the field experiment allowed the evaluation of the metal accumulation capability of native plant species selected. At the end of the observation period, the plant species that showed the greatest ability to accumulate Pb was *T. flavum* while *C. salviifolius* accumulated the greatest amount of Zn. However, these plant species have suffered from the high metal concentration in plant tissue, so that vital plants at the end of the experiment were equal to 11% and 10% for *T. flavum* and *C. salviifolius* respectively. *S. canina* has shown a higher biomass production and a higher ability to tolerate high concentrations of both metals compared to other plant species: the percentage of vital plants at the end of the experiment was equal to 68%. For these characteristics *S. canina* seems suitable for application to phytoextraction treatment in mining areas.

The application of chelating agents to the soil did not increase considerably metal mobility and metal accumulation in plant probably because the low soil C.E.C. determined low chelant retention in soil. The application of chelants to this

type of soil needs to be optimized for example by the addition of materials with high cation exchange capacity such as zeolites or compost. Also the use of different chelants can be experimented.

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