Contribution of *Cistus ladanifer* L. to natural attenuation of Cu and Zn in some mine areas of the Iberian Pyrite Belt

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ABSTRACT: The comparison between four groups of soils and rock rose plants (*Cistus ladanifer* L.) developed on these soils was made using three mine areas of different ages (Neves Corvo, Brancanes, Monte dos Mestres) and a control area (Lombador). Copper and zinc soil-plant relationship was different in Neves Corvo, ongoing exploitation of copper and zinc, when compared with the control area of Lombador reflecting the actual influence of the present exploitation. The rock rose plants seem to have contributed to the natural attenuation of Cu in soils of Brancanes area where mining stopped more than a century ago.

KEYWORDS: *Cistus ladanifer L., mining areas, control area, natural attenuation, copper mines*

INTRODUCTION

The role of green plants in natural attenuation is an important way of phytostabilazation of degraded areas, especially in the abandoned mine areas where well adapted and tolerant spontaneous plants grow. These plants contribute to decrease soil erosion, the mobility of contaminants in soil and to reduce or eliminate the risk to both human health and the environment.

The rock rose (*Cistus ladanifer* L.) is a typical Mediterranean plant well adapted to thin soils with low nutritional characteristics and water holding capacity as some of those found in the Iberian Pyrite Belt (IPB) (Carvalho Cardoso, 1965). This metallogenetic province is renowned by the existence of important polymetallic massive sulphide deposits and because was exploited for base metals since pre-Roman times.

The objective of this study was to evaluate the role of chemical elements uptake by rock rose (a well adapted plant to mine environments) in natural attenuation by phytostabilization of soils polluted during different periods of mining activity and abandoned.

MATERIALS AND METHODS

The capacity of rock rose to contribute to the natural attenuation of contaminated areas was evaluated by comparison, among different mine areas, the chemical elements in soils and plants. These areas were selected because of the similar geological environment and, the different periods of mining and abandon. The mines are located in the Vulcano Sedimentary formations of Upper Devonian epoch (Carvalho & Ferreira 1993). Three different areas of sampling were chosen. NC area - correspond to the Neves Corvo still active Cu and Zn mine where 19 soils and plants samples were collected. MM area - represent the Monte dos Mestres area which includes the following subareas: Courela das Ferrarias (a mine exploited until 1987), Cerro da Cachaçuda, Herdade do Castelo and Cerro das Guaritas all exploited for Mn (abandoned before 1980) and Cerro do Algaré exploited for copper and pyrite. In

MM area were collected 26 samples of soils and plants. The third area, named B – represent the Brancanes mine that was exploited until the end of the XIX century. In this area were collected 11 samples of soils and plants. For comparison, seven samples of soils and plants were collected in a reference area designated as L - Lombador area, which is located in the northern part of the area in turbidites of the Upper Visean age. The study areas are represented in Figure 1.

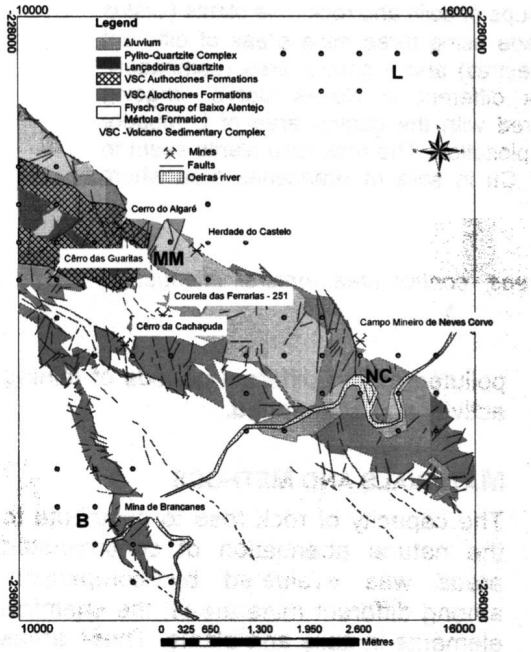

Fig.1. The study areas (NC, MM, B, L) of different mine sites with different periods of abandon.

A total of 112 samples of rock rose (roots and leaves) and 56 soil samples (fraction <0.18 mm) where these plants were grown were analyzed. Soil pH was determined in a soil/water suspension with 1/2.5 (m/v) proportion. Soils and plants were analyzed for Cu, Zn Al, Fe, Mn, Ca, K and P by ICP-OES after digestion with four acids ($HClO_4$+HNO_3+HCl+HF).

After analysis of basic statistics and Shapiro-Wilk normality test, it was concluded that the data did not assure the normality conditions necessary to perform certain statistical analysis. To follow usual procedures the data were lognormalised and normality was tested by normal probability curves.

One-way-ANOVA tests were made to control the quality of the data. To achieve the proposed objectives, multiple comparison of means of the four groups was made by Tukey ($p<0,05$) test. The Dunnett ($p<0,05$) test was used to compare the means of three groups of mining sites with the control group (Seaman *et al.* 1991). Pearson correlation coefficients were also obtained to confirm the tests results.

RESULTS AND DISCUSSION

The statistical parameters of central tendency obtained for the four groups of areas which reflect the geochemistry of different periods of the mine abandon are presented in Tables 1A and 1B.

Table.1A- Mean and median (mg kg^{-1}) of soil pH and Cu, Zn, Fe, Mn, Ca, P, Mg, Al, K in soil samples (S) and plants (F-Leaves; R-roots) in Lombador (control area) and Monte dos Mestres.

	Lombador (L)		Monte dos Mestres (MM)	
	Mean	Median	Mean	Median
CuS	24	20	74	47
CuF	9	9	34	26
CuR	10	10	12	9
ZnS	49	42	56	49
ZnF	66	63	78	67
ZnR	17	16	23	23
MnS	685	543	1074	776
MnF	835	860	876	727
MnR	304	268	300	289
FeS	27429	23600	28342	29450
FeF	623	593	768	604
FeR	608	600	908	850
CaS	1957	2200	2308	1900
CaF	9600	10100	7692	7150
CaR	6571	5200	6427	6150
PS	437	410	612	590
PF	1530	1460	1455	1505

MgS	5429	4500	4046	4500
MgF	2947	2613	2770	2750
MgR	655	699	745	756
AlS	62257	60300	65046	63500
AlF	1286	1200	1462	1350
AlR	1386	1400	1808	1850
KS	13114	11700	16542	15450
KF	5416	6400	5784	6000
KR	1984	2200	2295	2176
pH	6.0	6.2	6.0	6.1

Table 1B. Mean and median (mg kg^{-1}) of soil pH and Cu, Zn, Fe, Mn, Ca, P, Mg, Al, K in soil samples (S) and plants (F-Leaves; R-roots) in Neves Corvo and Brancanes areas.

	Neves Corvo		Brancanes	
	Mean	Median	Mean	Median
CuS	978	226	46	44
CuF	179	95	9	9
CuR	30	14	9	9
ZnS	165	83	52	54
ZnF	101	107	52	54
ZnR	28	23	20	19
MnS	1420	1017	966	1015
MnF	770	643	765	796
MnR	350	286	323	308
FeS	33479	30800	30945	29300
FeF	1538	1000	615	600
FeR	797	800	874	700
CaS	3000	2000	3418	2900
CaF	7377	7100	8107	8030
CaR	6109	5700	7139	6539
PS	700	600	827	800
PF	1406	1380	1548	1620
PR	387	354	374	330
MgS	5232	5400	4427	4900
MgF	2605	2600	2797	3003
MgR	758	789	695	666
AlS	63853	65000	68455	68500
AlF	1316	1226	1750	1550
AlR	1464	1498	1021	958
KS	15732	15000	18045	18100
KF	5311	5300	4816	6100
KR	2282	2200	2205	2186
pH	5.5	5.7	5.8	5.8

Comparing all the groups (Tukey test) by pairs it was concluded that Brancanes, Lombador and Monte dos Mestres are comparable for Cu and Zn in soils and Fe in leaves of the rock rose plants. None of these groups is comparable with Neves Corvo in what Cu, Zn and Fe is concerned, both in soils and plants. This is due to the present mine exploitation of these metals and the dispersion of newly exploited materials in the surrounding area.

In all the studied areas the concentrations of Mn, Al, K and Mg are statistically comparable among the areas. This indicates that these chemical elements, both in soils and plants, are independent from the mine exploitation.

In the control area, Lombador, the phosphorus, an essential element in plants nutrition, presents, in the relation soil-plant, a different behavior from the other areas. This can be related to the substratum rock in the Lombador area which is composed of metassediments (turbidites) and are not included in Volcano Sedimentary Complex as the other areas where mining works have occurred.

The correlation coeficients ($p< 0.05$) obtained for Lombador area showed that Cu in roots has good correlation with Zn ($r=0.81$) and Fe ($r=0.85$) in roots and with Al in soil (0.76) and roots ($r=0.82$) and K in leaves (0.90). Zinc in roots is well correlated with Zn in leaves (0.76) and Fe in roots (0.88) meaning that this may be related with the capacity of Zn to be translocated to the aboveground parts of the rock rose plants in Lombador, especially in low pH environment ($r=-0.79$). These results showed the importance of Cu and Zn uptake by plants (Wenzel & Jockwer 1999; Kidd *et al.* 2004) as these elements are essential micronutrients. The soil-root relationship, possibly more related with plant uptake, is higher in Cu than in Zn. The relation soil-leaf (possibly more related with translocation mechanisms is higher in Zn (Alvarenga *et al.* 2004).

In contrast, in the Neves Corvo mining area the correlations between each

element (Cu, Zn and Fe) in soil-root, soil-leaf and leaf-root samples, and low pH (3.45 minimum) are high. Therefore, mobility of those elements in the soil-plant system seems to be facilitated in this ongoing mining area.

The Dunett test considers a control area (Lombador) for comparison. In this area, phosphorus in soils is not comparable with the other mine areas groups which are in accordance with the Tucker test results. Phosphorous is an essential element in plant nutrition and its soil-plant relationship is different between the control area, where soils were developed on Visean age metassediments, and the mining areas whose substrata is composed of Volcano Sedimentary formations. The copper and zinc showed significant differences in the soil-plant system between the control area and Neves Corvo area. These differences indicate the obvious fact that those elements are presently mined in Neves Corvo, being present in the superficial environment of the area.

Comparing soil -plant- copper relationships between the Brancanes mine (that was abandoned over a century ago) and the Lombador control area shows that the element has already equilibrated with the environment as a result of natural attenuation.

CONCLUSIONS

The comparison between Tuckey and Dunnett tests indicated that the reference area of Lombador presents significant differences with the ongoing exploitation of Neves Corvo Cu and Zn mine. On the contrary, Cu relationship between the soil-plant is similar in the Lombador control area and in Brancanes test site which has been orphaned for over a century. This suggests that natural attenuation effects on Cu in the soil-plant system have already happened in Brancanes mining area. The rock rose species (*Cistus ladanifer, L.*) seems to play an important role in the natural attenuation process.

The major elements Mg, Ca, Al, K does not presented significant differences between the areas showing some independency of mining effects in these soil-plant systems. Phosphorus presents a different behavior between control and mining areas what may be related with parent material differences or plant physiology.

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