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Pinus pinaster Aiton (Maritime pine): a reliable indicator for delineating areas of anomalous soil composition for biogeochemical prospecting of Arsenic, Antimony and Tungsten

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ABSTRACT

Biogeochemical prospecting requires right selection of biological material. Accurate analysis of sampled materials, elimination or minimization of errors due to mixup of different plant parts of variable ages are equally important. The aim of this work is to evaluate the potential of different age needles and twigs of *Pinus pinaster* Aiton (maritime pine). *P. pinaster* is one of the important indicator species for biogeochemical prospecting. For this investigation we chose one of the old mining areas viz. Gatas, East Central Portugal which was contaminated with As, Sb and W. In this investigation, needles and twigs of different age have been collected for analysis of metals. It was observed that 2-year-old needes are the best material for recovery of As, Sb, W. The present work aslo elucidates the accumulation variation of As, Sb, W in twigs and needles of *P. pinaster* of different ages. The results highlight the sampling of plant parts and their age as important factors for biogeochemical prospecting. This investigation is based on principal components analysis (PCA). The data was also subjected to Biogeochemical Anomaly Index (BAI). © 2004 SDU. All rights reserved.

Keywords: Froth *Pinis pinaster*; Bioindicator; Biogeochemical prospecting; Arsenic; Antimony; Tungsten

1. INTRODUCTION

The function of metal accumulation in plants is of immense use for biogeochemical prospecting (Badri and Sringeul, 1994; Brooks, 1983; McInnes *et al.*, 1996). However, in many plant species the accumulation of a particular metal is not linear with the time and it is variable seasonally and with the age of the plant part sampled. Seasonally variability can be regulated by collecting samples in appropriate seasons. However, the “age and nature of the plant part collected” will be necessary for acurate investigation and application. The genus *Pinus* is important for its interactions with heavy metals. In *P. densiflora, P. thunbergii* and *P. pinaster* the bark is adsorbs wide range of heavy metals; *P. nigra* and *P. sylvestris* are the container plants to mitigate metals emitted by zinc smelter; *P. ponderosa* grows along river banks with heavy metal contaminated sediments; *P. strobus* and *P. taeda* are reported to inhibit the overall growth of root biomass. *P. virginiana* and *P. ridida* are tolerant to heavy metals and occur frequently on serpentine soils (Miller and Cumming, 2000; Prasad, 2001; Vázquez *et al.*, 1994). *P. pinaster* is distributed on serpentine soils and grows on mine refuse in Portugal. However its metal indicator and biogeochemical prospecting aspects have not been investigated. Therefore, the present work elucidates the metal accumulation pattern in twigs and needles as a functions of age in *P. pinaster* so as to eliminate errors in the selected sampling to achieve accuracy. This paper highlights the potential of *P. pinaster* for metal indicator value and for biogeochemical prospecting.

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2. EXPERIMENTAL

2.1. Area descriptions, methods and material studied

This study is a part of the series of studies on biogeochemical prospecting and mine reclamation that was attempted to evaluate the potential of plant species and communities established in soils contaminated with trace elements (Freitas *et al.*, 2004a,b). The study area includes two abandoned mines viz., Gatas and Santa mine. The area investigated is situated close to the Sarzedas village 39° 52' 30" N; 7° 32' 20" W (Castelo Branco county, central Portugal). The Sarzedas mineralisations are emplaced in quartzous veins striking N60°E (Santa mine) and N20°W (Gatas mine), filling tardi-hercinic fractures, which cut the "Schist-Graywake Complex". The acid rock veins cutting the complex are frequent and these are identical to ante-Ordovician veins appearing in the area. These veins show indication of hydrothermal alteration and they are mineralised by disseminated sulphides. However the main mineralisation is of the vein type and it is made of wolframite (ferberite), stibnite, pyrite, arsenopyrite and, seldom, by chalcopyrite, sphalerite and galena. The gold occurs in its native form.

In the study area, two transects were made on the mineralised zone and in the tailings. On these transects, soils and plants were collected in a 2 meters circle every 40 meters, ensuring that about 1/3 of the total of samples were in the contaminated area. Two transverse profiles within the mineralized area and tailings were chosen as sites for collection of materials. In these profiles soils were collected at intervals of 40m. Soil samples were always collected from B horizon (not always at the same depth because they were mountain soils with little thickness but variable) to minimise the influence of the organic matter present in superficial horizons. Each soil sample consisted on an homogenate of 4 sub-sample points located in an imaginary circle about 2 meters around the sampling point. The soil samples were dried at 80°C and passed through a 100 mesh sieve. Plant samples were cleaned in abundant fresh-water, rinsed with deionized water, air dried at room temperature by several days; after washing they were crushed (Kovalevskii, 1979; Brooks, 1983; Pereira *et al.*, 2003). Plants were identified following the local herbarium and and floras (Franco, 1971; 1984). Analytical methods included colorimetry for W (Quin and Brooks, 1972) atomic absorption spectrophotometry (Perkin Elmer 2380) for Ag, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, and hydride generation for As and Sb (Van Loon 1985; Vijan *et al.*, 1976).

In order to determine plant´s ability to accumulate heavy metals, and to use plants to detect metalliferous rocks, the Relative Index of Biogeochemical Anomaly (RIBA) was applied. This index is calculated based on metals concentration in soils and plant tissues and based on Principal Component Analysis (PCA). This allows plant selection (including their parts) that would better indicate ore deposits. This selection permits the organization of a hierarchy of metal tolerant species that can be used on biogeochemical prospecting. To obtain an index that can be considered responsible for the origin of the anomaly in plant material as a result of the soil, a Biogeochemical Anomaly Index (BAI) was estimated. It corresponds to the ratio between the absolute values of the biogeochemical and pedogeochemical anomaly.

Statistical analysis involved correlation analysis and principal components analysis (PCA). For carrying out these analyses, we presupposed that distribution of data was normal law, because, it was not possible to adjust each subset of data to normality. We assumed that multinormality arise as an adequate approximation to justify the parametric analyses to establish multi-dimensional relationships between the study variables (Fletcher, 1981; Pereira *et al.*, 2003; Singh *et al.*, 1994; C.V.R.M., 1988).

The particular algorithm of the PCA used was based on the standardization of the variables – the first step consisted on replacing the matrix of the mass data of chemical elements zij by the transformed panel of chemical elements tij, where tij= (zij - mj)/sj(n)1/2 (mj is the mean of the column j, sj is the respective standard deviation and n is the number of individuals. In this first analysis, individuals were all taken as principal elements and the main variables were those related to the elements that we knew to be in the origin of the mineralization, thereby confirming which secondary elements were associated to the anomaly and which samples were coupled to them. This procedure could verify which samples promote the origin of the anomalies caused by the mineralization and that will be important in the succeeding procedure.

In the second step of the analysis, the results obtained for each plant species and respective soil were handled together, taking into consideration that for each area, the principal elements in the factorial axis were those responsible for the soil contamination, as it is after them that we aim to verify if the concentrations in plant tissues show significant indication of soil anomalies. To distinguish the influence of the variables on the origin of the anomaly, each variable was designed in a straight line linking A to B (Figure 1). The sum of the obtained values by the distance to the center of the new projections should be equal to the dissimilarity between the anomaly and the background.

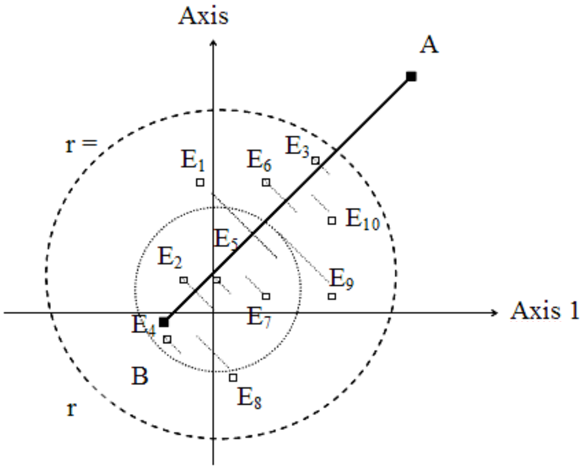

Figure 1. Scheme used to separate the influence of each variable in the origin of the anomaly

3. RESULTS AND DISCUSSION

The analytical results for soils are shown in Table 1. From the analytical data, it can be concluded that the elements present in the ore body are As, Sb and W. Beyond those elements we may observe that both Pb and Ag are accompanying the mineralisation and appear in more concentration in soils near the orebody.

The pH values, which are very low surrounding mineralised area could be justified by the presence of pyrite and others sulphide minerals in the orebody. These pH values support a high solubleness of heavy metals, allow much more dispersion and also bioavailability. The results obtained for the vegetal material are summarized in the Table 2.

Table 1
Soil data for composition of different metals (mg/kg)

	Variation	Mean	Median	Std. deviation
pH	3.3 –5.2	4.7	4.8	0.5
Ag	0.69 –1.91	0.98	0.92	0.32
As	11.1- 651.1	76.3	19.9	181.5
Co	5.4-14.9	8.8	8.41	2.6
Cr	50.7-129.1	96.5	100.2	26.3
Cu	15.5-78.2	40.7	35.1	21.1
Fe	21881-58644	39981	37356	12883
Mn	22-92	50	47	22
Ni	11.2-52.5	21.8	19.7	10.2
Pb	35.7-416.7	85.4	53.9	105.9
Sb	30.5-5986.4	663.1	87.8	1689.1
W	0.8-684.0	663.1	2.9	52.3
Zn	29-126.6	58.8	53.3	24.3

Table 2
Summary of of analytical data delineating soil composition and trace element accumulation in *Pinus pinaster* needles and twigs (mg/kg dry weight)

Plant Part	Year		Ag	As	Cu	Fe	Pb	Sb	W	Zn
Needles	1	Background	0.08	0.22	3.33	73	1.61	0.05	0.13	20.6
		Maximum	0.12	9.99	6.42	193	2.03	1.41	2.65	32.2
		Anomaly	0.09	3.64	2.86	128	1.87	0.74	1.68	20.7
Needles	2	Background	0.11	0.22	1.89	121	2.13	0.06	0.09	20.3
		Maximum	0.18	30.1	2.28	192	2.84	1.85	10.7	38.1
		Anomaly	0.16	10.33	1.86	155	2.65	0.89	6.52	22.6
Twigs	1	Background	0.13		4.73	85	1.30	0.03		21.5
		Maximum	0.28		7.04	166	2.60	2.19		35.4
		Anomaly	0.15	0.59	4.45	93	2.01	1.01	0.18	17.9

continued (Table 2)

Plant Part	Year		Ag	As	Cu	Fe	Pb	Sb	W	Zn
Twigs	2	Background	0.11	0.13	3.25	107	1.96	0.07	0.09	19.0
		Maximum	0.21	0.34	4.34	158	3.20	1.89	3.81	27.9
		Anomaly	0.13	0.25	2.77	85	2.19	1.01	2.44	15.5
Twigs	3	Background	0.1	0.12	1.65	38	1.02	0.02	0.08	14.7
		Maximum	0.15	0.32	1.84	72	1.90	0.17	2.48	21.6
		Anomaly	0.12	0.23	1.74	44	1.37	0.12	1.87	13.4

Based on these results (Tables 1 and 2), it can be observed that organs sampled do not show a similar distribution in order to the age, in other words, the element content in the vegetal material depend on, directly, both on the plant organ and also with age. These variations for all the analysed heavy metals in the vegetable material, in sampling points over the geochemical anomaly and, separately, over the geochemical background are presented in Figures 2-9.

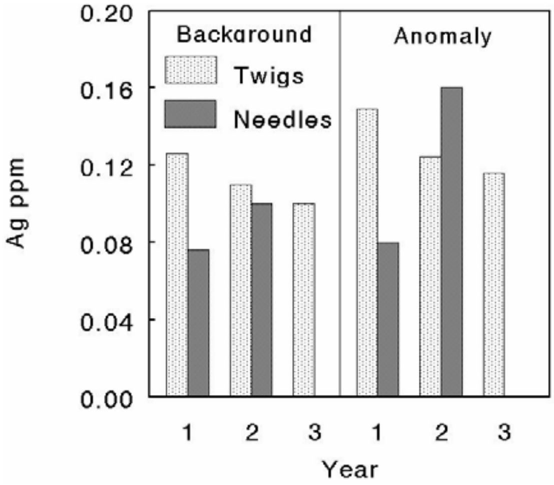

Figure 2. Ag content variation with the age of plant organ in *P. pinaster*

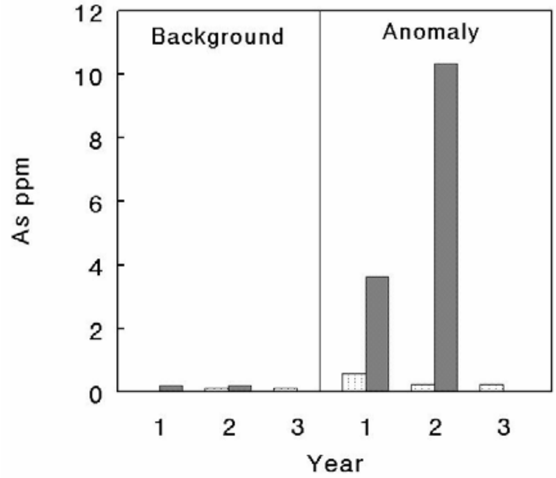

Figure 3. As content variation with the age of plant organ in *P. pinaster*

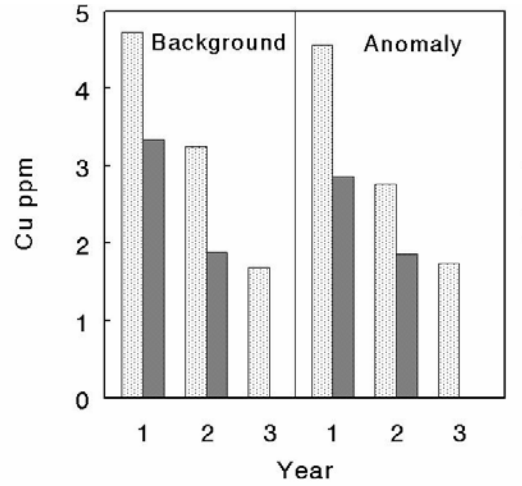

Figure 4. Cu content variation with the age of plant organ in *P. pinaster*

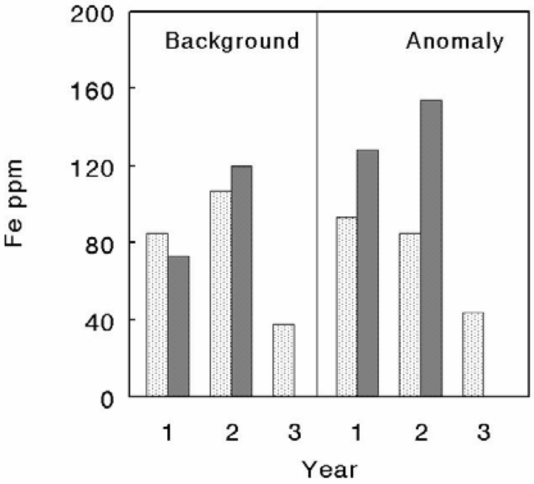

Figure 5. Fe content variation with the age of plant organ in *P. pinaster*

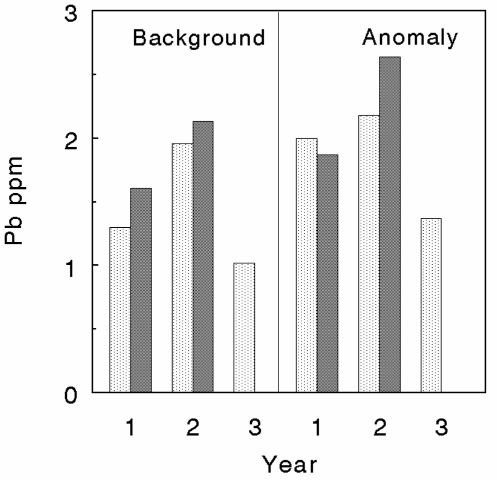

Figure 6. Pb content variation with the age of plant organ in *P. pinaster*

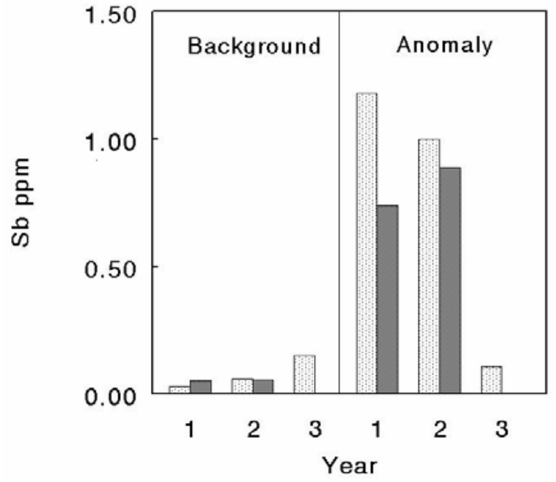

Figure 7. Sb content variation with the age of plant organ in *P. pinaster*

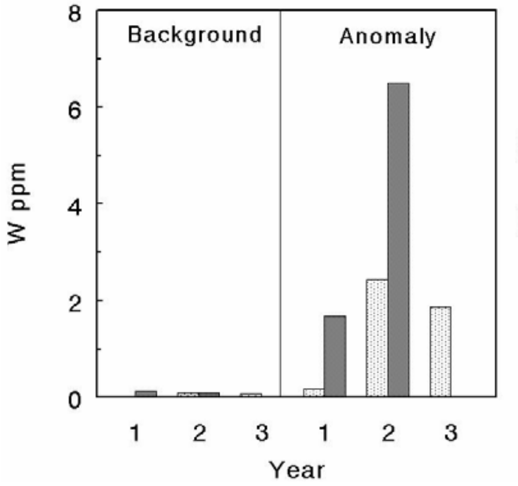

Figure 8. W content variation with the age of plant organ in *P. pinaster*

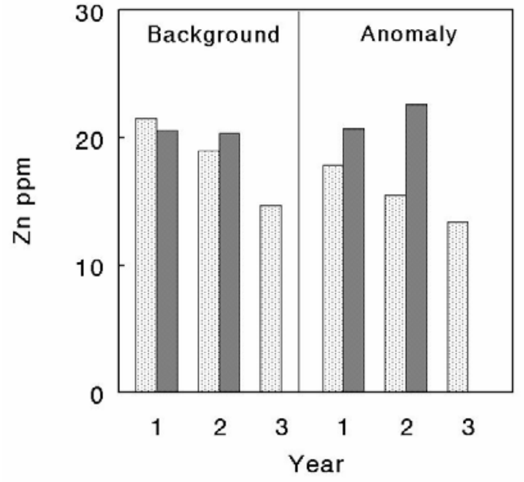

Figure 9. Zn content variation with the age of plant organ in *P. Pinaster*

Ag, exhibit concentrations slightly above geochemical anomaly. One-year-old twigs and 2-year-old needles accumulated highest amount of this element. The content of this element decreased with increased age of the twigs (Figure 2). The As content was mainly with needles and increased with the age of needles. Twigs do not accumulate this element with age, instead the content decreased with the age (Figure 3). Cu exhibit an distinct behaviour. Cu accumulation was higher in 1-year-old twigs and needles. The Cu content decreased with increased age (Figure 4). Fe present a distinct behaviour of accumulation in twigs. Fe accumulation in needles is age dependent, however, the content decreased in older twigs (Figure 5). The Pb variation as a function of age and organ was shown in Figure 6. Pb content in needles increased progressively with age. The Pb content is more in the 2-year-old twigs and subsequently decreased with age. As regards Sb first year twigs accumulated more. The Sb content decreased with increasing age in twigs compared to needles (Figure 7). The W exhibit distinct behaviour. This element is easily absorbed and retained maximum by 2-year-old needles (Figure 8). With regard to Zn content, exhibited a gradual decrease with increase in the age of twigs, however, the trend is exactly opposite for needles. Needles accumulate more metal with increased age (Figure 9). The data related to the biogeochemical anomaly index (BAI) was shown in the Table 3. The BAI support that As, Sb and W reflect the soil contamination but distinctly variable both with the plant part and its age.

Table 3
Biogeochemical anomaly index for the *P. pinaster*

	Ag	As	Cu	Cu	Fe	Pb	Sb	W	Zn
Needles 1 year	0	1.01	0	0	0	0	0.49	0.09	0
Needles 2 year	0	2.67	0	0	0	0	0.53	0.57	0
Twigs 1 year	0		0	0	0	0	1.45		0
Twigs 2 year	0	0.11	0	0	0	0	0.85	0.18	0
Twigs 3 year	0	0.16	0	0	0	0	0.67	0.38	0

4. CONCLUSIONS

The observed variation in contents and in the BAI for the sampled organs and relatively of its age show that it is very important to consider both the organ or its age in biogeochemical surveying involving *Pinus pinaster* Aiton. Thus, for optimum exploration of As, Sb and W, 2-year-old needles are the best material.

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