DETERMINATION OF Cu, Pb AND Zn IN HORSETAIL (*EQUISETUM SPP.*) GROWN ON MINE TAILINGS

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Abstract: Mine tailings are an unfavourable substrate for the plant growth because of their low pH, high metal and low nutrient contents. Horsetail (*Equisetum spp*.) is one of the plant species that spontaneously colonize tailings in nonferrous mining areas. The results indicated that despite the high Cu, Pb and Zn contents found in the tailings, only moderate to low concentration of these metals was found in the shoots of horsetail. The bioaccumulation factors calculated as the ratio between the metals concentration in plants and in tailings were low, suggesting the tolerance of horsetail to high metal contents. However, according to the bioaccumulation factors, horsetail does not classify as an accumulator for the studied elements. These results suggest the possibility of using horsetail in the development of remediation strategies for tailings.

Keywords: tailings, horsetail, metals, bioaccumulation factor

INTRODUCTION

Although one of the pillars of the economic growth, mining has a negative reputation because of the large amounts of associated wastes, which can cause soil, water and air pollution for decades or even centuries after closure (Johnson and Hallberg, 2005; Li, 2006; Dold, 2008; Sima et al., 2011; Levei et al. 2013a; Levei et al., 2013b). Thus, in order to increase the public acceptance of mining operations, the conservation or remediation of mining affected areas is mandatory throughout the whole operation life cycle. Generally, the available remediation technologies for metal contaminated sites are costly or do not offer a long-term nor aesthetic solution (Yoon et al., 2006).

Although it request long periods of time, one of the most effective restoration approach is the combination of limited treatment of critical factors with natural revegetation or colonization of metal tolerant plant species to volatilize, stabilize, extract or inactivate the pollutants in tailings (Li, 2006; Mendez and Maier, 2008; Mukhopadhyay and Maiti, 2010).

Tailings stored in tailings impoundment has generally no or poor vegetation cover due to toxic effects of pollutants, low pH, and lack of nutrients (Wong et al., 1998). Thus remediation approaches that use plants confronts with stress conditions such as extreme acidity, low water holding capacity, excess salinity, nutrients deficiency and high metal contents (Wong, 2003; Ye et al., 2002). Several substrate amelioration techniques and tolerant plant species are used for the tailings revegetation but the identification of self-sustaining, native plant specie that can tolerate high concentrations of toxic elements is still a challange (Narhi et al., 2012).

Horsetail (*Equisetum spp.*) is one of the plant species that spontaneously colonize tailing dumps, surviving in extreme conditions and having a high tolerance for low pH and high metal concentrations (Kurniati et al., 2014).

Horsetail requires a constant supply of moisture, thus in mining environments it can be found next to streams of acid mine drainage or mine galleries. Generally, is poor competitor and do not threaten other plant species, but is toxic for the grazing livestock.

The objective of this study was the determination of Cu, Pb, Zn in the tailings and horsetail shoots and the calculation of tailings to plant bioaccumulation factors for these metals.

MATERIALS AND METHODS

Romania has a long mining history of base (Cu, Cd, Pb, Zn) and precious (Au, Ag) metals, the majority of nonferrous mining and ore processing industry and consequently the highest number of tailings impoundments are located in the north and in the west of the country.

A number of 16 horsetail plants and the tailings adjacent to their roots were collected from 5 impoundments that store tailings resulted from the processing of non-ferrous metals in Certej (1-5), Baia Mare (6-11) and Aries (12-16) mining areas.

The plant samples were washed with tap water to remove the dusts and adhering materials, rinsed with ultrapure water, dried in an oven at 40°C until constant weight and milled to fine powder. The tailings were dried and ground to pass 250 μm sieve.

The content of metals in the tailings was determined by inductively coupled plasma atomic emission spectrometry using the Optima 5300 DV multichannel spectrometer (Perkin-Elmer, USA) after digestion. An amount of 1 g dried tailings was digested with 21 ml 37% HCl and 7 ml 65% HNO_3 in reflux conditions for 2 hours and diluted to 100 ml with ultrapure water.

The metal contents in the plants were determined by inductively coupled plasma mass spectrometry using the ELAN DRC II Spectrometer (Perkin Elmer, Canada) after digestion of 0.5 g plant sample with 6 ml of 65% HNO_3 and 2 ml of 30% H_2O_2. The extract was filtered and diluted to 25 ml.

RESULTS AND DISCUSSION

Concentrations of metals in the horsetail shoots were between 1.85 and 23.5 mg/kg Cu, 0.12 and 23.2 mg/kg Pb and 21.9 to 391 mg/kg Zn, while in the tailings the metal concentration ranger between 26.9-2640 mg/kg Cu, 26.4-9800 mg/kg Pb and 81.3-5330 mg/kg as shown in Table 1. The contents of all studied metals were one order of magnitude higher in samples 9-11 than in the other samples, suggesting that from the three studied mining areas the toughest conditions for plant survival are present in Baia Mare mining area. The average metal contents in tailings decreased in the order: Pb>Zn>Cu, while the median decreased in the order Zn>Pb>Cu, confirming the existence of several tailings samples with extreme metal concentrations.

In the horsetail plants both the average and the median metal contents decreased in the order: Zn>Cu>Pb indicating a more homogenous distribution of metals in the samples, and the existence of some tolerance mechanisms that allow its growing in substrates with high Pb content. Generally, the found metal contents in the horsetail shoots were comparable with their occurrence in plant tissues 2-20 mg/kg Cu, 0.1-5 mg/kg Pb and 15-150 mg/kg Zn (Markert, 1996), although individual values of Pb and Zn exceeded the presented range.

The hyperaccumulator plants should have more than 0.1% of Cu, 0.1% Pb or 1% of Zn in their shoots, irrespective of the metal concentration in the substrate (Reeves and Baker, 2000). In this study, none of the plant samples showed such high concentrations, suggesting that horsetail is not a hyperaccumulator for the Cu, Pb or Zn. However, the ability of these plants to tolerate metals may be useful for the development of remediation strategies.

Table 1.

The Cu, Pb and Zn contents (mg/kg) in horsetail shoots and tailings and the bioaccumulation factors

Sample	**Cu**			**Pb**			**Zn**		
	horsetail	**tailings**	**BAF**	**horsetail**	**tailings**	**BAF**	**horsetail**	**tailings**	**BAF**
1	2.71	35.0	0.077	0.67	38.4	0.017	125	189	0.661
2	3.06	41.2	0.074	4.00	81.0	0.049	122	220	0.555
3	4.60	62.8	0.073	0.15	170	0.001	33.7	180	0.187
4	2.99	51.7	0.058	0.12	131	0.001	91.9	226	0.407
5	3.57	78.0	0.046	0.24	26.4	0.009	22.9	81.3	0.282
6	6.41	138	0.046	2.07	354	0.006	177	237	0.747
7	17.5	527	0.033	23.2	570	0.041	143	797	0.179
8	10.6	891	0.012	9.34	1090	0.009	151	336	0.449
9	2.87	1790	0.002	12.2	9800	0.001	184	1840	0.100
10	4.46	2640	0.002	3.74	2040	0.002	188	2110	0.089
11	8.66	2344	0.004	4.57	6480	0.001	391	5330	0.073
12	2.10	33.1	0.063	0.45	218	0.002	64.9	497	0.131
13	2.96	50.4	0.059	0.51	158	0.003	26.7	271	0.099
14	23.5	799	0.029	1.77	41.6	0.043	21.9	167	0.131
15	1.85	26.9	0.069	2.85	93.6	0.030	42.4	263	0.161
16	3.35	55.8	0.060	0.18	338	0.001	136	1180	0.115
Min.	**1.85**	**26.9**	**0.002**	**0.12**	**26.4**	**0.001**	**21.9**	**81.3**	**0.073**
Max.	**23.5**	**2640**	**0.077**	**23.2**	**9800**	**0.049**	**391**	**5330**	**0.747**
Average	**6.32**	**598**	**0.044**	**4.13**	**1352**	**0.013**	**120**	**870**	**0.273**
Median	**3.46**	**70.4**	**0.052**	**1.92**	**194**	**0.005**	**123**	**267**	**0.170**

The bioaccumulation factors depend not only on the plant species, but also on the metals concentration and its availability in the soil. The ability of horsetail to accumulate metals from tailings was evaluated by the bioaccumulation factors (BAFs), calculated as the ratio between the metal content in the horsetail shoots and the metal content in the tailings (Yoon et al., 2006). In our study, BAFs were similar to the typical soil-to-plant transfer factors: 0.01-0.1 for Cu and Pb and 1-10 for Zn (Kloke et al., 1984).

Despite the fact that several studies (Anh et al., 2011) found *Equisetum* as a Zn accumulator, in our study the low BAF values (BAF<1) indicated that horsetail is not an accumulator for any of the studied elements, although have a high tolerance for high metal concentrations, and could act as an excluder.

CONCLUSIONS

The results indicate that despite the high Cu, Pb and Zn contents found in the tailings, only moderate to low concentration of these metals was found in the shoots of horsetail (*Equisetum spp.*).

The bioaccumulation factors demonstrate that horsetail is not an accumulator for Cu, Pb and Zn, although have developed tolerance for high metal concentrations.

These results suggest the possibility of using horsetail in the development of remediation strategies for tailings.

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