ELEMENTAL COMPOSITION OF PLANT SPECIES FROM ABANDONED TUNGSTEN MINING AREA: ARE THEY USEFUL FOR BIOGEOCHEMICAL EXPLORATION AND/OR PHYTOREMEDIATION PURPOSES?

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ABSTRACT

Mining activities is one of the main sources of environmental pollution, globally through the increased levels of metals. Some plant species appear to have ability to restore the harmful effects of these metals. The aim of this study is to evaluate the element (W, Mo, Zn, Fe, Cu, Co, Bi, Mn, Cd, Cr, As) composition of some plant species spread around the abandoned tungsten mining area of Uludağ Mount in order to find a proper candidate for phytoremedation or biogeochemical exploration purposes. The selected species were *Anthemis cretica* L. subsp *carpatica, and Trisetum flavescens* (L.) P. Beauv*.* Trace element contents of different parts of plants were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) after acid digestion process. Validation parameters were evaluated in terms of accuracy, repeatability, reproducibility, detection and quantification limits. Our results indicate that contents of many examined heavy metals in soils of these species were increased depending on mining activities.

Keywords: Tungsten, trace element, phytoremediation, phytomining, inductively coupled plasma-mass spectrometry.

1. Introduction

Mining activities leading to heavy metal contamination are also a main cause of land degradation in the Uludag Mountain region as well as in the whole world. The Etibank Wolfram mine work is the main source of heavy metal contamination on this mount. Tungsten is an important element for use in the production of some special steel and is added to steel as ferrotungsten alloys (Gürmen *et al*, 1999; Yücel and Özçelebi, 2000). It was reported that this element is mainly related to acid magmas and must be located in a surface part of Earth's silicate magmatic crust (Kobiashvili, 1964). Present technology used to obtain low-grade scheelite concentrates under alkaline conditions involves hydrometallurgical processes (Gürmen *et al*, 1999). Tungsten (W) is a scarce and stable heavy metal in nature, but it is locally accumulated at high concentrations as a waste of mines, industries, agricultural and military activities (Wilson and Pyatt 2006; Clausen and Korte 2009). Over the last decade, W has attracted the attention of scientists and governmental institutes, since it was shown to be toxic for living organisms (Koutsospyros *et al*. 2006; Steinberg *et al*. 2007). Ore tailings, metal dust, and other remnants of the exploitation of metals may affect vegetation, which has not previously been exposed to high concentration of metals (Ernst, 1990, 1996). Plant composition or distribution in areas contaminated by heavy metal may indicate a specific assemblage of plant species (Ellenberg, 1988; Ernst, 1990; Brown, 1995). Plants growing in metal-enriched substrates take up metals to varying degrees in response to external and internal factors (Marschner, 1995). Partitioning of metals between solid and liquid phases of the soil is strongly affected by soil properties. Factors known to affect the solubility and plant availability of metals include their chemical characteristics, loading rate, pH, cation exchange capacity, redox potential, soil texture, clay content, and organic matter content (Marschner, 1995; Greger, 1999).

Plants have shown several response patterns to the presence of high metal concentrations in the soils. Most are sensitive to high metal concentration and others have developed resistance, tolerance, and accumulate them in roots and above ground tissues such as shoot, flower, stem, and leaves. In plants, W has primarily been used as an inhibitor of the molybdoenzymes, since it antagonizes molybdenum for the Mo-cofactor of these enzymes. However, recent advances indicate that, beyond Mo-enzyme inhibition, W has toxic attributes similar with those of other heavy metals. These include hindering of seedling growth, reduction of root and shoot biomass, ultrastructural malformations of cell components, aberration of cell cycle, disruption of the cytoskeleton and deregulation of gene expression related with programmed cell death. Adamakis *et al* (2012) was reviewed W toxicity in plants and plant cells, and the mechanism by which W was trapped in the roots, the mortality of the metal inside the plant bod and concluded that, research is also needed in the context of W management and development of phytoremediation technologies.

In the previous study, we concluded that the element composition of soils and some plant species around the tungsten mining area were changed by mining activites (Güleryüz *et al*., 2002). In this study, *Anthemis cretica* and *Trisetum favescens* were studied for their potential phytoremediation properties in tungsten contaminated soils.

2. Material and method

The study was carried out around Etibank Wolfram Mine Work between 2100 and 2487 m altitude of Ulu dağ Mountain. The mining activity was operated from 1976 to 1989. Waste-removal pools and waste canals were constructed on the granite substratum. Two sample sites were selected from unpolluted areas (Site I and II) and one from waste removal pool (Site-III). Soil and plant samples were taken from three different places at each sampling site. Soils samples were sifted with a standard 2-mm sieve and then dried in air. Plant parts were separated carefully, washed, and then were dried in an oven until their weights become constant. Dried samples were grounded.

Elan 9000 inductively coupled plasma–mass spectrometry (ICP-MS) (PerkinElmer SCIEX, Shelton, CT, USA) was used to determine the contents of As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Z, and W in the plant tissues (roots, leaves and flowers) separately. Perkin-Elmer Ryton cross-flow nebulizer, a Scott-type double-pass spray chamber, a standard glass torch, nickel sampler and skimmer cones (i.d.:1.1 mm and 0.9 mm, respectively) were the components of ICP-MS equipment. Additionally, the optimum instrument conditions were as follows: RF power: 1000 W; plasma argon flow rate: 17.0 L min^{-1}; nebulizer gas flow rate: 0.85 L min^{-1}; sample uptake rate: 1.5 mL min^{-1}; dwell time: 50 ms; scanning mode: peak hopping; and detector mode: dual. The classical open wet digestion procedure was applied to the samples (300-500 mg) with 3mL HNO_3 and 1mL H_2O_2 in a borosilicate glass vessel.

A single-element standard solution of tungsten at a concentration of 1000 µg mL^{-1} (PerkinElmer) and a multi-element standard solution of 30 elements (Merck 110580) were used to prepare Working solutions for external calibration. Calibration curves were constructed with seven points (5.6–3000 µg L^{-1} for W).

The differences among the sampling sites regarding the element contents of plants and soil samples were tested by one-way ANOVA. We used Tukey's HSD test to determine the differences among sample sites.

3. Results and discussion

The mean contents heavy metals were outlined in Table 1. Tungsten contents were increased in soils of both species as well as plant parts (Table 1; $P<0.05$). Similar tendency was observed for Fe, Zn, Cu, Bi, Mn and Cd. On the other hand, although Mo contents were high in soil samples from waste removal pools, there was no significant decrease in *A. tinctoria* except *T. flavescens*. According to Table 1 there are different responses from two plant species against to increasing tungsten amount. These may show the different defense strategies for tungsten stress. The mean leaf W contents of *A. tinctoria* and *T. flavescens* sampled from polluted site were reached to 41.1 and 34.1 mg kg^{-1} DW, respectively. In addition leaf W content was observed about four times than the roots in both species. To the best of our knowledge, there are no values for tungsten content of normal plants in order to assess the phytoremediation capabilities. Nevertheless, these values can be used for background purposes because of the mean values of 41.1 mg kg^{-1} DW for the leaves of the polluted samples. This value may be show the potential phytoremediation capability of the selected species.

4. Conclusion

We conclude that the element contents of the investigated species were changed depending on the increased tungsten and element concentrations. Further investigations have to be performed for the assessment of the tungsten phytoremediation purposes.

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Table1: Mean values of heavy metals determined in organs (mg/kg DW) of *Anthemis cretica* and *Tricetum flavescens* collected from unpolluted sites (Site-I and II) and mine waste pool (Site III) around tungsten mine work [For mean soil element values, different letters indicate significant differences between the sampling sites according to Tukey's HSD Test (rejection level 0.05). *n*=3, Means ± Standard Deviation]

Elements	**Plant Organ / Soil**	***Anthemis cretica***			***Tricetum flavescens***		
		Site-I	**Site-II**	**Site-III**	**Site-I**	**Site-II**	**Site-III**
W	Flowers	1.1^{b} ± 0.4	1.6^{b} ± 1.1	13.1^{a} ± 9.2	0.9^{a} ± 0.3	2.2^{a} ± 1.7	0.4^{a} ± 0.2
	Leaves	4.1^{a} ± 2.1	0.7^{b} ± 0.2	41.1^{a} ± 24.0	2.7^{b} ± 1.0	3.5^{b} ± 0.4	34.1^{a} ± 15.5
	Roots	4.9^{b} ± 2.5	0.4^{c} ± 0.3	9.3^{a} ± 0.4	1.6^{b} ± 0.6	1.1^{b} ± 0.5	8.3^{a} ± 0.8
	Soil	60.9^{b} ± 12.7	26.8^{b} ± 9.4	1378.6^{a} ± 672.3	31.7^{b} ± 8.1	43.3^{b} ± 16.3	1092.8^{a} ± 223.5
Mo	Flowers	1.1^{a} ± 0.3	0.6^{a} ± 0.4	0.7^{a} ± 0.6	2.9^{a} ± 0.7	0.4^{b} ± 0.2	0.1^{b} ± 0.1
	Leaves	1.5^{a} ± 0.7	0.3^{a} ± 0.3	0.9^{a} ± 0.8	4.0^{a} ± 1.2	0.5^{b} ± 0.4	1.5^{ab} ± 1.2
	Root	1.9^{a} ± 1.2	0.1^{a} ± 0.1	0.3^{ab} ± 0.2	3.7^{a} ± 0.7	0.8^{b} ± 0.5	1.4^{b} ± 1.1
	Soils	0.6^{ab} ± 0.2	0.4^{b} ± 0.2	0.8^{a} ± 0.01	0.3^{b} ± 0.0	0.4^{ab} ± 0.1	0.7^{a} ± 0.2
Zn	Flowers	20.5^{a} ± 4.7	50.7^{a} ± 23.7	130.4^{a} ± 76.4	22^{a} ± 3.2	35.6^{a} ± 10.2	28.7^{a} ± 6.2
	Leaves	47.7^{b} ± 6.2	42.3^{b} ± 18.5	178.8^{a} ± 24.1	4.0^{a} ± 1.2	24.7^{b} ± 9.3	184.8^{a} ± 92.8
	Roots	37.5^{b} ± 4.8	38.3^{b} ± 13.4	144.2^{a} ± 18.5	51.5^{b} ± 17.2	26.3^{b} ± 7.3	196.1^{a} ± 69.5
	Soils	55.2^{b} ± 16.7	16.1^{b} ± 2.8	376.9^{a} ± 25.6	14.3^{b} ± 1.4	28.7^{b} ± 1.8	352.5^{a} ± 91.7
Fe	Flowers	12.6^{b} ± 3.6	19.6^{b} ± 8.6	173.8^{a} ± 104.7	9.9^{a} ± 0.2	9.0^{a} ± 3.6	12.2^{a} ± 6.7
	Leaves	68.4^{a} ± 14.7	16.6^{b} ± 1.6	64.6^{a} ± 33.6	18.5^{a} ± 1.0	9.3^{a} ± 2.0	45.1^{a} ± 28.5
	Roots	64.4^{a} ± 30.8	17.0^{a} ± 13.5	26.4^{a} ± 18.5	55.8^{a} ± 17.2	7.9^{b} ± 3.5	29.1^{ab} ± 11.8
	Soils	236.1^{b} ± 87.5	152.8^{b} ± 36.6	1426.4^{a} ± 75.2	130.5^{b} ± 16.6	130.3^{b} ± 16.5	1192.1^{a} ± 402.7
Cu	Flowers	8.5^{a} ± 1.4	9.3^{a} ± 4.4	21.0^{a} ± 8.4	2.9^{a} ± 0.1	2.9^{a} ± 0.6	4.0^{a} ± 1.0
	Leaves	17.6^{b} ± 9.3	7.8^{b} ± 3.2	41.5^{a} ± 11.5	3.3^{b} ± 0.9	2.4^{b} ± 0.7	14.4^{a} ± 2.4
	Roots	15.1^{b} ± 4.5	6.1^{b} ± 3.0	30.5^{a} ± 9.0	7.0^{b} ± 1.1	3.6^{b} ± 1.5	50.1^{a} ± 5.1
	Soils	9.6^{b} ± 1.5	6.0^{b} ± 0.2	224.6^{a} ± 35.4	5.5^{b} ± 0.3	7.2^{b} ± 0.5	127.5^{a} ± 40.7

Table 1 (Continued)

Element	Plant Organ / Soil	*Anthemis cretica*			*Tricetum flavescens*		
		Site-I	**Site-II**	**Site-III**	**Site-I**	**Site-II**	**Site-III**
Co	Flowers	0.11[a] ± 0.02	0.65[a] ± 0.48	0.08[a] ± 0.01	0.09[ab]± 0.04	0.17[a] ± 0.05	0.02[b] ± 0.03
	Leaves	0.22[a] ± 0.06	0.16[ab]± 0.04	0.06[b] ± 0.01	0.11[a] ± 0.02	0.18[a] ± 0.05	0.11[a] ± 0.10
	Roots	0.35[a] ± 0.09	0.24[a] ± 0.23	0.03[a] ± 0.01	0.46[a] ± 0.14	0.24[a] ± 0.25	0.05[a] ± 0.02
	Soil	4.93[b] ± 2.52	0.37[c] ± 0.33	9.28[a] ± 0.40	0.30[a] ± 0.06	0.35[a] ± 0.04	0.09[b] ± 0.01
Bi	Flowers	0.16[b] ± 0.05	0.17[b] ± 0.10	10.16[a] ± 0.71	0.08[a] ± 0.05	0.10[a] ± 0.02	0.17[a] ± 0.13
	Leaves	0.43[b] ± 0.44	0.19[b] ± 0.01	6.03[a] ± 2.18	0.18[b] ± 0.14	0.19[b] ± 0.04	3.98[a] ± 0.74
	Roots	1.16[a] ± 0.47	0.17[a] ± 0.17	4.84[a] ± 3.26	1.02[b] ± 0.28	0.17[b] ± 0.08	5.79[a] ± 1.62
	Soil	2.67[b] ± 0.74	0.71[b] ± 0.34	43.16[a] ± 8.04	1.30[b] ± 0.48	0.98[b] ± 0.14	29.52[a] ± 8.21
Mn	Flowers	520[a] ± 186	991[a] ± 234	1189[a] ± 1073	728[a] ± 86	649[ab]± 170	321[b] ± 173
	Leaves	1099[a] ± 347	1791[a] ± 506	1175[a] ± 171	1027[a] ± 99	493[c] ± 88	788[b] ± 86
	Roots	1276[a] ± 550	605[a] ± 424	563[a] ± 7	916[a] ± 274	269[b] ± 64	1029[a] ± 149
	Soils	1375[b] ± 471	664[b] ± 181	6689[a] ± 465	476[b] ± 53	909[b] ± 136	2767[a] ± 359
Cd	Flowers	0.28[b] ± 0.11	0.68[b] ± 0.27	1.72[a] ± 0.54	0.03[a] ± 0.00	0.19[a] ± 0.16	0.02[a] ± 0.03
	Leaves	0.76[b] ± 0.27	0.42[b] ± 0.26	1.69[a] ± 0.06	0.04[b] ± 0.03	0.29[b] ± 0.26	1.04[a] ± 0.21
	Roots	1.49[a] ± 0.74	0.84[a] ± 0.52	2.35[a] ± 0.56	0.65[b] ± 0.11	0.88[b] ± 0.42	4.35[a] ± 1.60
	Soils	0.22[b] ± 0.03	0.02[b] ± 0.00	2.77[a] ± 0.22	0.08[b] ± 0.01	0.26[b] ± 0.01	2.48[a] ± 0.64
Cr	Flowers	1.1[a] ± 0.1	1.4[a] ± 0.8	1.1[a] ± 0.3	1.3[a] ± 0.2	0.8[ab]± 0.4	0.2[b] ± 0.2
	Leaves	1.8[a] ± 0.5	0.6[c] ± 0.1	1.2[b] ± 0.1	1.5[a] ± 0.2	0.5[c] ± 0.1	1.1[b] ± 0.1
	Roots	2.2[a] ± 0.4	1.1[ab]± 0.1	0.6[b] ± 0.1	2.1[a] ± 0.6	1.0[b] ± 0.4	1.4[ab]± 0.5
	Soils	7.1[a] ± 2.7	2.84[ab]± 2.1	0.5[b] ± 0.1	2.6[ab]± 2.0	6.5[a] ± 2.3	0.5[b] ± 0.2
As	Flowers	0.04[a] ± 0.02	0.20[a] ± 0.12	0.05[a] ± 0.04	0.04[a]± 0.03	0.05[a] ± 0.03	0.03[a] ± 0.01
	Leaves	0.24[a] ± 0.13	0.06[a] ± 0.01	0.08[a] ± 0.03	0.11[a] ± 0.03	0.08[a] ± 0.03	0.05[a] ± 0.03
	Roots	0.36[a] ± 0.13	0.11[b] ± 0.11	0.01[b] ± 0.00	0.33[a] ± 0.15	0.07[b] ± 0.06	0.02[b] ± 0.01
	Soils	1.07[a] ± 0.38	0.40[b] ± 0.09	0.95[ab]± 0.15	0.44[b] ± 0.07	1.06[a] ± 0.16	0.91[a] ± 0.15