

Pb-Zn Accumulation in Plants Grown in and Around a Pb-Zn Mine

Güllü Kirat^{1*}, Nasuh Aydın^{2**}

¹Faculty of Architecture and Engineering, Department of Geological Engineering,
Bozok University

²Faculty of Architecture and Engineering, Department of Geological Engineering,
Balıkesir University

Received: 27 December 2013

Accepted: 5 September 2014

Abstract

The study area is located northeast of Akdağmadeni town center, 12 km from the town (Fig. 1). *Astragalus pycnocephalus* Fischer (local name: Kevan) and *Verbascum euphraticum* L. (local name: mullein) plants growing in nature around the mining area were chosen to be studied. The plants and the soil in which they grew were sampled and studied.

The vicinity of the Akdağmadeni Pb-Zn mining area is being polluted due to natural causes and mining activities. The surrounding areas and the plants growing in the study area are strongly affected by the pollution. The amount of Pb changes between 29.87 and 7839.53 mg/kg, and Zn changes between 48.6 and 9909.13 mg/kg in the soil where *A. pycnocephalus* grew. The concentration of Pb changes between 52.96 and 9909.13 mg/kg and the concentration of Zn changes between 115.1 and 10000 mg/kg in the soil where *V. Euphraticum* grew. Depending on the Pb and Zn concentrations in soil, *A. Pycnocephalus* and *V. Euphraticum* are determined as indicator plants.

A. pycnocephalus and *V. euphraticum* at some locations are determined as hyperaccumulators for Pb and Zn due to the determined concentration values (Pb:>1000 mg/kg, Zn:>10000 mg/kg), calculated enrichment coefficient, and translocation factor values (>1).

Keywords: coefficient, hyperaccumulator, polluted, translocation factor

Introduction

Plant samples are collected in and around the Pb-Zn deposit in the study area. Some of these plants are multi-year trees and some of them are seasonal or multi-year herbaceous plants. *A. pycnocephalus* and *V. euphraticum* plants are sampled in the study area by considering local taxonomy.

Metal concentrations in plants alter with plant species. Plant uptake of heavy metals from soil occurs either with

the mass flow of water into the roots, or through transport crossing the plasma membrane of root epidermal cells. Under normal growth conditions plants can potentially accumulate certain metal ions an order of magnitude greater than the surrounding medium [1].

A. pycnocephalus is one of the largest genera of vascular plants in North America, South America, Europe, Asia, and on tropical African mountains, and is distributed around semiarid steppe regions. It is represented by approximately 3,000 taxa in the world and is also the largest genus in Turkey, where it is represented by 463 taxa (including subspecies and types), 210 (41%) of them endemic, and is classified in 63 sections [2, 3].

*e-mail: gullu.kirat@bozok.edu.tr

**e-mail: nasuhaydin@hotmail.com.tr

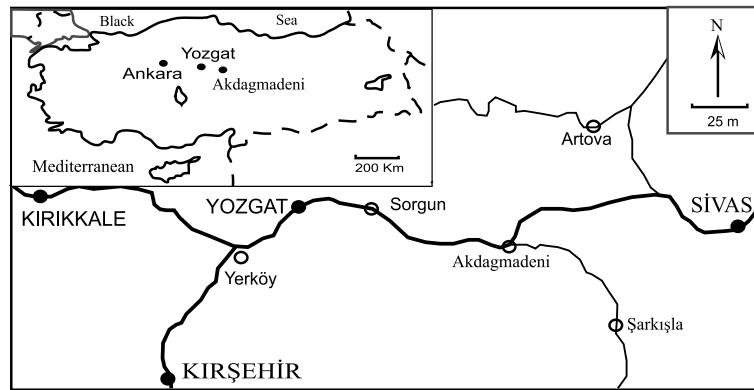


Fig. 1. Map of the study area.

The roots of some *A. pycnocephalus* are well known in traditional medicine as remedies for animal bites and poisons, wounds, burns, leukemia, and uterine cancer. They are also famous for their antimicrobial, antiperspirant, anti-inflammatory, diuretic, and tonic effects [3].

V. euphraticum, common name mulleins, comprises about 360 species of flowering plants in the Scrophulariaceae family, predominantly distributed in Asia, Europe, and North America [4].

The flowers and leaves of the *V. euphraticum* plant are analgesic, spasmolytic, anti-inflammatory, antiseptic, emollient, astringent, diuretic, expectorant, and vulnerary [5]. Homeopathic formulations containing fresh leaves are used in the treatment of long-standing headaches accompanied with oppression of the ear. Ointments prepared from leaves are used for burns and earache. Topically, the poultice of the leaves is a good healer of wounds and is also applied to ulcers, tumors, and piles. A poultice made from the seeds and leaves is used to draw out splinters [6].

Our study is needed to understand the concentrations of heavy metals by soil components and plant roots. It allows optimizing the plant nutrition in soils with a low content of nutrient elements and accumulation of heavy metals in plants on the soils. Knowledge about metal compounds in soil provides a deeper insight to evaluating the main supply of plants with these metals [3].

Environmental conditions play an important role for the uptake of heavy metal by plants, with the soil-plant transfer of metals, being a very complex process governed by several factors (natural and anthropogenic) such as soil heavy metal content, the sorptive capacity of the soil. These factors are known to control the processes of mobility and availability of metals in soils [7].

According to recent studies, in order to be considered as a hyperaccumulator, a plant should contain 1000 mg/kg Pb and >10,000 mg/kg Zn, and its translocation factor and enrichment coefficient must be greater than 1 [8-13]. Additionally, it must contain 10-to-500 fold more metal compared to the plants that grew in the unpolluted locations [8, 7, 14].

The heavy metals are a serious problem from the viewpoint of environmental pollution. It has been

defined as chemical pollution by many researchers and hyperaccumulator plants were used in order to remove the heavy metals from the environment. The hyperaccumulator plants take the heavy metals into their system and remove them from the soil [4, 8, 5, 15-18].

In the last decade, many researchers have studied the metal hyperaccumulator function of some plants

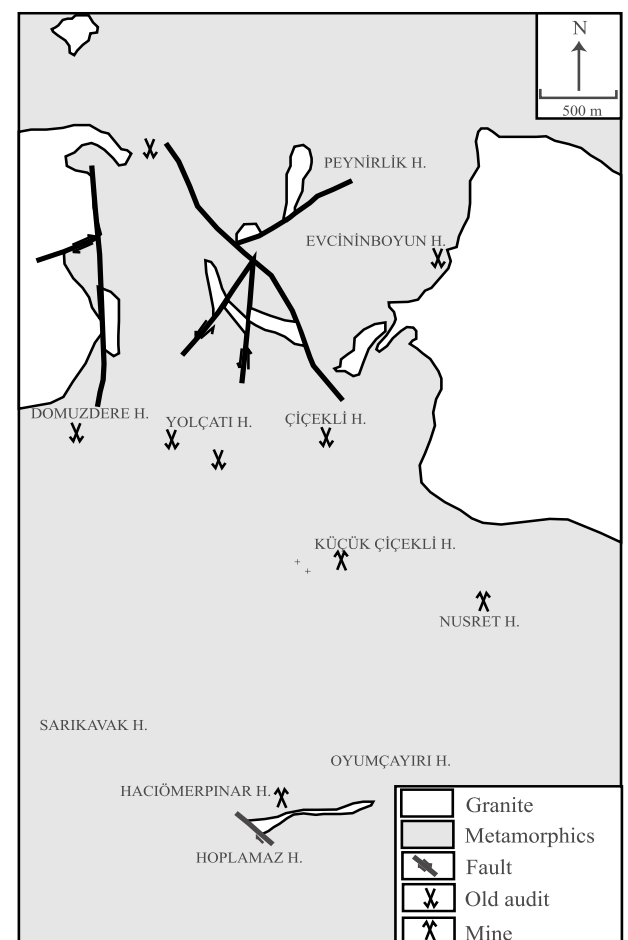


Fig. 2. Topographic map of the Akdağmadeni Pb-Zn Mine and its surroundings, and sample locations of the plant and soil samples. (●: *Astragalus pycnocephalus* Fischer, □: *Verbascum euphraticum* L.).

Table 1. Pb (mg/kg) content, enrichment coefficient, and translocation factor of the soil, and the roots, stems and leaves of *A. pycnocephalus* in the study area (L: Leaves, S: Stem, R: Root, S: Soil, S.D.: Standard Deviation, L.N.: Location Number).

Pb (mg/kg)								
L.N.	Soil	Root	Stem	Leaf	Enrichement coefficient			Translocation factor
					L/S	S/S	R/S	
A-1	346.22	677.46	2914.94	1434.09	4.1421	8.4193	1.9567	2.1169
A-2	411.44	437.21	414.94	386.89	0.9403	1.0085	1.0626	0.8849
A-3	741.58	3443.6	3415.52	2548.71	3.4369	4.6057	4.6436	0.7401
A-4	5986.5	3948.46	9130.07	5993.81	1.0012	1.5251	0.6596	1.518
A-5	653.14	1241.4	2783.52	1503.52	2.302	4.2618	1.9007	1.2111
A-6	399.86	448.07	1476.84	658.3	1.6463	3.6934	1.1206	1.4692
A-7	7839.53	9422.71	>10000	>10000	-	-	1.2019	-
A-8	2339.36	7767.66	>10000	>10000	-	-	3.3204	-
A-9	960.63	1012.94	1070.2	867.03	0.9026	1.1141	1.0545	0.856
A-10	7234.4	2778.43	3254.78	2584.74	0.3573	0.4499	0.3841	0.9303
A-11	67.64	103.93	420.74	287.03	4.2435	6.2203	1.5365	2.7618
A-12	133.68	128.54	157.96	140.52	1.0512	1.1816	0.9616	1.0932
A-13	29.87	84.67	86.51	75.36	2.5229	2.8962	2.8346	0.89
A-14	263.49	333.29	416.93	345.66	1.3119	1.5823	1.2649	1.0371
A-15	34.37	68.46	129.08	77.13	2.2441	3.7556	1.9919	1.1266
A-16	108.44	82.14	325.9	182.68	1.6846	3.0053	0.7575	2.224
Mean	1721.88	1998.69	1857.00	1220.39	-	-	-	-
S.D.	2709.51	2874.62	2443.03	1621.26	-	-	-	-

[1, 2, 6-10, 19-21]. Hyperaccumulator plants function depending on the species, the conditions of the soil (organic matter content, cation exchange capability, etc.), and the properties of the heavy metals [19].

The objective of this study is to determine the concentrations of Pb and Zn in *V. Euphraticum* and *A. Pycnocephalus* growing on a contaminated site, and to compare metal concentrations to those in the roots, stems, and leaves in soils. Additionally, the soil and these samples were analyzed in order to determine the hyperaccumulator and indicator plants for soils contaminated with Pb and Zn. Information obtained from this study should provide understanding of using native plants to remedy metal-contaminated sites.

Materials and Methods

Site Description

The study area is located 120 km east of Yozgat city and 25 km south of Akdagmadeni province. Akdagmadeni Pb and Zn deposits are located in Akdagmadeni Massive Complex, located in northern eastern Central Anatolian Crystalline Massive Complex (Fig. 2).

Akdagmadeni Pb and Zn deposits are in the Anatolide Tectonic Unit [22]. The Ankara-Erzincan suture zone extends E-W to the north and is related with a thrust zone from south to north of study area.

The study was carried out in the environs of Akdagmadeni, one of the most polluted regions of central Turkey (Fig. 1). This area has been affected by mining activity since medieval times. Severe metal contamination is a phenomenon mainly of the last century, due to intensive Zn-Pb ore exploitation, processing, and smelting activity [23].

Most soils in this region developed on metamorphic rocks and granite are covered largely by pine forests. The original soil cover was destroyed by excavation of Zn-Pb deposits in the center of the mining area, where the ore-bearing rock outcrops.

The majority of the study area is afforested. Pine plantations prevail because they can be maintained successfully not only by forestry practices but also on mining waste; since pine is relatively resistant to soil metal contamination. The remaining parts of the study area are covered by various vegetation types. These plant communities consist of species preferring shallow, dry, calcareous soil, and tolerating high concentrations of metals.

Table 2. Zn (mg/kg) content, enrichment coefficient, translocation factor of the soil, and the roots, stems and leaves of *A. pycnocephalus* in the study area (L: Leaves, S: Stem, R: Root, S: Soil, S.D.: Standard Deviation, L.N.: Location Number).

Zn (mg/kg)								
L.N.	Soil	Root	Stem	Leaf	Enrichment coefficient			Translocation factor
					L/S	S/S	R/S	
A-1	364.9	815.9	2633.7	1213.4	3.325	7.218	2.236	1.487
A-2	590	768.8	819.9	620.4	1.052	1.39	1.303	0.807
A-3	449.2	1668.7	1988.4	1665.5	3.708	4.427	3.715	0.998
A-4	2939.7	1745.7	2836.5	1771.7	0.603	0.965	0.594	1.015
A-5	359.6	812	1436.1	875.2	2.434	3.994	2.258	1.078
A-6	298	619.5	1164.9	522.1	1.752	3.909	2.079	0.843
A-7	>10000	>10000	>10000	>10000	–	–	–	–
A-8	974.2	2616.1	4135.2	3005.1	3.085	4.245	2.685	1.149
A-9	981.4	1148.4	990.4	936.2	0.954	1.009	1.17	0.815
A-10	>10000	4917	4855.4	4333.5	–	–	–	0.881
A-11	177.4	440.5	1018.2	819.9	4.622	5.74	2.483	1.861
A-12	203.8	350.4	435.4	253.9	1.246	2.136	1.719	0.725
A-13	48.6	362	256.4	617.5	12.706	5.276	7.449	1.706
A-14	410.2	576.5	534.7	508	1.238	1.304	1.405	0.881
A-15	92.4	209.3	278.9	318.4	3.446	3.018	2.265	1.521
A-16	148.2	196.3	448.7	423	2.854	3.028	1.325	2.155
Mean	574.1	1149.8	1588.9	1192.3	–	–	–	–
S.D.	739.8	1239.3	1431.1	1128.5	–	–	–	–

There are more than one Pb-Zn mining operation in the study area and its vicinity. Primary sulphide and oxide minerals found in the Akdağmadeni Pb-Zn mine are sphalerite, galenite, pyrite, chalcocopyrite, pyrotin, bornite, molybdenite, sulfosalts, magnetite, hematite, ilmenite, and rutile. Secondary minerals found in the mine are limonite, sericite, martite, chalcocine and covellite. Besides, graphite is commonly present in wall rock and ore bodies. Garnet, clinopyroxene, epidote, tremolite, calcite, quartz, chlorite, and a lesser amount of vezuvian, wollastonite, actinolite, clinozoisite, titanite, fluorite, and ilvaite are present as gangue minerals. In addition, fluorite and barite veinlets are present in marble and syenite [15].

Skarn zones were formed along the contacts of the regionally exhumed metamorphic rocks and intruded by younger acidic volcanic rocks. The skarn formations form a belt along the contacts and skarn zones are better developed along the marble and granite contacts compared to contacts with the other kind of metamorphic rocks [16, 17]. The magmatic rocks in the study area are made up of only quartz monzonites and subvolcanic rocks that crop out in limited areas.

Akdağmadeni Pb-Zn deposits are located in skarn zones that are formed along contacts of regional metamorphics and adamellit plutons. Skarn formations occurred as different

phases both in regional metamorphics and intrusive rocks. Uneconomical magnetite mineralization was formed and overprinted by late-stage Pb-Zn mineralization.

Plant Analysis

Native plant samples were randomly collected from the study area. Then the samples were packed, numbered, and delivered to the laboratory. The roots, stems, and leaves of the plant samples were separated. All the samples were first washed in tap water and then in distilled water and dried.

Inductively coupled plasma mass spectrometry (ICP-MS) has become a popular technique in multi-element analysis since the first commercial instrument became available in the 1980s. Semi quantitative analysis by ICP-MS has proven to be a powerful tool for fast screening. In addition, it does not require the element of interest to be present in the calibration standard, making it especially useful for the analysis of unknown samples [24].

Higher temperatures are required for ashing up or flameless burning of the plant samples and previous studies have suggested temperatures varying from 475°C up to 600°C [25]. The dried plant samples (approximately 2.0-3.0 g) were ashed by heating at 250°C, and then

Table 3. Pb (mg/kg) content, enrichment coefficient, translocation factor of the soil, and the roots, stems and leaves of *V. euphraticum* in the study area (L: Leaves, S: Stem, R: Root, S: Soil, S.D.: Standard Deviation, L.N.: Location Number).

L.N.	Pb (mg/kg)							
	Soil	Root	Stem	Leaf	Enrichment coefficient			Translocation factor
					L/S	S/S	R/S	
V-1	843.32	462.45	191.13	2096.62	2.486	0.227	0.548	4.534
V-2	9241.73	6143.34	550.3	7584.19	0.821	0.06	0.665	1.235
V-3	8545.35	1622.78	372.8	7640.52	0.894	0.044	0.19	4.708
V-4	8498.78	1567.77	146.9	2166.5	0.255	0.017	0.184	1.382
V-5	9909.13	5419.98	357.28	>10000	1.009	0.036	0.547	–
V-6	7236.58	3318.4	n.a.	5041.63	0.697	–	0.459	1.519
V-7	1415.04	542.41	133.33	748.59	0.529	0.094	0.383	1.38
V-8	2641.19	2139.62	n.a.	2063.24	0.781	–	0.81	0.964
V-9	146.94	78.65	47.84	35.56	0.242	0.326	0.535	0.452
V-10	2177.57	1888.51	291.22	659.72	0.303	0.134	0.867	0.349
V-11	63.47	n.a.	26.26	44.39	0.699	0.414	0.002	–
V-12	113.47	n.a.	66.23	68.51	0.604	0.584	0.001	–
V-13	52.96	26.46	25.61	79.58	1.503	0.484	0.5	3.008
V-14	114.02	64.56	176.37	131.31	1.152	1.547	0.566	2.034
Mean	3642.8	1939.6	198.8	2181.6	–	–	–	–
S.D.	4018.5	2061.3	163.8	2796.1	–	–	–	–

n.a.: not available

the temperature was gradually increased to 500°C for two hours [26]. The ashed samples were sent to ACME Analytical laboratories for analysis.

The ashed samples were digested for an hour at 95°C by using the mixture of HCl-HNO₃-H₂O (6 ml of the mixture of 1:1:1 was used per 1.0 g of the ashed sample). Then the ashed samples were analyzed by Aqua Regia digestion after extraction by using a microwave digestion system [24]. Precision values were calculated according to repeated analysis values. The ashed samples were analyzed by ICP-MS for ultralow detection limits, which are as follows: Pb 0.01 mg/kg, Zn 0.1 mg/kg.

Soil Analysis

Soil samples were taken from surroundings of the roots of the sampled plants and from 25 to 30 cm depths.

Soil samples were air-dried indoors at room temperature for approximately two weeks. They were then gently disaggregated, cleaned of extraneous material, and sieved through a nylon sieve of 2 mm [27]. The <2 mm material was homogenized and a quarter was milled in an agate mill to an analytical grain size of <0.125 mm.

Soil samples were digested for an hour at 95°C by using the mixture of HCl-HNO₃-H₂O (6 ml of the mixture of 1/1/1 was used per 1.0 g). Then the soil samples were

analyzed by 1:1:1 Aqua Regia digestion after extraction by using a microwave digestion system.

Pb and Zn analysis were done by ICP-MS at ACME Analytical laboratories. Ultralow detection limits of the elements are as follows: Pb 0.01 mg/kg, Zn 0.1 mg/kg.

Results and Discussion

Concentrations of Pb and Zn in Soils

Tables 1, 2, 3 and 4 show Pb-Zn analytical results of soil samples on which *A. pycnocephalus* and *V. euphraticum* grew. Mean Pb and Zn values in the soil of these plants were 1,721.9 mg/kg and 3,642.8 mg/kg Pb; 574.1 mg/kg ve 1,531 mg/kg Zn, respectively. The mean Pb concentration in Florida soils is 77 mg/kg [28], while the global baseline level of Pb in uncontaminated surface soils is 20 mg/kg [29]. The reason of the higher mean values in soil in the study area is very high concentrations (Pb: A7: 7839.5 mg/kg, V5: 9,909.1 mg/kg; Zn: A4: 2,939.7 mg/kg, V4: 4,539.3 mg/kg) of Pb and Zn values in soil in some of the sample locations.

The relationship between Pb-Zn concentrations (logarithmic) in soil and plant roots, stems, and leaves are shown in Figs. 3 and 4. The fact is that the distributions of

Table 4. Zn (mg/kg) content, enrichment coefficient, translocation factor of the soil, and the roots, stems, and leaves of *V. euphraticum* in the study area (L: Leaves, S: Stem, R: Root, S: Soil, S.D.: Standard Deviation, L.N.: Location Number).

Zn (mg/kg)								
L.N.	Soil	Root	Stem	Leaf	Enrichement coefficient			Translocation factor
					L/S	S/S	R/S	
V-1	834.8	843	450.4	2170.5	2.6	0.54	1.0098	2.5747
V-2	2919.9	3099.5	550.3	2150.1	0.7364	0.188	1.0615	0.6937
V-3	3543.3	1076.4	372.8	1933.7	0.5457	0.105	0.3038	1.7965
V-4	4539.3	2158.7	378.2	1408.6	0.3103	0.083	0.4756	0.6525
V-5	>10000	8975.7	671.6	>10000	–	–	–	1.1141
V-6	>10000	5409.2	n.a.	8093.1	–	–	–	1.4962
V-7	1384.6	1770	504.6	1135.2	0.82	0.364	1.278	0.6414
V-8	3672.9	3337	n.a.	2619.1	0.713	–	0.909	0.7849
V-9	210.1	368.1	317.4	446.6	2.126	1.511	1.752	1.2133
V-10	607.9	689.4	252.7	1262.1	2.076	0.416	1.134	1.8307
V-11	154.3	n.a.	225.7	256.1	1.66	1.463	0.001	-
V-12	237.6	n.a.	418.9	488.1	2.054	1.763	-	-
V-13	115.1	566.8	328.8	328	2.85	2.857	4.924	0.5787
V-14	151.6	378.4	339	381.4	2.516	2.236	2.496	1.0079
Mean	1531	2389.4	400.9	1744	–	–	–	–
SD	1656.8	2572.5	127.6	2071.9	–	–	–	–

n.a.: not available

the elements in the plant root, stem, and leaf show positive correlation with the element distributions in the soil (Figs. 3 and 4).

The Pb concentration in the contaminated soils changes between 400 and 800 mg/kg, whereas in the mining areas concentration values reach up to 1,000 mg/kg [30]. Pb concentration in soil is 10 to 35 mg/kg and Zn concentration is 70 to 90 mg/kg [31], and Pb concentration in soil is determined as 17 mg/kg and Zn concentration is determined as 36 mg/kg in different studies [32]. Chinese Environmental Quality Standards state threshold values for Pb and Zn in soil as ≤ 250 mg/kg and ≤ 200 mg/kg [33]. The upper limit of Pb concentration for European Commission (EC) is 300 mg/kg and 90-300 mg/kg for agricultural soils [34]. As reported [29], Zn concentrations in soil are 10-300 mg/kg and mean value is approximately 50 mg/kg. Soil samples taken from near mining areas have higher Pb and Zn concentrations than average values stated above. Therefore, it can be stated that these samples have a Pb-Zn anomaly (Tables 1 to 4).

Pb and Zn Concentrations in Plants

Metal concentrations in plants depend on the plant's species, the ionic and complex forms of elements in soil, pH of soil, redox conditions and amount of organic matter, as well as plant species, cultivars, and age. The

combination of elevated soil pH and high organic matter in the study space may have played a role in the limited plant availability of heavy metals in the soil [1]. Uptake of Pb in plants is regulated by pH, particle size, and cation exchange capacity of the soils as well as by root exudation and other physico-chemical parameters [35].

The mineral matter is made of sand, silt, and clay size particles – the basic texture of the soil. Organic matter includes plant and animal materials in various stages of decomposition. Organic matter has the ability to moderate major changes in soil pH, which is a measure of acidity or alkalinity as determined by the amount of positively charged hydrogen (H^+) ions in the soil solution.

Two common plants in the study area were sampled, their stems, roots and leaves were analyzed and results the presented in Tables 1-4. The Pb and Zn concentrations are high in different organs of plants growing in and around the mining area.

Metals can be accumulated in plant leaves through both root transfer and/or foliar transfer after deposition of atmospheric particles on the leaf surfaces. According to the pollution context, the foliar transfer of metals can be ignored, when ultra-fine particles interact with plant leaves and especially as Pb has low mobility in soil and is weakly phytoavailable by root uptake. Thus, supplementary studies are needed to compare the two pathways of exposure in terms of metal transfer, their

location and speciation in plant organs, and finally their environmental and health impacts [1].

The highest Pb concentrations in the study area are recorded as >10,000 mg/kg in the stems and leaves of *A. Pycnocephalus* (locations A7 and A8) and leaves of

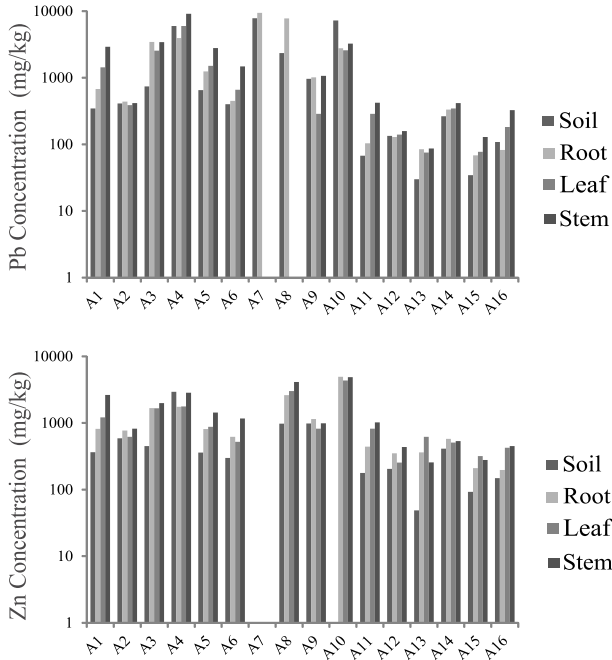


Fig. 3. The distribution of the elements according to sample locations, in the roots, stems and leaves of *A. pycnocephalus* plant and soil ((a) Pb an (b) Zn are given as mg/kg).

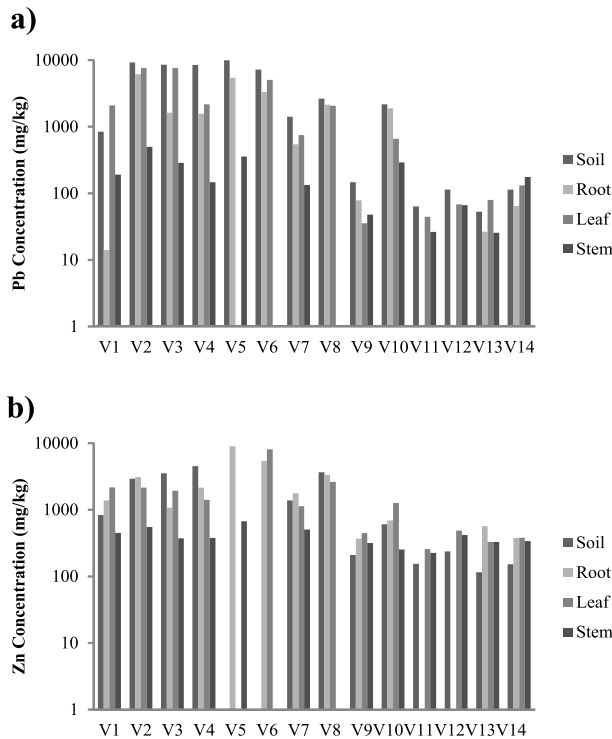


Fig. 4. The distribution of the elements according to sample locations in the roots, stems, and leaves of *V. euphraticum* plant and soil ((a) Pb an (b) Zn are given as mg/kg).

V. euphraticum (location V5). Plant leaves are known to reflect the elements inputs for a known exposure time [35]. Plant leaves collected from urban areas of Portugal accumulated up to 78 mg/g Pb dry weight in leaves and is suitable for monitoring Pb in air [36].

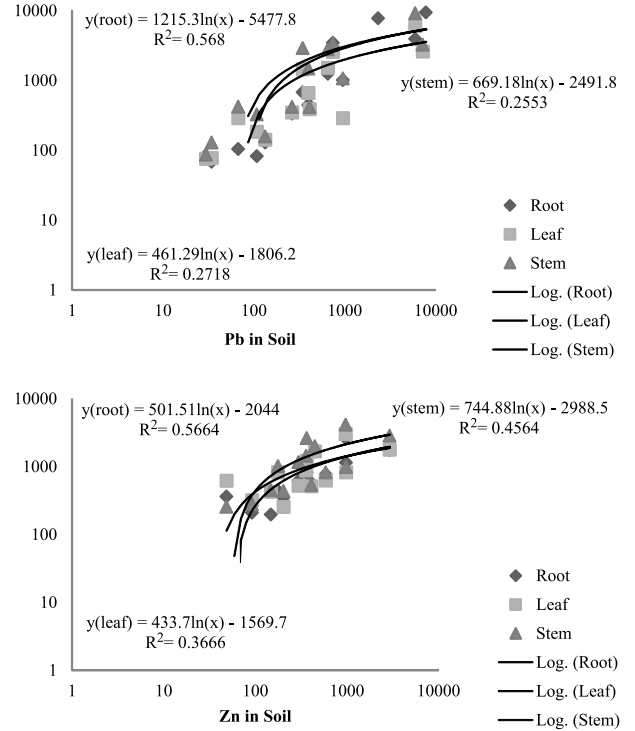


Fig. 5. Correlations between Pb and Zn contents of soil and plant (*A. pycnocephalus*), (mg/kg).

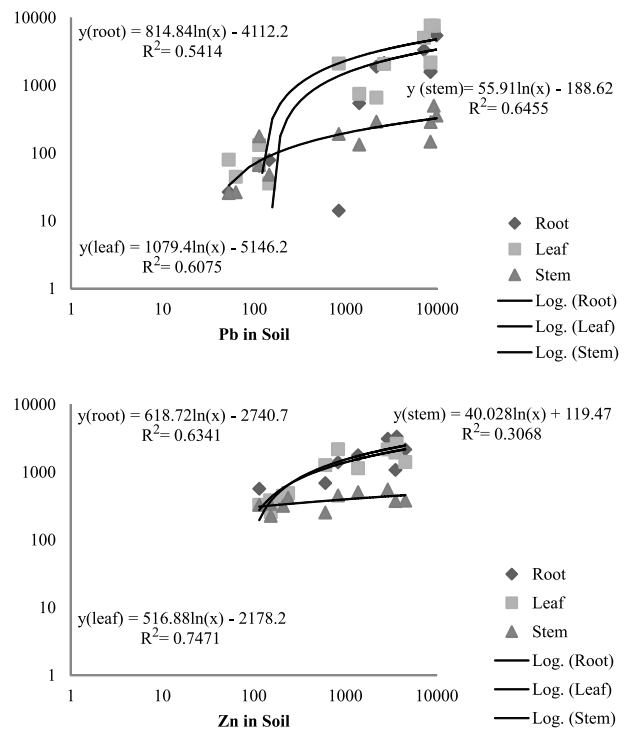


Fig. 6. Correlations between Pb and Zn contents of soil and plant (*V. euphraticum*), (mg/kg).

The highest Zn concentration in the study area is recorded as >10,000 mg/kg in the roots, stems, and leaves of *A. Pycnocephalus* (locations A7), and leaves of *V. euphraticum* (location V5). The lowest concentrations are determined in roots of *A. pycnocephalus* (68.46 mg/kg in sample A15) and stems of *V. euphraticum* (25.61 mg/kg at location V13) (Tables 1 to 4).

Sample locations of *A. pycnocephalus* and *V. euphraticum* are shown in Fig. 2. On the other hand, as can be seen in Figs. 5 and 6; correlation coefficients between experimental findings (of this study) Pb soil/Pb root ($r=0.75$), Pb soil/Pb stem ($r=0.51$), and Pb soil/Pb leaf ($r=0.52$); Zn soil/Zn root ($r=0.75$), Zn soil/Zn stem ($r=0.68$), and Zn soil/Zn leaf ($r=0.61$) of *A. pycnocephalus*; Pb soil/Pb root ($r=0.74$), Pb soil/Pb stem ($r=0.80$), and Pb soil/Pb leaf ($r=0.78$); Zn soil/Zn root ($r=0.80$), Zn soil/Zn stem ($r=0.55$), and Zn soil/Zn leaf ($r=0.86$) of *V. euphraticum* are important depending on sample quantity. In accordance with obtained data, direct proportionalities between Pb and Zn in plant samples of these chosen plant types in the study area are indicators (Figs. 5 and 6).

Metal concentrations in plants growing in uncontaminated soils were 0.3-18.8 and 6-126 mg/kg for Pb and Zn, respectively, whereas the highest metal concentrations in plants growing in contaminated soils were 1506 and 710 mg/kg for Pb and Zn, respectively [1]. [33] determined the median Pb content of the plants as 30 mg/kg; median Zn content is measured as ash weight (which can be 10-to-40 fold higher than dry weight) and as 20 mg/kg. Pb and Zn values of plants in the study area have anomalous values since they are not coherent with average values given in the literature (Table 1 to 4).

The enrichment factor for all the samples taken for Pb and Zn are presented in Tables 1 to 4. The case of plants' enrichment coefficient lower than 1 can be procured by saturation of roots and leaves by metal when inner metal concentration of plants is high. Enrichment factors smaller than 1 can be explained by saturation of roots and leaves by metal when inner metal concentrations of plants is high [6].

The translocation factor is defined as the ratio between the element concentrations in the leaves and in the roots. Translocation factors higher than 1 indicate that the metals were transported from the roots to stems and leaves [6, 7, 19]. Translocation factor from roots to leaves for Pb is calculated as 0.74 to 2.76 (*A. pycnocephalus*) – 0.35 to 4.71 (*V. euphraticum*); 0.73 to 2.16 (*A. pycnocephalus*) – 0.58 to 2.6 (*V. euphraticum*) for Zn. Translocation factors of Pb are greater than 1 for *A. pycnocephalus* and *V. euphraticum* (except for the locations, A2, A3, A9, A10, A13; V8, V9, V10), and the same factor of Zn is greater than 1 for *A. pycnocephalus* and *V. euphraticum* (except for locations A2, A3, A6, A9, A10, A12, A14; V2, V4, V7, V8, V13) (Tables 1 to 4).

Samples obtained from the study area have higher element concentrations compared to those growing in the uncontaminated areas: In *A. Pycnocephalus*, Pb is 17.3-to-1,826-fold and Zn is 8.55-to 161.8 fold; in *V. euphraticum* Pb is 5.12-to 110-fold and Zn is 7.52-to 22.3-fold. Pb and

Zn contents of *A. pycnocephalus* are between or greater than the stated fold factors in all locations.

Conclusion

The Akdağmadeni Pb-Zn ore deposit is one of the numerous lead-zinc deposits operated in Central Anatolia, Turkey. This deposit is located in Akdağ Massive, which is a part of the Kırşehir Crystalline Complex.

In this study *A. pycnocephalus* and *V. euphraticum* plants that naturally grew in and around Akdağmadeni Pb-Zn mining area and the soils in which these plants grew were sampled. The plant and soil samples were analyzed and it was found that the Pb and Zn elements found in the soil were also accumulated in the roots, stems, and leaves of the plants.

Pb and Zn contents in *A. pycnocephalus* and *V. euphraticum* plants and the soil on which these plants grew near the Akdağmadeni lead-zinc deposit is determined. Moreover, hyperaccumulator and indicator plants are determined for Pb and Zn elements. There are some conditions for determination of hyperaccumulator plants. Firstly, Pb (>1000 mg/kg) and Zn (>10,000 mg/kg) concentrations must be indicated values. Secondly, time factors must be between 10-and 500-fold. In addition, translocation coefficient and enrichment factor must be greater than 1 based on these conditions.

Pb and Zn contents of *A. pycnocephalus* and *V. euphraticum* samples and the soil samples in which these plants grew are studied. In this study, hyperaccumulator and indicator plants are also determined for Pb and Zn elements.

Pb concentration of *A. pycnocephalus* in locations A3-A5, A7-A10 (root), A1, A3-A10 (stem), and A1, A3-A5, A7, A8, A10 (leaf); *V. euphraticum* in locations V2-V6, V8, V10 (root) and V1-V6, V8 (leaf) is greater than 1000 mg kg⁻¹. Fold values are between 10 and 500, and even greater in mining areas (10-2000 fold) in all sample locations except for locations V2, V3, and V5. In addition, translocation coefficients and enrichment factors of most sample locations are greater than 1. All these facts indicate that these are hyperaccumulator plants for Pb.

Zn is concentrated more than >10,000 mg/kg in *A. pycnocephalus* at location A7 and in *V. euphraticum* at the location V5. Fold factors are between 10 and 500, and higher values are also found (10 to 971 fold at mining area). Moreover, translocation coefficients and enrichment factors are higher than 1 (it is lower than 1 for stem/soil and root/soil). These results indicate that the *A. pycnocephalus* plant is a hyperaccumulator for Zn.

Since there is a direct proportion between the elements in the plant and soil samples, it can be referred that these plants are indicator plants.

This study is to compare metal concentrations in the plants and the soils. Higher concentrations of Pb and Zn are determined in some of the plant and soil samples. Studied plants can be used for remediation of soils contaminated by Pb and Zn mineralization.

Acknowledgement

This study was carried out within grants The Scientific And Technological Research Council Of Turkey (TÜBİTAK).

References

- YOON J., CAO X., ZHOU Q., MA L.Q., Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. *Sci. Total Environ.*, **368**, 456-464, **2006**.
- SAĞIROĞLU A., ŞAŞMAZ A., ŞEN Ö., Hyperaccumulator plants of the Keban mining district and their impact on the environment. *Pol. J. Environ. Stud.* **15** (2), 317-325, **2006**.
- MINKINA T.M., MOTUZOVA G.V., MANDZHIEVA S.S., NAZARENKO O.G., Ecological resistance of the soil-plant system to contamination by heavy metals. *J. Geochem. Explor.*, **123**, 33-40, **2012**.
- BAKER A.J.M., MCGRATH S.P., REEVES R.D., SMITH J.A.C., Metal Hyperaccumulator Plants: A Review of the Ecology and Physiology of a Biological Resource for Phytoremediation of Metal Polluted Soils. In: *Phytoremediation of Contaminated Soil and Water*, Terry, N. and G. S. Banuelos (Eds.). CRC Press, Boca Raton, pp: 85-107, **2000**.
- BARRUTIA O., ARTETXE U., HERNÁNDEZ A., OLANO J.M., GARCÍA-PLAZAOLA J.I., GARBISU C., BECERRIL J.M., Native Plant Communities in an Abandoned Pb-Zn Mining Area of Northern Spain: Implications for Phytoremediation and Germplasm Preservation, *International Journal of Phytoremediation*, **13**, 256-270, **2011**.
- YANQUN Z., YUAN L., JIANJUN C., LI Q., SCHVARTZ C., Hyperaccumulation of Pb, Zn and Cd in herbaceous grown on lead – zinc mining area in Yunan, China. *Environ. Int.*, **31**, 755-762, **2005**.
- XIAOHAI L., YUNTAO G., KHAN S., GANG D., AIKUI C., LI L., LEI Z., ZHONGHAN L., XUECAN W., Accumulation of Pb, Cu, and Zn in native plants growing on contaminated sites and their potential accumulation capacity in Heqing, Yunan. *J. Environ. Sci.*, **20**, 1469-1474, **2008**.
- GRATAO P.L., POLLE A., LEA P.J., AZEVEDO R.A., Making the life of heavy metals-stressed plant a little easier. *Functional Plant Biology*. **32**, 481-494, **2005**.
- LORESTANI B., CHERAGHI M., YOUSEFI N., Accumulation Of Pb, Fe, Mn, Cu and Zn In Plants and Choice Of Hyperaccumulator Plant In The Industrial Town Of VIAN, IRAN. *Arch. Biol. Sci., Belgrade*, **63** (3), 739-745, **2011**.
- GUNDUZ S., UYGUR F.N., KAHRAMANOĞLU I., Heavy metal Phytoremediation potentials of *Lepidum sativum* L., *Lactuca sativa* L., *Spinacia oleracea* L. and *Raphanus sativus* L, *Agriculture and Food Science Research*, **1** (1), 001-005, **2012**.
- RODRIGUEZ J.H., SALAZAR M.J., STEFFAN L., PIGNATA M.L., FRANZARING J., KLUMPP A., FANGMEIER A., Assessment of Pb and Zn contents in agricultural soils and soybean crops near to a former battery recycling plant in Córdoba, Argentina. *J. Geochem. Explor.*, **2014**, (Article in press).
- YANQUN Z., YUAN L., SCHVARTZ C., LANGLADEC L., FAN L., Accumulation of Pb, Cd, Cu and Zn in plants and hyperaccumulator choice in Lanping lead-zinc mine area, *China Environment International*, **30**, 567-576, **2004**.
- BAKER A.J.M., BROOKS R.R., Terrestrial higher plants which accumulate metallic elements – a review of their distribution, ecology and phytochemistry. *Biorecovery*, **1**, 81-126, **1989**.
- SHEN Z.G., LIU Y.L., Progress in the study on the plants that hyperaccumulate heavy metal. *Plant Physiol Commun*, **34**, 133-9, **1989**.
- ÇOLAKOĞLU A., GENÇ Y., Macro-Micro Textures and Genetic Evolution of Lead-Zinc Deposits of Akdağmadeni (Yozgat) Region, *Geological Bulletin of Turkey*, **44**, 1, **2001**.
- SAĞIROĞLU A., Features and interpretations of the different types of skarn formations of the Akdağmadeni mining district, *Bulletin of the Geological Society of Turkey*, **27**, 69-8, **1984a**.
- SAĞIROĞLU A., Fluid inclusion studies on the contact metasomatic deposits of Akdağmadeni, *Bulletin of the Geological Society of Turkey*, **27**, 141-144, **1984**.
- BROOKS R.R. (ed), *Plants that hyperaccumulate heavy metals*. Wallingford, CAB International, p. 384, **1998**.
- SARMA H., Metal Hyperaccumulation in plants: A Review Focusing on Phytoremediation Technology. *Journal of Environmental Science and Technology*, **4** (2), 118-138, **2011**.
- ŞAŞMAZ A., YAMAN M., Determination of Uranium and Thorium in Soil and Plant Parts around Abandoned Pb-Zn-Cu Mining Area. *Communication Soil Science and Plant Analysis*, **39** (17-18), 2568-2583, **2008**.
- KIRAT G., Reflections Of The Soil Metal Contents In Plants Around Görgü Pb-Zn Deposits Malatya, Turkey Firat University, Graduate School of Natural and Applied Sciences, 210 p. Elazığ. **2009**.
- KETIN İ., Tectonic units of Anatolia: *Bulletin of the Mineral Research and Exploration*, **66**, 20-34, **1966**.
- CABALAJ., KRUPA P., MISZ-KENNAN M., Heavy metals in mycorrhizal rhizospheres contaminated by ZnPb mining and smelting around Olkusz in southern Poland. *Water Air Soil Poll.*, **199**, 139e149, **2009**.
- HAJARA E.W.I., SULAIMAN A.Z.B. SAKINAH A.M.M., Assessment of Heavy Metals Tolerance in Leaves, Stems and Flowers of *Stevia rebaudiana* Plant. *Procedia Environmental Sciences*, **20**, 386-393, **2014**.
- REICHMAN S.M., ASHER C.J., MULLIGAN D.R., Menzies, N.W., Seedling responses of three Australian tree species to toxic concentrations of zinc in solution culture. *Plant Soil*, **235**, 151-158, **2001**.
- SASMAZ A., Translocation and accumulation of boron in roots and shoots of plants grown in soils of low B concentration in Turkey's Keban Pb-Zn mining area. *International Journal of Phytoremediation*, **10**, 302-310, **2008**.
- SALMINEN R., CHIEF-ED., BATISTA M.J., BIDOVEC M., DEMETRIADES A., DE VIVO B., DE VOS W., DURIS M., GILUCIS A., GREGORAUSKIENE V., HALAMIC J., HEITZMANN P., LIMA A., JORDAN G., KLAVER G., KLEIN P., LIS J., LOCUTURA J., MARSINA K., MAZREKU A., O'CONNOR P.J., OLSSON,S., OTTESEN R.T., PETERSELL V., PLANT J.A., REEDER S., SALPETEUR I., SANDSTRÖM H., SIEWERS U., STEENFELDTA., TARVAINENT., FOREGS Geochemical Atlas of Europe, Part 1 - Background information, methodology and maps: Geological Survey of Finland, Espoo, pp. 525, **2005**. Also available at <http://www.gtk.fi/publ/foregsatlas/>.
- CHEN M., MAL.Q., HARRIS W.G., Baseline concentrations of 15 trace metals in Florida surface soils. *J. Environ. Qual.*, **28**, 1173-81, **1999**.

29. KABATA-PENDIAS A., PENDIAS H., Trace elements in soils and plants. CRC Press, Boca Raton, FL. **1992**.
30. SHARMA P., DUBEY R.S., Lead Toxicity in Plants, Braz. J. Plant Physiol., 17 (1), 35-52, **2005**.
31. SMITH W.H., 'Air pollution and forest'. Second edition. (Springer Verlag: New York), **1990**.
32. ROSE A.W., HAWKES H. E., WEBB J. S., Geochemistry in Mineral Exploration, second ed., Academic Press, Newyork, 657s, **1979**.
33. ZHUANG X., "Nano-imaging with STORM", Nature Photonics, **3**, 365-367, **2009**.
34. ATAYESE M.O., EIGBADON A.I., OLUWA K.A., Adesodun, J.K., Heavy Metal Contamination Of Amaranthus Grown Along Major Highways In Lagos, Nigeria, African Crop Science Journal, **16** (4), 225-235, **2009**.
35. AKINCI I., AKINCI S. YILMAZ K., Response of tomato (Solanum lycopersicum L.) to lead toxicity: Growth, element uptake, chlorophyll and water content. African Journal of Agricultural Research, **5** (6), 416-423, **2010**.
36. FREITAS H., NABAIS V., PAIVA J., Heavy metals pollution in the urban areas and roads of Portugal using Nerium oleander L. In: Proceedings of the International Conference Heavy metals in the Environment. (8^o, 12th -16th September, 1991) CEP consultants Ltd. Edinburgh. FARMER, J.G. ed., **1**, 240-242, **1991**.