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## Pb – Zn - Cd ACCUMULATOR PLANTS GROWN AROUND THE GÖRGÜ Pb – Zn MINE, YEŞİLYURT-MALATYA, TURKEY

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**ABSTRACT**

A study was carried out to identify Cd, Pb and Zn concentrations which exist in the roots and stems of Astragalus pycnocephalus Fischer and Verbascum euphraticum L. plants which grow in the Görgü Pb-Zn mining area. A total of 60 samples were collected, 30 samples from plants and 30 samples from the soils where the plants grow. When the anaytical results gained are statistically examined, according to correlation coefficients graphic between the soil and plant, finding positive correlation between (A. Pycnocephalus) soil-root (Cd, r =0.77), soil-stem (Cd, r =0.86) and soil-stem (Pb, r =0.77) could mean that these could be indicator plants and can be used for remediation of the soils polluted by Cd and Pb metals. It is observed that the metallic concentration times values of the plants in this study taken from polluted areas compared to the plants taken from unpolluted areas, are quite high in total 44 samples. Transition factor is >1 in some sample locations and range between 0.13 and 2.07. Enrichment coefficients is>1 for the location of V11 (Cd, root/soil). A. Pycnocephalus and V. Euphraticum, in some locations, according to transition factor, enrichment coefficients, times values and element concentrations could be identified as accumulator/hyperaccumulator for Cd, Pb and Zn elements..

### 1. Introduction

Mining industry has a destructive effect on the contamination of the environment because of the heavy metals (Navarro et al., 2008; Zhuang, 2009). Besides these mining works, industrial emissions, the use of fertilizers and pesticides increase the amount of heavy metals in the environment (Alloway, 1994; Yoon et al., 2006). Agricultural lands which are on the mining and its neighbouring area has the disadvantage of the accumulation of heavy metals in the soil in great amount which cause the increase of the content of heavy metals in food products and this increase affects the public health in adramatic way (Adriano, 2001; Pruvot et al., 2006). That's why, the heavy metals which exist in mineralization areas can be avoided thanks to growing the plants which are capable of collecting heavy metals in their structure (Wong, 2003; Yanqun et al., 2005). Also, techniques such as ditch opening, chemical stabilization, soil washing and burying are used to remove the heavy metals from the soil but these techniques are expensive, so they are not practical (Mehes-Smith et al., 2013). Remedial techniques carried out in a specific area are cheaper and more appropriate than a regional research field (Mitch, 2002; Pulford ve Watson, 2003). Generally, the use of plants in the improvement of the environment is an old and cheap method and that gives no damage to the environment.

Baker and Walker (1990) studied the plants in three groups: the ones which do not take metals into their structure directly, the ones which take them directly and the ones which take them into their structure in excessive amounts (accumulator and hyperaccumulator). The plants which can take the metals in their structure are grown in such areas to remove heavy metallic contamination. They are also used to find mine deposits containing the metal.

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There are many plant species discovered in Anatolia and the world for this purpose (Brook et al.,1995; Özdemir, 2003; 2005; 2009. Dunn, 2007). The metallic constructions are low in the plants which take place in non-metal containing group as metals are not carried from the roots to the branches but the metallic construction is high in the roots (Mehes-Smith et al., 2013). Heavy metal constructions accumulate in the tissues by moving from the plant roots to the top in a metal accumulator/hyperaccumulator (Salt et al., 1998; Kachout et al., 2009). Like accumulators, metal indicators accumulate the metals in the top tissues of the plants as well (Mganga et al., 2011; Mehes-Smith et al., 2013). While some species of plants only accumulate specific metals, some other plants accumulate many other metals in their structure (Mganga et al., 2011). Some kinds of plants die or undergo a physiological and morphological change as they continuously accumulate metals in their structure. These plants are biologically and ecologically important because they can be used as a contamination indicator. Also, they can absorb contaminants as accumulators (Mganga et al., 2011; Mehes-Smith et al., 2013).

The purpose of this study can be listed as below: 1. Identification of Cd, Pb ve Zn constructions in the *V. Euphraticum* and *A. Pycnocephalus* plant samples, 2. The comparison of element constructions in the plants with those of the soil in which they grow and their statistical examine 3. Identification of the accumulator/hyperaccumulator and indicator plants.

## 2. Geology of the Region and Mineralization

The study area is situated between the villages of Görgü and Seyitusagı in the city of Yesilyurt, Malatya (Figure 1). There are basically old Malatya metamorphics and Permo-Carbonifer which is formed from limestone and marbles in the region (Önal et al., 1990; Cengiz et al., 1991). They are found as comprised of schists. Malatya metamorphic rocks are overlained by volcano- sedimentary unit cut with andesitic volcanic rocks. Volcanits which exist in the study area near the business expose in a narrow area (Sağıroğlu, 1988). The third unit in the study area consists of alluvial deposits and soil cover. The mineralization exists in the fault zones which cut Malatya metamorphites (Figure 2).

According to Sağıroğlu (1988), Malatya metamorphites almost form from limestones in the study area. They observed as light grey limestones, mixed series, dark grey limestones and limestones breccia from the bottom to the top (Figure 2).

Volcanic rocks can be seperated from alteration zones and manganese dentritics and the units in the region as they are in the yellowish cream colour. Fault zones are exposed along these rocks (Sağıroğlu, 1988) (Figure 2).

In the northern part of the study area is a unit consisting of an alluvium and soil cover, which includes a wide area and slope rubble in places (Figure 2).

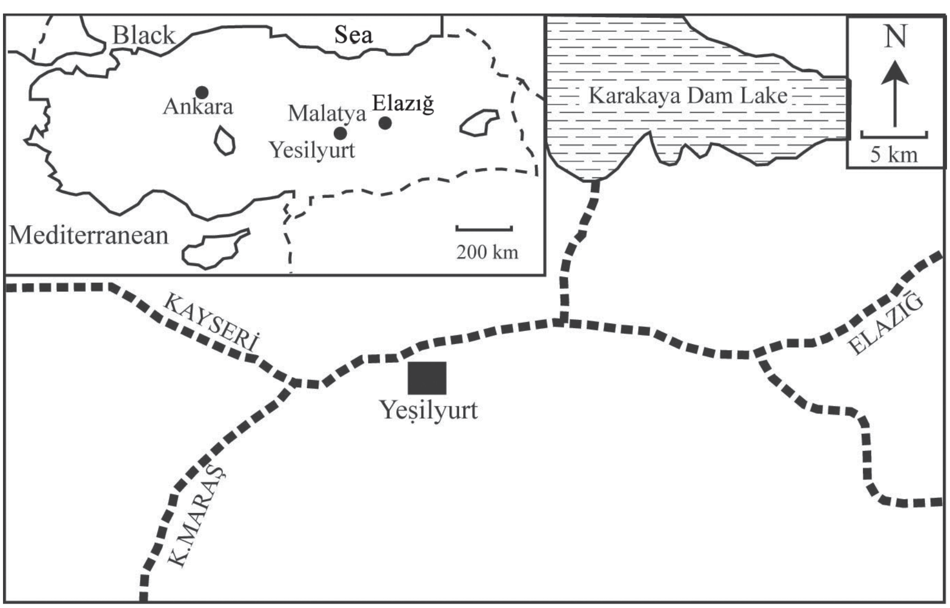


Figure 1- Location map of the study area.

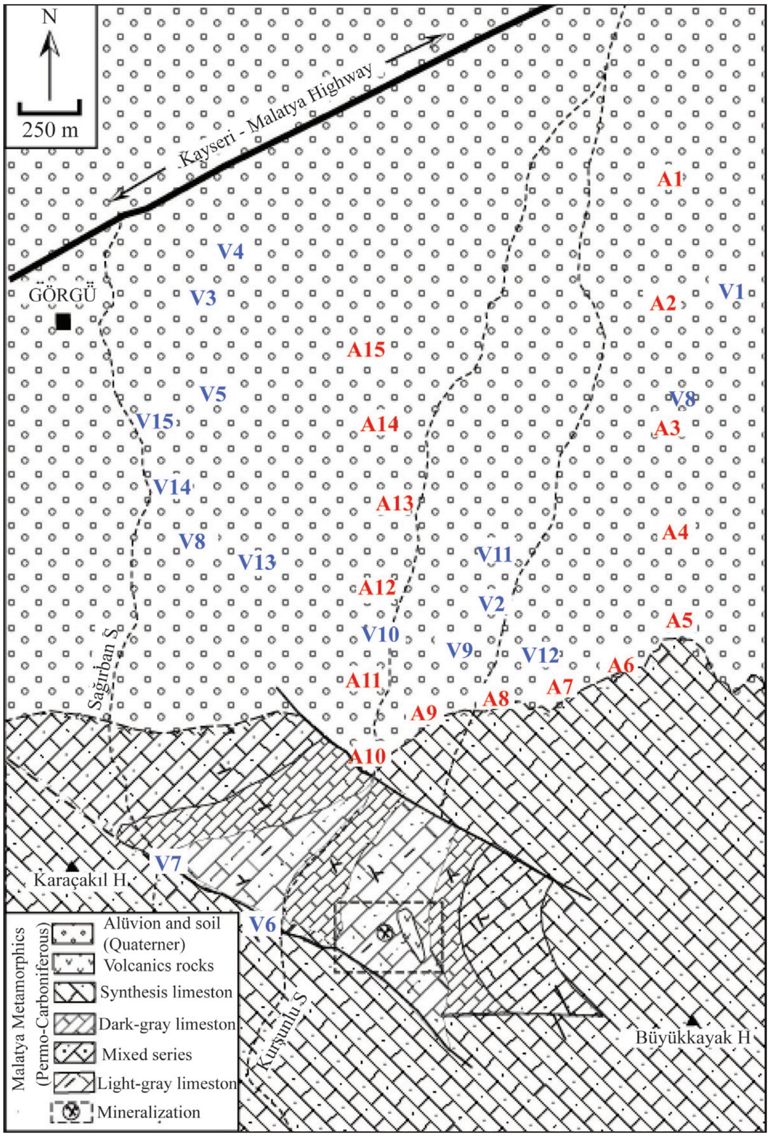


Figure 2- Distribution map of the geology of the study area (after Sağıroğlu, 1988), *A. pycnocephalus* plant samples (sample number is given in red color) and *V. euphraticum* plant samples (sample number is given in blue color).

There are two fault zones in the north-west direction and parallel to each other in the study area. No mineralization or alteration have been found in these two fault zones (Sağıroğlu, 1988).

This mineralization which is thought to have relation with dacitic-andesitic volcanism exists between volcano-sedimanter rocks and limestones contact and also in the units of both (Özen, 1991). Volcano-sedimanter rocks which are in grey, greenish grey, grayish blue and greenish brown colours have a structure which is rather weathered, cracked and with cavities. Also, sericitization and claying are seen locally in these rocks. The mineralogical composition of the host rock is formed from plagioclase, tremolite-actinolite, calcite, chlorite, titanite, apatite and opaque minerals (Güdücü, 1994).

The Görgü Pb-Zn mineralization forms from two different mineralizations which are classified as carbonated and sulfidic ones (Pratt, 1990). Carbonated ore (e.g., $ZnCO_3$, $PbCO_3$) exists around the cracks which start from the surface to the deeper parts where there is meteoric waters. This mineralization is in the yellow, brown-yellow colours and in the form of limonite rich Zn-carbonate. Ore minerals are simitsonite, limonite, zincite, hydrozincite, anglezite-serousite. The sulfidic ore (e.g., ZnS, PbS) continues vertically at a depth of 30-40 m. It is usually dark gray and exists scattered in limestones (Sağıroğlu, 1988). Ore minerals are galena, sphalerite, pyrite and marcasite (Sağıroğlu, 1988; Güdücü,1994).

## 3.Material and Method

In the PhD study performed by Kırat (2009), two seperate analyzes were carried out for *A. pycnocephalus* and *V. euphraticum* plants. Within the scope of this study, 30 specimens were taken from these two plants and the soil in which these plants were grown. Cd, Pb and Zn elemental analyses of the taken samples were carried out at ICP-MS (Inductively Coupled Plasma - Mass Spectrophotometer) and Yozgat-Bozok University, Science and Technology Application and Research Center (BILTEM).

ICP-MS device has the calibrations to carry out qualitative, quantitative and isotope ratio measurements. The Li, Be, and B measurements allow the passage of low-mass ions through the cell in the KED (Kinetic Energy Discrimination) mode in He. The quadrupole scan rate is 90.000 amu/s for each element. The system has a frequency of 2.0 MHz quadrupole for better peak resolution in complex samples and the linear dynamic range for the MS-detector in the system is 1-109 cps. Detection limits of analyzed soil and plant samples are Cd: 0.01 mg/kg, Pb: 0.01 mg/kg, Zn: 0.1 mg/kg.

### 3.1. Plant Analysis

In the study area, a total of 30 samples (Figure 3) were taken sybranchatically from the roots and branches of *A. pycnocephalus* and *V. euphraticum* plant samples (Figure 2). The roots and branches of the samples were separated and passed through the tap water first and pure water respectively. The plant samples which were dried at room temperature were then dehumidified by being kept waiting for 24 hours at 80-90°C in the oven.

4-5 g of dried plant samples were taken from each organ separately and placed in an ash oven. The samples which were placed in this oven were ashed at a temperature of 50°C for the beginning and burned to 550°C with an increase in temperature of 50°C per hour. Previous researchers have determined this temperature range to be between 475 - 550°C (Reichman et al., 2001).

### 3.2. Soil Analysis

A total of 30 soil samples were taken from the soil on which the plant specimens were grown (Figure 2). Soil specimens were taken at the depth of approximately 15-20 cm in the location where it was taken care not to have any metallic contamination and where the plant samples were taken, with the help of plastic shovels and by removing the plant roots. The collected soil samples were bagged, numbered and brought to the laboratory by passing through a 2 mm spaced plastic sieve. These samples were dried at room temperature for about two weeks.

To measure the pH values of soil samples, test tubes were prepared by mixing 10 ml of pure water (1: 2.5) with 4 g of soil sample. These prepared tubes were occasional mixed within 20-25 minutes and then their pH values were measured by pH meter (Table 1 and table 4).

A mixture was prepared from ash-derived plant sample, one gram of the soil on which the plants were grown and adding to 2 ml of concentrated $HNO_3$ by

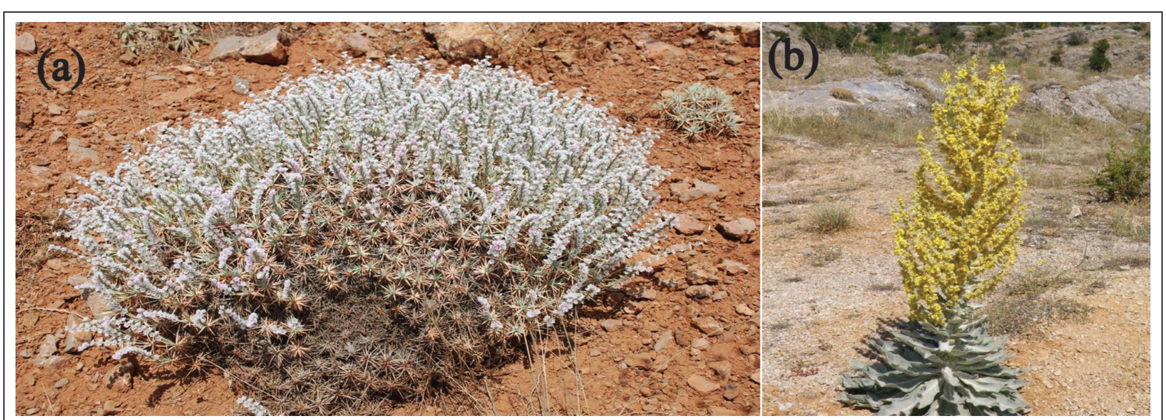


Figure 3- A view of (a) *A. pycnocephalus* and (b) *V. euphraticum* plants growing around the study area.

taking into account the sample preparation methods recommended by Hajara et al. (2014). The resulting mixture was dried by evaporating on a heating plate. The dried mixture was again mixed with HCl-$HNO_3$-$H_2O$ (from each acid 6 ml of a 1: 1: 1 mixture solution in each case). And the resulting mixture was completed with pure water to 25 ml.

## 4. Results and Discussion

### 4.1. Concentrations of Cd, Pb and Zn in Soil

The chemical analysis results for the Cd, Pb and Zn elements in the soil were evaluated statistically (values of > 10000 mg/kg were not used in statistical evaluation) (Table 1-6). A positive correlation was observed between the Pb element (r = 0.2) and pH of the soil where *A. pycnocephalus* plant was grown, while there was a negative correlation between Cd element (r = -0.47) and Zn element (r = -0.24) (Table 1-3). A negative correlation was observed between the Cd element (r = -0.22) and the Pb element (r = -0.2), while a positive correlation was found between the pH of the soil of the *V. euphraticum* plant and the Zn element (r = 0.2) (Table 4-6).

Cd is among the trace elements associated with phosphorites. Concentrations were found at 20 mg/kg in the phosphites (Il'in and Kiperman, 2001), at 0.15 mg/kg in granite, at 1.5 mg/kg in shales, at 6.5 mg/kg in black shales and at 2100-2600 mg/kg in sfaleritte (Olade, 1987). The existence of Cd in the soil depends on some properties such as organic matter, pH, grain size and cation exchange capacity. The mean Cd concentration in uncontaminated mine fields on Earth soil is 0.3 mg (Reimann and Caritat, 1998). According to a survey of Soil and Herbage contamination (Environment Agency, 2007), the contamination mean is 0.39 mg/kg in the soil of the UK (Health Protection Agency, 2009). The concentration of Cd in the soil was determined as 0.1-0.5 mg/kg by Rose et al. (1979) and 0.03 - 0.32 mg/kg in World Health Organization (Nazir et al., 2015).

The concentration of Cd in the soil where *A. pycnocephalus* plant grows ranges from 42.2-110.2

Table 1- Cd element distributions in *A. pycnocephalus* plant and statistical evaluations of distributions.

| Cd (mg/kg) | | | | | Enrichment Coefficient | | Transition Factor | Times |
|---|---|---|---|---|---|---|---|---|
| **Sample** | **pH** | **Soil** | **Root** | **Branch** | **R/S** | **B/S** | **B/R** | **B/Cd** |
| **A1** | 5.2 | 86.2 | 6.7 | 8.6 | 0.08 | 0.10 | 1.28 | 8.6 |
| **A2** | 5.3 | 93.6 | 7.8 | 10.2 | 0.08 | 0.11 | 1.31 | 10.2 |
| **A3** | 5.1 | 87.3 | 8.3 | 9.3 | 0.10 | 0.11 | 1.12 | 9.3 |
| **A4** | 4.9 | 75.7 | 7.4 | 6.7 | 0.10 | 0.09 | 0.91 | 6.7 |
| **A5** | 4.7 | 56.2 | 8.1 | 6.4 | 0.14 | 0.11 | 0.79 | 6.4 |
| **A6** | 5.4 | 61.3 | 6.3 | 7.1 | 0.10 | 0.12 | 1.13 | 7.1 |
| **A7** | 5.7 | 42.2 | 7.2 | 8.8 | 0.17 | 0.21 | 1.22 | 8.8 |
| **A8** | 6.9 | 45.7 | 4.9 | 3.5 | 0.11 | 0.08 | 0.71 | 3.5 |
| **A9** | 4.6 | 101.1 | 21.5 | 16.2 | 0.21 | 0.16 | 0.75 | 16.2 |
| **A10** | 5.1 | 98.7 | 14.7 | 23.3 | 0.15 | 0.24 | 1.59 | 23.3 |
| **A11** | 6.3 | 87.9 | 9.6 | 11.4 | 0.11 | 0.13 | 1.19 | 11.4 |
| **A12** | 7.01 | 65.6 | 5.1 | 6.3 | 0.08 | 0.10 | 1.24 | 6.3 |
| **A13** | 4.4 | 110.2 | 23.8 | 25.8 | 0.22 | 0.23 | 1.08 | 25.8 |
| **A14** | 4.6 | 85.6 | 7.5 | 10.1 | 0.09 | 0.12 | 1.35 | 10.1 |
| **A15** | 5.0 | 79.4 | 5.5 | 8.2 | 0.07 | 0.10 | 1.49 | 8.2 |
| **Minimum** | | 42.2 | 4.9 | 3.5 | | | | |
| **Maksimum** | | 110.2 | 23.8 | 25.8 | | | | |
| **Arithmetic mean** | | 78.4 | 9.6 | 10.8 | | | | |
| **Median** | | 85.6 | 7.5 | 8.8 | | | | |
| **Standard deviation** | | 20.3 | 5.8 | 6.3 | | | | |

R/S: Root/Soil, B/S: Branch/Soil, B/R: Branch/Root, B/Cd: Branch/Cd

Table 2- Pb element distributions in *A. pycnocephalus* plant and the statistical evaluations of distributions.

| **Pb (mg/kg)** | | | | **Enrichment Coefficient** | | **Transition Factor** | **Times** |
|---|---|---|---|---|---|---|---|
| **Sample** | **Soil** | **Root** | **Branch** | **R/S** | **B/S** | **B/R** | **B/Pb** |
| **A1** | 5639 | 450.7 | 789 | 0.08 | 0.14 | 1.75 | 157.8 |
| **A2** | 2198 | 124.4 | 83 | 0.06 | 0.04 | 0.67 | 16.6 |
| **A3** | >10000 | 832.7 | 454 | <0.08 | <0.05 | 0.55 | 90.8 |
| **A4** | >10000 | 1053.3 | 651 | <0.11 | <0.07 | 0.62 | 130.2 |
| **A5** | 5935 | 628 | 342 | 0.11 | 0.06 | 0.54 | 68.4 |
| **A6** | 3138 | 753.3 | 96 | 0.24 | 0.03 | 0.13 | 19.2 |
| **A7** | >10000 | 762.3 | 378 | <0.08 | <0.04 | 0.50 | 75.6 |
| **A8** | >10000 | 1420 | 298 | <0.14 | <0.03 | 0.21 | 59.6 |
| **A9** | 5572 | 324.3 | 94 | 0.06 | 0.02 | 0.29 | 18.8 |
| **A10** | >10000 | 926.7 | 181 | <0.09 | <0.02 | 0.20 | 36.2 |
| **A11** | >10000 | 1094 | 269 | <0.11 | <0.03 | 0.25 | 53.8 |
| **A12** | >10000 | 1367 | 447 | <0.14 | <0.04 | 0.33 | 89.4 |
| **A13** | >10000 | 1467 | 284 | <0.15 | <0.03 | 0.19 | 56.8 |
| **A14** | 3160 | 438.1 | 287 | 0.14 | 0.09 | 0.66 | 57.4 |
| **A15** | >10000 | 1527.1 | 211 | <0.15 | <0.02 | 0.14 | 42.2 |
| **Minimum** | 2198 | 124.4 | 83 | | | | |
| **Maksimum** | >10000 | 1527.1 | 789 | | | | |
| **Aritmetik Ortalama** | 4273.7 | 877.9 | 324.3 | | | | |
| **Median** | 4366 | 832.7 | 287 | | | | |
| **Standard deviation** | 1621.6 | 441.2 | 200.2 | | | | |

R/S: Root/Soil, B/S: Branch/Soil, B/R: Branch/Root, B/Pb: Branch/Pb

Table 3 – Zn element distributions in *A. pycnocephalus* plant and the statistical evaluations of distributions.

| **Zn (mg/kg)** | | | | **Enrichment Coefficient** | | **Transition Factor** | **Times** |
|---|---|---|---|---|---|---|---|
| **Sample** | **Soil** | **Root** | **Branch** | **R/S** | **B/S** | **B/R** | **B/Zn** |
| **A1** | >10000 | 981 | 1798 | <0.10 | <0.18 | 1.83 | 17.98 |
| **A2** | 9883 | 974 | 748 | 0.10 | 0.08 | 0.77 | 7.48 |
| **A3** | 8244 | 385 | 287 | 0.05 | 0.03 | 0.75 | 2.87 |
| **A4** | >10000 | 899 | 478 | <0.09 | <0.05 | 0.53 | 4.78 |
| **A5** | >10000 | 1034 | 736 | <0.10 | <0.07 | 0.71 | 7.36 |
| **A6** | 6088 | 321 | 179 | 0.05 | 0.03 | 0.56 | 1.79 |
| **A7** | 7244 | 1530 | 362 | 0.21 | 0.05 | 0.24 | 3.62 |
| **A8** | >10000 | 787 | 515 | <0.08 | <0.05 | 0.65 | 5.15 |
| **A9** | >10000 | 917 | 1491 | <0.09 | <0.15 | 1.63 | 14.91 |
| **A10** | >10000 | 1083 | 1254 | <0.11 | <0.13 | 1.16 | 12.54 |
| **A11** | >10000 | 1347 | 1208 | <0.13 | <0.12 | 0.90 | 12.08 |
| **A12** | >10000 | 727 | 1236 | <0.07 | <0.12 | 1.70 | 12.36 |
| **A13** | >10000 | 1380 | 1687 | <0.14 | <0.17 | 1.22 | 16.87 |
| **A14** | >10000 | 755 | 1377 | <0.08 | <0.14 | 1.82 | 13.77 |
| **A15** | 7988 | 723 | 986 | 0.09 | 0.12 | 1.36 | 9.86 |
| **Minimum** | 6088 | 321 | 179 | | | | |
| **Maksimum** | >10000 | 1530 | 1798 | | | | |
| **Aritmetik Ortalama** | 7889.4 | 922.9 | 956.1 | | | | |
| **Median** | 7988 | 917 | 986 | | | | |
| **Standard deviation** | 1393.9 | 335.8 | 524.9 | | | | |

R/S: Root/Soil, B/S: Branch/Soil, B/R: Branch/Root, B/Zn: Branch/Zn

Table 4 - Cd elemental distributions in *V. euphraticum* plant and statistical evaluations of distributions.

| Cd (mg/kg) | | | | | Enrichment Coefficient | | Transition Factor | Times |
|---|---|---|---|---|---|---|---|---|
| **Sample** | **pH** | **Soil** | **Root** | **Branch** | **R/S** | **B/S** | **B/R** | **B/Cd** |
| **V1** | 4.9 | 119 | 7.53 | 7.8 | 0.06 | 0.07 | 1.04 | 7.8 |
| **V2** | 5.1 | 37.8 | 12.1 | 6.4 | 0.32 | 0.17 | 0.53 | 6.4 |
| **V3** | 4.7 | 438 | 15.3 | 4.4 | 0.03 | 0.01 | 0.29 | 4.4 |
| **V4** | 5.9 | 140 | 15.7 | 8.2 | 0.11 | 0.06 | 0.52 | 8.2 |
| **V5** | 4.5 | 225 | 8.1 | 6.7 | 0.04 | 0.03 | 0.83 | 6.7 |
| **V6** | 5.1 | 173 | 23.3 | 5.1 | 0.13 | 0.03 | 0.22 | 5.1 |
| **V7** | 5.7 | 115 | 54.4 | 7.2 | 0.47 | 0.06 | 0.13 | 7.2 |
| **V8** | 5.9 | 544 | 19.1 | 34.3 | 0.04 | 0.06 | 1.80 | 34.3 |
| **V9** | 4.5 | 21.6 | 4.3 | 6.5 | 0.20 | 0.30 | 1.51 | 6.5 |
| **V10** | 5.3 | 87 | 10.4 | 5.4 | 0.12 | 0.06 | 0.52 | 5.4 |
| **V11** | 5.8 | 4.1 | 10.1 | 1.9 | 2.46 | 0.46 | 0.19 | 1.9 |
| **V12** | 5.9 | 96 | 9.3 | 14 | 0.10 | 0.15 | 1.51 | 14 |
| **V13** | 6.4 | 22 | 8.7 | 3.5 | 0.40 | 0.16 | 0.40 | 3.5 |
| **V14** | 6.6 | 19 | 2.4 | 2.7 | 0.13 | 0.14 | 1.13 | 2.7 |
| **V15** | 4.7 | 34.9 | 6.5 | 5.8 | 0.19 | 0.17 | 0.89 | 5.8 |
| **Minimum** | | 4.1 | 2.4 | 1.9 | | | | |
| **Maksimum** | | 544 | 54.4 | 34.3 | | | | |
| **Arithmetic mean** | | 138.4 | 13.8 | 8.0 | | | | |
| **Median** | | 96 | 10.1 | 6.4 | | | | |
| **Standard deviation** | | 157.8 | 12.5 | 7.8 | | | | |

R/S: Root/Soil, B/S: Branch/Soil, B/R: Branch/Root, B/Cd: Branch/Cd

Table 5 - Pb elemental distributions in *V. euphraticum* plant and statistical evaluations of distributions.

| Pb (mg/kg) | | | | Enrichment Coefficient | | Transition Factor | Times |
|---|---|---|---|---|---|---|---|
| **Sample** | **Soil** | **Root** | **Branch** | **R/S** | **B/S** | **B/R** | **B/Pb** |
| **V1** | >10000 | 243 | 462 | <0.02 | <0.05 | 1.90 | 92.4 |
| **V2** | >10000 | 762.5 | 434 | <0.08 | <0.04 | 0.57 | 86.8 |
| **V3** | >10000 | 283 | 128 | <0.03 | <0.01 | 0.45 | 25.6 |
| **V4** | >10000 | 756.6 | 131 | <0.08 | <0.01 | 0.17 | 26.2 |
| **V5** | >10000 | 134.2 | 84 | <0.01 | <0.01 | 0.63 | 16.8 |
| **V6** | 7767 | 154.1 | 58 | 0.02 | 0.01 | 0.38 | 11.6 |
| **V7** | >10000 | 640 | 243 | <0.06 | <0.02 | 0.38 | 48.6 |
| **V8** | 8906 | 340.7 | 89 | 0.04 | 0.01 | 0.26 | 17.8 |
| **V9** | >10000 | 250.1 | 109 | <0.03 | <0.01 | 0.44 | 21.8 |
| **V10** | 7483 | 278 | 52 | 0.04 | 0.01 | 0.19 | 10.4 |
| **V11** | 6918 | 343.3 | 278 | 0.05 | 0.04 | 0.81 | 55.6 |
| **V12** | >10000 | 443 | 282 | <0.04 | <0.03 | 0.64 | 56.4 |
| **V13** | >10000 | 691 | 337 | <0.07 | <0.03 | 0.49 | 67.4 |
| **V14** | 9984 | 357 | 124 | 0.04 | 0.01 | 0.35 | 24.8 |
| **V15** | 9831 | 235 | 245 | 0.02 | 0.02 | 1.04 | 49 |
| **Minimum** | 6918 | 134.2 | 52 | | | | |
| **Maksimum** | >10000 | 762.5 | 462 | | | | |
| **Arithmetic mean** | 8481.5 | 394.1 | 203.7 | | | | |
| **Median** | 8336.5 | 340.7 | 131 | | | | |
| **Standard deviation** | 1281.5 | 214.6 | 133.8 | | | | |

R/S: Root/Soil, B/S: Branch/Soil, B/R: Branch/Root, B/Pb: Branch/Pb

Table 6 - Zn elemental distributions in the *V. euphraticum* plant and statistical evaluations of the distributions.

| Zn (mg/kg) | | | | Enrichment Coefficient | | Transition Factor | Times |
|---|---|---|---|---|---|---|---|
| **Sample** | **Soil** | **Root** | **Branch** | **R/S** | **B/S** | **B/R** | **B/Zn** |
| **V1** | >10000 | 289 | 598 | <0.03 | <0.06 | 2.07 | 5.98 |
| **V2** | 7998 | 743 | 708 | 0.09 | 0.09 | 0.95 | 7.08 |
| **V3** | >10000 | 732 | 744 | <0.07 | <0.07 | 1.02 | 7.44 |
| **V4** | >10000 | 444 | 532 | <0.04 | <0.05 | 1.20 | 5.32 |
| **V5** | >10000 | 1145 | 860 | <0.11 | <0.09 | 0.75 | 8.6 |
| **V6** | >10000 | 1043 | 431 | <0.10 | <0.04 | 0.41 | 4.31 |
| **V7** | 7512 | 967 | 789 | 0.13 | 0.11 | 0.82 | 7.89 |
| **V8** | >10000 | 630 | 455 | <0.06 | <0.05 | 0.72 | 4.55 |
| **V9** | 5020 | 703 | 239 | 0.14 | 0.05 | 0.34 | 2.39 |
| **V10** | >10000 | 765 | 233 | <0.08 | <0.02 | 0.30 | 2.33 |
| **V11** | 8903 | 631 | 211 | 0.07 | 0.02 | 0.33 | 2.11 |
| **V12** | 6269 | 157 | 264 | 0.03 | 0.04 | 1.68 | 2.64 |
| **V13** | >10000 | 509 | 700 | <0.05 | <0.07 | 1.38 | 7 |
| **V14** | >10000 | 2436 | 349 | <0.24 | <0.03 | 0.14 | 3.49 |
| **V15** | 9986 | 1874 | 367 | 0.19 | 0.04 | 0.20 | 3.67 |
| **Minimum** | 5020 | 157 | 211 | | | | |
| **Maksimum** | >10000 | 2436 | 860 | | | | |
| **Aritmetik Ortalama** | 7614.7 | 871.2 | 498.7 | | | | |
| **Median** | 7755 | 732 | 455 | | | | |
| **Standard deviation** | 1787.9 | 592.9 | 222.4 | | | | |

R/S: Root/Soil, B/S: Branch/Soil, B/R: Branch/Root, B/Zn: Branch/Zn

mg/kg (mean 78.4 mg/kg) while the concentration of Cd in the soil where *V. Euphraticum* plant grows ranges from 4.1-544 mg/kg (mean 138.4 mg/kg) (Table 1-6).

Pb is an element which has a low mobility in the soil. However, this mobility changes depending on the Fe-Mn oxides and the amount of insoluble organic matter. When Pb coexists with soluble organic complexes or anionic complexes, its mobility increases. Pb is associated with clay minerals, Mn oxides, Fe-Al hydroxide and organic materials in the soil. It is associated with $CaCO_3$ or phosphate concentrations in some soils (Kabata-Pendias and Pendias, 2001). According to the world mean, Pb is 44.0 mg/kg in uncontaminated soil (Kabata-Pendias and Pendias, 2001), it is 18.8 mg/kg in the soil of rural areas (Al Obaidy and Al Mashhadi, 2013), Rose et al. (1979) found a mean value of 17 mg/kg in uncontaminated soil. The value determined by WHO (Nazir et al., 2015) is between 0.061 mg/kg and 0.46 mg/kg and the mean value in the soil in the surface is 32 mg/kg (Kabata-Pendias and Pendias, 2001; Wuana et al., 2011). Pb is 2198 - > 10000 mg/kg in the soil of *A. pycnocephalus* plant in the study area and it is is in the range of 6918 - > 10000 mg/kg in the soil where *V. euphraticum* plant grows. It is significantly higher than the above mentioned values (Table 1-6).

The Zn element is found in the soil together with zinc sulphides, Fe-Mn oxides, mafic minerals (hornblende and biotite) and chalcophile elements (Cu and Pb) (Rose et al., 1979). In the soil, the total Zn concentration is 10 - 300 mg/kg and in rural areas it is 16.15 mg/kg (Alloway, 1995). According to Kabata-Pendias and Pendias (2001) it is 100 mg/kg in uncontaminated soil . The mean value is 36 mg/kg in the soil according to Rose et al. (1979) and it is in the range of 0.033-0.349 mg/kg according to World Health Organization and (Nazir et al., 2015). Zn concentration in the study area is in the range of 6088 - > 10000 mg/kg (*A. pycnocephalus*) and 5020 - > 10000 mg/kg (*V. euphraticum*), it is higher than the values indicated by some of the above researchers (Table 1-6).

The results obtained in this study conducted in and around Görgü village, and table 1 - table 6 show that the results obtained from Kırat (2009) are almost the same; it is 82.2 mg/kg in Cd, it is 5649 mg/kg in Pb, it is > 10000 mg/kg in Zn (*A. pycnocephalus*) and it is 109 mg/kg Cd,: it is > 10000 mg/kg in Pb and Zn (*V. euphraticum*).

4.2. Cd, Pb and Zn Element Concentrations in the Plants

In plants grown in soil contaminated with heavy metals, higher concentrations of heavy metals are observed compared to plants growing in soil not affected by contamination (Guttormsen et al., 1995; Dowdy and Larson, 1995; Naser et al., 2012; Vural, 2014).

Generally, the Cd concentration specified by WHO for plants is 0.02 mg/kg, the Pb concentration is 2 mg/kg and the Zn concentration is 50 mg/kg (Nazir et al., 2015; Shah et al., 2011). According to Rose et al. (1979), the Cd concentration is 4.3 mg/kg, the Pb concentration is 30 mg/kg and the Zn concentration is 570 mg/kg on average.

The lowest concentration of Cd in the branch of *A. pycnocephalus* plant is 3.5 mg/kg in the A8 location, the highest concentration is 25.8 mg/kg in the A13 location and the mean is 10.8 mg/kg. The lowest concentration of Cd in the branch of *V. Euphraticum* is 1.9 mg/kg in the V11 location, the highest concentration is 34.3 mg/kg in the V8 location and the mean is 8.0 mg/kg.

In the root of *A. pycnocephalus* plant, the lowest concentration of Cd is 4.9 mg/kg, the highest concentration is 23.8 mg/kg and the mean is 9.6 mg/kg . The lowest concentration of Cd in the root of the *V. Euphraticum* plant is 2.4 mg/kg and the highest concentration is 54.4 mg/kg the mean is 13.8 mg/kg at 2.4 mg/kg. The element concentrations and mean values in the study area were found to be higher than the indicated values (Table 1-6).

It is determined that the results obtained in this study conducted in Görgü village and its surroundings and given in table 1, table 6 are similar to Kırat (2009)'s values obtained at same region from where Cd is 5.03 mg/kg, Pb is 445.7 mg/kg, Zn is 881 mg/kg (at the root of the *A. pycnocephalus*), and Cd is 6.53 mg/kg, Pb is 343 mg/kg and Zn is 409 mg/kg (at the root of *V. euphraticum*).

Sperman correlation coefficients (> 10000 mg/kg values are not taken into account) between *A. pycnocephalus* and *V. euphraticum* plants and Cd, Pb and Zn elements in the soil where this plant grows were calculated and given in figure 4 - 5 and Schroll (1975) evaluated the correlation between soil and plant samples at 95% and 99% confidence level (Özdemir and Demir, 2010). It was found from *A. pycnocephalus* plant that r =0.77 (n = 15, p <0.01, 99%) for Cd values of soil and root, r = 0.86 (n = 15, p <0.01, 99%) for Cd values of soil and branch; r = 0.77 (n = 6, p <0.01, 99%) for Pb values of soil and branch, r = 0.4 (n = 6) for Pb values of soil and root; r = 0.5 ( n = 5, p <0.05, 95%) for Zn values of soil and root, r = 0.3 (n = 5) for Zn values of soil-root. For *V. euphraticum* plant, r is 0.58 (n = 15, p <0.05, 95%) for Cd values of soil-root, r = 0.55 (n = 15, p <0.05, 95%) for Cd values of soil and branch; r = 0.14 (n = 6) for Pb values of soil and root, r = 0.1 (n = 6) for Pb values of soil and branch; r = 0.5 (n = 6, p <0.05, 95%) for

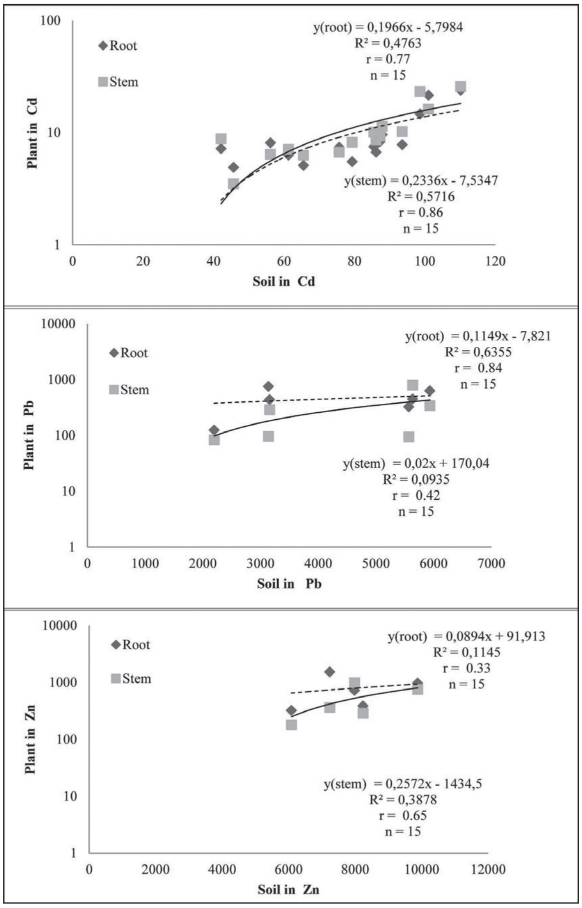


Figure 4- Correlation and distribution relation between the presence of Cd, Pb and Zn element rates in the soil and the rates in the root and branch of the plant in A. pycnocephalus plant samples.

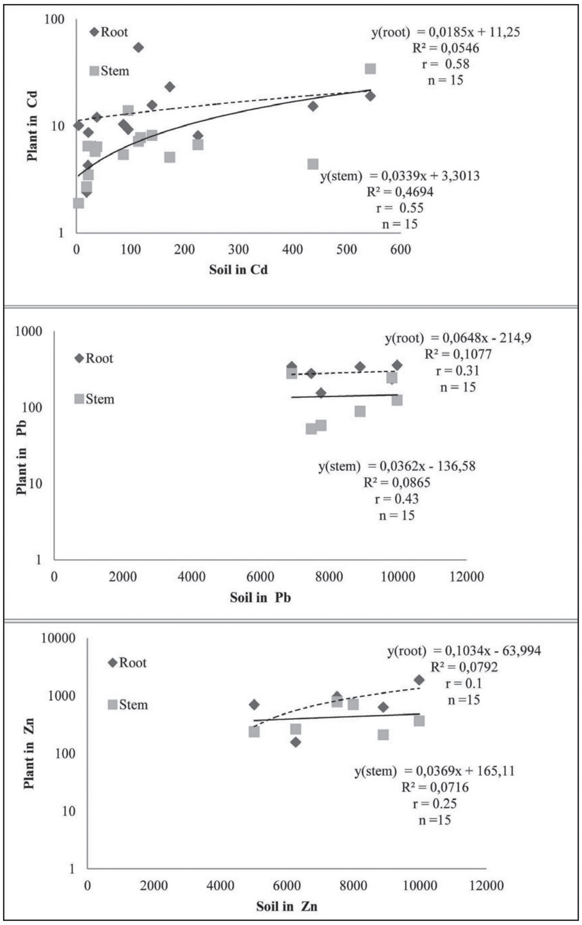


Figure 5- Correlation and distribution relation between the presence rates of Cd, Pb and Zn elements in the soil and their presence in the root and branch of the plant in *V. euphraticum* plant samples.

Zn values of soil and root, and r = 0.1 (n = 6) for Zn values of soil and branch.

*A. pycnocephalus* plant root for Pb; its roots and branches for Zn; The root and branch of *V. euphraticum* plant was seen not to be statistically significant ($p < 0.05$, 95% confidence level) for Cd, Pb and Zn. In the biogeochemical prospect, the root and branches of *A. pycnocephalus* plant for Cd, its branches for Pb can be suggested to identify indicator plants ($p < 0.01$, 99% confidence level) and they can be used to improve contaminated areas. It can be said that this plant species may be accumulator plant due to the excessive amounts of Cd and Pb values in the soil and excessive amounts of Cd and Pb the *A. pycnocephalus* plant can absorb.

There are 4 rules to define the hyperaccumulator: 1) branches of the plant /root of the plant >1 (transition factor> 1) (Xiaohai et al., 2008); 2) plant / soil > 1 (coefficient of enrichment> 1) (Rotkittikhun et al., 2006; Harrison and Chirgawi, 1989); 3) the branches of the plant/the ratio of the metal (Cd: 1 mg/kg, Pb: 5 mg/kg, Zn: 100 mg/kg) ranged from 10 to 500 times (time value) (Fifield and Haines, 2000; Allen, 1989; Shen and Liu, 1998; Yanqun et al., 2005); and 4) the concentration of element in the plant (Cd > 100 mg/kg, Pb> 1000 mg/kg, and Zn > 10000 mg/kg) (Mganga et al., 2011, Ernst, 2006, Brooks, 1998, Mehes-Smith et al., 2013).

The transition factor ranged from 0.13 (A6 and V7) to -2.07 (V1) for all samples taken. Transition factor for *A. pycnocephalus* plant is in 11 locations for Cd (A1-A3, A6, A7, A10-A15) for Pb, in 1 location (A1) for Zn in 7 locations (A1, A9, A10, A12-A15), and for *V. euphraticum* plant in 5 locations for Cd (V1, V8, V9, V12, V14) for Pb in 2 locations (V1, V15) and transition factor in 5 locations for Zn (V1, V3, V4, V12, V13) ) is greater than 1 (Table 1-6). In the study area, that the transition factor is > 1 indicates that the metals are transported from the root to the branches.

The enrichment coefficient is mainly dependent on the soluble fraction of the metal and the organic material in the soil (Xiaohai et al., 2008). This coefficient is an important factor when considering the potential for improvement in plants. The enrichment coefficient is less than 1, either because the metal concentration in the soil is increased or the metal concentration in the plant is low (Zhao et al., 2003). In the study area, the enrichment coefficient of the *V. euphraticum* plant is 2.46 in the V11 location. In general, the enrichment coefficient at all locations where *A. pycnocephalus* and *V. euphraticum* plants are taken is less than 1 (Table 1-6).

The Cd values of *A. pycnocephalus* plant in A2, A9-A11, A13-A14, (Zn) A1, A9-A14 locations and Cd values of *V. euphraticum* plant in V8 location are between 10-500 times. In both plant species, Pb is between 10 and 500 times in all locations. The Pb values are higher than 1000 mg/kg for the root of *A. pycnocephalus* plant in the A4, A8, A11-13, and A15 locations (Table 1-6).

Times values range from 1.79-157.8 in all collected samples. Time values of *A. pycnocephalus* plant is greater than 10 in 6 locations for Cd, for Pb in all locations and 7 locations for Zn. Time values in *V. euphraticum* plant is greater than 10 for Cd in 1 location and for Pb in all locations while they are less than 10 for all Zn values (Table 1-6).

When plant specimens in the study area were compared with plants grown in the soil not affected by contamination (Cd: 1 mg/kg, Shen and Liu, 1998); *A. pycnocephalus* plant at A2, A9, A10, A11, A13, A14 locations and *V. euphraticum* plant at V8 location are between 10.2-25.8 times. Samples taken from all locations (A1-A15 and V1-V15) contain 10.4-157.8 times Pb compared to the ones which were not affected by contamination (Pb: 5 mg/kg; Shen and Liu, 1998). In the A1, A9-A14 locations, the time values of Zn in *A. pycnocephalus* plant are found between 12.08-17.98, whereas all time values in *V. euphraticum* plant are <10 (Zn: 100 mg/kg; Shen and Liu, 1998) (Table 1-6).

## 5. Conclusions

The following results were obtained by statistically evaluating the results of the analyzes to better determine the elemental distributions of Cd, Pb and Zn in the soil and their distributions in the *A. pycnocephalus* and *V. Euphraticum* plants in the study area:

1. The elemental values of Cd, Pb and Zn change depending on the pH values.

2. It has been determined that the concentrations of Cd, Pb and Zn obtained from the soil in the study area are higher than the values given in the literature.

3. Medium and low positive correlations were observed between soil-root and soil-branch for Cd, Pb and Zn in *A. pycnocephalus* and *V. euphraticum* plants. It was seen that for Cd the root and branches of *A. pycnocephalus* plant, its root for Pb, its branches for Zn; for Cd the root and branches of *V. euphraticum* plant can be used to determine indicator plants and to improve the environmental contamination.

4. Concentration values of Cd, Pb and Zn in *A. pycnocephalus* and *V. euphraticum* plants were observed to have higher metal concentrations than those planted in soil not affected by contamination. Transition factor for Cd in *A. pycnocephalus* plant is A1-A3, A6, A7, A10-A15, for Pb is A1 for Zn is A1, A9, A10, A12-A15 and for Cd in *V. euphraticum* plant is V1, V8, V9, V12, V14, for Pb is V1, V15 and for Zn is V1, V3, V4, V12, V13 which are greater than 1 at the specified locations. At the V11 location (Cd, Root/Soil), the enrichment coefficient of the *V. euphraticum* plant is > 1. Times values in in the *A. pycnocephalus* plant for Cd are A2, A9-A11, A13, A14, for Pb they are A1-A15 and for Zn they are at A1, A9-A14; in *V. euphraticum* plant for Cd it is V8 for Pb they are V1 and V15. As it is seen in these locations they range from 10 to 500. According to the analysis results obtained, plant samples of *A. pycnocephalus* and *V. euphraticum* can be described as an accumulator / hyperaccumulator for Cd, Pb and Zn.

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