Gümüşköy (Kütahya) Maden Sahasında Karasal Bitkilerde Zn ve Sb Bioakümülasyonları

Jeoloji Müh. Zhala Zakariya SALEH

Yüksek Lisans Tezi

Jeoloji Mühendisliği Anabilim Dalı
Danışman: Prof. Dr. Ahmet ŞAŞMAZ

Temmuz-2017

T.C.

FIRAT ÜNİVERSİTESİ

FEN BİLİMLERİ ENSTİTÜSÜ

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Tezin Enstitüye Verildiği Tarih : 28 Haziran 2017

Tezin Savunulduğu Tarih : 20 Temmuz 2017

Tez Danışmanı : Prof.Dr. Ahmet ŞAŞMAZ

Prof.Dr. Ahmet SAĞIROĞLU

Yrd. Doç. Dr. Özlem ERDEM (Tunceli Üni.)

Temmuz 2017

ACKNOWLEDGEMENTS

I would like to thank to my supervisor Prof.Dr. Ahmet ŞAŞMAZ because of the continuous support of my MSc thesis and FUBAP personal (Fırat University Project Center) for the support with **FUBAP MF.16.74** project number..

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GÜMÜŞKÖY (KÜTAHYA) MADEN SAHASINDA KARASAL VE Sb BIOAKÜMÜLASYONLARI

Gümüşköy (Kütahya) Ag, As ve Pb yatağı, Kütahya'nın yaklaşık 25 km batısında yer almaktadır. Yörede Permo-Karbonifer'den Kuvaterner'e kadar zaman aralığında oluşan metamorfik, volkanik ve sedimanter birimler yüzeylemektedir. Türkiye'nin en önemli gümüş ataklarından birisi olan cevherleşmeler, Miyosen yaşlı Tavşanlı volkanitlerinin içerisinde ve Şahin Formasyonu ile kontaklarında yer alırlar. Gümüşköy yatakları Gümüsköy, Şahin, Gözeçukuru, Sığıreğreği ve Dulkadir köyleri arasında bulunmaktadır. Yatakta yaygın cevher mineralleri pirit, galenit, barit, sfalerit, realgar, orpiment, antimuanit, Fe ve Mn oksitler, arjantit, frayberjit ve pirarjirit, gang mineralleri ise kuvars, kalsedon, çört, dolomit ve kalsittir.

Bu çalışma 12 farklı bitki türünün [Onosma sp. (ON), Tripleurospermum maritimum (TR), Silene compacta (SL), Carduus nutans (CR), Alyssum saxatile (AL), Centaurea cyanus (CE), Anchusa arvensis (AN), Glaucium flavum (GL), Cynoglossum officinale (CY), Phlomis sp. (PH), Isatis sp. (IS) ve Verbascum Thapsus (VR)] kök ve dallarındaki Zn ve Sb birikimi ve dağılımı incelenerek, topraktan bitkinin farklı kısımlarına Zn ve Sb taşınımı ve alımı irdelenmiştir. Çalışma alanındaki bu bitkiler, ılıman karasal iklime sahip, Gümüşköy (Kütahya) Ag-Pb maden sahasının yüzey topraklarında doğal olarak büyümüşlerdir. Bitki örnekleri ve ilişkili topraklar araziden toplanmış ve ICP-MS'de Zn ve Sb içeriklerini belirlemek için analiz edilmiştir. Bitki örneklerinin dal, kök ve topraklarındaki ortalama çinko değerleri sırasıyla 4994, 3008 ve 2560 ppm; antimuan 915, 458 ve 373 ppm şeklindedir. Çalışma alanındaki bitkilerin kökleri (ECR) ve dalları (ECS) için ortalama zenginleşme katsayıları çinko için 1.98 ve 1.06; antimuan için 0.50 ve 0.46 şeklinde sıralanmıştır. Bu bitkiler ECR ve ECS temelinde gruplara ayrılmıştır. Çinko için GL, SL, ON, PH ve VR bitkileri; antimuan için PH ve GL bitkileri; 1'den büyük veya 1' e yakın ECR ve ECS değerlerine sahip olmasından dolayı çok iyi birer biyoakümülatör/hiperakümülatör bitkiler olarak gruplandırılmıştır. Bu yüzden, bu

bitkiler fitoremedasyonunda özellikle yararlı olabilir ve dolayısıyla da çinko ve antimuanca kirlenmiş alanların rehabilitasyon çalışmalarında kullanılabilirler.

Anahtar kelimeler: Zn ve Sb alımı, karasal bitkiler, zenginleşme katsayısı, translokasyon faktörü, fitoremedasyon, Gümüşköy maden sahası

ABSTRACT

THE Zn AND Sb BIOACCUMULATIONS IN THE TERRESTRIAL PLANTS AT THE GÜMÜŞKÖY (KÜTAHYA) MINING AREA

Gümüşköy Ag, As ve Pb ore deposit is located to about 25 km. west of Kütahya. In this region, the units cropping out in the study area are composed of metamorphic, volcanic and sedimentary rocks and their ages range from Upper Paleozoic to Quaternary. Gumusköy Ag deposit is the one of the biggest silver deposits in Turkey, occurred in Tavşanlı volcanic- Miocene in age and their contacts between Tavşanlı volcanic and Şahin Formation- Permo-Carboniferious in age. Gümüşköy deposit was found among Gümüşköy, Şahin, Gözeçukuru, Sığıreğreği and Dulkadir villages. Primary ore minerals are in order; pyrite, galena, sphalerite, realgar, antimuanite, orpiment, barite, Fe and Mn oxides, argentite, freibergite and pyrargyrite. The main gangue minerals are quartz, calcedony, chert, dolomite and calcite,

This study investigated silver (Ag),arsenic (As) and lead (Pb) uptake and transport from the soil to different plant parts by documenting the distribution and accumulations of Ag, As and Pb in the roots and shoots of 12 plant species [Onosma sp. (ON), Tripleurospermum maritimum (TR), Silene compacta (SL), Carduus nutans (CR), Alyssum saxatile (AL), Centaurea cyanus (CE), Anchusa arvensis (AN), Glaucium flavum (GL), Cynoglossum officinale (CY), Phlomis sp. (PH), Isatis sp. (IS) and Verbascum Thapsus (VR)]. All of these plants were growing naturally in surface soils of the Gumuskoy Ag-Pb mining area (Kutahya, Turkey), a region with a mild continental climate. Plant samples and their associated soils were collected and analyzed for Zn and Sb concentrtaions by inductively coupled plasma mass spectrometry (ICP-MS). Mean values in the soils, roots, and shoots of all plants were 4994, 3008 ve 2560 ppm for Zn; 915, 458 ve 373 ppm for Sb, respectively. The mean enrichment factors for root (ECR) and shoot (ECS) of these plants were 1.98 ve 1.06 for Zn; 0.50 ve 0.46 for Sb respectively. The plants in the study area were separated into different groups based on ECS and ECRs. The results showed that GL, SL, ON, PH and VR plants for Zn; PH and GL plants for Sb were very good hyperaccumulator plants due to their ECSs and ECRs are higher than 1 or close to 1. Therefore, these plants may be particularly useful in phytoremediation studies and they can be used to rehabilitate or clean areas contaminated with Zn and Sb.

Key Words Zn and Sb uptake, terrestrial plants, enrichment coefficient, translocation factor, phytoremediation, Gümüşköy mining area

1. INTRODUCTION

Heavy metals are the most important environmental contaminants, and their toxicity is a problem of increasing significance for evolutionary, ecological, environmental and nutritional reasons. The term ‘‘*heavy metals*’’ refers to any metallic element that is toxic or poisonous even at low concentration and has a relatively high density (Marfo, 2014). ‘‘Heavy metals’’ are the metalloids and metals with atomic density greater than 4 g/cm^3 , or 5 times or more, greater than water (Gill, 2014). Heavy metals include iron (Fe), chromium (Cr), silver (Ag), cadmium (Cd), zinc (Zn), lead (Pb), nickel (Ni), arsenic (As), cobalt (Co) and iron (Fe), the PGEs (Tchounwou *et al.*, 2012). Environment; is defined as the external environment in which the living beings that live on the earth continue their relationships throughout their lives and is also called "Ecosystem" for short (Costanzo *et al.*, 2005). Furthermore, water, soil and air are considered as the main physical elements of nature. They all together have an impact on the vital activities of living organisms on earth thus when these elements are polluted, they can negatively effect on any living organisms living in the area and cause structural damage on the inanimate environment elements and disturb their qualities and this is called "Environmental Pollution". Besides the comfort that the developing technology brings to life, the size of the pollution that this development gives to the nature and the environment increases with increasing speed. These developments aimed at making life more perfect, healthier and prolonged life. However, in recent years it has damaged water, air, soil vegetation and animal, but also it ruined natural resources both in rural and urban areas. Environmental pollutions can be categorized based on sources such as: 1) Migrations and irregular urbanization. 2) Energy, water, paper, coal etc. used per person. Increase. 3) The destruction of forests, fires and erosion. 4) Overgrazing and destruction of natural vegetation cover. 5) Air pollution caused by heat in houses and workplaces. 6) Motor vehicles and marine vehicles. 7) Mineral, lime, stone and sand quarries, 8) Fertilizers and pesticides, 9) Atmospheric events and natural disasters. 10) The supply of sewage waters to the receiving environment without purification and use in the water. 11) Solid wastes and rubbish. 12) Drying of wetlands and lakes. 13) Misuse of land. 14) Illegal fishing. 15) Radiation from medical devices such as TV, computer and x-ray. 16) Industrial and urban noise (Egboka *et al.*, 1989). Metal intake abilities of plants vary in large intervals and the plants which take up high amounts of metals are defined as “hyperaccumulator plants.’’ Criteria for “*hyperaccumulator plants*’’ are described as metal contents in shoot dry matter (Cd >100 ppm, Cu >1000 ppm, Pb>1000 ppm, Zn>10000 ppm), the ability to store heavy metals in above-ground parts 10-500 times more than in usual plants, and an enrichment coefficient >1 (Ensley et al., 2000; Lasat, 2002; Fayiga et al., 2004). The inorganic substance intake ability of plants is also considered for the rehabilitation of contaminated environments due to industrial and mining activities. This relatively new approach is called phytoremediation, which is defined as the use of plants to remove, destroy or sequester hazardous substances from the environment. Phytoremediation has become a topical research field in the last decades as it has emerged as a cheap and effective natural way of rehabilitation of the environment. Many metal hyperaccumulators have so far been discovered as a result of scientific work on the subject (Brown et al., 1995; Landberg et al., 1996; Lasat et al., 1996; Robinson et al., 1998; Desouza et al., 2000; Wei et al., 2002; Ozturk et al., 2003; Sagiroglu et al., 2006).

Two types of heavy metals will be focused on in this research, Zn (Zinc) and Sb (Antimony).

Table 1. Properties of Zinc (Zn) and Antimony (Sb) (Lebrun, N. and Perrot, P., 2006)

	Zinc Properties	**Antimony Properties**
Name:	Zinc	Antimony
Symbol:	Zn	Sb
Group:	Trans. Met.	Metal
Crystal Structure:	Hexagonal	Rhombohedral
Atomic number:	30	51
Atomic weight:	65.38	121.75
Shells:	2,8,18,2	2,8,18,18,5
Filling orbital:	3d10	5p3
Melt:	419.58°C	630°C
Boil:	907°C	1750°C
Electronegativity:	1.65	2.05
Covalent radius:	1.25 Å	1.40 Å
Atomic radius:	1.53 Å	1.53 Å
Atomic volume:	9.2 cm^3/mol	18.23 cm^3/mol
First ionization potential:	9.394 V	8.641 V

2nd ionization potential:	17.964 V	16.53 V
3rd ionization potential:	39.722 V	25.30 V
Oxidation states:	2	(±3),5
Density @ 293 K:	7.14 g/cm³	6.684 g/cm³
Specific heat:	0.39 J/gK	0.21 J/gK
Heat of vaporization:	115.30 kJ/mol	77.140 kJ/mol
Heat of fusion:	7.322 kJ/mol	19.870 kJ/mol
Electrical conductivity:	0.166 10^6/cm ohm	0.0288 10^6/cm ohm
Thermal conductivity:	1.16 W/cmK	0.243 W/cmK

Zinc is quite uniformly distributed in magmatic rocks, whereas in sedimentary rocks is likely to be concentrated in argillaceous sediments (Table 3). Zinc has been known as the metal since the middle Ages, but industrial extraction and Zn refining only began in Europe in the late 18th Century. It is very mobile during weathering processes and its easily soluble compounds that are readily precipitated by reaction with carbonates. Some of the most common compounds are Sphalerite, ZnS; Smithsonite, $ZnCO_3$; Hemimorphite, $Zn_4Si_2O_7(OH)_2.H_2O$; Zinc bloom, $Zn_5(OH)_6(CO_3)_2$; Zincite, ZnO and Willemite, Zn_2SoiO_4 (Table 3). This means that the metal has the potential for forming a variety of compounds with inorganic and organic groups.

Table 2. Selected properties of Zinc.

Element	Atomic number	Atomic mass	Atomic[a] radius (pm)	Density (20 °C, g cm^{-3})	Valence[b]	Melting point (°C)
Zn, zinc	30	65.38	153	7.13	**+2**	419.55

Table 3. Zinc contents in common Zn minerals (Landner and Reuther, 2002)

Mineral	Chemical composition	Zn (%)
Sphalerite	ZnS	67.0
Smithsonite	$ZnCO_3$	52.0
Hemimorphite	$Zn_4Si_2O_7(OH)_2 \cdot H_2O$	54.2
Zinc bloom	$Zn_5(OH)_6(CO_3)_2$	56.0
Zincite	ZnO	80.3
Willemite	Zn_2SiO_4	58.5

Zinc metal is most commonly used as a protective coating of other metals, such as steel and iron. Zinc metal dust is widely used in paint coatings, as a catalyst, and as a reducing and precipitating agent in organic and analytical chemistry (Goodwin 1998). The consumption of zinc by industry was 265,000 metric tons (53.4% of total consumption) for galvanizing; 103,000 metric tons (20.8% of total consumption) for zinc-based alloys; and 86,800 metric tons (17.5% of total consumption) for bass and bronze (Kaur *et al.*, 2014). Zinc is relatively harmless compared to several other metals with similar chemical properties. But, only exposure to high doses has toxic effects, making acute zinc intoxication a rare event. In addition to acute intoxication, high-dose and long-term zinc supplementation interferes with the uptake of copper. Hence, many of its toxic effects are in fact due to copper deficiency. Zinc deficiency caused by malnutrition and foods with low bioavailability, aging, certain diseases, or deregulated homeostasis is a far more common risk to human health than intoxication (Plum et al., 2010).

Zinc is usually found in soils and its concentration ranges between 10 to 300 ppm, with a mean of about 50 ppm (Malle, 1992). Mean Zn for worldwide soils is calculated as 64 ppm (Finkelman, 1999). Japanese agricultural soils contain Zn in the range of mean values from 59 to 99 ppm, with the lowest value for sandy Acrisols and the highest for Andosols (Takeda et al. 2004). Zinc contents in agricultural soils of Sweden ranges from 6 to 152 ppm, with mean value of 65 ppm (Eriksson, 2001)., The geometric mean of Zn in cultivated soils in the USA was reported to be 43 ppm, in the range of <3–264 ppm (Holmgren *et al.*, 1993). Although Zn is very mobile in most soils, clay fractions and SOM are capable of holding Zn quite strongly, especially at neutral and alkaline pH regime (Kabata-Pendias, 2007). The median Zn has been estimated for world ocean water from 0.5 to 4.9 ppb (Reimann *et al.*, 1999). However, Zn concentrations in open oceans, lakes and rivers vary considerably. Zinc is present in aquatic systems in the divalent state and the chemical speciation of Zn^{2+}, by analytical-chemical methods remains indispensable (Table 5).

Antimony (Sb) naturally existing in the environment with a low concentration. Its present in the earth's crust is around 0.2–0.3 ppm (Gebel, 1997). While the top soils layer has an enriched Sb. Moreover, the soils texture contains antimony concentrations ranges between 0.3 and 8.6 ppm (Johnson et al., 2005). In Japanese soils, the median Sb contents vary from 0.7 to 1.0 ppm, for Cambisols and Acrisols, respectively (Taylor *et al.*, 2012). The 90 percentage of Finnish soil contains the Sb level ranges between <0.2 and 0.9 ppm (Mount *et al.*, 2015).

Table 4. Selected properties of Antimony.

Element	Atomic number	Atomic mass	Atomic radius (pm)	Density (20 °C, g cm^{-3})	Valence	Melting point (°C)
Antimony (Sb)	51	121.76	133	6.68	5s25p3	631/1587

In contaminated soils, near industrial sites, Sb is quite high in surface layers and decreases with depth which indicates that it is rather non-reactive and mostly immobile and will not contaminate the groundwater. However, under specific conditions, mobility and leaching of Sb from the mineral stibnite, near a Sb-smelter in New Zealand has been observed (Craw, 2008). Also (Ashley *et al.*, 2003) confirmed the mobility of Sb in Fe free or low-Fe systems. Higher concentrations are typically linked to anthropogenic sources. The main natural sources are volcanic eruptions, sea salt spray, forest fires, and wind-blown dusts. Industrial sources include fossil fuel combustion, incineration of wastes, cement kilns, and metallurgical industries. However, it is known to be easily taken up by plants if present in soluble forms in growth media, Antimony is not essential to plants. Its concentration varies from <20 to 130 ppb in food plants that grown in soils of historical mining areas. In these soils, Sb occurs mainly in the sulfide form, SbS, which is slightly phyto-available, at the range of 0.06–0.59% of the total Sb content (Hammel et al., 2000). Antimony and its compounds were considered as pollutants of priority interest by the USEPA, Since 1979. It may enter the food chain and present a health risk for animals and humans if Sb is taken up by crop plants, even if the plants themselves remain unaffected. Owing to the limited knowledge about Sb toxicity, it is difficult to assess the health risks of exposure to elevated concentrations of Sb. assuming an average Sb concentration in vegetables grown in a contaminated garden of 100 ppm dry weight (Li and Thornton, 1993). There is a lack of reports revealing the Sb toxicity to plants. Only results of the experiment curried out by He and Yang (1999) show that Sb3+, at the highest dose (1000 ppm), significantly reduced the yield of rice, in the pot experiment, as compared with the impact of Sb^{5+} addition.

Antimony has various uses, and these are still expanding (Filella et al., 2002). While it can be used for hardening of leads when they are in metallic forms, such as lead–acid batteries, cable coverings and shells, and in semiconductors. Antimony trioxide (Sb_2O_3) is widely used as a flame-retardant, e.g. in textiles, papers, plastics and adhesives. Therefore, textiles and plastics are major sources of Sb in municipal waste (Albdiry et al., 2012). Furthermore, antimony trioxide is used as a paint pigment, ceramic pacifier, catalyst, mordant and glass decolorizer. Antimony was already known to the ancients. The significant enrichment of antimony is dated back to roman times as it has been revealed by a peat core in a bog from swiss. This shows that the anthropogenic fluxes of antimony can be back dated to more than 2000 years (Shotyk *et al.*, 1996). World reserves of antimony are in excess of 2 million tons and are located principally in Bolivia, China, Russia, South Africa, and Mexico. Current world production of antimony is about 140,000 tons per year (Carlin and Butterman, 2004).

Table 5. Abundance of Zinc and Antimony in the environment (Kabata-Pendias, 2007).

Environmental compartment	Zn	Sb
Earth's crust (mg kg^{-1})	52 – 80	0.1 – 0.9
Ingeous rocks (mg kg^{-1})		
Mafic	40 – 120	0.1 – 1
Acid	40 – 100	0.2 – 2
Sedimentary rocks (mg kg^{-1})		
Argillaceous	80 – 120	0.8 – 4
Sandstones	15 – 30	0.05
Calcareous	10 – 25	0.15 – 0.3
Raw energy material (mg kg^{-1})		
Coal, hard[b]	52 – 19000	0.6 – 1.2
Fly ash[c]	194	3.8
Crude oil	0.5 – 85	0.003 – 0.5
Petrol	<0.2 – 3	>0.005
Soils (mg kg^{-1})	63	
Light sandy	31 – 61	0.05 – 1.33
Medium loamy	47 – 61	0.05 – 2
Heavy loamy	35 – 75	0.3 – 0.6
Calcareous	50 – 100	–
Organic	57 – 100	0.08 – 0.6
Waters (μg l^{-1})		0.03 – 0.05
Snow	2.6 – 3	0.02 – 0.05
Rain	1.2 – 6.6	0.24
Ocean, sea	0.04 – 4.9	0.005 – 0.1
Air[d] (ng m^{-3})	0.03 – 15	
Urban/industrial	550 – 16000	1 – 55
Rural	10 – 200	0.003
South Pole	0.002 – 0.05	0.002 – 0.22[f]
Greenland	18 – 41	

Many studies have been carried out to investigate the geology of Gümüşköy (Kütahya) deposit and the region. It is known that the deposits in the region have been operating since ancient times and many studies related to them (gallery, tunnel, tree coals, ceramic pots, mill stones) have been encountered (Vıcıl, 1982, Yigitguden, 1984; Arık 2002). There is an average of 3-4 m thickness between Aktepe and Gümüsköy and an area of approximately 12 km². In the case of a charcoal taken from Gümüşköy eruption, the presence of 3900 ± 85 years of 14th Century isotope age indicates that the mining operations on the site extend from Phrygian to Assyrian and Trojan VI periods (Yiğitgüden, 1984). Kartalkanat (2008) determined the age of the tree as 3534 ± 24 years in C^{-14} isotope analysis of wood carp taken from the patios of silver operation operated by Eti Gümüş in Gümüşköy, Kütahya. These data were collected in Kütahya-Gümüşköy on average. It is an important finding that mining has been done in the last 1500 years. Concerning the tectonic evolution of the region, Vıcıl (1982) have reported that these structures developed both before and after mineralization. The authors talked about the occurrence of east - west direction volcanics along the north - south axis curves around the Aktepe mine as a result of the tectonic activity affecting the Tertiary aged tubers and the existence of many volcanic associated with this main fault system. Yiğitgüden (1984) found that the rocks are thrown by a vertical strike volcane and that the mineralization develops due to this Voclane. Alpergun (1996) shows that the tectonic traces in the region are quite large, especially the Paleozoic schists exhibit a folded and fractured structure with excessive amounts of Neogene tuff, tuffite and carbonates. The rocks are folded and broken by Alpine orogeny and the mineralization followed these broken lines. Vıcıl (1982) stated that there are three sahada ores in the form of Gözepe and Sığıregre, mainly Aktepe, and that the mineralizations are polymetallic. According to Vıcıl (1982), Aktepe mineralization occurred mainly in 2 phases and silver enrichment was mostly realized in the first two periods of the primary mineralization process. The volcanic rocks in the region are the result of a volcanic belt and volcanic events occurring in this belt, like the volcanics in all of Western Anatolia, and it is argued that the type of polymetallic ores is defined. As a result of the researches he has done, he stated that Aktepe's deposit is an epi-mesothermal deposit, according to the paragenesis, succession and mineral relations in the field. Yigitguden (1984) reported that the mineralizations detected in the sintered silicate are barite - sphalerite - silvered galenite - antimony, silvered galena - sphalerite mineral in tuffs, silvered galena - sphalerite gangue minerals, barite occurrences in dolomite, barite gangue and thin antimony veins. Karabaş (1997) stated that the mineralization in the region has developed as two phases. In the first stage, high temperature hydrothermal solutions ascend along the main fault system to silicify the tuffs and to form fine veins of several meters in length. During this silicification, silver became enriched with significant metal enrichments. The epithermal enrichment period, which is defined as the second stage, is much younger and its activity in the field still continues. In addition to the mining activities in the region during the historical period, the old manufacturing pans are considered as high grade silver ore.

Arık (2002) stated that rocks belonging to two volcanoes developed in two different periods around Gümüsköy deposits and that the first volcanic acidic and neutral feature is Miocene. The products of this volcanism, rhyolite and rhyodacitic features, indicate that the tuffite and tuffs are locally extensively silicified and settle before the type of veins and scattered mineralization in these rocks. Secondary Pliocene. Volcanism is represented by basaltic and rarely andesitic-like lavas, and basic volcanism is not directly related to mineralization. Arık (2002) stated that there is a significant zonation from the surface to the deep in the Gümüsköy deposits and that silica deposits generally occur in the uppermost parts of the deposits. It is known that As and Sb veins are found in the uppermost parts of the deposits. If the present operation center of Aktepe deposit is considered as a center, there is a zoning in the lateral direction and it is mentioned that there are As, Sb and Tl enrichments in the Gözeçukuru deposit where Ag, As, Sb mineralizations are located in accordance with this zoning and a little further to the center.

Yaldiz (2007) is working in the region; He argued that the common skin and lung cancer observed in the village of Dulkadir, which is very close to the mineral deposits, is due to the arsenic distribution in dangerous amounts. Dulkadir, Sahin and mineral deposits and especially People living in the distance of the eye deposit are at many different risks, such as skin cancer, lung cancer, heart rhythm disorders. People who have been affected by the dust produced by agriculture and livestock activities in these deposits during the past years living in ore deposits and in other villages around the Gözeçukuru deposit have been affected more by the water from the surrounding waters and from the plants that are drenched with these polluted waters. Men are more likely to be affected because there are more men who perform these activities. Arik and Yaldiz (2010) reported that the soil in the region and the plants in the same region were contaminated by many heavy metals in important areas such as willow, pine, oak and pear.

The aim of this study is to investigate Zn and Sb accumulation and transport from the soil to the roots and shoots of 12 terrestrial plants grown in contaminated soils of the Gumuskoy mining area, Kutahya, Turkey.

2. MATERIALS AND METHODS

2.1 The Study Area

The study area is located in the west of Kütahya, Turkey and between 38°960–39°480N latitude and 29°480–29°710E longitude with altitudes between 1100 - 1320 m (Figure 1).

Figure 1. Location map of the study area.

2.2. Geological Settings

Gümüşköy (Kütahya) is one of the Turkish city that has rich underground sources, metallic mine and industrials for raw materials. Numerous metallic materials like boron, kaolin, silver, chromium, alunite, antimony, cupper-lead-zinc, iron ore, manganese, magnesite, cement raw materials, feldspar, gypsum and fluoride are present in Kütahya. The formation of volcanic, sedimentary and metamorphic rocks ongoing from Permian to present day. In the study area, ore deposits represented by Ag, Zn, Sb, As, Tl and Pb occur among Dulkadir, Gümüşköy and Sahin villages (Figure 2). Soil and plants are contaminated by the heavy metals as the results of both natural and mining works. Kartalkanat (2008) specified that Gümüşköy had a long mining history of about 3500 years, according to ^{14}C absolute age determinations. As a result, Gümüşköy and its surrounding with both ancient and modern mining studies have been polluted by these metals (Arik et al. 2009; Özen & Arik 2016; Sasmaz et al. 2015; Sasmaz et al. 2016).

The study area consist of several formations starting with the Şahin formation consisting of metamorphic rocks with low-grade metamorphism overlying the Carboniferous-Permian limestone. Karaağaç formation, which is represented by Permian - Triassic marbles, comes in conformity with Şahin formation. Enne mélange stands tectonically above other units and the settlement age is Upper Cretaceous. Miocene aged and lower basal conglomerate, and rhyolitic and rhyodacitic syncretic tuffs, tuffites and agglomerates are present uncomfortably on the pre-Cenozoic basement. The Lower Pliocene aged tuff, carbonate and clay composed of alternations of sandstone, conglomerate and tuff are easily distinguishable from other units with light green color and stand on other units uncomfortably. Upper Pliocene aged Emet formation consists of clayey limestone, limestone and dolomitic limestones. Within the Emet formation, dolomite and dolomitic limestones are observed only around Aktepe in the region. Taşlıtepe volcanics, which is the product of the basic volcanism that developed during the Late Pliocene - Quaternary period, cuts off all the units. The Bozyer formation and alluvial deposits formed by the poorly adhered rugged rocks during the Quaternary period cover all units uncomfortably (Arık, 2002).

bZ]v&[illegible]

Şahin Formation is a low grade metamorphic green, pink and beige colored mainly in the study area; It is composed of phyllite, clayey-schist, sericite-schist, chlorite-muscovite schists, metachromite, metaconglomera, calcschist, marble, unconscious, muscovite schist, mica schist, graphitic mica schist and quartzite. The unit is described by Arik (2002) and presents large surface areas on the east and south of the study area, especially around Şahin village (Figure 2). In conformity with this unit, black colored bituminous marbles belonging to Karaağaç Formation come and their age is Ercan et al. (1990) as Permian. Again, the carbon content of the graphitic schists in the lower parts of the formation.

It is thought to have been gained during the Carboniferous period. According to this evidence, the age of the Sahin Formation is considered Permo-

Carboniferous. The presence of metamorphic rocks such as metamorphic rocks, metaconglomera, calcschists, marbles, mica schists, mica schists, muscovite schists and graphitic micaschists in the unit reflects a shallow sedimentary environment consisting primarily of clayey, sandy limestone and marls. Such an occurrence reflects the fact that the crumb from the land is dense and can occur in a coastal environment favorable to carbonate precipitation in shallow and occasionally rising and falling depending on the time. Based on the mineral paragenesis of metamorphic rocks by Arık (2002), it has been stated that the formation may have undergone low-grade regional metamorphism. It is suggested that the schists belonging to the study area and nearby metamorphic rocks are covered schists covering the Menderes massif (Ercan et al., 1982; Oygür and Erler, 1999) and metamorphism during the Hercynian orogeny by Akdeniz and Konak (1979)

Figure 2. View of the Şahin Formation in the field

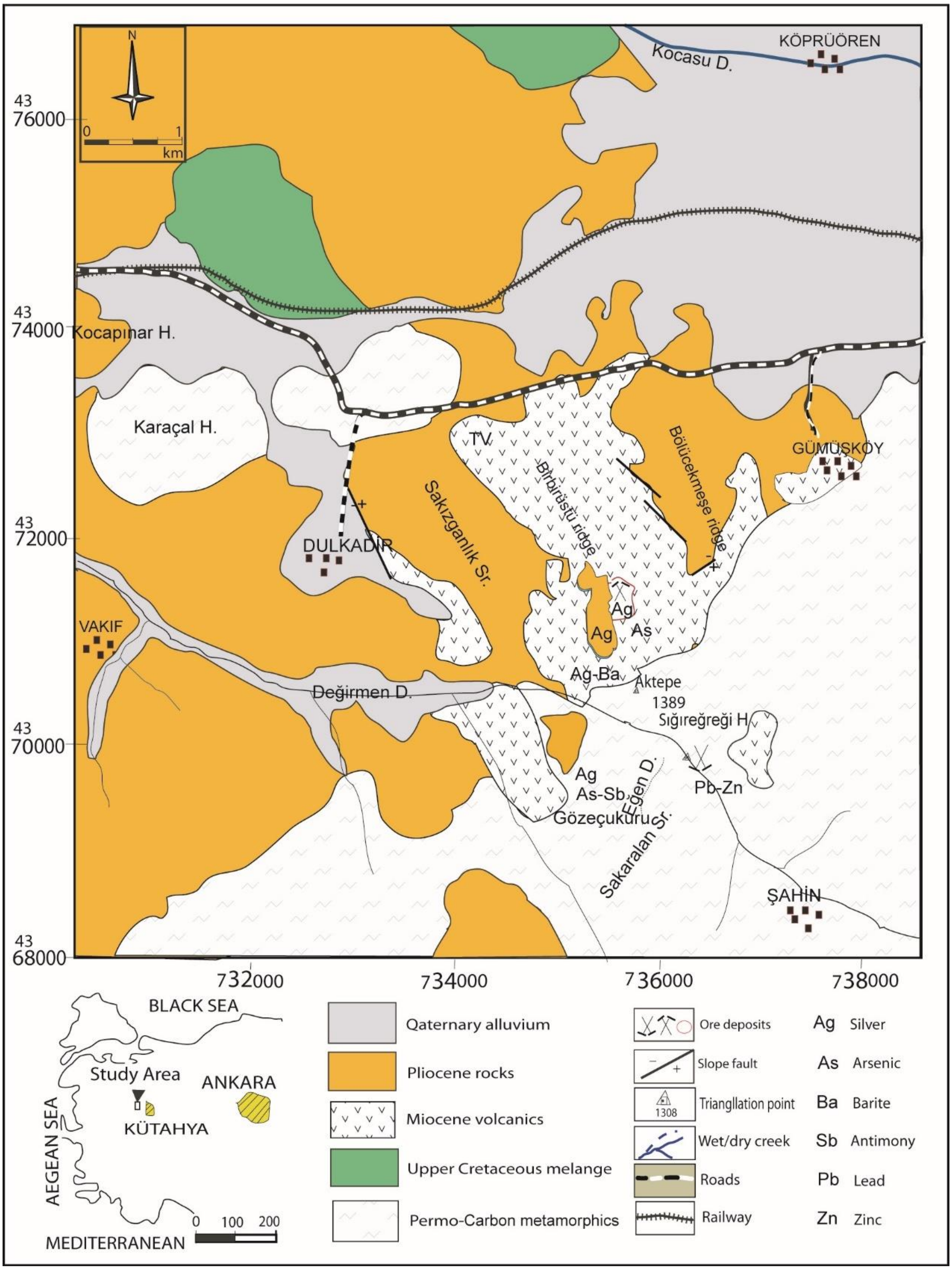

Figure 3. Geological map of the study area (Arik, 2002).

K a r a a ğ a ç   F o r m a t i o n

Were firstly identified as Mesozoic Marbles by Vıcıl (1982) and later as Karaağaç Formation due to their widespread appearance in Karaağaç region by Arik (2002). The region is unconformably overlain by the Sahin Formation, and Enne is covered by the melange and other young units (Figure 4). The unit is observed to the west of the study area (Figure 3) and is mainly represented by gray and beige colored, bituminous, cryptocrystalline textured marbles. The lower part of the unit is thicker and the unit is thinner. The unit is very cracked and fractured and the unit is approximately 400 m according to Arık (2002). There is no fossil that can illuminate the age of Karaağaç formation. The unit is unconformably overlain by the Permian-Carboniferous Şahin formation. According to Kalafatçıoğlu (1964), the age of the unit was determined as Triassic - Lower Cretaceous. Accordingly, the unit began to sediment in the Permian, and sedimentation continued in the Triassic period and consequently the Permian-Triassic age was given (Arik, 2002).

Figure 4. View of Karaağaç Formation

Enne melange

The zone has basic and ultrabasic rocks and carbonate rocks with lateral passages and is represented by spillite, serpentine, radiolarite and carbonate blocks of various dimensions. The unit gives a surface release between the silver plants in the study area and Aliköy (Figure 4). In the formation, there are metamorphic rocks composed of gabbro, pyroxenite, diabase, doleritite, basalt and pyroclastic rocks, serpentinite, talc and talcshistites and pelagic sediments represented by radiolarite, radiolarian chert, red and green shale, greywacke and limestones. The Enne Melange, which stands tectonically on the Karaağaç Formation in the study area, consists of magmatic and pelagic sediments of the oceanic environment at the end of Cretaceous and carbonate rocks of different ages and sizes from the older units (Arik, 2002). Arik (2002) and Yaldız (2007) who work in the region stated that the unit is of Upper Cretaceous age.

Tavşanlı volcanics

Tavşanlı volcanics were first defined by Ercan et al. (1982) by this name. The unit gives wide surface areas in Gümüşköy, Dulkadir and Şahin villages in the study area, especially in Aktepe region (Figure 5). The unit consists of dacite, rhyodacite and rhyolitic tuffites in varying colors ranging from gray to brown tones and intensively altered. In places, there are pyroclastic rock fragments and fine crystalline quartz, opal, calcinedonite, coarse crystalline barite, fine crystalline galenite, sphalerite and antimonite. Aglomera in the base sections of the unit is yellowish pink, gray and white color. Pumice fragments are quite common at the north of Aktepe summit and at Gözeçukuru. White and beige pumas are similar to crystal tudes at first glance. However, it is recognized as being very porous and lightweight. It is usually spherical and elliptical. Upper Pliocene Emet formation comes unconformably over this unit and the thickness of rhyolitic and rhyodacitic tuffs is found to be about 40 m according to the data obtained from the soundings (Arık, 2002). Based on the leaf fossils (Fagus Feromae Ung.) Found in the tuff and tuffites at the base of the study area, one part was given Miocene age (Vıcıl, 1982). The continuation of the same volcanism around Kütahya and Emet is characterized by the calc-alkaline quartzlatite of volcanic rocks and it is reported that they show 19.6 to 17.2 million years according to radiometric analysis (Sunder *et* al 1979). According to this data, the age of the unit was accepted as Middle - Upper Miocene.

Figure 5. View of Tavşanlı volcanics in the field

Ç o k k ö y f o r m a t i o n

The Çokköy Domanic formation was first described by Baş (1983). The unit consists mainly of green and gray marls, beige colored claystone, sandstone, conglomerate, tuff and locally limestone layers. The survey area of the Çokköy Formation yields topmost in the west and northwest (Fig. 3). The unit is often seen in light green, brown, white, gray and beige color, although it has different shades of color in different places within the study area. While the tuffs are dominant in the lowest levels of the unit, marls in the central part and limestones in the upper part are predominant, and these units are located horizontally or close to the horizon in the region (Arık, 2002). Gün et al. (1979), Working on the study area based on the Ostracoda and Gastropod fossils they found in the unit, they gave the Lower Pliocene age to the Çokköy Formation. Arik (2002) determined that the unit had a maximum thickness of 200 m and that it was the same as the Upper Pliocene Emet Formation and laterally and vertically passing through this unit, and that it was a lacustrine basin product from the beginning of Pliocene.

Emet formation

Emet formation is one of the units with the widest spread in the study area (Figure 6) and it is distributed in many places such as Gümüşköy and Aktepe western part. The unit is mainly composed of thin bedded, light colored limestone, limestone and dolomite. The unit was first defined and named by Emet in the Mediterranean and Konak (1979). The unit is thin and medium bedded, white and gray in color and has plenty of porosity. In the lower part of the unit, the layer thicknesses exceed 1 meter and generally stand horizontally or close to the horizon. If it is towards the upper layer, the layer thicknesses are thinner. Arik (2002) and Yaldiz (2007) reported that they observed widespread formation of barite, galena and quartz in cracks and voids with silicification around Aktepe, and that dolomites contained less void than limestones. The unit is in conformity with the Lower Pliocene aged. The thickness of the formation cut by Upper Pliocene-Quaternary Taşlıtepe volcanics is reported to be about 200 m (Arik, 2002). Therefore, a part of the upper Pliocene age was given by Arik (2002), and according to the freshwater fossils found in the area, the grabental coming from the region in Pliocene shows that it collapses in the resulting lake environment.

Figure 6. View of the Emet formation

Taşlıtepe volcanics

Taşlıtepe volcanics were first named as Karaköy volcanics by Bas (1983) and later by Arik (2002) as Taşlıtepe volcanics because of their typical appearance around Taşlıtepe. The unit is located to the adjacent south of the study area (Figure 3) and consists mainly of basalt and andesites with dark and abundant gas voids. When these rocks are examined petrographically, it is found that they are generally composed of porphyritic texture, composed of plagioclase and pyroxenes in the form of large crystals. In some cases, olivine and amphibole are also found. Taşlıtepe volcanics have been assigned by Upper Pliocene - Quaternary age to the age of the upper and lower units by Arik (2002). The thickness of the unit is 80 m, Arık (2002) reported that the volcanic rocks in the study area are formed by partial melting of the upper crust, lower crust and upper mantle, which are heated by convection currents due to intragranular grabenization.

Bozyer formation

Bozyer formation was first named as Kocayataktepe formation by Baş (1983) and later by Arik (2002) as Bozyer formation. The unit mainly consists of rough and fine grained gravels, rugged rocks such as sand and clay, mostly in red and brown colors. The unit is observed in the north of the study area and covers a very large area and based on the pebbles in it, Arik (2002) stated that this unit is of Quaternary age (Arik, 2002).

2.3. Mineralizations

The first scientific studies in the region began in the 1970s, and with the vast number of researches in recent years there have been many studies on the mining geology of the region. In the beginning of 1970s, Geological mapping and exploration studies using the drilling were carried out in this region and these studies continued until 1997 (Özker, 1970, Vıcıl, 1982, Erler et al., 1983, Yiğitgüden, 1984, Kafkas, 1994, Etibank, 1995, Alpergun, 1996, Karabas, 1997). In recent years, studies have begun to be published that examine both the mineralogical geology and the damages caused by the deposits in the region (Arık, 2002, Yaldız, 2007, Arık and Nalbantçilar, 2009).

The only silver deposit operated in Turkey, Kütahya-Gümüşköy silver deposit has 178 gr / t Ag grade and 21.5 million tons reserves. This is equivalent to 3827 tons of metal silver reserves (DPT, 2001). The Gümüşköy deposits present in the area that are spread between Gümüsköy, Şahin and Dulkadir villages, about 25 km west of Kütahya. The deposit is limited to Kavacik valley, the Tasoluk fountain in the west, Gözeçukuru in the south and Şahin village in the east and Sığreğreği Tepe in the north (Figure 3). The largest mineralizations are seen in the vicinity of Aktepe, and a significant amount of ore exploitation is made from this area (Figure 7). The ore production in the region is carried out by the open operation method, and the large-scale tonnage machines continue to operate in the region. Often the mineralizations observed in this area are represented by the soil cover in different colors ranging from intense dark brown to gray (Figure 8). Particularly siliceous and barite sections were not affected much by this alteration and they were protected in the field in a solid manner (Figure 8).

Figure 7. View of the barite and sulphide minerals

Figure 8. View of the mineralized area

2.4. Sample Collection and Preparation

The plants and soil samples in the present study were collected from soils of the Gümüşköy mining district, Kütahya, Western Turkey. These plants generally live for 1 or 2 years (annual) and indigenously grow on the soils of the mining area. The plant species in the Gümüşköy region can grow under severe climate conditions due to their deep-reaching root systems. The Zn and Sb concentrations were measured in 12 plant species: *Onosma* sp. (ON), *Tripleurospermum maritimum* (TR), *Silene compacta* (SL), *Carduus nutans* (CR), *Alyssum saxatile* (AL), *Centaurea cyanus* (CE), *Anchusa arvensis* (AN), *Glaucium flavum* (GL), *Cynoglossum officinale* (CY), *Phlomis* sp. (PH), *Isatis* sp. (IS) *ve Verbascum Thapsus* (VR. These plants in the study area were chosen due to dominant and native species.

Soil depths change between 6.0 and 0.3 m. The soils are black and light–dark brown in color, with a peaty clay texture (23.6 % sand, 51.4 % silt and 19.3 % clay) and loamy. The soil pH values change between 7.2 and 6.4 with an organic matter content of 2.32 %– 6.48 %. Soils were taken from around the plant roots at a depth of 30–40 cm. The soil samples were ground using hand mortars after drying in an oven at 100°C for 4 h. Soil samples were digested in a mixture of HCl:HNO3:H2O (1:1:1, v/v; 6 mL per 1.0 g of soil) for 1 h at 95°C. This treatment dissolved all soil samples minerals except for silicates, and the digests were analyzed using ICP-MS techniques for Zn and Sb at the ACME Analytic Laboratory (Vancouver, Canada) (www.acmelab.com). The determination of Zn and Sb performed by using inductively coupled plasma mass spectrometer (A Perkin-Elmer ELAN 9000).

Plant samples were randomly taken from sites of the Gümüşköy mining area. Three samples of shoots and roots were collected from each sampling site. The root samples were taken at a depth of 30–40 cm below the surface (Figure 9 and 10). The studied shoot and root samples were thoroughly washed with tap water, rinsed with distilled water, and dried at 100°C in an oven for 30 min and then at 60°C for 24 h. The dried plants (about 2.0–3.0 g samples) were ashed by heating at 300°C for 24 h. The ashed samples were digested in HNO3 for 1 h, followed by digestion in a mixture of HCl:HNO3:H2O (1:1:1, v/v; 6 mL per 1.0 g of the ashed sample) for 1 h at 95°C. The digests were analyzed using ICP-MS for Zn and Sb and the plant concentrations were calculated on a dry matter basis.

Figure 9. View of the *Verbascum thapsus* showing its root and soil area

Figure 10. View of the *Isatis* sp.

2.5. **ECR (**The enrichment coefficients for root)

The enrichment coefficients (ECR) for root were calculated by dividing to soil concentration of plant root concentration for each plant. This coefficient is an indicator indicating metal amount accumulated to plant root from soil (Chen et al., 2005). The ECR in hyperaccumulator plants is greater than 1, but the ECR for metal excluder plant is lower than 1 (Wei et al., 2002).

2.6. **ECS (**The enrichment coefficients for shoot)

The enrichment coefficients (ECS) for shoot were found by dividing to soil concentration of plant shoot concentration for each plant. This coefficient shows the accumulation ability for each plant (Zhao et al., 2003). This value shows the accumulating ability of the metals to the shoot from the soil and this is very important for similar studies. Therefore, the ECS defines the absorbing and storing ability of a plant. The ECS in hyperaccumulator plants is greater than 1, but the ECS for metal excluder plant is lower than 1 (Wei et al., 2002). If the ECR and ECS values are close to 1 (as 0.90 or 0.80 values), then, these plants can also accept as the best or good plants for bioaccumulations (Sasmaz et al., 2016).

2.7. **TLF (**Translocation factor)

The translocation factor (TLF) was the metal ratio transported to that of shoot from the plant roots. Hyperaccumulator plants have higher translocation factors than 1. This factor indicates the metal transfer capacity from root to shoot (Sasmaz et al., 2009). This value shows the transfer ability (not accumulating) of the metals to the shoot from the root and this is very important for phytoremediation studies (Sasmaz et al., 2016).

3. RESULTS

Gümüşköy deposit is the most important Zinc and Antimony deposit in Turkey where intensive mining studies have been carried out since 1970. In this study, it was aimed to determine the soil around the deposits and the heavy metal pollution in the plants. In this context, it was planned to take systematic sampling of plants and tombs from around the deposits, but having irregular geometry of the deposits made systematic sampling difficult. In addition, the fact that the vegetation cover is very poor, especially the growing of limited plant species on and around the deposits, made such sampling impossible. Specimens were generally taken locally from over and around the deposits. In almost all samples taken from the region, heavy metal concentrations were high. In this study, the effects of Zn and Sb collected around the Gümüşköy deposit and the changes in the surrounding soil and vegetation and the possible environment are examined.

The geochemical characteristics of Zinc are different to those of Antimony, also their concentration in the rocks has been enriched 100 times less than the Antimony (Table 1). The mean distribution of Zinc in the earth's crust is estimated at about 52 -80 ppm while it's much fewer in case of Antimony as it has been estimated between 0.1 -0.9 ppm.

3.1. Zinc concentration in the study area

Twelve different plant species collected from the study area and the Zn contents in the root and shoot of these plants were determined and their soil uptake capacities were calculated. It was therefore decided that these plants could be used as a bio accumulator plant for Zinc and Antimony or for phytoremediation studies. The results of Zinc analysis in the roots and shoots of the plants in the region are given in (Table 8, Figure 11). As can be seen on this figure and table, the samples of each plant have variation values for Zinc in the soil, root and branch. Here, the Zinc changes in the example are shown both numerically and graphically. Furthermore, for each plant sample, the value obtained by dividing the root Zinc to the soil Zinc ratio shows the degree of Zinc uptake in the soil (ECR) of the plants root, and if this value is equal to or greater than 1, this plant shows that the root has very well obtained the metal in the ground. Similarly, the value of the metal in the plant shoot is divided by the value of the metal in the soil, and the result is the coefficient of enrichment for the shoot (ECS), which indicates the degree of metal uptake in the shoot, if it is bigger than 1, it indicates that the plant shoot is in very good in obtaining the metal from the earth. Similarly, the transfer degree of the metals in the root of the plant to the shoot and different parts is defined as TLF, If the TLF values are 1 or more, it means that the plant has the ability to transfer the metals in the root very well to the shoot, which is considered particularly important in phytoremediation studies, especially in cleaning contaminated areas.

Table 6. The coordinates points of the samples

Sample No	X	Y	Plant Name
AL-01	735692	4 371826	*Alyssum saxatile L.*
AL-02	736024	4 371928	
AL-03	735512	4 372087	
AL-04	736142	4 369385	
AL-05	736354	4 371120	
AN-01	736098	4 368895	*Anchusa arvensis L.*
AN-02	735648	4 370336	
CE-01	735523	4 371421	*Centaurea cyanus L.*
CE-02	736019	4 371387	
CE-03	736189	4 371139	
CR-01	736157	4 371641	*Carduus nutans (CR) ()*
CR-02	736188	4 371217	
CR-03	735571	4 372366	
CY-01	735923	4 370195	*Cynoglossum officinale*
CY-02	735735	4 370862	
GL-01	735512	4 369195	*Glaucium flavum*

GL-02	735358	4 369015	
IS-01	735833	4 371748	*Isatis L.*
IS-02	735990	4 371018	
IS-03	736042	4 371508	
IS-04	735611	4 369125	
ON-01	736118	4 371332	*Onosma sp.*
ON-02	735708	4 369431	
ON-03	736052	4 371556	
PH-01	735774	4 370752	*Phlomis sp.*
PH-02	735560	4 371503	
PH-03	736145	4 371178	
PH-04	735603	4 371486	
SL-01	735592	4 369007	*Silene compacta*
SL-02	735517	4 369088	
SL-03	735511	4 368977	
SL-04	735584	4 368815	
SL-05	735406	4 368962	
SL-06	735753	4 369266	
TR-01	735890	4 371412	*Tripleurospermum maritimum*
TR-02	736143	4 371218	
VR-01	736052	4 371606	*Verbascum thapsus*
VR-02	735770	4 370753	
VR-03	735571	4 369077	
VR-04	736014	4 371427	
VR-05	735517	4 368894	
VR-04	736014	4 371427	
VR-05	735517	4 368894	

Table 7. The Zinc concentration of root and shoot and soils of the study area and TLF, ECR and ECS results for Zinc.

	Zn in soil	Zn in root	Zn in shoot	ECR=root/soil	ECS=shoot/soil	TLF= shoot/root
AL-01	3839	2045	2616	0.53	0.68	1.28
AL-02	5006	4948	2456	0.99	0.49	0.50
AL-03	13134	6697	5826	0.51	0.44	0.87
AL-04	11234	3812	4377	0.34	0.39	1.15
AL-05	10542	3741	5982	0.35	0.57	1.60
Average	8751	4249	4252	0.55	0.51	1.08
AN-01	5086	964	831	0.19	0.16	0.86
AN-02	1521	1988	1019	1.31	0.67	0.51
Average	3303	1476	925	0.75	0.42	0.69
CE-01	12058	4676	2137	0.39	0.18	0.46
CE-02	9356	3747	4263	0.40	0.46	1.14
CE-03	4800	1447	1610	0.30	0.34	1.11
Average	8738	3290	2670	0.36	0.32	0.90
CR-01	11142	10960	6835	0.98	0.61	0.62
CR-02	5854	297	2151	0.05	0.37	7.25
CR-03	3559	3609	1098	1.01	0.31	0.30
Average	6852	4955	3361	0.68	0.43	2.73
CY-01	4800	1022	1547	0.21	0.32	1.51
CY-02	618	267	274	0.43	0.44	1.03
Average	2709	644	910	0.32	0.38	1.27
GL-01	1398	1697	1270	1.21	0.91	0.75
GL-02	1854	3881	2914	2.09	1.57	0.75
Average	1626	2789	2092	1.65	1.24	0.75
IS- 01	3067	1790	1385	0.58	0.45	0.77
IS-02	10540	3958	1846	0.38	0.18	0.47
IS- 03	11325	3965	1255	0.35	0.11	0.32
IS- 04	1021	1413	664	1.38	0.65	0.47
Average	6488	2781	1288	0.67	0.35	0.51
ON-01	6982	2773	3096	0.40	0.44	1.12
ON-02	10852	6777	12325	0.62	1.14	1.82

ON-03	8091	7824	7953	0.97	0.98	1.02
Average	8642	5791	7791	0.66	0.85	1.32
PH-01	4818	967	299	0.20	0.06	0.31
PH-02	3520	1455	2044	0.41	0.58	1.40
PH-03	2005	2779	2929	1.39	1.46	1.05
PH-04	2032	2269	3101	1.12	1.53	1.37
Average	3094	1868	2093	0.78	0.91	1.03
SL-01	7355	3272	2277	0.44	0.31	0.70
SL-02	742	461	221	0.62	0.30	0.48
SL-03	384	880	474	2.29	1.23	0.54
SL-04	66	430	215	6.53	3.27	0.50
SL-05	322	1110	782	3.45	2.43	0.70
SL-06	538	942	844	1.75	1.57	0.90
Average	1568	1182	802	2.51	1.52	0.64
TR-01	9292	1024	974	0.11	0.10	0.95
TR-02	11389	2803	2059	0.25	0.18	0.73
Average	10340	1914	1516	0.18	0.14	0.84
VR-01	1290	1424	2265	1.10	1.76	1.59
VR-02	5140	4216	4220	0.82	0.82	1.00
VR-03	1323	2604	1373	1.97	1.04	0.53
VR-04	6482	1997	1591	0.31	0.25	0.80
VR-05	1589	10420	3569	6.56	2.25	0.34
Average	3165	4132	2604	2.15	1.22	0.85

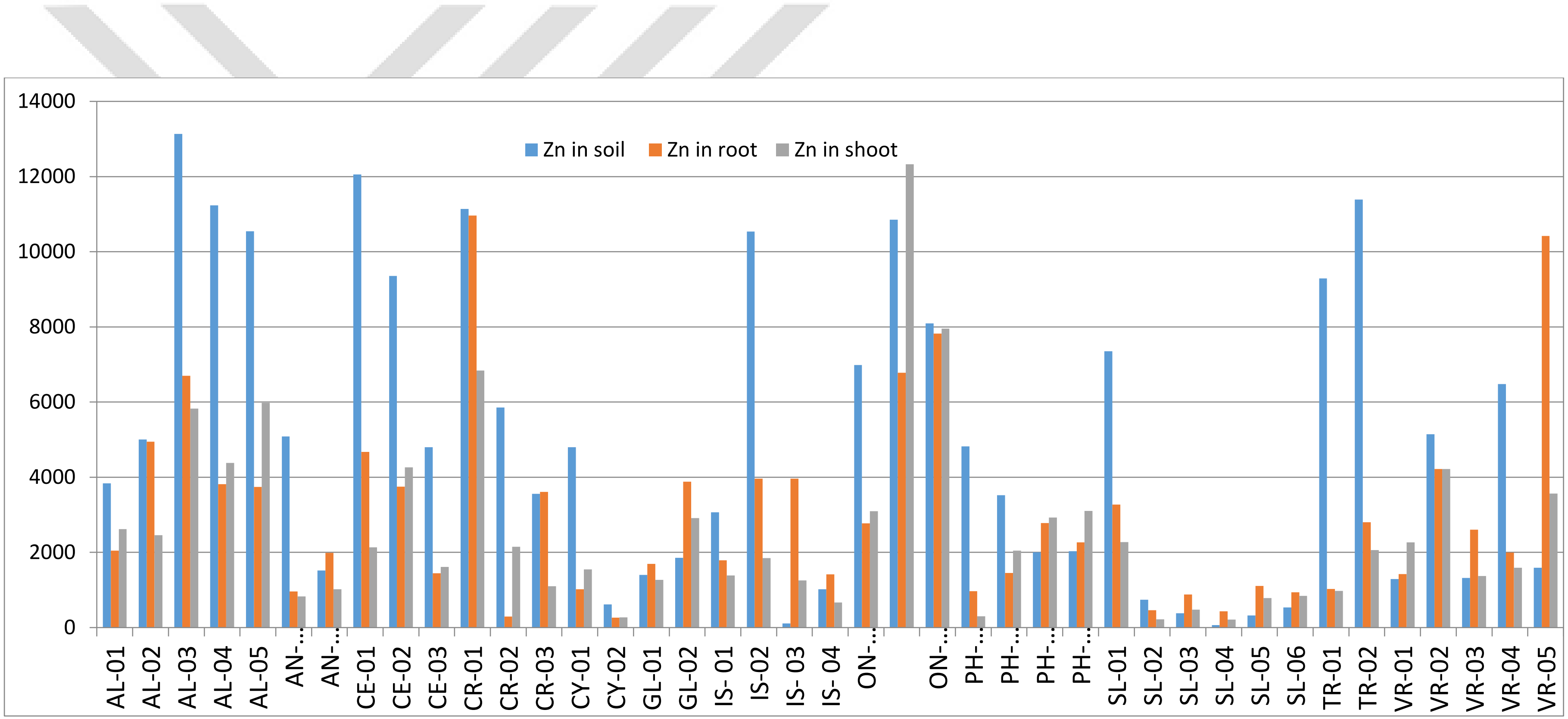

Figure 11. The histogram of the results of the Zinc analysis of the soil, plant roots and stems of the plants in the study area.

When the ECR, ECS and TLF values of the specimens belonging to the study area are examined, Plants with values of ECR and ECS of 1 or close to 1 are GL, SL, ON, PH and VR (Figure 13). This shows that *Glacium*, *Silena*, *Onosma*, *Phlomis* and *Verbascum* may be a bioaccumulator plant for Zinc. Therefore, these plants can be accepted as indicator plants for Zinc in mining operations, and it is possible to utilize these plants for the purification of Zinc contaminated soils. When the translocation factors of the plants in the study area were examined, it was determined that most of these plants were very high in TLF values (Figure 13). Especially, plants such as CR, AL, CY, CE, ON, PH show that the capacity of carrying or transferring Zinc to the root part of the root is very high.

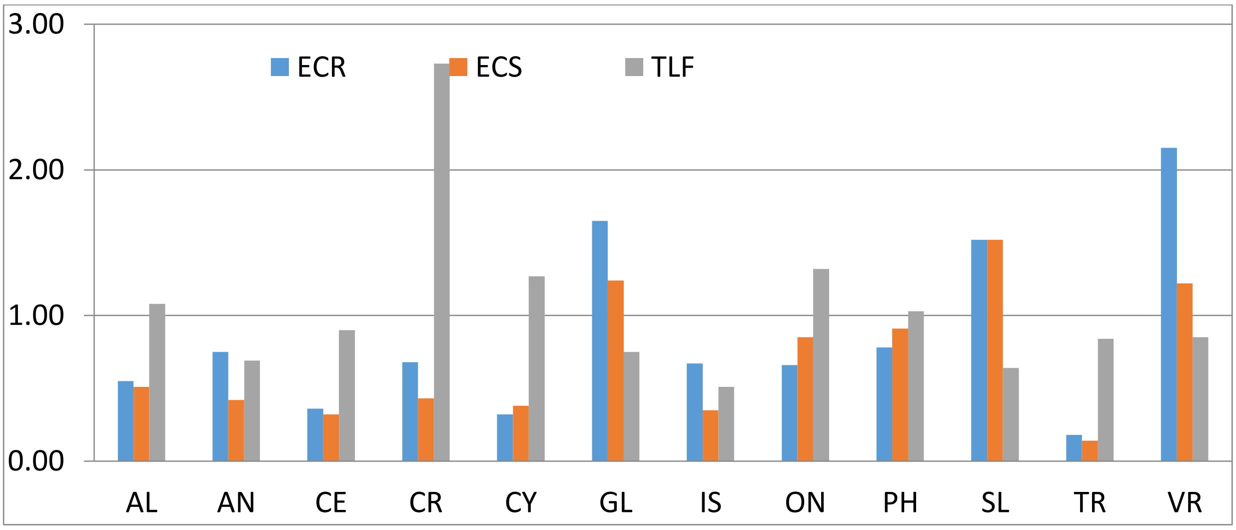

Figure 12. The histogram of the ECR, ECS and TLF results of the Zinc analysis of the soil, plant roots and stems of the plants in the study area.

When the amounts of Zinc taken up by the plant in the root and its body were assessed from a toxic point of view, almost all the plants' roots and bodies were polluted with Zinc. These values show that both the soil and vegetation in the study area are sometimes hundreds of times more polluted than Pais and Jones (2000) compared to the Zinc content of 0.01-0.5 ppm in the plants. Therefore, surface and groundwater from intense pollution in the local soils is also naturally affected and contaminated. The fact that plants in the study area are so dirty that animals and people who feed on them due to the herbaceous plants that make up the rings of the food chain are also heavily influenced by it.

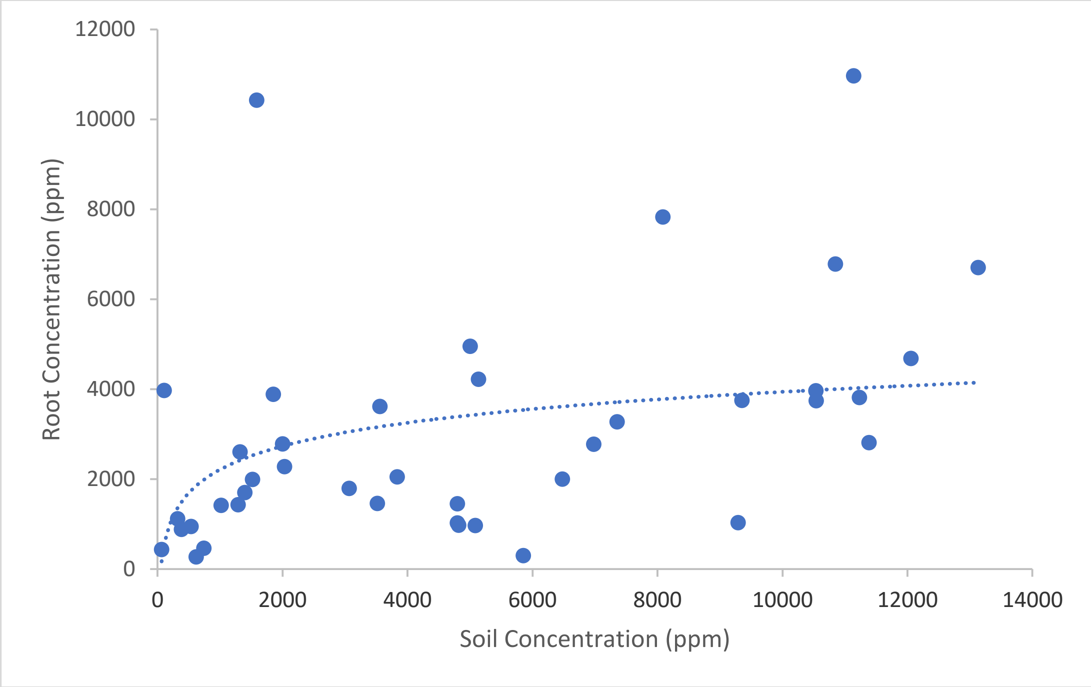

Figure 13. Shows the ratio of zinc concentration distributed between root and soil (ECR).

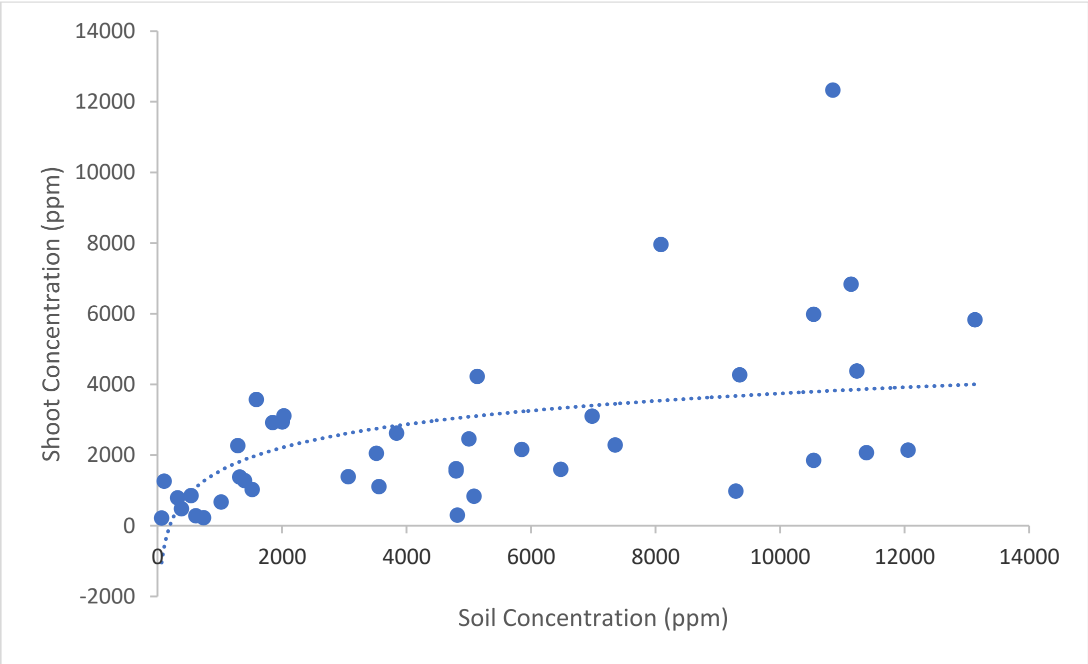

Figure 14. Shows the ratio of zinc concentration between soil and shoot (ECS)

3.2 Antimony concentration in the study area

The distribution of Sb in 12 different plant species and plant roots and shoot in the study area were examined and it was tried to determine where these plants had taken the soil Sb. It has also been decided whether these plants will be used as a bioaccumulator plant for Sb or in phytoremediation studies. The results of Sb analysis in the roots, shoots and soil of the plants in the region are given in (Table 9, Figure 16). As can be seen on this figure and table, the samples of each plant have variation values of Sb in root, and Shoots. Hence, the Sb value changes in each example are shown both numerically and graphically. ECR of each plant has been obtained by dividing the Sb ratio within the root to the soil Sb ratio. This shows the amount of Sb up taken by the root, and if this value is equal to or greater than 1, this plant shows that the root has very well obtained the metal in the Soil (Figure 17). Similarly, ECS obtained by dividing the value of the metal in the plant shoot by the value of the metal in the soil, and the result is the, which indicates the degree of metal uptake in the shoot, when ECS is bigger than 1, it indicates that the plant shoot has the ability in obtaining the metal from the earth (Figure 18). Finally, TLF is obtained by dividing the transfer rate of the metals in the root of the plant to the shoot and different parts. When the value of TLF are 1 or more, it shows that the plant has the ability to transfer the metals in the root to the shoot, which is considered particularly important in phytoremediation studies, especially in cleaning contaminated areas (Figure 15).

When the ECR, ECS and TLF values of the specimens belonging to the study area are examined, the plants with values of ECR and ECS of 1 or close to 1 are PH, and GL (Figure 15). This suggests that both *Glaucium flavum* and *Phlomis* sp. plants are a good Sb bioaacumulator. Therefore, these plants can be accepted as indicators plants for Sb in mining studies and it will be possible to utilize these plants for the cleaning of Antimony contaminated soils. When the translocation factors of the plants in the study area are examined; Most of these plants were found to have very high TLF values (Figure 15). In particular, plants such as AL, CE, CR, CY, ON, PH, SL, TR and VR seem to have a very high capacity to transport or transfer Sb to the stem root.

Table 8. The Sb concentrations of root and shoot and soils of the study area and TLF, ECR and ECS results for Sb.

	Sb In soil	**Sb in root**	**Sb shoot**	**ECR**	**ECS**	**TLF**
AL-01	141	86	114	0.61	0.81	1.33
AL-02	270	572	113	2.12	0.42	0.20
AL-03	479	305	172	0.64	0.36	0.56
AL-04	1453	240	206	0.16	0.14	0.86
AL-05	500	98	261	0.20	0.52	2.66
Average	569	260	173	0.74	0.45	1.12
AN-01	2407	2232	2066	0.93	0.86	0.93
AN-02	373	160	68	0.43	0.18	0.43
Average	1390	1196	1067	0.68	0.52	0.68
CE-01	711	166	246	0.23	0.35	1.48
CE-02	259	19	28	0.07	0.11	1.50
CE-03	835	105	381	0.13	0.46	3.64
Average	601	97	218	0.14	0.30	2.20
CR-01	233	82	145	0.35	0.62	1.77
CR-02	105	218	114	2.07	1.08	0.52
CR-03	1560	295	299	0.19	0.19	1.01
Average	633	198	186	0.87	0.63	1.10
CY-01	124	40	72	0.32	0.58	1.81
CY-02	450	18	7	0.04	0.01	0.36
Average	287	29	39	0.18	0.30	1.08
GL-01	2466	2254	1722	0.91	0.70	0.76
GL-02	2578	2488	2123	0.97	0.82	0.85
Average	2522	2371	1923	0.94	0.76	0.81
IS- 01	116	84	76	0.72	0.66	0.91
IS-02	845	190	49	0.22	0.06	0.26
IS- 03	849	139	36	0.16	0.04	0.26
IS- 04	2114	2055	921	0.97	0.44	0.45
Average	981	617	271	0.52	0.30	0.47
ON-01	395	79	183	0.20	0.46	2.34
ON-02	1453	188	730	0.13	0.50	3.88
ON-03	444	86	178	0.19	0.40	2.06
Average	764	118	364	0.17	0.46	2.76
PH-01	2301	565	299	0.25	0.13	0.53
PH-02	114	149	228	1.31	2.00	1.53

PH-03	194	172	174	0.89	0.89	1.01
PH-04	203	134	196	0.66	0.97	1.47
Average	703	255	224	0.78	1.00	1.13
SL-01	2342	376	1693	0.16	0.72	4.51
SL-02	451	66	15	0.15	0.03	0.22
SL-03	442	123	24	0.28	0.05	0.20
SL-04	951	218	98	0.23	0.10	0.45
SL-05	1426	124	116	0.09	0.08	0.94
SL-06	875	157	88	0.18	0.10	0.56
Average	1081	177	339	0.18	0.18	1.15
TR-01	482	30	33	0.06	0.07	1.07
TR-02	699	64	65	0.09	0.09	1.01
Average	590	47	49	0.08	0.08	1.04
VR-01	122	81	145	0.67	1.19	1.79
VR-02	375	183	407	0.49	1.09	2.22
VR-03	2554	2302	525	0.90	0.21	0.23
VR-04	701	160	128	0.23	0.18	0.80
VR-05	2125	1682	762	0.79	0.36	0.45
Average	1175	882	393	0.62	0.61	1.10

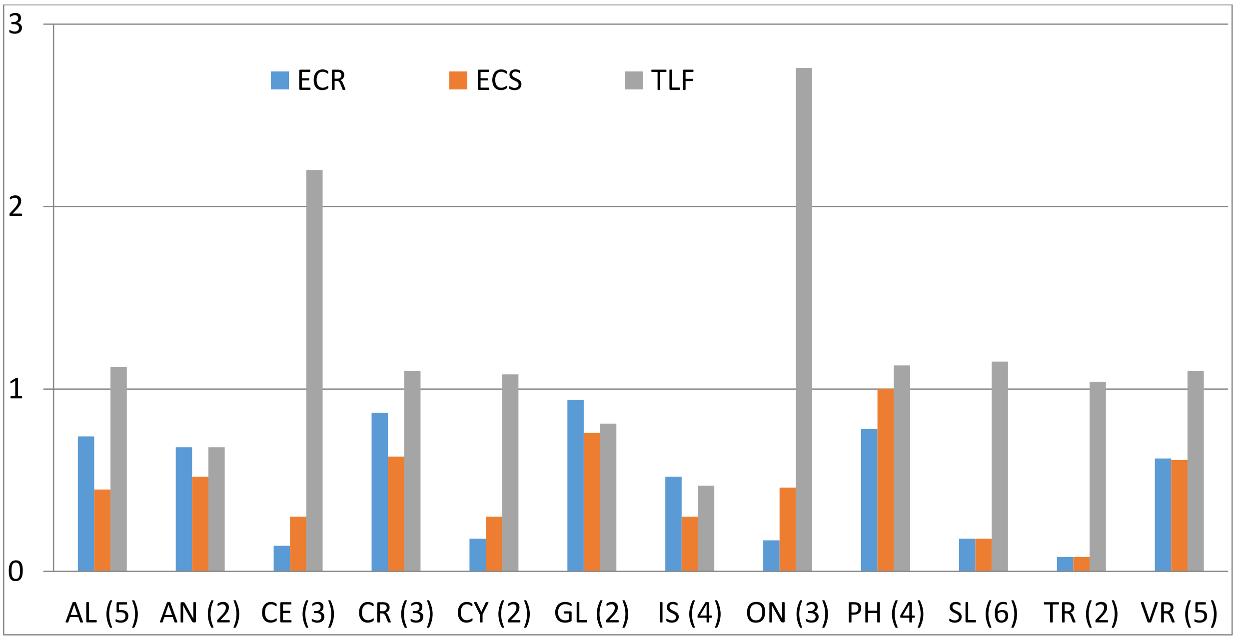

Figure 15. The ECR, ECS and TLF results of the Sb analysis of the soil, plant roots and shoots of the plants in the study area.

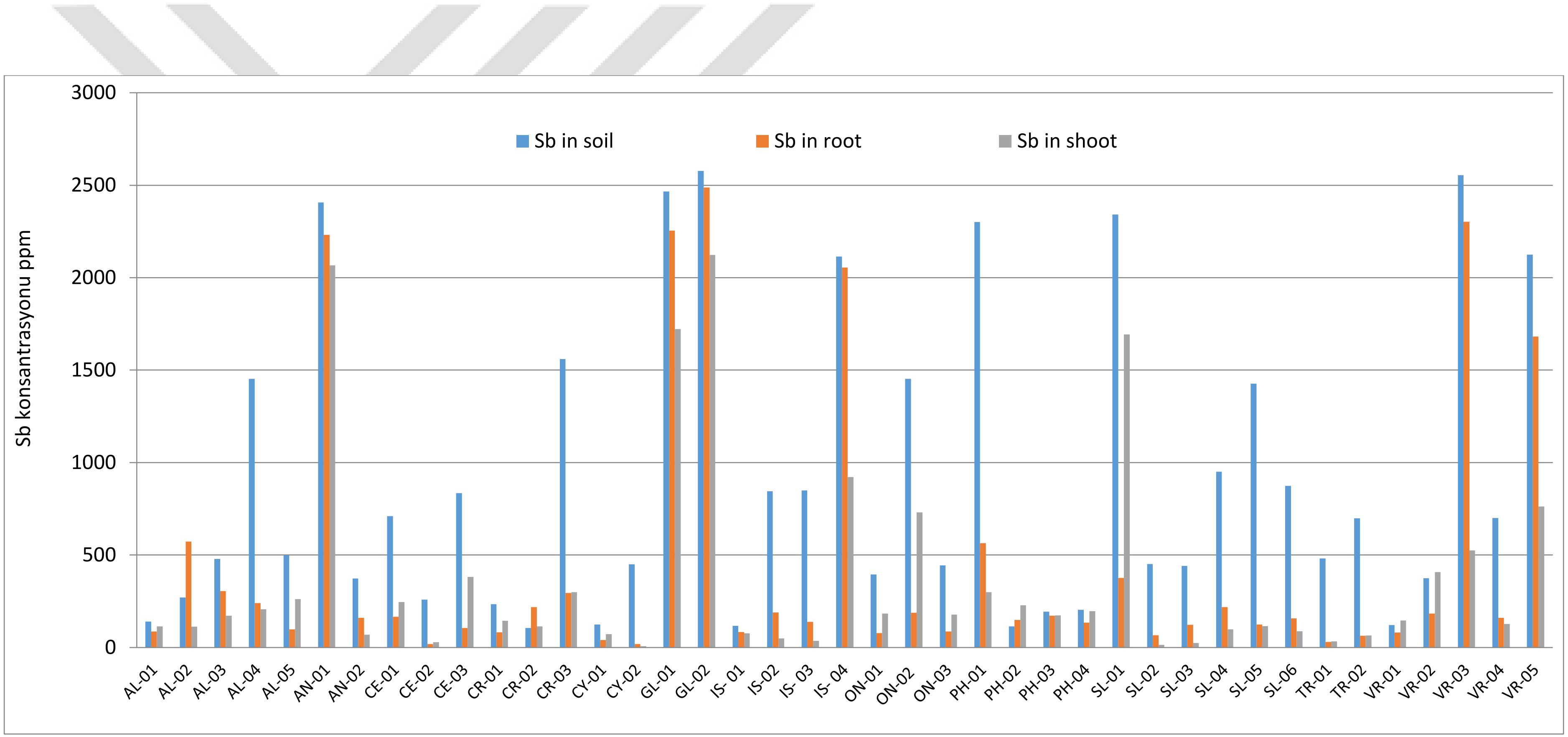

Figure 16. The histogram of the results of the Zinc analysis of the soil, plant roots and stems of the plants in the study area

When the amount of Sb taken from the root by the plant was assessed from a toxic point of view, almost all of the plants' root and shoot were contaminated by the Sb. These values indicate that both the soil and the plants in the study area were contaminated by hundreds and sometimes thousands of Antimony, compared to Pais and Jones (2000) 0.009-1.7 mg / kg (toxic when 5-10 mg / kg). Therefore, surface and groundwater from intense pollution in the local soils is also naturally affected and contaminated.

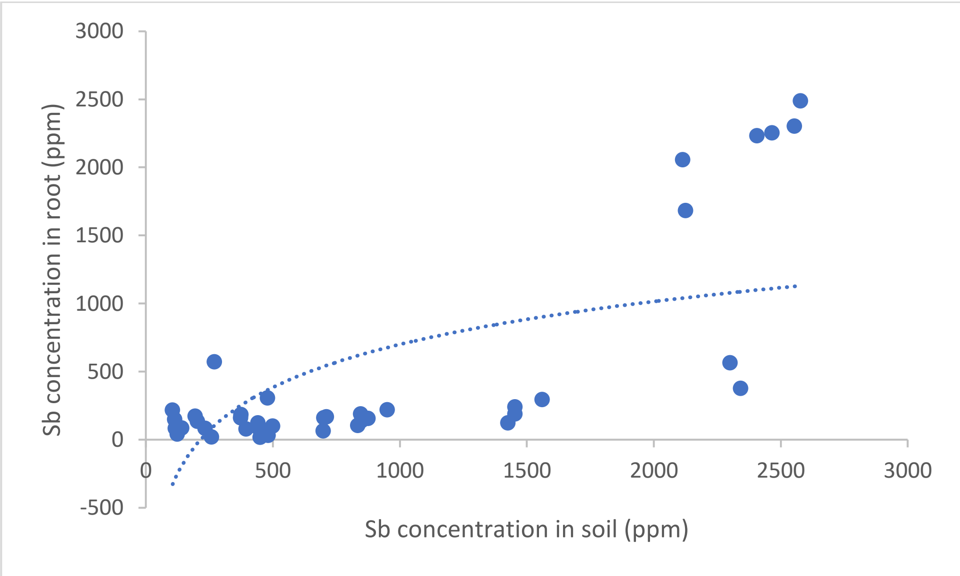

Figure 17. Shows the ratio of zinc concentration distributed between root and soil (ECR).

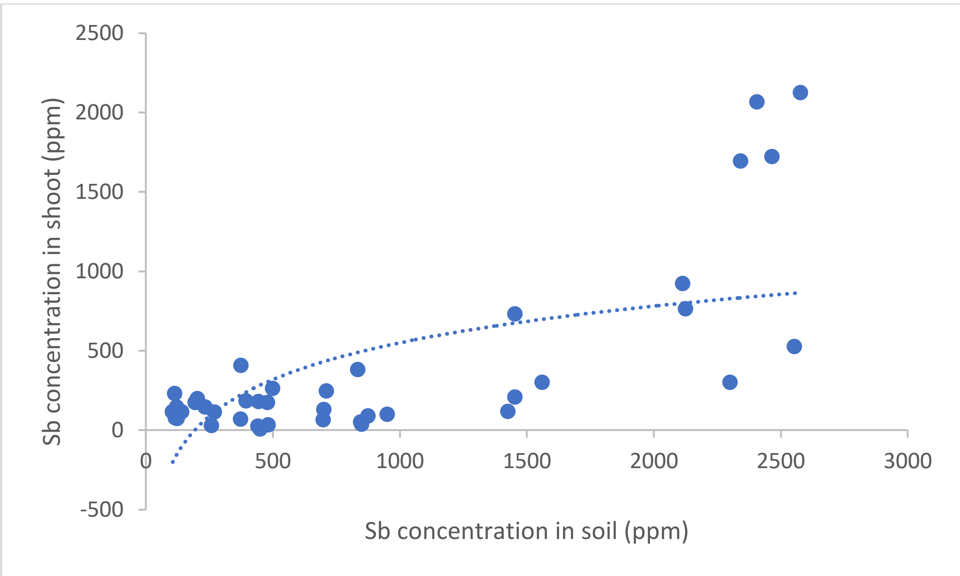

Figure 18.Shows the ratio of zinc concentration distributed between shoot and soil (ECS).

This result can be clearly seen both in the district of the mine site and in the resources and stream waters around the Şahin village.

The fact that plants in the study area are so polluted, the herbaceous plants that are eaten by the animals and people also polluted and leads to entering the pollutants in to the rings of the food chain which may also be heavily influenced by it. When the correlations of the Zinc and Sb metals in the study area are examined; We found that zinc is highly correlated with Cu, Pb, Mn, Ag, Cd, Fe and Se. and it was negatively correlated to As, U, Sr, Pb, Hg, Sc, Ti, Sb. In another hand, antimony had a high correlation with As, U, Pb, Ca, and Hg. There is negative correlation between Sb with Cu, Ag, Mn, Na, K and Zn.

It is possible to distinguish two groups of these metals. The first group metals are Cu, Pb, Zn, Cd, Ag, Mn, Fe and Se, and these metals show high correlations among themselves. The second group of metals is composed of As, Sb, U, Sr, Hg, P and Tl, and these metals show high positive correlations among themselves (Table 10). The first and second group metals have high negative correlations with each other. The first group in the region has weak negative correlations with heavy metals and elements such as K, P, Sc, Sr, Ca and U (Table 10). This shows that I and II in the study area. Almost all of the group metals derive from the same source, but at different times it is perhaps the product of different ore phases and shows that the region is moved in this way. Similarly, the presence of metals such as Sr and Ba, which are known to concentrate in the last phase of the magmatic process in the ore deposits in the region, show positive correlations with the second group metals and the richness of ore-bearing solutions are rich in Sr, supporting the argument that these solutions may have evolved into magmatic finite phase solutions.

Table 9. Correlation associations of heavy metals in soil samples of study area

	Cu	Pb	Zn	Ag	Mn	Fe	As	U	Sr	Cd	Sb	Ca	P	Ba	Hg	Na	K	Sc	Tl	Hg	Se
Cu	1.00																				
Pb	0.76	1.00																			
Zn	0.76	0.71	1.00																		
Ag	0.55	0.40	0.63	1.00																	
Mn	0.83	0.77	0.79	0.49	1.00																
Fe	0.62	0.65	0.64	0.14	0.70	1.00															
As	-0.07	0.31	-0.08	-0.42	-0.01	0.42	1.00														
U	-0.35	0.12	-0.21	-0.44	-0.26	0.25	0.79	1.00													
Sr	-0.46	-0.01	-0.39	-0.55	-0.35	0.09	0.81	0.90	1.00												
Cd	0.76	0.82	0.72	0.34	0.79	0.79	0.22	-0.04	-0.13	1.00											
Sb	-0.12	0.31	-0.01	-0.37	-0.09	0.31	0.92	0.78	0.76	0.13	1.00										
Ca	-0.19	0.06	0.17	-0.15	-0.03	0.06	0.30	0.17	0.19	0.07	0.48	1.00									
Pb	-0.33	-0.03	-0.36	-0.43	-0.30	0.05	0.76	0.77	0.90	-0.14	0.68	0.00	1.00								
Ba	0.04	0.42	0.25	-0.07	0.28	0.37	0.37	0.29	0.23	0.55	0.39	0.50	0.01	1.00							
Hg	-0.01	0.48	-0.07	-0.12	0.06	0.09	0.51	0.48	0.36	0.19	0.52	0.25	0.19	0.54	1.00						
Na	0.02	-0.18	0.00	-0.27	-0.03	0.01	-0.09	-0.24	-0.19	0.02	-0.13	0.23	-0.19	0.02	-0.18	1.00					
K	0.19	-0.03	0.39	0.41	0.14	-0.17	-0.75	-0.59	-0.66	0.06	-0.58	0.07	-0.65	0.03	-0.35	0.30	1.00				
Sc	-0.14	-0.40	-0.41	-0.37	-0.20	-0.01	0.26	0.06	0.20	-0.25	0.04	-0.33	0.42	-0.44	-0.33	0.16	-0.47	1.00			
Tl	-0.41	0.11	-0.26	-0.48	-0.30	0.10	0.80	0.87	0.90	-0.08	0.81	0.30	0.81	0.25	0.52	-0.11	-0.57	0.05	1.00		
Hg	-0.01	0.48	-0.07	-0.12	0.06	0.09	0.51	0.48	0.36	0.19	0.52	0.25	0.19	0.54	1.00	-0.18	-0.35	-0.33	0.52	1.00	
Se	0.73	0.72	0.76	0.40	0.67	0.75	0.29	0.08	-0.02	0.76	0.25	0.12	0.06	0.14	0.04	0.02	0.02	-0.12	0.11	0.04	1.00

4. DISCUSSION

Gümüşköy (Kütahya) The Ag, Pb, Zn and Tl deposit has been known for many years and is the largest Zinc and Antimony deposit of Turkey which has been mined during the historical periods. As a result of the isotope studies on the charcoals belonging to the mining activities in the region, it shows that mining work has been done in the last 1500-2000 years.

Zinc and Antimony metal contents of the soil taken from the study area are determined and these metals are on average Zinc in Soil were 4993, root were 3008 and shoot were 2560 ppm. While for Antimony the average in soil were 700 in soil, 920 in root and 444 in shoot ppm. Correlational relationships of the metals in the study area are examined. Based on these correlations, many metals observed in the field of work generally present two types of correlation relationships. The first group metals are Cu, Pb, Zn, Cd, Ag, Mn, Fe and Se, and these metals show high correlations among themselves. The second group of metals consists of As, Sb, U, Sr, Hg, P and Tl, and this group also shows high positive correlations among the metals. The first and second group metals show high negative correlations with each other. The first group in the region has weak negative correlations with heavy metals and elements such as K, P, Sc, Sr, Ca and U. This shows that I and II in the study area. Almost all of the group metals derive from the same source, but at different times it is perhaps the product of different ore phases and shows that the region is moved in this way. Similarly, in the ore deposits in the region, there are positive correlations between metals such as Sr and Ba, which are known to intensify during the last phase of the magmatic process, and the fact that ore-bearing solutions are rich in Sr also support the argument that these solutions may have evolved into magmatic final phase solutions. When the correlations between soil and plant roots and branches for Ag, As and Pb in the study area are examined; As the amount of metal in the soil increases, the amount of metal in the plant roots and branches increases proportionally.

A large number of samples were taken from one or more annual plants grown in the region and chemical analyzes of their soil, roots and soils were made in ICP-MS and Zn and Sb contents were determined. The ratios of Zn and Sb contents of different parts of plants, ECR and ECS and TLF were examined for each plant separately. Plants important in ECR and ECS in terms of Zn are *Glacium, Silena, Onosma, Phlomis* and *Verbascum*. At the roots and branches of these plants there was a significant transfere of Zinc from the soil. Similarly, when the TLF values of plants for Zinc are examined, the plants with high transferring ability of Zinc from the plant root are CR, AL, CY, CE, ON, PH. When these plants are examined in terms of Sb, they show that PH, and GL are taken as Sb for the plant roots and shoot from the soil in terms of ECR and ECS values. In these plants, the transport of radial Sb has been effective in plants such as AL, CE, CR, CY, ON, PH, SL, TR and VR.

The results of the chemical analysis of both the soil and the plant carried out in the study area show that the pollution in the region is very large. In particular, all these plants, which have been collected from the region, have taken up toxic metals in the high amount such as Zn and Sb in the earth. Especially animals and humans in the region are negatively affected indirectly or directly from these plants. Minerals, such as Zn and Sb, have been included in the most toxic and undesirable elements class in recent years by standards such as WHO, EU and USEPA. These organizations have reduced the level of heavy metals above ground, water and plants to several ppb in 1990 standards. According to these organizations, the targeted figure in the dimensions of the pollution here must be close to zero values.

Average levels of Zinc in study area Soil were 4993 ppm, root were 3008 ppm and shoot were 2560 ppm. While for Antimony the average in soil were 700 in soil, 920 in root and 444 in shoot ppm. This were observed to be at least 100 and often thousands more times contaminated compared to the soil in uncontaminated areas. This dense contamination of the soils in the region causes intensive pollution of the surface waters and resources that are fed from the region. The regions where the most intensive pollution is in the region are Aktepe, Kayabaşı T. Gözeçukur region, Koca T. Şahin village and its surroundings, Koca Valley and Şahin Valley. The soils in these areas are heavily polluted. Because of the mining activity that took place in the region in the past years, the region was heavily polluted. The local soils were affected more than the average pollution. However, this contamination of the soil, then chain has leads to contamination of groundwater. The plants growing in the region are polluted with heavy metals as well as the soils which resulted in polluting the plants and animals eating them. Thus, all living organisms in the area are naturally affected. Improvement studies should be carried out on and around such deposits, agriculture and agriculture should not be done in overcrowded areas. Surfaces and underground waters originating from the region should not be used for drinking and irrigation purposes. The heavy waters of this area should be precipitated by means of small ponds. In this respect, the pollution caused by the area should be prevented from polluting the areas below. Rehabilitation operations should be especially forested with visual and heavily contaminated areas, with appropriate terracing and greening. In this way, all living creatures living in and around the area should be brought to a position where they can be harmed very less. Care should be taken to select bioaccumulator plants that have the ability to clear toxic elements in the area during conversion to a green area. Thus, even if not in a short time, it is aimed to clean or minimize pollution in the region in the long term. Such processes start with the production of minerals in modern countries, and when the deposits are exhausted, improvement works have been completed.

This work has been completed with limited opportunities and completed within about a year. It is thought that the output of this study is very important in terms of environmental health. Especially intensely polluted areas in the area should be protected and people and animals must be prevented from entering these areas. Because these regions are used for grazing animals by the people of the region as dense grassland areas. Hence, the herbs that grow in contaminated areas of heavy metals are taken by these animals to their structures. Later on, these milk and meat products are consumed by the people of the region and therefore the local people face significant risks from the environmental point of view.

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