Bulletin of MTA (2014) 148: 85-106

Bulletin of the
Mineral Research and Exploration

http://bulletin.mta.gov.tr

# TRACE/HEAVY METAL ACCUMULATION IN SOIL AND IN THE SHOOTS OF ACACIA TREE, GÜMÜŞHANE-TURKEY

Alaaddin VURAL[a]

[a] *Gümüşhane University, Faculty of Engineering and Natural Sciences, Dept. of Geological Engineering, Gümüşhane-Turkey*

Keywords:
Geochemistry,
Biogeochemistry, Trace
element, Heavy metal,
Acacia, Gümüşhane.

**ABSTRACT**

In this study, heavy metal/trace element accumulation was investigated in soils along the road passing through Gümüshane city center and shoots of 1-2 years of acacia trees (Robinia pseudoacacia L.) grown in these soils. Heavy metal contents in soils and plants were analyzed by Enrichment Factor (EF), Geo-accumulation index ($I_{geo}$) parameters, and by Bio Accumulation Factor (BAF), respectively. According to geo-accumulation index ($I_{geo}$) data, it is seen that the soil was unpolluted in terms of Cr, Co, Cu, Rb, Sr; unpolluted to moderately polluted in terms of V, Ni and Zn; moderate to excessively polluted in terms of As, and moderate to excessively polluted in terms of Pb. According to EF parameters, on the other hand, it is observed that the soil was non to slightly enriched in terms of Cr, Co, Sr and Ba; non to moderately enriched in terms of Ni and Cu; slightly to significantly enriched in terms of Zn; significant to very highly enriched in terms of As and slightly to over excessively enriched in terms of Pb. Although trace/heavy metal contents of acacia shoots were usually within normal values for acacia, it was determined that Cu, Fe, Mo, Ni, Sr and Zn concentrations were within and/or above upper limits of normal values in certain sampling points.

## 1. Introduction

Investigations related to trace element/heavy metal within the perspective of environmental geochemistry have been increasingly continuing everyday (Wheeler and Rolfe, 1979; Kovacs et al., 1981; Kabata-Pendias and Pendias, 1994; Kabata-Pendias, 2000; Kocaer and Baskaya, 2003; Bosco et al., 2005; Önder and Dursun, 2005; Birch and Scollen, 2003; Murakami et al., 2009; Yaylalı-Abanoz and Tüysüz, 2009; Yaylalı-Abanoz et al., 2011; Ahdy and Khaled 2009; Rodriguez-Barroso et al., 2009; Machender et al., 2011; Miao et al., 2011;Vural and Şahin 2012*a*, *b*). Therefore, the roles of many sciences, especially the geochemistry, have been increasing on the environmental awareness, the quality of environment and on the environmental health.

In this study, it was aimed at detailing the findings related to heavy metal accumulation which was obtained by Vural and Şahin (2012*a* and *b*) along the auto road passing through Gümüşhane city center. Studies related to investigating the dimensions of pollution in the field and factors effective in the formation of it have still been performed by the investigator within scope of environmental geochemistry. Because of geological characteristics of the region, the negative effects which the urbanization had brought up were investigated in multi dimensions, and geological, hydrogeological and biochemical studies both in soil and on plants still continue. However, in this study, the geochemical and biogeochemical characteristics of heavy metals/trace elements of the soil along the auto road and acacia shoots grown up in this soil were taken into consideration.

---

* *Corresponding author : vural@gumushane.edu.tr*

For this purpose, total of 45 samples were collected from the soil and from the shoots of acacia in the field. Analyses of soil samples and acacia shoots in the field were performed in the Department of Research and Development of the General Directorate of ETİ Maden and in the laboratory of Trabzon Provincial Food Control Directorate using ICP-AES, respectively. Within the study, the change of trace element contents in soil with respect to reference values, the source of this change and biological transmission rates from trace element into acacia shoots in the soil were investigated.

## 2. Material and Method

### 2.1. Study Area

The study area is located within Gümüşhane provincial borders towards the eastern part of the Pontide tectonic unit and covers a 20 $km^2$ area with 2x10 km (Figure 1).

Rocks cropping out in the study area which extend along the state road passing through city center are divided into two groups as Late Paleozoic basement rocks and Mesozoic-Cenozoic cover rocks. Basement rocks in the region are represented by Early-Middle Carboniferous Pulur-Kurtoğlu metamorphic rocks (Topuz et al., 2007) and unmetamorphosed Middle-Late Carboniferous Gümüşhane granitoid (Yılmaz 1972, 1974; Topuz et al., 2010; Dokuz, 2011). Gümüşhane granitoidas well which crops out in the study area is mainly composed of microdiorite with quartz, granite and dacitic porphyries (Yılmaz, 1972; Çoğulu, 1975; Topuz et al., 2010). This rock assemblage was named as Köse Composite Plutonic in and around Köse, outside the study area by Dokuz

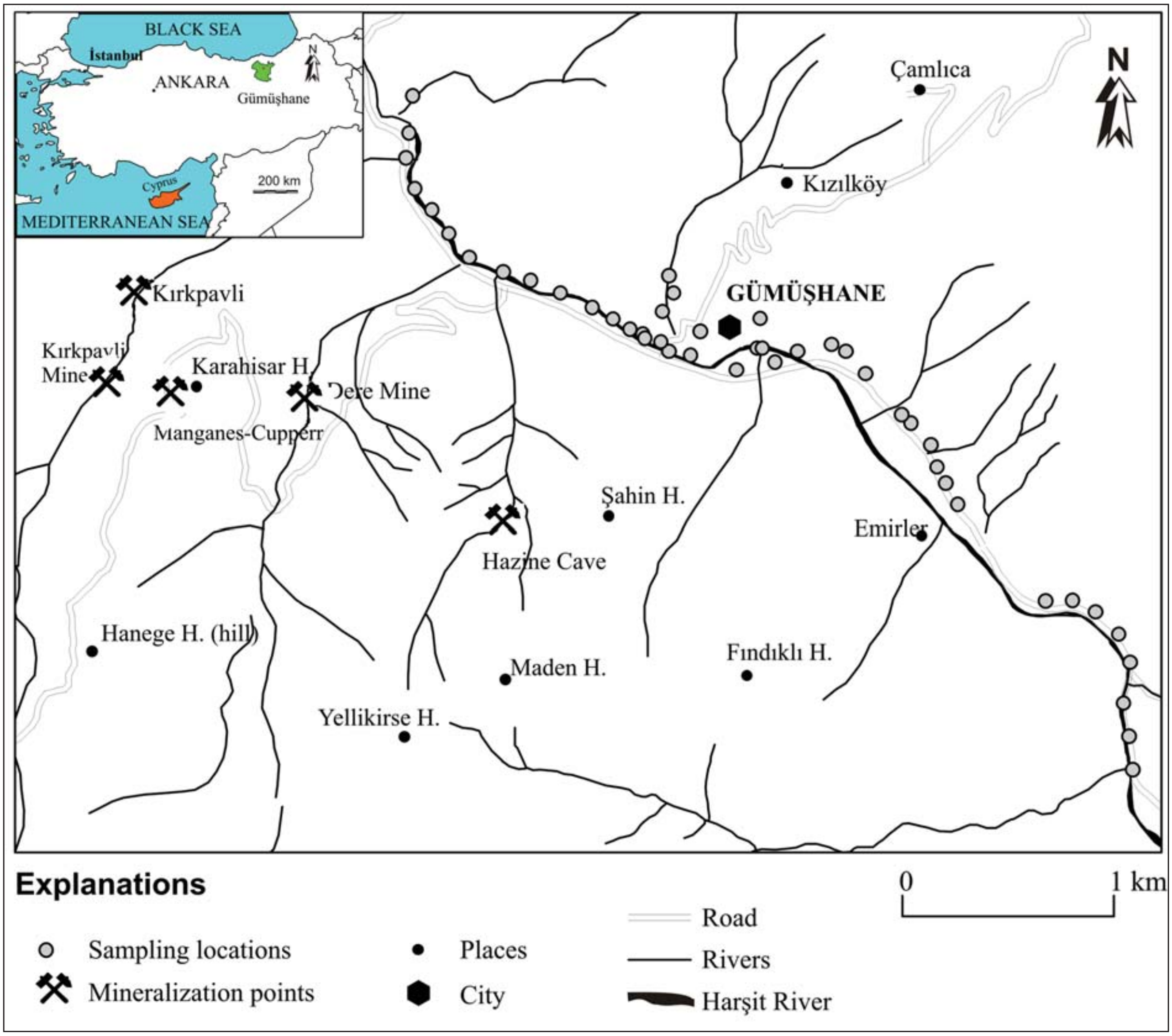

Figure 1- Location map of the study area

(2011). The lowermost section of the Mesozoic deposit is represented by unconformably overlying Early Jurassic volcano sedimentary unit over Variscan basement. This unit, which was named as Şenköy formation, is interpreted as rift facies related with the opening of Neotethys Ocean (Kandemir, 2004). The formation begins with basal conglomerate and continues upward with basalt, diabase, chert and dacitic tuff bearing turbiditic calcerous pebble stone, sandstone, siltstone and marls (Adamia et al., 1977; Kandemir, 2004; Eyüboğlu et al., 2006). Şenköy formation is overlain by Late Jurassic–Early Cretaceous Berdiga formation of which its bottom is formed by platform carbonate in massive character in general (Pelin, 1977). Carbonates are overlain by Late Cretaceous Kermutdere formation. This formation begins with yellow, sandy limestones at the bottom and continues with red colored clastic carbonates and gray colored turbidites (Tokel, 1972). All these units are cut by late Cretaceous intrusions especially on the road between Gümüşhane–Trabzon and outside the study area (Kaygusuz et al., 2008, 2010).

All Pontides have uplifted above the water level starting from Paleocene to Middle Eocene. This situation is represented by a widespread unconformity which is dedicated to the collision of Pontides with Anatolide-Tauride block and the closure of northern branch of Neotethys. Late Cretaceous volcanic and/or sedimentary rocks in Gümüşhane region are unconformably overlain by Middle-Late Eocene marine volcanosediments (Aslan and Aliyazıcıoğlu, 2001; Kaygusuz et al., 2010). These rocks, which are also named as Alibaba formation (Tokel, 1972) or as Kabaköy formation (Güven, 1993) begin with conglomerates, nummulitic limestones interbedded with sandstone and tuff, and continue with andesite and related pyroclastics towards upper layers. The unit ends with alternation of occasionally eroded limestone, sandstone, marl and tuff (Aliyazıcıoğlu, 1999). These units are again cut by synchronous intrusive rocks (Karslı et al., 2010; Eyüboğlu et al., 2011). These rocks, which crop out in the close vicinity of the study area, in and around Gözeler, were named as Gözeler granite. Quaternary travertine, debris flows and alluvials are the youngest units in the region.

Gümüşhane granitoid in the study area spreads out along Harşit Stream and continues until city exit from Bağlarbaşı locality to Trabzon.It also overlies Alibaba formation with a tectonic contact on the exit of Gümüşhane. The general stratigraphic succession of the region is typically observed within the study area (Figure 2).

At the same time, Gümüşhane and its vicinity is one of the most significant mine provinces bearing many lead, zinc, copper and gold mineralizations. The tectonism which is closely related with mineralization is affective in the region. Sulfide mineralization which developed due to young granitic intrusives were emplaced along these tectonic lines and formed Cu, Pb, Zn, Au and Ag mineralization (Güner et al., 1985; Kahraman et al., 1985; Güner and Yazıcı, 2005; Aslan and Akçay 2011; Akçay et al., 2011).

The origin of soil formation in the study area is mainly the Gümüşhane granitoid with lesser amount of Eocene volcanic rocks.

## 2.2. Sampling Method and Analyses

In order to carry out geochemical and biogeochemical studies, 45 samples were collected from soil and 1-2 years old shoots of acacia tree which had grown over this soil along the road passing through Gümüşhane city center (Figure 1). Sampling was performed approximately 10 km along road. Samples were collected along road and its surroundings, since Gümüşhane had been located in a narrow valley and Iran-Turkey state road passing through the city center has an intense traffic. When analyzing heavy metal/trace element contents in the soil, the collected samples from which the soil was originated become important. The element contents of granitic and volcanic rocks in the region were statistically assessed and values obtained were used as the reference values. For soils which are considered to have originated from granitoid rocks, the trace element values of Topuz et al. (2010); for soils which are considered to have originated from volcanic rocks the trace element values of Aslan (2010); and for chromium and arsenic elements, the trace element values of Turekian and Wedepohl (1961); and Taylor and McLennan (1995) were used.

Soil samples were collected at a depth of 25 centimeters and directly put into nylon bags from zones (a) and (b) of the soil then were again put into another nylon bag to prevent it from other factors. Maximum care was taken during collection and preservation of samples in order to avoid them from contamination. Soil samples were dried up in oven 2

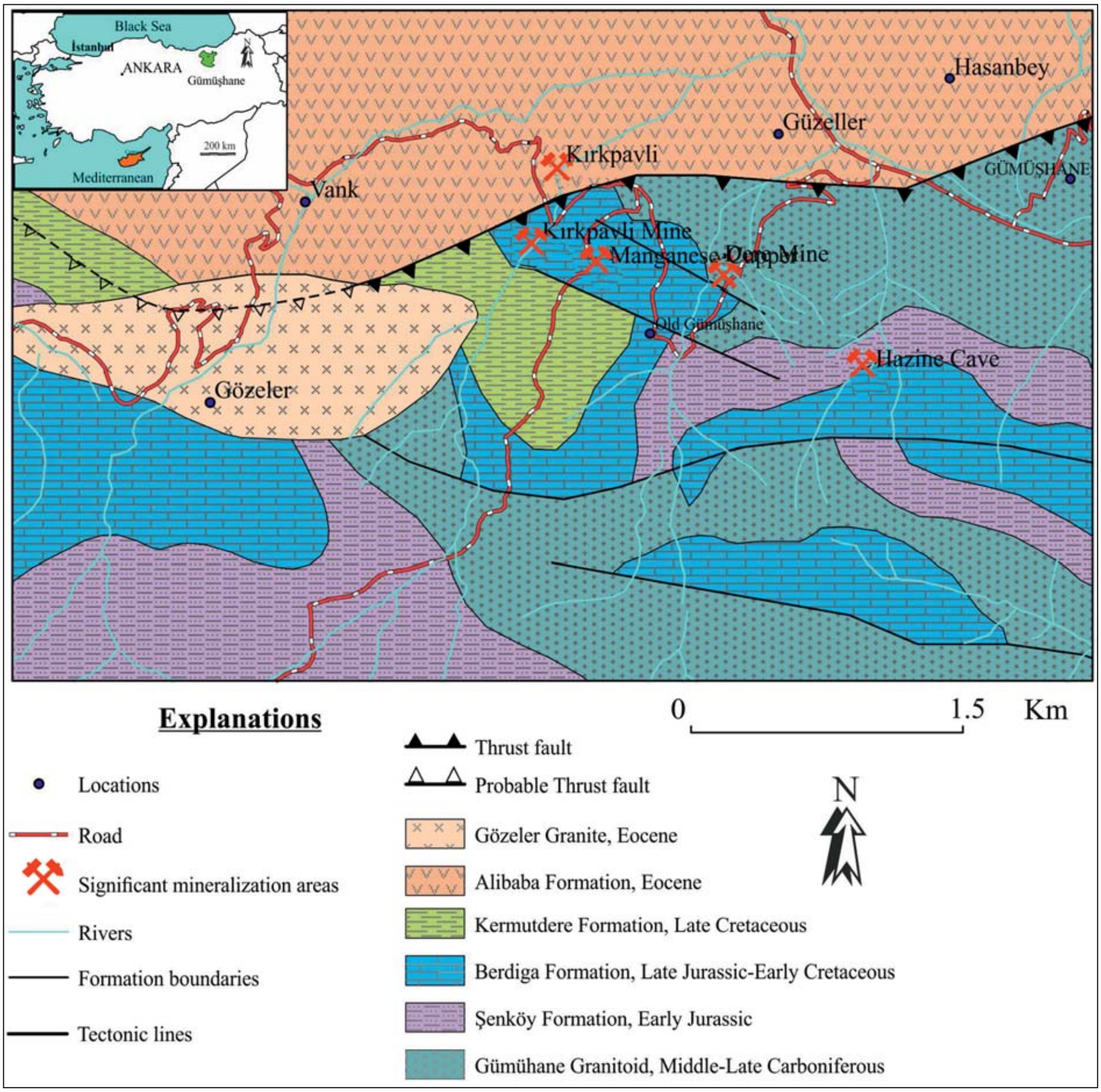

Figure 2-Geological map of the study area and its vicinity (modified from Güven, 1993)

days at a temperature of 60 °C and pulverized down to 250 mesh size by grinder. Pulverized samples were then weighted on platinum crucible between 0.5-1 in the laboratory of Department of Research and Development of the General Directorate of Eti Maden Management (Ankara) and 2-3 spatulas of (6 units $Na_2CO_3$+1 unit $Na_2B_4O_7$) mixture were added. Platinum cover was then closed and kept one hour under the temperature of 1000 °C. It was then dissolved in a 400 ml cup with 50 ml hydrochloric acid (HCl) and 100 ml boiling water. Filtering was made from black banded filter paper into 250 ml balloon, and concentrations of elements were estimated in ICP-AES instrument. Results of analyses of soil samples were given in table 1.

Plant samples each weighing 200 gr were taken from 1-2 years old shoots of acacia trees in localities from where soil samples had been collected, then washed in distilled-deionized water and dried up in oven 24 hours under 80 °C temperature. Dried samples were then grinded and powdered. Samples each weighing 1 gram were disintegrated in microwave oven 4 hours at a temperature of 500 °C. Samples were weighted in teflon cups of the microwave oven ranging between 0.8-1.0 gr and at a

0.1 mg sensitivity. Later on, 6 ml concentrated $HNO_3$ and 1.5 ml $H_2O_2$ (peroxide) were added on to cups and placed into microwave oven after cups had been closed. Hence, samples were disintegrated by means of microwave beam, pressure and acid, and then rendered into a crystalline solution. Teflon cup contents were taken into measured balloon and were equalized to 25 ml by pure water. Metal contents of solutions obtained were determined by being analyzed in ICP-AES instruments of Trabzon Provincial Food Control Laboratories. Results were given in table 2.

The procedure suggested by Duran et al. (2007) was applied in ICP-AES measurements. Within this framework, standard solutions were prepared by diluting 1000 mg/l solutions from each metal (Merck, Darmstadt/Germany). These standard solutions were read on the instrument, and drawing concentrations (mg/l) against emission intensity graphs their standard calibration graphics were obtained. Using these graphics, the metal contents of samples were determined. The accuracy tests of results were checked by two methods; adding/regaining tests and standard reference material analyses. CRM 1568a Rice Flour was used as the standard reference material.

Values obtained by the method used in this study (microwave disintegration / ICP-AES) and certified contents of reference material in terms of some metals were identified and these values were given in table 3. As it is seen from table 3, there is not much difference between certified and obtained values.

Table 1- Results of chemical analyses of soil samples (concentration values in mg/kg)

| Sample Nr. | Al | Fe | Zr | Sr | Rb | Ba | Cd | Co | Cr | Cu | Mn | Ni | Pb | Zn | Y | As | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GÇ-1 | 76899.39 | 28116.59 | 51.49 | 144.16 | 99.67 | 556 | BDL | BDL | 105 | 34 | 797 | 36 | 20 | 72 | 17 | 9 | BDL |
| GÇ-2 | 101668.08 | 32452.98 | 77.65 | 72.08 | 164.59 | 900 | BDL | BDL | 97 | 35 | 710 | BDL | 49 |  | 19 | 13 | BDL |
| GÇ-3 | 106537.14 | 35040.82 | 44.95 | 72.08 | 170.08 | 1110 | BDL | BDL | 113 | 34 | 850 | 30 | 22 |  | 27 | 20 | BDL |
| GÇ-4 | 73406.37 | 36439.66 | 73.97 | 216.24 | 97.84 | 712 | BDL | BDL | 98 | 55 | 859 | 44 | 64 | 252 | 14 | 2 | BDL |
| GÇ-5 | 86849.21 | 36579.54 | 55.58 | 216.24 | 100.58 | 723 | BDL | BDL | 68 | 51 | 649 |  | 58 | 106 | 15 | 5 | BDL |
| GÇ-6 | 79069.30 | 35670.30 | 56.80 | 216.24 | 92.36 | 847 | BDL | 19 | 116 | 56 | 914 | 28 | 74 | 175 | 19 | 11 | 71 |
| GÇ-7 | 84520.52 | 39656.98 | 67.43 | 216.24 | 98.76 | 586 | BDL | BDL | 51 | 55 | 972 | 50 | 63 | 156 | 20 | 15 | BDL |
| GÇ-8 | 76581.84 | 30354.72 | 55.99 | 144.16 | 85.95 | 369 | BDL | BDL | 71 | 53 | 1759 | 34 | 240 | 406 | 12 | 12 | BDL |
| GÇ-9 | 93094.30 | 36509.60 | 80.92 | 144.16 | 130.76 | 949 | BDL | BDL | 104 | 54 | 865 | 56 | 56 | 74 | 20 | 5 | 33 |
| GÇ-10 | 69595.80 | 39377.21 | 44.95 | 216.24 | 54.86 | 545 | BDL | BDL | 84 | 76 | 931 | 53 | 55 | 158 |  | 13 | BDL |
| GÇ-11 | 94999.59 | 36789.37 | 65.39 | 72.08 | 158.19 | 847 | 10 | BDL | 106 | 41 | 975 | 32 |  | 81 | 16 | 14 | 55 |
| GÇ-12 | 86108.26 | 44552.90 | 78.06 | 144.16 | 85.04 | 536 | BDL | BDL | 105 | 79 | 1318 | 45 | 441 | 153 | 20 | 6 | BDL |
| GÇ-13 | 99021.85 | 30424.67 | 53.94 | 72.08 | 193.85 | 487 | BDL | BDL | 104 | 48 | 988 | 22 | 19 | 127 | 10 |  | 118 |
| GÇ-14 | 73618.07 | 44203.19 | 43.32 | 216.24 | 40.23 | 401 | BDL | BDL | 65 | 84 | 1065 | 43 | 73 | 177 | 17 | 20 | BDL |
| GÇ-15 | 73088.82 | 36299.77 | 44.95 | 216.24 | 61.27 | 644 | BDL | 33 | 172 | 76 | 1097 | 39 | 146 | 191 | 14 | 9 | BDL |
| GÇ-16 | 80392.41 | 36089.95 | 71.11 | 216.24 | 114.30 | 645 | 2 | BDL | 114 | 58 | 989 | 56 | 133 | 199 | 20 | 9 | 47 |
| GÇ-17 | 84308.83 | 33152.40 | 67.43 | 72.08 | 127.10 | 665 | BDL | BDL | 109 | 34 | 886 | 28 | 26 | 85 | 19 | BDL | BDL |
| GÇ-18 | 84732.22 | 41125.76 | 55.99 | 216.24 | 80.47 | 534 | BDL | BDL | 111 | 70 | 899 | 46 | 56 | BDL | 20 | 2 | 39 |
| GÇ-19 | 84414.68 | 39237.33 | 65.80 | 288.33 | 96.93 | 802 | BDL | BDL | 95 | 51 | 877 | 42 | 36 | BDL | 19 | 11 | BDL |
| GÇ-20 | 87748.92 | 38537.91 | 59.26 | 216.24 | 100.58 | 882 | 14 | BDL | 106 | 62 | 873 | 47 | 27 | 122 | 19 | 13 | 8 |
| GÇ-21 | 97116.57 | 38467.97 | 73.97 | 144.16 | 117.96 | 805 | 4 | BDL | 73 | 66 | 868 | 47 | 71 | 131 | 21 | 18 | BDL |
| GÇ-22 | 89389.58 | 46651.16 | 68.66 | 288.33 | 82.30 | 521 | BDL | BDL | 48 | 86 | 1072 | 40 | 52 | 134 | 13 | BDL | BDL |
| GÇ-23 | 102091.48 | 49588.71 | 78.46 | 216.24 | 108.81 | 557 | BDL | BDL | 85 | 87 | 1214 | 56 | 43 | BDL | 25 | 30 | BDL |
| GÇ-24 | 90659.77 | 41755.23 | 71.52 | 216.24 | 79.55 | 536 | BDL | BDL | 78 | 77 | 1012 | 46 | 60 | 146 | 22 | 10 | BDL |
| GÇ-25 | 83726.66 | 53365.56 | 95.63 | 360.41 | 19.20 | 328 | BDL | BDL | 241 | 71 | 1023 | 195 | BDL | BDL | 19 | 9 | BDL |
| GÇ-26 | 93835.25 | 41615.35 | 70.70 | 144.16 | 83.21 | 529 | BDL | BDL | BDL | 60 | 1039 | 52 | 39 | 127 | 23 | 19 | BDL |
| GÇ-27 | 87166.75 | 33781.87 | 109.11 | 144.16 | 177.40 | 1074 | BDL | BDL | 114 | 29 | 734 | 14 | BDL | BDL | 27 |  | BDL |
| GÇ-28 | 97010.72 | 37698.61 | 71.11 | 216.24 | 103.33 | 944 | 6 | BDL | 66 | 44 | 817 | 30 | 67 | 114 | BDL | 10 | BDL |
| GÇ-29 | 64832.59 | 33152.40 | 49.86 | 216.24 | 73.15 | 515 | 12 | BDL | 193 | 59 | 750 | 42 | 85 | BDL | 15 | BDL | 84 |
| GÇ-30 | 98757.23 | 34621.17 | 68.25 | 72.08 | 180.14 | 920 | BDL | BDL | 120 | 33 | 1035 | 35 | BDL | BDL | BDL | 18 | 130 |
| GÇ-31 | 83938.35 | 42314.77 | 73.15 | 288.33 | 101.50 | 781 | 10 | BDL | 115 | 65 | 1055 | 36 | 50 | 174 | 17 | 8 | 52 |
| GÇ-32 | 88701.57 | 35810.18 | 57.62 | 144.16 | 142.65 | 865 | BDL | BDL | 109 | 43 | 880 | 38 | 33 | 95 | 12 | 1 | 17 |
| GÇ-33 | 92882.61 | 35600.36 | 83.37 | 144.16 | 142.65 | 844 | 6 | BDL | 131 | 51 | 860 | 40 | 38 | 104 | 20 | 42 | BDL |
| GÇ-34 | 77428.63 | 35670.30 | 53.54 | 216.24 | 80.47 | 715 | BDL | 3 | 96 | 36 | 826 | 31 | 29 | 110 | 13 | 11 | BDL |
| GÇ-35 | 76052.60 | 36299.77 | 50.27 | 216.24 | 67.67 | 580 | BDL | BDL | 89 | 67 | 864 | 32 | 89 | 182 | BDL | 24 | BDL |
| GÇ-36 | 84996.85 | 39307.27 | 141.40 | 288.33 | 78.64 | 782 | BDL | BDL | 86 | 67 | 692 | 40 | 49 | 195 | BDL | 14 | BDL |
| GÇ-37 | 106166.67 | 39447.15 | 87.05 | 72.08 | 149.96 | 770 | BDL | BDL | 77 | 38 | 1009 | 50 | 45 | 126 | 24 | 18 | BDL |
| GÇ-38 | 108283.65 | 35110.76 | 86.23 | 72.08 | 171.91 | 918 | BDL | BDL | 75 | 30 | 832 | 31 | 3 | 86 | 24 | 21 | BDL |
| GÇ-39 | 99709.87 | 34970.88 | 77.65 | 144.16 | 144.48 | 524 | 0.1 | BDL | 65 | 38 | 790 | 32 | 12 | 89 | 17 | 12 | BDL |
| GÇ-40 | 85843.64 | 30564.55 | 68.25 | 144.16 | 117.04 | 808 | BDL | BDL | 134 | 37 | 32 | 37 | BDL | BDL | 9 | 56 | BDL |
| GÇ-41 | 97804.59 | 46091.62 | 59.26 | 288.33 | 67.67 | 661 | BDL | BDL | 56 | 92 | 749 | 41 | 64 | 105 | 15 | 17 | BDL |
| GÇ-42 | 98175.06 | 33362.22 | 78.87 | 72.08 | 167.34 | 957 | BDL | BDL | 85 | 15 | 811 | 25 | 16 | 132 | 19 | 21 | 75 |
| GÇ-43 | 98333.84 | 32662.80 | 86.64 | 72.08 | 160.02 | 741 | BDL | BDL | 96 | 41 | 719 |  | 28 | 122 | 10 | 5 | 61 |
| GÇ-44 | 85684.87 | 37838.49 | 69.47 | 216.24 | 92.36 | 737 | 15 | BDL | 80 | 48 | 784 | 36 | 51 | 138 | 18 | 10 | BDL |
| GÇ-45 | 67531.74 | 36859.31 | 64.98 | 288.33 | 85.04 | 621 | BDL | BDL | 81 | 65 | 967 | 74 | 106 | 325 | 13 | 16 | 74 |

BDL: Below Detection Limit

Table 2- Element contents of shoots of acacia (concentration values in mg/kg)

| Sample Nr. | Al | As | Ba | Cd | Co | Cr | Cu | Fe | Mn | Mo | Ni | Sn | Sr | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GÇA-1 | 99.9 | 2.08 | 14.7 | BDL | 0.90 | 2.05 | 10.5 | 693.3 | 8.6 | 42.1 | 1.49 |  | 61.2 | 12.5 |
| GÇA-2 | 90.2 | BDL | 8.5 | BDL | 0.88 | 1.14 | 2.8 | 88.7 | 8.1 | 42.1 | BDL | BDL | 39.5 | 10.3 |
| GÇA-3 | 62.0 | BDL | 9.5 | BDL | 0.73 | 0.86 | 5.3 | 63.8 | 8.1 | 23.8 | BDL | BDL | 49.6 | 16.7 |
| GÇA-4 | 74.8 | BDL | 11.4 | BDL | 0.89 | 0.91 | 4.8 | 79.1 | 6.5 | 44.1 | BDL | BDL | 40.4 | 31.7 |
| GÇA-5 | 48.5 | BDL | 4.9 | BDL | 0.79 | 0.62 | 2.8 | 47.2 | 5.9 | 49.5 | BDL | BDL | 26.2 | 8.6 |
| GÇA-6 | 146.7 | BDL | 7.1 | BDL | 0.83 | 2.15 | 4.3 | 139.5 | 6.8 | 56.4 | BDL | BDL | 60.3 | 12.5 |
| GÇA-7 | 54.1 | BDL | 4.6 | BDL | 0.83 | 1.08 | 5.4 | 74.3 | 7.0 | 48.1 | BDL | BDL | 40.9 | 13.6 |
| GÇA-8 | 30.4 | BDL | 7.4 | BDL | 0.94 | 0.96 | 3.3 | 53.0 | 5.7 | 42.1 | BDL | BDL | 37.7 | 28.3 |
| GÇA-9 | 33.4 | BDL | 5.4 | BDL | 0.48 | 0.98 | 2.9 | 47.4 | 7.3 | 10.2 | BDL | BDL | 31.2 | 16.7 |
| GÇA-10 | 32.8 | BDL | 4.2 | BDL | 0.73 | 0.74 | 2.8 | 38.6 | 4.1 | 7.3 | BDL | BDL | 19.6 | 11.9 |
| GÇA-11 | 27.8 | BDL | 14.0 | BDL | 0.81 | 0.77 | 2.9 | 53.3 | 12.5 | 25.2 | BDL | BDL | 50.8 | 14.2 |
| GÇA-12 | 38.9 | BDL | 8.8 | BDL | 0.58 | 1.07 | 3.0 | 55.0 | 5.5 | 14.8 | BDL | BDL | 50.2 | 11.8 |
| GÇA-13 | 44.3 | BDL | 18.5 | BDL | 0.93 | 0.92 | 3.6 | 60.8 | 14.0 | 32.5 | 1.74 | BDL | 73.0 | 13.3 |
| GÇA-14 | 43.2 | BDL | 7.4 | BDL | 0.68 | 0.84 | 4.0 | 47.9 | 5.9 | 8.9 | BDL | BDL | 38.1 | 10.9 |
| GÇA-15 | 88.2 | BDL | 7.2 | BDL | 0.51 | 1.23 | 7.6 | 94.8 | 8.8 | 19.9 | 1.09 | BDL | 35.2 | 21.3 |
| GÇA-16 | 62.7 | BDL | 12.5 | BDL | 0.89 | 1.88 | 34.4 | 89.9 | 12.0 | 17.5 | 5.41 | BDL | 22.6 | 47.0 |
| GÇA-17 | 88.2 | BDL | 5.7 | BDL | 0.83 | 0.86 | 6.3 | 90.2 | 7.3 | 19.2 | BDL | BDL | 34.2 | 10.0 |
| GÇA-18 | 199.5 | BDL | 10.6 | BDL | 0.93 | 2.19 | 6.2 | 197.1 | 8.3 | 21.0 | 1.45 | BDL | 77.1 | 18.4 |
| GÇA-19 | 69.0 | BDL | 4.9 | BDL | 0.56 | 1.04 | 4.3 | 63.0 | 3.7 | 32.7 | BDL | BDL | 34.9 | 10.0 |
| GÇA-20 | 76.2 | BDL | 6.9 | BDL | 0.90 | 1.12 | 10.2 | 84.0 | 7.3 | 33.5 | 1.43 | BDL | 53.2 | 36.3 |
| GÇA-21 | 38.0 | BDL | 6.0 | BDL | 0.80 | 0.33 | 5.4 | 40.3 | 5.3 | 30.2 | BDL | BDL | 33.5 | 10.0 |
| GÇA-22 | 46.2 | 1.99 | 6.0 | BDL | 0.71 | 0.71 | 3.6 | 59.7 | 5.9 | 18.8 | BDL | BDL | 24.5 | 20.4 |
| GÇA-23 | 36.0 | BDL | 4.1 | BDL | 0.83 | 0.66 | 5.0 | 46.0 | 5.3 | 11.3 | BDL | BDL | 27.4 | 20.6 |
| GÇA-24 | 50.3 | BDL | 6.0 | BDL | 0.86 | 0.65 | 5.3 | 56.5 | 6.8 | 21.4 | 1.18 | BDL | 31.4 | 15.4 |
| GÇA-25 | 35.6 | BDL | 5.3 | BDL | 0.63 | 0.63 | 4.8 | 36.8 | 5.4 | 13.1 | BDL | BDL | 35.5 | 17.3 |
| GÇA-26 | 203.0 | BDL | 9.4 | BDL | 0.61 | 2.48 | 4.6 | 193.3 | 7.9 | 16.4 | 1.11 | BDL | 32.5 | 16.5 |
| GÇA-27 | 61.7 | BDL | 4.1 | BDL | 0.77 | 1.01 | 8.8 | 61.0 | 8.2 | 25.7 | BDL | BDL | 36.0 | 14.9 |
| GÇA-28 | 103.9 | BDL | 10.4 | BDL | 0.60 | 1.30 | 2.4 | 97.9 | 5.9 | 11.6 | BDL | BDL | 37.2 | 9.5 |
| GÇA-29 | 24.3 | BDL | 10.6 | BDL | 0.74 | 0.54 | 3.8 | 25.5 | 4.2 | 8.5 | BDL | BDL | 32.7 | 7.5 |
| GÇA-30 | 23.8 | BDL | 4.8 | BDL | 0.77 | 0.76 | 6.2 | 26.7 | 4.4 | 34.2 | BDL | BDL | 22.9 | 14.4 |
| GÇA-31 | 65.9 | BDL | 11.4 | BDL | 0.86 | 9.05 | 6.8 | 104.0 | 9.0 | 11.2 | 5.86 | 9.9 | 43.5 | 16.3 |
| GÇA-32 | 17.1 | BDL | 4.5 | BDL | 0.51 | 0.47 | 3.5 | 23.8 | 3.6 | 14.8 | BDL | BDL | 32.9 | 12.1 |
| GÇA-33 | 24.4 | BDL | 8.8 | BDL | 0.66 | 0.60 | 3.2 | 29.6 | 4.3 | 31.1 | 1.69 | BDL | 28.3 | 16.6 |
| GÇA-34 | 13.3 | BDL | 5.8 | BDL | BDL | 0.32 | 3.0 | 17.9 | 4.3 | 29.7 | BDL | BDL | 19.5 | 7.9 |
| GÇA-35 | 19.5 | BDL | 6.8 | BDL | BDL | 0.47 | 2.3 | 27.8 | 6.1 | 21.4 | BDL | BDL | 30.4 | 7.5 |
| GÇA-36 | 34.8 | BDL | 4.4 | BDL | 0.55 | 0.87 | 1.8 | 35.8 | 5.2 | 34.3 | BDL | BDL | 64.3 | 7.2 |
| GÇA-37 | 23.1 | BDL | 3.1 | BDL | 0.59 | 0.50 | 2.7 | 35.4 | 5.7 | 46.4 | BDL | BDL | 32.7 | 12.9 |
| GÇA-38 | 25.0 | BDL | 5.7 | BDL | 0.64 | 0.81 | 3.3 | 30.7 | 7.6 | 7.9 | BDL | BDL | 38.7 | 10.9 |
| GÇA-39 | 17.9 | BDL | 5.9 | BDL | 0.78 | 0.72 | 4.3 | 28.0 | 6.2 | 20.8 | BDL | BDL | 30.2 | 18.4 |
| GÇA-40 | 10.6 | BDL | 6.2 | BDL | 0.61 | 0.59 | 4.7 | 16.1 | 5.4 | 25.5 | 1.70 | BDL | 20.2 | 13.8 |
| GÇA-41 | 10.1 | BDL | 13.3 | BDL | BDL | 0.39 | 4.4 | 19.4 | 6.7 | 34.8 | BDL | BDL | 33.0 | 14.3 |
| GÇA-42 | 22.4 | BDL | 16.3 | BDL | 0.65 | 0.74 | 3.9 | 33.0 | 7.3 | 46.1 | BDL | BDL | 51.1 | 12.6 |
| GÇA-43 | 23.2 | BDL | 14.8 | BDL | 0.92 | 1.95 | 4.4 | 38.5 | 10.9 | 38.2 | 2.62 | BDL | 76.2 | 13.0 |
| GÇA-44 | 21.4 | BDL | 8.6 | BDL | 0.80 | 0.37 | 1.6 | 31.0 | 3.5 | 10.9 | BDL | BDL | 23.6 | 3.8 |
| GÇA-45 | 14.6 | 1.82 | 8.4 | BDL | 0.46 | 11.73 | 5.1 | 96.6 | 6.6 | 42.3 | 9.85 | 11.7 | 38.5 | 12.3 |

BDL: Below Detection Limit

Table 3- Certified reference material analysis as an accuracy test for microwave/ICP-AES method (CRM 1568*a* Rice Flour)

|  | Al | As | Ba | Cd | Co | Cr | Cu | Fe | Mn | Mo | Ni | Pb | Se | Sn | Sr | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Certificated Value (mg/kg) | 4.4±1.0 | 0.29±0.03 | * | 0.022±0.002 | 0.018 | * | 2.4±0.3 | 7.4±0.9 | 20.0±1.6 | 1.46±0.08 | * | (<0.010) | 0.38±0.04 | -0.0047 | * | 19.4±0.5 |
| Detected Value (mg/kg) | 4.3±0.5 | BDL | 0.43±0.02 | BDL | BDL | BDL | 2.2±0.2 | 7.6±0.4 | 18.8±0.2 | BDL | BDL | BDL | BDL | BDL | 0.18±0.01 | 17.5±0.5 |
| Error (%) | 2.3 | - | - | - | - | - | 8.3 | 2.7 | 6.0 | - | - | - | - | - | - | 9.8 |

BDL: Below Detection Limit

## 3. Results and Discussion

### 3.1. Trace element contents in soil

Descriptive statistical parameters were estimated belonging to trace element/heavy metal contents in the soil beside the road passing through Gümüşhane city center (Table 4).

According to descriptive statistical parameters, the elements and related ranges are as follows; aluminum (Al) 108283.65-64832.59 mg/kg (ave: 87839.83 mg/kg), iron (Fe) 28116.59-53365.56 mg/kg (ave. 37627.11 mg/kg), zircon (Zr) 141.40-43.32 mg/kg (ave. 69.11 mg/kg), strontium (Sr) 360.41-72.08 mg/kg (ave. 179.40 mg/kg), rubidium (Rb) 193.85-19.2 mg/kg (ave. 109.95 mg/kg), barium (Ba) 1110-328 mg/kg (ave. 706.07 mg/kg), cadmium (Cd) 15-0,1 mg/kg (ave. 7,91 mg/kg), cobalt (Co), 33-3 mg/kg (ave.18,33), chromium (Cr) 241-48 mg/kg (ave.99.70), copper (Cu) 92-15 mg/kg (ave. 54,47 mg/kg), manganese (Mn) 1759-32 mg/kg (ave. 904.6 mg/kg), nickel (Ni) 195-14 mg/kg (ave. 43,60 mg/kg), lead (Pb) 441-3 mg/kg (ave. 67.2 mg/kg), zinc (Zn) 406-72 mg/kg (ave. 147.69), yttrium (Y) 27-9mg/kg (ave. 17.82 mg/kg), arsenic (As), 56-1 mg/kg (ave. 14.47 mg/kg) and tin (Sn) 130-8 mg/kg (ave. 61.71 mg/kg). The pH values of soils in the study area were estimated in laboratories of Department of Forest of the Vocational High School in Gümüşhane as ranging between 7.50–8.70 and it was detected that these were close to low alkaline character close to neutral (Table 4).

Besides, inter elemental *Pearson correlation coefficients* were estimated. Accordingly; elements and related correlation coefficients are as follows; Mn and Co (0.97), Ni and Cr (0.52), Zn and Mn (0.62), As and Sn (0.62), Pb and Co (0.99), Pb and Mn (0.63) moderate to high grade positive, As and Co (-0.85), Cu and Ba (-0.58) moderate to high negative (Table 5).

### 3.2. Heavy metal/trace element contents in shoots of Acacia Tree

Elements and related concentration values are as follows of shoots of ocacia; barium (Ba) 3.14-18.50 mg/kg (ave. 8.10 mg/kg), cobalt (Co), 0.46-0.94 mg/kg (ave. 0,74 mg/kg), chromium (Cr) 0.32-11.73 mg/kg (ave. 1.38 mg/kg), copper (Cu) 1.59-34.40 mg/kg (ave. 5.17 mg/kg), iron (Fe) 16.08-693.32 (ave. 74.93 mg/kg), manganese (Mn) 3.54-14 mg/kg (ave. 6.43 mg/kg), molybdenum (Mo), 7.34-56.45 mg/kg (ave. 23.05 mg/kg), nickel (Ni) 1.09-9.85 mg/kg (ave. 2.82 mg/kg), tin (Sn) 9.93-11.70 mg/kg (ave. 10.81 mg/kg), strontium (Sr), 19.55-77.15 mg/kg (ave. 38.94 mg/kg), zinc (Zn) 3.77-47 mg/kg

Table 4- Statistical data of elements in soil (concentration values in mg/kg)

| | Al | Fe | Zr | Sr | Rb | Ba | Cd | Co | Cr | Cu | Mn | Ni | Pb | Zn | Y | As | Sn | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | 87839.48 | 37627.11 | 69.11 | 179.40 | 109.95 | 706.07 | 7.91 | 18.34 | 99.74 | 54.47 | 904.6 | 43.60 | 67.2 | 147.69 | 17.83 | 14.47 | 61.71 | 8.09 |
| Min. | 64832.59 | 28116.59 | 43.36 | 72.08 | 19.22 | 328 | 0.1 | 3 | 48 | 15 | 32 | 14 | 3 | 72 | 9 | 1 | 8 | 8.09 |
| Max. | 108283.65 | 53365.56 | 141.40 | 360.41 | 193.85 | 1110 | 15 | 33 | 241 | 92 | 1759 | 195 | 441 | 406 | 27 | 56 | 130 | 7.50 |
| Cardinality | 45 | 45 | 45 | 45 | 45 | 45 | 10 | 3 | 44 | 45 | 45 | 42 | 40 | 35 | 40 | 40 | 14 | 8.70 |
| | | | | | | | | | | | | | | | | | | 45 |

Table 5- Correlation coefficients of trace element concentrations in soil

| | *Al* | *Fe* | *Zr* | *Sr* | *Rb* | *Ba* | *Cd* | *Cr* | *Cu* | *Mn* | *Ni* | *Pb* | *Zn* | *Y* | *As* | *Sn* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | 1 | | | | | | | | | | | | | | | |
| Fe | 0.04 | 1 | | | | | | | | | | | | | | |
| Zr | 0.34 | 0.17 | 1 | | | | | | | | | | | | | |
| Sr | -0.55 | 0.66 | 0.01 | 1 | | | | | | | | | | | | |
| Rb | 0.68 | -0.56 | 0.22 | -0.81 | 1 | | | | | | | | | | | |
| Ba | 0.45 | -0.36 | 0.25 | -0.40 | 0.64 | 1 | | | | | | | | | | |
| Cd | -0.45 | 0.24 | -0.61 | 0.30 | -0.52 | 0.24 | 1 | | | | | | | | | |
| Cr | -0.27 | 0.02 | 0.02 | 0.11 | -0.15 | -0.07 | 0.35 | 1 | | | | | | | | |
| Cu | -0.34 | 0.74 | -0.14 | 0.69 | -0.74 | -0.58 | 0.22 | -0.03 | 1 | | | | | | | |
| Mn | -0.10 | 0.31 | -0.15 | 0.06 | -0.20 | -0.44 | -0.09 | -0.08 | 0.36 | 1 | | | | | | |
| Ni | -0.14 | 0.60 | 0.20 | 0.49 | -0.49 | -0.41 | -0.11 | 0.52 | 0.34 | 0.14 | 1 | | | | | |
| Pb | -0.31 | 0.17 | -0.05 | 0.09 | -0.35 | -0.35 | -0.17 | 0.11 | 0.37 | 0.63 | 0.19 | 1 | | | | |
| Zn | -0.58 | -0.05 | -0.07 | 0.36 | -0.40 | -0.41 | -0.01 | -0.04 | 0.30 | 0.62 | 0.30 | 0.47 | 1 | | | |
| Y | 0.41 | 0.28 | 0.39 | -0.14 | 0.17 | 0.32 | -0.37 | -0.04 | -0.05 | 0.14 | 0.05 | -0.08 | -0.30 | 1 | | |
| As | 0.21 | -0.09 | 0.06 | -0.19 | 0.17 | 0.13 | -0.14 | 0.03 | -0.10 | -0.35 | -0.11 | -0.19 | -0.06 | 0.08 | 1 | |
| Sn | 0.13 | -0.56 | -0.09 | -0.36 | 0.43 | -0.25 | -0.16 | 0.16 | -0.36 | 0.24 | -0.36 | 0.03 | 0.30 | -0.43 | 0.62 | 1 |

(ave. 15.16 mg/kg), arsenic (As), 1.82-2.08 mg/kg (ave. 1.96 mg/kg), aluminum (Al) 10.15-203.01 mg/kg (ave. 52.82 mg/kg) (Table 6). As lead (Pb) values in shoots of acacia could not be detected, it remained below the detection limit.

Table 6- Descriptive statistical values of trace elements in shoots of acacia

| | Ba_Acc. | Co_Acc. | Cr_Acc. | Cu_Acc. | Fe_Acc. | Mn_Acc. | Mo_Acc. | Ni_Acc. | Sn_Acc. | Sr_Acc. | Zn_Acc. | As_Acc. | Al_Acc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | 8.10 | 0.74 | 1.38 | 5.17 | 74.93 | 6.77 | 26.62 | 2.82 | 10.81 | 38.94 | 15.16 | 1.96 | 52.82 |
| Geometric Mean | 7.39 | 0.72 | 0.94 | 4.34 | 53.92 | 6.43 | 23.05 | 2.13 | 10.78 | 36.59 | 13.70 | 1.96 | 40.49 |
| Min. | 3.14 | 0.46 | 0.32 | 1.59 | 16.08 | 3.54 | 7.34 | 1.09 | 9.93 | 19.55 | 3.77 | 1.82 | 10.15 |
| Max. | 18.50 | 0.94 | 11.73 | 34.40 | 693.32 | 14.00 | 56.45 | 9.85 | 11.70 | 77.15 | 47.00 | 2.08 | 203.01 |
| Cardinality | 45 | 42 | 45 | 45 | 45 | 45 | 45 | 13 | 2 | 45 | 45 | 3 | 45 |

Correlation coefficients of trace elements in shoots of acacia with each other and the alkalinity of them were calculated. Following results were obtained; Mn and Ba (0.65), Ni and Cr (0.89), Sr and Ba (0.56), Sr and Mn (0.54), Zn and Cu (0.72), As and Ba (0.56), As and Cu (0.62), As and Fe (0.73), As and Mn (0.58) and the alkalinity of the soil and As (0.64) moderate to strong positive correlation;Mnand Cu (0.42), As and Sr (0.47) weak positive correlation; As and Cr (-0.90) strong negative correlation. Besides; there is as negative correlation between the alkalinity of the soil and Ni (Table 7).

Table 7- Pearson correlation coefficients between trace element concentrations of acacia shoots and alkalinity of soil

| | Ba_Acc. | Co_Acc. | Cr_Acc. | Cu_Acc. | Fe_Acc. | Mn_Acc. | Mo_Acc. | Ni_Acc. | Sn_Acc. | Sr_Acc. | Zn_Acc. | As_Acc. | Al_Acc. | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ba_Acc. | 1,00 | | | | | | | | | | | | | |
| Co_Acc. | 0,37 | 1,00 | | | | | | | | | | | | |
| Cr_Acc. | 0,18 | -0,10 | 1,00 | | | | | | | | | | | |
| Cu_Acc. | 0,20 | 0,28 | 0,13 | 1,00 | | | | | | | | | | |
| Fe_Acc. | 0,32 | 0,24 | 0,20 | 0,24 | 1,00 | | | | | | | | | |
| Mn_Acc. | 0,65 | 0,42 | 0,20 | 0,42 | 0,25 | 1,00 | | | | | | | | |
| Mo_Acc. | 0,14 | 0,25 | 0,07 | -0,05 | 0,18 | 0,11 | 1,00 | | | | | | | |
| Ni_Acc. | 0,04 | -0,26 | 0,89 | 0,25 | -0,14 | 0,05 | 0,13 | 1,00 | | | | | | |
| Sn_Acc. | -1,00 | -1,00 | 1,00 | -1,00 | -1,00 | -1,00 | 1,00 | 1,00 | 1,00 | | | | | |
| Sr_Acc. | 0,54 | 0,31 | 0,16 | -0,07 | 0,36 | 0,54 | 0,32 | -0,18 | -1,00 | 1,00 | | | | |
| Zn_Acc. | 0,14 | 0,33 | 0,04 | 0,72 | 0,06 | 0,35 | 0,03 | 0,07 | -1,00 | -0,02 | 1,00 | | | |
| As_Acc. | 0,56 | 0,99 | -0,90 | 0,62 | 0,73 | 0,58 | -0,18 | -1,00 | | 0,47 | 0,20 | 1,00 | | |
| Al_Acc. | 0,13 | 0,22 | 0,12 | 0,17 | 0,51 | 0,26 | 0,05 | -0,36 | -1,00 | 0,37 | 0,17 | 0,95 | 1,00 | |
| pH | -0,01 | -0,01 | -0,32 | -0,19 | -0,05 | -0,12 | -0,23 | -0,50 | -1,00 | 0,08 | -0,21 | 0,64 | -0,05 | 1,00 |

### 3.3. Heavy metal/trace element accumulations in the soil (pollution)

In the assessment of trace element accumulations in soil, the reference values of the soil are compared with element concentrations estimated in soil. In order to calculate the trace element accumulations in Gümüşhane Region, the values of Gümüşhane granitoid and Eocene volcanic rocks which are the source of soil were used. Therefore, the reference values of Topuz et al. (2010) for the soil that had developed on Gümüşhane granitoid, the trace element values of Aslan (2010) for the soil cover that had developed on Eocene volcanic rocks, and the values of Turekian and Wedepohl (1961) and Taylor and McLennan (1995) for chromium and arsenic elements were used. The geometric average values were used for element concentrations showing logarithmic distribution when benefited from trace element values of Topuz et al. (2010) and Aslan (2010). However, the arithmetic average values were used for elements showing normal distribution. For major element concentrations in the study area, bar graphics were drawn. Accordingly, the elements and number of sample locations of which are above the reference values in soils are as follows; Cd (9), Ba (26), Co (2), Cr and Mn (44), Cu and Ni (all locations), Sn (14), Zn (35), As (36), Pb (38). The pH values of soils in sample location showever, were detected as ranging between neutral to alkaline (Figure 3a, b).

Geochemical normalizations are widely used to determine the pollution resulting from human especially the human induced pollution in soil. The purpose here is to proportionate pollution with respect to normal concentrations with a normalization factor (Daskalakisand O'Connor, 1995; Aloupi and Angelidis, 2001; Condrad and Chisholm-Brause, 2004; Feng et al., 2004). There is not any certain acceptance in the selection of element to be used in

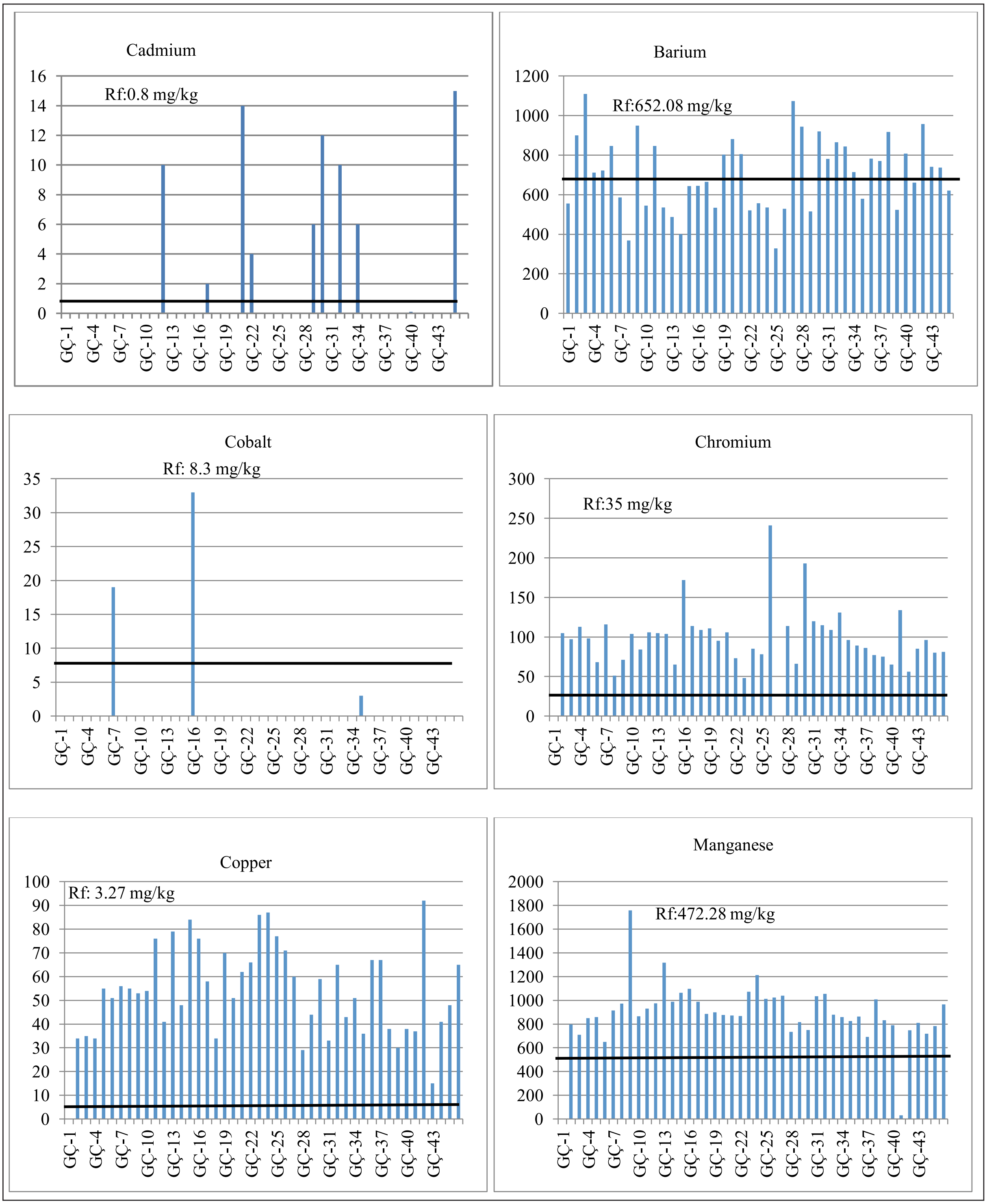

Figure 3- a. Trace element concentrations, reference and pH values of soils in the study area

normalization but, the elements which are not geochemically active (inert) and encountered in all conditions such as; Al, Fe, Li, Zr, Sc and Sr are used (Feng et al., 2004; Acevedo-Figueroa et al., 2006; Ghrefat and Yusuf 2006; Chen et al., 2007; Loska et al., 1997; Saur and Juste 1994; Sutherland 2000; Reimann and De Caritat, 2000).

The parameters which are widely used for the assessment of element enrichments in soil are

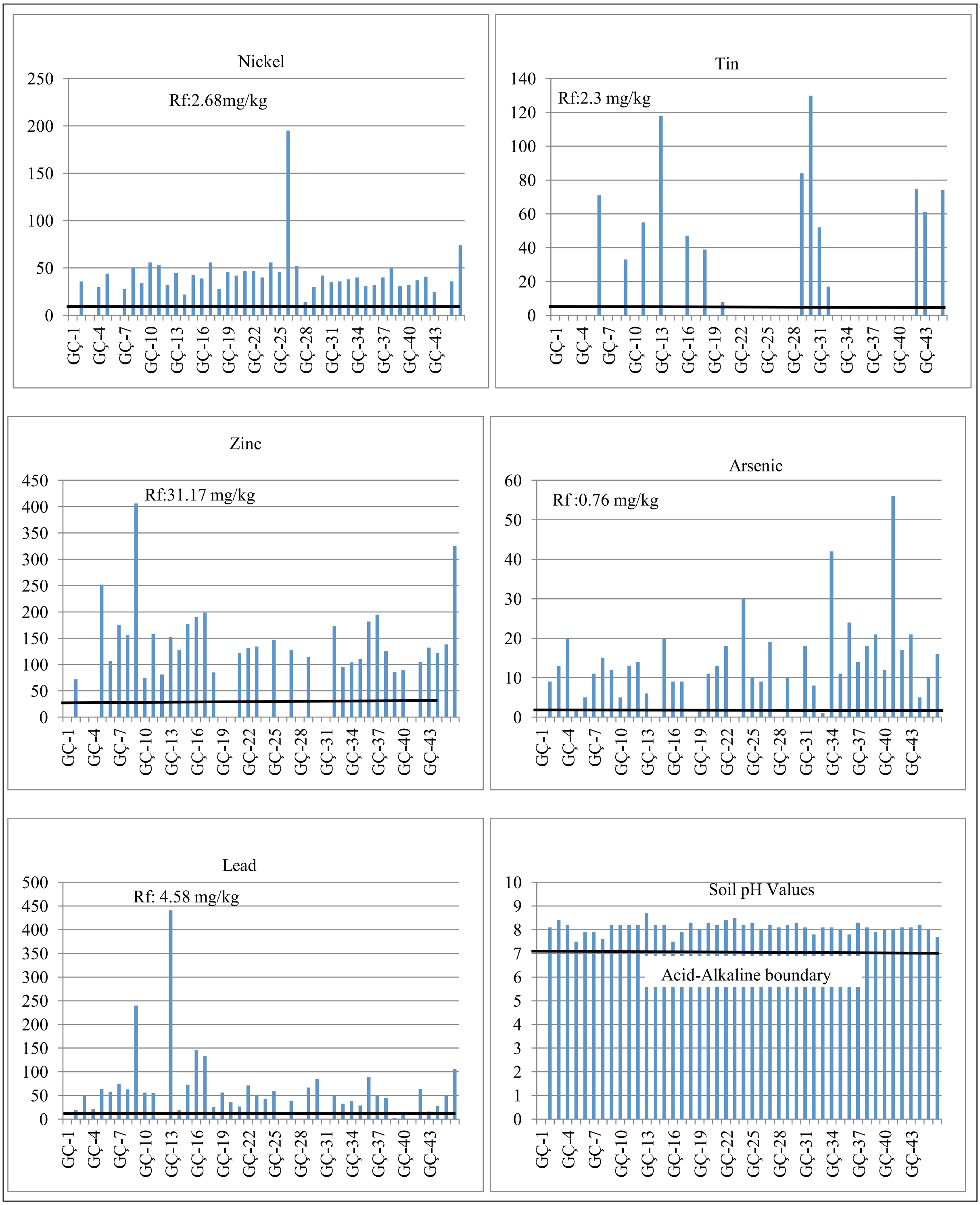

Figure 3- b. Trace element concentrations, reference and pH values of soils in the study area (Continue)

Enrichment Factor (EF), Geoaccumulation Index ($I_{geo}$), Contamination Factor (CT), Contamination Factor Degree ($CF_{deg}$). The Enrichment Factor and geoaccumulation index were used in this study.

### *3.3.1. Enrichment Factor (EF)*

The Enrichment Factor (EF) was used by Buat-Menard and Chesselet (1979) for the assessment of metal accumulation in soils. The Enrichment Factor has also been used in assessing various environmental conditions in time and in the estimation of contribution of the human induced effect in metal pollution (Buat-Menard and Chesselet, 1979; Groengroeft et al., 1998; Morillo et al., 2002; Adamo et al., 2005; Vald'es et al., 2005). Although there have been discussed some drawbacks about the usage of Enrichment Factor for the assessment of elemental accumulations in various environments in detail by Reiman and De Caritat (2000), this factor is widely used in the assessment of enrichment factors and in comparing the pollution of different environmental conditions because it is accepted as a universal formula. In this study, Zr element was selected as the reference element as it has some features such that, its geochemistry resembles to the geochemistry of trace elements and its natural sediment concentrations are regular (Daskalakis and O' Connor, 1995). Zircon is mostly used as stable lithogenic element in alteration studies or for the assessment of more reactive heavy metals in sediments, in reducing dispersive data and in determining sensitive reference values as normalizer (Rubio et al. 2000; Zhang et al., 2006; Cobela-Garcia and Prego, 2003; Machender et al., 2011).

The following formula is used in calculating the Enrichment Factor;

$$EF=\frac{(Me/Zr)_{sample}}{(Me/Zr)_{reference}}$$

Here;

$(Me/Zr)_{sample}$ is the ratio of metal concentration with respect to zircon amount in the soil,

$(Me/Zr)_{reference}$ is the ratio of element reference value with respect to reference Zr used for the normalization.

If EF is less than 5.0 then, the soil is accepted as unimportant in terms of pollution as such minor enrichments could originate from differences in local soil material compounds and in reference soils used in EF estimations (Kartal et al., 2006). Nonetheless; there is also observed difference in the range of contamination degree and in its classification. Birch (2003) classified EF as follows; EF<1 (no enrichment), EF<3 (minor), 3<EF<5 (moderate), 5<EF<10 (moderately severe), 10<EF<25 (severe), 25<EF<50 (very severe), 50<EF (highly severe).

Enrichment factors were calculated for 12 trace elements in soils at 45 sampling locations along the state auto road passing through Gümüşhane city center (Table 8).

Results were taken as follows; Sr (0.6-3.62) in "no enrichment-minor" class; Ba (0.77-5.52) "no enrichment-moderately severe" class; Cd is an important heavy metal that has risk for environment and living organisms when it is assessed in terms of trace element accumulation.Cd content was detected in 10 sampling locations (0.26–49.14) as "no enrichment-highly severe" class; Co was detected in 3 sampling locations (0.98–12.88) in "no enrichment–severe" class; Cr (0.25-1.61) as "no enrichment–minor" class; Cu (8.49-86.57) as "moderately severe–highly severe" class; Mn (0.14-9.70) as "no enrichment–moderately severe" class; Ni (7.17-113.92) as "moderately severe–very highly severe" class. Pb element is one of the most significant pollutant heavy metal of today and it was detected as (1.11-180.51) "minor-very highly severe" class. Arsenic (As) element is an important pollutant material and is seen in all over the world. EF for As is around 5 mg/kg in unpolluted soils (Goldschimdt, 1958; ATSDR, 2000), however it reaches 1400 mg/kg or even 2700 mg/kg in polluted soils (EPA, 1982). EF value of As element is between 1.74-82.05 mg/kg in the study area "minor-very highly severe". EF value for Sn element was detected as (8.54-138.45) "moderately severe–very highly severe" (Table 8, 9).

### *3.3.2. Geo-accumulation Index ($I_{geo}$)*

Geo-accumulation Index ($I_{geo}$), which was suggested by Muller (1969, 1981) has been used in many investigations since 1970 and aims at detecting the increasing pollution comparing today's metal content with pre industrialization values (Miko et al.. 2000; Loska et al., 2003; Vural and Şahin, 2012 *a-b*). Geo-accumulation index is calculated as shown below;

$$I_{geo}=\log_2\left[\frac{C_n}{1.5 * B_n}\right]$$

$C_n$ is the metal concentration analyzed,

$B_n$ is the reference value of element n,

However, value of 1.5 corresponds to coefficient used for normal fluctuations in environments like very small anthropogenic effects.

Table 8- Enrichment factors (EF) of trace element accumulations in soil

| EF(Sr) | EF(Rb) | EF(Ba) | EF(Cd) | EF(Co) | EF(Cr) | EF(Cu) | EF(Mn) | EF(Ni) | EF(Pb) | EF(Zn) | EF(Y) | EF(As) | EF(Sn) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2.03 | 2.10 | 2.42 | | | 0.85 | 29.48 | 4.78 | 39.06 | 12.41 | 6.56 | 2.23 | 17.48 | |
| 0.67 | 2.30 | 2.59 | | | 0.52 | 20.12 | 2.82 | | 20.16 | | 1.65 | 16.74 | |
| 1.16 | 4.11 | 5.52 | | | 1.05 | 33.77 | 5.84 | 37.28 | 15.64 | | 4.06 | 44.49 | |
| 2.12 | 1.44 | 2.15 | | | 0.55 | 33.19 | 3.58 | 33.23 | 27.64 | 15.99 | 1.28 | 2.70 | |
| 2.82 | 1.97 | 2.91 | | | 0.51 | 40.97 | 3.60 | | 33.34 | 8.95 | 1.82 | 9.00 | |
| 2.76 | 1.77 | 3.34 | | 5.87 | 0.85 | 44.01 | 4.97 | 27.54 | 41.62 | 14.46 | 2.26 | 19.36 | 79.11 |
| 2.32 | 1.59 | 1.94 | | | 0.32 | 36.41 | 4.45 | 41.43 | 29.85 | 10.86 | 2.00 | 22.25 | |
| 1.87 | 1.67 | 1.47 | | | 0.53 | 42.26 | 9.70 | 33.93 | 136.96 | 34.05 | 1.45 | 21.43 | |
| 1.29 | 1.75 | 2.62 | | | 0.54 | 29.79 | 3.30 | 38.66 | 22.11 | 4.29 | 1.67 | 6.18 | 25.81 |
| 3.49 | 1.33 | 2.71 | | | 0.78 | 75.48 | 6.39 | 65.87 | 39.09 | 16.50 | | 28.92 | |
| 0.80 | 2.63 | 2.90 | 30.59 | | 0.68 | 27.99 | 4.60 | 27.34 | | 5.82 | 1.65 | 21.41 | 53.24 |
| 1.34 | 1.18 | 1.54 | | | 0.56 | 45.18 | 5.21 | 32.21 | 180.51 | 9.20 | 1.73 | 7.69 | |
| 0.97 | 3.90 | 2.02 | | | 0.80 | 39.72 | 5.65 | 22.78 | 11.25 | 11.05 | 1.25 | | 138.45 |
| 3.62 | 1.01 | 2.07 | | | 0.63 | 86.57 | 7.59 | 55.46 | 53.84 | 19.18 | 2.65 | 46.17 | |
| 3.49 | 1.48 | 3.20 | | 12.88 | 1.59 | 75.48 | 7.53 | 48.47 | 103.76 | 19.95 | 2.10 | 20.02 | |
| 2.20 | 1.75 | 2.03 | 5.63 | | 0.67 | 36.41 | 4.29 | 44.00 | 59.76 | 13.14 | 1.90 | 12.66 | 41.83 |
| 0.77 | 2.05 | 2.21 | | | 0.67 | 22.51 | 4.06 | 23.20 | 12.32 | 5.92 | 1.90 | | |
| 2.80 | 1.56 | 2.13 | | | 0.83 | 55.82 | 4.96 | 45.90 | 31.96 | | 2.41 | 3.57 | 44.09 |
| 3.18 | 1.60 | 2.73 | | | 0.60 | 34.60 | 4.11 | 35.66 | 17.48 | | 1.95 | 16.72 | |
| 2.64 | 1.84 | 3.33 | 47.25 | | 0.75 | 46.71 | 4.55 | 44.31 | 14.56 | 9.67 | 2.17 | 21.94 | 8.54 |
| 1.41 | 1.73 | 2.43 | 10.82 | | 0.41 | 39.83 | 3.62 | 35.50 | 30.67 | 8.31 | 1.92 | 24.33 | |
| 3.04 | 1.30 | 1.70 | | | 0.29 | 55.92 | 4.82 | 32.55 | 24.20 | 9.16 | 1.28 | | |
| 2.00 | 1.51 | 1.59 | | | 0.45 | 49.50 | 4.78 | 39.87 | 17.51 | | 2.15 | 38.23 | |
| 2.19 | 1.21 | 1.68 | | | 0.45 | 48.07 | 4.37 | 35.93 | 26.80 | 9.58 | 2.08 | 13.98 | |
| 2.73 | 0.22 | 0.77 | | | 1.05 | 33.15 | 3.30 | 113.92 | | | 1.34 | 9.41 | |
| 1.48 | 1.28 | 1.67 | | | 0.00 | 37.89 | 4.54 | 41.09 | 17.62 | 8.43 | 2.20 | 26.87 | |
| 0.96 | 1.77 | 2.20 | | | 0.44 | 11.87 | 2.08 | 7.17 | | | 1.67 | | |
| 2.20 | 1.58 | 2.97 | 16.88 | | 0.39 | 27.62 | 3.55 | 23.57 | 30.10 | 7.53 | | 14.06 | |
| 3.14 | 1.59 | 2.31 | 48.14 | | 1.61 | 52.83 | 4.64 | 47.06 | 54.47 | | 2.03 | | 106.63 |
| 0.77 | 2.87 | 3.02 | | | 0.73 | 21.59 | 4.68 | 28.65 | | | | 26.37 | 120.56 |
| 2.86 | 1.51 | 2.39 | 27.34 | | 0.66 | 39.67 | 4.45 | 27.49 | 21.84 | 11.17 | 1.57 | 10.94 | 44.99 |
| 1.81 | 2.69 | 3.36 | | | 0.79 | 33.31 | 4.71 | 36.84 | 18.30 | 7.74 | 1.41 | 1.74 | 18.67 |
| 1.25 | 1.86 | 2.26 | 14.39 | | 0.65 | 27.31 | 3.18 | 26.80 | 14.56 | 5.86 | 1.62 | 50.38 | |
| 2.93 | 1.63 | 2.99 | | 0.98 | 0.75 | 30.02 | 4.76 | 32.35 | 17.31 | 9.65 | 1.64 | 20.55 | |
| 3.12 | 1.46 | 2.58 | | | 0.74 | 59.50 | 5.31 | 35.57 | 56.57 | 17.00 | | 47.75 | |
| 1.48 | 0.60 | 1.24 | | | 0.25 | 21.15 | 1.51 | 15.80 | 11.07 | 6.47 | | 9.90 | |
| 0.60 | 1.87 | 1.98 | | | 0.37 | 19.49 | 3.58 | 32.09 | 16.52 | 6.80 | 1.86 | 20.68 | |
| 0.61 | 2.16 | 2.38 | | | 0.36 | 15.53 | 2.98 | 20.08 | 1.11 | 4.68 | 1.88 | 24.35 | |
| 1.35 | 2.02 | 1.51 | 0.26 | | 0.35 | 21.85 | 3.14 | 23.02 | 4.94 | 5.38 | 1.48 | 15.45 | |
| 1.53 | 1.86 | 2.65 | | | 0.82 | 24.20 | 0.14 | 30.29 | | | 0.89 | 82.05 | |
| 3.53 | 1.24 | 2.50 | | | 0.39 | 69.31 | 3.90 | 38.65 | 34.51 | 8.32 | 1.71 | 28.69 | |
| 0.66 | 2.30 | 2.71 | | | 0.45 | 8.49 | 3.17 | 17.71 | 6.48 | 7.86 | 1.63 | 26.63 | 60.18 |
| 0.60 | 2.01 | 1.91 | | | 0.46 | 21.13 | 2.56 | | 10.33 | 6.61 | 0.78 | 5.77 | 44.56 |
| 2.26 | 1.44 | 2.37 | 43.18 | | 0.48 | 30.84 | 3.48 | 28.95 | 23.45 | 9.33 | 1.75 | 14.39 | |
| 3.22 | 1.42 | 2.14 | | | 0.52 | 44.66 | 4.59 | 63.62 | 52.12 | 23.48 | 1.35 | 24.62 | 72.08 |

Table 9- Statistical parameters of enrichment factors in the study area

| Statistical Descriptor Parameters | *EF (Sr)* | *EF(Rb)* | *EF(Ba)* | *EF(Cd)* | *EF(Co)* | *EF(Cr)* | *EF(Cu)* | *EF(Mn)* | *EF(Ni)* | *EF(Pb)* | *EF(Zn)* | *EF(Y)* | *EF(As)* | *EF(Sn)* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | 2.00 | 1.78 | 2.38 | 24.45 | 6.58 | 0.64 | 37.80 | 4.31 | 36.45 | 33.87 | 10.83 | 1.81 | 21.90 | 61.34 |
| Interval | 3.02 | 3.89 | 4.76 | 47.88 | 11.90 | 1.36 | 78.08 | 9.55 | 106.75 | 179.39 | 29.75 | 3.28 | 80.32 | 129.90 |
| Cardinality | 45 | 45 | 45 | 10 | 3 | 44 | 45 | 45 | 42 | 40 | 35 | 40 | 40 | 14 |
| Max. | 3.62 | 4.11 | 5.52 | 48.14 | 12.88 | 1.61 | 86.57 | 9.70 | 113.92 | 180.51 | 34.05 | 4.06 | 82.05 | 138.45 |
| Min. | 0.60 | 0.22 | 0.77 | 0.26 | 0.98 | 0.25 | 8.49 | 0.14 | 7.17 | 1.11 | 4.29 | 0.78 | 1.74 | 8.54 |

Muller (1969, 1981) and Chen et al. (2007) classified $I_{geo}$ as follows; $I_{geo}<0$ uncontaminated, 0-1 uncontaminated-moderately contaminated, 1-2 moderately contaminated, 2-3 moderately- heavily contaminated, 3-4 heavily contaminated, 4-5 heavily to extremely contaminated and >5 extremely contaminated.

The Geo-accumulation Index ($I_{geo}$) for the study area was calculated and results were given in table 10.

Table 10- Geoaccumulation indexes of soil elements

| Igeo (Sr) | Igeo (Rb) | Igeo (Ba) | Igeo (Cd) | Igeo (Co) | Igeo (Cr) | Igeo (Cu) | Igeo (Mn) | Igeo (Ni) | Igeo (Pb) | Igeo (Zn) | Igeo (Y) | Igeo (As) | Igeo (Sn) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| -1.07 | -1.01 | -0.81 |  |  | 1.00 | 2.79 | 0.17 | 3.20 | 1.54 | 0.62 | -0.93 | 2.99 |  |
| -2.07 | -0.29 | -0.12 |  |  | 0.89 | 2.83 | 0.00 |  | 2.84 |  | -0.77 | 3.52 |  |
| -2.07 | -0.24 | 0.18 |  |  | 1.11 | 2.79 | 0.26 | 2.94 | 1.68 |  | -0.26 | 4.14 |  |
| -0.48 | -1.04 | -0.46 |  |  | 0.90 | 3.49 | 0.28 | 3.49 | 3.22 | 2.43 | -1.21 | 0.82 |  |
| -0.48 | -1.00 | -0.44 |  |  | 0.37 | 3.38 | -0.13 |  | 3.08 | 1.18 | -1.11 | 2.14 |  |
| -0.48 | -1.12 | -0.21 |  | 0.61 | 1.14 | 3.51 | 0.37 | 2.84 | 3.43 | 1.90 | -0.77 | 3.28 | 4.36 |
| -0.48 | -1.03 | -0.74 |  |  | -0.04 | 3.49 | 0.46 | 3.68 | 3.20 | 1.74 | -0.70 | 3.73 |  |
| -1.07 | -1.23 | -1.41 |  |  | 0.44 | 3.43 | 1.31 | 3.12 | 5.13 | 3.12 | -1.43 | 3.40 |  |
| -1.07 | -0.62 | -0.04 |  |  | 0.99 | 3.46 | 0.29 | 3.84 | 3.03 | 0.66 | -0.70 | 2.14 | 3.26 |
| -0.48 | -1.88 | -0.84 |  |  | 0.68 | 3.95 | 0.39 | 3.76 | 3.00 | 1.76 |  | 3.52 |  |
| -2.07 | -0.35 | -0.21 | 3.06 |  | 1.01 | 3.06 | 0.46 | 3.03 |  | 0.79 | -1.02 | 3.63 | 3.99 |
| -1.07 | -1.24 | -0.87 |  |  | 1.00 | 4.01 | 0.90 | 3.52 | 6.01 | 1.71 | -0.70 | 2.40 |  |
| -2.07 | -0.05 | -1.01 |  |  | 0.99 | 3.29 | 0.48 | 2.49 | 1.47 | 1.44 | -1.70 |  | 5.10 |
| -0.48 | -2.32 | -1.29 |  |  | 0.31 | 4.10 | 0.59 | 3.46 | 3.41 | 1.92 | -0.93 | 4.14 |  |
| -0.48 | -1.72 | -0.60 |  | 1.41 | 1.71 | 3.95 | 0.63 | 3.32 | 4.41 | 2.03 | -1.21 | 2.99 |  |
| -0.48 | -0.82 | -0.60 | 0.74 |  | 1.12 | 3.56 | 0.48 | 3.84 | 4.28 | 2.09 | -0.70 | 2.99 | 3.77 |
| -2.07 | -0.66 | -0.56 |  |  | 1.05 | 2.79 | 0.32 | 2.84 | 1.92 | 0.86 | -0.77 |  |  |
| -0.48 | -1.32 | -0.87 |  |  | 1.08 | 3.83 | 0.34 | 3.56 | 3.03 |  | -0.70 | 0.82 | 3.50 |
| -0.07 | -1.05 | -0.29 |  |  | 0.86 | 3.38 | 0.31 | 3.42 | 2.39 |  | -0.77 | 3.28 |  |
| -0.48 | -1.00 | -0.15 | 3.54 |  | 1.01 | 3.66 | 0.30 | 3.59 | 1.98 | 1.38 | -0.77 | 3.52 | 1.21 |
| -1.07 | -0.77 | -0.28 | 1.74 |  | 0.48 | 3.75 | 0.29 | 3.59 | 3.37 | 1.49 | -0.63 | 3.99 |  |
| -0.07 | -1.29 | -0.91 |  |  | -0.13 | 4.13 | 0.60 | 3.35 | 2.92 | 1.52 | -1.32 |  |  |
| -0.48 | -0.89 | -0.81 |  |  | 0.70 | 4.15 | 0.78 | 3.84 | 2.65 |  | -0.38 | 4.73 |  |
| -0.48 | -1.34 | -0.87 |  |  | 0.57 | 3.97 | 0.51 | 3.56 | 3.13 | 1.64 | -0.56 | 3.14 |  |
| 0.26 | -3.39 | -1.58 |  |  | 2.20 | 3.85 | 0.53 | 5.64 |  |  | -0.77 | 2.99 |  |
| -1.07 | -1.27 | -0.89 |  |  |  | 3.61 | 0.55 | 3.73 | 2.51 | 1.44 | -0.50 | 4.07 |  |
| -1.07 | -0.18 | 0.13 |  |  | 1.12 | 2.56 | 0.05 | 1.84 |  |  | -0.26 |  |  |
| -0.48 | -0.96 | -0.05 | 2.32 |  | 0.33 | 3.16 | 0.21 | 2.94 | 3.29 | 1.29 |  | 3.14 |  |
| -0.48 | -1.46 | -0.93 | 3.32 |  | 1.88 | 3.59 | 0.08 | 3.42 | 3.63 |  | -1.11 |  | 4.61 |
| -2.07 | -0.16 | -0.09 |  |  | 1.19 | 2.75 | 0.55 | 3.16 |  |  |  | 3.99 | 5.24 |
| -0.07 | -0.99 | -0.32 | 3.06 |  | 1.13 | 3.73 | 0.57 | 3.20 | 2.87 | 1.90 | -0.93 | 2.82 | 3.91 |
| -1.07 | -0.50 | -0.18 |  |  | 1.05 | 3.13 | 0.31 | 3.28 | 2.27 | 1.02 | -1.43 | -0.18 | 2.30 |
| -1.07 | -0.50 | -0.21 | 2.32 |  | 1.32 | 3.38 | 0.28 | 3.35 | 2.47 | 1.15 | -0.70 | 5.21 |  |
| -0.48 | -1.32 | -0.45 |  | -2.05 | 0.87 | 2.87 | 0.22 | 2.99 | 2.08 | 1.23 | -1.32 | 3.28 |  |
| -0.48 | -1.57 | -0.75 |  |  | 0.76 | 3.77 | 0.29 | 3.03 | 3.70 | 1.96 |  | 4.40 |  |
| -0.07 | -1.36 | -0.32 |  |  | 0.71 | 3.77 | -0.03 | 3.35 | 2.84 | 2.06 |  | 3.63 |  |
| -2.07 | -0.42 | -0.35 |  |  | 0.55 | 2.95 | 0.51 | 3.68 | 2.71 | 1.43 | -0.43 | 3.99 |  |
| -2.07 | -0.23 | -0.09 |  |  | 0.51 | 2.61 | 0.23 | 2.99 | -1.19 | 0.88 | -0.43 | 4.21 |  |
| -1.07 | -0.48 | -0.90 | -3.58 |  | 0.31 | 2.95 | 0.16 | 3.03 | 0.81 | 0.93 | -0.93 | 3.40 |  |
| -1.07 | -0.78 | -0.28 |  |  | 1.35 | 2.91 | -4.47 | 3.24 |  |  | -1.85 | 5.63 |  |
| -0.07 | -1.57 | -0.57 |  |  | 0.09 | 4.23 | 0.08 | 3.39 | 3.22 | 1.17 | -1.11 | 3.91 |  |
| -2.07 | -0.27 | -0.03 |  |  | 0.70 | 1.61 | 0.20 | 2.68 | 1.22 | 1.50 | -0.77 | 4.21 | 4.44 |
| -2.07 | -0.33 | -0.40 |  |  | 0.87 | 3.06 | 0.02 |  | 2.03 | 1.38 | -1.70 | 2.14 | 4.14 |
| -0.48 | -1.12 | -0.41 | 3.64 |  | 0.61 | 3.29 | 0.15 | 3.20 | 2.89 | 1.56 | -0.85 | 3.14 |  |
| -0.07 | -1.24 | -0.66 |  |  | 0.63 | 3.73 | 0.45 | 4.24 | 3.95 | 2.80 | -1.32 | 3.82 | 4.42 |

According to this index, following results were obtained; Sr (-2.07;+0.26), Ba (-1.58;+0.18) and Mn (-4.47, +1.31) “uncontaminated”-“moderately contaminated”; Rb (-3.39; -0.05), “uncontaminated”; Cd (-3.58;+3.64), “uncontaminated-heavily contaminated”; Co (-2.05;1.41) was detected in 3 sampling locations, “uncontaminated-moderately contaminated”; Cr (-0.13;2.20), “uncontaminated-moderately contaminated-heavily contaminated”; Cu (1.61;4.23), “moderately contaminated”, “heavily contaminated-extremely contaminated”; Ni (1.84; 5.64), “moderately contaminated”,“heavily contaminated - extremely contaminated”; Pb ($I_{geo}$ -1.19; +6.01), “moderately contaminated”,“heavily contaminated-extremely contaminated”; Zn ($I_{geo}$: 0.62; 3.12), “uncontaminated, moderately contaminated” - “heavily contaminated”; Y (-1.85; -0.26) “uncontaminated”; As (-0.18; +5.63), “uncontaminated” - “heavily – extremely contaminated”, Sn (1.21;5.24), “moderately to heavily contaminated”, “extremely contaminated” (Table 10, 11).

Table 11- Statistical parameters of geoaccumulation for soil element contents of soils on Gümüşhane auto road

| Statistical Descriptor Parameters | Igeo (Sr) | Igeo (Rb) | Igeo (Ba) | Igeo (Cd) | Igeo (Co) | Igeo (Cr) | Igeo (Cu) | Igeo (Mn) | Igeo (Ni) | Igeo (Pb) | Igeo (Zn) | Igeo (Y) | Igeo (As) | Igeo (Sn) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | -0.90 | -0.99 | -0.52 | 2.02 | -0.01 | 0.85 | 3.38 | 0.25 | 3.35 | 2.81 | 1.54 | -0.91 | 3.33 | 3.88 |
| Irregularity | -0.61 | -1.30 | -0.53 | -2.27 | -1.36 | 0.43 | -0.79 | -5.50 | 1.25 | -0.45 | 0.73 | -0.57 | -1.05 | -1.30 |
| Interval | 2.32 | 3.34 | 1.76 | 7.23 | 3.46 | 2.33 | 2.62 | 5.78 | 3.80 | 7.20 | 2.50 | 1.58 | 5.81 | 4.02 |
| Cardinality | 45 | 45 | 45 | 10 | 3 | 44 | 45 | 45 | 42 | 40 | 35 | 40 | 40 | 14 |
| Max. | 0.26 | -0.05 | 0.18 | 3.64 | 1.41 | 2.20 | 4.23 | 1.31 | 5.64 | 6.01 | 3.12 | -0.26 | 5.63 | 5.24 |
| Min. | -2.07 | -3.39 | -1.58 | -3.58 | -2.05 | -0.13 | 1.61 | -4.47 | 1.84 | -1.19 | 0.62 | -1.85 | -0.18 | 1.21 |
| Confidence Level(95.0%) | 0.21 | 0.19 | 0.12 | 1.55 | 4.50 | 0.14 | 0.16 | 0.23 | 0.17 | 0.38 | 0.19 | 0.12 | 0.36 | 0.62 |

### 3.3.3. *Trace element contents in plants and trace element patterns*

The transfer of metals from soil to plants is important in terms of plant formation and heavy metal pollution (Kabata and Pendias, 2000). Many mechanical and experimental methods have been studied for the investigation of element transfer from soils or soil solutions into plants (Kraus et al., 2001; Yaylalı-Abanuz and Tüysüz 2009). The relation between the metal contents of various soils and plants could be explained by transfer factor (Krauss et al., 2001). Although a linear function is preferred in many cases, soil-plant transfer of metal does not give a linear relation. Some investigators use Ferundlich type function to predict the transfer of elements into various plants grown in polluted soils (Krauss et al., 2001;Yaylalı-Abanuz and Tüysüz, 2009).

The relationship of concentration of an element in plant or soil could be calculated by the formula;

$$c_{plant} = bxc_{soil}^{a}$$

As there is not any linear relationship in element transfer from soil to plant, this formula can be rendered into linear form by a logarithmic transformation;

$$log\ c_{plant} = axc_{soil} + log\ b$$

Here;

$c_{plant}$ is metal concentration in plant

$c_{soil}$ is the metal concentration in plant

Values (a) and (b) are the empirical Ferundlich coefficients (Sposito, 1984). As trace element concentrations in plants and soils do not display a normal distribution, logarithmic values in regression analyses were used in order to obtain a linear distribution. This model, which is used in investigating the element transfer between the plant and soil in which the plant grows, is not only easy model to use but also is an easy method used for explaining the relationship between these (Krauss et al., 2001). The coefficient (b) also reflects element intake capacity of the element from soil to plant (Krauss et al., 2001; Yaylalı-Abanuz and Tüysüz, 2009). Within the scope of study, the correlation coefficients between shoots of acacia tree and the soil in which this tree had grown up were calculated but there was not observed any significant relationship between them (Figure 4a, b). High correlation values were taken between shoots of acacia tree and the soil in which the tree grows because of insufficient data in terms of these elements. Therefore, these are not realistic correlation values. There is no strong correlation between the element concentrations of acacia shoots and soil in which these shoots had grown up. So, it means that there was not observed a direct relationship between element concentrations of acacia shoots and soils in which those trees had grown up. The absence of a good correlation is an expected result when the fact that the trace element accumulations of tree shoots are less than the trace element accumulation of tree leaf and flowers is taken into consideration.

It is considered to take satisfactory results if this study would be carried out for leaves and flowers of acacia tree.

The element concentrations in acacia shoots are decreasingly ordered as; Fe>Al>Sr>Mo>Zn>Sn>Ba>Mn>Cu>Ni>As>Cr>Co in table 6. It is clear that molybdenum values in acacia shoots are high. As molybdenum values are lower than the detection limits in soil analyses in which acacia trees grow up, the possibility for examining the relationship between soil and the plant could not be performed. This situation is a lack which should be corrected in further studies, and acacia shoots to present high values in terms of molybdenum is another worth investigating. Studies on this topic still continue and

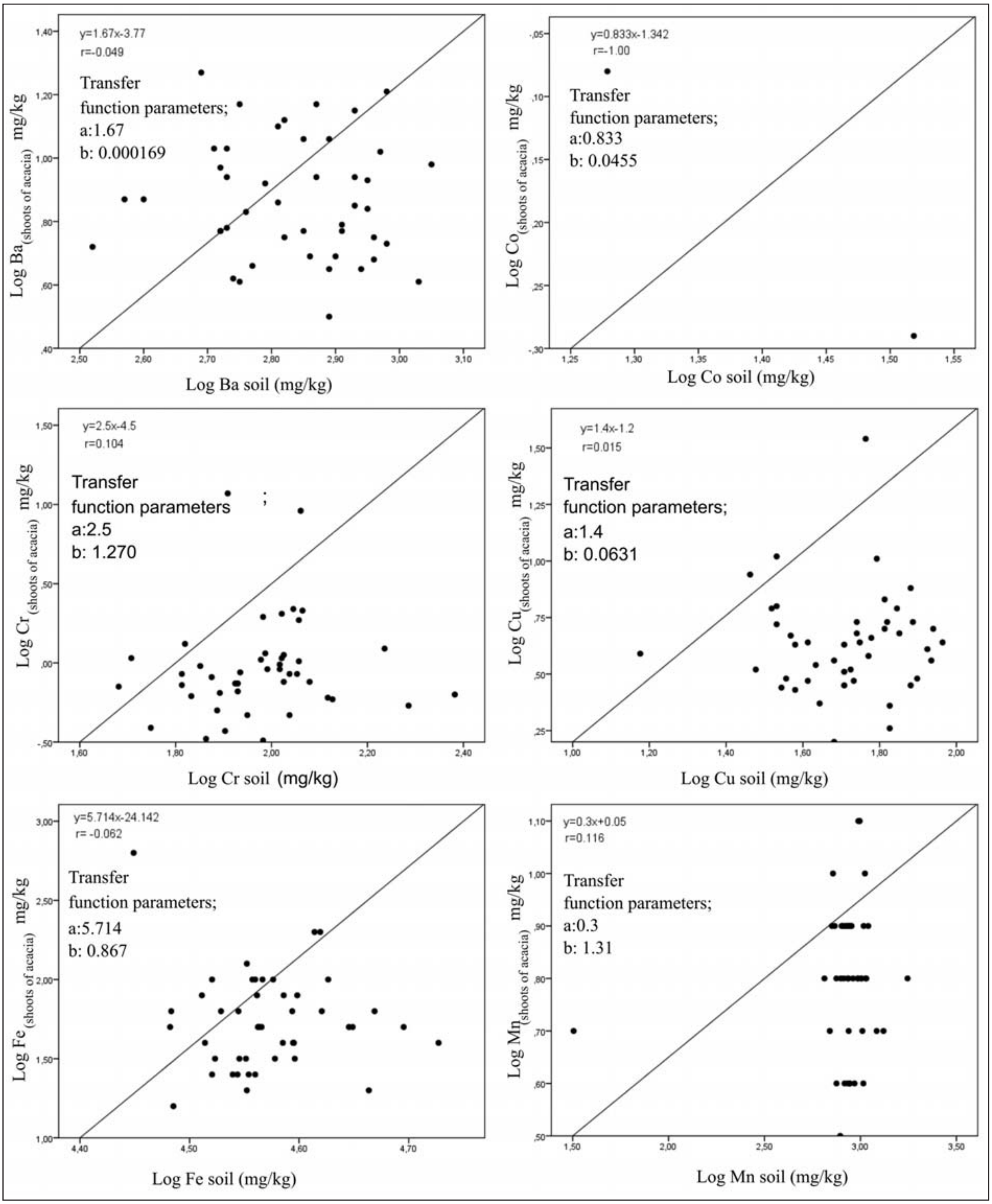

Figure 4- (a) Relationships between shoots of acacia and element in the soil in which the acacia tree has grown (data in logarithmic)

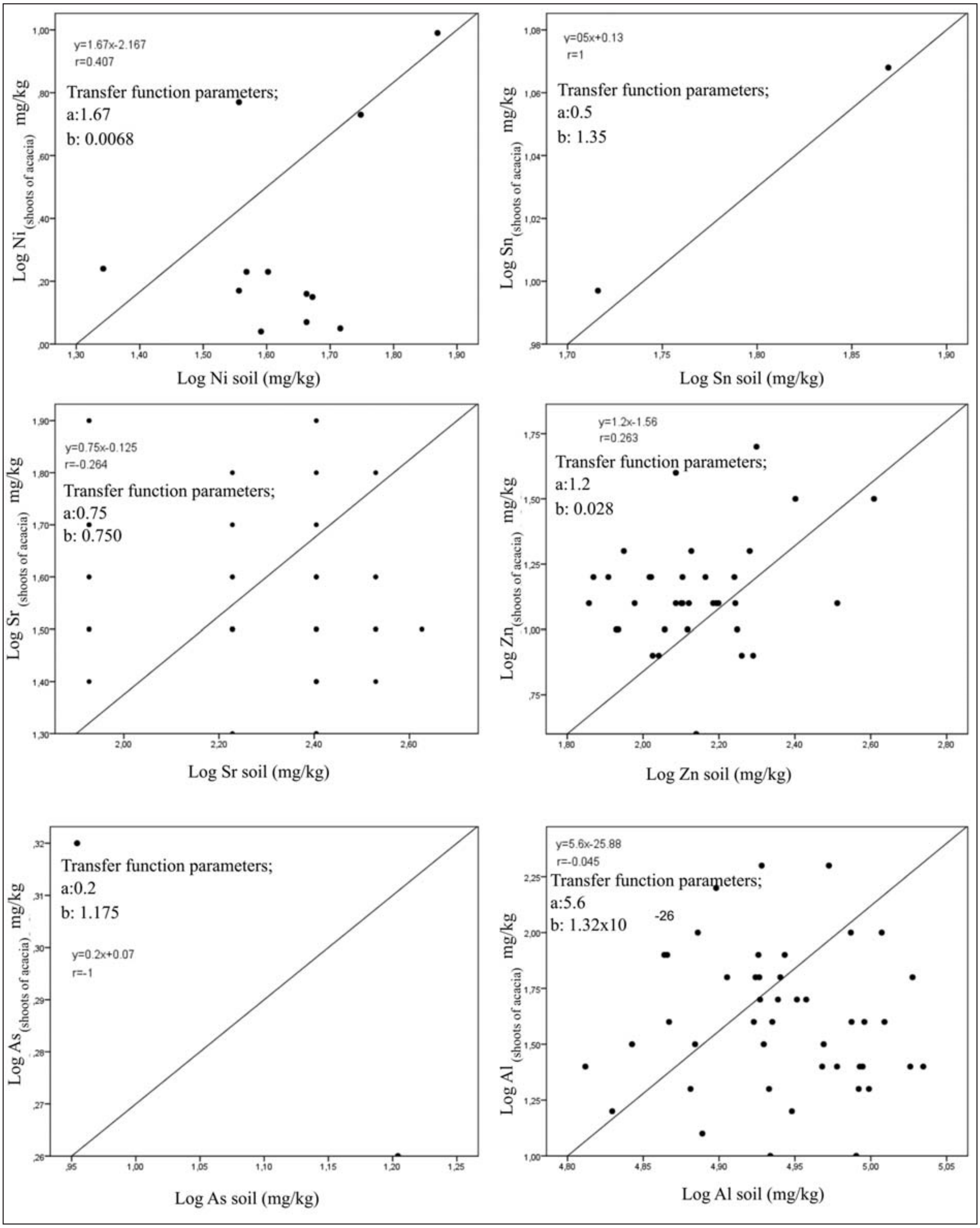

Figure 4- Cont.

these indicate that acacia shoots could be used in soil geochemistry analyses especially for mineral investigations. Using coefficient b, heavy metal accumulations in plants can be detected, and these plants can be used both in geochemistry studies for mineral explorations and in rehabilitating soils which have been subjected to heavy metal contamination. Slope coefficient in acacias is ordered as; Fe>Al>Cr>Ba=Ni>Cu>Zn>Co>Sr>Sn>Mn>As (Figure 4). The plant capacity which affects the element accumulation is expressed with this coefficient. Small coefficients indicate intensive element contributions from soil to its body which contains low metal concentrations, or small amount element contributions from soil which has high metal concentration. In case of low coefficient, the relation between plant and soil is not linear. There is a linear correlation between them when the coefficient approaches 1. This situation is partly related with the element content of the plant, and any increase in soil directly reflects to plant (Krauss et al., 2001, Yaylalı-Abanuz and Tüysüz 2009). This model $log\ c_{plant} = axc_{soil} + log\ b$ is very suitably used in correctly detecting the element intake of plants from the soil (Krauss et al., 2001).

### *3.3.4. Heavy metal accumulation relationship in soil and plant systems and their use in biogeochemical studies of acacia shoot*

Trace elements were absorbed and transported from soil via roots to the other organs of the plant. The relation of transmit from polluted soil to plant is handled with parameters such as; Biological Absorption Constant (BAC), Transfer Factor (TF), Bioaccumulation Factor (BAF) (Luoma and Bryan, 1979; Cui et al., 2004). Element transfer from soil to plant was investigated in this study by means of Bioaccumulation Factor. BAF is estimated by a formula given below;

$$BAF=M_{plant}/M_{soil}$$

Here; $M_{plant}$ is the element content in plant organs, and $M_{soil}$ corresponds to element content of soil in which plant grows (Louma and Bryan, 1979). This equation is used in predicting the transmission rate capacity of each element into plant and plant systems growing in the soil, to show the skill for biological element transport and migration.

Enrichments of trace elements in shoots of acacia relative to soils in which they grow and their related complementary statistical parameters were calculated and box diagrams of elements for BAF were drawn (Table 12, Figure 5).

When BAF values belonging to elements/metal in soil and acacias growing in this soil was studied, following results were obtained as follows; Ba (0.0038-0.038), Co (0.0154-0.0439), Cr (0.0026-0.1448), Cu (0.0271-0.5931), Fe (0.0004-0.0247), Mn (0.0032-0.1680), Ni (0.0214-0.1628), Sn (0.1581-0.909), Sr (0.0723-0.9015), Zn (0.0273-0.2972), As (0.1138-0.2311) and Al (0.0001-0.0025). So, transmission rates for Ba, Co, Fe, Al and partly Mn elements from soil to plant were found to be low. So, taking all these data into account, Al, Mn, Ba and Co elements are not considered to be very productive for biogeochemical studies. Since BAF values of Cu, Ni, Zn, Sn and As elements are higher or equal than 0.1, these can be used in biogeochemical analyses. BAF value of Cu element is seen in a wide range (0.027-0.593), but concentrates are between the range of 0.06-0.11 (Figure 5). BAF value of Cu element to increase up to 0.593 shows that acacia shoots can be used in biogeochemical studies. BAF value for Ni element is between the ranges of 0.021-0.0163, but concentrates are between the ranges of 0.03-0.08. BAF value of Zn is 0.27-0.3, however it mainly possesses a BAF value of 0.1. There was not sufficient data in shoots of acacia, but BAF value obtained for tin element is 0.1. The sufficient determination for As element in acacia shoots could not be performed, nevertheless BAF value for this element was detected as 0.113-0.2. BAF value of Sr element ranges between 0.072-0.9, and the most of data cumulates around 0.12-0.3. Therefore; Sr element can be used in biogeochemical studies. The value of molybdenum in acacia was detected higher than the expected value. The value of molybdenum element could not be detected in soil samples as the content of this element in soil was low. The detection

Table 12- Descriptive statistical parameters of the bioaccumulation factor for shoots of acacia tree.

| | *BAF(Ba)* | *BAF(Co)* | *BAF(Cr)* | *BAF(Cu)* | *BAF(Fe)* | *BAF(Mn)* | *BAF(Ni)* | *BAF(Sn)* | *BAF(Sr)* | *BAF(Zn)* | *BAF(As)* | *BAF(Al)* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | 0.0124 | 0.0297 | 0.0146 | 0.1069 | 0.0021 | 0.0112 | 0.0615 | 0.1745 | 0.2464 | 0.1146 | 0.1724 | 0.0006 |
| Min. | 0.0038 | 0.0154 | 0.0026 | 0.0271 | 0.0004 | 0.0032 | 0.0214 | 0.1581 | 0.0723 | 0.0273 | 0.1138 | 0.0001 |
| Max. | 0.0380 | 0.0439 | 0.1448 | 0.5931 | 0.0247 | 0.1680 | 0.1628 | 0.1909 | 0.9015 | 0.2972 | 0.2311 | 0.0024 |
| Total | 0.5580 | 0.0593 | 0.6412 | 4.8105 | 0.0958 | 0.5020 | 0.7380 | 0.3490 | 11.0890 | 4.0094 | 0.3449 | 0.0276 |
| Cardinality | 45 | 2 | 44 | 45 | 45 | 45 | 12 | 2 | 45 | 35 | 2 | 45 |

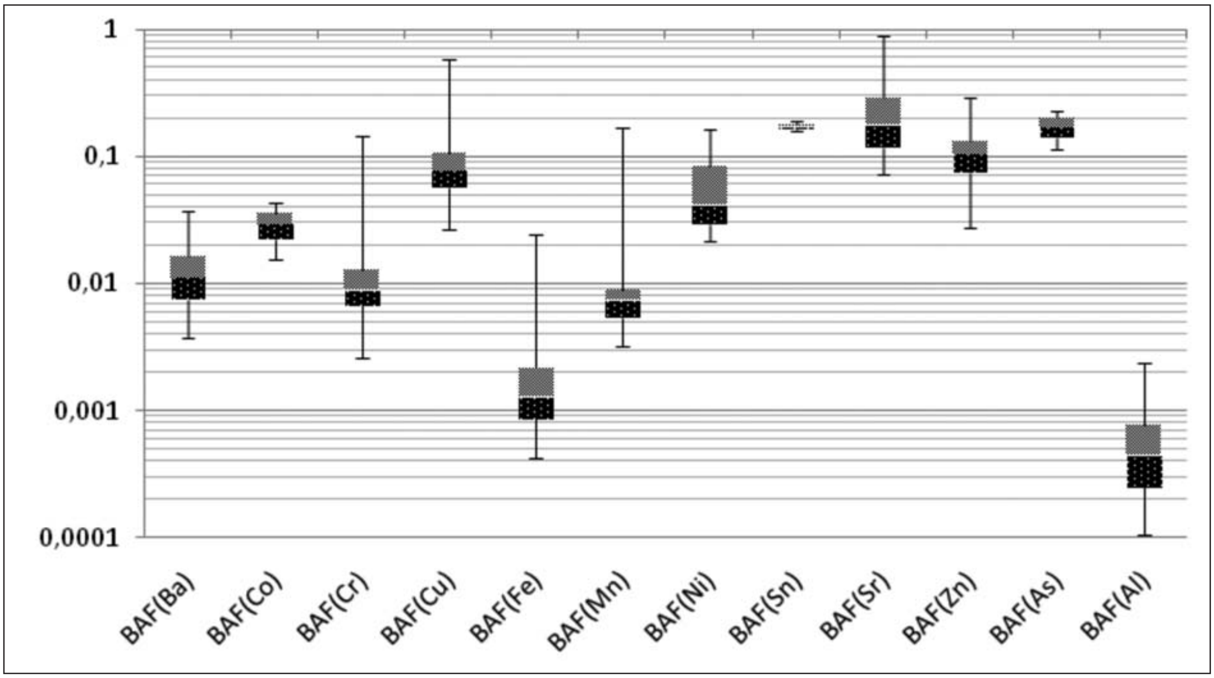

Figure 5-Box diagram belonging to Bioaccumulation Factors (BAF) for the elements of acacia shoots.

of molybdenum values in acacia shoots is because of its nature. As it is known; elements which are rarely found in nature such as; Mo, Mn, Co, Pb, Ni and Sr could reach very high values on leaves as their mobility coefficients are high in water.The molybdenum element was observed in high values in shoots of acacia tree, though it could not be detected in soil in this study as well (7.34-56.45 mg/kg). These values showed that molybdenum gave better results in shoots of acacia tree than soil in biogeochemical studies.

The correlation of element transfer from soil to acacia shoots and the correlation with pH of the soil in which the plant grows was made. Accordingly; weak positive correlation was observed between Fe and Ba with Cu; Sr and Ba; Zn and Cu with Mn; and Al and Fe. However; strong positive correlation between Cr and Ni, and weak negative correlation between Al and Ni, and the alkalinity of the environment with Cr and Ni were observed (Table 13).

The pH values of the environment are effective on the mobility of all cations. As pH decreases, the mobility of cations increases with increasing in acidity of the soil. However, the high mobility of trace elements in the soil increases the element transmission from soil to plant and supplies soil profiles to pass into water systems. Also; pH values have an important effect on the takeout of nutrition and elements in soil profiles (Kabata-Pendias, 2000). The pH value also enables the alteration of minerals in the soil and transforms minerals into less soluble compounds (Kabata-Pendias and Pendias, 1992). The alkaline pH values ranging between 7 and 8.5 can account for the low correlation in element transfer to plant.

## 4. Results

In this study, the environmental biogeochemical characteristics of heavy metal/trace elements in soils and in shoots of acacia trees in soils were investigated along the auto road passing through Gümüşhane city center. In this study, concentrations of heavy metals such as; Al, Fe, Zr, Sr, Rb, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, Y, As and Sn, and the contamination degrees of these elements in the soil were studied. Elements in the soil are ordered in abundance as; Al>Fe>Mn>Ba>Pb>Zn>Sr>Cr>Ni>Rb>Zr>Sn>Cu>As>Co>Y>Cd. In order to determine the degree of contamination in the area, $I_{geo}$ and EF parameters were calculated. According to these parameters; the contamination order as; Pb>Zn>Cu>Ni>Mn was obtained. High $I_{geo}$ and EF values for Pb, Zn and Cu in the soil along the auto road indicate the presence of an anthropogenically induced contamination (related with traffic and industrial facilities) in terms of these

Table 13- Correlation values between bioaccumulation factors and the pH of the soil.

| | *BAF(Ba)* | *BAF(Cr)* | *BAF(Cu)* | *BAF(Fe)* | *BAF(Mn)* | *BAF(Ni)* | *BAF(Sr)* | *BAF(Zn)* | *BAF(Al)* | *pH* |
|---|---|---|---|---|---|---|---|---|---|---|
| BAF(Ba) | 1.000 | | | | | | | | | |
| BAF(Cr) | 0.099 | 1.000 | | | | | | | | |
| BAF(Cu) | 0.128 | 0.009 | 1.000 | | | | | | | |
| BAF(Fe) | 0.359 | 0.122 | 0.342 | 1.000 | | | | | | |
| BAF(Mn) | -0.060 | -0.060 | 0.078 | -0.039 | 1.000 | | | | | |
| BAF(Ni) | 0.139 | 0.774 | 0.156 | -0.147 | -0.096 | 1.000 | | | | |
| BAF(Sr) | 0.389 | -0.087 | 0.116 | 0.111 | -0.020 | -0.048 | 1.000 | | | |
| BAF(Zn) | 0.050 | -0.201 | 0.486 | 0.188 | 0.365 | -0.380 | 0.066 | 1.000 | | |
| BAF(Al) | 0.172 | 0.048 | 0.129 | 0.454 | -0.125 | -0.397 | -0.032 | 0.111 | 1.000 | |
| pH | 0.034 | -0.313 | -0.144 | -0.044 | -0.071 | -0.444 | 0.214 | 0.081 | -0.115 | 1.000 |

elements. It is also predicted that mine sites in the vicinity of the study area would have direct or indirect effect on this contamination. However, there is a need for more detailed investigation to understand the dimensions of the effect. Low $I_{geo}$ and EF parameter for Mn and Ni elements indicate that there is not any contamination in soil in terms of these elements. So, while there is observed a depletion in terms of elements such as; Mn, Cr and Ni in soils along the road, there was detected an enrichment (contamination) in terms of Pb, As, Zn and Cu elements.

In the study; Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sn and Zn contents in shoots of acacia tree were determined. Cd, Hg and Pb concentrations remained below the detection limits. Ni and As elements were determined in acacia shoots in locations 6 and 2, respectively. When plant transmission parameters from soil were calculated, it was seen that (BAF and TF) Al, As, Ba, Co, Cr and Mn contents ranged in normal limits, and Cu, Fe, Mo, Ni, Sr and Zn elements were above the upper limits and/or even more at some locations.

## Acknowledgement

The author would like to thank to the General Directorate of Eti Maden Management (Ankara) and to Muhsin Gani, to the Directorate of Provincial Food Control, Trabzon, to Ali Gündoğdu and Cemalettin Baltacı (Gümüşhane University) and to his students Erdem Şahin, Osman Barış Aslan, Veysel Dündar and Emre Önal for their helps during field studies.

*Received: 04.12.2012*
*Accepted: 08.01.2014*
*Published: june 2014*

## References

Acevedo-Figueroa, D., Jiménez, B.D., Rodríguez-Sierra, C.J. 2006. Trace metals in sediments of two estuarine lagoons from Puerto Rico, *Environmental Pollution* 141, 336-342.

Adamia, S., Lordkipanidze, M., Zakariadze, G. 1977. Evolution of an active continental margin as exemplified by the Alpine history of the Caucasus. *Tectonophysics*, 40, 183–199.

Adamo, P., Arienzo, M., Imperato, M., Naimo, D., Nardo, G., Stanziones, D. 2005. Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port, *Chemosphere* 61, 800-809.

Ahdy, H.H., Khaled, A. 2009. Heavy Metal Contamination in Sediments of the Western Part of Egyptian Mediterranean Sea, *Austrlian J. of Basic Applied Sci*3(4) 3330-3336

Akçay, M., Gündüz, Ö., Yaşar, R., Gümrük, O. 2011. Hazine Mağara ve Kırkpavli (Gümüşhane) Polimetalik Pb-Zn-Cu-Au-Ag Madenlerinin Jeokimyasal ve Kökensel Özellikleri. *64. TJK Kurultayı Bildiri Özleri Kitabı* s-183-184.

Aliyazıcıoğlu, İ. 1999. Kale (Gümüşhane) Yöresi Volkanik Kayaçlarının Petrografik, Jeokimyasal ve Petrolojik incelenmesi, Yüksek Lisans Tezi, KTÜ Fen Bilimleri Enstitüsü. Trabzon.

Aloupi, M., Angelidis, M.O. 2001. Geochemistry of natural and anthropogenic metals in the coastal sediments of the island of Lesvos, Aegean Sea, *Environmental Pollution* 113, 211-219.

Aslan, Z. 2010. U–Pb zircon SHRIMP age, geochemical and petrographical characteristics of tuffs within calc-alkaline Eocene volcanics around Gümüşhane (NE Turkey), Eastern Pontides. N*eues Jahrbuch für Mineralogie - Abhandlungen: Journal of Mineralogy and Geochemistry* 187(3), 329-346.

Aslan, M., Aliyazıcıoğlu, İ. 2001. Geochemical and petrological characteristics of the Kale (Gümüşhane) volcanic rocks: implications for the Eocene evolution of eastern Pontide arc volcanism, northeast Turkey. *International Geology Review* 43, 595–610.

Aslan, N., Akçay, M. 2011. Mastra (Gümüşhane) Au-Ag Yatağının Jeolojik, Mineralolojik ve Jeokimyasal

Özellikleri. *64. TJK Kurultayı Bildiri Özleri Kitabı*, 25-29 Nisan 2011, Ankara, 181-182.

ATSDR (Agency for Toxic Substances and Disease Registry). *Toxicological Profile for Arsenic*. 2000.

Birch, G. 2003. A scheme for assessing human impacts on coastal aquatic environments using sediments, In C.D. Woodcoffe & R. A. Furness (Eds.), *Coastal GIS 2003. Wollongong University Papers in Center forMaritime Policy,* 14, Australia.

Birch, G.E.,Scollen, A. 2003. Heavy metals in road dust, gully pots and parkland soils in a highly urbanized sub-catchment of Port Jackson, *Australia. Austr. J. Soil Res*. 41: 1329-1342.

Bosco. M.I., Varrica, D., Dongarra, G. 2005. Case study: Inorganic pollutants associated with particulate matter from an area near a petrochemical plant. *Environ. Res*. 99, 18–30.

Buat-Menard, P., Chesselet, R. 1979. Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter, *Earth Planet Sci Lett* 42:398–411

Chen, C.W., Kao, C.M., Chen, C.F., Dong, C.D. 2007. Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan, *Chemosphere*, 66, 1431–1440.

Cobela-Garcia A, Prego, R. 2003. Heavy metal sedimentary record in a Glacian Ria (NW Spain): background values and recent contamination. *Mar Pollut Bull* 46:1253–1262.

Condrad, C.F., Chisholm-Brause, C.J. 2004. Spatial survey of trace metal contaminants in the sediments of Elizabeth River, Virginia. *Marine Pollution Bulletin* 49, 319-324.

Cui. Y., Zhu, Y., Zhai. R., Chen, D., Huang, Y., Qui, Y., Liang, J. 2004. Transfer of metals from soil to vegetables in an area near a Smelter in Nanning/China. *Environment International*. 30, 785-791.

Çoğulu, E. 1975. Gümüşhane ve Rize Granitik Plutonlarının Mukayeseli Petrojeolojik ve Jeokronolojik Etüdü, İTÜ Fen Bilimleri Fakültesi, İstanbul, Doktora Tezi.

Daskalakis, K., D., O'Connor, T.P. 1995. Normalization and elemental sediment contamination in the Coastal United States. *Environmental Science and Technology* 29, 470-477.

Dokuz, A. 2011. A slab detachment and delamination model for the generation of Carboniferous high-potassium I-type magmatism in the Eastern Pontides, NE Turkey: The Köse composite pluton. *Gondwana Res*. 9 (4), 926-944.

Duran, C., Gundogdu, A., Bulut, V.N., Soylak, M., Elci, L., Şentürk, H.B., Tüfekçi, M. 2007. Solid-phase extraction of Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) ions from environmental samples by flame atomic absorption spectrometry (FAAS). *Journal of Hazardous Materials* 146 (1-2), 347-355.

EPA. 1982. Exposure and risk assessment for arsenic. Washington, DC: U.S. Environmental Protection Agency. Code of Federal Regulation. PB 85-221711. EPA 440/4-85-005. 1.1-4.68.

Eyüboğlu, Y., Bektas, O., Seren, A., Maden, N., Jacoby, W.R., Özer, R. 2006. Three-directional extensional deformation and formation of the Liassic rift basins in the eastern Pontides (NE Turkey). *Geologica Carpathica* 57(5), 337-346.

Eyüboğlu, Y., Chung, SL., Dudas, F.O., Santosh, M., Akaryali, E. 2011. Transition from shoshonitic to adakitic magmatism in the Eastern Pontides, NE Turkey: Implications for slab window melting. *Gondwana Research* 19, 413-429.

Feng, H., Han, X., Zhang, W., Yu, L. 2004. A preliminary study of heavy metal contamination in Yantze River intertidal zone due to urbanization, *Marine Pollution Bulletin* 49, 910-915.

Ghrefat, H., Yusuf, N. 2006. Assessing Mn, Fe, Cu, Zn and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. *Chemosphere* 65, 2114-2121.

Goldschmidt V.M. 1958. Geochemistry. Ed.: Muir A., Oxford, Oxford University Press, s. 468.

Groengroeft, A., Jaehnig, U., Miehlich, G., Lueschow, R., Maass, V. ve Stachel, B., 1998. Distribution of metals in sediments of the Elbe Estuary in 1994. *Water Science and Technology 37*, 109-116.

Güner, S., Er, M., Gümüşel, A., Boğuşlu, M.1985. Gümüşhane-Eski Gümüşhane yöresindeki cevherleşmelere ait jeoloji raporu. *Maden Tetkik ve Arama Genel Müdürlüğü Rapor No: 8029*, 525 s Ankara (unpublished).

Güner, S.,Yazıcı, E.N. 2005. Gümüşhane Yöresi epitermal altın aramaları prospeksiyon raporu. *Maden Tetkik Arama Genel Müdürlüğü Rapor No: 10743*, 45 s Ankara (unpublished).

Güven, İ.H., 1993. Doğu Pontidlerin Jeolojisi ve 1/250 000 ölçekli kompilasyonu. *Maden Tetkik ve Arama*, Ankara (unpublished)

Kabata-Pendias, A.2000 Trace element in soils and plants, 3rd edn. CRC Press, USA. 413 s.

Kabata-Pendias, A., Pendias, H. 1992 Trace elements in the biological environment. Wyd. Geol., Warsaw, 300 s.

Kabata-Pendias, A. ve Pendias, H. 1994. Trace Element in Soil and Plants (Second edition ed.). Florida: CRC.

Kahraman, İ., Kansız, H., Dursun, A., Yılmaz, H., Erçin, A.İ. 1985. Gümüşhane yöresinin jeolojisine ve cevherleşmelerine ait jeoloji raporu. *Maden Tetkik ve Arama Rapor No:7956*, Ankara (unpublished).

Kandemir, R. 2004. Gümüşhane ve Yakın Yöresindeki Erken-Orta Jura Yaşlı Şenköy Formasyonunun Çökel Özellikleri ve Birikim Koşullar. Doktora Tezi, Karadeniz Teknik Üniversitesi, Fen Bilimleri Enstitüsü, Trabzon.

Karslı, O., Dokuz, A., Uysal, İ., Aydin, F., Kandemir, R., Wijbrans, J. 2010. Generation of the Early Cenozoic adakitic volcanism by partial melting of mafic lover crust, Eastern Turkey: Implications for crustal thickening to delemination. *Lithos* 114: 109–120.

Kartal, S., Aydın, Z., Tokalıoğlu, S. 2006. Fractionation of metals in street sediment samples by using the BCR sequential extraction procedure and multivariate statistical elucidation of the data, *J. Hazard. Mater.,*132, 80–89.

Kaygusuz, A., Wolfgang, S., Şen, C., Satır, M. 2008. Petrochemistry and petrology of I-type granitoids in an arc setting: the composite Torul pluton, Eastern Pontides, NE Turkey. *International Journal of Earth Sciences*, 97, 739–764.

Kaygusuz, A., Arslan, M., Siebel, W., Şen, C. 2010. Geochemical and Sr-Nd Isotopic Characteristic of Post-Collisional Calc-Alkaline Volcanics in the Eastern Pontides (NE Turkey). *Turkish J.Earth Sci* 20, 137-159.

Ketin, İ. 1966. Anadolu'nun Tektonik Birlikleri. *MTA Dergisi*, 66, 20-34.

Kocaer F, Baskaya H.S. 2003. Remediation Technologies for Metal-Contaminated Soils, *Uludag Univ. Eng. Archit. Fac. J.,* 8(1): 121-131.

Kovacs, M., Podani, J., Klincsek, P., Dinka, M., Torok, K. 1981. Element composition of the leaves of some deciduous trees and the biological inducators of heavy metals in an urban-industrial environment. *Acta Botanica Acadcmiac Scicntiarum Hunsaricae* 27: 43-52.

Krauss, M., Wilcke, W., Kobza, J., Zech, W. 2001. Predicting heavy metal transfer from soil to plant: potential use of Freundlich-type functions. *J Plant Nutr Soil Sci* 165,3–8

Loska K., Cebula J., Pelczar J., Wiechula D., Kwapulinski J. 1997**.** Use of enrichment, and contamination factors together with geoaccumulation indexes to evaluate the content of Cd, Cu, and Ni in the Rybnik Water Reservoir in Poland. *Water, Air, Soil Pollut*. 93, 347.

Loska, K., Wiechula, D., Barska, B., Cebula, E., Chojnecka, A. 2003. Assessment of arsenic enrichment of cultivated soils in Southern Poland, *Polish Journal of Environmental Studies*, 12(2): 187-192.

Luoma S.N., Bryan G W. 1979. Heavy metal bioavailability: Modeling chemical and biological interactions in sediment bound zinc[M]. In: Chemical modeling in aqueous systems (E. A. Jenne, ed.). Washington, DC: ACS Symposium Series 93. *American Chemical Society* 577-604.

Machender, G., Dhakate R., Pransanna, L., Govil, P.K. 2011. Assessment of heavy metal contamination in soils around Balanagar industrial area, Hyderabad, India. *Environ Earth Sci*. 63. 945-953.

Miao L., Ma, Y., Xu, R., Yan W. 2011. Environmental biogeochemical characteristics of rare earth elements in soil and soil grown plants of the Hetai goldfield, Guangdong Province, China. *Environ Earth Sci*. 63:501-511.

Miko, S., Peh, Z., Bukovec, D., Prohic, E., Kastmüller, Z. 2000. Geochemical baseline mapping and Pb pollution assessment of soils in the karst in Western Croatia, *Natura Croatica* 9 (1):41-59.

Morillo, J., Usero, J.,Gracia, I. 2002. Partitioning of metals in sediments from the Odiel River (Spain). *Environment International* 28, 263–271.

Murakami, M., Fujita, M., Furumai, H., Kasuga, I., Kurisu, F. 2009. Sorption behavior of heavy metal species by soakaway sediment receiving urban road runoff from residential and heavily trafficked areas. *J Hazard Mater* 164:707-12.

Müller, G. 1969. Index of geoaccumulation in sediments of the Rhine River, *GeoJournal,* 2(3): 108-118.

Müller, G. 1981. Die Schwermetallbelastung der Sedimenten des Neckars und Seiner Nebenflüsse. *Chemiker-Zeitung* 6, 157.

Önder, S., Dursun Ş. 2005. Air borne heavy metal pollution of Cedrus libani (A. Rich.) in the city centre of Konya (Turkey). *Atmospheric Environment* 40, 1122-1133.

Pelin, S. 1977. Alucra (Giresun) Güneydoğu Yöresinin Petrol Olanakları Bakımından Jeolojik İncelemesi. Doçentlik Tezi, Yayın No: 87, , K.T.Ü., Trabzon.

Reimann C., De Caritat P. 2000. Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry. *Environ. Sci. Technol.* 34, 5084-5091.

Rodríguez-Barroso, M.R., Benhamou, Y., El Moumni, B., El Hatimi I., Garica-Morales, J.L. 2009. Evalution of Metal contamination from North of Morrocco: geochemical and statistical approaches, *Environ Monit Asses* 159, 169-181.

Rubio, B., Nombela, M.A., Vilas, F. 2000. Geochemistry of major and trace elements in sediments of the Ria de Vigo (VW Spain): an assessment of metal pollution.*Mar. Pollut Bull* 40, 968-980.

Saur, E., Juste, C. 1994. Enrichment of trace elements from long-range aerosol transport in sandy podozolic soils of southwest France. *Water Air Soil Pollut* 73, 235-246.

Sposito, G. 1984. The surface chemistry of soils. Oxford University Press, New York.

Sutherland, R.A. 2000. Bed sediment associated trace metals in an urban stream, Oahu, Hawaii. *Environ Geological.*, 39, 611-627

Taylor, S.R., McLennan, S.M. 1995. The geochemical evolution of the continental crust. *Reviews of Geophysics* 33, 241-265.

Tokel, S. 1972. Stratigraphical and volcanic history of Gümüşhane region (Kuzeydoğu Turkiye), Ph. Thesis, University College, London.

Topuz G., Altherr, R., Siebel, W., Schwarz, W.H., Zack, T., Hasözbek, A., Barth, M., Satır, M., Şen, C. 2010. Carboniferous high-potassium I-type granitoid magmatism in the Eastern Pontides: The Gümüşhane pluton (NE Turkey). *Lithos* 116, 92-110.

Topuz, G., Altherr, R., Schwarz, W.H., Dokuz, A., Meyer, H.P. 2007. Variscan amphibolitefacies metamorphic rocks from the Kurtoğlu metamorphic complex (Gümüşhane area, Eastern Pontides, Turkey). *Int. J. Earth Sci. (Geol. Rundsch)* 96, 861-873.

Turekian, K.K.,Wedepohl, K.H. 1961. Distribution of the elements in some major units of the earth's crust. *Bulletin of the Geological Society of American* 72, 175-192.

Vald'es, J., Vargas, G., Sifeddine, A., Ortlieb, L., Guinez, M., 2005. Distribution and enrichment evaluation of heavy metals in Mejillones Bay (23°S), Northern Chile: Geochemical and statistical approach, *Marine Pollution Bulletin* 50, 1558-1568.

Vural, A., Şahin, E., 2012*a*. Gümüşhane İli Şehir Merkezinden Geçen Devlet Karayolundaki Akasyalarda Ve Toprakta Trafiğe Bağlı İz Element Birikimine Ait İlk Bulgular. *65. TJK Kurultayı Bildiri Özleri Kitabı*; 2-6 Nisan 2012, Ankara,162-163.

Vural, A., Şahin, E., 2012*b*. Gümüşhane Şehir Merkezinden Geçen Karayolunda Ağır Metal Kirliliğine Ait İlk Bulgular. *Gümüşhane Üniversite, Fen Bilimleri Enstitüsü Dergisi* 2, (1), 21-35.

Wheeler G.L., Rolfe G.L. 1979. Relationship between daily traffic volume and the distribution of lead in roadside soil and vegetation. *Environ Pollut*.18, 265.

Yaylalı-Abanuz, G., Tüysüz, N., Akaryalı, E. 2011. Soil Geochemical Prospection for Gold Deposit in the Arzular Area (NE Turkey), *Journal of Geochemical Exploration* 112, 107-117

Yaylalı-Abanuz, G., Tüysüz, N., 2009. Heavy metal contamination of soils and tea plants in the eastern Black Sea region, NE Turkey. *Environ Earth Sci*. 59:131-144.

Yılmaz, Y.1972. Petrology and structure of the Gümüşhane granite and surrounding rocks, North-Eastern Anatolia.Doktora Tezi, Londra Üniversitesi, 260 s.

Yılmaz, Y. 1974. Geology of the Gümüşhane granite (Petrography), İstanbul Üniversitesi Fen Fakültesi, Mecm. B., 39, 157-172

Zhang, X. Bao, Z.Y., Tang, J.H. 2006 Application of the enrichment factor in evaluation of heavy metal contamination in the environmental geochemistry. *Geol Sci Technol Infrom* 25(1), 65–72.