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**ORIGINAL RESEARCH ARTICLE**

# On the elemental contents of aspen (*Populus tremula* L.) leaves grown in the mineralization area

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## ABSTRACT

The aim of this study is to investigate the behavior of major and trace elements in aspen leaves grown in an intensely altered region from a geochemical point of view. In this context, major and trace element contents of aspen leaves (*Populus tremula* L.) grown on Gümüştuğ (Gümüşhane/Türkiye) antimony mineralization were investigated. For this purpose, 56 leaf samples were collected from the field by grid method and at intervals of approximately 50–60 m. After routine sample preparation processes, analyzes were carried out to determine the major and trace element concentrations. Subsequently, elemental concentrations of aspen leaves were evaluated by different statistical methods. As a result, major elements Ca, Mg, Na, K, Al and S concentrations were determined in the range of 2%–3%, 0.23%–0.85%, up to 0.02%, 0.79%–2.01%, 0.01%–0.03% and 0.13%–0.43%, respectively. The trace element concentrations were determined in the range of 127–339 ppm, 86.7–265.30 ppm, 0.1–1.21 ppm, 13.5–453.20 ppm, 6.0–12.0 ppm, 14.0–82.0 ppm and 0.1–0.60 ppm for Mn, Sr, La, Ba, Ti, B and Se, respectively. Considering that the samples were taken from aspen leaves grown on the antimony mineralization, the concentrations of the antimonite element were determined above the detection limit in only a few sampling points in the study. But the concentrations of B, Mn, Sr, La of aspen (*Populus Tremula* L.) leaves are remarkable.

***Keywords:*** Aspen (*Populus Tremula* L.); Major Elements; Trace Element; Geochemistry; Mineralization

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## 1. Introduction

Due to its geographical location, Gümüşhane (NE Türkiye) has a transitional climate between the Black Sea Climate and the Continental Climate. This provided an advantage for the region and enabled Gümüşhane to host a serious plant diversity. Therefore, many endemic plants grow in the region[1–5]. The region is also one of the important metallogenic belts of Türkiye and hosts many metallic mineralizations such as copper, lead, zinc, gold, silver, antimonite[6–9]. Considering the metallogenic richness and plant diversity of the region, Gümüşhane and its surroundings have a great potential for biogeochemical studies. Although the history of biogeochemical studies goes back to ancient times, their use for mineral exploration has increased remarkably after the first quarter of the 20th century[10,11]. After the second half of the 20th century, it started to be used not only for mineral exploration purposes, but also for phytoremediation purposes and reclamation of metal contaminated sites, with the increase in environmental sensitivity in the society[12,13].

The elemental uptake abilities of plants vary widely. Some plants even uptake some elements in much higher concentrations than others. What is important in mineral exploration and environmental biogeo-

biogeochemistry studies is which plants uptake which elements at a higher rate. Thus, plants that can uptake elements at a higher rate from the environment, thanks to their roots, serve as a kind of sounding function for the region between a few cm and a few meters from the surface, provide information to researchers and come to the forefront in geochemical exploration studies according to soil geochemistry. Likewise, such plants can be widely used to remove (for remediation) metals from naturally or anthropogenically contaminated areas. Therefore, studies for biogeochemical purposes, with the motivation of both mineral exploration and the improvement of the areas contaminated by the heavy metal and trace elements (phytoextraction technology[14]), continue to increase day by day[1,15–21].

Aspen tree (*Populus tremula* L.) grows widely in Eurasia, in a wide geography from the coldest northern regions to the temperate regions. It spreads from northern Norway to all of Europe, northern parts of Asia, northern Africa, Japan in the east, and many geographies. They are widely used in landscaping especially in residential and industrial areas of cities in temperate regions. It is frequently encountered in almost all geographical regions of Türkiye. Especially in relatively wet areas. The ability of aspen leaves to bioaccumulate elements, including Rare Earth elements (REE), has been reported in various studies[22]. Aspen leaves are biochemical and ecological indicators because they can absorb the elements in their structure by holding the dust in the air with their leaves and because they can accumulate the elements they take from the soil with their roots in their leaves[22].

In this study, the elemental contents (major, trace elements and some REEs) of aspen leaves (*Populus tremula* L.) grown in the antimony mineralization area, intensely hydrothermal altered site, in a high topography of Gümüşhane were investigated. The obtained findings will thus contribute to the understanding of the biochemical properties of aspen leaves, and to the studies of mineral exploration and remediation of contaminated soils.

## 2. Material and method

### 2.1 Geographic and geology features of the area

The study area is 1.5 km southwest of Gümüştuğ village (Torul-Gümüşhane/Türkiye) and 55 km southwest of Gümüşhane. There is antimonite mineralization in the area that has been exploited in the past and is currently abandoned (**Figure 1**). The site is in a very mountainous topography and the altitude is between 2,000–2,750 m (a.s.l). The region has inland climate characteristics, summers are mild/hot and dry, winters are cold and mostly snowy. Snow can remain unmelted until mid-July, especially in high areas. The hottest month is August and the coldest is January.

The region is one of the important and remarkable regions of Türkiye with its geological and metallogenic features. The base of the Eastern Pontides is made up of Early Carboniferous metamorphic rocks[23] and Late to Early Carboniferous plutonic rocks[24–30]. These basement rocks are uncomformably overlain by Early and Middle Jurassic volcano-sedimentary rocks[31,32] and crosscutting plutonic rocks of Mid to Late Jurassic[33–35]. Late Jurassic to Early Cretaceous period is characterized with extensive carbonate deposits corresponding to the stability period from a magmatic and tectonic perspective[36]. Late Cretaceous units consist of plutonic, volcanic and sedimentary rocks[37–46]. Cenozoic units consist of plutonic, volcanic and sedimentary rocks[47–65]. The oldest rocks in the region are comprised of Quaternary travertines and alluviums[66,67].

The study area is located in the Southern Zone of the Eastern Pontides (**Figure 1**). Permo-Carboniferous plutonic rocks make up the oldest units in the study area[26]. These basement rocks are overlaid by Early-Mid Jurassic volcano-sedimentary rocks (Zimonköy Formation). Late Jurassic to Early Cretaceous Berdiga Formation conformably overlain these units. Late Cretaceous rocks are represented by the Kermutdere Formation. This formation starts at the base with sandy limestones, continue with red limestones and ending with volcano-sedimentary series. Eocene Alibaba Formation are uncomformably overlies Late Cretaceous units and consist of andesite and basalt lavas and their pyroclastic equivalents, intercalated with sedimentary rocks. All these units are cut by Lutetian (44 My) aged Avliyana Granitoid[55] (**Figure 1**). The youngest units of the study area are made up of Quaternary alluviums and active travertines[66,67].

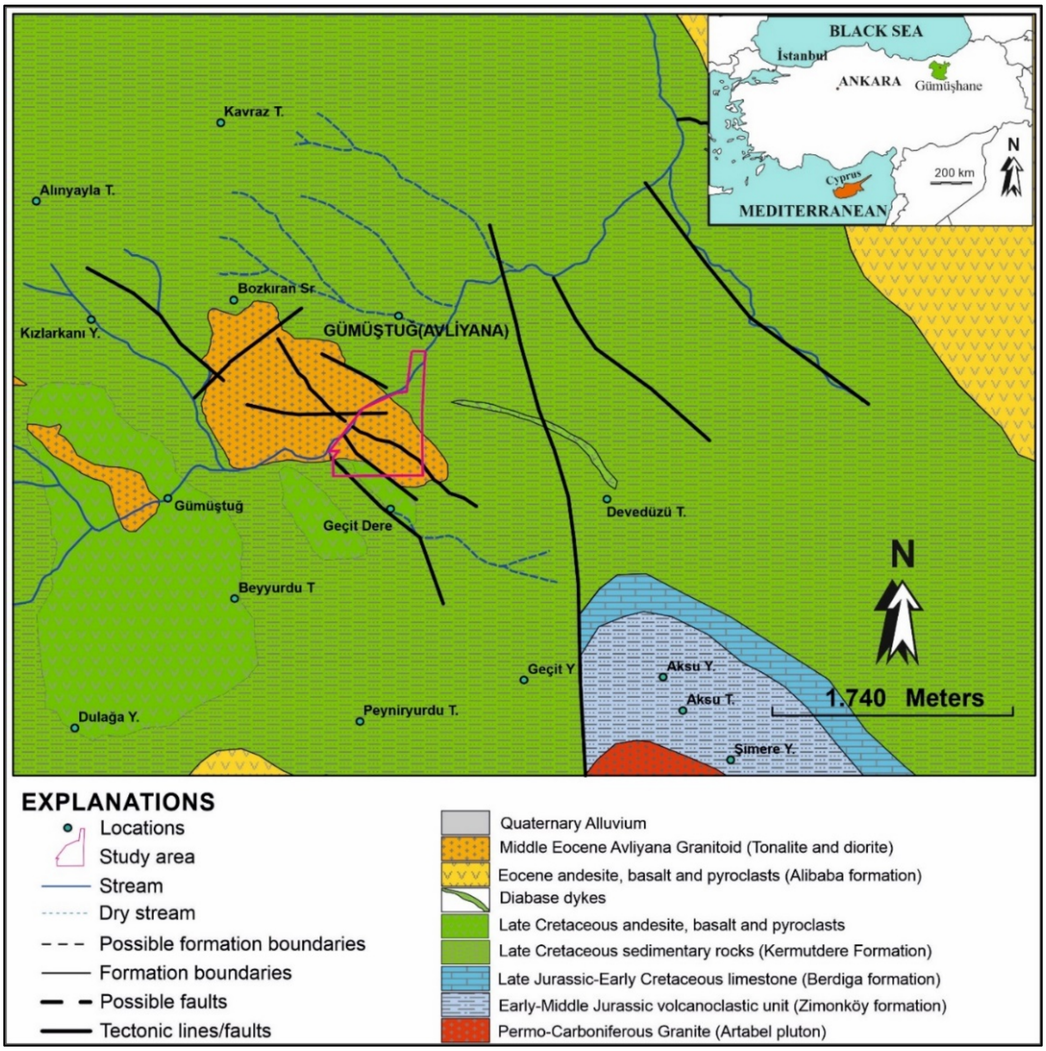


**Figure 1.** Study site location and geology map[68,69].

## 2.2 Sampling and analysis procedure

There is a well-developed hydrothermal alteration as well as mineralization where aspen grows. Depending on the alteration, soil development is also quite good. 56 aspen (*Populus tremula* L.) leave samples were collected from the hydrothermally altered Gümüştuğ antimony mineralization area, approximately 50–60 m apart, by grid method in September–October 2018. Routine sampling procedures were applied during sample collection and preparation for analysis and utmost care has been taken throughout all processes to avoid contamination of the samples. The collected samples were carefully washed three times with deionized water to eliminate putative metallic surface contamination and were dried under natural conditions in a shadowy place in Gümüşhane University Geological Engineering Mineral Deposits and Geochemistry laboratory. Subsequently, the moisture was removed in the oven at 60 °C for 6 h and the dried samples were then powdered with steel mills. The powdered samples were sent to the Accredited ACME LAB (Canada) and analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for major and trace elements, respectively.

## 2.3 Statistical analysis

First, descriptive statistics of element concentrations of aspen (*Populus tremula* L.) leaves were calculated within the scope of statistical studies. The element concentrations of leaves were tested with different methods, such as histogram, boxplots, Q-Q plot, Kolmogrow-Smirnov and Shapiro-Wilk Test. The Pearson correlation coefficient and Spearman correlation coefficients were calculated to determine the relationships between the elements in the leaves. Pearson correlation coefficients were used to determine the relations of normally distributed elements with each other, while Spearman correlation coefficients were used to determine the relations of non-normally distributed elements with each other.

# 3. Results

**Table 1** and **Figure 1** show the descriptive statistics parameters of the elements. Major elements concentrations of Ca, Mg, Na, K, Al, P and S (in %) range from 2 to 3, 0.23 to 0.8, up to 0.02, 0.79 to 2.01, 0.01 to 0.03, 0.15 to 0.30 and 0.1 to 0.43, respectively. Trace element concentrations (Mn, Sr, La, Ba, Ti, B and Se (in ppm)) are between from 127 to 339, 86.7 to 265.30, 0.1 to 1.21, 13.5 to 453.20, 6.0 to 12.0, 14.0 to 82.0 and 0.1 to 0.60, respectively.

The element concentrations in aspen (*Populus tremula* L.) leaves, considering their maximums, the minimums, and the averages, are ordered from largest to smallest as Ca > K > Mg > S > P > Ba > Al > Na > B > Ti > La > Se. (**Table 1**, **Figure 2**). The most abundant element in leaves is Ca, while the smallest concentrations are Se.

To determine the realistic average values of element concentrations in leaves, whether the element concentrations in the leaves show normal or logarithmic distribution were tested with histogram, boxplots, Kolmogorov-Smirnov and Shapiro-Wilk Test. According to most of the results of these methods, it was decided whether the data showed normal distribution or not. However, Boxplot and histogram graphs are not given in the study, only Kolmogorov-Smirnov and Shapiro-Wilk Test results are given (**Table 2**). Considering the results, it was found that K, S, Fe, P, Mn, and Sr elements showed normal/near-normal distribution and the others did not show normal distribution. Thus, the mean element contents in the leaves can be used as

**Table 1.** Descriptive statistics of element concentrations in aspen (*Populus tremula* L.) leaves from antimony mineralization area (Ca, Mg, K, Na, Al, S and P in %, others in ppm)

| | N | Minimum | Maximum | Mean | Std. deviation |
|---|---|---|---|---|---|
| Mn | 56 | 127.000 | 339.000 | 200.000 | 37.989 |
| Fe | 56 | 0.024 | 0.047 | 0.034 | 0.005 |
| Sr | 56 | 86.700 | 265.300 | 139.080 | 35.655 |
| Cd | 56 | 0.510 | 4310 | 0.975 | 0.649 |
| Ca | 56 | 2.000 | 39.00 | 2.584 | 0.412 |
| P | 56 | 0.148 | 0.299 | 0.220 | 0.038 |
| La | 56 | 0.100 | 1,210 | 0.309 | 0.230 |
| Mg | 56 | 0.231 | 0.846 | 0.391 | 0.120 |
| Ba | 56 | 13.500 | 453.200 | 57.954 | 85.154 |
| Ti | 56 | 6.000 | 12.000 | 8018 | 1471 |
| B | 56 | 14.000 | 82.000 | 35.696 | 14.831 |
| Al | 52 | 0.010 | 0.030 | 0.013 | 0.005 |
| Na | 56 | 0.001 | 0.023 | 0.004 | 0.003 |
| K | 56 | 0.790 | 2.010 | 1.311 | 0.322 |
| S | 56 | 0.130 | 0.430 | 0.285 | 0.066 |
| Se | 56 | 0.100 | 0.600 | 0.316 | 0.112 |

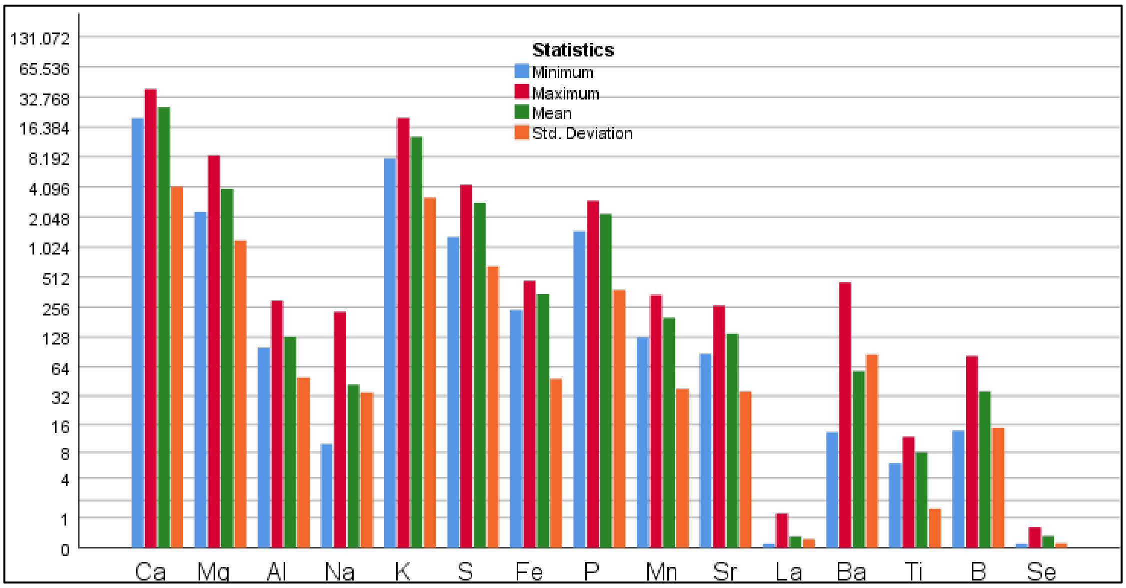


**Figure 2.** Bar diagram of elements concentrations in aspen (*Populus tremula* L.) leaves (all elements in ppm).

**Table 2.** The tests of normality of element concentrations in aspen (*Populus tremula* L.) leaves (areas highlighted in yellow show normally distributed elements)

| | **Kolmogorov-Smirnov[a]** | | | **Shapiro-Wilk** | | |
|---|---|---|---|---|---|---|
| | **Statistic** | **df** | **Sig.** | **Statistic** | **df** | **Sig.** |
| Ca_ppm | 0.221 | 56 | 0.000 | 0.831 | 56 | 0.000 |
| Mg_ppm | 0.126 | 56 | 0.027 | 0.894 | 56 | 0.000 |
| Al_ppm | 0.449 | 52 | 0.000 | 0.587 | 52 | 0.000 |
| Na_ppm | 0.272 | 56 | 0.000 | 0.578 | 56 | 0.000 |
| K_ppm | 0.075 | 56 | 0.200* | 0.967 | 56 | 0.134 |
| S_ppm | 0.084 | 56 | 0.200* | 0.981 | 56 | 0.508 |
| Fe_ppm | 0.101 | 56 | 0.200* | 0.973 | 56 | 0.248 |
| P_ppm | 0.084 | 56 | 0.200* | 0.974 | 56 | 0.268 |
| Mn | 0.085 | 56 | 0.200* | 0.955 | 56 | 0.034 |
| Sr | 0.087 | 56 | 0.200* | 0.909 | 56 | 0.000 |
| La | 0.247 | 56 | 0.000 | 0.755 | 56 | 0.000 |
| Ba | 0.367 | 56 | 0.000 | 0.474 | 56 | 0.000 |
| Ti | 0.219 | 56 | 0.000 | 0.909 | 56 | 0.000 |
| B | 0.117 | 56 | 0.055 | 0.916 | 56 | 0.001 |
| Se | 0.188 | 56 | 0.000 | 0.896 | 56 | 0.000 |

*. This is a lower bound of the true significance.
a. Lilliefors Significance Correction.

arithmetic mean for normal distributed elements and geometric mean/median/harmonic mean values for others (**Table 3**). When the average element concentrations of aspen leaves are considered, the concentrations of B, Mn, Sr, La are remarkable. Boron was detected below 10 ppm in most plants and up to 15 ppm in very few plants[70]. In aspen leaves, it is in the range of 33–36 ppm. Mn was also found above the average in most plants[70]. Sr has also been reported at values below 100 ppm in plants, except alfalfa and clover[70]. It is reported that aspen (*Populus tremula* L.*)* leaves are a good bioaccumulator for rare earth elements (La-Lu series). This study confirms it, at least for La. When the element contents of aspen leaves compared to other plants under similar conditions were compared, it was observed that aspen tree leaves showed higher element accumulation ability than many other plants. Likewise, it is understood that the aspen, which is grown in altered/mineralized areas, has a higher rate of element accumulation ability than the aspen grown in unaltered areas where there is no mineralization development[71].

When the relations between the elements are examined by taking into account the Pearson and Spearman correlation coefficients, it was determined that positive correlation between Ca and Sr, La, Ba elements; a positive correlation between Mg and S (0.59), P (0.52), La (0.47, weak), Ba (0.58); a positive correlation between Al and Na (0.45, weak), Ti (0.65); a positive correlation between S and Mg (0.64), Na (0.54), P (0.69), and B (0.59); a positive correlation between Sr and Ca (0.60), Mn (0.48, weak), La (0.47, weak) and a negative correlation between Sr and K (−0.50); a positive correlation between La and Sr (0.64, according to Pearson correlation coefficient), Ba (0.69); positive correlation between Ba and Ca (0.58), Mg (0.48, weak), Na (0.51); positive correlation between Ti and Al (0.65), P (0.53), Ba (0.53); a positive correlation between B and S (0.59), P (0.60), Ba (0.53) (**Table 4**). It indicates that elements with positive correlation of more than 0.5 with each other exhibit similar behavior patterns for the environment and tree in question. It indicates that elements with negative correlations below −0.5 exhibit opposite behavior patterns for the environment and tree in question.

**Table 3.** Mean, median, harmonic mean and geometric mean of element concentrations in leaves of aspen (*Populus tremula* L.) (areas highlighted in yellow indicate accepted averages of the elements)

| | Mean | Median | Harmonic mean | Geometric mean |
|---|---|---|---|---|
| Ca_ppm | 25,839.29 | 25,000.00 | 25,307.19 | 25,556.78 |
| Mg_ppm | 3,905.36 | 3,775.00 | 3,609.47 | 3,748.57 |
| Al_ppm | 128.85 | 100.00 | 115.99 | 121.46 |
| Na_ppm | 41.96 | 35.00 | 30.50 | 35.4 |
| K_ppm | 13,108.93 | 13,300.00 | 12,317.72 | 12,713.54 |
| S_ppm | 2,851.79 | 2,800.00 | 2,674.67 | 2,768.87 |
| Fe_ppm | 344.29 | 340.00 | 337.55 | 340.94 |
| P_ppm | 2,197.68 | 2,195.00 | 2,132.88 | 2,165.27 |
| Mn | 200.00 | 198.50 | 193.36 | 196.63 |
| Sr | 139.08 | 137.35 | 131.20 | 135.00 |
| La | 0.309 | 0.23 | 0.22 | 0.25 |
| Ba | 57.954 | 30.50 | 30.73 | 37.39 |
| Ti | 8.018 | 8.00 | 7.77 | 7.89 |
| B | 35.70 | 33.00 | 30.58 | 33.00 |
| Se | 0.32 | 0.30 | 0.28 | 0.30 |

**Table 4.** Pearson (yellow area) and Spearman (green area) correlation coefficients of element in leaves of aspen (*Populus Tremula* L.)

| | Ca | Mg | Al_ | Na | K | S | P | Mn | Sr | La | Ba | Ti | B | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca | **1.00** | 0.55** | 0.16 | 0.21 | –0.08 | 0.35** | 0.27* | 0.23 | 0.73** | 0.47** | 0.58** | 0.35** | 0.32* | 0.34* |
| Mg | 0.54** | **1.00** | 0.11 | 0.45** | 0.09 | 0.59** | 0.52** | –0.24 | 0.16 | 0.48** | 0.58** | 0.32* | 0.47** | 0.38** |
| Al | 0.23 | –0.02 | **1.00** | 0.45** | –0.12 | 0.26 | 0.30* | 0.00 | 0.20 | 0.21 | 0.31* | 0.65** | 0.10 | 0.14 |
| Na | 0.33* | 0.68** | 0.34* | **1.00** | 0.03 | 0.36** | 0.39** | –0.25 | 0.07 | 0.42** | 0.51** | 0.40** | 0.32* | 0.07 |
| K_ | –0.15 | 0.28* | –0.16 | 0.43** | **1.00** | 0.34* | 0.39** | –0.44** | –0.42** | –0.44** | –0.21 | –0.19 | 0.06 | 0.00 |
| S | 0.35** | 0.64** | 0.15 | 0.54** | 0.40** | **1.00** | 0.69** | –0.21 | –0.16 | 0.15 | 0.41** | 0.40** | 0.59** | 0.29* |
| P | 0.19 | 0.52** | 0.30* | 0.53** | 0.40** | 0.66** | **1.00** | –.291* | –0.16 | 0.04 | 0.36** | 0.53** | 0.60** | 0.11 |
| Mn | 0.20 | –0.33* | –0.02 | –0.48** | –0.48** | –0.25 | –0.34* | **1.00** | 0.44** | 0.20 | –0.12 | 0.10 | –0.03 | –0.03 |
| Sr | 0.60** | –0.04 | 0.31* | –0.15 | –0.55** | –0.29* | –0.19 | 0.48** | **1.00** | 0.48** | 0.44** | 0.29* | –0.04 | 0.15 |
| La | 0.42** | 0.06 | 0.31* | –0.04 | –0.54** | –0.10 | –0.27* | 0.38** | 0.64** | **1.00** | 0.69** | 0.36** | 0.26 | 0.32* |
| Ba | 0.60** | 0.45** | .365** | 0.50** | 0.01 | 0.31* | 0.37** | –0.03 | 0.40** | 0.23 | **1.00** | 0.41** | 0.43** | 0.29* |
| Ti | 0.32* | 0.13 | 0.62** | 0.19 | –0.20 | 0.32* | 0.51** | 0.11 | 0.33* | 0.31* | 0.46** | **1.00** | 0.37** | 0.27* |
| B | 0.37** | 0.40** | 0.13 | 0.28* | 0.14 | 0.56** | 0.58** | –0.05 | –0.02 | –0.14 | 0.53** | 0.36** | **1.00** | 0.21 |
| Se | 0.26 | 0.31* | 0.15 | 0.11 | –0.01 | 0.32* | 0.13 | 0.00 | 0.00 | 0.25 | 0.26* | 0.29* | 0.25 | **1.00** |

## 4. Conclusions

Element contents of leaves of aspen tree grown on antimonite mineralization area were determined. It was observed that the elements in the leaf were ordered as Ca > K > Mg > S > P > Ba > Al > Na > B > Ti > La > Se. According to normality test, histogram and boxplot diagrams, it was found that K, S, Fe, P, Mn, Sr elements showed normal/near normal distribution and the others show non-normal distribution. Thus, the average element concentrations in the leaves calculated as arithmetic mean for normal distributed elements and geometric mean/median/harmonic mean values for others. So average of K, S, Fe, P, Mn and Sr are calculated as 13,109, 2,852, 344.28, 21,978 ppm, respectively. Average concentrations of Ca, Mg, Al, Na, La, Ba, Ti, B, Se are calculated as 25,000, 3,775, 100, 35.00, 0.23, 30.50, 8.00, 33.00, 0.30 ppm, respectively. It was determined that the average B, Mn, Sr and La concentrations of aspen leaves were significantly higher than their concentrations in other plants.

## Author contributions

Corresponding author contributed to the study conception and design. Material preparation, data collection and analysis were performed by Alaaddin Vural.

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## Data availability

Data (the concentrations of elements in the aspen (*Populus tremulus* L.) are available on request from the corresponding author.

## Declarations

This article does not contain any studies with human participants or animals performed by the author.

## Conflict of interest

The author declares no conflicts of interest.

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