# Investigation of elemental composition of *Dianthus leucophaeus* Sibth. var. *leucophaeus* from tungsten mining area

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**Abstract:** The accumulation of metals in both aquatic and terrestrial ecosystems poses a relevant environmental risk as a consequence of several contaminating human activities such as mining or melting. In this regard, heavy metal accumulation in environment constitutes a serious health problem for animals and humans via biomagnification processes in the trophic chain. Some metals and metalloids such as Zn, Cu, Fe, Mg and Mn are taken up by plant roots to different extents to maintain the essential biochemical and cellular processes. Others with unknown biological role can enter into plant tissues and damage normal processes, either passively or due to their similarity with essential ions. The aim of this study is to evaluate the behaviour of *D. leucophaeus* which spread on the abandoned W mining area of Uludağ Mount. Thus, elemental composition (W, Mo, Zn, Fe, Cu, Cd, Mn, Pb, Cr, Co, B, and Bi) of this plant species in order to understand the contribution of elemental composition of surviving capability of this plant. Elemental contents of different parts of plants were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) after acid digestion processes. Our results indicate that contents of many elements in soils of these species were increased depending on mining activities.

**Keywords**: *Dianthus leucophaeus*, tungsten, element, inductively coupled plasma-mass spectrometry.

## 1. Introduction

Many anthropogenic activities which caused the heavy metal contamination in soil, water and air, threat the natural ecosystems by different ways. According to Ernst (1990) heavy metal-rich sites such as abandoned mining areas have characteristic plant species. These species can tolerate the high concentrations of heavy metals in their environment and they have capability to survive in metal-enriched environments by accumulating or excluding toxic metals (Brooks *et al*. 1998). So, they can be regarded as the main tool of the novel remediation approach called phytoremediation and the geochemical exploration called phytomining (Maestri *et al*. 2010). The restoration of heavy metal-contaminated soils can performed by the technique of phytoextraction which uses the roots of plants to take up metals from soils and transfer them into the shoots (Ali *et al*., 2013). For this reason, phytoextraction is related to metal uptake by plant roots and accumulation in above ground parts of plants. The subgroup of accumulator species, hyperaccumulators, are often endemic to naturally mineralized soils and they accumulate high concentrations of metals in their foliage (Baker and Brooks, 1989). These plants have capability to accumulate heavy metals in their aboveground tissues, without developing any toxicity symptoms. The screening of plant species in regarding to determine the heavy metal accumulation is the crucial for the phytoremediation aspects. The aim of this study was to understand the variations in the elemental composition of *Dianthus leucophaeus* Sibth. & Sm. var. *leucophaeus* which naturally growing in soils around the abandoned tungsten mine work from Uludağ Mountain, Turkey. The contents of W, Mo, Zn, Fe, Cu, Cd, Mn, Pb, Cr, Co, B, and Bi in different parts (roots, leaves and flowers) of plants and surrounding soils were determined to evaluate the variation in elemental composition of species and to understand whether this species is useful for phytomonitoring and/or phytoremediation purposes for tungsten-contaminated soil or not.

## 2. Material and Method

### *2.1. Material*

The study was carried out around Etibank Wolfram Mine Work of Uludağ Mountain. *Dianthus leucophaeus* Sibth. & Sm. var. *leucophaeus* belonging to *Caryophyllaceae* family is endemic. Calyx widest in the lower part, lanceolate, apiculate or acuminate. Petals limbs pink, whitish above, entire or subentire. Bracteoles as in *D. pallens* or with green subulate patent apices (Davis 1982). Species is distributed on the Uludag mountain sides at the altitudes between 1500 and 2400 m. It's flowering specimens can be seen among the dwarf shrub (*Juniperus communis* and *Astragalus angustifolius*) and hard cushion (*Festuca punctoria* and *Acantholimon ulucinum*) communities on June and July (Güleryüz, 2000).

Figure 1. *Dianthus leucophaeus* (photo by G .Güleryüz)

*2.2. Method*

Two sampling sites were selected as unpolluted areas (Site I and II) and one sampling site was selected from waste removal pool (Site-III). W, Mo, Zn, Fe, Cu, Cd, Mn, Pb, Cr, Co, B, and Bi in the plant tissues (roots, leaves and flowers) and soil samples were determined by Elan 9000 inductively coupled plasma–mass spectrometry (ICP-MS) (PerkinElmer SCIEX, Shelton, CT, USA). The components of ICP-MS were outlined elsewhere (Güleryuz *et al*., 2016). Additionally, the optimum instrumental conditions were as follows: RF power: 1000 W; nebulizer gas flow rate: 0.85 L $min^{-1}$; sample uptake rate: 1.5 mL $min^{-1}$; scanning mode: peak hopping; and detector mode: dual. Open wet digestion using $HNO_3$ and $H_2O_2$ (3:1, *v/v*) was applied to the approximately 500 mg of leaf samples. Soil samples were digested according to method of Bednar *et al*. (2010). The differences among the sampling sites regarding the element contents of plants and soil samples were tested by one-way ANOVA.

## 3. Results and discussion

Tables 1 and 2 represent the mean elemental contents (W, Mo, Zn, Fe, Cu, Cd, Mn, Pb, Cr, Co, B, and Bi) of soil samples and the different organs of *D. leucophaeus* in respectively. There were significant differences among the sample sites regarding the soil elemental contents, except for the Pb, Co and B contents (P< 0.05). The mean W, Mo, Zn, Fe, Cu, Cd, Mn, and Bi contents in the soil taken from the waste removal pool were higher than those of the unpolluted sites (Table 1). High concentration of these elements were found that indicates the contamination in soils. Highest mean W content in soils of waste removal pool ( 2027.02 ± 90.10 mg/kg DW) (Table 1) was determined. In considering W limits in a non-polluted soil as 0.4 to 5.0 mg/kg DW (Kabata-Pendias and Mukherjee, 2007), this value points out the certain effects of mining activities on this area. Similarly, these activities were resulted in a contamination with regard to molybdenum, zinc, iron, copper, cadmium manganese and bismuth (Table 1). For example, Cu is one of the pollutants in the soils of waste removal pool. The mean Cu content in the soils of this site was higher than the upper Cu limit of a non-polluted soil (15 mg/kg) (Temmerman *et al*. 1984) reaching to 2415 ± 69 mg/kg DW. On the other hand, we found not found significant significant difference between sample sites in terms of soil Pb, Co and B contens (P>0.05) (Table 1). The results of study also suggest that tungsten-mining activity both affects the elemental composition of the soil and *D. leucophaeus* as well as other natural species growing on this area such as *Marrubium astracanicum* (Güleryüz *et al*., 2016), *Anthemis tinctoria* and *Trisetum flavescens* (Erdemir *et al*., in press). The increased contents of W, Zn, Fe, Cu, Cd, Mn, and Bi in soil from polluted site caused to increase in concentrations of these elements in the in *D. leucophaeus*. Considering the tungsten content which is reported for the plants growing in the unpolluted soil (<0.1 mg/kg DW; Rodushkin *et al*. 1999; Wilson and Pyatt 2009); the high W concentration in above ground parts (6.8 ± 1.16 mg/kg DW; Table 2) may indicate a tungsten accumulation in this plant. Also, Cd and Zn were accumulated in plant organs especially in above ground parts such as others. This data supports the results of studies indicating the Cd and Zn accumulation in *Dianthus chinensis* which is other species of this genus (Hung-Yu and Chen, 2005). Bismuth composition of *D. leucophaeus* is the most insteresting part of our results. Because bismuth is one of the elements that’s function is not known according to Kabata-Pendias (2001) and Wei *et al*. (2011). In these works, Bi contents in terrestrial vascular plants is mentioned less than 20 μg/kg. This level is too lower than the determined value in this species (7.06 ± 1.16 mg/kg DW) and the leaves seem to be the main bismuth accumulating parts (Table 2).

## 4. Conclusion

Consequently, it can be seen that elemental composition of soils has been changed due to tungsten mining activities and these changes reflected in accumulation of some examined elements of *D. leucophaeus* especially, tungsten and bismuth.

Table 1. Average acid soluble contents of elements in soil at different sides (non-polluted, Sites I and II) and within the waste-removal pool (polluted, Site III) of the abandoned tungsten mine work in Uludağ Mount, Bursa Turkey. [For mean element values, different letters indicate significant differences between the sampling sites according to Tukey’s HSD Test (rejection level 0.05). *n*=3, Means ± Standard Deviation]

| Element (mg/kg DW) | Sampling Sites | | |
|---|---|---|---|
| | I | II | III |
| W | $70^{b} \pm 18$ | $79^{b} \pm 1$ | $2027^{a} \pm 90$ |
| Mo | $2.6^{b} \pm 0.2$ | $2.2^{b} \pm 0.4$ | $8^{a} \pm 1$ |
| Zn | $273^{b} \pm 24$ | $216^{b} \pm 31$ | $3532^{a} \pm 799$ |
| Fe | $12176^{b} \pm 974$ | $11951^{b} \pm 1965$ | $379257^{a} \pm 96580$ |
| Cu | $66^{b} \pm 6$ | $79^{b} \pm 8$ | $2415^{a} \pm 69$ |
| Cd | $2.9^{b} \pm 0.2$ | $2.2^{b} \pm 0.3$ | $13^{a} \pm 4$ |

| | | | |
|---|---|---|---|
| Mn | $1213^{b} \pm 59$ | $925^{b} \pm 76$ | $5728^{a} \pm 954$ |
| Pb | $56^{a} \pm 4$ | $37^{a} \pm 8$ | $57^{a} \pm 12$ |
| Cr | $11^{a} \pm 1$ | $10^{a} \pm 1$ | $8^{b} \pm 1$ |
| Co | $3.4^{a} \pm 0.2$ | $3.4^{a} \pm 0.7$ | $2.4^{a} \pm 0.4$ |
| B | $26^{a} \pm 3$ | $23^{a} \pm 3$ | $28^{a} \pm 5$ |
| Bi | $11^{b} \pm 1$ | $10^{b} \pm 1$ | $548^{a} \pm 188$ |

Table 2. Mean values of heavy metals determined in organs and whole plant (mg/kg DW) of *Dianthus leucophaeus* collected from unpolluted sites (Site-I and II) and mine waste pool (Site III) around tungsten mine work [For mean element values, different letters indicate significant differences between the sampling sites according to Tukey's HSD Test (rejection level 0.05). *n*=3, Means ± Standard Deviation]

| **Element** | **Plant Organ** | **Site-I** | **Site-II** | **Site-III** |
|---|---|---|---|---|
| | Flowers | $0.7^{b} \pm 0.3$ | $0.7^{b} \pm 0.3$ | $1.4^{a} \pm 0.2$ |
| | Leaves | $0.3^{b} \pm 0.1$ | $0.05^{b} \pm 0.03$ | $5.5^{a} \pm 0.9$ |
| **W** | Aboveground Total | $1.0^{b} \pm 0.3$ | $0.8^{b} \pm 0.3$ | $6.9^{a} \pm 1.2$ |
| | Roots | $0.08^{b} \pm 0.02$ | $0.24^{b} \pm 0.11$ | $3.8^{a} \pm 1.0$ |
| | Total | $1.1^{b} \pm 0.3$ | $1.0^{b} \pm 0.3$ | $10.6^{a} \pm 2.1$ |
| | Flowers | $0.04^{b} \pm 0.02$ | $0.4^{a} \pm 0.1$ | $0.4^{a} \pm 0.1$ |
| | Leaves | $0.16^{b} \pm 0.02$ | $0.15^{b} \pm 0.04$ | $0.25^{a} \pm 0.02$ |
| **Mo** | Aboveground Total | $0.20^{b} \pm 0.02$ | $0.5^{a} \pm 0.1$ | $0.7^{a} \pm 0.1$ |
| | Roots | $0.20^{b} \pm 0.03$ | $0.06^{c} \pm 0.02$ | $1.7^{a} \pm 0.1$ |
| | Total | $0.4^{c} \pm 0.1$ | $0.6^{b} \pm 0.1$ | $2.4^{a} \pm 0.1$ |
| | Flowers | $22^{b} \pm 4$ | $27^{b} \pm 7$ | $73^{a} \pm 6$ |
| | Leaves | $20^{b} \pm 2$ | $35^{b} \pm 19$ | $156^{a} \pm 36$ |
| **Zn** | Aboveground Total | $42^{b} \pm 4$ | $62^{b} \pm 17$ | $229^{a} \pm 40$ |
| | Roots | $11^{b} \pm 1$ | $15^{b} \pm 4$ | $46^{a} \pm 9$ |
| | Total | $53^{b} \pm 3$ | $77^{b} \pm 18$ | $275^{a} \pm 38$ |
| | Flowers | $13^{ab} \pm 3$ | $9^{b} \pm 1$ | $15^{a} \pm 1$ |
| | Leaves | $11^{b} \pm 3$ | $12^{b} \pm 1$ | $25^{a} \pm 6$ |
| **Fe** | Aboveground Total | $24^{b} \pm 5$ | $21^{b} \pm 2$ | $39^{a} \pm 7$ |
| | Roots | $8^{b} \pm 1$ | $5^{b} \pm 1$ | $21^{a} \pm 3$ |
| | Total | $31^{b} \pm 6$ | $26^{b} \pm 3$ | $60^{a} \pm 7$ |

to be contiuned Table 2

| | | | | |
|---|---|---|---|---|
| | Flowers | $2.6^{b} \pm 0.7$ | $2.1^{b} \pm 0.7$ | $5.1^{a} \pm 0.3$ |
| | Leaves | $2.2^{b} \pm 0.6$ | $3.1^{b} \pm 0.8$ | $7.6^{a} \pm 1.2$ |
| **Cu** | Aboveground Total | $4.8^{b} \pm 1.3$ | $5.2^{b} \pm 1.4$ | $12.7^{a} \pm 0.9$ |
| | Roots | $3.5^{b} \pm 1.2$ | $2.4^{b} \pm 0.7$ | $10.4^{a} \pm 1.3$ |
| | Total | $8.3^{b} \pm 1.1$ | $7.6^{b} \pm 2.1$ | $23.1^{a} \pm 0.7$ |
| | Flowers | $0.24^{b} \pm 0.06$ | $0.25^{b} \pm 0.05$ | $0.9^{a} \pm 0.2$ |
| | Leaves | $0.5^{b} \pm 0.2$ | $0.7^{b} \pm 0.1$ | $1.4^{a} \pm 0.5$ |
| **Cd** | Aboveground Total | $0.7^{b} \pm 0.2$ | $0.9^{b} \pm 0.2$ | $2.3^{a} \pm 0.7$ |
| | Roots | $0.5^{b} \pm 0.1$ | $0.5^{b} \pm 0.1$ | $1.3^{a} \pm 0.2$ |
| | Total | $1.2^{b} \pm 0.2$ | $1.4^{b} \pm 0.2$ | $3.6^{a} \pm 0.8$ |
| | Flowers | $655^{a} \pm 255$ | $427^{a} \pm 61$ | $678^{a} \pm 159$ |
| | Leaves | $730^{b} \pm 124$ | $686^{b} \pm 51$ | $1675^{a} \pm 208$ |
| **Mn** | Aboveground Total | $1385^{b} \pm 375$ | $1113^{b} \pm 55$ | $2353^{a} \pm 365$ |
| | Roots | $346^{a} \pm 78$ | $173^{b} \pm 56$ | $372^{a} \pm 61$ |
| | Total | $1731^{b} \pm 448$ | $1287^{b} \pm 26$ | $2725^{a} \pm 309$ |
| | Flowers | $1.7^{b} \pm 0.9$ | $0.9^{b} \pm 0.1$ | $2.0^{a} \pm 0.4$ |
| | Leaves | $0.5^{b} \pm 0.1$ | $0.7^{b} \pm 0.1$ | $1.7^{a} \pm 0.2$ |
| **Pb** | Aboveground Total | $2.3^{ab} \pm 1.1$ | $1.6^{b} \pm 0.2$ | $3.7^{a} \pm 0.2$ |
| | Roots | $1.1^{a} \pm 0.3$ | $0.7^{b} \pm 0.1$ | $1.8^{a} \pm 0.2$ |
| | Total | $4.3^{a} \pm 0.8$ | $2.4^{b} \pm 0.3$ | $5.5^{a} \pm 0.4$ |
| | Flowers | $0.8^{a} \pm 0.2$ | $0.6^{a} \pm 0.3$ | $0.7^{b} \pm 0.1$ |
| | Leaves | $0.7^{b} \pm 0.1$ | $0.8^{b} \pm 0.2$ | $1.0^{a} \pm 0.1$ |
| **Cr** | Aboveground Total | $1.5^{a} \pm 0.2$ | $1.4^{a} \pm 0.2$ | $1.7^{a} \pm 0.1$ |
| | Roots | $0.8^{a} \pm 0.2$ | $1.1^{a} \pm 0.1$ | $0.9^{a} \pm 0.3$ |
| | Total | $2.3^{a} \pm 0.4$ | $2.5^{a} \pm 0.2$ | $2.6^{a} \pm 0.4$ |
| **Co** | Flowers | $0.13^{a} \pm 0.03$ | $0.5^{a} \pm 0.1$ | $0.19^{a} \pm 0.05$ |
| | Leaves | $0.21^{a} \pm 0.01$ | $0.14^{ab} \pm 0.03$ | $0.05^{b} \pm 0.01$ |

| | | | | |
|---|---|---|---|---|
| | Aboveground Total | $0.3^{a} \pm 0.1$ | $0.3^{a} \pm 0.1$ | $0.24^{a} \pm 0.06$ |
| | Roots | $0.17^{a} \pm 0.02$ | $0.09^{b} \pm 0.02$ | $0.04^{c} \pm 0.01$ |
| | Total | $0.5^{a} \pm 0.1$ | $0.4^{ab} \pm 0.1$ | $0.3^{b} \pm 0.1$ |
| **B** | Flowers | $14^{a} \pm 2$ | $7^{b} \pm 1$ | $10^{ab} \pm 1$ |
| | Leaves | $18^{a} \pm 2$ | $19^{a} \pm 3$ | $14^{a} \pm 2$ |
| | Aboveground Total | $31^{a} \pm 7$ | $27^{a} \pm 4$ | $24^{a} \pm 4$ |
| | Roots | $17^{a} \pm 4$ | $11^{ab} \pm 2$ | $11^{a} \pm 1$ |
| | Total | $49^{a} \pm 12$ | $38^{a} \pm 6$ | $35^{a} \pm 4$ |
| **Bi** | Flowers | $0.16^{b} \pm 0.06$ | $0.10^{b} \pm 0.02$ | $0.7^{a} \pm 0.1$ |
| | Leaves | $0.05^{b} \pm 0.03$ | $0.07^{b} \pm 0.03$ | $3.6^{a} \pm 0.5$ |
| | Aboveground Total | $0.21^{b} \pm 0.09$ | $0.17^{b} \pm 0.02$ | $4.3^{a} \pm 0.6$ |
| | Roots | $0.15^{b} \pm 0.03$ | $0.05^{b} \pm 0.03$ | $2.8^{a} \pm 0.2$ |
| | Total | $0.4^{b} \pm 0.1$ | $0.22^{b} \pm 0.03$ | $7.0^{a} \pm 0.6$ |

**References**


Ali H., Khan E. and Sajad M.A. (2013), Phytoremediation of heavy metals-concepts and applications, *Chemosphere*, **91**, 869-881.

Baker A.J.M. and Brooks R.R. (1989), Terrestrial higher plants which hyperaccumulate heavy elements: a review of their distribution, ecology and phytochemistry, *Biorecovery*, **1**, 81-126.

Bednar A.J., Jones W.T., Chappell M.A., Johnson D.R., and Ringelberg D.B. (2010), A modified acid digestion procedure for extraction of tungsten from soil, *Talanta*, **80**,1257–1263.

Brooks R.R, Chiarucci A. and Jaffre T. (1998), Revegetation and stabilisation of mine dumps and degraded terrain. In *Plants that hyperaccumulate heavy metals. Their role in phytoremeditation, microbiology, archeology, mineral exploration and phytomining*, edited by R.R. Brooks. CAB International, Wallingford.

Davis P.H. (1982*), Flora of Turkey and the East Aegean Islands*. Vol: 9. Edinburg University Press, Edinburg.

Erdemir U.S., Arslan H., Güleryüz G. and Güçer Ş. Elemental Composition of Plant Species from an Abandoned Tungsten Mining Area: Are They Useful for Biogeochemical Exploration and/or Phytoremediation Purposes?, *Bulletin of Environmental Contamination and Toxicology*, in press.

Ernst W.H.O. (1990), Mine vegetation in Europe. In *Heavy Metal Tolerance in Plants*: Evolutionary Aspects, edited by A.J. Shaw. CRC Press, Boca Raton, Florida.

Güleryüz G. (2000). Alpine flowers of Uludağ. Governorship of Bursa Provincial Directorate of Tourism. Dönence Basım ve Yayın Hizmetleri, İstanbul, Turkey.

Güleryüz G., Erdemir U.S., Arslan H. and Güçer Ş. (2016), Elemental composition of *Marrubium astracanicum* Jacq. growing in tungsten-contaminated sites, *Environmental Science and Pollution Research*, **23**, 18332-18342.

Hung-Yu L. and Chen Z.S. (2005), Phytoextraction of rainbow pink (*Dianthus chinensis*) growing in cadmium, lead, zinc contaminated soil of Taiwan, Proceeedings of the 9th International Conference on Environmental Science and Technology. Rhodes Island, Greece, 1-3 September 2005, A860-A864.

Kabata-Pendias A.P.H. (2001), Trace elements in soils and plants. CRC Press, Boca Raton, pp 177-178.

Kabata-Pendias A. and Mukherjee A.B. (2007), *Trace Elements from Soil to Human*, Springer, Berlin.

Maestri E., Marmiroli M., Visioli G. and Marmiroli N. (2010), Metal tolerance and hyperaccumulation: costs and trade-offs between traits and environment, *Environmental and Experimental Botany*, **68**,1-13.

Rodushkin I., Ödman F. and Holmström H. (1999), Multi-element analysis of wild berries from northern Sweden by ICP techniques, *Science of the Total Environment*, **231**,53-65.

Temmerman L.O., Hoening M. and Scokart P. O. (1984). Determination of normal levels and upper limit values of trace elements in soils. *Zeitschrift für Pflanzenernährung und Bodenkunde*, **147,** 687-699.

Wei C., Deng Q., Wu F., Fu Z. and Xu L. (2011), Arsenic, Antimony, and Bismuth Uptake and Accumulation by Plants in an Old Antimony Mine, China, *Biological Trace Element Research*, **144**,1150-1158.

Wilson B. and Pyatt F.B. (2009), Bioavailability of tungsten and associated metals in calcareous soils in the vicinity of an ancient metalliferous mine in the Corbières Area, southwestern France, *Journal of Toxicology and Environmental Health A*, **72**, 807-816.