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Determination of some trace elements in various lichens as biomonitors of pollution and assessment of pollution status

Kirliliğin biyomonitörleri olarak çeşitli likenlerdeki bazı eser elementlerin belirlenmesi ve kirlilik durumunun değerlendirilmesi

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Abstract

Some trace elements in various lichens as biomonitors of pollution were investigated. Also, the pollution status was assessed by enrichment factor, contamination factor, and pollution load index. Investigated elements were Ta, Bi, Hf, Nb, Ga, Sc, Li, Y, Ce, and Sr. The lichen species were *Rhizoplaca chrysoleuca*, *Umbilicaria vellea*, *Aspicilia calcarea*, *Pseudevernia furfuracea*, and *Cetraria islandica*. According to the results, lichen species accumulate Sr element well. The highest trace element accumulated by *Pseudevernia furfuracea* (21.7±1.0 mg/kg; 75%), *Rhizoplaca chrysoleuca* (31.9±1.6 mg/kg; 61%), *Umbilicaria vellea* (16.3±0.8 mg/kg; 59%), *Aspicilia calcarea* (77.9±3.8 mg/kg; 88%), and *Cetraria islandica* (22.7±1.1 mg/kg; 75%) was determined as Sr. The highest CFs in lichens investigated were calculated for Sr, Ta, and Li. PLI values for *Cetraria islandica*, *Aspicilia calcarea*, and *Umbilicaria vellea* were greater than 1. As a result, it has been proven that these lichen species can be used as good biomonitors of pollution.

Keywords: Accumulation, biomonitor, lichen, pollution

Öz

Çeşitli likenlerde kirliliğin biyomonitörleri olarak bazı eser elementler incelenmiştir. Ayrıca, kirlilik durumu zenginleştirme faktörü, kirlilik faktörü ve kirlilik yükleme indeksi ile değerlendirildi. Araştırılan elementler Ta, Bi, Hf, Nb, Ga, Sc, Li, Y, Ce ve Sr'dur. Liken türleri *Rhizoplaca chrysoleuca*, *Umbilicaria vellea*, *Aspicilia calcarea*, *Pseudevernia furfuracea* ve *Cetraria Islandica*'dır. Elde edilen sonuçlara göre liken türleri Sr elementini iyi akümüle ettiği belirlendi. *Pseudevernia furfuracea* (21,7±1,0 mg/kg; %75), *Rhizoplaca chrysoleuca* (31,9±1,6 mg/kg; %61), *Umbilicaria vellea* (16,3±0,8 mg/kg; %59), *Aspicilia calcarean* (77,9±3,8 mg/kg; 88%) ve *Cetraria islandica* (22,7±1,1 mg/kg; 75%) tarafından akümüle edilen en yüksek eser element Sr olarak belirlendi. İncelenen likenlerde en yüksek CF'ler Sr, Ta ve Li için hesaplanmıştır. *Cetraria islandica*, *Aspicilia calcarea* ve *Umbilicaria vellea* için PLI değerleri 1'den büyüktü. Sonuç olarak, bu liken türlerinin kirlilik için iyi bir biyomonitör olarak kullanılabileceği kanıtlanmıştır.

Anahtar kelimeler: Akümülasyon, biyomonitör, liken, kirlilik

1 Introduction

Some elements are globally important and have various usage areas. The demand for metals is increasing and the primary metallic resources are simultaneously running out. This is one of the important social and environmental challenges today. As a result of the increasing demand for critical metals, many metals are at the edge of supply risk. Also, the problems resulting from waste generation are increasing globally [1]. The consumption of raw materials required to produce technological goods causes the release of pollutants into the environment [2].

The globally used elements investigated in this study are described as follows. Bismuth (Bi) has been used medicinally for centuries [3]. It is required in various sectors (e.g. energy storage, and electrochemical sensing, forming liquid alloys) [4]. There is increased use of Bi in the manufacturing of various materials [3]. Cerium finds applications in different fields (e.g. alloys, catalysts, and light-emitting diodes) [5]. Gallium (Ga) increases the solubility of rare earth elements in chalcogenide glasses [6]. Ga and its compounds of it lead to human health problems [7]. Scandium is required in various applications (e.g. electronic, and automotive industries). Therefore, scandium demand grows [8, 9]. Scandium-reinforced alloys are used in military weapons [9]. Yttrium is utilized in various fields (e.g. metallurgical industries, astronavigation, ceramics, and fields) [10-12]. It has adverse health effects. Because, it causes diseases of the lung and liver [12, 13]. Hafnium (Hf) is important to produce highly resistant materials. Dust that contains Hf is toxic via dietary and respiratory [14]. Niobium (Nb) and tantalum (Ta) are refractory metals having unchallenged technological importance for modern society. They have growing importance as strategic metals because of the intrinsic properties of them [15]. Lithium (Li) has electrochemical activity and high redox potential [16, 17].

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Nonradioactive strontium (Sr) accounts for 0.02–0.03% of the Earth's crust [18]. It and its derivates of it are required in various applications (e.g. fireworks, ceramics, medicines, and electronics) [19-21].

As reported by WHO [22], atmospheric pollution is a major source of pollution exposure to humans [22, 23]. International Agency for Research on Cancer classifies outdoor air pollution as carcinogenic to humans [22-24]. The development of methods using various living (e.g. lichens, algae, and plants) as biomonitors result in high interest because of their easy of operation, rapidity, and inexpensiveness [25]. The lichens are among the oldest colonist on the earth particularly terrestrial habitats, with records dating back to about 400–600 million years ago [26-28]. The lichens are required as biomonitors of airborne trace elements. They are undoubtedly the most versatile biomonitors [29, 30]. Contrary to vascular plants, they lack roots, waxy, multi-layered cuticles, and stomata, relying on dry and wet atmospheric deposition for the uptake of nutrients and water [30-34]. Lichens are capable of accumulating atmospheric metals over time [23]. Therefore, the elemental content of lichens has been frequently used as a dependable representative of air pollution [30, 35, 36].

This study focuses on the accumulation of trace elements (Ta, Bi, Hf, Nb, Ga, Sc, Li, Y, Ce, and Sr) in different lichen species (*Pseudevernia furfuracea*, *Cetraria islandica*, Rhizoplaca chrysoleuca, *Aspicilia calcerea*, and *Umbilicaria vellea*). There are very few studies on the composition of some of that trace elements in lichens. Carreras et al. [37] reported Sr concentration in the lichen U. amblyoclada. Bubach et al. [38] reported Cs, Hf, Sr, Sc, and Ta concentrations in Usnea sp. Koroleva and Revunkov [39] reported Sr concentration in epiphytic lichen Hypogymnia physodes. Landis et al. [40] reported that Bi, Ce, Li, Nb and Ta concentrations in H. physodes. Parviainen et al. [23] reported Sr concentration in Xanthoria parietina. The following points are aimed in our study; (i) determination of the accumulation amounts and percentages of the trace elements in lichen species (ii) assessment of the element pollution by calculating enrichment factors, contamination factors, and pollution load indexes (iii) determination of whether that lichens are biomonitors of pollution. In this context, this study is quite new, original, and a study that will make a sound in the literature.

2 Material and methods

Pseudevernia furfuracea, *Cetraria islandica*, *Rhizoplaca chrysoleuca*, *Aspicilia calcerea*, and *Umbilicaria vellea* lichens investigated were collected from Oltu-İnci village (Erzurum, Turkey). The lattitude and longitude of the study area are as follows: Lattitude: 40º35'30", Longitude: 41º50'00". There was not any agricultural and industrial activities etc. at the study region. These lichens were selected because of their common dispersion in that area. Identification of lichen species is done by Prof. Dr. Ali Aslan. The collected lichens are dried at 25ºC at room temperature and powdered by a grinder. Analysis procedure for lichens are as following: samples are cold-leached with HNO_3. After cooling a modified Aqua Regia solution of equal parts concentrated HCl, HNO_3 and DI H_2O are added to samples for leaching in heating block of hot water bath. Samples are made up to volume with dilute HCl before filtration. Lichens are analyzed by ICP/MS (ICP/MS-Perkin-Elmer ELAN 9000) for evaluation of trace elements (Hf, Ta, Nb, Li, Sr, Bi, Y, Sc, Ce, and Ga). Terrigenous or anthropogenic origin of elements in samples were evaluated by the calculated enrichment factor (EF) [23]. Enrichment factors for different lichen species were calculated by:

$$EF = \frac{[E_{lichen}/Al_{lichen}]}{[E_{crust}/Al_{crust}]} \quad (1)$$

where EF: enrichment factor, Elichen: element value in lichen (mg/kg), Allichen: Al value in lichen (mg/kg), Ecrust: element value in the Earth's crust (mg/kg) Alcrust: Al value in the Earth's crust (mg/kg).

Degree of contamination in Erzurum (Oltu, İnci, Turkey) region were evaluated by the calculated contamination factor (CF) [39]. Contamination factors were calculated by:

$$CF = C_i/C_b \quad (2)$$

where CF: contamination factor, Ci: element value in lichen (mg/kg), Cb: element value in control area (mg/kg). In this study, eastern Alps and northern Apennines were chosen as control [41] (for all elements, except elements Ta and Ga which do not exist in their study). Ta and Ga values were taken from Markert [42].

Pollution load index (PLI) indicating how much the sample exceeds metal concentrations of natural environments and also giving indication of overall toxicity status for the sample is defined as the nth root of multiplication of CFs [43]. PLI was calculated by:

$$PLI = (CF_1 x CF_2 x CF_3 x \ldots\ldots\ldots\ldots x CF_n)^{1/n} \quad (3)$$

where, CF_1 is the CF of the first element, CF_2 is the CF of the second element value, CF_3 is the CF of the third element value, CF_n is the CF of the nth element in the lichens species.

3 Results and discussion

Trace elements accumulated by *Pseudevernia furfuracea* are given in Figure 1.

According to Figure 1, the highest element concentration was 21.7±1.0 mg/kg for Sr (Figure 1(a)). In the literature, Parviainen et al. [23] reported Sr concentrations between 5.6 and 377 mg/kg in lichen Xanthoria parietina from Spain. Bubach et al. [38] reported Sr concentrations in lichen Usnea sp. between 29.05 and 50.8 mg/kg. The lowest element concentration was 0.008±0.002 mg/kg for Ta in our study. The Bi, Hf, Nb, Ga, Sc, Li, Y, and Ce concentrations in *Pseudevernia furfuracea* were 0.02±0.01, 0.044±0.002, 0.16±0.008, 0.5±0.02, 0.9±0.04, 1.15±0.05, 1.158±0.06, and 3.2±0.16 mg/kg, respectively (Figure 1(a)). The trace elements in *Pseudevernia furfuracea* were Ta<Bi<Hf<Nb<Ga<Sc<Li<Y<Ce<Sr. Considering these

values, it can be said that the best accumulation by *Pseudevernia furfuracea* is for Sr. The distribution percentages of the trace elements accumulated by *Pseudevernia furfuracea* are given in Figure 1(b). According to Figure 1(b), the highest element value was 75% for Sr, while the lowest element value was 0.027% for Ta. Also, Bi and Hf values in *Pseudevernia furfuracea* were below 1%. Ce, Y, Li, Sc, Ga, and Nb values were 11%, 4%, 4%, 3%, 2%, and 1%, respectively.

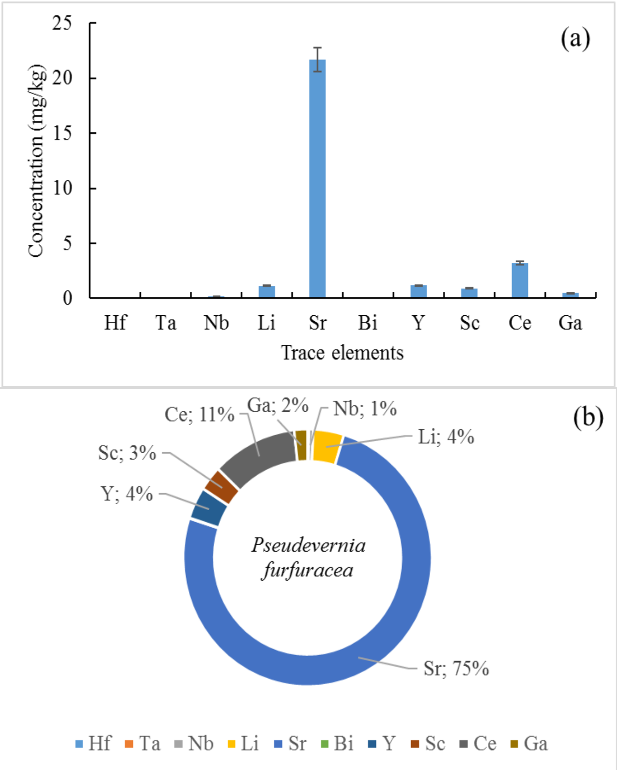

Figure 1. Trace elements accumulated by *P.furfuracea*

Trace elements accumulated by *Cetraria islandica* are given in Figure 2.

Maximum element concentration was 22.7±±1.1 mg/kg for Sr, while minimum element concentration was 0.008±0.002 mg/kg for Ta (Figure 2). Bi, Hf, Nb, Ga, Sc, Y, Li, and Ce concentrations in *Cetraria islandica* were 0.02±0.01, 0.043±0.002, 0.16±0.008, 0.4±0.02, 0.8±0.04, 1.183±0.05, 1.65±0.08, and 3.5±0.17 mg/kg respectively. Different concentrations were reported in the literature. Landis et al. [40] reported that Bi concentrations in lichen H. physodes between 0.002 and 0.149 µg/g while Ce concentrations were between 0.803 and 16.815 µg/g. Bubach et al. [38] reported Sc concentrations in lichen Usnea sp. between 0.18 and 1.75 mg/kg.

The trace elements in *Cetraria islandica* were Ta<Bi<Hf<Nb<Ga<Sc<Y<Li<Ce<Sr. Given these values, similar to *Pseudevernia furfuracea*, it can be said that the best accumulation by *Cetraria islandica* is for Sr. The distribution percentages of the trace elements accumulated by *Cetraria islandica* are shown in Figure 2(b). According to Figure 2(b), the highest element value was 75% for Sr, while the lowest element value 0.027% for Ta. Also, Bi and Hf values in *Cetraria islandica* were below 1%. Ce, Li, Y, Sc, Ga, and Nb values were 11%, 5%, 4%, 3%, 1%, and 1%, respectively.

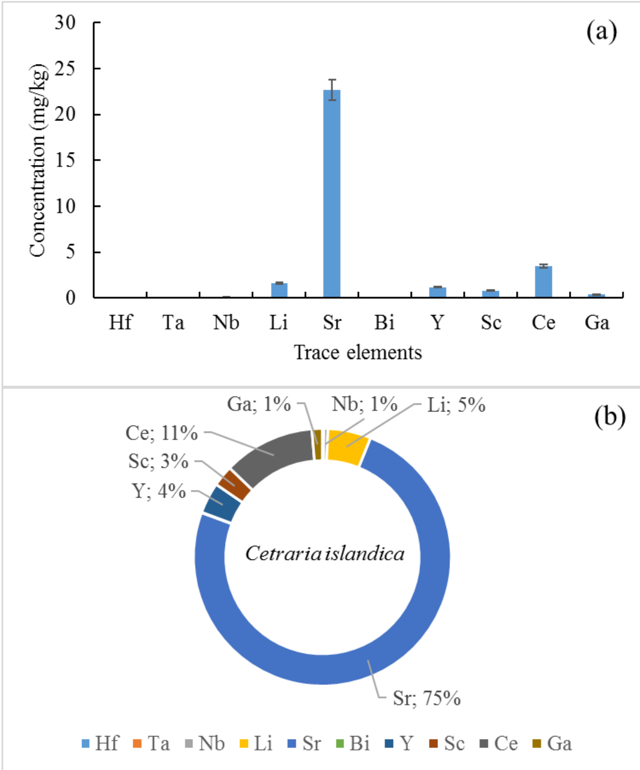

Figure 2. Trace elements accumulated by *C. islandica*

The trace elements accumulated by *Rhizoplaca chrysoleuca* are given in Figure 3.

According to Figure 3(a), the highest element concentration was 31.9±1.6 mg/kg for Sr, while minimum element concentration was 0.008±0.002 mg/kg for Ta. Landis et al. [40] reported Ta concentrations in lichen H. physodes between 0.004±0.001 and 0.099 µg/g. Bubach et al. [38] reported Ta concentrations in lichen Usnea sp. between 0.0051 and 0.14 mg/kg. In our study, Bi, Hf, Nb, Ga, Sc, Li, Y, and Ce concentrations in *Rhizoplaca chrysoleuca* were 0.03±0.01, 0.193±0.01, 0.49±0.02, 1.1±0.05, 1.3±0.06, 2.07±0.1, 4.489±0.22, and 11.1±0.5 mg/kg respectively. The trace elements in *Rhizoplaca chrysoleuca* were Ta<Bi<Hf<Nb<Ga<Sc<Li<Y<Ce<Sr. Given these values, similar to *Cetraria islandica* and *Pseudevernia furfuracea*, it can be said that the best accumulation by *Rhizoplaca chrysoleuca* is for Sr. The distribution percentages of the trace elements accumulated by *Rhizoplaca chrysoleuca* are given in Figure 3(b). According to Figure 3(b), the highest element value was 61% for Sr, while the lowest element value was 0.027% for Ta. Also, Bi and Hf values in *Rhizoplaca chrysoleuca* were below 1%. Ce, Y, Li, Sc, Ga, and Nb values were 21%, 9%, 4%, 2%, 2%, and 1%, respectively.

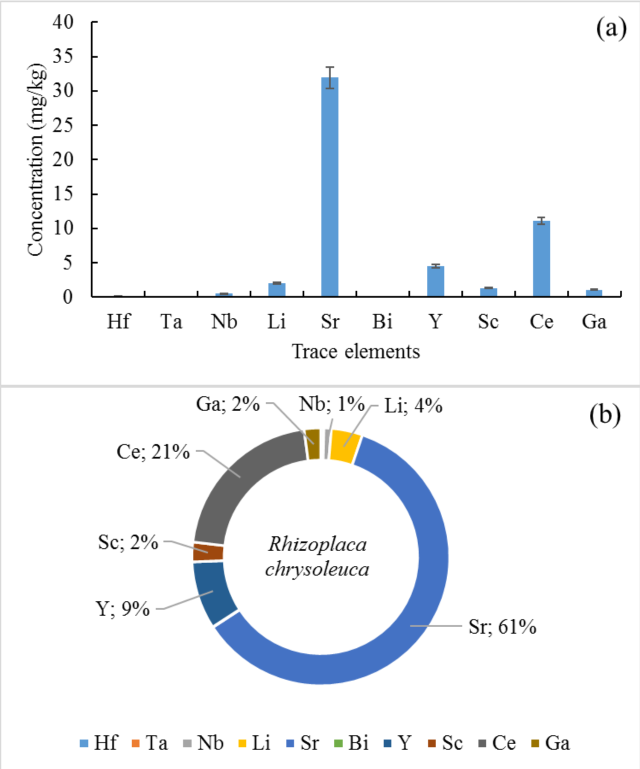

Figure 3. Trace elements accumulated by *R. chrysoleuca*

The trace elements accumulated by *Aspicilia calcarea* are given in Figure 4.

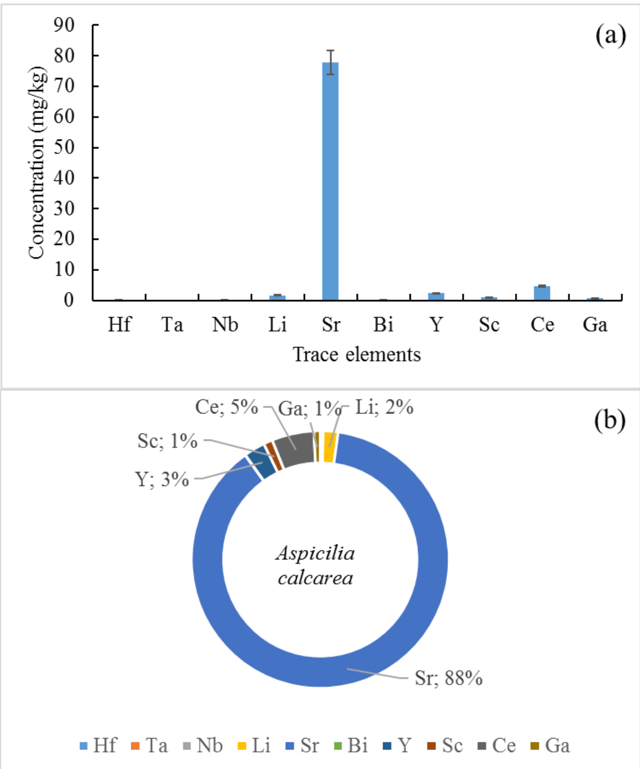

Figure 4. Trace elements accumulated by *A.calcarea*

According to Figure 4(a), the highest element concentration was 77.9±3.8 mg/kg for Sr, while the minimum element concentration was 0.008±0.002 mg/kg for Ta. Bi, Hf, Nb, Ga, Sc, Li, Y, and Ce concentrations in *Aspicilia calcarea* were 0.03±0.01, 0.095±0.004, 0.22±0.01, 0.7±0.03, 1.0±0.05, 1.65±0.08, 2.365±0.11, and 4.7±0.23 mg/kg respectively. Different concentrations were reported in the literature. Landis et al. [40] reported Nb concentrations in lichen H. physodes between 0.066 and 1.296 µg/g. Bubach et al. [38] reported Cs concentrations in lichen Usnea sp. between 0.0170 and 0.1100 mg/kg. The trace elements in *Aspicilia calcarea* were Ta<Bi<Hf<Nb<Ga<Sc<Li< Y<Ce<Sr. It can be said that the best accumulation by *Aspicilia calcarea* is for Sr. The distribution percentages of the trace elements accumulated by *Aspicilia calcarea* are given in Figure 4(b). According to Figure 4(b), the highest element value was 88% for Sr, while the lowest element value 0.027% for Ta. Also, Bi, Hf, and Nb values in *Aspicilia calcarea* were below 1%. Ce, Y, Li, Sc, and Ga values were 5%, 3%, 2%, 1%, and 1%, respectively.

The trace elements accumulated by *Umbilicaria vellea* are given in Figure 5.

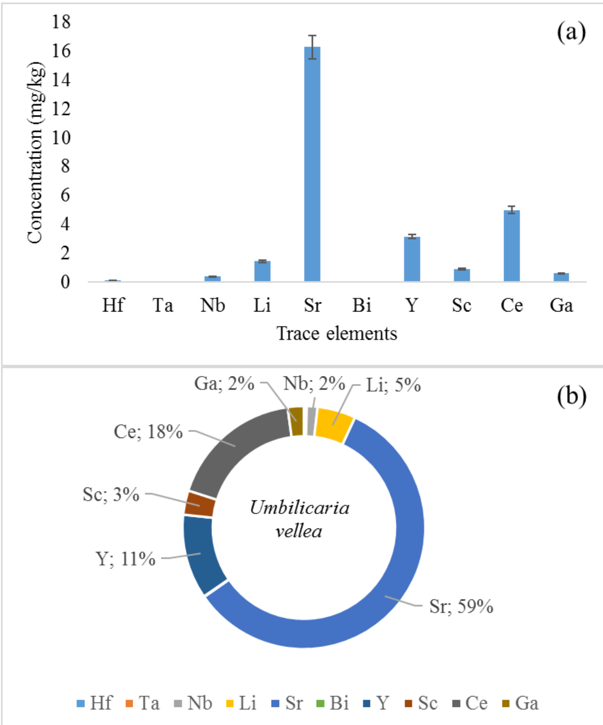

Figure 5. Trace elements accumulated by *U. vellea*

According to Figure 5(a), the highest element concentration was 16.3±0.8 mg/kg for Sr, while minimum element concentration was 0.004±0.001 mg/kg for Ta. Bi, Hf, Nb, Ga, Sc, Li, Y, and Ce concentrations in *Umbilicaria vellea* were 0.02±0.01, 0.1±0.05, 0.4±0.02, 0.6±0.03, 0.9±0.04, 1.43±0.07, 3.15±0.15, and 5.0±0.25 mg/kg respectively. Different concentrations were reported in the literature. Landis et al. [40] reported Li concentrations in lichen H. physodes between 0.235 and 7.185 µg/g. Bubach et al. [38] reported Hf concentrations in lichen Usnea sp. between 0.018 and 0.046 mg/kg. The trace elements in *Umbilicaria vellea* were Ta<Bi<Hf<Nb<Ga<Sc<Li

<Y<Ce<Sr. It can be said that the best accumulation by *Umbilicaria vellea* is for Sr. The distribution percentages of the trace elements accumulated by *Umbilicaria vellea* are given in Figure 5(b). According to Figure 5(b), the highest element value was 59% for Sr, while the lowest element value was 0.014% for Ta. Also, Bi and Nb values in *Umbilicaria vellea* were below 1%. Ce, Y, Li, Sc, Nb, and Ga values were 18%, 11%, 5%, 3%, 2% and 2%, respectively.

A comparison of trace elements accumulated by *Pseudevernia furfuracea*, *Cetraria islandica*, *Rhizoplaca chrysoleuca*, *Aspicilia calcarea*, and *Umbilicaria vellea* are given in Figure 6. According to Figure 6(a), the highest Hf concentration was 0.193±0.01 mg/kg for *Rhizoplaca chrysoleuca*, while the minimum Hf concentration was 0.043±0.002 mg/kg for *Cetraria islandica*. The Hf concentrations for *Aspicilia calcarea*, *Pseudevernia furfuracea* and *Umbilicaria vellea* were 0.095±0.004, 0.044±0.002, and 0.1±0.05 mg/kg, respectively. Hf values of lichen species were *Rhizoplaca chrysoleuca*> *Umbilicaria vellea*> *Aspicilia calcarea*> *Pseudevernia furfuracea*> *Cetraria islandica*. It was determined that Hf, one of the trace elements, was well accumulated by *Rhizoplaca chrysoleuca*. According to Figure 6(b), maximum Ta concentration was 0.008±0.002 mg/kg for *Cetraria islandica*, *Rhizoplaca chrysoleuca*, *Aspicilia calcarea* and *Pseudevernia furfuracea*, while minimum Ta concentration was 0.004±0.001 mg/kg for *Umbilicaria vellea*. Ta values of lichen species were *Rhizoplaca chrysoleuca* =*Aspicilia calcarea*=*Pseudevernia furfuracea*=*Cetraria islandica*> *Umbilicaria vellea*. The best Ta accumulation was determined as *Rhizoplaca chrysoleuca*, *Aspicilia calcarea*, and *Pseudevernia furfuracea*. The highest Nb concentration was 0.49±0.02 mg/kg for *Rhizoplaca chrysoleuca*, while the lowest Nb concentration was 0.16±0.008 mg/kg for *Cetraria islandica* and *Pseudevernia furfuracea*. Nb concentrations for *Aspicilia calcarea* and *Umbilicaria vellea* were 0.22±0.01 and 0.40±0.02 mg/kg, respectively. The Nb values of lichen species were *Rhizoplaca chrysoleuca*> *Umbilicaria vellea*> *Aspicilia calcarea*> *Pseudevernia furfuracea*=*Cetraria islandica*. Similarly to Hf, the best Nb accumulation was determined as *Rhizoplaca chrysoleuca* (Figure 6(c)). Maximum Li concentration was 2.07±0.1 mg/kg for *Rhizoplaca chrysoleuca*, while minimum Li concentration was 1.15±0.05 mg/kg for *Pseudevernia furfuracea*. The Li concentrations for *Cetraria islandica*, *Aspicilia calcarea* and *Umbilicaria vellea* were 1.65±0.08, 1.65±0.08, and 1.43±0.07 mg/kg, respectively. The Li values of lichen species were *Rhizoplaca chrysoleuca*> *Cetraria islandica*= *Aspicilia calcarea*> *Umbilicaria vellea*>*Pseudevernia furfuracea*. Similarly to Hf and Nb, the best Li accumulation was determined as *Rhizoplaca chrysoleuca* (Figure 6(d)). According to Figure 6(e), the maximum Sr concentration was 77.9±3.8 mg/kg for *Aspicilia calcarea*, while the lowest Sr concentration was 16.3±0.8 mg/kg for *Umbilicaria vellea*. The Sr concentrations for *Cetraria islandica*, *Rhizoplaca chrysoleuca*, and *Pseudevernia furfuracea* were 22.7±1.1, 31.9±1.6, and 21.7±1.0 mg/kg, respectively. The Sr values of lichen species were *Aspicilia calcarea*> *Rhizoplaca chrysoleuca*> *Cetraria islandica*> *Aspicilia calcarea*> *Pseudevernia furfuracea*> *Umbilicaria vellea*. Contrary to Hf, Nb, and Li, the best Sr accumulation was determined as *Aspicilia calcarea*. According to Figure 6(f), the highest Bi concentration was 0.03±0.01 mg/kg for, *Rhizoplaca chrysoleuca* and *Aspicilia calcarea*, while the minimum Bi concentration was 0.02±0.01 mg/kg for *Cetraria islandica*, *Pseudevernia furfuracea* and *Umbilicaria vellea*. The Bi values of lichen species were *Rhizoplaca chrysoleuca*=*Aspicilia calcarea*> *Cetraria islandica*= *Pseu devernia furfuracea*= *Umbilicaria vellea*. The best Bi accumulation was determined as *Rhizoplaca chrysoleuca* and *Aspicilia calcarea*. Maximum Y concentration was 4.489±0.22 mg/kg for *Rhizoplaca chrysoleuca*, while minimum Y concentration was 1.158±0.06 mg/kg for *Pseudevernia furfuracea*. The Y concentrations for *Cetraria islandica*, *Aspicilia calcarea*, and *Umbilicaria vellea* were 1.183±0.05, 2.365±0.11, and 3.15±0.15 mg/kg, respectively.

The Y values of lichen species were *Rhizoplaca chrysoleuca*> *Umbilicaria vellea*> *Aspicilia calcarea*>*Cetraria islandica*> *Pseudevernia furfuracea*. The best Y accumulation was determined as *Rhizoplaca chrysoleuca* (Figure 6(g)). Te highest Sc concentration was 1.3±0.06 mg/kg for *Rhizoplaca chrysoleuca*, while minimum Sc concentration was 0.8±0.04 mg/kg for *Cetraria islandica*. The Sc concentrations for *Aspicilia calcarea*, *Pseudevernia furfuracea*, and *Umbilicaria vellea* were 1.0±0.05, 0.9±0.04, and 0.9±0.04 mg/kg, respectively. Sc values of lichen species were *Rhizoplaca chrysoleuca*> *Aspicilia calcarea*> *Pseudevernia furfuracea*=*Umbilicaria vellea*>*Cetraria islandica*. The best Sc accumulation was determined as *Rhizoplaca chrysoleuca* (Figure 6(h)). According to Figure 6(i), the maximum Ce concentration was 11.1±0.5 mg/kg for *Rhizoplaca chrysoleuca*, while the minimum Ce concentration was 3.2±0.16 mg/kg for *Pseudevernia furfuracea*. Ce concentrations for *Cetraria islandica*, *Aspicilia calcarea*, and *Umbilicaria vellea* were 3.5±0.17, 4.7±0.23, and 5.0±0.25 mg/kg, respectively. The Ce values of lichen species were *Rhizoplaca chrysoleuca*> *Umbilicaria vellea* >*Aspicilia calcarea*> *Cetraria islandica*>*Pseudevernia furfuracea*. The best Ce accumulation was determined as *Rhizoplaca chrysoleuca*. According to Figure 6(j), the maximum Ga concentration was 1.1±0.05 mg/kg for *Rhizoplaca chrysoleuca*, while minimum Ga concentration was 0.4±0.02 mg/kg for *Cetraria islandica*. The Ga concentrations for *Aspicilia calcarea*, *Pseudevernia furfuracea*, and *Umbilicaria vellea* were 0.7±0.03, 0.5±0.02, and 0.6±0.03 mg/kg, respectively. Ga values of lichen species were *Rhizoplaca chrysoleuca*>*Aspicilia calcarea*>*Umbilicaria vellea* >*Aspicilia calcarea*> *Pseudevernia furfuracea*> *Cetraria islandica*. The best Ga accumulation was determined as *Rhizoplaca chrysoleuca*.

Accumulation values of trace elements in different lichen species were determined. From the results it was observed that Sr concentration was higher while Ta concentration was lower in all species.

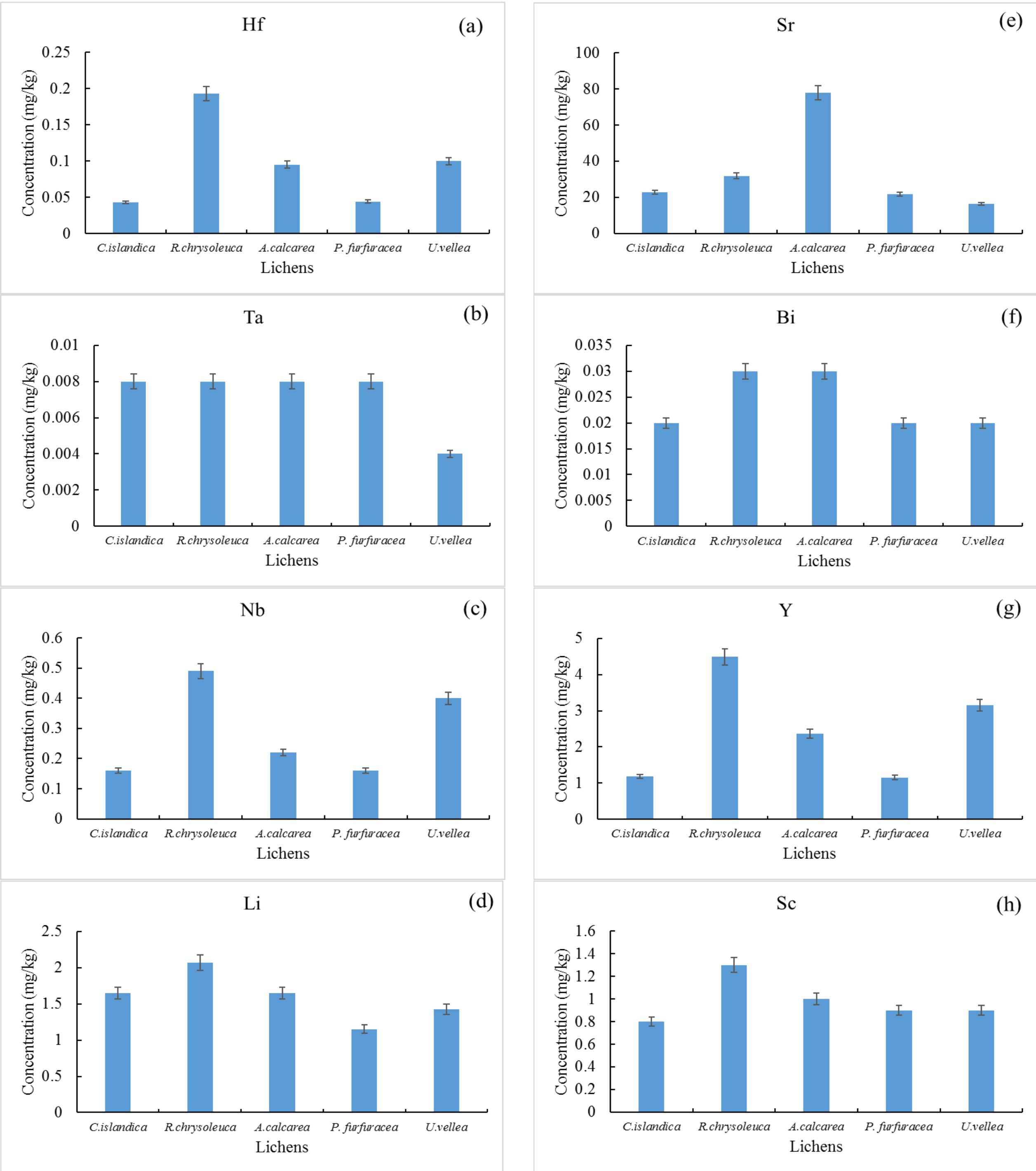

Figure 6. Comparison of trace elements accumulated by lichen species

The possible reason of this can be described by the accumulation characteristics of the elements as well as the trace element uptake preference by lichens. In the present study, the he pollution status values were calculated. The enrichment factors calculated for different lichen species are given in Table 1.

When Table 1 was examined, the highest EF value in *Cetraria islandica* was 7.91 for Bi, while the minimum value was 0.37 for Hf. The maximum EF value in *Rhizoplaca chrysoleuca* was 11.87 for Bi, while minimum value was 0.40 for Ta. The maximum EF value in *Aspicilia calcarea* was 11.87 for Bi, while the minimum value was 0.40 for Ta. The maximum EF value in *Pseudevernia furfuracea* was 7.91 for Bi, while the minimum value was 0.38 for Hf. The maximum EF value in *Umbilicaria vellea* was 7.91 for Bi, while the lowest value was 0.20 for Ta. EF values < 10 are considered as terrigenous, whereas EF values > 10 are considered to be impacted by anthropogenic activity [23].

According to Table 1, EF values for *Rhizoplaca chrysoleuca* (Bi: 11.87 and Y:10.25) and *Aspicilia calcarea* (Sr:11.18 and Bi:11.87) were greater than 10. EF values for *Cetraria islandica*, *Pseudevernia furfuracea* and *Umbilicaria vellea* were <10.

Table 1. Enrichment factors

	Lichens				
Trace elements	*Cetraria islandica*	*Rhizoplaca chrysoleuca*	*Aspicilia calcarea*	*Pseudevernia furfuracea*	*Umbilicaria vellea*
Hf	0.37	1.67	0.82	0.38	0.87
Ta	0.40	0.40	0.40	0.40	0.20
Nb	0.67	2.05	0.92	0.67	1.68
Li	4.15	5.20	4.15	2.89	3.59
Sr	3.26	4.58	11.18	3.12	2.34
Bi	7.91	11.87	11.87	7.91	7.91
Y	2.70	10.25	5.40	2.64	7.19
Sc	2.96	4.80	3.69	3.33	3.33
Ce	2.75	8.72	3.69	2.51	3.93
Ga	1.18	3.25	2.07	1.48	1.77

The contamination factors are given in Table 2.

Table 2. Contamination factors

	Lichens				
Trace elements	*C.islandica*	*R.chrysoleuca*	*A.calcarea*	*P.furfuracea*	*U.vellea*
Hf	1.19	0.16	0.59	0.07	1.34
Ta	8.00	0.00	8.00	0.00	4.00
Nb	6.15	0.08	2.76	0.06	6.91
Li	7.67	0.27	6.12	0.19	7.61
Sr	1.63	19.53	3.99	5.44	3.00
Bi	0.63	0.05	0.63	0.03	0.63
Y	3.26	1.38	1.72	0.67	4.67
Sc	2.47	0.53	1.90	0.47	1.90
Ce	5.22	2.12	2.21	1.45	3.46
Ga	4.00	0.28	2.55	0.20	3.05

There are six categories corresponding to CF values [45]: Category 1 (C1) CF < 1 no contamination; Category 2 (C2) 1 < CF < 2 suspected contamination; Category 3 (C3) 2 < CF < 3.5 slight contamination; Category 4 (C4) 3.5 < CF < 8 moderate contamination; Category 5 (C5) 8 < CF < 27 severe contamination; Category 6 (C6) CF > 27 extreme contamination. The highest CF value (8.00) was determined for Ta (C5) in *Cetraria islandica*. Li (C4) > Nb (C4) > Ce (C4) > Ga (C4) > Y (C3) > Sc (C3) > Sr (C2) > Hf (C2) > Bi (C1), followed it. CFs were calculated at the C4 category for four elements, C3 category for two elements, C2 category for two elements, and C1 category for one element. The highest CF value (19.53) was determined for Sr (C5) in *Rhizoplaca chrysoleuca*. Ce (C3) > Y (C2) > Sc (C1) > Ga (C1) > Li (C1) > Hf (C1) > Nb (C1) > Bi (C1) > Ta (C1), followed it. CFs were calculated at the C3 and C2 categories for one element, and C1 category for seven elements. The highest CF value (8.00) was determined for Ta (C5) in *Aspicilia calcarea*. Li (C4) > Sr (C4) > Nb (C3) > Ga (C3) > Ce (C3) > Sc (C2) > Y (C2) > Bi (C1) > Hf (C1), followed it. CFs were calculated at the C4 category for two elements, C3 category for three elements, C2 category for two elements, and C1 category for two elements. The highest CF value (8.00) was determined for Sr (C4) in *Pseudevernia furfuracea*. Ce (C2) > Y (C1) > Sc (C1) > Ga (C1) > Li (C1) > Hf (C1) > Nb (C1) > Bi (C1) > Ta (C1), followed it. CFs were calculated at the C2 category for one elements, and C1 category for eight elements. The highest CF value (7.61) was determined for Li (C4) in *Umbilicaria vellea*. Nb (C4) > Y (C4) > Ta (C4) > Ce (C3) > Ga (C3) > Sr (C3) > Sc (C2) > Hf (C2) > Bi (C1), followed it. CFs were calculated at the C4 category for three elements, C3 category for three elements, C2 category for two elements, and C1 category for one element. As a result, the highest CF values in lichens investigated were determined for Sr, Ta and Li. Carreras et al. [37] investigated the lichen U. amblyoclada. They reported CF values of Sr in city center, university campus and residential area in Cordoba city as 0.828, 1.055 and 0.817, respectively. These CF values are lower than the ones obtained in our study for Sr. Koroleva and Revunkov [39] investigated epiphytic lichen Hypogymnia physodes. They reported CF values of Sr in the Kaliningrad region and Sambian peninsula region as 1.9 and 2.3 that classified as C3 and C2, respectively. These CF are lower than the ones obtained in our study for Sr, except *Cetraria islandica*.

The coal burning may result in important problems in environment. During spontaneous combustion of coal volatization of coal and mineral matter may result in atmospheric pollution. High tantalum concentrations were reported in coal samples [46]. Therefore, the combustion of coal may have caused Ta emissions in the air resulting in high CF for Ta.

During last years, anomalous accumulations of lithium were discovered in coal samples [47-50]. Lithium has an affinity to inorganic fractions in coals; however, it is also related to organic fractions. Primary Li carriers in coals are thought to be lithium bearing clay minerals, and partially mica and tourmaline [49, 50]. Lithium is one of the semi-volatile elements according to enrichment behaviour in coal ash. Li in coals are probably to be enriched in ash fraction of coal. Lithium was found to be enriched in a range of 27% to 73% more in fly ash than in bottom ash [50, 51]. Therefore, in the studied area, the combustion of coal causing fly ashes may have resulted in Li emissions in the air and in high CF for Li. Lichens are sensitive to air pollution, resistant and able to live where pollution is present. Lichens are bioindicators of air pollution by absorbing air pollutants. They react differently to different levels of pollutants. Since they do not have an advanced root system, they exchange water and mineral matter with all their surfaces. Thus, they accumulate air pollutants in their bodies [52]. Therefore, climate and weather conditions effect the element accumulations by lichens. Moreover, habitat of lichens, the substrate they are on, metal-containing rock and soil affects the amount of metal accumulated in the lichen thallus [53-55].

In this study, pollution load index (PLI) values were calculated within the scope of this study. PLI below 1 indicates that elemental loads are near the background level, and above 1 indicates the extent of pollution. PLI indicates how much a sample exceeds the metal concentrations of natural environments and give an indication of the overall toxicity status of a sample [43]. According to obtained data, the highest PLI value was determined as 3.08 for *Cetraria islandica*, while the lowest PLI value was determined as 0.16 for *Pseudevernia furfuracea*. PLI values were *Cetraria islandica*> *Umbilicaria vellea*> *Aspicilia calcarea*> *Rhizoplaca chrysoleuca*> *Pseudevernia furfuracea*. PLI values for *Cetraria islandica*, *Aspicilia calcarea*, and *Umbilicaria vellea* were greater than 1.

4 Conclusion

The important results were obtained in the study. The highest trace element accumulated by *Pseudevernia furfuracea* (21.7±1.0 mg/kg; 75%), *Rhizoplaca chrysoleuca* (31.9±1.6 mg/kg; 61%), *Umbilicaria vellea* (16.3±0.8 mg/kg; 59%), *Aspicilia calcarea* (77.9±3.8 mg/kg; 88%), and *Cetraria islandica* (22.7±1.1 mg/kg; 75%) was determined as Sr. The best Sr accumulation was 77.9±3.8 mg/kg for *Aspicilia calcarea*. *Aspicilia calcarea* is good biomonitor of Sr. The lowest trace element accumulated by lichen species was determined as Ta. The lowest Ta accumulation was calculated as 0.004±0.001 mg/kg for *Umbilicaria vellea*. Bi and Hf elements accumulated by *Pseudevernia furfuracea*, *Rhizoplaca chrysoleuca*, *Umbilicaria vellea*, and *Cetraria islandica* and the Bi, Hf and Nb elements determined in *Aspicilia calcarea* had values below 1%. *Rhizoplaca chrysoleuca* is a good biomonitor of Ce, Ga, Sc, Y, Bi, Li, Nb, Hf. EF values for *Rhizoplaca chrysoleuca* (Bi: 11.87 and Y:10.25) and *Aspicilia calcarea* (Sr:11.18 and Bi:11.87) were greater than 10. EF values for *Cetraria islandica*, *Pseudevernia furfuracea* and *Umbilicaria vellea* were lower than 10. According to CF values, the highest CF values in lichens were considered for Sr (19.53), Ta (8.00), and Li (7.67). According to obtained data, the highest PLI value was determined as 3.08 for *Cetraria islandica*. PLI values were *Cetraria islandica*> *Umbilicaria vellea*> *Aspicilia calcarea*> *Rhizoplaca chrysoleuca*> *Pseudevernia furfuracea*. PLI values for *Cetraria islandica*, *Aspicilia calcarea*, and *Umbilicaria vellea* were greater than 1. In this context, it has been proven that these lichen species can be used as a good biomonitor of pollution.

Conflict of interest

The author declares that there is no conflict of interest.

Similarity rate (iThenticate): %18

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