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Lichens as Biomonitors of Air Pollutants Deposition: Strategically Important Element Pollution

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Abstract
Investigation of various species of lichen as biomonitors of air pollutants deposition and evaluation of element pollution were aimed. Maximum accumulation was 43.9±2.1 mg/kg in *X. somloensis*. Strontium in lichen species was quite high. Percentages of strontium for *L. pulmonaria*, *C. furcata*, *U. longissima*, *X. somloensis* and *F. caperata* were between 58% and 78% indicating the efficient accumulation of strontium. Lichens also accumulated strategically important elements. Maximum contamination factors in lichens were for strontium and tantalum. Maximum contamination factors of hafnium, niobium, lithium, gallium, and bismuth were for *L. pulmonaria* while maximum contamination factors of strontium, yttrium, scandium, and cerium were for *X. somloensis*. Maximum contamination factor of tantalum was for *F. caperata*. Enrichment factors for *L. pulmonaria*, *C. furcata*, and *F. caperata* were higher than 10, only for bismuth while lower than 10 for *U. longissima*. Enrichment factors for *X. somloensis* were higher than 10. Pollution load indexes for *L. pulmonaria* and *U. longissima* were higher than 1. The presence of strategically important elements in lichens showed that lichen species can be used as biomonitors of air pollutants.

1. Introduction

Environmental pollution threats the ecosystem and health of humans because of toxicity. The major factors that contributed to the pollution of the environment are anthropogenic activities, industrialization, and development [1,2]. Nowadays, one of the main leading global problems is the presence of various pollutants in the environment. They not only affect the health of humans but also overshadow the life of other creatures [3]. Chemical pollution of the environment globally affects ecosystem function, services, and biodiversity [4,5].

The strategically important elements have various usage fields. As a result of the wide usage of these elements, they are released into the environment. The strategically important elements have pollutant characteristics and strategic importance, at the same time. In the present paper hafnium (Hf), tantalum (Ta), niobium (Nb), strontium (Sr), lithium (Li), bismuth (Bi), cerium (Ce), yttrium (Y), gallium (Ga), and scandium (Sc) were investigated. Gallium has no known biological functions in living [6]. It is extensively used in the semiconductor industry. Ga arsenide is applied in different electronic components. Furthermore, gallium has been extensively used in medicine [7] because of its immunomodulating, anti-inflammatory, analgesic, and anti-hypercalcemic activities [6]. Bismuth is a rarely heavy metal. It has good chemical stability and peculiar physical and chemical properties [8]. The development in communication and

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microelectronics has been reflected in a concomitant increase in demand for Ta and Nb [9]. Lithium has strategic importance for various applications (e.g., lithium-ion batteries for mobile devices) [10,11]. Hafnium is a typical reactive element. Therefore, there is interest in using hafnium in nickel-based alloy systems [12]. Sr is a common trace element in the environment. It has commercial uses (e.g., glass, ceramics, and ferrite magnets). Strontium consumption via various ways can have adverse health effects (e.g., osteomalacia and abnormal bone development [13]. Yttrium is used in magnetic garnets [14]. It has the effect of refining grains of Mg alloys, can reduce the amount of Ca required in magnesium-based alloys, and may improve properties of them as well [15]. The high content of yttrium in different products results in accumulation in the body through food chain and endanger health by inhibiting the growth of pre-osteoblasts [16,17]. Cerium (Ce) is the most abundant rare earth metal found in the earth's crust [18]. Long-term ingestion of rare earth elements influences on activities of digestive enzymes [19,20]. Cerium minerals have been processed for industrial applications [18]. Scandium (Sc) is a valuable metal and used in production of high-strength and lightweight aluminum alloys and solid oxide fuel cells [21].

Different papers about the various applications of lichens were reported in the literature [22-25]. Apart from that papers, there are also some ones stating lichens as air pollution bioindicator/biomonitor [26-29]. Amount of elements accumulated in lichen thallus proportionally represents the presence of them in the atmosphere. When it comes to epiphytic species, thallus acts as a vehicle for transmitting particles by direct deposition from the air. Therefore, lichen serves as a valid instrument and proxy to assess air quality and potential contamination sources of elements [29-31]. Their prolonged exposure time to environmental factors, lack of cuticles or stomata and the absence of mechanisms of excretion make lichens behave like bioaccumulators of aerosol [29,32]. Lichens can accumulate even minor elements to measurable concentrations [33].

The aim of the present study is determination of accumulation of some strategically important elements in various lichens (*L. pulmonaria*, *C. furcata*, *U. longissima*, *X. somloensis* and *F. caperata*). When the literature is examined, there are few studies on accumulation of strategically important elements in lichens, and therefore we focused on the following issues in our study; (1) We identified various lichens (*L. pulmonaria*, *C. furcata*, *U. longissima*, *X. somloensis* and *F. caperata*) in Artvin, Murgul (Turkey) (2) We determined the strategically important elements in lichens (3) We calculated the accumulation amounts and percentages of the strategic elements in lichen species (4) We assessed the element pollution by calculating enrichment factors, contamination factors, and pollution load indexes.

2. Material and Method

2.1. Sampling and Analysis

Lobaria pulmonaria, *Cladonia furcata*, *Usnea longissima*, *Xanthoparmelia somloensis* and *Flavopormelia caperata* lichens investigated were collected from Murgul (Artvin, Turkey). The identification of lichen species was done by Prof. Dr. Ali Aslan. The lichens were dried and powdered. Analysis procedures are briefly given: samples were cold-leached with HNO_3. After cooling a modified Aqua Regia solution of equal parts concentrated HCl, HNO_3 and DI H_2O were added to sample for leaching in a heating block of the hot water bath. Samples were made up to volume with dilute HCl before filtered. Samples were analyzed by ICP/MS (ICP/MS-Perkin-Elmer ELAN 9000) for the evaluation of Hf, Ta, Nb, Li, Sr, Bi, Y, Sc, Ce, and Ga.

2.2. Pollution Status

Terrigenous or anthropogenic origin of elements in lichen species were evaluated by the calculated enrichment factor (EF) [29]. 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, E_{lichen}: element value in lichen (mg/kg), Al_{lichen}: Al value in lichen (mg/kg), E_{crust}: element value in the Earth's crust (mg/kg) Al_{crust}: Al value in the Earth's crust (mg/kg).

Degree of contamination in Artvin (Murgul) region were evaluated by the calculated contamination factor (CF) [34]. Contamination factors were calculated by:

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

where CF: contamination factor, C_i: element value in lichen (mg/kg), C_b: element value in control area (mg/kg). In this study, eastern Alps and northern Apennines were chosen as control [35] (for all elements, except elements Ta and Ga which do not exist in their study). Ta and Ga values were taken from Markert [36].

Pollution load index (PLI) indicating how much the sample exceeds metal concentrations of natural environments and also giving an indication of overall toxicity status for the sample is defined as the nth root of multiplication of CFs [37]. PLI was calculated by:

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

where, CF_1 is the CF of the first element, C_{F2} is the CF of the second element value, C_{F3} is the CF of the third element value, C_{Fn} is the CF of the n_{th} element in the lichens species.

3. Results and Discussion

3.1. Accumulation by *Lobaria pulmonaria*

Strategically important elements accumulated by *Lobaria pulmonaria* are given in Figure 1.

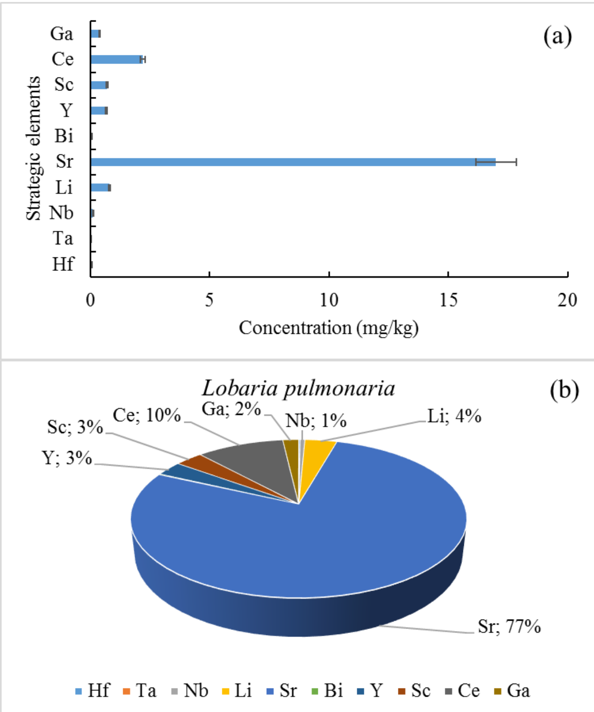

Figure 1. Strategically important elements accumulated by *Lobaria pulmonaria*

Figure 1(a) shows that the highest element concentration was 17±0.8 mg/kg for Sr. In the literature, Rivera et al. [38] reported Sr concentration as 9 µg/g in lichen *Himantormia lugubris*. In our study, the lowest element concentration was 0.006±0.001 mg/kg for Ta. Rivera et al. [38] reported Ta concentration as 0.00275 µg/g in lichen *Himantormia lugubris*. Parviainen et al. [28] reported Sr concentration of 14 mg/kg in lichens from Spain. Reported highest Sr concentration by Kousehlar and Widom [26] was 354.67 ppm in the lichens from Middletown, southwest Ohio. In our study, Hf, Bi, Nb, Ga, Y, Sc, Li, and Ce concentrations in *Lobaria pulmonaria* were 0.031±0.001, 0.04±0.002, 0.12±0.006, 0.4±0.02, 0.657±0.03, 0.7±0.03, 0.81±0.04, and 2.2±0.1 mg/kg, respectively. Rivera et al. [38] reported Hf and Sc concentrations as 0.0377 and 0.319 µg/g in lichen *Himantormia lugubris*, respectively. Parviainen et al. [28] reported Ce concentration of 3.8 mg/kg in lichens from Spain. Reported highest Ce and Ga concentration by Kousehlar and Widom [26] was 150.42 and 9.66 ppm in the lichens from Middletown, southwest Ohio, respectively. In our study, the strategic elements in *Lobaria pulmonaria* were Sr > Ce > Li > Sc > Y > Ga > Nb > Bi > Hf > Ta.

Considering these values, it can be said that the best accumulation by *Lobaria pulmonaria* is for Sr. The distribution percentages of the strategic elements accumulated by *Lobaria pulmonaria* are given in Figure 1(b). According to Figure 1(b), the highest element value was 77% for Sr, while the lowest element value 0.027% for Ta. Also, Bi and Hf values in *Lobaria pulmonaria* were below 1%. Y, Sc, Ce, Ga, Nb, and Li values were 3%, 3%, 10%, 2%, 1%, and 4%, respectively.

3.2. Accumulation by *Cladonia furcata*

Strategically important elements accumulated by *Cladonia furcata* are given in Figure 2.

According to Figure 2(a), the highest element concentration was 20±1.0 mg/kg for Sr, while the lowest element concentration was 0.006±0.001 mg/kg for Ta. In the literature, Rivera et al. [38] reported Sr and Ta concentrations as 36 and 0.0115 µg/g in lichen *Physconia muscigena*. In our study, the Hf, Bi, Nb, Ga, Sc, Li, Y, and Ce concentrations in *Cladonia furcata* were 0.038±0.001, 0.06±0.003, 0.16±0.008, 0.6±0.03, 1.2±0.06, 1.53±0.07, 1.95±0.09, and 4.6±0.23 mg/kg respectively.

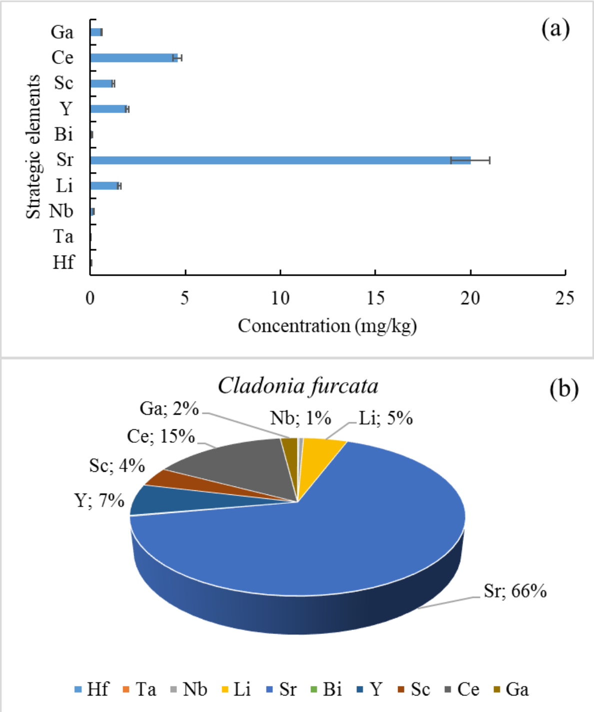

Figure 2. Strategically important elements accumulated by *Cladonia furcata*

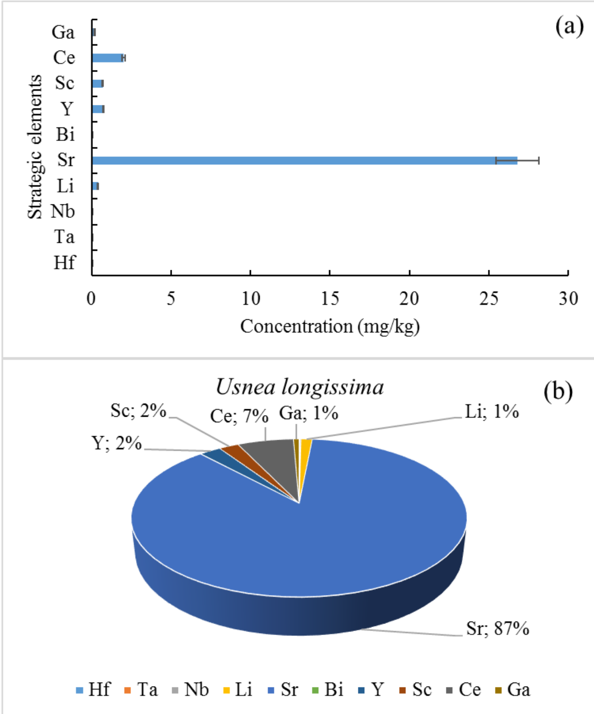

Figure 3. Strategically important elements accumulated by *Usnea longissima*

Rivera et al. [38] reported Hf and Sc concentrations as 0.196 and 1.86 µg/g in lichen *Physconia muscigena*. In our study, the strategic elements in *Cladonia furcata* were Sr>Ce>Y>Li>Sc>Ga>Nb>Bi>Hf>Ta. It can be said that the best accumulation by *Cladonia furcata* is for Sr. The distribution percentages of the strategic elements accumulated by *Cladonia furcata* are given in Figure 2(b). According to Figure 2(b), the highest element value was 66% for Sr, while the lowest element value 0.027% for Ta. Also, Bi and Hf values in *Cladonia furcata* were below 1%. Y, Sc, Ce, Ga, Nb, and Li values were 7%, 4%, 15%, 2%, 1%, and 5%, respectively.

3.3. Accumulation by *Usnea longissima*

Strategically important elements accumulated by *Usnea longissima* are given in Figure 3.

According to Figure 3(a), the highest element concentration was 26.8±1.3 mg/kg for Sr, while the lowest element concentration was 0.006±0.001 mg/kg for Ta. In the literature, Rivera et al. [38] reported Sr and Ta concentrations between 17 and 63 µg/g and between <0.002 and 0.0044 µg/g in lichen *Usnea antarctica*, respectively. Furthermore, the highest Sr and Ta concentrations in *Usnea aurantiacoatra* were reported as 51 and 0.0031 µg/g, respectively.

In the present study, Bi, Hf, Nb, Ga, Li, Sc, Y, and Ce concentrations in *Usnea longissima* were 0.02±0.001, 0.021±0.001, 0.04±0.002, 0.2±0.01, 0.4±0.02, 0.7±0.03, 0.757±0.03, and 2.0±0.1 mg/kg respectively. In the literature, Rivera et al. [38] reported Hf and Sc concentrations between 0.0088 and 0.0447 µg/g and between 0.158 and 1.051 µg/g in lichen *Usnea antarctica*, respectively. Furthermore, the highest Hf and Sc concentrations in *Usnea aurantiacoatra* were reported as 0.0278 µg/g and 0.576 µg/g, respectively. In the present study, the strategic elements in *Usnea longissima* were Sr>Ce>Y>Sc>Li>Ga>Nb>Hf>Bi>Ta. It can be said that the best accumulation by *Usnea longissima* is for Sr. The distribution percentages of the strategic elements accumulated by *Usnea longissima* are given in Figure 3(b). According to Figure 3(b), the highest element value was 87% for Sr, while the lowest element value 0.027% for Ta. Also, Bi, Nb, and Hf values in *Usnea longissima* were below 1%. Y, Sc, Ce, Ga, and Li values were 2%, 2%, 7%, 1%, and 1%, respectively.

3.4. Accumulation by *Xanthoparmelia somloensis*

Strategically important elements accumulated by *Xanthoparmelia somloensis* are given in Figure 4.

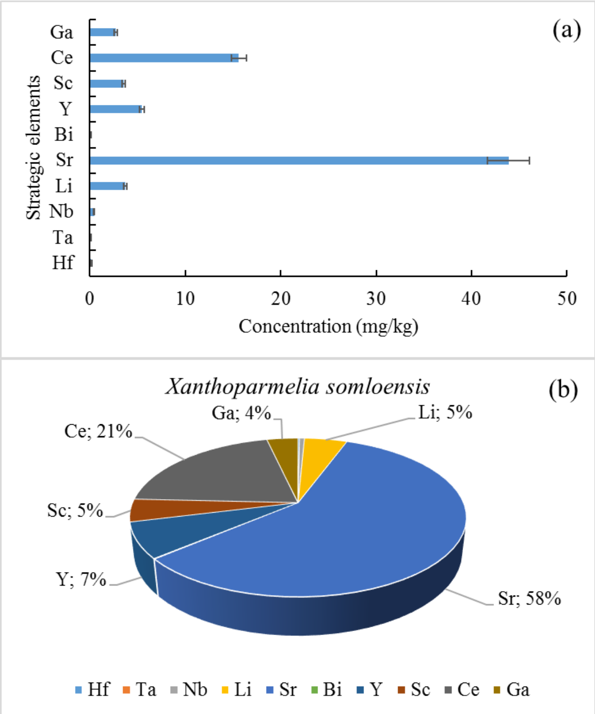

Figure 4. Strategically important elements accumulated by *Xanthoparmelia somloensis*

According to Figure 4(a), the highest element concentration was 43.9±2.1 mg/kg for strontium, while the lowest element concentration was 0.002±0.001 mg/kg for Ta. In the literature, Rivera et al. [38] reported Sr and Ta concentrations as 304 and 0.0655 µg/g in lichen *Rhizoplaca aspidophora*, respectively. In our study, the bismuth, hafnium, niobium, gallium, scandium, lithium, yttrium, and cesium concentrations in *Xanthoparmelia somloensis* were 0.08±0.004, 0.126±0.006, 0.43±0.02, 2.7±0.13, 3.5±0.17, 3.7±0.18, 5.457±0.27, and 15.6±0.7 mg/kg respectively. Rivera et al. [38] reported Hf and Sc as 0.933 and 14 µg/g in lichen *Rhizoplaca aspidophora*, respectively. In our study, the strategic elements in *Xanthoparmelia somloensis* were Sr>Ce>Y>Li>Sc>Ga>Nb>Hf>Bi>Ta. It can be said that the best accumulation by *Xanthoparmelia somloensis* is for Sr. The distribution percentages of the strategic elements accumulated by *Xanthoparmelia somloensis* are given in Figure 4(b). According to Figure 4(b), the highest element value was 58% for Sr, while the lowest element value 0.0026% for Ta. Also, Bi and Nb values in *Xanthoparmelia somloensis* were below 1%. Y, Sc, Ce, Ga, and Li values were 7%, 5%, 21%, 4%, and 5%, respectively.

3.5. Accumulation by *Flavopormelia caperata*

Strategically important elements accumulated by *Flavopormelia caperata* were given in Figure 5.

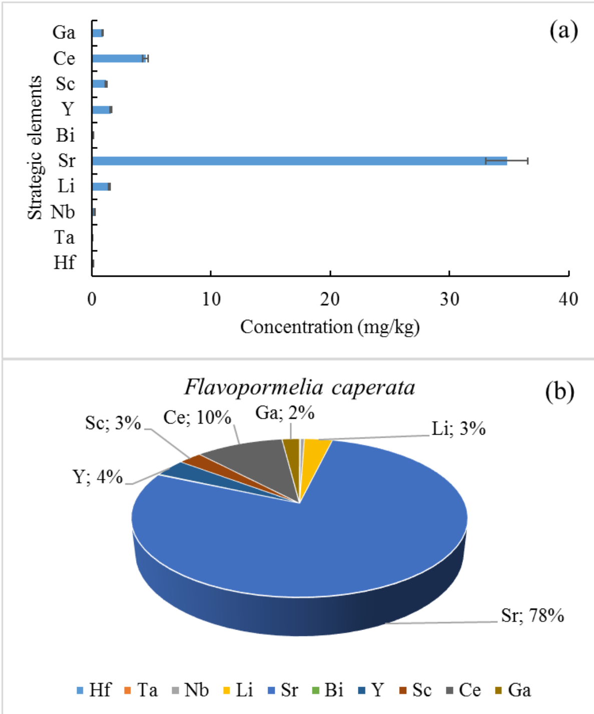

Figure 5. Strategically important elements accumulated by *Flavopormelia caperata*

According to Fig. 5(a), the highest element concentration was 34.8±1.7 mg/kg for Sr, while the lowest element concentration was 0.004±0.002 mg/kg for Ta. In the literature, Rivera et al. [38] reported Sr and Ta concentrations as 57 and 0.0157 µg/g in lichen *Sphaerophorus globosus*, respectively. In our study, the Hf, Bi, Nb, Ga, Sc, Li, Y, and Ce concentrations in *Flavopormelia caperata* were 0.045±0.002, 0.08±0.004, 0.2±0.01, 0.9±0.04, 1.2±0.06, 1.44±0.07, 1.595±0.08, and 4.5±0.22 mg/kg respectively. Rivera et al. [38] reported Hf and Sc concentrations as 0.209 and 1.64 µg/g in lichen *Sphaerophorus globosus*, respectively. In our study, the strategic elements in *Flavopormelia caperata* were Sr>Ce>Y>Li>Sc>Ga>Nb>Bi>Hf>Ta. It can be said that the best accumulation by *Flavopormelia caperata* is for Sr. The distribution percentages of the strategic elements accumulated by *Flavopormelia caperata* are given in Fig. 5(b). The highest element value was 78% for Sr, while the lowest element value was 0.0089% for Ta. Also, Bi and Nb values in *Flavopormelia caperata* were below 1%. Y, Sc, Ce, Ga, and Li values were 4%, 3%, 10%, 2%, and 3%, respectively.

The highest Hf concentration was 0.126±0.006 mg/kg for *Xanthoparmelia* *somloensis*, while the lowest Hf concentration was 0.021±0.001 mg/kg for *Usnea longissima*. The Hf concentrations for *L. pulmonaria, C. furcata,* and *F. caperata* were 0.031±0.001, 0.038±0.001, and 0.1±0.005 mg/kg, respectively. The Hf values of lichen species were *Xanthoparmelia somloensis* > *Flavopormelia caperata* > *Cladonia furcata* > *Lobaria pulmonaria* > *Usnea longissima*. It was determined that Hf, one of the strategic elements, was well accumulated by *Xanthoparmelia somloensis*. The highest Ta concentration was 0.006±0.001 mg/kg for *L.pulmonaria, C.furcata,* and *U.longissima* while the lowest Ta concentration was 0.002±0.001 mg/kg for *Xanthoparmelia somloensis*. Ta values of lichens were *L.pulmonaria = C.furcata = U.longissima* > *F.caperata* > *X.somloensis.* The best Ta accumulation was determined for *L.pulmonaria, C.furcata,* and *U.longissima.* The highest Nb value was 0.43±0.02 mg/kg for *Xanthoparmelia somloensis,* while the lowest Nb value was 0.04±0.002 mg/kg for *Usnea longissima*. The Nb concentrations for *L.pulmonaria, C.furcata,* and *U.longissima* were 0.12±0.006, 0.16±0.008 and 0.20±0.01 mg/kg, respectively. The niobium values of lichen species were *Xanthoparmelia somloensis* > *Flavopormelia caperata* > *Cladonia furcata* > *Lobaria pulmonaria* > *Usnea longissima.* The best Nb accumulation was determined for *Xanthoparmelia somloensis*. The highest Li concentration was 3.7±0.18 mg/kg for *Xanthoparmelia somloensis,* while the lowest Li concentration was 0.4±0.02 mg/kg for *Usnea longissima*. The Li concentrations for *L.pulmonaria, C.furcata,* and *U.longissima* were 0.81±0.04, 1.53±0.07, and 1.44±0.07 mg/kg, respectively. The Li values of lichen species were *Xanthoparmelia somloensis* > *Cladonia furcata* > *Flavopormelia caperata* > *Lobaria pulmonaria* > *Usnea longissima.* The best Li accumulation was determined for *Xanthoparmelia somloensis*. The highest Sr concentration was 43.9±2.1 mg/kg for *X.somloensis,* while the lowest Sr concentration was 17±0.8 mg/kg for *Lobaria pulmonaria*. The Sr concentrations for *Cladonia furcata, Usnea longissima,* and *Flavopormelia caperata* were 20±1.0, 26.8±1.3, and 34.8±1.7 mg/kg, respectively. The Sr values of lichen species were *Xanthoparmelia somloensis* > *Flavopormelia caperata* > *Usnea longissima* > *Cladonia furcata* > *Lobaria pulmonaria.* The best Sr accumulation was determined as *Xanthoparmelia somloensis*. The highest Bi concentration was 0.08±0.004 mg/kg for, *Xanthoparmelia somloensis* and *Flavopormelia caperata,* while the lowest Bi concentration was 0.02±0.001 mg/kg for *Usnea longissima*. The Bi concentrations for *Lobaria pulmonaria* and *Cladonia furcata* were 0.04±0.002 and 0.06±0.003 mg/kg, respectively. The Bi values of lichen species were *Xanthoparmelia somloensis = Flavopormelia caperata* > *Cladonia furcata* > *Lobaria pulmonaria* > *Usnea longissima.* The best Bi accumulation was determined as *Xanthoparmelia somloensis* and *Flavopormelia caperata.* The highest Y concentration was 5.457±0.27 mg/kg for *Xanthoparmelia somloensis,* while the lowest Y concentration was 0.657±0.03 mg/kg for *Lobaria pulmonaria*. The Y concentrations for *C.furcata, U.longissima,* and *F.caperata* were 1.95±0.09, 0.757±0.03, and 1.595±0.08 mg/kg, respectively. The Y values of lichen species were *Xanthoparmelia somloensis* > *Cladonia furcata* > *Flavopormelia caperata* > *Usnea longissima* > *Lobaria pulmonaria.* The best Y accumulation was determined as *Xanthoparmelia somloensis*. The highest Sc concentration was 3.5±0.17 mg/kg for *Xanthoparmelia somloensis,* while the lowest Sc concentration was 0.4±0.02 mg/kg for *L.pulmonaria* and *U.longissima*. The Sc concentrations for *C.furcata* and *F.caperata* were 1.2±0.06. The Sc values of lichen species were *Xanthoparmelia somloensis* > *Cladonia furcata = Flavopormelia caperata* > *Usnea longissima = Lobaria pulmonaria.* The best Sc accumulation was determined for *Xanthoparmelia somloensis*. The highest Ce concentration was 15.6±0.7 mg/kg for *Xanthoparmelia somloensis,* while the lowest Ce concentration was 2.0±0.1 mg/kg for *Usnea longissima*. The Ce concentrations for *L.pulmonaria, C.furcata,* and *F.caperata* were 2.2±0.1, 4.6±0.23, and 4.5±0.22 mg/kg, respectively. The Ce values of lichen species were *Xanthoparmelia somloensis* > *Cladonia furcata* > *Flavopormelia caperata* > *Lobaria pulmonaria* > *Usnea longissima.* The best Ce accumulation was determined as *Xanthoparmelia somloensis*. The highest Ga concentration was 2.71±0.13 mg/kg for *Xanthoparmelia somloensis,* while the lowest Ga concentration was 0.2±0.01 mg/kg for *Usnea longissima*. The Ga concentrations for *L.pulmonaria, C.furcata,* and *F.caperata* were 0.4±0.02, 0.6±0.03, and 0.9±0.04 mg/kg, respectively. The Ga values of lichen species were *Xanthoparmelia somloensis* > *Cladonia furcata* > *Flavopormelia caperata* > *Lobaria pulmonaria* > *Usnea longissima.* The best Ga accumulation was determined for *Xanthoparmelia somloensis*.

3.7. Assessment of pollution status

In this study, after the accumulation values of strategically important elements in different lichens were determined, pollution status values were calculated. In this context, the enrichment factors are given in Table 1.

Table 1. Enrichment factors calculated for different lichen species

Lichens	Value									
Lobaria pulmonaria	0.27	0.30	0.50	2.04	2.44	15.83	1.50	2.59	1.73	1.18
Cladonia furcata	0.33	0.30	0.67	3.84	2.87	23.74	4.45	4.43	3.61	1.77
Usnea longissima	0.18	0.30	0.17	1.01	3.85	7.91	1.73	2.59	1.57	0.59
Xanthoparmelia somloensis	1.09	0.10	1.80	9.30	6.30	31.65	12.46	12.93	12.25	7.98
Flavopormelia caperata	0.39	0.20	0.84	3.62	5.00	31.65	3.64	4.43	3.53	2.66

When Table 1 was examined, the highest EF value in *Lobaria pulmonaria* was 15.83 for Bi, while the lowest was 0.27 for Hf. Maximum EF value in *Cladonia furcata* was 23.74 for Bi, while the lowest was 0.30 for Ta. Maximum EF value in *Usnea longissima* was 7.91 for Bi, while the lowest value was 0.17 for Nb. Maximum EF value in *Xanthoparmelia somloensis* was 31.65 for Bi, while the lowest value was 0.10 for Ta. The highest EF value in *Flavopormelia caperata* was 31.65 for Bi, while the lowest value was 0.20 for Ta. Enrichment factors lower than 10 are considered as terrigenous and enrichment factors higher than 10 are considered to be impacted by anthropogenic activities [29]. According to Table 1, enrichment factors for *L.pulmonaria, C.furcata,* and *F.caperata* were higher than 10, only for Bi. Enrichment factors for *U.longissima* were lower than 10. Enrichment factors for *X.somloensis* were higher than 10 (Bi:31.65, Y:12.46, Sc:12.93, and Ce:12.25).

The contamination factors are given in Figure 6.

Lichen species										
Lobaria pulmonaria	0.86	6.00	4.62	3.77	1.22	1.25	1.81	2.16	3.28	4.00
Cladonia furcata	0.04	0.00	0.03	0.41	16.35	0.05	1.08	0.56	1.40	0.15
Usnea longissima	0.48	6.00	1.15	0.98	1.64	0.42	0.70	1.26	1.43	1.33
Xanthoparmelia somloensis	0.26	0.00	0.37	3.76	26.79	0.19	7.77	2.78	10.93	2.03
Flavopormelia caperata	0.17	12.00	0.54	0.38	1.30	0.42	0.21	0.43	0.41	0.44

Value	Category	Value	Category	Value	Category
Cf<1.0	C1	1.0-2.0	C2	2.0-3.5	C3
3.5-8.0	C4	8.0-27.0	C5	>27.0	C6

Figure 6. The contamination factors

There are six categories corresponding to CF values [39]: Category 1 (C1) contamination factor < 1 no contamination; Category 2 (C2) 1 < contamination factor < 2 suspected contamination; Category 3 (C3) 2 < contamination factor < 3.5 slight contamination; Category 4 (C4) 3.5 < contamination factor < 8 moderate contamination; Category 5 (C5) 8 < contamination factor < 27 severe contamination; Category 6 (C6) contamination factor > 27 extreme contamination. The highest CF value was determined for Ta (C4) in *Lobaria pulmonaria* while Nb (C4), Ga (C4), and Li (C4) followed it. These results indicated moderate contamination. The elements that indicated slight contamination were Ce (C3) and Sc (C3) while Y (C2), Bi (C2), and Sr (C2) indicated suspected contamination. Hf (C1) indicated no contamination.

CFs were calculated at the C4 category for three elements, C3 category for two elements, C2 category for three elements, and C1 category for one element. The highest CF value was determined for Sr (C5) in *Cladonia furcata* indicating severe contamination. As a result, it can be said that the source of Sr in the lichen *Cladonia furcata* is probably anthropogenic emissions. Ce and Y were at C2 category indicating suspected contamination. Sc (C1), Li (C1), Ga (C1), Bi (C1), Hf (C1), Nb (C1), and Ta (C1) indicated no contamination. CFs were calculated at the C1 category for seven elements, C2 category for two elements, and C5 category for one element. Most of the CFs were classified as C1. The highest CF value was determined for Ta (C4) in *Usnea longissima* indicating moderate contamination. Sr, Ce, Ga, Sc and Nb were at C2 category indicating suspected contamination. Li (C1), Y (C1), Hf (C1), and Bi (C1) indicated no contamination. CFs were calculated at the C1 category for four elements, C2 category for five elements, and C4 category for one element. The highest CF value was determined for Sr (C5) in *Xanthoparmelia somloensis* and Ce (C5) followed it. These results indicated severe contamination. Y and Li were at C4 category indicating moderate contamination. Sc and Ga were at C3 category indicating slight contamination. Nb (C1), Hf (C1), Bi (C1), and Ta (C1) indicated no contamination. CFs were calculated at the C5, C4, and C3 categories for two elements, C1 category for one element. As a result, it can be said that the source of Sr and Ce in the lichen *Xanthoparmelia somloensis* is probably anthropogenic emissions. The highest CF value was determined for Ta (C5) in *Flavopormelia caperata* indicating severe contamination. As a result, it can be said that the source of Ta in the lichen *Flavopormelia caperata* is probably anthropogenic emissions. Sr was at C2 category indicating suspected contamination. Nb (C1), Ga (C1), Sc (C1), Bi (C1), Ce (C1), Li (C1), Y (C1), and Hf (C1) indicated no contamination. CFs were calculated at the C1 category for eight elements, C5 and C2 category for one element. Most of the CFs were classified as C1.

As a result, the highest contamination factors in lichens investigated were determined for strontium and tantalum. Biological behaviours of Sr resemble those of calcium because of chemical similarity of them. The close relationship between calcium and strontium has been proven in studies with various plant systems, algae and yeasts. It has been shown that strontium may substitute for calcium in binding processes at biological cell surfaces as well as in active uptake via divalent cation transport systems [40]. Therefore, it is not surprising the high value of Sr in lichen species. Near to the studied region, the copper flotation wastes from a mine are stored in the empty pit mine, the ore of which is finished. It is known that high concentrations of strontium are detected in drinking water in the area close to where these wastes are stored. Strontium is probably dispersed by atmospheric transport to near region of these flotation waste deposits and is subsequently deposited in lichens. The transportation and redeposition on Earth by dry or wet deposition of Sr released into the air from various activities is reported by WHO [41]. Main sources of Ta in the environment are geologic, mostly as a result of rock weathering, but a potential anthropogenic source of it is from coal combustion [42,43]. As a result of combustion of coal may caused high Ta in lichens investigated. Maximum contamination factors of Hf, Nb, Li, Ga, and Bi were for *L. pulmonaria* and maximum contamination factors of Sr, Y, Sc, and Ce were calculated for *X.somloensis*. Additionally, maximum contamination factor of Ta was calculated for *F.caperata.*

In this study, pollution load index (PLI) values were calculated within the scope of this study. PLI lower than 1 indicates that elemental load is near the background level, and higher than 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 for a sample [37]. According to obtained data, PLI values for *L.pulmonaria* and *U.longissima* were higher than 1. PLIs for *Lobaria pulmonaria* and *Usnea longissima* were 2.43 and 1.14, respectively. PLI values for *C.furcata*, *X.somloensis*, and *F.caperata* were 0.19, 0.89, and 0.57, respectively.

4. Conclusion and Suggestions

In this study, we identified *L.pulmonaria*, *C.furcata*, *U.longissima*, *X.somloensis*, and *F.caperata* lichens. The highest strategically important element accumulated by *Lobaria pulmonaria* (17±0.8 mg/kg), *Cladonia furcata* (20±1.0 mg/kg), Usnea longissima (26.8±1.3 mg/kg), *Xanthoparmelia somloensis* (43.9±2.1 mg/kg), and *Flavopormelia caperata* (34.8±1.7 mg/kg) was determined as Sr. The best Sr accumulation was by *Xanthoparmelia somloensis*. Among the strategically important elements accumulated by lichens, the highest Sr percentage was found to be 78% in *Flavopormelia caperata*. The lowest strategic element accumulated by lichen species was determined as Ta. The lowest Ta accumulation was determined as 0.002±0.001 mg/kg for *Xanthoparmelia somloensis*. Maximum CF values were for Sr and Ta. Maximum CF values of Hf, Nb, Li, Ga, and Bi were for *L. pulmonaria* and maximum CF values of Sr, Y, Sc, and Ce were for *X. somloensis*. The maximum CF value of Ta was for *F. caperata*. In general, EF values were higher than 10. The PLIs for *L. pulmonaria* and *U. longissima* were greater than 1. As a result, lichens can be used as biomonitors of air pollutants.

Conflict of Interest Statement

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The study is complied with research and publication ethics.

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