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Analysis of Trace Element Concentrations of Some Lichens of Turkey

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In this study, concentrations of six different elements (Ca, K, Fe, Ba, Ti and Sr) were measured in twelve lichen species from two geographically different regions (Northern Anatolia: Provinces of Trabzon, Ordu, Artvin and Giresun and Eastern Anatolia: Erzurum province) in Turkey. An annular ^{55}Fe and ^{241}Am radioactive source was used for excitation of characteristic K X-rays using radioisotope excited energy dispersive X-ray fluorescence method of multiple standard addition. The incident beam and fluorescence X-rays emitted from the target were detected and analyzed with an Ultra-LEGe detector. Five of the six elements (Ca, K, Fe, Ba and Ti) are available in the twelve lichen species living in 12 different habitats. But, Sr is the only available element in some lichens living in some certain localities. Moreover, some lichens living in some localities contain very high concentrations (almost 5-10 folds) of Ti and Ba (for example: Ordu-Ünye Çinarsuyu, Erzurum-Kösk village for Ti, 0.384, 0.342 %, respectively and Trabzon-Maçka, Solma plateau for Ba and 0.306 %).

Key Words: Element analysis, Lichen, Soil, EDXRF, Turkey.

INTRODUCTION

Lichens are highly sensitive to atmospheric pollution and this makes them good indicator plants for air pollution. However, species, which can tolerate high levels of air pollution, like *Lecanora conizaeoides* Nyl ex Cromb, also exist. Today it is possible to utilize lichens to determine qualitatively and/or quantitatively air pollution caused by SO_2, heavy metal and radioactivity[1]. Lower plants, especially mosses and lichens, due to their higher capacity for metal accumulation, are probably the organisms that are the most frequently used for monitoring metal pollution in urban environments[2].

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Lichens pay effort for the continuity of the union in a morphological or physiological manner that is different from their free state. There is very close relationship between inorganic elements and metabolism of living organisms including lichens. Inorganic elements have three important functions (structural, electrochemical and catalytic) in the occurrence of metabolic activities in all living organisms. They play very specific roles in the setting of ion balances, buffer solutions and supply of osmotic regulations and stabilizations of macromolecules (electrochemical). They participate in the formation of several enzymes by binding to specific proteins as prosthetic groups (cofactors) and, moreover, also in the formation of NADP and ATP, which have important roles in energy metabolism and redox reactions.

Recently, much research has been made using the characteristic X-ray fluorescence technique. This technique is preferred in order to define various elements in the substance and to determine the characteristic features of such elements. This technique is less time consuming. It enables us to obtain more sensitive results and it is economical. Besides, sample analysis with the energy-dispersive X-ray fluorescence (EDXRF) technique is used in several areas such as analyzing environmental pollution, medicine, pharmacy, biochemical research, quality control system and oil industry[3].

It has recently been getting more considerable effort to determine the concentrations of trace elements in several substances at the last years using X-ray spectroscopy techniques. For example: in food materials[4], in plants[5], in insects[6] and in mineralogy[7]. However, no reports have ever compared the elemental concentrations of some lichens species which had been living in two different regions.

Artvin, Giresun, Ordu and Trabzon provinces are located in northwest Anatolia and these provinces with a marine climate are rich in terms of the diversity of lichen species. Erzurum province is located in Eastern Anatolia in Turkey and this province has a terrestrial climate and is poor in the diversity of lichen species.

Here an attempt has been made to determine differences of some trace element concentrations in twelve lichen species found in two the geographically different regions (Eastern Anatolia and Northern Anatolia) using EDXRF spectroscopy technique.

EXPERIMENTAL

Twelve lichen species (Table-1) were collected from trees, rock and soil from twelve different stations in Northern Anatolia Region (Artvin, Giresun, Ordu and Trabzon: the average altitude of this region which is on the coastal Black Sea, changes from 0-1750 m) and Eastern Anatolia Region (Erzurum: the average altitude of this region is 1800 m) in August 2005. A stereo-microscope, a light-microscope and the usual spot tests were used to identify the samples with reference to Purvis *et al.*[8]. Sample specimens have been stored in the private herbarium of Kazim Karabekir Faculty of Education, Atatürk University, Erzurum (Turkey).

TABLE-1
LICHEN SAMPLES COLLECTED FROM THE STUDY AREAS

Sample No.	Lichen	Black sea region (Northern Anatolia)	Substrata	Altitude (m)	Nature of site	Coordinates	Herbarium number
1.	*Bryoria fuscescens*	Artvin-Murgul Korucular village	*Fagus orientalis*	675	Rural	41°18'30" N 41°38'20" E	Aslan 705
2.	*Peltigera polydactyla*	Artvin-Murgul Basköy village	mosses	550	Rural	41°17'50" N 41°32'50" E	Aslan 700
3.	*Cetrelia olivetorum*	Giresun-Dereli Kulakkaya village	*Fagus orientalis*	1550	Rural	40°33'30" N 38°27'00" E	Aslan 710
4.	*Evernia divaricata*	Giresun-Tirebolu Kisecik plateau	*Pinus sylvestris*	1750	Rural	40°50'00" N 38°53'00" E	Aslan 724
5.	*Xanthoria parietina*	Ordu-Ünye-Ç?harsuyu	*Robinia* sp.	5	Sub rural	40°59'50" N 37°52'30" E	Aslan 717
6.	*Cladonia foliacea*	Trabzon-Maçka-Solma plateau	Soil	1650	Rural	40°51'30" N 39°32'30" E	Aslan 712
7.	*Xanthoparmelia pulla*	Senkaya-Yürekli village	Siliceous rock	1850	Rural	40°40'15" N 42°30'50" E	Aslan 695
8.	*Physcia aipolia*	Eastern Anatolia region Erzurum-Oltu-Gökçedere village	*Alnus glutinosa*	1700	Rural	40°37'00" N 41°59'50" E	Aslan 702
9.	*Dermatocarpon intestiniforme*	Erzurum-Oltu-Inci village-Eskitarmut area	Sileceous rock	1650	Rural	40°35'30" N 41°50'00" E	Aslan 720
10.	*Ramalina polymorpha*	Erzurum-Center-Hamam deresi	Sileceous rock	1850	Sub rural	39°58'50" N 41°26'45" E	Aslan 701
11.	*Umbilicaria vellea*	Erzurum-Center-Kösk village	Sileceous rock	1800	Rural	40°05'50" N 41°26'40" E	Aslan 730
12.	*Xanthoria elegans*	Erzrum-Senkaya-Yürekli village	Calcareous rock	1850	Rural	40°40'15" N 42°30'50" E	Aslan 729

Artvin is situated at a height of 550 m, standing high on a rock above the Çoruh river on the Black Sea coast on the border with Georgia. Vegetation varies from the bed of the Çoruh Valley upwards. Mainly *Quercus* populations are visible at the lower sides of the Valley. The upper sides of the Valley are covered by mixed forests of *Ulmus, Alnus, Carpinus, Abies, Quercus, Populus, Tilia*, up to about 1400 m. From this altitude, up to 2000 m, *Pinus* forests take place. Above 2000 m, alpinic zone which is composed of mainly steppes covered by mountain meadows. This greenery runs from the top all the way down to the Black Sea coastal[9]. Artvin has a wet climate that forms a transition between the terrestial climate and the climate of the East Black Sea Region. Here the winters are cold and snowy and the summers are mild and rainy. Annual precipitation averages *ca.* 700 mm and the temperatures averages 13 °C[10].

The surface area of Erzurum is the fourth biggest in Turkey. The majority of the province is elevated. Most plateaus are about 2.000 m high from sea level and the mountainous regions beyond the plateaus are 3.000 m and higher. The northern mountain ranges are the second row elevations of the North Anatolian Mountains. The two depression plains between these mountainous areas are Erzurum Plains and Hasankale Plains. Steppe formations are prevalent in the geography, occupying about 60 % of the surface area, much of it fertile. Forest areas are not large mainly consisting of scots pines and oaks[9]. Continental climate rules in the province with long and harsh winters and short and mild summers. The lowest temperature average is -8.6 °C and the highest average temperature is 19.6 °C. Yearly average precipitation is 453 mm[10].

Trabzon has a total area of 4.685 km^2 and it is bordered by the provinces of Rize, Giresun and Gümushane. The total area is 22.4 % plateaux and 77.6 % hills. Dense pine forests cover the mountains and an abundance of crops flourish in the lower elevations and valleys. The unusual and varied landscape has shaped the industry and culture of the area. Being situated along a sea-side and surrounded towards south by steep mountains running parallel to the coast[9]. Trabzon has a typical Black sea climate with rain the year round and temperatures reaching up to around 27 °C in the summer. Winters are cool and damp and the lowest temperature is around 5 °C in January. In summers the temperature is pleasantly cool and in winter it is mild with an annual average temperature of 14.5 ºC. It has a relatively high rainfall all year round. It receives a lot of rain, especially in winters and springs[10].

Ordu is 4 m altitude from sea level and situated in the East Black sea region. Its surface is of 5.963 km^2 and covers 6.563 km^2. Ordu is one of the calmest and greenest sites along the Black Sea coast. Due to its rainy climate, the land is fertile, with vegetable and fruit gardens and wide forests covering the whole area. There are clean and restful atmosphere and extensive hazelnut plantations. The grafted plants were exposed to nursery conditions and they were irrigated at certain intervals[9]. Typical Black Sea humid climate dominates Ordu. Winters pass chilly, summers pass tepid, approximately every months of year is rainy. Annual rainfall is approximate

1600 mm. It has average temperature of 13.9 °C, maximum temperature 33 °C, minimum temperature -7.2 °C, average annual rainfall 1196.6 mm, average number of frozen day 9, average number of snow days 6.1 and average relative moisture of 76 %[10].

Giresun is 50-60 km from the coast. There are some high plateaux above 2.000 m such as Kümbet, Kulakkaya, Bektas and Tamdere. Majority of the plains, which cover relatively small areas, are situated near the coastal area, altitudes ranging from 50 to 3.000 m. The northern part of the province is mostly seen hazelnut gardens from the coastal up to altitudes of 800 m. *Alnus, Castanea, Abies* and *Picea* in the lower and *Carpinus, Quercus* and *Fagus* in the higher altitudes are occasionally seen among these gardens. *Abies, Pinus* and *Picea* exist between 1600 and 2000 m and over 2000 m, the high plateaux are covered with meadows[9]. In Giresun it is dominated by oceanic climate. A mild and high precipitation climate prevails along the coast, with a mean annual temperature of 14.2 °C in the centre of Giresun. Average temperatures are lowest in February (6.9 °C) and highest in August (22.3 °C) and mean annual precipitation is 1.305 mm, the highest precipitation occuring in October and November and the lowest in May and June[10].

Metals are emitted into the Artvin, Erzurum, Trabzon, Giresun and Ordu environments from different sources, *i.e.*, transportation, industrial activities, fossil fuels, agriculture and other human activities.

The selected 12 lichen samples were prepared as the experimental materials. After cleaned from soil particles in distilled water, lichen samples dried at room-temperature. Every lichen sample was dried at 70 °C to determine dry weight and then powdered using a Spex mill. To reduce the particle size effects, the powder obtained was sieved using a 400 mesh sieve and then was mixed for 20 min. A five-tone hydraulic press was used to compress the sample powder into a solid thin pellet of 13 mm diameter.

It is well known that the measurement of thin samples in EDXRF presents several advantages over the methods using thick samples. In the latter case, the increase of background by multiple scattering within the sample causes absorption and enhancement effects that dominate over the gain in characteristic line intensity resulting from the increase in sample thickness[11]. However, the absorption and enhancement effects are less significant and can be easily corrected or neglected for thin samples. For the measurement of metal concentrations, *ca.* 100 mg homogeneous specimens were positioned according to the geometry of Fig. 1, were irradiated by 5.96 keV photons emitted by an annular 1.85 GBq ^{55}Fe radioactive source for potassium, calcium and titanium and were irradiated by 59.543 keV photons emitted by an annular 1.85 GBq Am-241 radioactive source for iron, strontium and barium. To detect the radiation scattered from a sample, Ultra-LEGe detector (FWHM 150 eV at 5.9 keV, active area 30 mm^2, thickness 5 mm and polymer window thickness 0.4 μm) was used. 8192-16384 channels of a multichannel analyzer were employed in data acquisition. In qualitative analysis, characteristic X-rays emitted by excited atoms of the sample were registered for time intervals of 5000 s. Spectra were analyzed using the Nucleus program (Tennelec, Oak Ridge). Qualitative analysis of spectral peaks showed that the samples contain potassium, calcium, titanium, iron, strontium and barium. A representative example of a spectrum is given in Fig. 2 for elements excited by the ^{55}Fe radioactive source and Fig. 3 for elements excited by the ^{241}Am radioactive source.

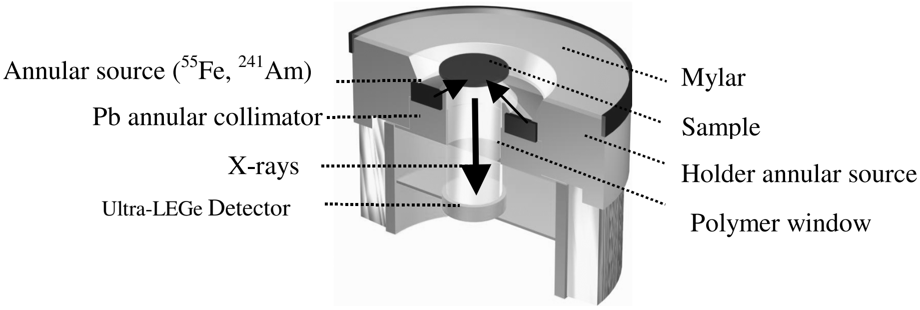

Fig. 1. Geometry of the experimental set-up

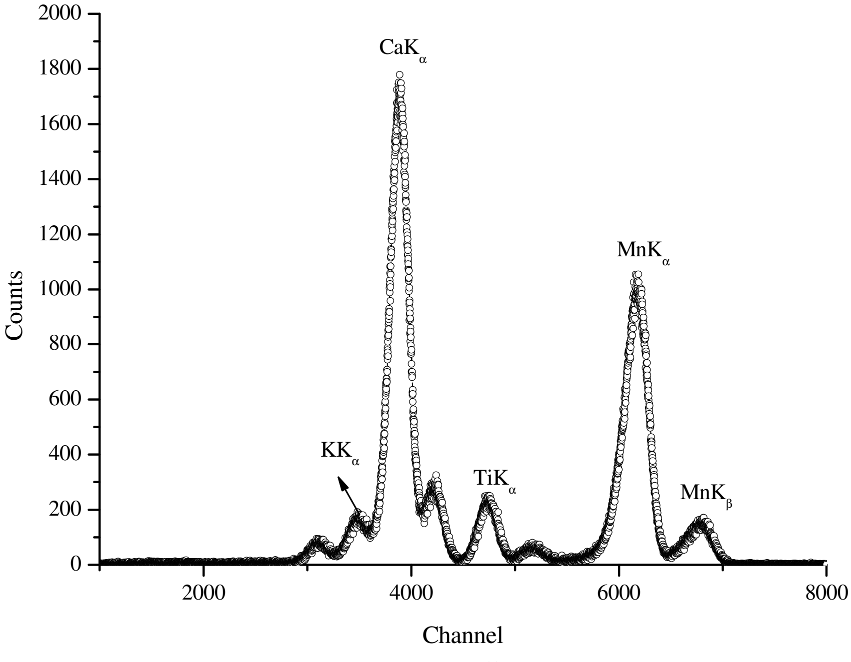

Fig. 2. X-ray spectrum, using ^{55}Fe source, lichens

In this paper, the standard addition method was used to obtain the elemental concentration[3]. The method involves the addition of known quantities of the analyte to the specimen. If the analyte is presented at low levels and no suitable standards are available, standard addition may prove to be an alternative, especially if the

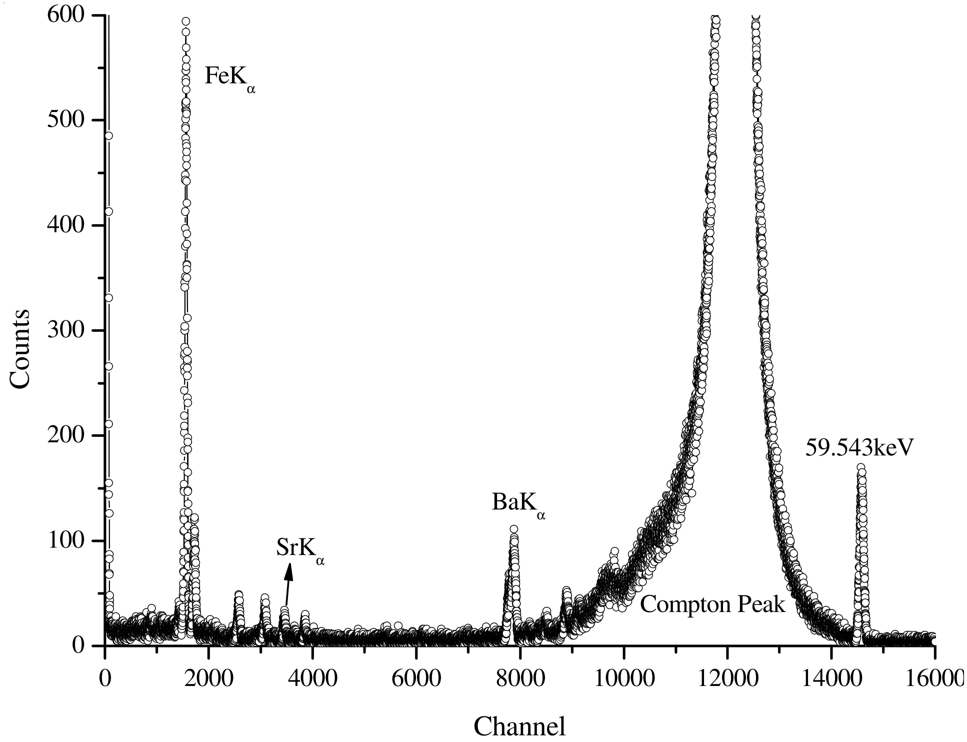

Fig. 3. X-ray spectrum, using ^{241}Am source, lichens

analyst is interested in only one analyte element. The principle is as follows: Adding a known amount of analyte I (ΔC_i) to the unknown sample gives an increased intensity $I_i + \Delta I_i$. Assuming a linear calibration, the following equations apply:

$$I_i = M_i C_i \tag{1}$$

For the original samples and

$$I_i + \Delta I_i = M_i(C_i + \Delta C_i) \tag{2}$$

for the sample with the addition. From eqns. 1 and 2, C_i can be determined by the elimination of the calibration factor M_i. C_i can also be obtained by plotting the intensity measured *versus* concentration of the addition. The intensities used for calibration must be corrected for background and line overlap[12]. In order to minimize the absorption effect, the K_α net peak areas for copper, strontium and barium obtained from the sample spectra were normalized by dividing them by Compton net peak areas. The K_α net peak areas for potassium, calcium and titanium obtained from the sample spectra were normalized by dividing them by MnK_α peak areas.

The detection limits for EDXRF is related to sample preparation and analysis time. Typically achieved detection limits vary between ~1-100 ppm in X-ray fluorescence spectroscopy systems. In order to determine the detection limit of EDXRF for Sr, we used the reference material which was prepared by the International

Atomic Energy Agency. Characteristic X-ray peak intensities for Sr was obtained through spectrum analysis of the reference material. Sensitivity of this element was calculated by using:

$$C_i = \frac{I_i}{S_i} \qquad (3)$$

where C_i is the concentration (mg kg^{-1}), I_i is the characteristic X-ray intensity (cps) and S_i is the elemental sensitivity (cps mg^{-1} kg) for the element i.

The detection limit was calculated by:

$$DL_i = \frac{3}{S_i}\sqrt{\frac{I_i(BG)}{t}} \qquad (4)$$

where DL_i is the detection limit (mg kg^{-1}), I_i (BG) is the background intensity (cps) under element I peak and t is the counting time (s). Detection limit for Sr was calculated to be 8 ppm.

RESULTS AND DISCUSSION

The presented work has shown that different specimens of lichens can be analyzed by the EDXRF technique, employing the standard addition method for sample preparation. The concentrations of six elements in twelve lichen species are shown in Table-2. The concentrations of K, Ca and Fe were always higher than the other trace element concentrations in the lichens. The overall error in the measurements is estimated to be 6-9 %. The erroneous resulting areas from uncertainties in the various parameters are used to calculate the concentration, including errors due to peak area evaluation (≤ 4-6 %), sample thickness and weighing (≤ 1-4 %), source intensity (≤ 3 %) and systematic errors (≤ 5-8 %). Measurements are made for all samples at different mixing time. Each sample is analyzed and it appears that all the results are in good agreement with experimental uncertainties.

In this work, 12 different lichen species, four of which morphologically had fruticose and the others had foliose structure, were collected from five different stations in every location. The highest values of Ca was in *Xanthoparmelia pulla* and *Ramalina polymorpha* (6.564 ± 0.394 % and 3.566 ± 0.214 %, respectively) living Eastern Anatolia, although *Peltigera polydactyla* living in Northern Anatolia had the highest value of K (0.640 ± 0.045 %). The average Ti concentrations in lichen species living in Eastern Anatolia was higher than in the other species living in Northern Anatolia. There was considerable difference in Ba concentration of *Cladonia foliacea* living in Northern Anatolia. It is noticed that all lichen species collected from Eastern Anatolia had Sr (excluded *Physcia aipolia*), but we couldn't determine any Sr amount in most lichen species (*Bryoria fuscescens, Peltigera polydactyla, Cetrelia olivetorum* and *Evernia divaricata*) collected from Northern Anatolia. It is thus suggested that Sr may not be a necessary element for metabolism of lichens. But if there is Sr in the substrate on which lichens live, lichens

TABLE-2
ELEMENT CONCENTRATIONS OF LICHEN SPECIES AND SUBSTRATA

		Sample No.												Certified value (µg/g)
		1	2	3	4	5	6	7	8	9	10	11	12	
Elemental Concentration (%)	Ca	1.175±0.070	1.276±0.077	1.492±0.092	2.563±0.154	1.979±0.119	2.866±0.172	6.564±0.394	1.689±0.101	1.855±0.111	3.566±0.214	2.605±0.156	1.647±0.099	2600
	K	0.249±0.017	0.640±0.045	0.181±0.013	0.250±0.018	0.471±0.033	0.107±0.008	0.206±0.014	0.417±0.029	0.371±0.026	0.234±0.016	0.257±0.018	0.377±0.026	1840±200
	Fe	1.501±0.121	0.285±0.023	0.629±0.052	0.319±0.025	5.434±0.435	3.064±0.245	2.682±0.215	1.682±0.135	5.653±0.452	1.939±0.155	3.750±0.300	2.457±0.197	430±50
	Ti	0.046±0.004	0.019±0.002	0.021±0.002	0.025±0.002	0.342±0.027	0.130±0.012	0.234±0.019	0.142±0.011	0.288±0.023	0.177±0.014	0.384±0.031	0.237±0.019	5-35
	Ba	0.061±0.004	0.025±0.002	0.076±0.005	0.016±0.001	0.092±0.006	0.306±0.021	0.084±0.006	0.036±0.003	0.110±0.008	0.041±0.003	0.091±0.006	0.046±0.003	5.5
	Sr	ND	ND	ND	ND	0.038±0.003	0.074±0.006	0.041±0.003	ND	0.042±0.003	0.037±0.003	0.044±0.004	0.039±0.003	8.5-25

Elemental concentration (%)							
Sample rock from Erzurum	Sample bark of *Alnus glutinosa* from Erzurum	Sample soil from Maçka-Trabzon	Sample bark of Giresun and Ordu	Sample bark of *Fagus orien talis* from Murgul-Artvin	Sample rock from Murgul district, Artvin	Sample soil from Murgul- Artvin	
1.420±0.016	3.128±0.126	1.029±0.015	3.478±0.146	3.778±0.146	1.312±0076	1.019±0.045	Ca
4.657±0.294	4.737±0.292	5.850±0.311	4.737±0.292	4.737±0.292	4.553±0.294	5.784±0.323	K
14.757±0.611	ND	6.100±0.276	ND	ND	14.551±0.843	7.122±0.398	Fe
0.123±0.007	0040±0.001	0.205±0.001	0.037±0.001	0.025±0.001	0.133±0.007	0.210±0.011	Ti
0.367±0.016	ND	1.670±0.067	ND	ND	0.337±0.016	1.760±0.087	Ba
ND	ND	0.010±0.001	ND	ND	ND	0.030±0.002	Sr

ND = Not detected

may absorb the element and accumulate it in their bodies such as other metals, even though they don't need physiologically all of these elements. As a matter of fact, it has been well known that uptake of metals and other inorganic elements and higher or lower element accumulation abilities of lichens are directly related to morphological, anatomical, physiological features, surface area, large intercellular space, high cell membrane permeability, pH and having thin or thick or no upper or lower cortex of the species. The work on heavy metal pollution using lichens as indicators is reported by Aslan *et al.*[13].

In this study, these lichen species were collected from two different geographical regions in 12 well known stations that are environmentally very clean. Although concentrations of Ti show largely high concentrations in some lichen species living on some areas (*Umbilicaria vellea*, Erzurum-Kösk village and *Xanthoria parietina*, Ordu-Ünye Çinarsuyu) with comparison to others, all of these lichen species living on very different ecologic habitats have at least an amount of Ti. It is also unknown whether Ti has any role in metabolism of livings. On the other hand, these localities are small rural or sub-rural sites, but not industrial areas. So, pollution of soil is not possible. However all of these elements (included Ti) found in the study are soil originated. It means that they are not atmospheric pollutants. Therefore these elements cannot be carried from an area to the other areas *via* air movements. It is believed that these two regions (Eastern and Northern Anatolia) naturally contain different concentrations of Ti in their habitats. Ti is one of valuable metals. Since Ti concentrations are at high levels in Erzurum-Kösk village and Ordu-Ünye-Çinarsuyu localities in comparison to the others, this finding can be used in searching for Ti mines as a clue. We must here agree that if we could have found the same species of these lichens in these different localities, we would have been exactly sure that the idea is strongly true. So, it is necessary to do more research in an experimental design as we mentioned.

Bryoria fuscescens (on *Fagus orientalis*) and *Peltigera polydactyla* (on moss) which were collected from different stations of the same district (Murgul) accumulated different amounts of K, Fe, Ti and Ca, but similar amounts of Ca. That may be because *Bryoria fuscescens* is a futicose species and *Peltigera polydactyla* is a foliose species and maybe their different substrata. Two fruticose species *Cladonia foliacea* and *Ramalina polymorpha*, collected from different locations (Trabzon and Erzurum) and substrata (soil and rock), accumulated fairly different amounts of Fe, Ba, Sr, while they accumulated quite close amounts of Ca, Ti and K. On the other hand, *Ramalina polymorpha* was collected from a sub-rural area while *Cladonia foliacea* was collected from rural area. In another study previously done in Erzurum, *Ramalina capitata* and *Ramalina pollinaria* were found to have accumulated lower amounts of Ti, Ca, Fe, Sr and Ba except K than *R. polymorpha* in this study[14,15].

Xanthoria elegans and *X. parietina*, collected from different localities (from Ordu and Erzurum provinces, Turkey) and substrata (rock and *Robinia* sp.) accumulated different amounts of K, Fe, Ba while they accumulated quite close amounts of Sr[16].

Especially species growing on soil accumulated more Ba and Sr than the others[14,15]. In this study Ca, K, Ba, Ti, Fe was measured in eight foliose species in eight stations while Sr was measured in only five foliose samples. These are *Xanthoria parietina, Xanthoparmelia pulla, Dermatocarpon intestiniforme, Umbilicaria vellea* and *Xanthoria elegans*.

Taking into account the foliose species with regard to accumulation of Ca, Fe, K, Ti, Ba and Sr, lower amounts of Fe, Ca and K were detected in foliose species used in this study than the other studies done in Turkey, but more amounts in terms of Ti, Ba and Sr[13-15]. Especially Fe was accumulated by *Xanthoria parietina, Dermatocarpon minatum* and *Peltigera praetextata* in Trabzon and *Umbilicaria polyrrhiza* in Murgul-Artvin (*ca.* 3-8 folds). *Xanthoria parietina, Dermatocarpon minatum* and *Peltigera praetextata* were collected near the city center of Trabzon. As for *Umbilicaria polyrrhiza* it might have been collected in Murgul-Artvin from rocks in Fe. Foliose species used in this study absorbed more amounts of Ti, Ba and Sr than those of the other studies in Turkey[13,15,16]. This is so because the wind, the amounts of rainfall, soil and rock types and also anatomical and morphological features of the species are different.

Metal-absorbing capabilities of lichens are directly related to their anatomical and morphologic structure. As the surface gets wider, lichens accumulate more metals.

Other factors that increase metal uptake are wide intercellular space, high cell permeability, humidity, high amount of atmospheric pollutants and thin upper cortex or no upper cortex[17]. When we take into account the foliose species used in the studies of element analyses in Turkey including this work, lower amounts of Fe, Ca, K and Sr were detected in foliose species used in this study than the other studies done in Turkey, but more amounts in terms of Ti and Ba[13-15,18]. The most amounts of Ca are accumulated by *Protoparmeliopsis muralis, Xanthoparmelia stenophylla* and *X. pulla*. *Dermatocarpon miniatum* absorbs the highest amounts of K. *Protoparmeliopsis muralis* and *Umbilicaria vellea* accumulate Ti more than the foliose lichen samples. *Umbilicaria polyrrhiza* absorbs most Fe in respect to the other foliose species. *Xanthoparmelia stenophylla, Xanthoria parietina* and *Dermatocarpon miniatum* accumulate lower amounts of Fe, respectively in comparison with *Umbilicaria vellea*. The highest amounts of Ba is absorbed by *Umbilicaria polyrrhiza* while Sr by *Xanthoparmelia pulla*, *Dermatocarpon intestiniforme* and *Umbilicaria vellea*.

Conclusion

In this study *Cladonia foliacea*, growing on soil, accumulated the highest amounts of Ba and Sr, while Fe and Ti were accumulated by *Dermatocarpon intestiniforme, Umbilicaria vellea* and *Xanthoria parietina*. On the other hand, the highest amounts of K were accumulated by *Peltigera polydactyla* while Ca by *Xanthoparmelia pulla*. Sr was not detected in *Bryoria fuscescens, Peltigera polydactyla, Cetrelia olivetorum, Evernia divaricata* and *Physcia aipolia*. According to the results, foliose species can generally accumulate higher amounts of elements than the others[17,18].

As a result, it is noticed that generally there are differences in concentrations of these trace elements in different lichen species living in two geographically different regions regardless of differences of industrial pollutions in these regions. It has been known that there is no report is available from its habitat. If a lichen species contains a higher concentration of an element than its normal concentration of that element in varying amounts, then that element is a valuable element like Ti that is found in sub-rural and ecologically clean locations. It is thought that these kind findings can be useful to determine in mining researches as a clue. In addition, according to present results, it is suggested that although Sr is not a necessary element for lichen metabolism, lichen species can take it into their bodies from their habitats (if there is) and store it.

REFERENCES

1. J.E. Sloof and B.T. Wolterbeek, *J. Environ. Radioact.*, **16**, 229 (1992).
2. S.M. Al-Shayeb, M.A. Al-Rajhi and M.R.D. Seaward, *Sci. Total Environ.*, **168**, 1 (1995).
3. E. Tirasoglu, Ö. Sögüt, G. Apaydin, V. Aylikçi and N. Damla, *J. Quant. Spectros. Radiat. Transfer*, **102**, 396 (2006).
4. L. Perring, D. Andrey, M. Basic-Dvorsak and D. Hammer, *J. Food Compos. Anal.*, **18**, 655 (2005).
5. R. Dumlupinar, F. Demir, G. Budak, A. Karabulut, N. Kadi, H. Karakurt and S. Erdal, *J. Quant. Spectros. Radiat. Transfer*, **103**, 331 (2007).
6. Ö.K. Erman, A. Gürol and R. Dumlupinar, *Fresen. Environ. Bull.*, **7**, 697 (2006).
7. M. Alvarez and V. Mazo-Gray, *X-Ray Spectrometry*, **20**, 67 (2005).
8. O.W. Purvis, B.J. Coppins, D.L. Hawksworth, P.W. James and D.M. Moore, The Lichen Flora of Great Britain and Ireland, Natural History Museum Publications in Association with The British Lichen Society, London (1992).
9. S. Kiliçoglu, N. Araz and H. Devrim, Meydan Larousse, Büyük Lügat ve Ansiklopedi, Meydan Yayinevi, 19, Istanbul (1986).
10. Y. Akman, Iklim ve Biyoiklim (Biyoiklim Metodlari ve Türkiye IklimLeri), Kariyer Matbaacilik, Ankara(1999).
11. E. Tirasoglu and M. Ertugrul, *J. Radioanal. Nucl. Chem.*, **237**, 147 (1998).
12. B.J.B. Nyarko, D. Adomako, Y. Serfor-Armah, S.B. Dampare and D.E.H.K. Adotey Akaho, *Radiat. Phys. Chem.*, **75**, 954 (2006).
13. A. Aslan, G. Budak, E. Tirasoglu, A. Karabulut, Y. Karagöz, G, Apaydin, B. Ertugral and U. Çevik, *Fresen. Environ. Bull.*, **13**, 740 (2004).
14. A. Aslan, G. Budak and A. Karabulut, *J. Quant. Spectros. Radiat. Transfer*, **88**, 423 (2004).
15. A. Aslan, G. Budak, E. Tirasoglu and A. Karabulut, *J. Quant. Spectros. Radiat. Transfer*, **97**, 10 (2006).
16. M. Rossbach and S. Lambrecht, *Croat. Chim. Acta*, **79**, 119 (2006).
17. J. Garty, *Environ. Exper. Bot.*, **27**, 127 (1987).
18. D. Mendil, M. Tuzen, K. Yazici and M. Soylak, *Bull. Environ Contam. Toxicol.*, **74**, 190 (2005).

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