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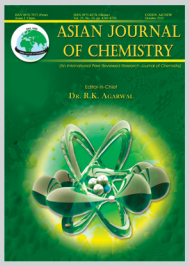

Comparison of Trace Element Levels of Lichen Species Living on Different Habitats

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In this paper, concentrations of 18 trace elements, Al, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Se, Si and Zn were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) in 16 lichen species living in four different habitats at 39 localities in Ardahan (Turkey). Cd, Na, Ni and Pb are the only available elements in some lichens living in some certain localities. Cd, Na, Ni and Pb are not necessary elements for the lichen metabolism, but the lichen species can take them into their bodies from their habitats or atmosphere (if there are) and store them even if it haven't got any role in the lichen metabolism. Moreover, some lichens living in some localities contain high concentrations (almost 177 folds of Fe: Ardahan-Hanak Altas: 1.13266 %), 104 folds of Ca (Posof, 2 km to Kursunçavus, mainroadside: 3.1066.6 %), 96 folds of Na (Ardahan-Hanak Altas: 0.090 %), 36 folds of Ni (Ardahan-Hanak Altas: 0.002386 %), 30 folds of Cr (Ardahan-Hanak Altas: 0.001853 %), 27 folds of Al (Ardahan, Göle 20 km to Ardahan mainroad side: 0.6960 %) and 22 folds of Mn (Ardahan-Hanak, Altas: 0.03946 %). The highest values of Al, Cr, Cu, K, Mn, Ni, P, S and Zn were determined in *Dermatocarpon miniatum*, while the highest values of Cd, Fe, Mg and Na were accumulated by *Peltigera rufescens*. On the other hand, the highest amounts of B and Se were accumulated by *Peltigera canina*, Ca by *Rhizoplaca chrysoleuca* and Pb by *Parmelia sulcata*.

Key Words: Ardahan, ICP-OES, Lichen, Trace elements, Turkey.

INTRODUCTION

Monitoring of air pollution with living organisms provides low-cost information on the nature and quantity of pollutants[1,2].

Bioaccumulation of trace metals from atmospheric deposition is currently evaluated by some environmental biomonitors such as mosses, plant leaves and lichens[3]. In particular lichens whose mineral nutrition is dependent on wet and dry depositions from the atmosphere are regarded as suitable tools for monitoring the relative levels of atmospheric pollution. In fact they are able to accumulate and store many airborne substances found in the environment as reported in literature[4].

The advantages of using lichens as quantitative biological monitors of air metal deposition in comparison to conventional air sampling techniques rise from that lichens are present in most terrestrial habitats, are perennial, inexpensive and easy reproduced. The quality of lichen analysis is affected by specific matrix effect so the accuracy of an analytical methodology can only really be proven by analyzing lichen reference materials[5,6] or by comparing the results obtained for real samples by independent analytical techniques[7].

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). 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[8].

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[9].

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. It has recently been getting more considerable effort to determine the concentrations of trace elements in lichens at the last years using ICP-OES[10-12]. However, no reports have

ever compared the elemental concentrations of some lichens species, which had been living in Ardahan. Ardahan, which is stiuated in Northeastern of Anatolian of Turkey and with a terrestrial wet and cold climate, is rich in terms of the diversity of lichen species.

Aim of this paper is to validate, through trials carried out by two laboratories an analytical procedure consisting of a microwave oven digestion, associated with modern spectroscopic techniques such as ICP-OES for the determination of trace elements in lichens.

EXPERIMENTAL

Sampling: Sixteen lichen species (Table-1) were collected from four different habitats *Pinus* sp., rock, moss and soil in 39 stations of Ardahan (Turkey: the average altitude of this region changes from 138 m to 2302 m) in 2008 and 2009. A stereo-microscope, a light-microscope and the usual spot tests were used to identify the samples with reference to Purvis *et al*.[13]. Sample specimens have been stored in the herbarium of Biology Department, Karadeniz Technical University, Trabzon, Turkey.

Ardahan is a northeastern Anatolian province of Turkey with a surface area of 5.453 km^2, where Turkey borders with Georgia. It is surrounded by Acaristan Autonomous Republic to the north, Georgia and Armenia to the northeast, Kars to the south, Erzurum to the southwest and Artvin to the west. It usually has a high and rough terrain at northeastern portion especially along the border of eastern Anatolian and northeastern Anatolian regions. Ardahan is under the effects of hard terrestrial wet and cold climate, winter takes so long and cold[14]. The average temperatures is 3.6 ºC and the annual precipitations is 490.3 mm in Ardahan[15]. This is attractive open countryside, which however spends many months of the year under snow. At this altitude temperatures on average reach -20 ºC and can drop below freezing all year round, including summer months.

Phytogeographically, the area falls in Irano Turanean floristic region. Approximately, 5 % of Ardahan is covered with forest vegetation. *Pinus slyvestris* L. is the most dominant member of these forest being one of the main three population to affect the distribution of lichens together with *Populus, Salix* and *Prunus* sp.

Metals are emitted into the Ardahan environments from different sources, *i.e.*, transportation, industrial activities, fossil fuels, agriculture and other human activities.

Chemical analysis: The lichen samples were dried at 105 ºC for 24 h (to a constant weight). After grinding samples passed through a nylon sieve (0.5 mm) and 0.3 g of each sample was placed in pyrex reactors of a CEM MARSXpress microwave digestion unit. Digestion was carried out using a mixture of concentrated HNO_3: $HClO_4$ in 3:1 proportion. Afterwards, the samples were filtered in such a way as to make their volumes up to 100 mL with ultra-pure distilled water. A blank digest was carried out in the same way. The element standard solutions used for calibration were prepared by diluting stock solutions of 1000 mg/L of each element supplied from SCP Science. Heavy metals concentrations were measured by Varian 720 ES model ICP-OES[16-18]. The element analyses in lichen samples were recorded as means triplicate measurements. In the ICP-OES analysis, the following wavelength (nm) lines were used; Al 308.215, B 249.678, Ca 315.887, Cd 226.502, Cr 205.560, Cu 324.754, Fe 259.940, K 766.491, Mg 279.078, Mn 257.610, Na 588.995, Ni 231.604, P 214.914, Pb 220.353, S 181.972, Se 196.026, Si 251.611, Zn 213.857. The analytical process quality was also controlled by certified reference material of NCS DC73350 (leaves of poplar). The analysis of these standard reference materials showed good accuracy, with the recovery rates of the metals, between 90.3 and 108.9 % (Table-2). Recoveries were compared with the American Organization of Analytical Chemists criteria[19].

RESULTS AND DISCUSSION

The presented work has shown that different specimens of lichens can be analyzed and 18 trace elements Al, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Se, Si and Zn were determined by ICP-OES. The concentrations of 18 elements in 16 lichen species are shown in Table-3. The concentrations of Ca, Fe, Al, K, S, Mg and P were always higher than the other trace element concentrations in these lichens. 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, 18 different lichen species, 10 of which morphologically had foliose and the others had fruticose structure, were collected from 39 different localities. The highest values of Al, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Se, Si and Zn were in *Dermatocarpon miniatum, Peltigera canina, Rhizoplaca chrysoleuca, Dermatocarpon miniatum, Dermatocarpon miniatum, Dermatocarpon miniatum, Dermatocarpon miniatum, Ramalina polymorpha, Dermatocarpon miniatum, Dermatocarpon miniatum, Peltigera rufescens, Dermatocarpon miniatum, Dermatocarpon miniatum, Parmelia sulcata, Dermatocarpon miniatum, Peltigera canina, Peltigera horizontalis* and *Dermatocarpon miniatum* respectively. Among these trace elements the highest values of Al, Cr, Cu, K, Mn, Ni, P, S and Zn were determined in *Dermatocarpon miniatum*, living in Ardahan-Göle mainroad side, Hanak:Altas village-roadside and Çildir: Öncül village-roadside. These samples were collected from roadside and near the main road mostly.

The highest values of Ca was determined in *Rhizoplaca chrysoleuca* (Posof-20 km to Kursunçavus, mainroad side), *Xanthoparmelia stenophylla* (Hanak: Altas village) and *Hypogymnia physodes* (Posof: Center, control tower forests) (3.10666, 2.98666 and 2.49333 % respectively), B in *Anaptychia setifera* (0.00272 %, Posof: Alköy village), Cd in *Peltigera rufescens* (0.000066 %: Hanak-Altas village), Fe in *Peltigera rufescens* (1.13266 %: Hanak: Altas village), Mg in *Peltigera rufescens* (00.2018 %: Hanak-Altas village), Na in *Peltigera rufescens* (0.0090 %: Hanak: Altas village), Pb in *Parmelia sulcata* (0.00064 %: Posof: Kursunçavus), Se in *Peltigera canina* (0.000753 %: Hanak: Altas village), Si in *Peltigera leucophlebia* (0.02836 %: Göle: Yeniköy forests).

We noticed that we couldn't determine any Cd, Na, Ni and Pb in most of lichens. Sodium was not determined in

TABLE-1
LICHEN SAMPLES COLLECTED FROM THE STUDY AREA

No	Lichen	Locality	Coordinates	Altitude (m)	Substrate	Date
1	*Parmelia sulcata*	Ardahan, Posof-Kursunçavus	41°31'37.76"N, 42°37'16.40"E	1790	*Pinus* sp.	11.08.2008
2	*Hypogymnia physodes*	Ardahan, Posof-Center-Kontrol Tower forests	41°31'45.03"N, 42°43'59.90"E	2000	*Pinus* sp.	08.12.2008
3	*Cetraria islandica*	Ardahan, Posof-Center, Forest establishment storage	41°29'44.17"N, 42° 44'03.88"E	1381-1430	Soil	07.12.2008
4	*Cetraria islandica*	Ardahan, Posof- Center-Kontrol Tower forests	41°31'45.03"N, 42°43'59.90"E	2000	Soil	08.12.2008
5	*Cetraria islandica*	Göle-Eskidemirkapi	40°51'00.91"N 42°47'35.90"E	2155	Soil	11.12.2008
6	*Cladonia furcata*	Ardahan, Posof-Center, Forest establishment storage	41°29'44.17"N, 42° 44'03.88"E	1381-1430	Soil	07.12.2008
7	*Pseudevernia furfuracea*	Ardahan, Posof- Center-Kontrol Tower forests	41°31'45.03"N, 42°43'59.90"E	2000	Soil	08.12.2008
8	*Anaptychia setifera*	Ardahan, Posof-Alköy Forests	41°28'24.51"N, 42°46'37.27"E	1750-1900	*Pinus* sp.	01.08.2009
9	*Pseudevernia furfuracea*	Ardahan, Göle-Yenidemirkapi	40°50'54.50"N 42°43'12.80"E	2030	*Pinus* sp.	11.12.2008
10	*Pseudevernia furfuracea*	Ardahan, Hanak-Altas village	41°09'40.08"N, 42°52'27.76"E	1800	*Pinus* sp.	28.07.2009
11	*Pseudevernia furfuracea*	Ardahan, Göle-Çakirüzüm Forests	40°47'44.90"N, 42°31'59.35"E	2233	*Pinus* sp.	21.07.2008
12	*Rhizoplaca chrysoleuca*	Ardahan, Posof-Kontrol Tower forests	41°31'45.03"N, 42°43'59.90"E	2000	Siliceous rock	08.12.2008
13	*Rhizoplaca chrysoleuca*	Ardahan, Posof, 2 km to Kursunçavus, maninroad side	41°31'13.57"N, 42°39'26.02"E	1835	Siliceous rock	11.08.2008
14	*Cetraria islandica*	Ardahan, Göle-opposite of Çakirüzüm Forests	40°48'28.88"N, 42°33'21.61"E	2090	Soil	12.12.2008
15	*Ramalina polymorpha*	Ardahan-Çamlibel	41°12'15.39"N, 42°33'08.14"E	2302	Siliceous rock	31.07.2009
16	*Peltigera aphthosa*	Ardahan, Posof-Alköy Forests	41°28'24.51"K 42°46'37.27"D	1750-1900	Moss	01.08.2009
17	*Rhizoplaca chrysoleuca*	Ardahan, Çildir-Yildirimtepe Village	41°07'52.81"K 43°07'34.61"D	1990	Siliceous rock	08.08.2009
18	*Ramalina polymorpha*	Ardahan, Çildir-Öncül village	41°14'21.99"K 43°09'37.41"D	1762	Siliceous rock	15.08.2009
19	*Dermatocarpon miniatum*	Ardahan, Hanak-Altas village	41°09'40.08"N, 42°52'27.76"E	1735	Siliceous rock	28.07.2009
20	*Ramalina polymorpha*	Ardahan, Hanak-Altas village	41°09'40.08"N, 42°52'27.76"E	1735	Siliceous rock	28.07.2009
21	*Xanthoparmelia stenophylla*	Ardahan, Hanak-Altas village	41°09'40.08"N, 42°52'27.76"E	1735	Calcareous rock	28.07.2009
22	*Dermatocarpon miniatum*	Ardahan, Çildir-Öncül village	41°14'21.99"N, 43°09'37.41"E	1762	Siliceous rock	15.08.2009
23	*Peltigera rufescens*	Ardahan, Hanak-Altas village	41°09'40.08"N, 42°52'27.76"E	1735	Soil	28.07.2009
24	*Peltigera canina*	Ardahan, Hanak-Altas village	41°09'40.08"N, 42°52'27.76"E	1735	Soil	28.07.2009
25	*Rhizoplaca chrysoleuca*	Ardahan, Ardahan-ÇamLibel	41°12'15.39"K, 42°33'08.14" D	2302	Siliceous rock	31.07.2009
26	*Dermatocarpon miniatum*	Ardahan, Göle, 20 km to Ardahan-mainroad side	40°54'57.54"K 42°35'48.11"D	1980-2000	Siliceous rock	26.07.2009
27	*Peltigera rufescens*	Ardahan, Göle-20 km to Ardahan-mainroad side	40°54'57.54"K 42°35'48.11"D	1980-2000	Soil	26.07.2009
28	*Peltigera apthosa*	Ardahan, Göle-Yeniköy forests	40°58'00.27"N, 42°29'01.83"E	1960	Moss	27.07.2008
29	*Peltigera horizontalis*	Ardahan, Göle-Yeniköy forests	40°59'16.79"N, 42°25'58.78"E	1960-2019	Moss	27.07.2008
30	*Peltigera canina*	Ardahan, Kent Forests	41°02'45.75"N 42°35'24.37"E 41°02'52.74"N 42°36'19.00"E	1983-2034	Moss	09.12.2008
31	*Ramalina polymorpha*	Ardahan, center, Çamlibel	41°12'15.39"K, 42°33'08.14" D	2302	Siliceous rock	31.07.2009
32	*Peltigera leucophlebia*	Ardahan	41°02'34.52"N 42°26'32.44"E 40°51'13.48"N 42°47'35.28"E	1966-2124	Moss	26.07.2009

No	Lichen	Locality	Coordinates	Altitude (m)	Substrate	Date
33	*Peltigera horizontalis*	Ardahan-Yalnizçam forests	41°02'34.52"N 42°26'32.44"E 40°51'13.48"N 42°47'35.28"E	1966-2124	Moss	13.08.2008
34	*Peltigera canina*	Ardahan, Göle-Yeniköy forests	40°58'00.27"N 42°29'01.83"E 40°59'16.79"N 42°25'58.78"E	1960-2019	Moss	27.07.2008
35	*Umbilicaria vellea*	Ardahan, Göle-Eskidemirkapi	40°51'13.48"N 42°47'35.28"E	2124	Siliceous rock	11.12.2008
36	*Peltigera horizontalis*	Ardahan, Göle-Eskidemirkapi forests	40°51'00.91"N 42°47'35.90"E	2155	Moss	11.12.2008
37	*Peltigera praetextata*	Ardahan, Göle-Eskidemirkapi forests	40°51'00.91"N 42°47'35.90"E	2155	Moss	11.12.2008
38	*Rhizoplaca chrysoleuca*	Ardahan, Hanak-Altas Village	41°09'40.08"K 42°52'27.76"D	1735	Siliceous rock	28.07.2009
39	*Pseudevernia fufuracea*	Ardahan, Göle-Köprülü Plateau	40°50'11.04"N 42°24'03.37"E 40°50'32.35"N 42°24'17.55"E	2169-2274	*Pinus* sp.	28.07.2008

TABLE-2
RESULTS ON ELEMENT LEVELS OF REFERENCE MATERIALS

Element (mg kg^{-1})	NCS DC73350 (leaves of poplar)		Recovery (%)	AOAC[a] (%)
	Certified	Analytical value		
Cd	0.32 ± 0.07	0.32 ± 0.01	100.0	80-110
Cr	0.55 ± 0.07	0.56 ± 0.005	101.8	80-110
Cu	9.3 ± 1.0	8.4 ± 0.45	90.3	80-110
Fe	274 ± 17	287.66 ± 11.06	104.9	90-107
Mn	45 ± 4	43.6 ± 6.41	96.8	80-110
Pb	1.5 ± 0.3	1.63 ± 0.37	108.6	80-110
Ni	1.9 ± 0.3	2.00 ± 0.28	105.2	80-110
Zn	37 ± 3	35.93 ± 3.23	97.1	80-110
B	53 ± 5	54.5 ± 2.98	102.8	80-110
Al (%)	0.104 ± 0.006	0.109 ± 0.002	104.8	95-105
K (%)	1.38 ± 0.07	1.41 ± 0.05	102.1	97-103
Ca (%)	1.81 ± 0.13	1.85 ± 0.17	102.2	97-103
Mg (%)	0.65 ± 0.05	0.63 ± 0.02	96.9	95-105
Na	200 ± 13	198 ± 4	99.0	90-107
P	1680 ± 60	1641.46 ± 141	97.7	97-103
S (%)	0.35 ± 0.04	0.37 ± 0.01	105.7	90-107
Se	0.14 ± 0.04	0.13 ± 0.03	92.8	80-110
Si (%)	0.71 ± 0.08	0.72 ± 0.04	101.4	95-105

Parmelia sulcata, Hypogymnia physodes, Cetraria islandica, Cladonia furcata, Pseudevernia furfuracea, Anaptychia setifera, Rhizoplaca chrysoleuca, Ramalina polymorpha, Peltigera leucophlebia, Xanthoparmelia stenophylla, Dermatocarpon miniatum Peltigera horizontalis, Peltigera canina, Peltigera praetextata and *Umbilicaria vellea* collected from localities 1, 2, 3, 4, 6-17, 21, 22, 25, 26, 29-39.

Cadmium was not observed in *Cetraria islandica*, *Cladonia furcata, Pseudevernia furfuracea, Anaptychia setifera, Ramalina polymorpha, Peltigera leucophlebia, Peltigera canina, Peltigera horizontalis, Peltigera praetextata, Rhizoplaca chrysoleuca* collected from localities 3-9, 14-16, 20, 30-32, 34, 36-38 while Ni was not found in *Parmelia sulcata, Hypogymnia physodes, Cetraria islandica, Cladonia furcata, Anaptychia setifera, Pseudevernia furfuracea, Ramalina polymorpha, Rhizoplaca chrysoleuca, Peltigera horizontalis, Peltigera canina and Umbilicaria vellea* from localities 1-18, 20, 25, 29-32, 34-36, 38. On the other hand Pb was not determined in *Cetraria islandica, Cladonia furcata Pseudevernia furfuracea, Anaptychia setifera, Rhizoplaca chrysoleuca, Ramalina polymorpha, Peltigera leucophlebia, Dermatocarpon miniatum, Peltigera canina, Peltigera horizontalis, Umbilicaria vellea, Peltigera praetextata* collected from localities 3-12, 14-16, 18, 20, 22, 24, 28-36.

It is interesting that these samples are mostly foliose and collected from mosses mostly, but some were from barks and rocks. This may be reason that Cd, Na, Ni, Pb may not be a necessary element metabolism of lichens. But if there is Cd, Na, Ni, Pb in the substrate on which lichens live, lichens 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 is 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. A report on heavy metal pollution using lichens as indicators has been presented[20].

In this study, these lichen species were collected from Ardahan 39 localities that are environmentally very clean. Although concentrations of Cd, Na, Ni and Pb show significantly low concentrations in some lichen species living on some areas.

TABLE-3
ELEMENT CONCENTRATIONS OF LICHEN SPECIES AND SUBSTRATA (mg/kg)

Lichen	Al	Ca	Fe	K	Mg	Na	P	S	Si	Zn	B	Cd	Cr	Cu	Mn	Ni	Pb	Se
1	1443.10	5938.0	1395.8	2362.66	644.40	ND	849.86	956.93	89.1333	34.333	23.33	0.133	3.33	5.733	75.366	ND	6.4	6.066
2	801.33	24933.33	1107.33	2107.33	607.33	ND	450.00	699.33	135.266	28.866	19.33	0.26	2.33	2.66	75.73	ND	0.66	5.733
3	250.00	11226.66	365.33	2366.66	344.66	ND	867.33	522.00	205.60	23.00	16.933	ND	0.80	1.60	74.20	ND	ND	6.20
4	409.33	1433.33	574.66	2273.33	390.00	ND	556.66	515.33	167.20	24.533	23.733	ND	1.20	1.533	34.466	ND	ND	6.133
5	895.33	16866.66	1263.33	1788.0	536.00	83	467.33	443.33	106.6	21.533	21.00	ND	1.533	1.86	53.53	ND	ND	6.066
6	558.66	2916.0	892.0	1983.33	438.66	ND	854.66	590.66	155.866	15.20	19.466	ND	1.133	2.533	62.733	ND	ND	6.066
7	689.33	13200.0	1110.66	2244.66	554.66	ND	480.66	1202.66	60.066	32.60	20.20	ND	1.866	2.933	41.266	ND	ND	7.066
8	1326.66	5320.0	2016.0	2146.66	804.00	ND	1167.33	1310.66	190.66	29.73	27.20	ND	3.533	4.866	143.00	ND	ND	5.533
9	640.66	16246.66	943.33	1944.66	431.33	ND	861.33	1282.00	126.066	29.93	18.066	ND	1.933	3.33	41.066	ND	ND	5.266
10	748.00	14660.0	1204.0	1826.0	512.00	ND	505.33	1072.66	116.20	35.00	19.133	0.2	2.266	3.133	48.46	ND	ND	6.333
11	876.00	15166.66	1228.66	1681.33	484.00	ND	388.00	1091.33	125.40	41.33	19.266	0.133	3.733	3.46	42.33	ND	ND	7.133
12	842.00	18806.66	1569.33	1001.33	340.66	ND	612.00	714.66	84.266	26.133	15.733	0.133	2.33	2.933	26.60	ND	ND	6.00
13	1033.33	31066.66	1556.0	1113.33	354.66	ND	502.00	687.33	102.133	28.133	16.466	0.2	2.80	2.733	27.40	ND	4.6	5.40
14	269.33	24200.0	408.66	1295.33	252.66	ND	358.66	571.33	125.733	16.60	17.33	ND	0.66	1.40	20.066	ND	ND	7.133
15	682.00	4553.33	876.66	1397.33	360.66	ND	1123.33	1232.66	134.73	19.13	16.066	ND	1.80	3.00	19.133	ND	ND	6.06
16	415.33	297.33	651.33	4453.33	627.33	ND	1458.00	947.33	223.466	16.533	21.866	ND	1.266	2.933	44.60	ND	ND	6.40
17	2700.00	21006.66	3553.33	1557.33	676.66	ND	804.00	1016.00	104.933	34.66	17.80	0.266	6.933	3.266	52.933	ND	1.4	6.333
18	732.66	7360.0	1040.0	1816.66	412.00	0.9333	1106	1480.00	131.066	23.80	15.133	0.066	2.133	3.80	26.60	ND	ND	5.066
19	8953.3	3953.30	12220.0	5113.3	1869.33	9.6	1030.66	3253.33	90.40	38.80	21.133	0.8	18.53	17.26	394.6	23.86	1.6	6.26
20	417.3	5766.60	658.60	18776	336.60	2.93	1142.66	1317.33	104.20	19.06	14.06	ND	1.33	3.13	17.20	ND	ND	7.466
21	3366.6	29866.6	6266.6	2136	994.66	ND	584.00	814.66	120.20	28.00	15.33	0.4	8.533	7.60	93.30	5.533	0.4	7.466
22	2302.6	2146.60	5573.3	4600	1278.66	ND	1802.66	3826.6	329.00	29.80	16.73	0.331	6.26	11.40	192.30	12.06	ND	7.466
23	5966.6	7360.0	11326.6	2186.6	2018.00	90	836.00	1060.00	92.80	35.00	20.133	0.666	12.93	11.06	393.30	17.40	1.33	4.266
24	1880.00	8913.30	2700.0	3753.3	1403.33	15.8	1129.33	1442.66	125.26	31.66	26.60	0.2	5.93	6.40	81.06	0.66	ND	7.53
25	1442.6	24386.6	1719.0	2496.6	694.00	ND	1144.00	1200.66	114.46	36.00	14.40	0.266	4.53	3.93	34.53	ND	2.6	6.733
26	6960.0	2866.60	6640.0	3053.3	1295.3	ND	996.66	2946.6	75.80	97.866	15.733	0.466	12.46	11.86	197.53	5.80	0.66	5.33
27	3340.0	5153.30	3320.0	333.3	1058.6	11.8	1614.0	1183.33	143.00	29.066	16.33	0.266	7.26	9.20	141.06	0.86	0.86	6.46
28	3012.0	4180.00	3391.3	4920.0	936.66	5.066	1489.3	1017.3	283.60	23.80	17.133	0.133	6.86	8.86	243.00	2.60	ND	6.20
29	1406.6	4280.00	1930.6	2673.3	780.00	ND	927.33	934.66	437.40	25.533	19.533	0.66	3.80	4.06	144.00	ND	ND	6.06
30	1021.3	9013.30	1419.3	3493.3	1060.0	ND	1095.3	1269.3	200.06	31.20	20.133	ND	3.80	7.066	130.06	ND	ND	6.33
31	978.60	7793.30	1157.3	1236.6	343.33	ND	738.66	1233.33	133.93	18.20	12.733	ND	2.66	3.60	22.83	ND	ND	6.73
32	663.30	4893.30	857.3	2653.3	782.00	ND	652	885.33	212.53	15.20	21.80	ND	1.866	3.20	74.53	ND	ND	5.53
33	3186.6	7800.00	4640.0	2440.0	1263.3	ND	777.33	1048.66	182.8	24.20	17.66	0.20	11.00	7.53	246.6	1.13	ND	6.46
34	1176.0	4806.60	1504.6	2600.0	638.00	ND	697.33	924.00	279.3	20.46	16.93	ND	2.93	3.80	209.2	ND	ND	6.53
35	6726.6	1562.00	1552.0	2806.6	639.30	ND	996.00	1571.33	168.13	41.86	14.40	0.13	3.133	3.86	55.20	ND	ND	5.60
36	1354.6	5193.30	1774.6	3880.0	953.30	ND	1194.0	1624.66	142.86	25.73	19.20	0.20	3.66	6.133	86.33	ND	ND	7.20
37	1082.0	11946.6	63.80	1469.3	518.66	ND	972.00	1152.66	126.20	19.93	12.00	0.26	14.4	4.33	187.66	1.93	ND	6.33
38	734.00	18966.6	1024.0	1052.6	392.66	ND	317.30	834.66	125.30	23.26	14.46	0.13	1.30	2.73	31.86	ND	ND	6.06
39	2706.6	6366.60	3233.3	3393.3	1383.3	ND	1307.3	1626.6	140.30	33.93	21.00	0.20	8.20	7.86	156.13	0.53	1.33	6.06

These localities are small rural or sub-rural sites, but not industrial areas. So, pollution of soil is not possible. It is unknown whether Cd, Na, Ni and Pb have any role in metabolism of livings. However all of these elements (included Ni, Cd, Pb, Na) found in the study are soil originated. Pb and Cd, whose levels are acceptably small, are radioactive elements and observed low level in Pd can be air originated. Palladium cannot be carried from any vehicle to the soil *via* air movements. We think that these regions (Göle, Hanak, Çildir, Posof) naturally contain different concentrations of Ni, Cd, Pb, Na in their habitats. Nickel concentrations are in localities of Hanak and Çildir localities: Öncül village and Ayni sekilde Cd was determined in high amounts in Posof: control tower forests, Hanak:Altas, Posof: Kursunçavus and Göle:Yeniköy.

The concentration of crustose, fruticose and foliose species it is certain that foliose species absorbed more amount elements. Especially *Dermatocarpon miniatum* and *Peltigera rufescens* accumulate more then the others. Calcium is largely absorbed by *Rhizoplaca chrysoleuca* only. Especially Ca, K, S, Cd and Pb are absorbed by *Hypogymnia physodes, Cetraria islandica, Pseudevernia furfuracea, Rhizoplaca chrysoleuca*, which were collected from Ardahan (Posof: Center, Control tower forests) in different amounts.

Pseudevernia furfuracea accumulate Ca 1.3200 % (Posof: Kontrol Tower forests), while Ca was found 0.0024933 % in *Cetraria islandica* (Posof: Kontrol Tower forests) and 3.10666 % in *Rhizoplaca chrysoleuca* (Posof: 2 km to Kursuncavus village).

Rhizoplaca chrysoleuca (Posof: 2 km to Kursuncavus) absorbed K 0.111333 %, but *A. setifera* 0.214666% (Posof, Alköy Forests) and 0.210733 % in *Hpogymnia physodes* (Posof: Kontrol Tower forests).

Pseudevernia furfuracea (Posof: Kontrol tower forests) accumulated S 0.120266 %, on the other hand *Hypogymnia physodes* (Posof: Kontrol tower forests) absorbed S 0.069933 % and S 0.071466 % was detected in *Rhizoplaca chrysoleuca* (Posof: Kontrol Tower forests).

Cadmium 0.000026 % was determined in *Hypogymnia physodes* (Posof: Kontrol tower forests) *Rhizoplaca chrysoleuca* (Posof: Kontrol tower forests) has Cd 0.0000133 % and theree concentrations of Cd was detected in *Pseudevernia furfuracea* 0.00 % (Posof: Kontrol tower forest), 0.0000133 % (Göle: Yenidemirkapi), 0.0000133 % (Göle: Çakirüzüm forests) and 0.00002 % (Hanak: Altas village, mainroad side) respectively. *Hypogymnia physodes* (Posof: Kontrol tower forests) accumulated Pb 0.000066 %, but *Rhizoplaca chrysoleuca* (Posof:

Kontrol tower forests) *Pseudevernia furfuracea* (Göle: Yenidemirkapi village, roadside, Hanak: Altas village, roadside and Göle: Çakirüzüm forests) has not absorbed any Pb.

Pseudevernia furfuracea, Dermatocarpon miniatum, Ramalina farinacea, Xanthoparmelia stenophylla, Peltigera rufescens, Peltigera canina ve *Rhizoplaca chrysoleuca* were collected from Ardahan: Hanak, Altas village. *Dermatocarpon miniatum* absorbed highest amount of Al, Cd, Cr, Cu, Fe, K, Mn, Mg, Ni, P, Pb, S and Zn. Meanwhile *Xanthoparmelia stenophylla* (Hanak: Altas village, roadside) accumulated highest amount of Ca, *Peltigera rufescens* has Na (Hanak:Altas roadside) and *Peltigera horizontalis* (Göle:Yeniköy forests) has accumulated S in highest amounts.

For example Ni was found in *Dermatocarpon miniatum* (Hanak: Altas village, Çildir: Öncül village, Göle-Ardahan mainroad side, 20 km to Ardahan), *Xanthoparmelia stenophylla* (Hanak: Altas village), *Peltigera rufescens* (Göle-Ardahan mainroad side, 20 km to Ardahan), *P. leucophlebia* (Göle: Yeniköy village) *P. horizontalis* (Ardahan: center, Yalnizçam, Göle: Yeniköy village), *P. praetextata* and *Pseudevernia furfuracea*. The concentration of Ni determined as highest value (23.86mg/kg, Hanak: Altas village) in *D. miniatum* is 45 folds higher than the others.

Sodium were defined in *Cetreria islandica* (Göle: Eskidemirkapi), *Ramalina polymorpha* (Öncül köyü, Hanak: Altas), *Dermatocarpon miniatum* (Hanak: Altas village, Göle-Ardahan mainroad side, 20 km to Ardahan), *Peltigera rufescens* (Hanak: Altas village, Göle-Ardahan mainroad side, 20 km to Ardahan) and *P. canina* (Hanak: Altas village, Göle: Yeniköy) The highest concentration of Na was found in *Peltigera rufescens* (0.0090 %, Hanak: Altas village) and *Cetraria islandica* (0.0083%, Göle: Eskidemirkapi village). This value is 96 folds higher than that in the other species.

Lead was found in *Parmelia sulcata* (Posof: Kursunçavus village), *Rhizocarpon chrysoleuca* (Posof: center, 2 km to Kursunçavus, Posof: Kontrol tower forests, Çildir: Yildirimtepe village), *Dermatocarpon miniatum* (Hanak: Altas village, Çildir: Öncül Village, Göle-Ardahan mainroad side, 20 km to Ardahan), *Xanthoparmelia stenophylla* (Hanak: Altas village), *Peltigera rufescens* (Hanak: Altas village, Göle-Ardahan mainroad side, 20 km to Ardahan) and *Pseudevernia furfuracea* (Hanak: Altas village, Göle: Çakirüüzm forests, Göle: Yenidemirkapi village). The highest amount of Pb was defined in *Parmelia sulcata* (0.00064 %, Ardahan: Posof, Kursunçavus village).

Cadmium was determined on a small scale in *Parmelia sulcata* (Posof: center, Kursunçavus village), *Hypogymnia physodes* (Posof, center, Kontrol Tower forests), *Pseudevernia furfuracea* (Posof, center, Kontrol Tower forests, Hanak: Altas village), *Rhizoplaca chrysoleuca* (Posof, center, Kontrol tower forests, Posof: Center, 2 km to Kursunçavus, Çildir: Yildirimtepe, Hanak: Altas village), *Ramalina polymorpha* (Ardahan: Center, Çamlibel, Çildir: Öncül village, Hanak: Altas village), *Dermatocarpon miniatum* (Hanak: Altas village, Çildir: Öncül village, Göle-Ardahan mainroad side, 20 km to Ardahan), *Peltigera praetextata* (Göle: Eskidemirkapi forests), *Xanthoparmelia stenophylla* (Hanak: Altas village), *Peltigera rufescens* (Hanak: Altas village, Göle: Ardahan mainroad side, 20 km to Ardahan), *Peltigera canina* (Hanak: Altas village, Ardahan: center, Kent forests, Göle: Yeniköy Forests), *Peltigera leucophlebia* (Göle: Yeniköy Forests), *Peltigera horizontalis* (Göle: Eskidemirkapi forests) and *Umbilicaria vellea* (Göle: Eskidemirkapi forests). On the other hand the highest amount of Cd was found in *Dermatocarpon miniatum* (0.00008 %) collected from Hanak; Altas village.

Cd, Ni, Pb and Na, found in this study in low amount, was not detected in the other studies performed in Turkey. All of 16 different elements were found in *Dermatocarpon miniatum* and *Peltigera rufescens*. Cd, Ni, Pb and Na were detected in a little amount in some species (*e.g. Dermatocarpon miniatum, Peltigera rufescens* and *Xanthoparmelia stenophylla*) but on the other hand these elements were not seen in some species.

Comparising with the studies in Turkey, Cu was found in all species in this study the highest amount of Cu was detected in *Dermatocarpon miniatum* (0.0017 %: Hanak, Altas village and 0.0011 %: Göle, Ardahan mainroad side). On the other hand Cu was not found in the othet studies performed in Turkey. *Pseudevernia furfuracea* and *Xanthoparmelia stenophylla* were used in the other studies in Turkey. In this study Cu was found in *Pseudevernia furfuracea* (0.0078 %, Göle: Köprülü high plateau, Hanak: Altas village and Göle: Eskidemirkapi) and *Xanthoparmelia stenophylla* (0.0076 %, Hanak: Altas village). In addition higher amounts were determined in the same species in the studies performed in the other parts of Turkey. For instance K is 0.2 % in *Pseudevernia furfuracae* in this study while 4.158 % in the same species in Erzurum[21] and 3.175 % in Artvin: Murgul[20]. Also Fe is 0.42 % in Dermatocarpon miniatum in this study while 9.19 % in Erzurum (Aslan *et al*. 2004). Ca is 0.21 % in *Xanthoparmelia stenophylla* in this study but it is 2.615 % in Erzurum[21] and 3.846 % in Artvin: Murgul[20]. Concentrations of K, Ca and Fe are 3.707 ± 0.85, 6.563 ± 0.328 and 0.775 ± 0.039 respectively in Giresun and Ordu, but in this study these values of K, Ca and Fe are avarage 0.219 %[22]. Concentrations of Ca, K and Fe in *Ramalina polymorpha* from Erzurum are 3.566 ± 0.214, 0.234 ± 0.016 and 1.939 ± 0.155 % respectively[23] but Ca, K and Fe are 0.636, 0.580 and 0.070 % respectively in this study.

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.

Cadmium was not detected in *Cetraria islandica*, collected from roadside, center and in forests, but in *Peltigera leucophlebia, P. horizontalis, P. rufecens, P. canina, Umbilicaria vellea*, from roadside and also in forests and also in *Dermatocarpon miniatum* from roadside. About Ni it was found in some *Peltigera spp*. and *Xanthoparmelia* from roadside. Na was determined in fruticose and foliose lichens, collected from roadside (more in foliose sopecies). Foliose species were collected from Göle: yeniköy, Yalnizçam, Göle: Eskidemirkapi, Hanak: Altas, Göle:Ardahan mainroadside, Posof: Alköy and Posof: Center while fruticose ones from Posof: Alköy, Göle: Eskidemirkapi, Hanak: Altas, Göle: Çakirüzüm forests, Ardahan: Center: Çamlibel and Posof: Center, Control tower forests.

Rhizoplaca polymorpha, collected from roadside, absorbed all elements nearly the same amount while *R. chrysoleuca*, collected from roadside and most of foliose lichens, from roadside and also in forests, accumulated elements 2-3.5 folds.

Conclusion

In this study, *Dermatocarpon miniatum*, growing on siliceous rocks in Ardahan, Göle, Çildir and Hanak towns, accumulated the highest amounts of of Al, Cr, Cu, K, Mn, Ni, P, S and Zn, while Cd, Fe, Mg and Na were accumulated by *Peltigera rufescens*, on the other hand, the highest amounts of B and Se were accumulated by *Peltigera canina*, Ca by *Rhizoplaca chrysoleuca* and Pb by *Parmelia sulcata.* According to the results, foliose species can generally accumulate higher amounts of elements than the others[24,25].

As a result, it is noticed that generally there are differences in concentrations of these trace elements in different lichen species living in some geographically different regions regardless of differences of industrial pollutions in these regions. It has been known that there is no any reportable finding 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 valuable element like Cd, Na, Ni and Pb that are found in sub-rural and ecologically clean locations except Pb. 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 Cd, Na, Ni and Pb are not necessary elements for lichen metabolism, lichen species can take them into their bodies from their habitats (if there is) and store it.

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