The heavy metal biomonitoring study using lichen *Xanthoria parietina* (L.) Th. Fr. in Ankara province (Turkey)

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Abstract
For the purpose of biomonitoring air pollution level in Ankara (capital of Turkey) in terms of heavy metals, *Xanthoria parietina* (L.) Th. Fr. lichen samples were collected at 30 stations on different tree species, 29 of which are located in city center and 1 outside the city as a control station, between November 2020 and April 2021. After drying and cleaning dust and bark materials from the lichen thallus, the analysis of heavy metals (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb) was performed using ICP-MS and the amaount of chlorophyll-a and chlorophyll-b was measured with UV-Spectrophotometer. When mean of the heavy metal measurement results was compared with lichen reference values of International Atomic Energy Agency (IAEA), the ranking was as follows: Cr>Fe>Al>Co>V>Cu>As>Ni>Zn>Pb>Cd>Mn. As expected, the station in Çamlıdere district, which was selected as a control station 98 km from the city center of Ankara, has lower heavy metals concentration compared to the other stations. According to the results of heavy metals concentration from other stations, the main sources of air pollution in Ankara are motor vehicles, fossil fuels, and industrial activities, respectively.

Keywords *Biomonitoring, Air Pollution, Lichen, Heavy Metal, Xanthoria parietina, Ankara*

Introduction

Lichens are morphological and physiological associations between algae and fungi in which both the fungal component and the algal component benefit from each other. While the fungal component (=mycobiont) uses the organic food produced by the photosynthesis of the algae, the algal component (=photobiont) survives without the danger of desiccation with the water and minerals that the fungus takes up from the substrate and the atmosphere (Ahmadjian, 1982; Nash III, 2008; Yavuz, 2010; Yıldız et al., 2018). Generally, epiphytic foliose and fruticose lichen species are used in air pollution biomonitoring studies. Biomonitoring is an early warning system that detects and tracks changes in the ecosystem (Loppi et

al., 2003; Loppi et al., 2006). Air pollution studies with lichens have been conducted for about 50 years. These lichen studies involve measuring the amount of pollutants that accumulate in the thalli of air pollution-tolerant species, determining the morphological, anatomical, and physiological changes in the lichens due to these pollutants, and mapping the lichen species living in the region according to the pollution levels (Garty, 1993; Beyaztaş, 2008). Heavy metals, which constitute a significant part of the air pollutants group, are analyzed by flame atomic absorption spectrophotometry (FAAS), atomic absorption spectrophotometry (AAS) or inductively coupled plasma mass spectrometry (ICP-MS). Quality control of the measured heavy metals is performed using the International Atomic Energy Agency (IAEA) reference

material IAEA-336 (Tufan-Çetin and Sümbül, 2010). *Xanthoria parietina* (L.) Th. Fr. is a epiphytic foliose lichen species that fairly abundant in many regions of the world. Its toxic tolerance index is 7, which describes it as moderately tolerant of air pollution (Kirschbaum and Wirth, 1997).

The benefit of this species is its ease of identification, its availability for sampling in various environments, and its resistance to a certain amount of pollution. Its cosmopolitan character reduces biomonitoring costs, especially for developing countries (Kouadri et al., 2019). The aim of this study is to highlight air Pollution concentration level related to heavy metals using lichen *X.parietina* in Ankara, Turkey. While there is a study with *Pseudevernia furfuracea* (L.) Zopf by Yıldız et al. (2008) in Ankara, this is the first biomonitoring study with *X.parietina* in Ankara province.

Materials and methods

Study area

Ankara, the capital of Turkey, is located at 39°50'546"–39°59'474"N and 32°34'862"-32°56'387" E and at an altitude of 796–1,270 meters above sea level.

Figure 1. *The map of Ankara*
(http://cografyaharita.com/haritalarim/4l-ankara-ili-haritasi.png)

The hottest month in Ankara is July-August, and the coldest month is January. While the annual average temperature in Ankara is 11.7 °C, the annual average precipitation is 389.1 mm (www.meteoblue.com/tr).

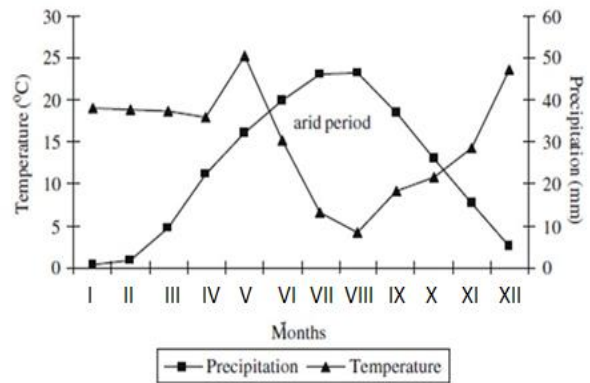The monthly temperature and precipitation values of the city are shown in Figure 2.

Figure 2. *Climate diagram of Ankara* (Yıldız et al. 2008)

The prevailing wind direction changes according to the terrain conditions. Figure 3. shows how many hours and in which direction the wind has blown annually in the last 30 years.
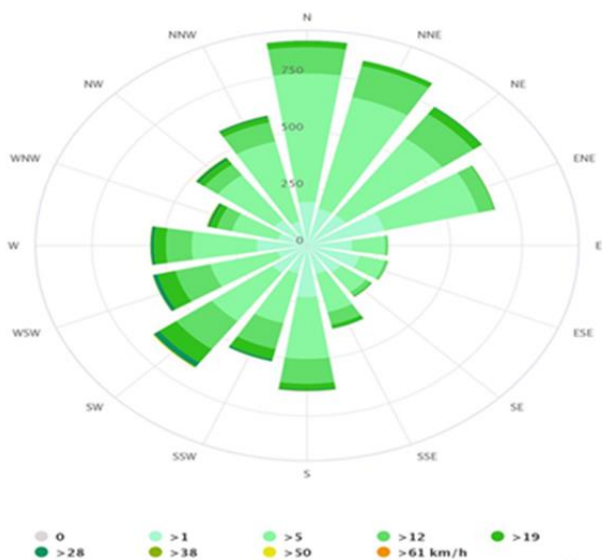

Figure 3. *Weathercock for the last 30 years* (www.meteoblue.com/tr)

Lichen samples were collected at 30 stations in Ankara. One of them, Çamlıdere District (20th station) outside the city with forest area, was selected as a clean control station (Table 1 and Figure 4).

Table 1. *General characteristics of the stations where Xanthoria parietina specimens were collected.*

Stations Number and locality	Altitude m asl	Latitude	Longitude	Date	Substrat
1. Ankara-Çankaya-Yaşamkent	934	39°51'10.181"N	32°39'36.059"E	20.11.2020	Fraxinus sp.
2. Ankara-Çankaya-Ahlatlıbel	1216	39°50'15.198"N	32°44'22.382"E	20.11.2020	Fraxinus sp.
3. Ankara-Çankaya-Mühye Köyü	927	39°51'53.448"N	32°53'18.559"E	20.11.2020	Populus alba
4. Ankara-Çankaya-50.Yıl Parkı	948	39°55'27.506"N	32°52'29.784"E	21.11.2020	Robinia sp.
5. Ankara-Mamak-Mavigöl	963	39°54'55.201"N	32°59'20.965"E	23.11.2020	Populus sp.
6. Ankara-Mamak-Şafaktepe Parkı	921	39°56'10.564"N	32°53'22.478"E	24.11.2020	Fraxinus sp.
7. Ankara-Mamak-Cebeci Asri Mezarlığı	892	39°56'50.126"N	32°53'20.249"E	24.11.2020	Fraxinus sp.
8. Ankara-Altındağ- Altınköy Parkı	1055	39°58'48.455"N	32°57'24.649"E	24.11.2020	Betula sp.
9. Ankara-Altındağ-Altınpark	896	39°58'80.524"N	32°52'51.562"E	25.11.2020	Betula sp.
10. Ankara-Çankaya-Botanik Parkı	981	39°53'12.938"N	32°51'22.179"E	26.11.2020	Populus sp.
11. Ankara-Çankaya- Seğmenler Park	987	39°53'47.244"N	32°51'45.469"E	26.11.2020	Betula sp.
12. Ankara- Demetevler-Lunapark	900	39°58'00.714"N	32°47'53.712"E	28.11.2020	Fraxinus sp.
13. Ankara -İvedik-Fatih Köybaşı Parkı	865	39°58'56.067"N	32°44'40.577"E	28.11.2020	Robinia sp.
14. Ankara-Yenimahalle-Ostim-Mehmet Ali Bey Parkı	880	39°57'55.743"N	32°44'40.853"E	29.11.2020	Salix sp.
15. Ankara-Yenimahalle-Karşıyaka Mezarlığı	896	39°59'31.031"N	32°46'38.820"E	29.11.2020	Fraxinus sp.
16. Ankara-Yenimahalle-Batıkent-Ali Dinçer Parkı	840	39°58'10.821"N	32°43'50.996"E	29.11.2020	Robinia sp.
17. Ankara-Sincan-Harikalar Diyarı	794	39°58'51.470"N	32°55'90.687"E	01.12.2020	Betula sp.
18. Ankara-Etimesgut-Emekliler Konağı Parkı	815	39°56'48.410"N	32°36'40.138"E	01.12.2020	Acer sp.
19. Ankara-Gölbaşı-Mogan Gölü	964	39°46'47.034"N	32°47'15.930"E	01.12.2020	Fraxinus sp.
20.* Ankara-Çamlıdere-Avdan Köyü Mevkii	1354	40°32'27.445"N	32°31'28.737"E	02.12.2020	Populus tremula
21. Ankara-Kahramankazan-Aile Yaşam Merkezi Karşısı Ağaçlık Alan	915	40°13'41.626"N	32°41'70.586"E	02.12.2020	Fraxinus sp.
22. Ankara-Ankara Üniversitesi Beşevler Yerleşkesi –Fen Fakültesi Bahçesi	786	39°56'15.288"N	32°49'40.277"E	04.12.2020	Fraxinus sp.
23. Ankara-Pursaklar-Kuzey Yıldızı Parkı	944	40°00'20.568"N	32°53'52.204"E	08.12.2020	Tilia sp.
24. Ankara-Keçiören-Bağlum-Şehit Yakup Çapat Parkı	1198	40°20'42.249"N	32°50'39.163"E	08.12.2020	Betula sp.
25. Ankara-Keçiören-Ihlamur Vadisi	842	39°58'28.368"N	32°52'25.331"E	08.12.2020	Betula sp.
26. Ankara-Çankaya-Eymir Gölü	956	39°49'50.416"N	32°50'36.368"E	09.03.2021	Populus sp.
27. Ankara-Keçiören-Sanatoryum Hastanesi Yanı	1063	40°00'16.880"N	32°51'11.121"E	19.04.2021	Fraxinus sp.
28. Ankara-Çankaya-Bağlıca-Karabağ Parkı	950	39°53'24.691"N	32°38'42.312"E	19.04.2021	Betula sp.
29. Ankara-Bilkent-Yök Yol Kenarı	962	39°52'48.556"N	32°45'44.336"E	21.04.2021	Fraxinus sp.
30. Ankara-Çankaya-İncek-Atatürk Parkı	1233	39°50'39.208"N	32°47'33.928"E	21.04.2021	Fraxinus sp.

*Control station
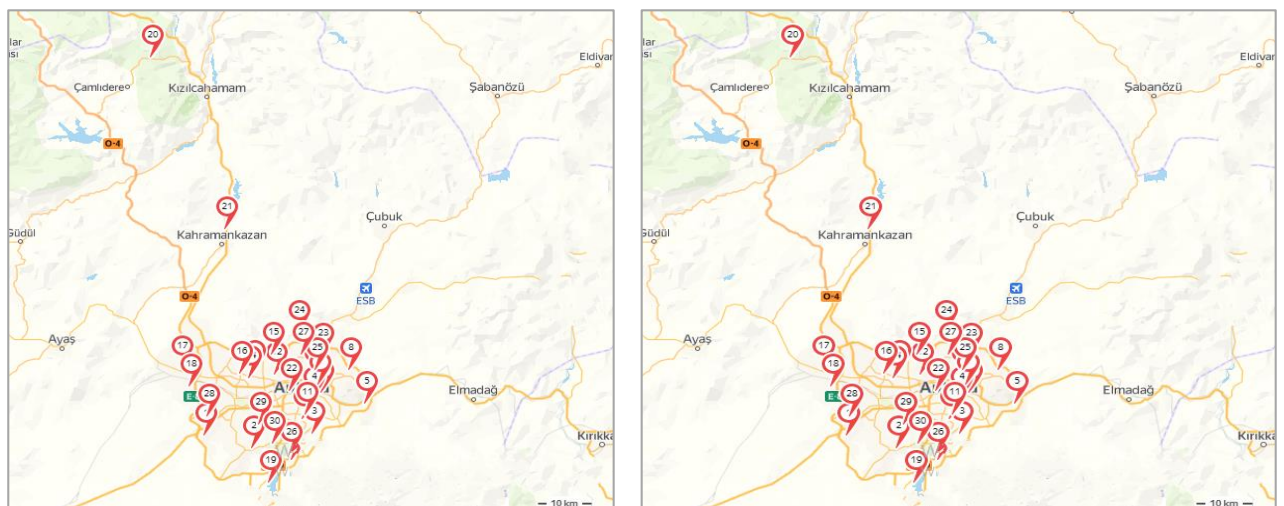
Figure 4. *Map of Xanthoria parietina collected stations*

Sample preparation and heavy metal determinations

The samples of *X. parietina* collected and dried at 30 stations in Ankara were cleaned from tree bark parti-cles and dust materials in their thallus under the stereomicroscope in the Lichenology Laboratory of the Department of Biology, Faculty of Science, Ankara University.

Then, the analysis of the elements Cu, Pb, Zn, Ni, Co, Cd, Cr, Al, As, Fe, Mn, V in the lichen samples was carried out with the instrument ICP-MS (Agilent Technologies / 7700X ICP-MS Systems) in the laboratory of Sinop University Scientific and Technological Research Application and Research Center (SUBITAM). The IAEA-336 reference values of the International Atomic Energy Agency were used as control values for the analysis of heavy metal elements.

Chlorophyll analysis of lichen samples

0.1 g of lichen sample was extracted in 8 ml of 80 % acetone. The resulting mixture was centrifuged at 5000 rpm for 5 minutes. The supernatant was measured in a UV spectrophotometer at wavelengths 647 nm and 664 nm. Subsequently, the values obtained were entered into the formula below and the values for chlorophyll-a, chlorophyll-b and total chlorophyll were calculated (Öncel et al., 2004). Calculations of the amount of chlorophyll were calculated according to the following equations of Arnon (1949).

$$\text{Chlorophyll-a} = 12{,}25 \times A^{664} - 2{,}55 \times A^{647} \qquad [1]$$

$$\text{Chlorophyll-b} = 20{,}31 \times A^{647} - 4{,}91 \times A^{664} \qquad [2]$$

$$\text{Chlorophyll (a+b)} = 17{,}76 \times A^{647} + 7{,}34 \times A^{664} \qquad [3]$$

Results

A total of 12 elements (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb) were analyzed with the device ICP-MS and the following results were obtained (Table 3).

Aluminum (Al): The average of aluminum values at all stations was 4268.18 ug/g. While the highest Al value was 11290.14 ug/g at the 23rd station, the lowest Al value was 1936.36 ug/g at the control station (20th station).

Vanadium (V): The average of vanadium values in all stations was 8.44 ug/g. The highest V value was 19.73 ug/g at the 23rd station, while the lowest V value was 4.01 ug/g at the control station (20th station).

Chromium (Cr): The average of chromium values at all stations was 12.35 ug/g. This value is above the FAO/WHO's Cr upper limit (Tonguç Yayıntaş et al. 2018). The highest Cr value was 26.19 ug/g at the 23rd station, while the lowest Cr value was 5.85 ug/g at the control station (20th station).

Manganese (Mn): The average of manganese values in all stations was 95.06 ug/g. While the highest Mn value was 169.56 ug/g at the 23rd station, the lowest Mn value was 41.90 µg/g at the control station (20th sta-

tion).

Iron (Fe): The average of iron values in all stations was 3581.09 ug/g. This average value is higher than FAO/WHO's Fe upper limit (Tonguç Yayıntaş et al. 2018). While the highest Fe value was 8209.24 ug/g at the 23rd station, the lowest Fe value was 1682.79 ug/g at the control station (20th station).

Cobalt (Co): The average of cobalt values at all stations was 1.81 ug/g. While the highest Co value was 5.82 ug/g at the 6th station, the lowest Co value was 0.68 ug/g at the control station (20th station).

Nickel (Ni): The average of nickel values at all stations was 8.04 ug/g. This value is above the FAO/WHO's Ni upper limit (Tonguç Yayıntaş et al. 2018). The highest Ni value was 15.71 ug/g at the 23rd station, while the lowest Ni value was 4.36 ug/g at the control station (20th station).

Copper (Cu): The average of copper values at all stations was 19.21 ug/g. This average is above the FAO/WHO's Cu upper limit (Tonguç Yayıntaş et al. 2018). The highest Cu value was 68.24 ug/g at the 22nd station, while the lowest Cu value was 5.93 ug/g at the control station (20th station).

Zinc (Zn): The average of zinc values in all stations was 89.46 ug/g. This average value is higher than FAO/WHO's Zn upper limit (Tonguç Yayıntaş et al. 2018). The highest Zn value was 191.46 ug/g at the 15th station, while the lowest Zn value was 34.06 ug/g at the 26th Station. The Zn value at our control station (20th station) was 46.78 ug/g.

Arsenic (As): The average of arsenic levels at all stations was 3.04 ug/g. The highest As value was 7.47 ug/g at the 23rd station, while the lowest As value was 1.32 ug/g at the 10th station. The As value at our control station (20th station) was 1.96 ug/g.

Cadmium (Cd): The average of cadmium levels at all stations was 0.21 ug/g. This is an acceptable value according to FAO/WHO's Cd upper limit (Tonguç Yayıntaş et al. 2018). The highest Cd value was 0.90 ug/g at 22th Station, while the lowest Cd value was 0.08 ug/g at the control station (20th Station).

Heavy metals	Max value (ug/g)	
Pb	2.00	Table 2.
Cd	0.50	Upper limits value
Ni	5.00	for trace elements
Cr	0.50	determined by
Cu	5.00	FAO/WHO
Fe	30.0	(2003)
Zn	30.0	(Tonguç Yayıntaş et al., 2018)

Table 3. *ICP-MS analysis result values of elements (µg/g)*

Stations	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
1.	5540.2	10.27	11.48	106.46	3991.4	1.87	8.45	16.35	64.37	3.02	0.14	5.36
2.	5224.5	9.32	11.18	99.61	3776.5	1.58	8.26	17.48	51.58	2.62	0.14	7.28
3.	4440.7	8.66	10.47	84.65	3293.4	1.55	7.57	10.13	57.36	2.39	0.15	6.95
4.	3726.9	7.32	10.86	77.59	2960.7	1.65	9.53	14.31	65.22	4.04	0.12	8.40
5.	6044.4	12.35	17.33	141.66	4781.8	2.25	10.84	16.34	83.90	2.85	0.19	10.37
6.	4586.6	9.19	18.52	101.27	4247.7	5.82	10.10	31.30	115.29	3.09	0.27	14.86
7.	4830.2	9.88	14.30	97.52	4043.3	1.99	9.63	18.90	71.74	2.91	0.16	11.20
8.	2739.7	5.80	7.69	46.05	2142.3	0.99	4.79	34.30	43.33	2.13	0.09	4.52
9.	4215.9	8.76	12.03	92.03	3564.8	1.88	10.18	13.37	75.44	3.87	0.16	9.52
10.	2283.5	4.85	6.70	48.40	1937.4	0.92	4.43	10.92	60.46	1.32	0.10	4.83
11.	2820.6	5.93	8.99	81.80	2493.7	1.60	6.33	20.07	82.41	1.72	0.20	7.87
12.	3347.8	6.83	9.94	70.77	2972.1	1.36	6.59	16.50	72.91	2.84	0.12	7.44
13.	3832.1	8.28	19.79	115.41	4688.5	1.85	9.99	17.65	173.85	6.07	0.34	23.63
14.	4984.7	10.47	22.95	118.05	5287.0	2.28	11.42	28.14	138.80	3.66	0.24	20.19
15.	5529.8	11.19	16.20	166.07	4619.9	2.34	10.42	13.77	191.46	3.33	0.17	13.78
16.	2881.6	5.61	9.22	57.90	2490.6	1.03	5.56	10.79	74.75	3.04	0.16	7.37
17.	2516.0	5.70	9.10	86.28	2285.7	1.23	7.26	39.93	135.81	3.05	0.29	13.56
18.	4145.6	8.61	13.63	167.22	3678.6	1.83	7.88	16.92	125.23	3.92	0.23	18.81
19.	3246.0	6.34	8.86	50.90	2584.8	1.06	6.19	15.98	63.41	2.12	0.11	6.38
20.*	1936.4	4.01	5.85	41.90	1682.8	0.68	4.36	5.93	46.78	1.96	0.08	4.53
21.	3410.4	8.75	10.49	111.38	3737.8	1.75	7.20	16.97	123.91	4.63	0.24	9.81
22.	3743.4	6.45	7.39	137.63	2800.0	1.90	5.86	68.24	132.55	1.59	0.90	5.96
23.	11290.	19.73	26.19	169.56	8209.2	3.92	15.71	26.41	186.74	7.47	0.33	24.71
24.	4486.4	8.46	10.79	102.04	3497.3	1.51	7.12	9.22	53.00	2.60	0.13	7.68
25.	5368.5	10.41	15.33	68.32	4746.6	1.92	8.68	15.47	91.09	3.47	0.19	11.25
26.	3062.6	5.92	7.67	46.58	2314.2	1.00	5.18	7.32	34.06	1.46	0.10	4.88
27.	4138.0	7.95	12.19	119.49	3532.5	1.60	7.86	13.56	73.70	2.56	0.20	10.19
28.	6817.3	12.49	16.93	116.24	5296.5	2.28	10.82	14.28	99.25	3.59	0.28	13.06
29.	3286.0	6.57	8.78	57.22	2840.5	1.19	6.56	10.58	38.96	1.69	0.10	6.19
30.	3569.2	7.03	9.72	71.89	2934.9	1.33	6.41	25.14	56.32	2.03	0.14	7.69
Average	4268.2	8.44	12.35	95.06	3581.1	1.81	8.04	19.21	89.46	3.04	0.21	10.28

*Control Station

Stations	Chl-a	Chl-b	Chl (a+b)	Chl (a/b)	Chl (b/a)
1.	5.341	2.584	7.925	2.066	0.483
2.	6.193	2.647	8.841	2.339	0.427
3.	6.878	2.566	9.445	2.680	0.373
4.	7.134	3.215	10.35	2.218	0.450
5.	11.72	4.055	15.78	2.892	0.345
6.	7.628	3.172	10.80	2.404	0.415
7.	7.776	3.382	11.15	2.298	0.434
8.	6.844	2.657	9.501	2.575	0.388
9.	11.66	4.756	16.42	2.452	0.407
10.	7.665	2.694	10.36	2.844	0.351
11.	12.05	4.194	16.07	2.874	0.347
12.	9.487	3.102	12.58	3.058	0.327
13.	10.38	3.262	13.64	3.347	0.314
14.	10.78	3.507	14.29	3.074	0.325
15.	5.965	1.968	7.933	3.030	0.329
16.	10.86	3.147	14.01	3.452	0.289
17.	6.457	2.310	8.768	2.794	0.357
18.	5.966	2.237	8.203	2.666	0.375
19.	4.684	1.420	6.105	3.297	0.303
20.*	13.04	3.738	16.78	3.490	0.286
21.	5.641	1.673	7.315	3.371	0.296
22.	10.11	3.004	13.12	3.366	0.297
23.	8.687	2.709	11.39	2.891	0.311
24.	11.85	3.523	14.88	3.364	0.297
25.	11.10	3.303	14.40	3.360	0.297
26.	5.509	1.610	7.120	3.421	0.292
27.	7.491	2.224	9.716	3.368	0.296
28.	6.604	1.789	8.393	3.691	0.270
29.	10.17	2.827	13.00	3.598	0.277
30.	11.36	4.029	15.39	2.819	0.354

*Control station

Table 4.

Chlorophyll analysis results (µg/ml)

Lead (Pb): The average of lead values at all stations was 10.28 µg/g. This is a higher value than the FAO/WHO's Pb upper limit (Tonguç Yayıntaş et al. 2018). The highest Pb value was 24.71 µg/g at 23th station, while the lowest Pb value was 4.52 µg/g at the 8th station. The Pb value at our control station (20th station) was 4.53 ug/g.

The results of chlorophyll analysis of *X. parietina* samples collected from 30 stations in Ankara are shown in Table 4.

Discussion

The average values of analysed elements were related to the average reference values of IAEA-336 and a tabular comparison was performed with other studies at element and region level (Figure 6 and Table 5).

At the 1st. 2nd. 5th. 15th. 23rd and 28th stations possess high Al value. the Al value is caused by vehicle exhaust and solid fuel combustion. The reason for the highest value at 23rd station is intensive city traffic. vicinity to Esenboğa Airport and N-S wind direction. Al ratio in Ankara is lower than in Isparta. higher than in İzmir (Tuncel and Karakaş. 2001; Yavuz. 2010).

Vehicle exhaust and coal combustion are the main causes at 5th. 15th. 23rd and 28th stations which are among the stations with high V pollution. Highest V value for 23rd station is vehicle exhaust and vicinity to airport due to aircraft landing and taking off traffic. V ratio is lower than in Isparta and Kocaeli. higher than in İzmir and Italy (Scerbo et al.. 1999; Tuncel and Karakaş. 2001; Doğrul. 2007; Yavuz. 2010).

Exhaust-induced Cr pollution occurred at 14th and 23rd stations with high Cr levels. The vehicle traffic of 14th station is under the influence of Ostim-İvedik Organize Sanayi plants during the day with east wind in the evening (THEP. 2021). Cr ratio is lower than in Isparta and İstanbul. higher than in Kocaeli. İzmir. and Italy (Scerbo et al.. 1999; Tuncel and Karakaş. 2001; İçel. 2005; Doğrul. 2007; Yavuz. 2010).

At 5th. 15th. 18th. 22nd. 23rd stations with high Mn values. Mn pollution has occurred due to vehicle exhaust. Mn ratio is lower than in Isparta. Kocaeli and İstanbul. higher than in İzmir and Ankara (Tuncel and Karakaş. 2001; İçel. 2005; Doğrul. 2007; Yıldız et al.. 2008; Yavuz. 2010).

The mixing of iron used in construction in the air as dust in the 23rd and 28th stations (construction activities) with high levels of Fe and the fact that the 14th station is in the vicinity of the organized industrial area of İvedik has increased Fe pollution here. Fe ratio is lower than in Isparta and Kocaeli. higher than in İzmir (Tuncel and Karakaş. 2001; Doğrul. 2007; Yavuz. 2010).

High Co pollution in 6th and 23rd stations is caused by vehicle traffic. There is not any Co measurement in other compared places.

High Ni values at 5th. 14th. 15th. 23rd. and 28th stations are due to vehicle exhaust and solid fuel combustion. Ni ratio is lower than in Isparta and İstanbul. higher than in Kocaeli and Italy (Scerbo et al.. 1999;İçel. 2005; Doğrul. 2007;Yavuz. 2010).

If we look at the 4 stations with high Cu values. the 17th station is located near the organized industrial area of Sincan. it is under the influence of the neighborhoods where coal is used in the north and northwest. fossil fuels and vehicle exhaust at 6th and 8th

stations and an increase in Cu values due to vehicle exhaust at the 22nd station. Cu ratio is higher than in Ankara (Yıldız et al.. 2008) . lower than in İstanbul and Isparta (İçel. 2005; Yavuz. 2010).

At 13th. 14th. 15th. 17th and 23rd stations. vehicle exhaust. proximity to industrial facilities and use of solid fuels caused Zn concentrations to increase. Zn ratio is lower than in Isparta. Kocaeli. İstanbul and İzmir. higher than in Italy and Ankara (Scerbo et al.. 1999;Yenisoy and Karakaş. 2001;İçel. 2005;Doğrul. 2007;Yıldız. 2008;Yavuz. 2010).

With the exception of 10th.11th. 22th. 26th and 29th stations. all other stations have higher As than the control station. Coal heating and vehicle traffic can be counted among the reasons for the higher values. As ratio is lower than in Isparta and İzmir. higher than in Kocaeli and Italy (Scerbo et al.. 1999;Yenisoy and Karakaş. 2001; Doğrul. 2007;Yavuz. 2010).

All stations are higher in Cd content than the control station. Proximity to industrial facilities (İvedik and Sincan organized industry area) at 13th and 17th stations and domestic fire and vehicle exhaust at 6th. 22nd. 23rd. and 28th stations increased Cd levels. Cd ratio is lower than in Isparta. Kocaeli. İstanbul and İzmir and higher than Italy (Scerbo et al.. 1999; Yenisoy and Karakaş. 2001; İçel. 2005; Doğrul. 2007;Yavuz. 2010).

With the exception of the 8th station. all other stations are higher in Pb content than the control station (20th station). At 13h. 14th. 15th and 17th stations with high Pb levels was the proximity to industrial facilities and at 6th. 18th and 23th stations Pb levels were high due to vehicle exhaust. Pb ratio is lower than in Isparta. Kocaeli. İstanbul and Italy and higher than Ankara (Scerbo et al.. 1999; İçel. 2005; Doğrul. 2007;Yıldız et al.. 2008; Yavuz. 2010).

As a result of the analyzes carried out. 23rd station ranks first among the stations with the highest heavy metal pollution. The reasons for this include the heavy traffic of the Esenboğa Airport Road on the route of the 23rd station. its location very close to the O-20 Ring Road. and the heating activities in the vicinity. As expected. the 20th station. which is the control station. is the station with the lowest heavy metal contamination. This showed us that the lichen *X. parietina* is a good bioindicator species for biomonitoring. The comparison of the thallus

of the lichen *X. parietina* at the 23rd station and the thallus of the lichen *X. parietina* at the 20th station is shown in Figure 5. The values in Isparta. Kocaeli. and İstanbul are gene rally higher due to industrial activities, vehicular traffic. and intensive heating of households (Scerbo et al.. 1999; Yenisoy-Karakaş. 2003; Yıldız et al.. 2008; Yavuz. 2010; Doğrul-Demiray et al.. 2012). Due to various reasons such as climate. geographic conditions and collection of *X. parietina* samples from different locations (different sources of pollution). heavy metals levels may vary among cities and countries. The IAEA-336 reference values provide a standard for these differences and make it possible to compare items at the international levels. As there is no IAEA-336 reference value for nickel. the Ni value used by Yavuz (2010) in his study was selected as a reference.

As shown in Figure 6 and table 5. our study with *X. parietina* in Ankara was compared with the studies conducted in Isparta. Kocaeli. İstanbul. İzmir and Italy with the same lichen species. Since no biomonitoring study has been conducted with *X. parietina* in Ankara so far. the measurement results of Yıldız et al. (2008) in Ankara with *Pseudevernia furfuracea* were taken as comparison data.

Figure 5. *a-23rd and b-20th stations Xanthoria parietina thallus*

Table 5. *Elements comparison with other studies. values expressed in μg/g*

Element	Avg	Avg/IAEA	Avg	Avg/IAEA	Avg	Ort/IAEA	Avg	Avg/IAEA	Avg	Avg/IAEA	Avg	Avg/IAEA	Avg	Avg/IAEA	IAEA
Al	4268.2	8,27	6206.5	9.13	***	***	***	***	3160.0	4.65	***	***	***	***	680.0
V	8.44	5.75	30.81	20.96	10.67	7.26	***	***	6.4	4.35	***	***	3.74	2.54	1.47
Cr	12.35	11.65	20.62	19.45	11.73	11.07	21.39	20.18	9,9	9.34	***	***	7.52	7.09	1.06
Mn	95.06	1.50	274.07	4.35	152.00	2.41	150.43	2.39	60.0	0.95	2.36	0.037	***	***	63.0
Fe	3581.1	8.32	5539.6	12.88	3686.0	8.57	***	***	2360.0	5.49	***	***	***	***	430
Co	1.81	6.24	***	***	***	***	***	***	***	***	***	***	***	***	0.29
Ni	8.04	3.28	48.42	19.76	7.47	3.05	17.07	6.96	***	***	0.29	0.119	6.26	2.55	2.45**
Cu	19.21	5.33	24.89	6.91	19.19	5.33	45.24	12.57	***	***	0.56	0.155	***	***	3.6
Zn	89.46	2.94	265.77	8.74	280.1	9.21	194.87	6.41	100.0	3.29	0.52	0.017	46.0	1.51	30.4
As	3.04	4.82	6.08	9.65	2.63	4.17	***	***	4.5	7.14	***	***	1.3	2.06	0.63
Cd	0.21	1.75	0.22	1.88	0.93	7.95	0.35	2.99	0.3	2.56	***	***	0.16	1.33	0.12
Pb	10.28	2.09	10.77	2.2	70.2	14.33	71.35	14.56	***	***	0.72	0.146	11.85	2.41	4.90

* Pseudevernia furfuracea - ** Non-certificate vale of Evernia prunastri - *** Unanalyzed elements

Chlorophyll amounts

The accumulation of heavy metals in plant tissues results in the breakdown of chlorophyll (Garty et al.. 1985; Ra et al.. 2005). The chlorophyll content of lichens is known to decrease with the increase in pollution. which is the physiological effect of pollution on lichens (Yıldız et al.. 2011). Chlorophyll-a is primarily destroyed because chlorophyll-a is the type of chlorophyll most affected by pollution. Where pollution becomes excessive. chlorophyll-b is destroyed. Chlorophyll b/a is the destroying signal during photosynthesis. The increase in the results of heavy metals may be explained by a reduction in chlorophyll-a. Any changes in chlorophyll a and b concentrations and reports could be explained by environmental stress such as pollution (Yıldız et al.. 2018). It is difficult to explain that the only reason is not environmental pollution. but weather conditions. seasons. the power of sunlight and the plant itself can also affect these changes (Yıldız et al.. 2008).
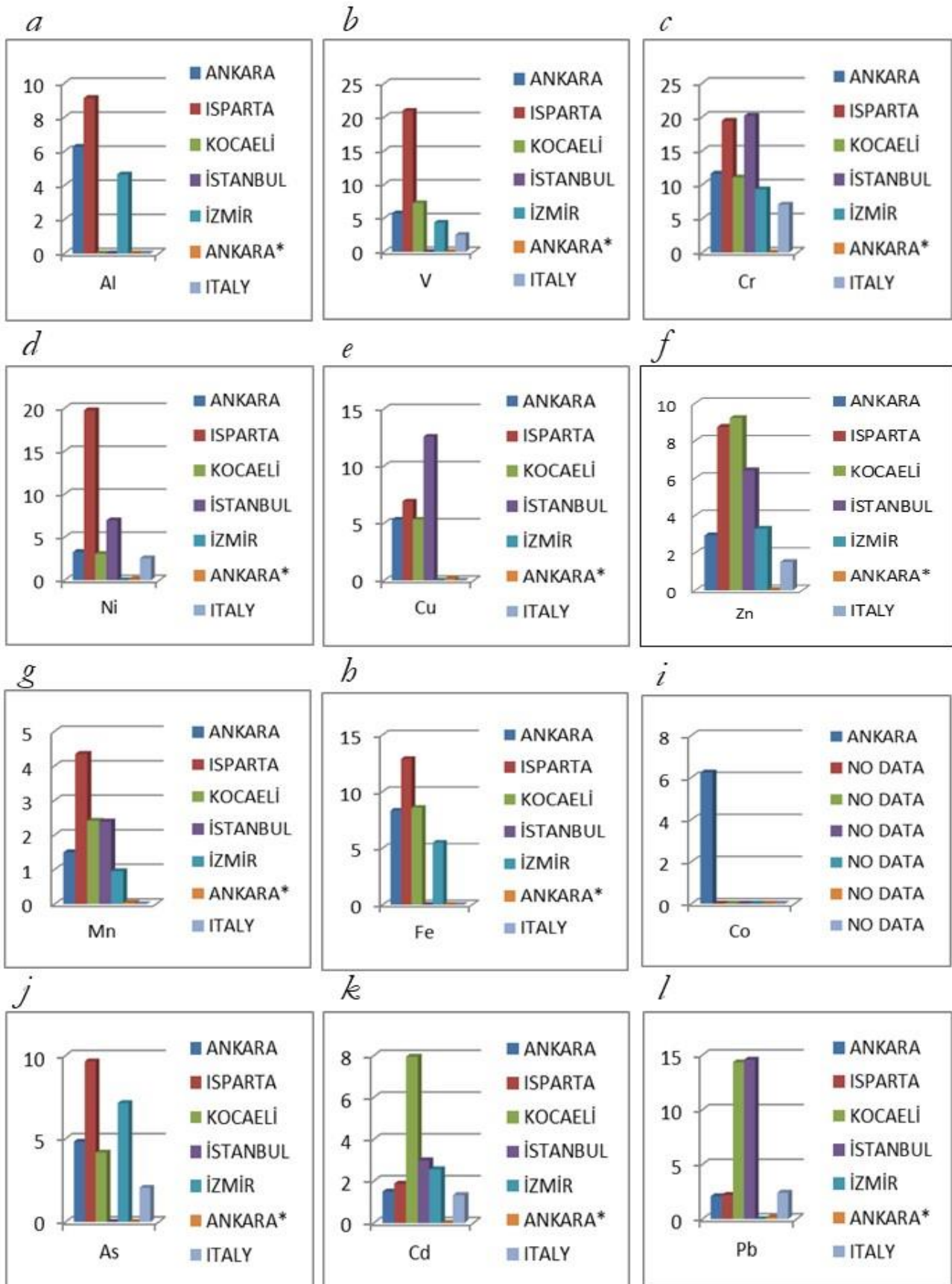
Figure 6. *Element level comparison with other studies a-Aluminium. b-Vanadium. c-Chromium. d-Nickel. e-Copper. f-Zinc. g-Manganese. h-Iron. i-Cobalt. j-Arsenic. k-Cadmium. l-Lead . Values in ordinates expressed in µg/g.*

The control station (20th station) selected as a clean sample was located in Çamlıdere District-Avdan Village. As expected. the chlorophyll-a value was higher at the control station than at all other stations (Figures 5.15 and 5.16). On average. pollution from motor vehicles is the main factor at the stations where the chlorophyll-a value is lower than at the control site. In addition. factors such as climatic conditions. the strength of sunlight. and the seasons also affect changes in chlorophyll levels.

High chlorophyll-a values at 9th. 11th. 13th. 14th. 16th. 22nd. 24th. 25th. 29th. and 30th stations indicated that photosynthetic activity of *X. parietina* samples was high at these stations. The reason for the lowest chlorophyll-a values at the 1st. 15th.18th.21th.26.th.19th stations was due to metal pollution. weather conditions. and solar radiation.

At 1st.2nd.4th.6th.7th.9th stations chlorophyll b/a ratio is higher than at the other stations and photosynthesis process is faster. so destruction in photosynthesis is lower (Yıldız et al.. 2008).

At the 1st.2nd.3rd.8th.10th.15th.17th.18th.21th.23th.26th.27th.28th.29th stations chlorophyll-b degradation is higher than at the other stations. Therefore. it can be said that heavy metal pollution negatively affects chlorophyll-b content at these stations.

Conclusions

Lichens have been used as bioindicator organisms for biomonitoring of air pollution for 50 years because of their physiology and sensitivity to pollutants in the atmosphere. If we look at the literature. this is the first study. because studies on biomonitoring of heavy metals with *X.parietina* have never been conducted in Ankara before. Our biomonitoring study we conducted with *X. parietina* at 30 sites in Ankara. the capital of Turkey and the second largest metropolis after İstanbul. showed that the thallus of *X. parietina* is a good bioindicator species that accumulates Mn. V. Cu. Cd. Pb. Zn. Ni. Co. Cr. Al. As. and Fe elements.

Main air pollution sources in our study are burning of coal in some neighborhoods of Ankara. the emission factors of industrial activities in centers such as İvedik-Ostim-Sincan organized industrial area. the intensive exhaust pollution from vehicles in the city and prevailing wind in the N-S/NE-SW direction. The findings of our experiments show that the accumulation of heavy metals depends on the nature of the exchange site. the affinity of the species to those parts of the region.

References

AHMADJIAN V. (1982) Algal/Fungal Symbioses. In: F. Round and D.J. Chapman (eds): Progress in Phycological Research. Elsevier Biomedical Press Amsterdam. pp. 179–233

ARNON D.I. (1949) Copper enzymes in isolated chloroplasts polyphenol oxidase in *Beta vulgaris*. Plant Physiology. 24:1-15. https://doi.org/10.1104/pp.24.1.1

BEYAZTAŞ T. (2008) Karabük civarında bulunan Pseudevernia furfuracea (L.) zopf. var. furfuracea liken türinde ağır metal kirliliğinin atomik absorpsiyon spektroskopisi ve rapd analizi ile araştırılması. (https://tez.yok.gov.tr/UlusalTezMerkezi/tezDetay.jsp?id=xoGKIY0cagWRd57Rue1kzw&no=kvr5X0Kwm84QXgprVMnpbQ/(23.10.2022)).

COĞRAFYA HARİTA. 2022. Ankara ili haritası. (www.cografyaharita.com/haritalarim/4l-Ankara-ili-haritasi.png/(23.10.2022))

DOĞRUL DEMİRAY A.. YOLCUBAL İ.. AKYOL N.H.. ÇOBANOĞLU G. (2012) Biomonitoring of airborne metals using the lichen *Xanthoria parietina* in Kocaeli province. Turkey. Ecological Indicators. 18:632-643. https://doi:org/10.1016/j.ecolind.2012.01. 024.

EMBERGER L. (1955) Ann. Biol. 31:249–255.

GARTY J.. RONAN R.. GALEN M. (1985) Correlation between chlorophyll degradation and the amount of some elements in the lichen *Ramalina duriaei* (de not.) Jatta. Environmental and Experimental Botany, 25:67–74. https://doi.org/10.1016/0098-8472(85)90049-8.

GARTY J. (1993) Lichens as bioindicators of heavy metal pollution. In: Plants as biomonitors: Indicators for heavy metals in the terrestrial environment. Markert. B. (ed). VCH. pp. 193-263.

KIRSCHBAUM U., WIRTH V. (1997) Les lichens bioindicateurs les reconnaître pour évaluer la qualité de l'air. Ed. Eugen Ulmer, Paris 128.

KOUADRI L., BENAMAR M.E.A., BENKHALIFA A. (2019) Evaluation by X-ray fluorescence (XRF) of major and trace elements accumulated in Xanthoria parietina (L.) Th. Fr. (1860) indicating levels of pollution in Blida area (Algeria). Algerian Journal of Environmental Science and Technology. 5: 1155- 1176.

LOPPI S.. PIRINTSOS S.A. (2003) Epiphytic lichens as sentinels for heavy metal pollution at forest ecosystems (Central Italy). Environmental Pollution. 121:327-332.

https://doi.org/10.1016/S0269-7491(02)00269-5.

LOPPI S.. PAOLI L.. GAGGI C. (2006) Diversity of epiphytic lichens and hg contents of *Xanthoria parietina* thalli as monitors of geothermal air pollution in the Mt. Amiata Area (Central Italy). Journal of Atmospheric Chemistry. 53:93–105. https://doi.org/10.1007/s10874 - 006-6648-y.

METEOBLUE (2022) Wheather cock for Ankara. (https://www.meteoblue.com/tr /(23.10.2022)).

NASH III T. H. (2008) Lichen Biology. Cambridge University Press.

ÖNCEL I.. ÜSTÜN A.S.. KELEŞ Y. (2004) Renk Maddelerinin (Pigment) Ekstraksiyonu ve Belirlenmesi in Bitki Fizyolojisi Laboratuvar Kılavuzu. Ankara Üniversitesi Fen Fakültesi Döner Sermaye İşletme Yayınları. No:48. Ankara. pp.72-74.

SCERBO R.. POSSENTI L.. LAMPUGNANIC L.. RISTORIA T.. BARALE R.. BARGHIGIANIA C. (1999). Lichen (*Xanthoria parietina*) biomonitoring of trace element contamination and air quality assessment in Livorno Province (Tuscany. Italy). The Science of the Total Environment. 241:91-106. https://doi.org/ 10.1016/S0048-9697(99)00333-2.

THEP (2021) Emisyon Envanteri. In: Ankara ili Temiz Hava Eylem Plani (2020-2024). Ankara, pp 82-83.

TONGUÇ YAYINTAŞ Ö.. YILDIZ A.. YILMAZ S.. İRKİN C. (2018) Determination of trace element level in some lichens from Mount Ida (Çanakkale. Turkey) By ICP-MS. (https://www.iiste.org/)).

TUFAN-ÇETİN Ö.. SÜMBÜL H. (2010) Hava kirliliğinin belirlenmesinde likenlerin kullanımı. (https://dergipark.org.tr/tr/pub/makufebed/issue /19425/206572/(23.10.2022)).

YENİSOY-KARAKAS. S.. TUNCEL. S.G. (2004) Geographic patterns of elemental deposition in the aegean region of Turkey indicated by the lichen. *Xanthoria parietina* (L.) Th. Fr. Science of the Total Environment. 329:43–60. https://doi.org/10.1016/ j.scitotenv.2004.03.003.

YAVUZ. M. (2010) Gölcük Tabiat Parkı Liken Florası ve Isparta Hava Kirliliğinin Likenlerle Derecelendiril-mesi. https://www.researchgate.net/profile/Mustafa-Yavuz-4/publication/292143350_Golcuk_Tabiat-Parki_ Liken_Florasi_ve_Isparta_Hava_Kirliliginin_Likenlerle_ Derecelendirilmesi/links/5816709408aeb720f6880f3a/.

Goelcuek-Tabiat-Parki-Liken-Florasi-ve-Isparta-Hava-Kirliliginin-Likenlerle-Derecelendirilmesi.pdf).

YILDIZ. A.. AKSOY. A.. TUĞ. G.N.. İŞLEK. C.DEMİREZEN. D. (2008). Biomonitoring of heavy metals by *Pseudevernia furfuracea* (L.) Zopf in Ankara (Turkey). Journal of Atmospheric Chemistry. 60:71-81. https://doi.org/10.1007/s10874-008-9109-y

YILDIZ A.. AKSOY A.. AKBULUT G.. DEMİREZEN D.. İSLEK C.. ALTUNER E.M.. DUMAN F. (2011) Correlation Between Chloropphyll Degradation and the Amount of Heavy Metals Found in *Pseudevernia furfuracea* in Kayseri (Turkey). Ekoloji, 20 (78):82-88. https://doi.org/10.5053/ekoloji.2011.7813

YILDIZ A.. VARDAR Ç.. AKSOY A.. ÜNAL E. (2018). Biomonitoring of Heavy Metals Deposition With Pseudevernia furfuracea (L.) Zopf in Çorum City. Turkey. Journal of Scientific Perspectives. 2(1):9-22. https://doi.org/10.26900/jsp.2018.02.

ZENGİN K.F.. MUNZUROGLU Ö. (2005) Fasulye fidelerinin (*Phaseolus vulgaris* L.Strike) klorofil ve karotenoid miktarı üzerine bazı ağır metallerin (Ni+2. Co+2. Cr+3. Zn+2) etkileri. https://dergipark.org.tr/tr/ pub/fudad/issue/47000/590382