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RESEARCH

Spatial evaluation of air quality by biomonitoring of toxic element accumulation in lichens in urban green areas and nature parks on the Anatolian side of Istanbul

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Abstract The city of Istanbul is constantly exposed to air pollution due to its high population, heavy traffic — sea and air transport — and urban industry. This study basically aims to determine the recent level of airborne heavy metals, using lichen biomonitoring method. The cosmopolitan foliose lichen *Xanthoria parietina* growing abundantly on trees was sampled from 16 urban green spaces in 8 districts on the Anatolian side of Istanbul. Multi-element analysis by ICP-MS was applied to measure the accumulation of 10 potentially toxic trace elements in lichen samples. Spatial distributions of element levels in the air in the sampling areas are shown by mapping. According to the analysis data, the sequence of element deposition levels in lichen samples was as follows; Al > Fe > Mn > Zn > Cr > Cu > Pb > V > Ni > As. Most of the measured atmospheric element amounts yielded results much higher than the reference material in all areas. It was detected that the highest pollution in terms of Al, Cu, Fe, Mn, and Ni elements was in Elmasburnu Nature Park area in Beykoz district, which is a touristic place by the sea. Changes in the city's air quality over the years have been evaluated by comparing element levels in these locations in a previous biomonitoring study and some differences were found. The resulting data is valuable for periodic monitoring of toxic elements in the air, for determining causes of air pollution, and for taking precautions.

Keywords Air quality · Heavy metals · Lichen monitoring · Elements · Bioaccumulation

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Introduction

Environmental pollution, global warming, and climate change, which have emerged as a result of factors such as population growth, industry, and developing technology and continue to increase all over the world, affect not only people but also other living organisms in the ecosystem. The biggest and most risky environmental problem declared by the World Health Organization (WHO, 2019) has been reported as "air pollution". It is stated that 7 million people in the world die every year due to diseases such as cancer, heart attack, and heart and lung diseases triggered by polluted air. Air pollution, which also contributes negatively to soil and water pollution, is one of the leading environmental problems in developed and developing countries due to the damage it causes to human health and the environment.

Biomonitoring is a biological method developed to measure the atmospheric pollution in a more economical, reliable and long-term way (Çobanoğlu

Özyiğitoğlu, 2020). Because they can accumulate more elements than their physiological needs during their long lives and are sensitive to many pollutants, lichens have been the most widely used organisms for years as a biomonitoring tool in the assessment of air pollution levels (Garty, 2001; Madheshiya et al., 2022; Rinino et al., 2005). Lichens are symbiotic organisms that usually consist of a fungal partner (mycobiont) and one or more photosynthetic algae partners (photobiont). Lichens, which do not have true root systems, have been considered very sensitive to air pollution for many years because they only absorb the necessary nutrients from rainwater and atmospheric moisture (Nash, 2008). It has been reported that lichen diversity in a region can be used to develop predictions about human health and especially lung cancer incidences (Cislaghi & Nimis, 1997).

Especially since the 2000s, studies on air quality biomonitoring have been intensifying. In some of these studies, to detect atmospheric accumulation of heavy metals; for example, *Ramalina muciformis* in the Israeli Nagev Desert (Garty et al., 2002), *Pyxine cocoes* in the eastern Himalayan region (Daimari et al., 2020), *Usnea* species in the Canadian territory of New Scotland (Klapstein et al., 2020), *Flavoparmelia caperata* in the city of Middletown, Ohio, USA (Kousehlar & Widom, 2020), different lichen species were used as application tools depending on the region.

The cosmopolitan epiphytic foliose lichen *Xanthoria parietina* has been used successfully worldwide as a bioindicator of atmospheric pollution (Brunialti & Frati, 2007; Dzubaj et al., 2008; Hissler et al., 2008; Scerbo et al., 1999, 2002). Heavy metal accumulation in lichen *X. parietina* was investigated in studies conducted in Huelva, Spain (Parviainen et al., 2019), and Morocco (Rhzaouii et al., 2015). The ability of *X. parietina* to biomonitor and bioaccumulate some heavy metals, PAHs, PCDDs, PCDFs, PCBs, and PBDEs was evaluated in an Italian study (Vitali et al., 2019), and the results proved that this lichen is biologically efficient and useful for monitoring. Numerous biomonitoring studies with this lichen species in Turkey were also reported in a review by Işık and Yıldız (2021). Some of these are the studies carried out with *X. parietina* in the vicinity of Yatağan Thermal Power Plant in Muğla province (Ölgen & Gür, 2012), in Düzce province (Bozkurt, 2017) and in Ordu province (Topçuoğlu et al., 1995). Likewise, airborne metal deposition in the major urban and the industrial districts of Kocaeli (on the eastern border of Istanbul) was monitored with lichen *X. parietina* (Doğrul-Demiray et al., 2012).

In the last 20 years, air quality lichen monitoring studies have increased considerably in Turkey as well as in the world, due to the global air pollution problem (Çobanoğlu, 2015). However, air quality lichen biomonitoring studies for the mega city Istanbul, which has lands on the Asian and European continents, have been quite limited. Therefore, this study aimed to determine the level of toxic elements, which are potential ecological and human health risks that can be found in the atmosphere of the city of Istanbul through lichen monitoring.

The first biomonitoring study from Istanbul was radionuclide analysis in lichen (*Xanthoria parietina*) and moss (*Leucodon immersus*) samples from Küçükçekmece district (Topçuoğlu et al., 1995). In a later study (Belivermiş et al., 2008), heavy metals and radionoclides in soil and in moss samples (*Hypnum cupressiforme, Scleropodium purum*) from some districts of Istanbul were determined. The accumulation of As, Cd, Cr, Cu, Pb, and Zn in lichen (*Cladonia rangiformis*) and moss (*Hypnum cupressiforme*) samples were evaluated by Coskun et al. (2009) in the Thrace region, which also includes Tekirdağ and the vicinity of Istanbul province. The latest air quality biomonitoring research in Istanbul was conducted on the European side by Kurnaz and Çobanoğlu (2017), and it was reported that the mean values of all measured elements accumulated in samples of epiphytic lichen *Physcia adscendens* were higher than the reference values. The biomonitoring study conducted by İçel and Çobanoğlu (2009) on both sides of Istanbul is based on the multi-element analysis of moss and lichen species and is the only study that has been done more than 10 years ago covering some localities on the Anatolian side of Istanbul. There is a great lack of information in Istanbul for many years on the biological monitoring of atmospheric element pollution.

In this study, it was mainly aimed to determine the latest state of pollution related to the level of toxic metals in the air in the Anatolian (Asian) Side of Istanbul, where there is a high population and heavy land and sea traffic, by performing a monitoring method. *Xanthoria parietina* (L.) Th. Fr., a moderately sensitive epiphytic lichen species that naturally spreads in urban green areas and is often preferred for biomonitoring, was used as a biological monitor of airborne elements in our study.

It is also aimed to interpret the extent to which anthropogenic emission sources contribute to air pollution with data analysis of the elements measured in lichens. Although instantaneous air quality measurements are made for greenhouse gases and particulate matter (PM) at some stations in the city, information based on biological measurements is almost non-existent, especially in terms of toxic metals. Therefore, this study contains sustainable and valuable biomonitoring data. In addition to evaluating the current air quality based on possible long-term element accumulation in the study area, comparison of lichen biomonitoring data with a single past study in Istanbul to identify differences in elemental levels, and interpretation of data from several other cities in Turkey and Europe are also included. An answer is sought to the question of what is the difference between the present data obtained and the past observations. It is of great importance to evaluate the air pollution that Istanbul, one of the largest metropolises in the world, is exposed to due to its human population, traffic density, and industrial zones.

Materials and methods

Study area and sampling procedure

Istanbul, Turkey's largest and most populous city, is located between the continents of Asia and Europe. According to Turkish Statistical Institute (TÜİK, 2021), the population of the city is over 15 million in 2020. The entire city, including the Prince Islands in the Sea of Marmara, is 5712 km^2. Istanbul's climate is temperate, and it shows a transition between the Black Sea climate and the Mediterranean climate. The average temperature of the year is 13.7 °C, and it is around 2–9 °C in winter and 18–28 °C in summer. The winds are moderately strong in Istanbul; the prevailing wind direction is predominantly from the northwest and southwest in winter, north in summer (TSMS, 2021).

The air quality index (adapted to EPA, Environmental Protection Agency) assessment performed continuously in the city by the Air Quality Monitoring Center within the Istanbul Metropolitan Municipality (IMM, 2019) is based on instant measurement of parameters such as PM_{10} and SO_2, NO_2, O_3, and CO. However, only Kartal (B) station is compatible with our sample localities. The inventory containing NO_x, CO, SO_2, VOC, and PM_{10} pollutants prepared by IMM points out the industry for SO_2, domestic heating for PM_{10}, and traffic as the main emission source for NO_x, CO, and VOC. The city is heavily influenced by air, sea, and land traffic. The large organized industrial zones on the Asian side of Istanbul are concentrated in two locations, Dudullu and Tuzla (Fig. 1).

Xanthoria parietina (L.) Th. Fr. (Turkish name is ruffled orange), the most common epiphytic foliose lichen in almost all areas of Istanbul (Çobanoğlu, 2021), possibly a pollution tolerant and nitrophilic species, was chosen as monitoring specimen. The samples were collected from trees in urban forest and wooded and hilly habitats in the study area.

Fig. 1 The location of the study area in the Asian side of Istanbul; the left map shows the sampling sites (1–16) and the districts (A–H); A Beykoz (1–4), B Kartal (5), C Maltepe (6), D Adalar (7–8), E Ataşehir (9), F Şile (10–13), G Üsküdar (14–15), H Pendik (16); and the right geographic map shows green areas, highways, and big organized industries with red landmarks

The lichens were sampled from urban green spaces, nature parks, and forests at 16 localities in 8 districts on the Asian (Anatolian) Side of Istanbul between October 2018 and October 2019 (Fig. 1). Care was taken to take lichen material from a height of at least 1 m above the trees and at least 300 m from the main road. The geographical location of each locality was determined with GPS (Global Positioning System) measuring tools (Table 1).

International standard reference lichen material (IAEA-336, *Evernia prunastri*) prepared by the International Atomic Energy Agency was provided in powder form.

Procedure for element analysis and spatial distribution

Lichen samples collected from its natural habitat were examined under a stereomicroscope in the laboratory and were freed from residues. Afterwards, the cleaned pure lichen samples were washed twice with distilled water to remove the dust remaining on the surface and left to dry for 1 night at room temperature. In the next step, lichen samples were dried in an oven at 60 °C for 12 h. Then, the dried lichen thalli of the samples were homogenized by grinding and powdered (Yenisoy-Karakas & Tuncel, 2004). All lichen samples were stored in sterile falcon tubes before chemical analysis. Solubilization process of the lichen samples was carried out in 3 repetitions using a Microwave digestion system (CEM Mars X-press). For digestion step, 6 ml of King's water (3:1 $HCl:HNO_3$) was added to each lichen sample weighing 0.1 g and microwaved at 160 °C for 15 min. After the treatment, the solubilized samples were added to 50 ml ultrapure water and taken into falcon tubes.

Trace elements (Al, As, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn) were measured after all this acid digestion process, by using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500 Tokyo, Japan) in the laboratory of the department of Mersin University Advanced Technology. With the same procedures applied, the certified reference material IAEA-336 was also analyzed and evaluated (Table 2; Figs. 2 and 3).

The data analyzed by ICP-MS was transferred to Surfer®15 software to determine the spatial distribution of airborne elements in the study area (Fig. 4).

Data analysis

The analysis results of our study were statistically evaluated with SPSS®21 software. The descriptive statistics of the sample populations were presented, and then it was determined whether the population formed according to each variable showed a normal distribution. It was determined that the distribution of the sampled areas was normal. Since the variances of normally

Table 1 Information about the 16 sampling sites in 8 districts studied in the Asian side of Istanbul

District		Sampling sites		Geographic coordinates (N–E)	Elevation (m)	Date
A	Beykoz	1	Polonezkoy Nature Park	41.6530–29.1240	160	28.10.2018
		2	Elmasburnu Nature Park	41.2277–29.2185	67	07.06.2019
		3	Kanlıca Forestry Department	41.0952–29.0716	125	07.06.2019
		4	Göztepe Nature Park	41.0952–29.0716	125	07.06.2019
B	Kartal	5	Aydos Forest	40.9445–29.2268	232	08.12.2018
C	Maltepe	6	Başıbüyük Forest	40.9596–29.1679	268	22.12.2018
D	Adalar	7	Kınalıada Island	40.9122–29.0519	49	24.03.2019
		8	Büyükada Island	40.8603–29.1171	66	25.04.2019
E	Ataşehir	9	Kayışdağı Forest	40.9743–29.1543	198	25.05.2019
F	Şile	10	Şile Central Entrance Road	41.1669–29.5944	33	11.09.2019
		11	Şile Castle	41.1817–29.6066	31	11.09.2019
		12	Serintepe Picnic Area	41.1692–29.6003	111	11.09.2019
		13	Atatürk Forest	41.1636–29.6389	126	11.09.2019
G	Üsküdar	14	Büyük Çamlıca Hill	41.0273–29.0685	306	29.09.2019
		15	Küçük Çamlıca Hill	41.0197–29.0649	206	29.09.2019
H	Pendik	16	Gözdağı Grove	40.5343–29.1529	179	07.10.2019

Table 2 The average elemental concentrations of *X. parietina* samples analyzed by ICP-MS by districts (A–H) and sampling sites (1–16)

		Average concentration values of elements (μg g^{-1})									
Sampling sites		**Al**	**As**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**V**	**Zn**
A Beykoz		5810	2.07	42.76	16.70	5109	131.2	9.00	8.78	21.58	61.21
	1	8780	2.54	54.75	11.60	7679	169.6	6.78	8.21	26.60	83.49
	2	10,027	1.77	23.92	26.88	8177	254.1	10.27	10.43	24.55	70.04
	3	9003	2.66	45.40	17.25	8142	230.7	10.21	13.35	28.25	85.14
	4	2667	2.14	50.38	12.53	2567	43.71	6.24	7.01	18.41	47.27
B Kartal	**5**	3122	1.36	46.82	17.12	3102	83.22	6.60	9.04	17.02	56.06
C Maltepe	**6**	2871	1.97	53.32	19.95	3058	65.56	6.88	7.73	17.64	79.25
D Adalar		2937	3.17	50.61	18.11	3470	60.47	6.65	22.15	17.42	124.5
	7	2840	3.85	49.45	10.67	2905	51.64	7.53	21.38	17.46	110.1
	8	3033	2.50	51.78	25.55	4036	69.30	5.76	22.92	17.39	138.9
E Ataşehir	**9**	2609	1.71	56.16	20.74	2856	59.17	6.88	8.23	17.72	89.20
F Şile		2386	1.41	57.03	11.68	2149	72.70	6.49	6.17	18.61	28.02
	10	1723	0.58	42.40	7.13	1418	132.9	<DL	5.51	14.97	19.70
	11	4345	1.33	44.90	22.50	4147	64.25	5.70	7.49	19.89	43.14
	12	1649	2.61	88.05	<DL	1497	25.71	<DL	<DL	24.58	27.74
	13	2108	1.10	54.90	8.55	1841	70.33	7.28	5.50	16.82	24.76
G Üsküdar		1584	0.35	32.03	12.54	1496	42.21	6.04	8.39	10.99	76.13
	14	1309	0.57	31.15	13.27	1239	35.65	<DL	9.32	10.59	87.53
	15	2135	0.13	33.78	11.82	2011	55.34	6.04	6.53	11.81	53.33
H Pendik	**16**	2188	1.47	58.46	24.27	2428	57.20	5.55	10.20	17.44	57.65
Mean		2938	1.69	49.65	17.64	2958	71.47	6.76	10.09	17.30	71.50
Median		3999	1.77	50.61	20.49	3769	94.20	7.28	9.49	19.51	59.43
SD		1259	0.80	8.90	4.17	1069	26.92	1.01	5.01	2.93	28.36
R-m		460	3.34	3.45	2.52	648	58.50	1.05	6.89	2.97	15.51
R–c		680	0.63	1.06	3.60	430	63	*	4.90	1.47	30.40

<*DL* below detection limit, *R–c* certified reference lichen IAEA-336, *R-m* measured reference

*non-certified

distributed populations are homogeneous, the Tukey test was used to compare the means (Kalıpsız, 1981; Özdamar, 2002). Data tables were created with Microsoft Office Excel 2016 program for statistical analysis and presented graphically (Tables 3 and 4 and Fig. 5).

Results and discussion

Elemental concentrations

Based on the results of the quantitative laboratory analyses by ICP-MS, the data regarding the average values of the elemental concentrations detected in the lichen samples by localities are reported in Table 2. The amount of element contents accumulated in the *X. parietina* samples revealed that the order of average concentrations for 10 elements in the study area was Al > Fe > Mn > Zn > Cr > Cu > Pb > V > Ni > As (Fig. 2).

The trace elements measured in this study are among the important heavy metals for human and environmental health, as specified by WHO (2019) due to their toxic effects. The term "heavy metals" is used to mean the toxic effect for all these elements that have chemically different metallic properties.

The distribution of each element in the districts according to their average levels is shown in Fig. 3. The top 3 elements Al, Fe, and Mn, which were found to be in the highest concentration, according to the certified reference, are likely to cause serious contamination in the area. It is known that metals in the air can be bound to particulate matter (PM) (Conti & Tudino, 2016; U.S. EPA, 2017). Vannini et al. (2019) showed that transplant lichens can easily take up airborne PM and PM-bound metals into their thalli (when not covered with nylon). The air quality for the PM_{10} parameter in 2019 measured by IMM (2019) at Kartal (B) station, the only locality compatible with

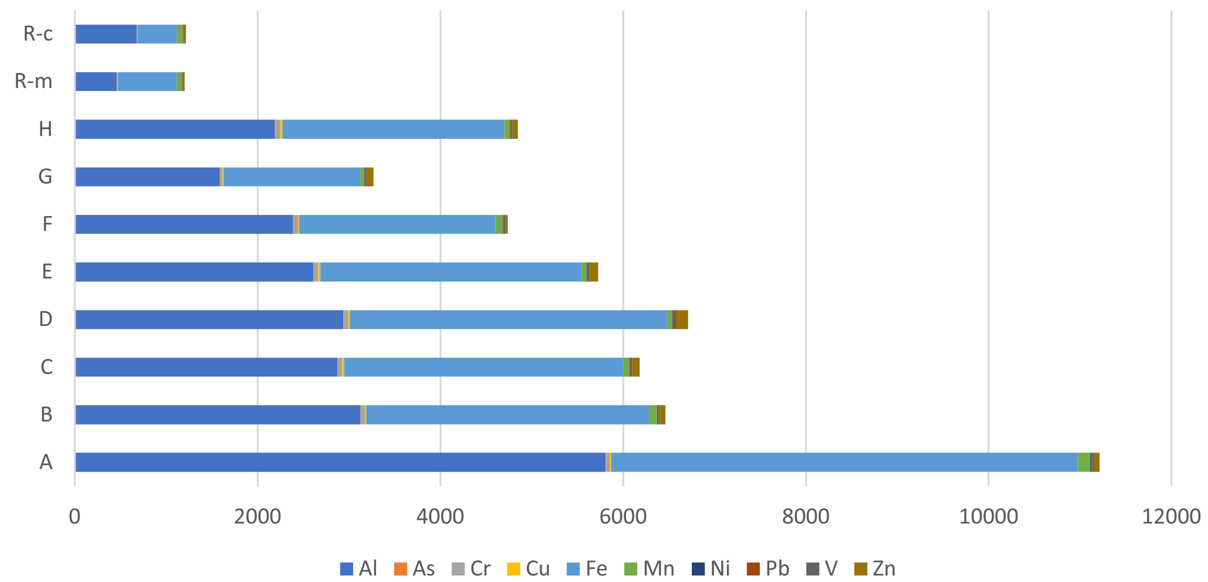

Fig. 2 Distribution of elemental concentration values (μg g^{-1}) by district averages. For abbreviations, see Table 2

our study, showed that it was bad for 111 days (above the limit) and very bad for 21 days (winter period). As a result, PM_{10} level may also have an effect on the high heavy metal contamination in the samples at the same station.

According to the data obtained, it was determined that Al, Cr, Cu, Fe, Ni, V, and Zn were 7 elements whose average concentration values were higher than the reference material measured in all sampled areas. As, Mn, and Pb elements were found to be higher in certain locations, while they are lower in others. Pb concentrations were higher than the certified reference value in all district averages.

Biomonitoring results can also be considered in terms of which elements in the air can be captured and accumulated in the lichen thallus. Accordingly, intracellular metal uptake in lichens can vary depending on many factors such as species, distance from the source of pollution, and climate (Garty, 2001). Rinino et al. (2005) reported that metals in the air are taken into the lichen thallus by being dissolved or captured as particles, and soluble metals tend to settle in extracellular or intracellular regions. With regard to the absorption mechanisms of metals in lichens, the heavy metals Cd, Cu, and Zn are reported to be the most taken into lichens (Brunialti & Frati, 2007) and the ones that stay in the thallus for a long time, 2–5 years residence time in most elements (Backor & Loppi, 2009). This may be another reason for the relatively high Cu and Zn ratios in our study.

Mapping studies were carried out to show the spatial distributions of each element, according to the localities, and 10 pollution maps created are shown in Fig. 4.

When the spatial distributions of the elements in the air are evaluated in the locations, A1, A2, A3, D7, D8, and H16 are the heavily polluted areas of the 16 studied regions in Asian side of Istanbul as sample areas with the highest measured mean values of the elements, while A4, B5, E9, G14, and G15 are the relatively cleanest areas. Especially in Elmasburnu Nature Park (A2) station, which is a touristic place by the sea in Beykoz district, Al, Cu, Fe, Mn, and Ni heavy metals yielded results far above the averages in other areas. The contamination here may have resulted from exposure to high levels of human influence. On the other hand, the sampling areas on Çamlıca hill in Üsküdar district (G14 and G15), the highest point of the city, were at the cleanest level. This result indicates that the altitude difference has a significant effect on air quality.

It is noteworthy that Prince's islands (D7 and D8) have the highest level of pollution in terms of As, Pb,

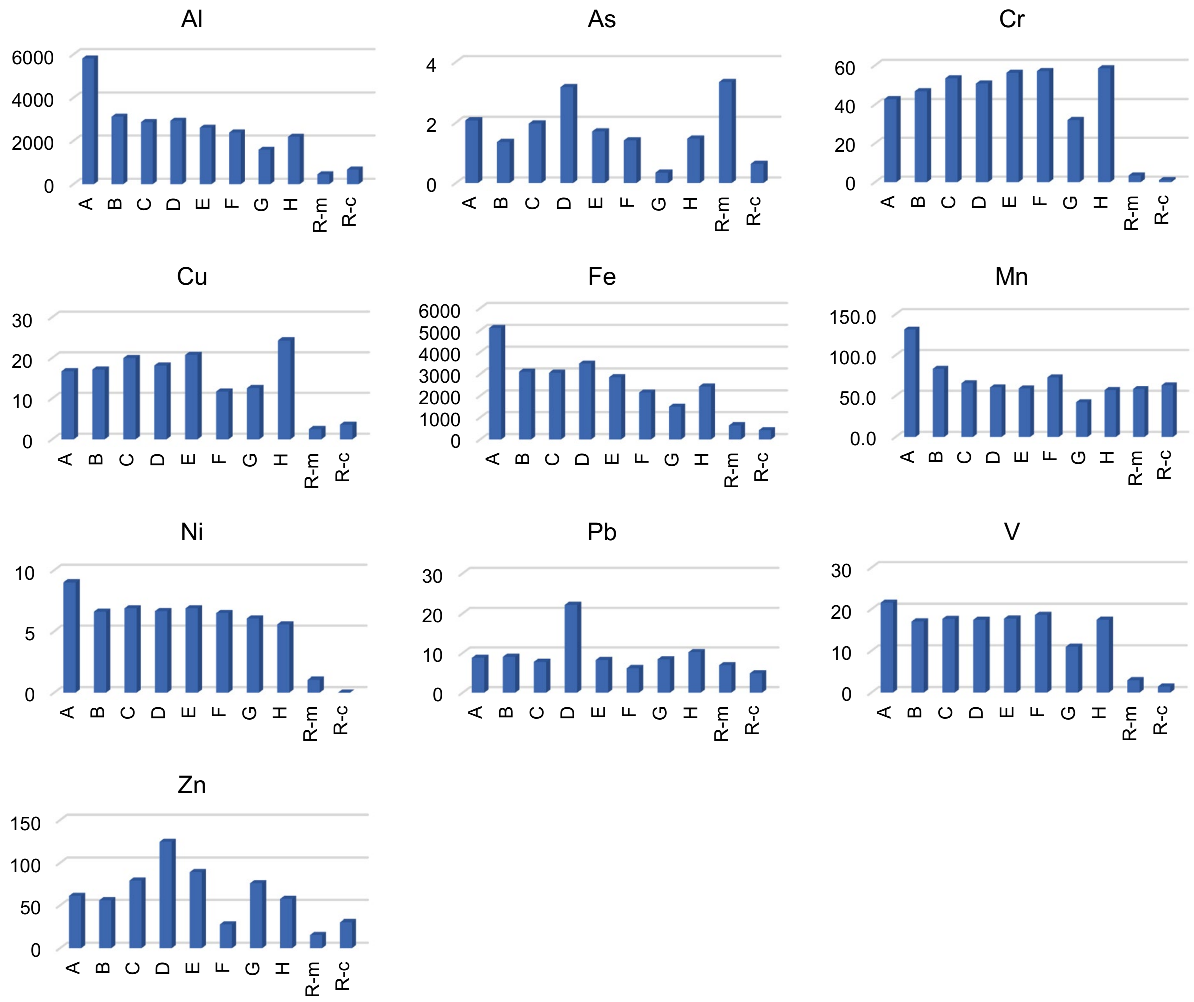

Fig. 3 Levels of each element in districts according to average values (µg g^{-1}). For abbreviations, see Table 2

and Zn, and it is also ahead of other places in terms of Cu, Fe, and Ni elements. While the standard Pb value determined by WHO (2019) is 10 µg/l in the EU, the value we obtained in Adalar (D7 and D8) area is 22 µg, which is well above the dangerous limit values for human health. The localities of A1, A2, and A3 in Beykoz, Al, Cu, Fe, Mn, Ni, and V reached the highest values, compared to other places. The elemental pollution of Göztepe nature park (A4) in Beykoz district is higher than the reference values, but lower than the other localities of the district.

Cr and Cu rates, which are 5th and 6th in the order of levels of the measured elements, are observed at the highest levels in Pendik (H16), compared to other districts. It is obvious that Cr, a heavy metal used in the leather industry, has reached the highest concentration with the effect of the leather industry facilities as well as chemical and textile products manufacturing plants in the district. In fact, this industrial area may have increased the amount of Cr in other stations by airborne long-distance transport.

Statistical analysis

Descriptive statistics showed that the distribution of the sampled localities formed according to each variable was normal. The mean of Al values of lichens was determined to be in the same group at $P < 0.05$ significance level according to Tukey comparison test. Al values of lichen samples found in Beykoz (A)

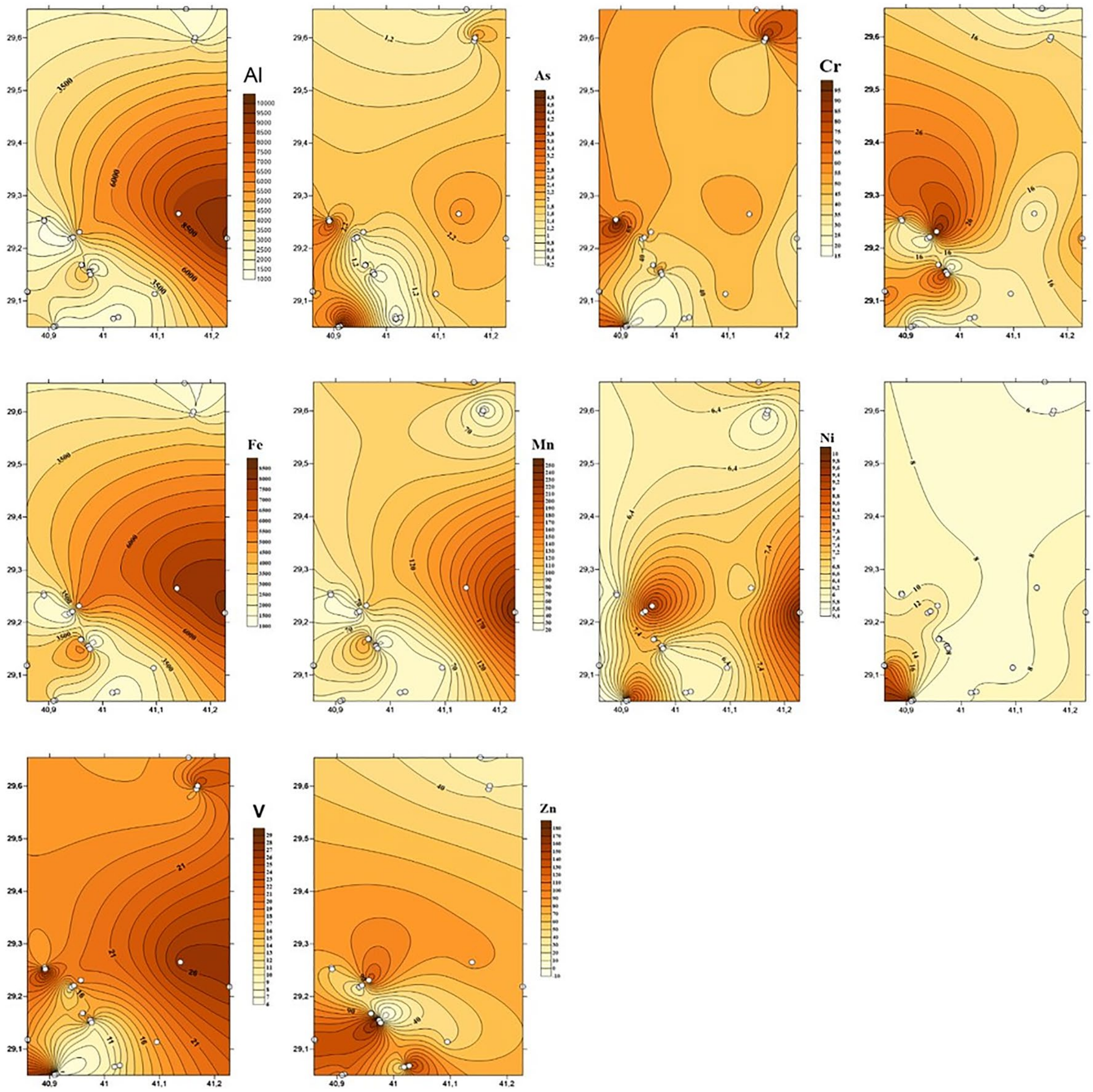

Fig. 4 Spatial distribution maps of airborne elements in lichen samples at the studied locations

Table 3 Comparison of descriptive statistics and averages values of Al (μg g^{-1}) in *X. parietina* samples

District in Istanbul	Number of samples	Range	Min.	Max.	Average	Standard error of the average	Standard deviation	Variants
A-Beykoz	13	11,491	1899	13,390	5810[a]	1156	4005	16,036,293
B-Kartal	9	4336	1074	5410	3122[a]	398	1195	1,427,350
C-Maltepe	12	2047	2776	4823	2871[a]	473	947	896,488
D-Adalar	4	2566	1557	4123	2937[a]	527	1053	1,109,810
E-Ataşehir	8	3292	1182	4474	2609[a]	495	1309	1,713,398
F-Şile	5	2696	1649	4345	2386[a]	503	1125	1,266,464
G-Üsküdar	6	2223	775	2998	1584[a]	322	788	620,668
H-Pendik	4	1956	1094	3050	2188[a]	309	757	573,358

The letter [a] shows group differences for the same subscale ($P < 0.05$)

Table 4 Comparison of descriptive statistics and averages values of Pb (μg g^{-1}) in *X. parietina* samples

District in Istanbul	Number of samples	Range	Min.	Max.	Average	Standard error of the average	Standard deviation	Variants
A = Beykoz	13	11.23	5.39	16.62	8.78^a	1.06	3.67	13.46
B = Kartal	9	14.54	0.00	14.54	9.04^a	1.36	4.09	16.76
C = Maltepe	12	2.45	6.03	8.48	7.73	0.57	1.13	1.28
D = Adalar	4	31.34	5.71	37.05	22.15^b	6.93	13.86	191.97
E = Ataşehir	8	9.60	0.00	9.60	8.23^a	1.73	4.58	21.02
F = Şile	5	7.49	0.00	7.49	6.17^a	1.55	3.47	12.07
G = Üsküdar	6	12.97	0.00	12.97	8.39^a	2.14	5.24	27.48
H = Pendik	4	10.75	0.00	10.75	10.2^a	2.15	5.27	27.78

The letters ^{a} and ^{b} show group differences for the same subscale ($P < 0.05$)

are higher than the others (Table 3). The locality with the lowest standard deviation is Pendik (H) region, while the highest point is Beykoz (A) region.

Mean Pb values of lichens were determined to be in two different groups at $P < 0.05$ significance level according to Tukey comparison test (Table 4). While the sampled locality groups in the first group are 2, 3, 6, 7, 8, 9, and 10, there is only locality 5 in the second group. While the locality with the lowest standard deviation was Maltepe (C); the locality with the highest was Adalar (D). Average values in *X. parietina* samples in the 8 districts were indicated in Fig. 5a for Al and in Fig. 5b for Pb.

Comparison with other lichen biomonitoring studies

In order to get a better picture of the elemental pollution level in the air in the Istanbul metropolis, comparative data are presented with the results obtained from other foreign locations. The data of this study were first compared with the results of the only previous biomonitoring study involving similar locations with the current study on the Asian side of Istanbul to see if there is a change in the current situation. In addition, elemental measurements by ICP-MS in similar lichen biomonitoring studies with the same species of lichen *Xanthoria parietina* in different cities in Turkey (Kocaeli, Düzce), Spain (Huelva), and Italy (Livorno) are compared with those in this study (Table 5) and displayed graphically in Fig. 6. The results were evaluated on the basis of elements and locations. The cities compared from Turkey were chosen based on their locations, and to the east of Istanbul are the provinces of Kocaeli (100 km), with dense industrial zones, and Düzce (200 km), on the same line further ahead.

In the biomonitoring studies selected for comparison, although lichen species, analysis method, and measurement units are the same; the pollution level in the compared regions may show some differences

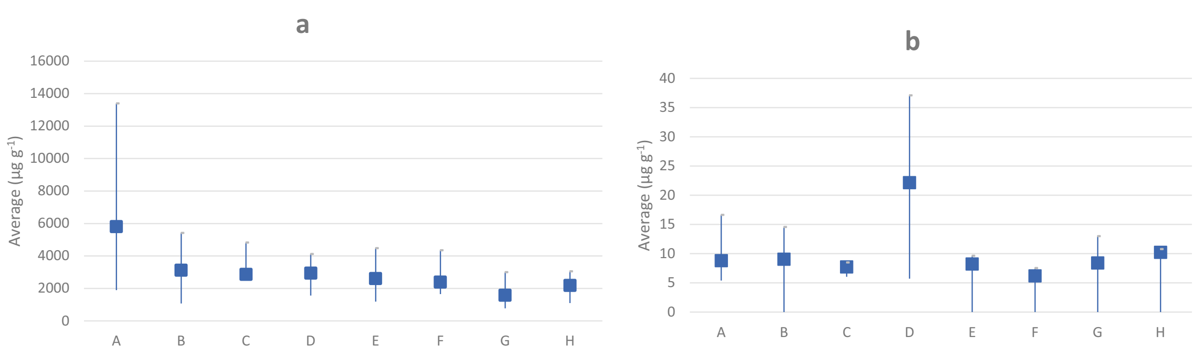

Fig. 5 Average, Min. and Max. values of Al (**a**) and Pb (**b**) in *X. parietina* samples in the districts

Table 5 Comparison of mean element concentrations (μg g^{-1}) measured in the thalli of *X. parietina* in 5 different biomonitoring studies and in the current study

Reference article	İcel and Çobanoğlu (2009)	Dogrul-Demiray et al. (2012)	Bozkurt (2017)	Parviainen et al. (2019)	Scerbo et al. (1999)	Özkök and Çobanoğlu (this study)
Research area	**Istanbul** TR-Turkey	**Kocaeli** TR-Turkey	**Düzce** TR-Turkey	**Huelva** ES-Spain	**Livorno** IT-Italy	**Istanbul Asian side** TR-Turkey
Al	18.5	1500	3612	2537	–	2938
As	–	1.9	1.6	–	1.3	1.7
Cr	21.4	–	13.1	11	7.52	49.7
Cu	45.2	15.9	16.4	769	–	17.6
Fe	9.7	3075	3321	4201	–	2959
Mn	150.4	90	140.1	57	–	71.5
Ni	17.1	6.1	8.3	7.9	6.26	6.8
Pb	71.4	40	10.3	31	11.85	10.1
V	–	9.5	13.2	–	3.74	17.3
Zn	194.9	166	87.3	138	46	71.5

– Unmeasured

depending on the details in the sampling procedure. In the evaluation made with average values without considering these differences, with an overview, the mean concentrations of As, Cr, and V elements were determined at the highest level in our study, compared to all the others (Scerbo et al., 1999; İcel & Çobanoğlu, 2009; Dogrul-Demiray et al., 2012; Bozkurt, 2017; Parviainen et al., 2019). Although the average level of arsenic in the air in İstanbul was found to be higher than in other cities, it ranks last in the element concentrations according to the data obtained in this study. The intense concentrations of Cr and V elements in the air, which are widely used in steelmaking, coating, and leather industries, seem likely to originate from the industry in Istanbul and nearby provinces.

According to the comparison table, Al element was found to be higher in Düzce (Bozkurt, 2017), and Cu and Fe were higher in Huelva (Parviainen et al., 2019), compared to our study.

In the study of İcel and Çobanoğlu (2009) more than a decade ago, the concentrations of Mn, Ni, Pb, and Zn, at the same time the elements with the highest values measured, were two to six folds higher than those

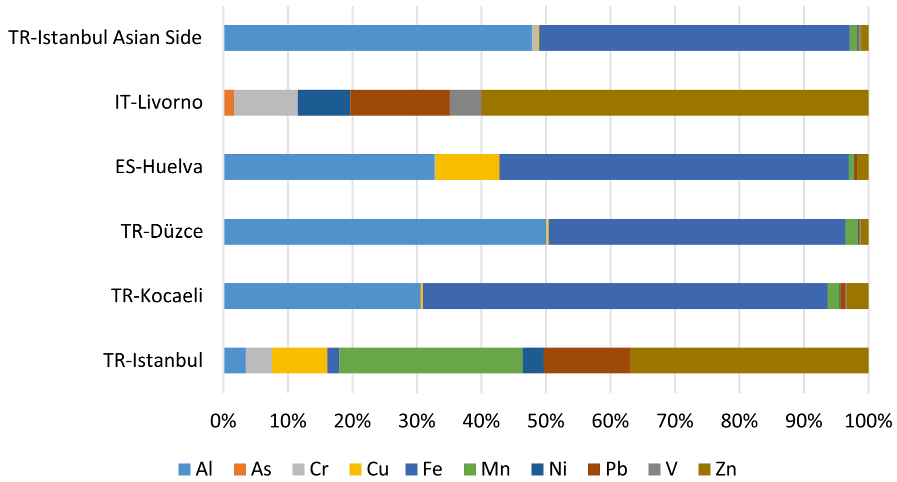

Fig. 6 Graphical representation (%) of trace elements measured in *X. parietina* in different cities on the base of Table 5

in our current study. The conclusion that can be drawn from this is that there is a decrease in the level of these heavy metals in the air in the Anatolian side of Istanbul today. The sampled areas of D8, D7, C, G14, A1, and F10 on the Anatolian side of Istanbul are common with those in this study. When a more specific comparison is made on the basis of locality, average concentration of Cu in the Kınalıada (D7) region in their study was 24.504 μg g^{-1}, while it was 11 μg g^{-1} in our study. Accordingly, it can be said that there has been a decrease in Cu pollution in the last 10 years. Despite the fact that motor vehicles are not allowed within the Prince's islands (Adalar district), it is noteworthy that highest Pb values are obtained in both studies (D7 and D8). The probable cause may be heavy ship traffic and winds transport of pollutants from the mainland. Dusts generated during industrial grinding processes and fuel fumes, especially lead, are also possible sources of these heavy metals in the city.

Today, it is known that emissions of pollutants can affect not only the environment of their source, but also over long distances. It is reported that there is a significant relationship between temperature, wind direction, wind speed, and humidity and air quality index (Kousehlar & Wisdom, 2020). Long range transport of some aerosols by easterly winds over the Gebze and Kocaeli industrial zones to the east of Istanbul may affect the air quality of the Asian side. In addition, due to the prevailing winds blowing from the north in Istanbul, it can be thought that atmospheric pollutants such as Pb may come from the Black Sea, especially from ship traffic. This possible wind effect is in question in the sampling areas in the southern districts of the Anatolian side, from west to east, Üsküdar (G), Adalar (D), Maltepe (C), Kartal (B), and Pendik (H), which are not deprived of green areas.

It has been shown that a significant part of the dust loading on Istanbul is Saharan dust from the deserts of Algeria, Libya, and Tunisia (İncecik & İm, 2013). It is also stated that the biggest contribution to PM_{10} levels in winter comes from traffic and combustion sources, and NO_X, $PM_{2.5}$, and O_3 emissions from Istanbul can be effective over long distances, especially in summer. Namely, it,can reach the eastern and southern Aegean region, a region from the western Black Sea to Egypt in the south, and the entire eastern Mediterranean and southern Europe. In some comparative studies with dust samples, the highest elemental concentrations in lichen thallus were observed for Cr, Zn, and Fe (Çobanoğlu, 2015). According to the data of this study, the very high concentrations of these elements in lichen samples may be due to airborne dust.

Conclusion

This study revealed the long-term accumulation of elemental pollution in the air through lichen biomonitoring from 8 districts in the Asian side of the Istanbul. There was a need to fill the gap in the lack of data on this subject, as past or ongoing studies on measurements of heavy metal levels in the air in Istanbul or based on biomonitoring were inadequate. The use of biological monitoring method with lichens provided the advantage of being able to reveal the spatial distribution of elements in urban locations. Biomonitoring has allowed focusing on air quality determination, particularly in terms of heavy metals released from anthropogenic emissions. The data of the study is also important in that it indicates long-term values that are captured by lichens that live in nature for a long time, rather than instant measurements.

The results from the present study showed that especially 7 toxic metals, Al, Cr, Cu, Fe, Ni, V, and Zn, were found in the urban atmosphere at a very high rate, compared to the reference. Al, Fe, Mn, Zn, and Cr element averages accumulated in the *X. parietina,* which is one of the species suitable for biomonitoring in big cities, were determined at the highest levels. Furthermore, among the sampled monitoring sites, those near sea level (at lower altitudes) were more polluted in terms of heavy metal distribution than those at higher altitudes. One of the clear results of the study was that the level of elemental pollution increased inversely with altitude.

Points considered to have a potential impact on the distribution of heavy metals polluting the air in the city are related to long-distance transport and wind effect, atmospheric dust, and elevation of the areas. High elemental levels were likely to be associated with lichens' retention of airborne dust and fuel fumes containing certain metals. In some coastal districts with high PM_{10} values, it seems likely that the PM-bound metals in the air have an effect on the detection of high metal ratios in our study in line with this. The emission sources of toxic elements are mostly industrial areas and motor vehicles in and around the city, and they are transported by air, causing an increase in pollution. Considering the high human population in the city of Istanbul, domestic and industrial wastes are among the possible consequences that affect the distribution of air polluting metals.

The decrease in natural areas together with many factors such as population density, unplanned urbanization, and industrialization brought about by being a metropolitan negatively affect the air quality of the city. In addition, despite the measures taken for climate change, since it is not possible to switch to clean energies completely and for economic reasons, fossil fuels are still used in many sectors. The dominant sources of atmospheric emissions in Istanbul are known as traffic, domestic heating, urban industry, sea and air transport, and dust. The lichen sampling areas selected are mostly hills, forests, groves, nature parks or natural recreation areas, but they are touristic places that people frequently visit. It has been concluded that the air quality of even these natural areas, which are thought to have clean air, is more polluted than expected in terms of heavy metals.

Periodic repetition of lichen monitoring studies at certain intervals is important for biological monitoring of air quality, as it reflects changes over time in the composition of atmospheric pollutants released into the air due to emissions from different sources. In this way, a comparative evaluation can be made with the data of previous biomonitoring studies. This study has contributed to the up-to-date data that complements some of the information deficiencies regarding Istanbul's air quality.

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Author contribution Conceptualization and design: Gülşah Çobanoğlu and Elif Aysu Özkök; methodology: Gülşah Çobanoğlu and Elif Aysu Özkök; material preparation, data collection, investigation, and analysis were performed by Elif Aysu Özkök; the first draft preparation: Elif Aysu Özkök; determination and supervision: Gülşah Çobanoğlu; writing, review, and editing: Gülşah Çobanoğlu; both authors read and approved the final manuscript.

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Data availability All the data generated or analyzed during this study are included in this published article.

Declarations

Competing interests The authors declare no competing interests.

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