



# Biomonitoring of atmospheric heavy metals in native lichen *Xanthoria parietina* around Salda Lake (Burdur – Turkey), a special environmental protection area

Gülşah Çobanoğlu<sup>1</sup> · Tuğçe Kaan<sup>2</sup>

Received: 12 April 2024 / Accepted: 12 June 2024  
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## Abstract

Exposure to air pollutants negatively affects human health as well as the ecosystem. The target study area, Salda Lake, which is a special environmental protection area with Turkey's and the world's geoheritage and unique natural values, has become one of the tourist attraction areas in recent years. However, quantitative data on airborne trace metals in the region remain poorly described. This study focuses on the spatial distribution of atmospheric heavy metals through lichen monitoring for the first time around Salda Lake. The concentration of airborne metals accumulated in *Xanthoria parietina* lichen thalli samples collected from 14 sites were evaluated by multi-element analysis with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The spatial distribution of toxic metals in the region was presented as separate pollution maps. Analysis data showed that Ni, Fe, Al, Cu and Zn accumulation levels in lichen thalli were significantly higher than reference. Visitor entrance, camping areas and the road line in the west and south of the lake were among the sample areas where metal contamination was evident. Due to the prevalence of chromium mineral deposits in the region, the high level of Cr content is also quite remarkable. It was concluded that Al, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the air are high enough to threaten human health and their levels vary depending on wind direction, human activities and traffic density. This study is important in terms of determining the level of air quality in this natural area and future perspectives.

**Keywords** Airborne trace metals · Heavy metal pollution · Lichen · Biomonitoring · Atmospheric pollutants

## Highlights

- First-ever biomonitoring in Salda provided data on long-term metal pollution.
- *X. parietina* around the lake was a good accumulator of airborne toxic elements.
- The effects of tourism and mining came to the fore in spatial metal contamination.
- Possible cause of pollution concentration in the west is the prevailing winds.
- The results were comparable to the literature performed with the same species.

✉ Gülşah Çobanoğlu  
gcoban@marmara.edu.tr

<sup>1</sup> Department of Biology, Faculty of Science, Marmara University, Istanbul, Türkiye

<sup>2</sup> Biology Department, Institute of Pure and Applied Sciences, Marmara University, Istanbul, Türkiye

## Introduction

Poor air quality, which is considered the biggest environmental risk factor today, affects not only humans but also the biodiversity and ecosystem health. In recent decades, air pollutants released into the atmosphere from many sources due to urbanization and industrialization have negative impacts on human health, environmental health and global climate change. The World Health Organization (WHO 2020) reported that people's risk of developing health problems, especially cardiovascular and respiratory diseases and lung cancer, increases due to exposure to the effects of air pollution, and 7 million deaths occurred globally in 2016. As they can be taken into the body through respiration and skin, they can accumulate in tissues and cause oxidative stress, DNA damage, cellular deterioration, various cancers and many diseases since they cannot be eliminated from the body. In case of excess metals in metabolism, they create a carcinogenic potential (Vigneri et al. 2017; Demir 2021). Heavy metals released into the atmosphere from different sources

can accumulate in the soil, sediment, plants, lichens, water resources, and seawater (Tchounwou et al. 2012).

Lichens with bioindicator properties, which are resistant to adverse climatic conditions but sensitive to air pollution, especially SO<sub>2</sub>, are widely used as biomonitors of airborne pollutants. They respond to air pollution to varying degrees depending on their species, and can reflect the amount of pollutants in the atmosphere, such as trace elements and organic chemicals that they have accumulated in their thalli due to their biological structure (Çobanoğlu Özyiğitoğlu 2020). It has been shown that there is a very high correlation between the diversity of lichen communities in northern Italy and the incidence of lung cancer (Cislaghi and Nimis 1997). In a study conducted in Algiers city (Algeria) by Ghenam et al. (2021), a significant correlation was found between air pollution levels determined by lichen biomonitoring and spatial variations of respiratory diseases asthma and bronchitis.

As living organisms in nature, the use of lichens as biological monitoring tools in the assessment of air quality is an approach that has been accepted for years in detecting long-term accumulation of atmospheric metals (Garty 2001). Airborne heavy metals, trace elements, radionuclides, persistent organic pollutants (POPs) and particulate matter (PM) can be detected by various methodologies suitable for lichen monitoring (Conti and Tudino 2016), resulting in much lower costs than air sampling. Monitoring air quality around pollution sources with lichens has become routine in many regions. In the lichen biomonitoring study carried out by Loppi (2000) around the geothermal power plant in Siena (Italy), it was determined that geothermal-derived hydrogen sulfide is both the main source of atmospheric sulfur and responsible for the decrease in lichen diversity in the environment. In another study conducted in Middletown, Ohio (Kousehlar and Wisdom 2020), it was found that toxic metals measured in lichen samples collected near steel and coke plants, the emission sources in the region, were at very high concentrations, but showed a sharp decrease at distances more than 3 km from the factories. It was also determined that atmospheric PM samples were rich in metal.

It has been reported in various studies that lichen species represent different bioaccumulation capacities against pollutants. Foliose epiphytic lichen species growing in urban and suburban areas near air pollution sources can best reflect the negative effects of pollution (Paoli et al. 2021). The epiphytic foliose *Xanthoria parietina* probably due to its thallus surface character and being widespread is one of the most frequently used lichen species in the biomonitoring of atmospheric pollutants (Scerbo et al. 2002; Nimis et al. 2001; Yeniso-y-Karakas and Tuncel 2004; Doğrul-Demiray et al. 2012; Bozkurt 2017; Vitali et al. 2019; Fortuna et al. 2021; Özkök and Çobanoğlu 2023).

This study focuses on monitoring atmospheric toxic elements through lichens around Lake Salda, Turkey's cleanest and deepest tectonic lake, which was declared as a 1st Degree Natural Protected Area in the Burdur Provincial Report in 1996 (TMMOB 2020). But, unfortunately, Burdur is among the provinces that exceeded the European Union (EU) limit values in terms of PM<sub>10</sub> measurement values in 2019 (Zeydan 2021). Recreational possibilities offered by Salda Lake with camping, local culture and touristic facilities, as well as some mining activities have a negative impact on the rapid pollution of the region in recent years. Poor air quality can threaten visitors as well as the public living in this area. However, since air pollution measurements are not made consistently in the region, there is no clear information about air quality. Lichen biomonitoring serves as a valuable tool for environmental monitoring in such rural natural areas where adequate monitoring devices are lacking. In addition, there has been no research in the literature on lichen monitoring around the Salda natural area so far. Our main goal is to obtain inferences based on lichen monitoring of the air quality around Salda Lake and to contribute to eliminating the lack of data on this issue. The study was designed to determine the spatial levels of atmospheric heavy metals and trace elements accumulated by native lichens around the lake using a long-term biomonitoring approach. This research will help provide the first basic biological data on air quality in the studied region and track future changes.

## Materials and methods

### Description of the study site

The study was conducted around Salda Lake, located at an altitude of 1193 m above sea level within the borders of the Yeşilova District of Burdur Province (Fig. 1B). Salda Lake with a maximum depth 190 m is known as the deepest lake in Turkey and the third deepest lake in the world (Temurçin et al. 2019). It is approximately 6.8 km wide and 9.2 km long and covers a lake area of 44.7 km<sup>2</sup>. The Lake draws attention with its unique structure, clear water, white sandy beach, and its “analog to Mars” due to the presence of microbialites, which are organo-sedimentary structures composed of hydrated magnesium carbonate, “hunhite”, in the rocks and sediments around the Lake (Balci et al. 2020). The activities for huntite mineral deposit and chrome mining operations in and around Salda Lake adversely affect the biodiversity in the region. The lake and its surroundings have been recently closed to mining licenses (TMMOB 2020). Mining around Salda Lake based on the data General Directorate of Mineral Research and Exploration of Turkey was shown in Fig. 1C.

The average temperature in Salda Lake and its surroundings, where the Mediterranean climate prevails, is 15 °C and varies between 30 °C in August and 2 °C in January. While January is the month with the highest rainfall with 162 mm, the least precipitation is in July with 16 mm. Northeast is the prevailing wind direction. The region contains wetlands, streams, dunes, woodlands, forests, mountain steppes, rocks, agricultural ecosystems and residential areas Salda Lake, which contains a very rich biodiversity in terms of flora and fauna, meets "Important Natural Area" and "Important Bird Area" criteria of IUCN (International Union for Conservation of Nature and Natural Resources) with its endemic species (Ceylan and Bulut 2019).

The land around the lake contains tectonic and karst depression areas. The fact that the lake water has an alkaline pH value ranging from 8.8 to 9.2 and its white beaches and turquoise color, which are the result of current magnesite formations, rise the popularity of the lake. In recent years, the destruction in the region has increased considerably due to the density of visitors, and the ecosystem of the lake has been under the threat of pollution as well as drought (Ceylan and Bulut 2019). Salda Lake was first declared as a 1st Degree Natural Protected Area in Turkey in 1989 and it was determined as a Special Environmental Protection Area in 2019 (<https://tvk.csb.gov.tr/salda-golu-i-91578>).

### Lichen sampling

*Xanthoria parietina* (L.) Th. Fr. (Fig. 1A), a native foliose epiphytic lichen species with orange colored-thalli, frilly lobes and often apothecia, was selected as the monitoring organism in the current biomonitoring study. The reason for choosing this species is that it is widely available in the research area and, as a pollution-tolerant species, it is among the best bio-accumulators of airborne trace elements (Fortuna et al. 2021; Nimis et al. 2001; Vitali et al. 2019). Since lichens develop slowly and unseasonably and their morphology remains the same throughout the year, sampling can be done in every season. Lichen samples were collected from the bark of various deciduous or evergreen trees between 23–26 June 2019 (Table 1), anticipating that this might reflect the air pollution caused by thermal power plants, coal mines and mining operations, which increases in the winter season, and the effects of visitor density starting in the spring.

Sampling was carried out at 14 different sites determined in the field at random points surrounding the lake along an area of approximately 15 km from north (37°59'39" N—29°65'45" E) to south (37°50'75" N—29°70'65" E) displayed in Table 1 and Fig. 1B. Composite biomonitoring samples, including 10 lichen thallus with a diameter of 1.5–2 cm (140 in total), were collected from each sampling site. During the fieldwork, care was taken to pick corticolous

lichen samples from tree branches or trunks at a height of at least 1 m above ground to prevent contamination from the soil, and at least 100 m from the main roads, based on the guidelines proposed by Bargagli and Nimis (2002). To minimize the possibility of contamination from tree bark, necessary steps in lichen sampling were followed, such as selection of the epiphytic species loosely attached to the substrate, careful cleaning of the lower surface of the thallus. The outermost part of the thallus, which had the least or no connection with the tree bark, was selected for the analyses. The collected samples were wrapped in paper towels, kept in paper bags and envelopes. Lichen samples were air-dried in the laboratory and stored in polyethylene bags until chemical analysis.

### Quantitative analysis

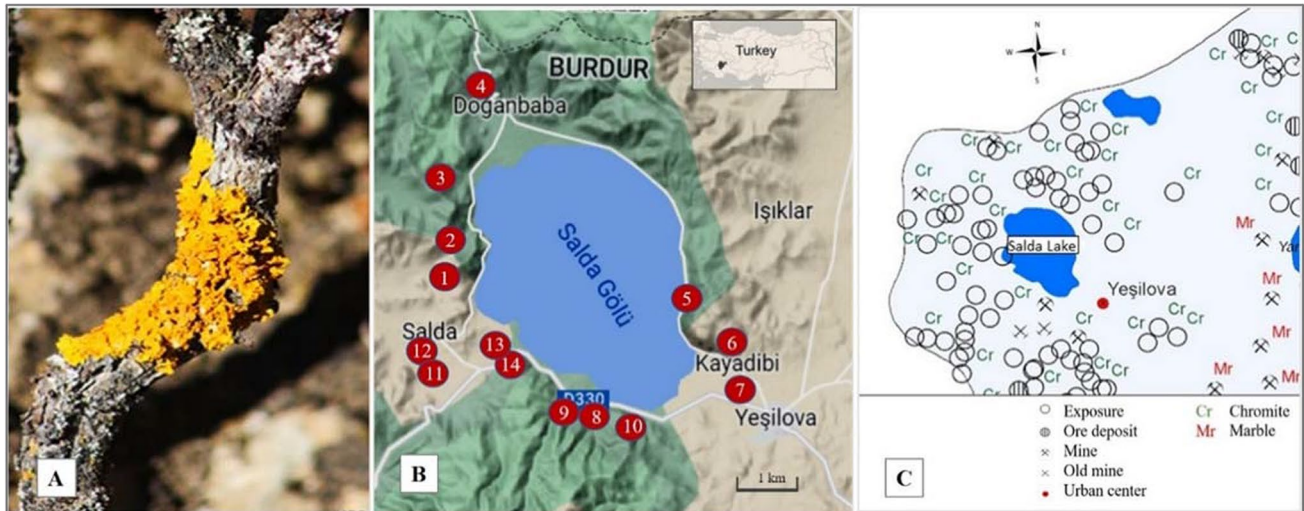
The composite lichen samples collected for analysis were carefully separated from their substrates (bark) with the help of forceps under a stereomicroscope and were cleaned of foreign matter and dust. The cleaned samples were washed twice with distilled water in petri dishes to remove the dust remaining on the thallus surface and left to dry for 2–3 h at room temperature. Subsequently, the samples were placed into an oven and dried again at 60 °C for 12 h. The dried thalli of the lichen samples were homogenized by grinding and powdered (Yenisoy-Karakas and Tuncel 2004). The powdered samples were then transferred into the sealed falcon tubes by labeling their weighed amounts and stored under sterile conditions for further analysis.

Solubilization of lichen samples was carried out with Microwave digestion system (CEM Mars X-press) with 3 subsequent repetitions. For this, 0.1 g of the lichen samples was placed into the microwave containers after adding 6 ml of King's solution (3:1 ratio, HCl: HNO<sub>3</sub>) in the fume hood. Then, the containers were closed and kept in the microwave at 160 °C for 15 min. Following these steps, the solubilized samples were taken into the falcon tubes and completed to 50 ml with ultrapure water.

After the cleaning, grinding and solubilization steps, Inductive Coupled Plasma-Mass Spectrometry (ICP-MS, Agilent 7500 Tokyo, Japan) analysis was conducted at Advanced Technology Education, Research and Application Center in Mersin University. Concentrations of 10 elements, Al, As, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn were measured in all lichen samples from Salda Lake region, including IAEA-336 certified reference lichen material provided by the International Atomic Energy Agency (Heller-Zeisler et al. 1999).

### Data analysis

The data obtained were evaluated by comparing with the reference values, and the spatial analysis of the elements in



**Fig. 1** a Epiphytic foliose orange lichen, *Xanthoria parietina* b Study area with sampling sites (1–14) around Salda Lake basin in Burdur province c Mining map of Salda Lake surroundings

the region was presented with the pollution maps created using the SURFER 17.1 software program (Fig. 4). In this software, the sampled points are placed according to the coordinate system by using the Kriging algorithm together with the gridding method. In this way, contour maps representing the distribution of air concentrations of each analyzed element in the study area were created. Analysis data was also shown in tables (Table 2) and graphs created with Microsoft Office Excel 2016 program (Figs. 2, 3 and 6). Atmospheric trace element levels were statistically assessed by multivariate hierarchical cluster analysis for differences between sampling sites in the study area using the PAST 4.12b software package. The Ward's method was applied to determine the correlation of monitoring sites with elemental concentration distribution. Group affinities of metal levels were shown by two-way stratigraphic dendrogram (Fig. 5A). Boxplots are also provided to visualize the outliers and the distribution pattern of each element in the dataset (Fig. 5B).

## Results and discussion

### Elemental composition of biomonitoring samples

The measured concentrations of airborne trace elements (Al, As, Cr, Cu, Mn, Fe, Ni, Zn, V, Pb) accumulated by epiphytic lichen samples taken from Salda were evaluated according to the criterion of comparison with the lichen reference material (IAEA-336) applied as a standard. Element concentrations and average values of the biomonitoring lichen samples along with the measured and certified values of the reference lichen were provided in Table 2. In the measured values, all of Cd, the majority of As, and

many of Pb and Cu were detected below the limit. For this reason, Cd is not shown in the table and is excluded from graphical evaluation.

The mean values of *X. parietina* monitoring samples from all areas were found to be 43.3 times higher for Ni, 8 times higher for Fe, 2.9 times higher for Al, 2.5 times for Cu and 1.7 times higher for Zn when compared with the measured reference lichen (R-m). All measured values of the As element in Salda samples were below the R-m value. Accordingly, airborne metals accumulated in abundance by lichen thalli in Salda were listed in decreasing order as Ni > Fe > Al > Cu > Zn > Pb > Mn > Cr > V > As. Compared to the certified reference (R-c) values (\*Ni non-certified), the average concentrations of the measured elements were found to be higher 25.4 times for Cr, 5.1 times higher for Fe, 4 times higher for V, 2.8 times for Al, 2.5 for As 1.8 for Cu, 1.2 times for Pb and 1.1 times for Zn. In this case, the ranking was as follows; \* Ni > Cr > Fe > V > Al > As > Cu > Pb > Zn > Mn (Table 2).

*Xanthoria parietina*, observed at each of the sampling sites in the Salda region, has been reported to be a physiologically toxic-tolerant lichen species suitable for measuring the spatial level of air pollution (Parviainen et al. 2019; Dzubaj et al. 2008). In terms of its performance in metal accumulation, it can be said that *X. parietina* in the present study was a good collector for Al, Cr, Cu, Fe, Mn, Ni, Pb and Zn, but their maximum concentrations vary by localities. In a biomonitoring study conducted with the same species in Poland, it was stated that *X. parietina* thalli showed the highest accumulation in terms of Cu, Fe, Mn and Zn, and the least accumulation in Pb and Ni (Parzych et al. 2016). When compared with the results of our study, the elements reported to have high accumulation levels are

similar, while those with the lowest accumulation differ; It was observed that Ni in our study was at the highest level in the ranking of average metal concentrations compared to the reference.

## Spatial analysis

The distribution of the mean concentration level of each element measured in *X. parietina* across the monitoring sites is shown in Fig. 2.

By evaluating the elemental data, spatial variation of pollution levels based on mean values across the monitoring sites is arranged from high to low as follows: 12 > 2 > 13 > 1 > 8 > 14 > 4 > 9 > 6 > 5 > 10 > 11 > 3 > 7 (Fig. 3). Among the monitoring sites, the four most intensively measured metals were significantly similar and followed the decreasing order of sites 2, 12, 9, 7, 13 for Ni, 2, 12, 11, 7, 13 for Fe, 12, 9, 10, 6, 11 for Al, and 2, 13, 7, 8, 12 for Cu. Maximum concentration levels were detected for Fe, Mn and Pb in site #12; for Cr in site #13; for Ni in site #2; for Al in site #1 (the forest land at the entrance of Lake Salda); for Zn in site #6. Although Cr, Fe and Ni concentrations were recorded above the reference in site #4 (Doğanbaba village), they were still below the average values in Salda.

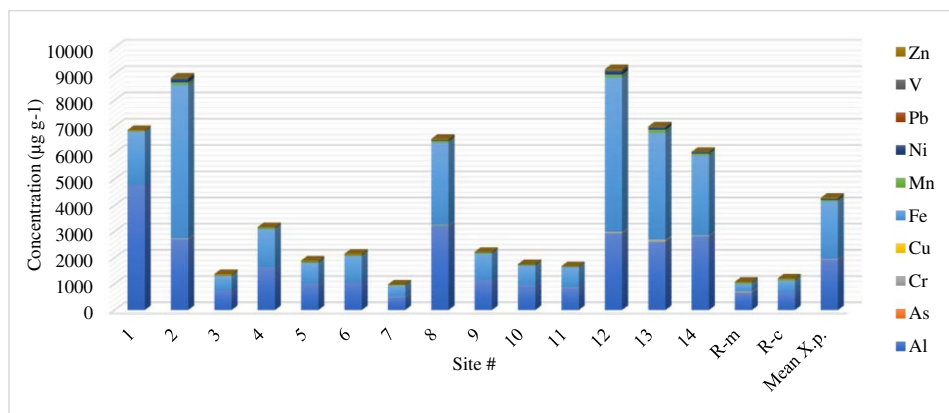
The ranking of the monitoring sites with the highest pollution level above the average in Salda is 12, 2, 13, 1, 8, 14, and the least polluted sites are 3, 7, 11, 10, 5, 6 (Fig. 3). The sample areas in the Central Village (#12, 13, 14), which are the monitoring areas in the west of Salda Lake, the rocky area further north (#1, 2), and the recreation facility area (#8), were determined as the most polluted areas with the highest Al, Cr, Cu, Fe, Ni, Pb, V, Mn and Zn concentrations. It turned out that the cleanest locations were around the rocky terrain located in the north of the Lake (#3) in Doganbaba village in the northwest and Kayadibi village (#5, 6, 7) in Yeşilova district in eastern parts of Salda Lake, and area behind the forest side of the

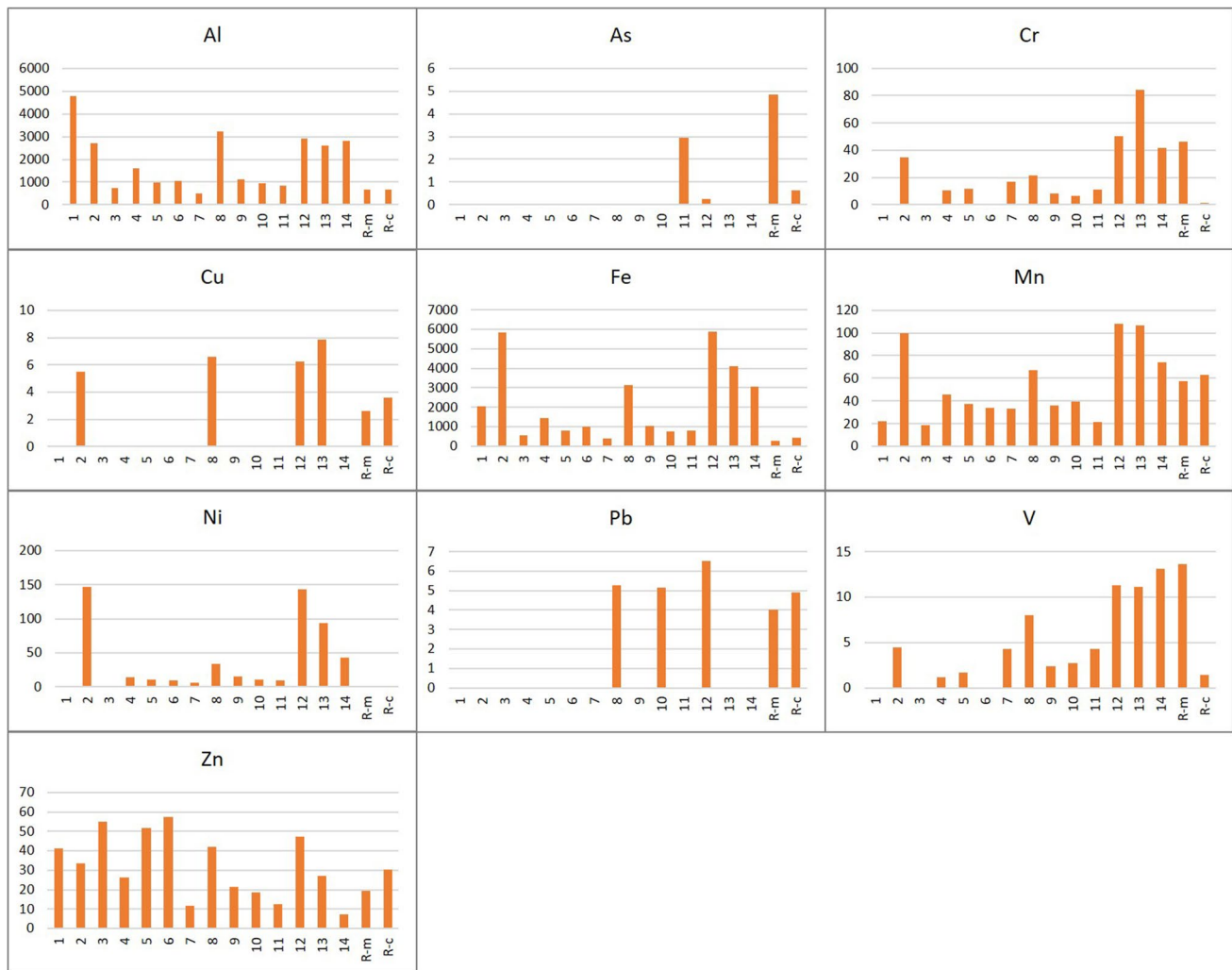
campsite (#10). Spatial distribution maps created for each element based on average concentrations in biomonitoring lichen samples in the study area are presented in Fig. 4.

Heavy metals from anthropogenic emissions enter the atmosphere as particles and/or byproducts from activities such as mining, smelting, fossil fuel combustion and waste incineration, sewage sludge, sewage effluents, commercial fertilizers and pesticides, and accumulate in lichens as reported in numerous studies (Kousehlar and Wisdom 2020; Loppi 2000; Vitali et al. 2019). Mining and smelting activities are considered the main sources of atmospheric heavy metals (Milow et al. 2022). It has also been pointed out that these air pollutants do not remain at the emission source and can spread over long distances with different meteorological factors such as wind direction, wind speed, and thermal slope (Çobanoğlu 2015). The monitoring areas in our study, where heavy metals such as Ni, Fe, Al, Cu and Cr are in high concentrations, correspond to the visit entrance, the campsites and the road route around the lake, especially in the west and south of the lake. The effect of the northeast prevailing wind is thought to contribute to the transport of atmospheric heavy metals to the west of the lake. This situation also reveals the negative impact of people and vehicle density. These heavy metals, detected at high levels in the study area, are among the metals with sufficient human evidence to be classified as carcinogenic (Tchounwou et al. 2012), and they have been shown to cause DNA damage through base pair mutation, deletion, or oxygen radical attack on DNA (Briffa et al. 2020).

Nickel, which ranks first among airborne heavy metals around Salda Lake with an average value of  $44.6 \mu\text{g g}^{-1}$ , was detected at the maximum level ( $146.6 \mu\text{g g}^{-1}$ ) in site #2. The European Union (EU) has set a target value for Ni, a human genotoxic carcinogen, of  $20 \text{ ng/m}^3$  for its concentration in ambient air (Communities 2001). The vast majority of nickel emissions are cited as anthropogenic sources, including the burning of oil for heat or energy production, nickel mining, burning of waste and sewage sludge, steel-making, electroplating, and coal combustion. High levels

**Fig. 2** Location-based contamination levels based on mean element values accumulated in thalli of *X. parietina* (*X.p.*) across the monitoring sites





**Fig. 3** Distribution of elemental concentration values ( $\mu\text{g g}^{-1}$ ) in monitoring sites (#1–14)

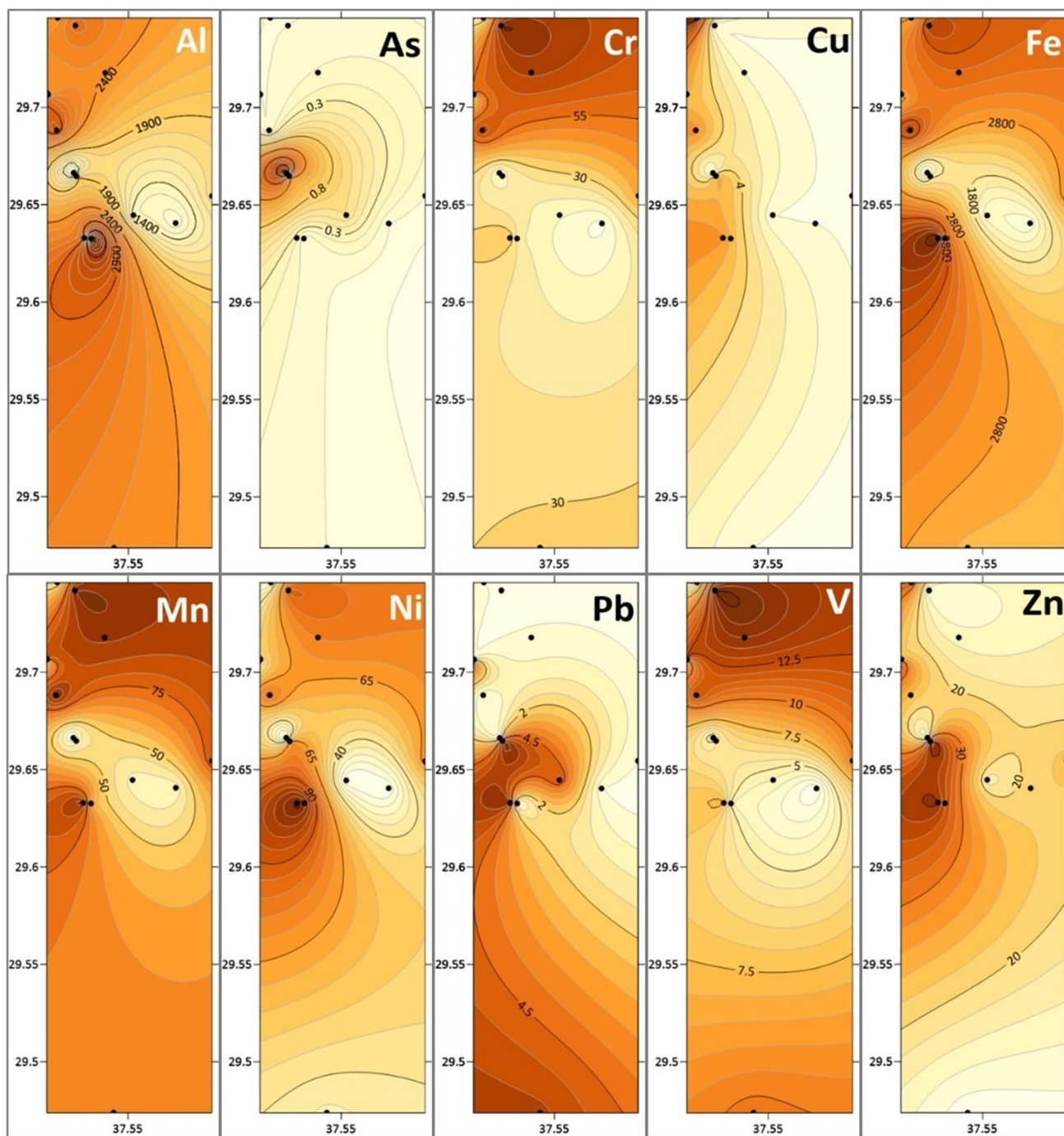
of Ni can be toxic to plants and humans since it causes respiratory system cancers (Briffa et al. 2020). Atmospheric Ni is closely associated with metallurgical industry emissions and the combustion of liquid fuels (Parzych et al. 2016) and probably released into the atmosphere from industry and vehicle exhausts in the Salda region.

Although copper is relatively lower, the significantly high levels of iron detected in the study region is alarming. While Cu increases mostly due to mining, traffic, fungicides and fertilizers used in agriculture, the main source of Fe is mining and heavy traffic. It has been noted that inhalation of iron-rich air pollution nanoparticles emitted from industrial and traffic-related sources can catalyze the formation of harmful reactive oxygen species (ROS), leading to oxidative stress and cell damage or death (Maher et al. 2020). Long-term exposure to Fe and Cu in airborne fine particulate  $\text{PM}_{2.5}$ , together with their combined effect on ROS, has been

consistently associated with increased CVD mortality from early childhood (Zhang et al. 2021).

Aluminum levels in the air were found to be high, most likely due to industrial emissions. Al concentrations did not exceed the Salda average in sampling sites #3, 5, 9 and 11, and the reference in site #7, but it was observed to increase up to 2.9 times in all other areas (Fig. 3 and 4). Compared to the mean value of *X. parietina* conducted in rural-industrial Düzce province ( $3149.2 \mu\text{g g}^{-1}$ ) (Bozkurt 2017) and in urban-industrial İstanbul Asia ( $2938 \mu\text{g g}^{-1}$ ) (Özkök and Çobanoğlu 2023), concentration level of Al in Salda ( $1915 \mu\text{g g}^{-1}$ ) appeared lower. However, it is not a coincidence that Al contents is mostly found in sample sites where people are crowded, such as areas close to the central village of Salda, human recreation areas and the shore and entrance part of the lake.

In humans, zinc is an important element primarily in cell-mediated immunity and also as an antioxidant and



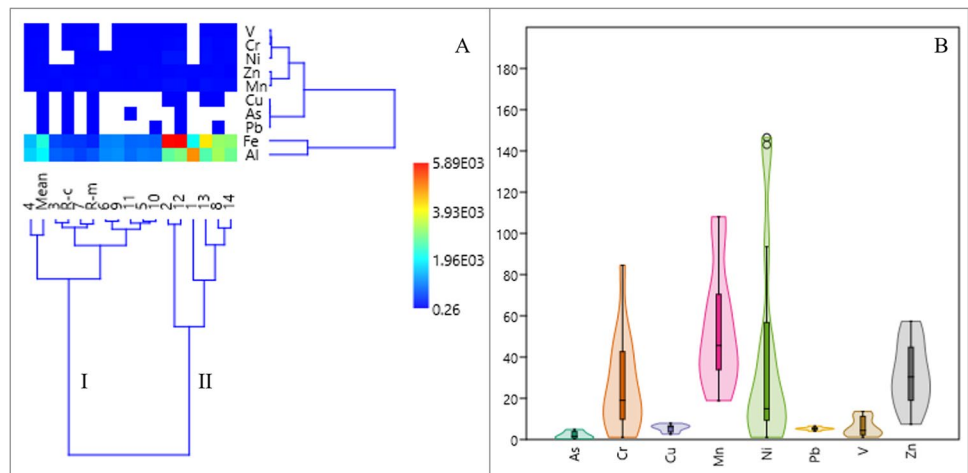
**Fig. 4** Spatial distribution levels of elements ( $\mu\text{g g}^{-1}$ ) in the Salda Lake region

anti-inflammatory (Prasad 2014). However, *Zn*, which is approximately 2 times the reference value in the work area air, is at a level that can threaten human health.

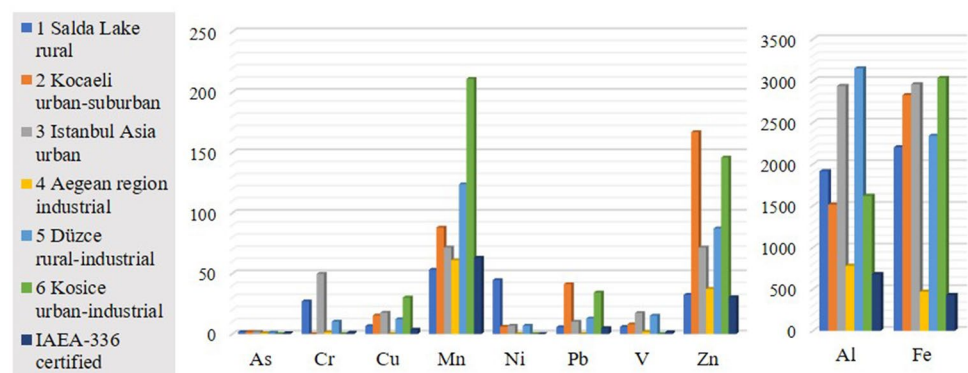
*Pb*, which humans are exposed to from sources such as food, water and contaminated dust, is a nonessential trace metal with no safety threshold (Stojsavljevic et al. 2024). Lead reached the highest value ( $6.51 \mu\text{g g}^{-1}$ ) in the 12th sample site, which turned out to be the most polluted

area in terms of heavy metal levels, and was found to be higher than the reference in the 8th and 10th sample sites, but remained below the limit value in the other sites around Salda Lake. The primary and secondary *Pb* standards are  $0.15 \mu\text{g/m}^3$  limited by EPA to protect human health and the environment from lead pollution in the air. Lead can be emitted into the air in the form of particles small enough to stay suspended in the air. Depending on

**Fig. 5** **a** Group affinities based on the average of the elements are shown by a two-way stratigraphic dendrogram (Ward's method, cophen. corr.: 0.8382) **b** Box plots for the distribution of element concentrations (excluding Al and Fe due to their higher numerical values), Error bars indicate standard deviations



**Fig. 6** Element levels ( $\mu\text{g g}^{-1}$ ) of different monitoring studies conducted with *X. parietina* in the literature (Al and Fe are presented on separate axes in order not to obscure those of other elements, as they have much higher concentration values than the others)



**Table 1** Geographic information on the sampling sites around Salda Lake

Site Number	Geographic coordinates	Tree substrate	Habitat/ Place name
1	37°54'23'' N—29°64'04'' E	cedar	rocky area to the west of the lake
2	37°55'25'' N—29°64'46'' E	juniper	Woodland to the west of the lake
3	37°57'49'' N—29°64'05'' E	cedar	Doganbaba beach in the northwest
4	37°59'39'' N—29°65'45'' E	cherry	lakeside, Doganbaba village
5	37°53'77'' N—29°71'79'' E	red pine	rocky area in the east of the lake
6	37°52'22'' N—29°74'20'' E	oak	wooded area, way to Kayadibi village
7	37°51'29'' N—29°74'60'' E	acacia	Kayadibi village, east side of the lake
8	37°50'76'' N—29°70'69'' E	oak	recreational facility area
9	37°51'24'' N—29°68'82'' E	mulberry	Hasmet tent garden
10	37°50'75'' N—29°70'65'' E	cedar	forest area, behind the Lake campsite
11	37°52'67'' N—29°63'29'' E	plum	Salda central village, roadside
12	37°53'05'' N—29°63'26'' E	acacia	Salda central village, roadside
13	37°52'28'' N—29°66'46'' E	black pine	lakeside, Salda central village
14	37°52'12'' N—29°66'63'' E	black pine	roadside woodland, exit from Salda

the exposure level, lead can adversely affect the nervous system, kidney function, immune system, reproductive and developmental systems and cardiovascular system, and the oxygen-carrying capacity of the blood (<https://>

[www.epa.gov/lead-air-pollution](https://www.epa.gov/lead-air-pollution)). Especially Salda central village seems to be under threat in terms of *Pb* in the air.

Due to the widespread chromium mineral deposits in the region, *Cr* contents are most likely quite pronounced around Salda Lake, especially at sampling sites #12 and

**Table 2** Elemental concentrations ( $\mu\text{g g}^{-1}$  dry weight) of the monitoring samples of *X. parietina*

Site #	Al	As	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
1	4780	<DL	<DL	<DL	2031	22.16	<DL	<DL	<DL	41.39
2	2698	<DL	34.53	5.5	5848	99.9	146.6	<DL	4.44	33.71
3	748	<DL	<DL	<DL	556	18.89	<DL	<DL	<DL	55.09
4	1622	<DL	10.33	<DL	1457	45.6	14.7	<DL	1.15	26.2
5	973	<DL	11.63	<DL	808	37.49	10.58	<DL	1.69	51.69
6	1060	<DL	<DL	<DL	996	34.14	9.01	<DL	<DL	57.34
7	498	<DL	16.63	<DL	407	33.6	5.85	<DL	4.32	11.75
8	3224	<DL	21.33	6.6	3130	67.1	33.25	5.29	8.04	42.14
9	1108	<DL	8.18	<DL	1035	36.19	15.16	<DL	2.43	21.3
10	939	<DL	6.43	<DL	741	39.23	10.58	5.17	2.74	18.51
11	830	2.94	10.88	<DL	786	21.62	9.38	<DL	4.31	12.64
12	2930	0.26	50.43	6.23	5888	108	143	6.51	11.31	47.34
13	2593	<DL	84.58	7.88	4087	106.3	93.45	<DL	11.14	27.29
14	2808	<DL	41.43	<DL	3055	73.75	43.55	<DL	13.11	7.43
Min	498	0.26	6.43	5.5	407	18.89	5.85	4.01	1.15	7.43
Max	4780	2.94	84.58	7.88	5888	108	146.6	6.51	13.11	57.34
Mean	1915	1.60	26.94	6.55	2202	53.14	44.59	5.66	5.88	32.42
S.D.	1261	1.90	24.13	1.00	1910	31.98	52.82	0.74	4.27	16.94
Median	1365	1.60	16.63	6.42	1246	38.36	14.93	5.29	4.32	30.50
95% C.I.	$\pm 320.2$	$\pm 1.3$	$\pm 6.9$	$\pm 0.5$	$\pm 485.0$	$\pm 8.1$	$\pm 14.5$	$\pm 0.4$	$\pm 1.2$	$\pm 4.3$
R-m	661	4.85	46.33	2.60	275	57.80	1.03	4.01	13.61	19.49
R-c	680	0.63	1.06	3.60	430	63	*	4.90	1.47	30.40
95% C.I.	$\pm 110$	$\pm 0.08$	$\pm 0.17$	$\pm 0.50$	$\pm 50$	$\pm 7$		$\pm 0.6$	$\pm 0.22$	$\pm 3.40$

<DL: below detection limit; \* not certified; # number; Min: Minimum; Max: Maximum; S.D.: Standard deviation; C.I.: Confidence Intervals; R-m: Reference-measured; R-c: Reference-certified (IAEA-336)

#13 with the higher levels (Fig. 1c). In addition to mining activities, building stones such as sand, gravel, granite, andesite, basalt, limestone and marble extracted by open pit operations are among the activities that cause air pollution in the form of dust emissions. In the report of the Union of Chambers of Turkish Engineers and Architects (TMMOB 2020), it is stated that marble quarries around the lake basin and mining activities, especially chromite, are among the activities that affect and pollute the lake and its immediate surroundings. The report also draws attention to the damage caused by agricultural activities such as the use of fertilizers and pesticides to forests, agricultural areas and water regime. Along with these, recent increase in tourism and leisure activities such as picnics, camping, bicycle and off-road tours, and festivals threaten the sensitive lake.

### Statistical analysis

The dendrogram constructed by hierarchical cluster analysis reflects some indicative results regarding the average concentrations of toxic elements (Table 2) measured in

lichen thalli samples in the monitored areas (Fig. 5A). Box plots for visualizing the distribution level of each metal in the data set are indicated in Fig. 5B.

The affinity of metal levels showed a distinct grouping for Fe and Al, while the others were grouped in two sub-groups: Mn, Zn, Ni, Cr, V and As, Cu, Pb (Fig. 5).

The spatial distribution of each element in *X. parietina* monitoring samples gave rise to two main clusters. Cluster I was divided into 2 sub-groups; one included both certified and measured reference lichen (*E. prunastri*), and sites #3, 7, 6, 9, 5, 10, 11, and the other grouped together with mean of Salda, and site #4. The areas with metal levels closest to the reference are sites 3 and 7.

In cluster II, sampling sites #2, 12, 1, 13, 8, and 14 were included together. Elements converged within the same group, with strong intercorrelations. This second cluster of the sampling sites based on metal pollution levels includes areas where human activities are concentrated, such as visitor entrances and recreation areas, mostly in the west and south of the lake. According to this conclusion, human density and wind factors emerge as two reasons for the low air quality in these areas.

## Comparison of results with five other biomonitoring studies

Trace element levels were compared with several lichen biomonitoring studies in Turkey, which were conducted with *X. parietina* samples around urban and industrial areas in Istanbul, an industrial city, Kocaeli, and Düzce, where urban and industrial areas are intertwined. Additionally, a similar study in the Aegean region covering many provinces and a study conducted in Kosice, the industrial city of Slovakia, were also included in this comparison. The results of these studies compiled from the literature based on the average concentrations of atmospheric elements monitored in *X. parietina* (Table 3) are shown in Fig. 6.

When compared with those in five other studies in terms of the first three elements, *Ni*, *Cr* and *Fe*, which are at higher concentrations in Salda than the certified reference, the *Ni* value in this study is the highest among the values measured in other places. Although the *Cr* in Salda is lower than in Istanbul (Özkök and Çobanoğlu 2023), it is at a much higher level than in the Aegean and Düzce (Bozkurt 2017). *Fe* in the air of Salda is at a value approaching the measurements in Turkey's industrial cities Kocaeli, Istanbul and Düzce, and was found to be very high compared to the Aegean region (Fig. 6).

The *Al* level in Salda is lower than in Düzce, Istanbul and Kosice-SR (Dzubaj et al. 2008), but higher than in the Aegean region (Yenisoy-Karakas and Tuncel 2004) and Kocaeli (Doğrul-Demiray et al. 2012). Although *Cu*, *Pb*, *Mn* and *Zn* levels are slightly higher than certified IAEA-336 in Salda, they are quite low compared to all other places (Table 3). These comparative results reveal that Salda's air quality is low enough to compete with many urban and industrial regions in terms of the amount of heavy metals in the air.

## Conclusions

Global warming, drought risk, unconscious agriculture, mining activities, quarries, increasing tourism activities and construction works are the main factors threatening Salda Lake and its surroundings, which is a unique natural heritage and 1st Degree Natural Protected Area. The lack of information based on biomonitoring on air pollution around this important natural area necessitated the study. Data obtained based on lichen biomonitoring are important in the study area where aerial measurement devices are not sufficient. In addition, while element measurements directly from air samples show instant results, lichen biomonitoring provides advantages in long-term evaluation of pollution. Epiphytic foliose biomonitoring lichen *X. parietina* provided reliable long-term data to estimate the extent of air quality in the Salda region by the level of toxic metals.

The results of the current biomonitoring study, based on elemental analysis of lichen samples around Salda Lake, provided evidence that the air quality in the region has seriously decreased in terms of heavy metals. Conclusive results showed that *Al*, *Cu*, *Fe*, *Mn*, *Ni*, *Pb* and *Zn* in the air were quite high and their levels varied mostly depending on wind direction and the intensity of human activities and traffic. It is clear that the high levels of airborne *Cr*, mostly detected in the lichens in the western and southern sample areas (#2, 8, 12, 13, 14) of the lake, originate from chromium mineral deposits and wastes released into the environment without appropriate reclamation processes, as well as the prevailing northeast wind.

Although the economy of Burdur Province, where Salda Lake is located, is largely based on agriculture and animal husbandry, it has become inevitable to be exposed to the impacts of atmospheric heavy metal pollution due to the natural stone, metal-machine manufacturing, iron joinery,

**Table 3** Mean concentrations ( $\mu\text{g g}^{-1}$ ) of elements in the current study and 5 other lichen biomonitoring studies of *X. parietina*

Monitoring area	Al	As	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
<sup>1</sup> Salda Lake TR, rural	1915	1.60	26.94	6.55	2202	53.14	44.59	5.66	5.88	32.42
<sup>2</sup> Kocaeli TR, urban-suburban	1513	1.63	*	15.26	2828	88	6.03	41.18	8.00	167
<sup>3</sup> Istanbul Asia TR, urban	2938	1.7	49.7	17.6	2959	71.5	6.8	10.1	17.3	71.5
<sup>4</sup> Aegean region TR, industrial	780	0.68	1.36	*	470	61	*	*	1.78	37.3
<sup>5</sup> Düzce TR, rural-industrial	3149.2	1.1	10.2	12.2	2340.1	123.8	6.8	12.8	15.2	87.3
<sup>6</sup> Kosice SR, urban-industrial	1620	*	*	30,1	3033	211	*	34,3	*	146
IAEA-336 certified	680	0.63	1.06	3.60	430	63	*	4.90	1.47	30.40

<sup>1</sup>The present study, TR Turkish Republic; <sup>2</sup> Doğrul-Demiray et al. (2012); <sup>3</sup> Özkök and Çobanoğlu (2023); <sup>4</sup> Yenisoy-Karakas and Tuncel (2004); <sup>5</sup> Bozkurt (2017); <sup>6</sup> Dzubaj et al. (2008), SR Slovak Republic; \* not measured

mining and building-construction materials industries that have come to the fore in recent years. With increasing tourism activity, extremely important environmental problems arise in and around Salda Lake. In order to keep this heritage alive, public awareness should be raised, the people of the region should live more consciously, and the protection of the lake should be given priority in the decisions taken by the authorities.

**Acknowledgements** We would like to thank Dr. Sevda İldan Özmen from Mersin University, Department of Advanced Technology, where the ICP-MS analysis was performed. We also thank Dr. Mustafa Yavuz for his help in creating the contour maps. We appreciate the anonymous reviewers for their constructive comments.

**Authors contribution** Authors GÇ, TK: design and methodology, collection of samples. TK: perform pre-analysis and mapping procedures and writing first draft of manuscript, GÇ: determination and supervision, writing and finalizing the manuscript. All authors read and approved the final manuscript.

**Funding** Open access funding provided by the Scientific and Technological Research Council of Türkiye (TÜBİTAK). This work was supported by Marmara University Scientific Research Projects Unit (BAPKO) with the number FEN-C-YLP-130219-0034.

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

## Declarations

**Ethical approval** This article does not contain any studies with human or animals' participants.

**Consent to participate** All authors given his/her consent to participate in the manuscript.

**Consent to publish** All authors have given his/ her consent for publication and authors have no conflicts of interest.

**Competing interest** The authors declare that they have no conflict of interests.

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