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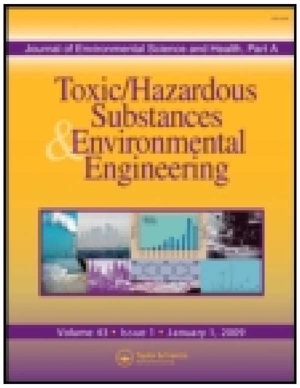

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Biomonitoring of metals in the vicinity of Soma coal-fired power plant in western Anatolia, Turkey using the epiphytic lichen, *Xanthoria parietina*

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In this study, epiphytic lichen *Xanthoria parietina* was applied as the biomonitor of air pollution to determine the environmental influence in the vicinity of Soma coal-fired power plant. Thalli of lichen *Xanthoria parietina* growing on olive, oak and poplar trees were collected with their substrate in 2004–2006. They were taken from 44 different stations located in 3×3 km grids within an area of 30 km in diameter around the Soma power plant near the town of Soma. Lichen samples were analyzed by using the ICP-MS for As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Se, Th, U, V and Zn elements and their concentrations were mapped. The sample analyses results were evaluated by using the statistical software (SPSS 11). Average element contents of samples were, in descending order, Fe > Zn > V > Pb > Cr > Cu > Ni > As > Co > U > Th > Se > Cd > Hg. Results obtained in the current study were generally found to be higher than the data reported in literature although some lower values exist for Cd, Co, Hg, Ni, Pb elements. The most polluted areas were found to be those in the vicinity of the coal-fired power plant, particularly along the direction of predominant wind and in the corridor which runs from west to southeast direction due to topographic conditions. We believe that this research which is conducted around a coal-fired power plant will shed light on future research on pollution.

Keywords: Biomonitoring, lichen, pollution, coal-fired power plant, Turkey.

Introduction

Lichens are slow-growing associations of fungi and green algae. These symbiotic association forms of common thalli have no roots or waxy cuticles and depend mainly on the atmospheric input of mineral nutrients. These features of lichens, combined with their extraordinary capability to grow in a large geographical range and to accumulate trace elements extending their needs, rank them among the best bioindicators of air pollution.

In general, bioindicators are organisms that can be used for the identification and qualitative determination of human-generated environmental factors, while biomonitors are organisms mainly used for the quantitative determination of contaminants and can be classified as being sensitive or accumulative.[1] Monitoring of air pollutants in large areas using automatic gauges is not commonly carried out owing to its high cost. Compared to conventional methods, biomonitoring is an easy, inexpensive and indirect method for determining pollutants and their distributions over large areas.[2]

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Numerous investigations of the interaction between air pollutants and lichens have been performed over the last three decades. The majority of the investigations for the accumulation of air pollutants by lichens focused on pollutants produced by smelters, power plants, and busy roads in urban and rural sites. Apart from unpolluted background regions, these studies of elemental accumulation in lichens around pollution sources yielded tables of elemental content of lichens near industrial/urban or other contaminated sites.[3] Recent studies referring to lichen biomonitoring have dealt mostly with airborne elements emitted by power plants using fossil fuels, as is the case in the present study.

The majority of the investigations of power plant emissions, airborne pollutants, and lichens as monitors were performed in different temperate zones. Lichens applied as monitors near coal-fired power stations in Portugal, for example, were found to accumulate metals such as Fe, Co, Cr, and Sb originating from coal and ash particles drifting through the air and positioned on the thalli.[4] Freitas[5] analyzed the comparative accumulation of Cr, Fe, Co, Zn, Se, Sb, and Hg in two vascular plants and in the epiphytic lichen (growing on trees), *Parmelia sulcata,* in an industrial region occupied by a thermal coal-fired power station, a chemical plant, and an oil refinery. The lichen was found to be the most effective bioaccumulator according to Freitas.[5]

Biomonitoring with lichens was also carried out to estimate the air quality in the La Spezia district, Italy, in relation to a coal-fired power plant and other industrial activities.[6] Samples of two different species of lichens (*Parmelia caperata* and *Parmelia rudecta*) were analyzed via instrumental neutron activation analysis (INAA) to determine the concentrations of metals around Dickerson coal-fired power plant.[7] Garty[8] has performed a study in Israel around Maor David coal-fired power plant with species of the lichen, *Ramalina duriaei,* within a distance about 25 km from the plant.

Relevant to the same type of power plant called Oroth Rabin, Garty et al.[9] applied three physiological parameters to assess stress symptoms in the lichen *Ramalina lacera* under air pollution produced by anthropogenic activity. Epiphytic lichen *Xanthoria parietina* was also used as a biomonitor in estimating the level and geographical gradients of air pollution in the Aegean region of Turkey by Yenisoy-Karakaş.[10] Uğur et al.[11] have studied types of lichens called *Rhizoplaca melanophthalma*, *Cladonia convulata*, *Cladonia pyxidata* and types of mosses called *Grimmia pulvinata*, *Hypnum cupressiforme* as bioindicators in order to measure ^{210}Po and ^{210}Pb deposition in the vicinity of Yatağan coal-fired power plant.

The main objectives of our study were; (i) to establish the first biomonitoring network in the vicinity of coal-fired power plants located in western Anatolia, Turkey in order to produce a baseline database for future studies at certain time intervals, (ii) to describe the metal contents of lichens collected from a relatively polluted site around Soma coal-fired power plant and (iii) to compare levels of air pollution with other studies.

Materials and methods

Description of the study area

This research takes place in Manisa, a city of Turkey in the Aegean Region. Soma coal-fired power plant which is located within a distance of 3 km to Soma township started to generate electricity in 1957 (Fig. 1). This was preferred as our study area since the power plant has been in operation for more than 50 years and it was the first coal-fired power plant in Turkey.

It has released pollutants to its environs during this long operation period. It has eight units, six of which produce 165 MW powers each while the other two units produce 22 MW. The power plant has four stacks with a height of 50 m, 150 m, 150 m and 275 m, respectively. Each of them has an electrostatic precipitator functioning with 99% efficiency. The weather in the region is occasionally rainy during the winter, but hot and dry during the summer. The local wind direction is generally through north to south, west to east and northwest to southeast in descending order (Fig. 2).

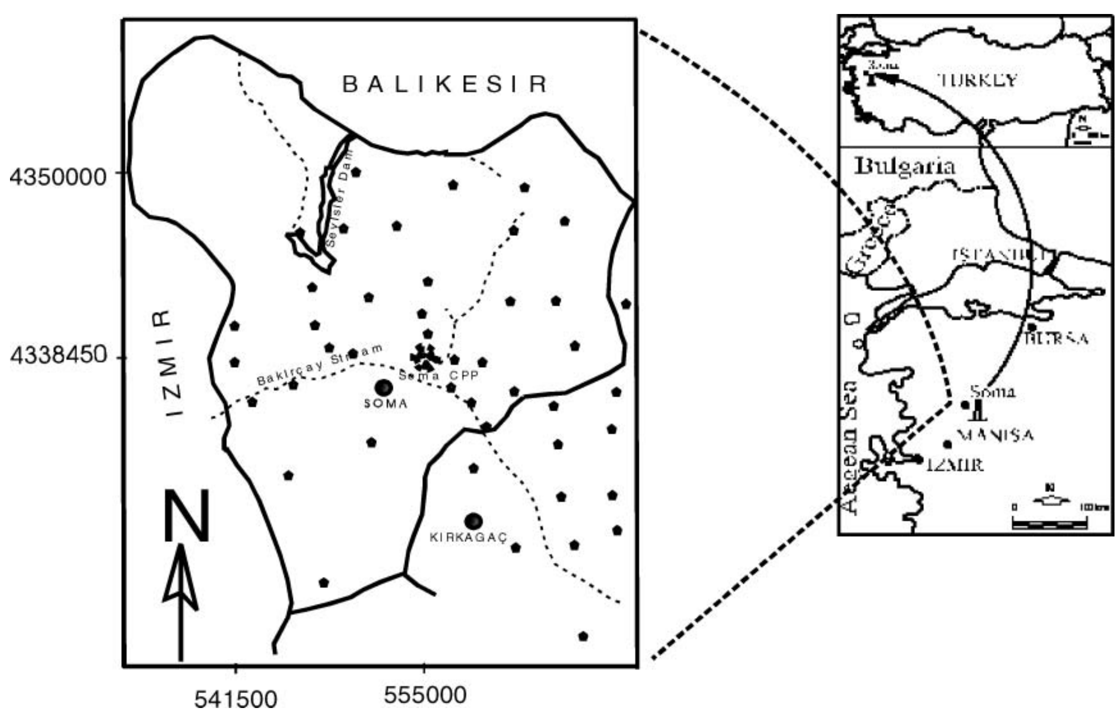

Fig. 1. Map of survey area of Aegean region and sampling sites (Projection: UTM, Datum: E50, units are in meters 'm').

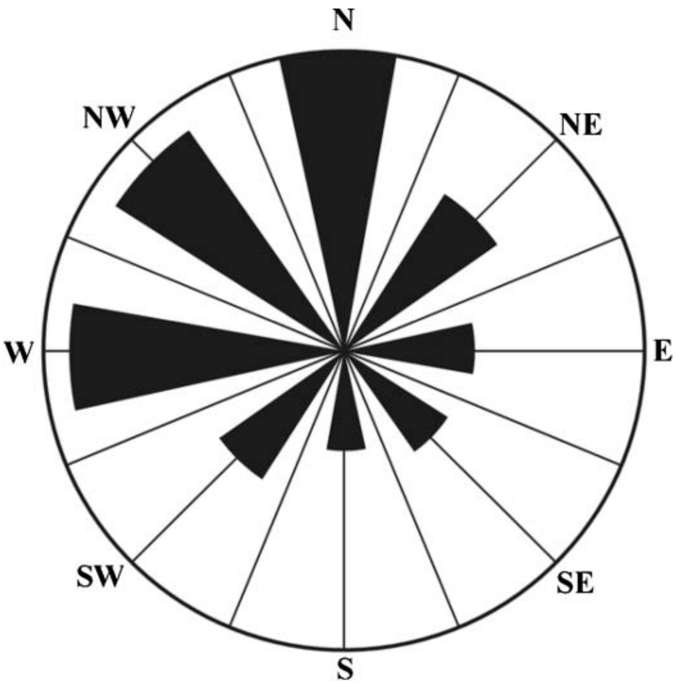

Fig. 2. The Soma town wind rose (black bars indicate the wind directions).

Sampling—preparation of the samples and analyses

Lichen *Xanthoria parietina* samples growing commonly on olive, oak and poplar trees were collected together with its substrate from the vicinity of Soma coal-fired power plant in 2004–2006. They were taken from 44 different stations located in 3×3km grids within an area of 30km in diameter around the power plant. Total survey area is 450 km^2. The map of survey area and sampling locations around Soma CPP are shown in Figure 1.

The reasons for using this type of lichen as a biomonitor are: 1) it is very common in the region, 2) it tolerates pollution, 3) it can be easily recognized in the field and separated from the substrate. This type of lichen, *Xanthoria parietina,* met all the above mentioned requirements within the area of the present study. However, it was not so easy to remove its thalli from the substrate. In some of the grids, no samples could be collected since there were no trees or the trees had no lichens. Several lichen thalli of different sizes were collected from all parts of the trunk within a distance of 1–2 m height from the ground.

At each sampling station within an area of 50×50 m^2, several sub-samples were taken and combined as one sample. Lichen samples were collected at least 300–500 m away from main roads, farms, villages and industries in order to avoid further contamination. After the identification of the sample (coordinates, elevation, directions, tree types and date, etc.), it was put in a paper bag, labeled and sealed. Polyethylene gloves were worn during the sampling and preparation processes. Each sample weighed approximately 10–15 g on the average. To separate the lichen thalli from the substrate, nylon tweezers were used. After separation from the substrate, dead tissue and extraneous materials (adhering bark, mosses, other lichen species, soil particles, etc.) were removed. Then, samples were dried to a constant weight at 85°C for 24 h and weighed. Afterwards, lichen samples were grinded with the Retsch vibration disc mill RS 100.

Preparation and packing of the samples were carried out in a clean room of our laboratory. Each sample along with a standard sample was put in a clean polyethylene bag. They were carried to Acme Analytical Laboratories Ltd. (ISO 9002 Accredited Co.) in packages in order to avoid contamination during transportation. Lichen sample (0.5g) was first leached with 2 mL HNO_3 and then 6 mL 2:2:2 of HCl-HNO_3-H_2O at 95°C for one hour. Afterwards, it was diluted to 20 mL and analyzed by ICP/ES-MS at ACME laboratory, Canada (Group 1VE-MS/Ultra trace by ICP Mass Spec.: ICP Mass Spec. analysis of vegetation samples using a 0.5 g split digested in HNO_3 then Aqua Regia and analyzed by ICP-MS for ultra low detection limits). The detection limits and the upper limits the system can detect were 1 ppb for Hg; 0.01 ppm for Cd, Co, Cu, Pb, Th and U; 0.1 ppm for As, Cr, Ni, Se and Zn; 2 ppm for V; 10 ppm for Fe; 100 ppm for Hg and Se; 2000 ppm for Cd, Co, Th, and U; 10000 ppm for As, Cr, Cu, Ni, Pb, V and Zn; and 400,000 ppm for Fe, respectively.

Quality control procedures

For quality assurance, lichen standard reference material (SRM)-IAEA 336 was analyzed by ICP-MS. As can be seen from Table 1, the average concentrations of the most metals were either very close to the average certified concentrations of SRM or they took place at intervals of certified values of SRM except for As, Cr, Se, Th and V. Table 1 also gives the ratios of found/certified values for lichen standard. It was observed that the average ratios of found/certified values were in the interval of 0.57–2.54 for all of the elements. It can be observed in Table 1 that the results obtained by ACME were compared with the results produced by the reference values determined by IAEA. As the ratio gets closer to 1, it means that the probability of making mistakes in measuring gets smaller. The fact that the range of values obtained after experiments conducted in 15 different laboratories by nuclear and related techniques were compatible with our result seemed to increase the reliability of the present study.

Data analysis

The metal levels accumulated by *Xanthoria parietina* around Soma coal-fired power plant were mapped using the coordinates of sampling points by means of some com-

Table 1. Element concentrations (μg g^{-1}), ratios of found/certified value observed in standard reference material analyzed by ICP-MS.

Element	*Found*	*IAEA 336*	*Confidence interval (95%)*	*Found/certified*
As	1.1	0.63	0.55–0.71	1.74
Cd	0.11	0.117	0.100–0.134	0.94
Co	0.27	0.29	0.24–0.34	0.93
Cr	2.7	1.06	0.89–1.23	2.54
Cu	3.66	3.6	3.1–4.1	1.01
Fe	360	430	380–480	0.84
Hg	0.173	0.20	0.16–0.24	0.87
Ni	0.9	–	–	–
Pb	4.72	4.9	4.3–5.5	0.96
Se	0.4 <	0.22	0.18–0.26	1.82 <
Th	0.08	0.14	0.12–0.16	0.57
U	0.03	0.04	–	0.75
V	2	1.47	1.25–1.69	1.36
Zn	33.8	30.4	27.0–33.8	1.11

puter software. The Kriging algorithm was used to interpolate the data. On these maps, counter lines were used to portray the surface relief as a set of lines that connect the points which have the same value. The results of lichen analysis were evaluated using the statistical software (SPSS 11). Summary of the statistics were given in Table 2.

Results and discussion

Comparison with literature values

The concentrations of elements in 44 lichen samples collected from the Aegean region of Turkey around Soma coal-fired power plant were analyzed using the ICP-MS technique. Statistical summary of elemental concentration obtained from all lichen data set (*Xanthoria parietina*) was given in Table 2 including the number of samples, arithmetic and geometric means with associated standard deviations, range, median and coefficient of variation (CV). Furthermore, in Table 2, background values were given in the last column.

Around the Soma coal-fired power plant, arithmetic means of concentration values of elements in the lichen samples were aligned from the highest to the lowest value as follows: Fe > Zn > V > Pb > Cr > Cu > Ni > As > Co > U > Th > Se > Cd > Hg. The local variation in element concentrations was expressed in terms of coefficient of variation (CV) and defined as standard deviation (S.D.) $\times$ 100/mean to compare the magnitudes of variation. The concentrations of Th, U and Zn elements have the highest CV values. These results indicate that these concentrations are distributed in a wide range of values.

Krichner and Daillant[12] have reported that the uranium concentrations were changed in the range of 0.15–1.45 μg g^{-1} at the anthropogenic sources of uranium which

Table 2. Average values of elements (in μg g^{-1} d.w.) in lichen samples around Soma coal-fired power plant.

		Element concentrations (μg g^{-1})				
Element (number of samples)	*Arithmetic mean ± SD*	*Median*	*Geometric mean*	*Min.-max.*	*CV (%)*	*BG values*
As (44)	14.2 ± 6.5	13.1	12.8	5.2 − 30.2	46	2.3
Cd (44)	0.46 ± 0.26	0.40	0.40	0.16–1.53	57	0.08
Co (44)	6.78 ± 3.24	6.59	6.06	1.70–17.79	48	1.40
Cr (44)	19.0 ± 8.3	16.8	17.3	7.2–34.2	44	5.0
Cu (44)	17.57 ± 7.58	15.48	16.29	8.54–42.60	43	6.26
Fe (44)	7531 ± 2925	7255	6956	2730–13070	39	2090
Hg (44)	0.134 ± 0.026	0.137	0.131	0.070–0.192	20	0.058
Ni (44)	15.7 ± 7.5	13.4	14.2	5.9–34.0	48	4.9
Pb (44)	23.99 ± 9.70	22.44	22.01	7.68–45.27	40	5.66
Se (44)	0.6 ± 0.1	0.6	0.6	0.4–1.1	25	0.2
Th (44)	1.68 ± 1.51	1.35	1.10	0.24–6.38	90	0.18
U (44)	2.24 ± 1.62	1.54	1.57	0.40–6.96	72	0.20
V (44)	28 ± 14	25	25	10–68	52	7
Zn (44)	115.8 ± 52.9	107.9	104.4	50.0–239.9	85	46.0

Table 3. The comparison of power plant area data with literature values (μg g^{-1}).

Element	*Average ± sd *1*	*Average ± sd *2*	*Average ± sd 3*	*Average ± sd 4*	*This study average ± sd*
As	3.9 ± 1.0	5.0 ± 2.0			14.2 ± 6.5
Cd	1.2 ± 0.2				0.46 ± 0.26
Co				0.57 ± 0.08	6.78 ± 3.24
Cr	3.8 ± 1.2	4.6 ± 1.5	9.4 ± 6.5	5.8 ± 1.1	19.0 ± 8.3
Cu			13.4 ± 7.1	7.3 ± 4.0	17.57 ± 7.58
Fe	1400 ± 600	1620 ± 780		1218 ± 74	7531 ± 2925
Ni			36 ± 21	5.3 ± 0.9	15.7 ± 7.5
Pb			120 ± 73	8.5 ± 1.7	23.99 ± 9.70
Se	1.1 ± 0.8	1.1 ± 0.5			0.6 ± 0.1
Th	0.34 ± 0.17	0.38 ± 0.19			1.68 ± 1.51
V	8.5 ± 2.6	6.8 ± 2.1		6.1 ± 0.8	28 ± 14
Zn	64 ± 8	68 ± 24	57 ± 30	38.1 ± 7.8	115.8 ± 52.9

* Ölmez et al.[7] (A coal-fired power plant, Washington D.C.).
*1: Parmelia caperata (5 samples).
*2: Parmelia rudecta (6 samples).
3 Garty[8] (A coal-fired power plant, Israel), Ramalina duriaei (125 samples).
4 Garty et al. [9] (A coal-fired power plant, Israel), Ramalina lacera (10 samples).

was found in coal-fired power plant. In addition, Loppi et al.[13] have reported that concentrations of uranium were found in lichens close to anthropogenic sources of U, such as coal-fired power plants (0.59–0.7 μg g^{-1}), uranium mines (up to 151 μg g^{-1}) and yellow cake production plants (1.26–6.16 μg g^{-1}). In the light of these findings, the arithmetic mean of uranium concentration at the present study was about 1.5-3 times higher than this range (2.24 μg g^{-1}).

Results obtained in the current study were generally found to be higher than the data reported in literature although some lower values exist for Cd, Co, Hg, Ni, Pb, Se elements. Ölmez et al.[7] have reported average concentrations of metal in both lichen species *Parmelia caperata* and *Parmelia rudecta* (Table 3). As seen in this table the concentrations of all the elements except for Cd and Se were observed to be higher in our study. As and Se, which are mainly associated with emissions from the coal-fired plant, especially show a very close relation.[7] The As/Se ratio calculated for each sample was almost constant and equal to 4.0 for the Dickerson power plant. However, for the Soma coal-fired power plant average ratio was equal to 23. The difference between these values might have resulted from low and high concentration for Se and As, respectively. Karayigit et al.[14] have reported that the As content in Turkish lignite coal is higher than the currently available ranges for most world coals. In another study performed in Israel around Maor David coal-fired power plant with a lichen species of *Ramalina duriaei* within a distance about 25 km from the plant, the average concentrations of

Table 4. Comparison of the lichen data with the previously reported results within the same region (μg g^{-1}).

Element	*Average ± sd *1 (N)*	*Average ± sd *2 (N)*	*Average BG ± sd *2*	*This study average ± SD (N)*
As	6.5 ± 1.3 (16)	–	–	14.2 ± 6.5 (44)
Cd	0.14 ± 0.12 (18)	1.93 ± 0.42 (10)	0.34 ± 0.11 (10)	0.46 ± 0.26 (44)
Co	–	10.18 ± 1.40 (10)	5.00 ± 1.05 (10)	6.78 ± 3.24 (44)
Cr	4.3 ± 2.2 (18)	13.30 ± 0.99 (10)	8.36 ± 0.69 (10)	19.0 ± 8.3 (44)
Cu	4.9 ± 1.7 (18)	8.14 ± 0.79 (10)	4.00 ± 0.69 (10)	17.57 ± 7.58 (44)
Fe	2110 ± 1000 (18)	4005 ± 83 (10)	1564 ± 43 (10)	7531 ± 2925 (44)
Hg	0.26 ± 0.29 (13)	–	–	0.134 ± 0.026 (44)
Ni	3.8 ± 2.0 (18)	16.64 ± 2.72 (10)	10.88 ± 1.08 (10)	15.7 ± 7.5 (44)
Pb	5.6 ± 5.6 (18)	58 ± 5 (10)	22.05 ± 1.61 (10)	23.99 ± 9.70 (44)
Se	0.37 ± 0.29 (17)	–	–	0.6 ± 0.1 (44)
V	4.7 ± 2.9 (18)	–	–	28 ± 14 (44)
Zn	27 ± 24 (18)	112 ± 8 (10)	88.96 ± 2.43 (10)	115.8 ± 52.9 (44)

N shows the number of samples.
*1 Yenisoy-Karakaş[10] (Soma and Yatağan coal-fired power plants, Turkey), *Xanthoria parietina.*
*2 Uğur et al.[11] (Yatağan coal-fired power plant, Turkey) *Rhizoplaca melanophthalma* (Epilitic lichen).
*2 BG, Uğur et al.[11]

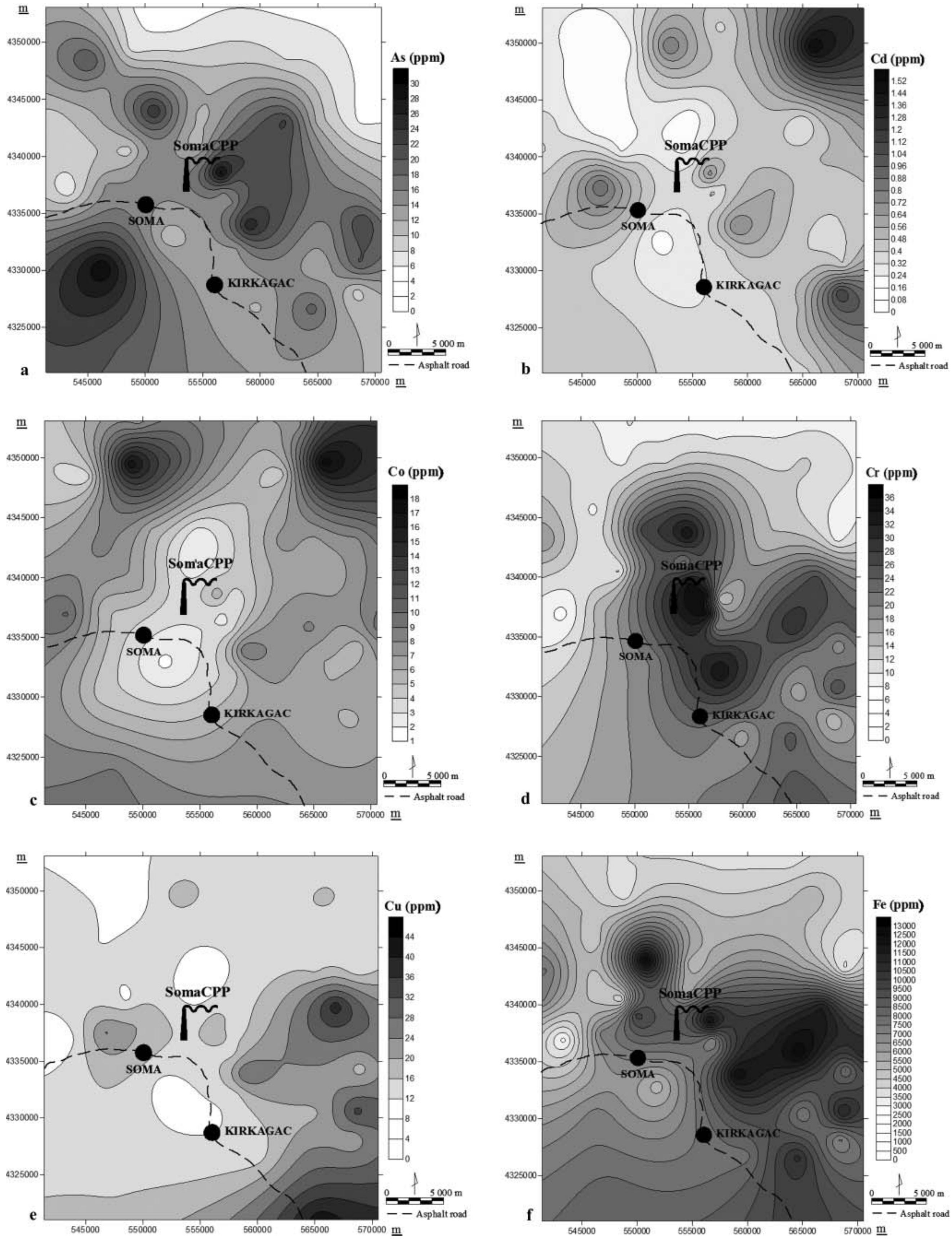

Fig. 3. The distribution map of element concentrations (a) arsenic, (b) cadmium, (c) cobalt, (d) chromium, (e) copper, (f) iron, (g) mercury, (h) nickel, (i) lead, (j) selenium, (k) thorium, (l) uranium, (m) vanadium and (n) zinc (Projection: UTM, Datum: E50, units are in meters'm').

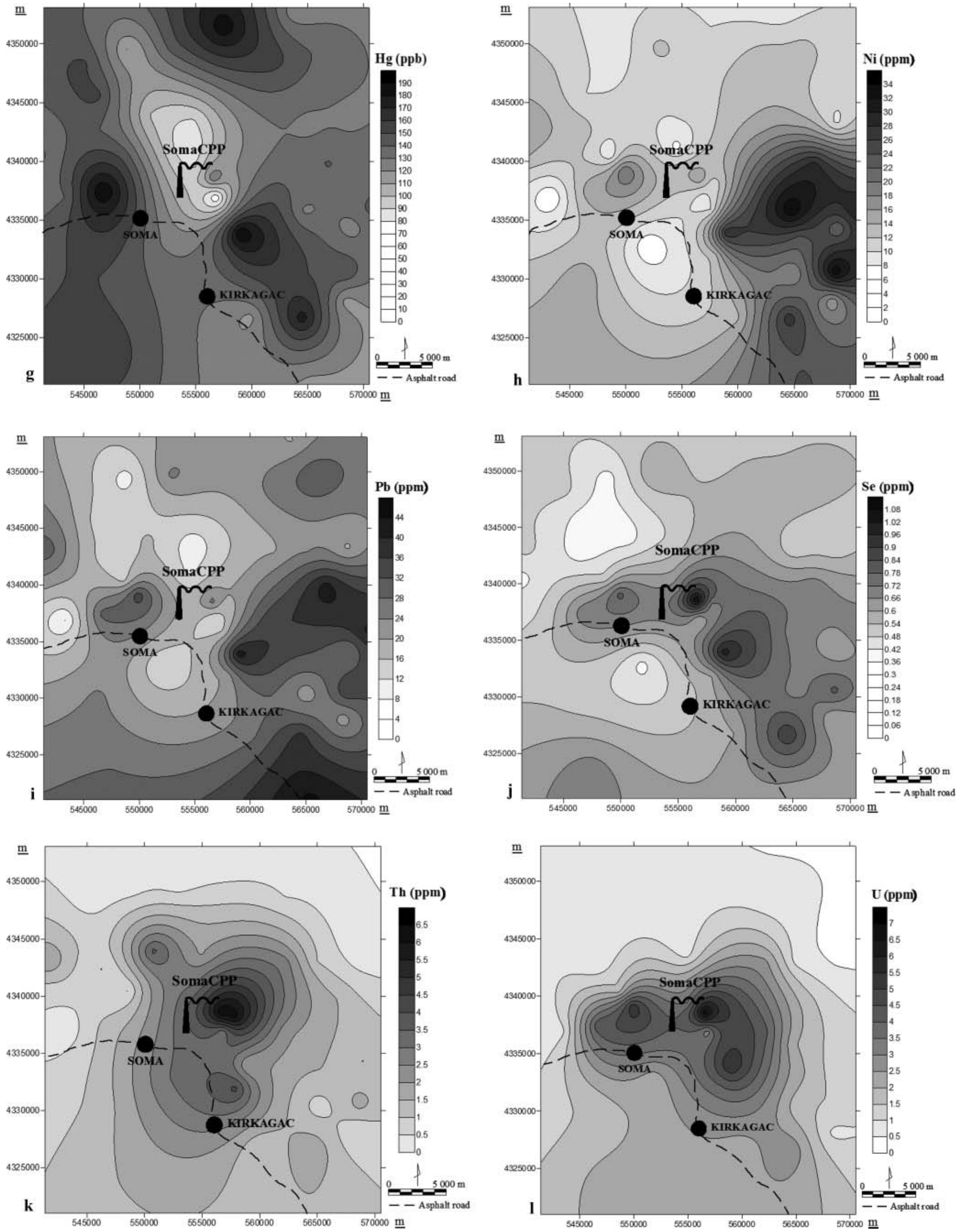

Fig. 3. (Continued)

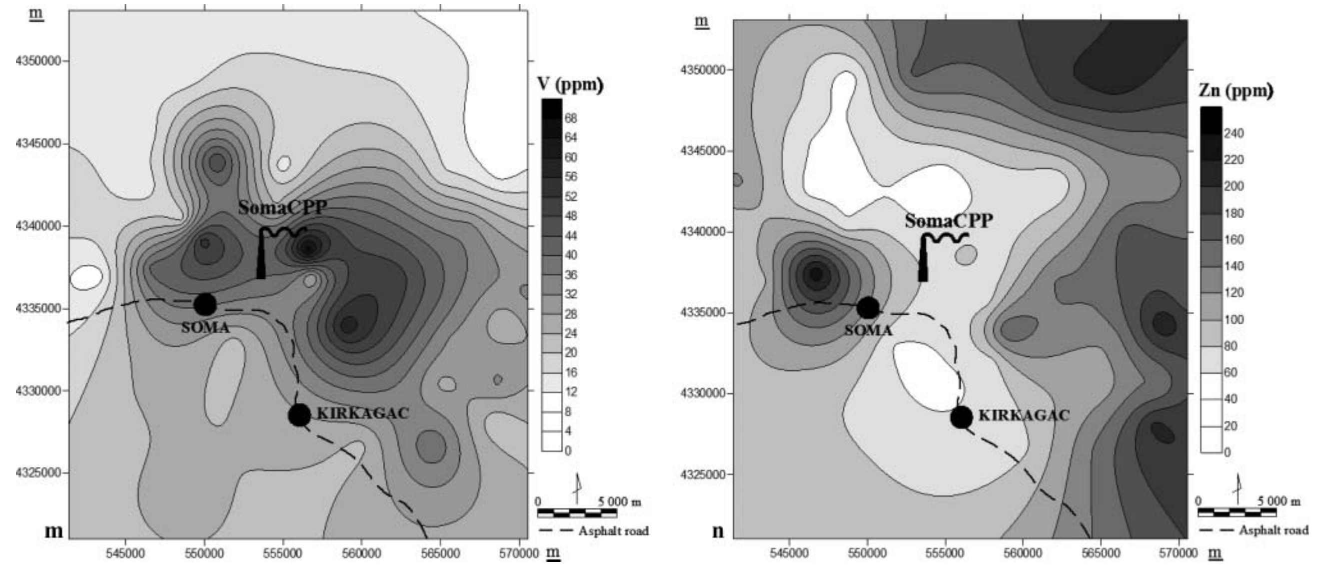

Fig. 3. (Continued)

Ni and Pb elements have occurred to be higher than those obtained in the current study.

Garty[8] have reported that the coal used in the power plant was imported from South Africa and contained high amounts of Cr. In comparison with the literature data, the concentration of Cr in the coal used in Soma coal-fired power plant was very high. The mean Pb/Zn ratio in lichen samples that was given in Garty[8] was 2.11. However, in our study it was calculated as 0.20. This result was derived from high Pb content and low Zn content. In another study conducted by the same author around the Oroth Rabin coal-fired power plant[9], the amount of elemental concentrations of all metals were lower than those measured in our study.

Comparison of the data obtained in this study on lichen with the previously reported results within the same region is one of the observation methods used in environmental research. When we compare our data with literature for regional scale surveys, we see that the concentrations of all elements except Cd, Co, Hg and Pb were considerably higher than the other studies (Table 4). The average values of As, Cr, Cu, Fe, Se, V and Zn concentrations in our study were relatively higher than all literature values. This was closely related with burning lignite, which is extensively used as an energy source for electricity production and domestic heating in Turkey.

The distribution map of metal concentrations

The distributions of all metals analyzed were shown on the maps (Figs. 3a–3n). Generally, higher metal concentrations for As, Cr, Fe, Se, Th, U, V were recorded in samples collected from nearby the Soma coal-fired power plant. It is observed that metal concentrations of Cu, Ni, Pb in east and southeast of the power plant were in higher values. As seen in Figure 3b and 3c, higher concentrations of Cd and Co were found throughout northeast direction. The higher metal concentrations of Hg and Zn were also observed throughout west, northeast and southeast directions.

Dominating wind directions were from north to south, from west to east and from northwest to southeast (Fig. 2). Therefore, metal pollution that has been observed mainly along the southeast direction can be considered as to result from the power plant. Topographic map belonging to investigation area was shown in Figure 4. As seen in this figure, there was a corridor running from west to southeast direction. In addition, coal beds are situated along

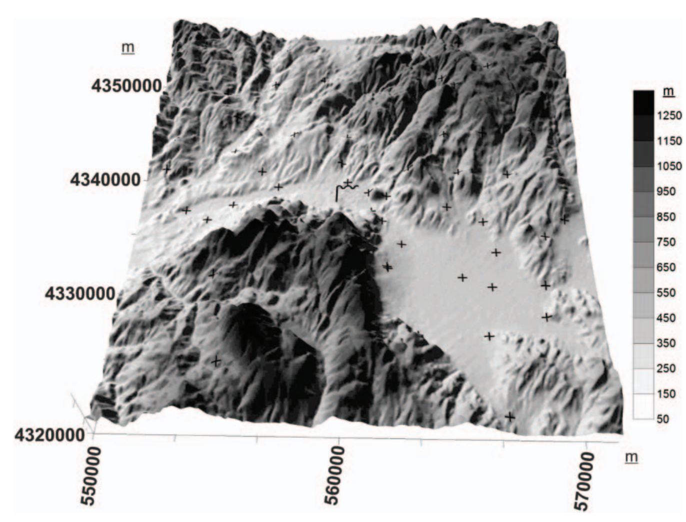

Fig. 4. Topographic map of investigation area (+; sampling location site; projection: UTM, Datum: E50, units are in meters 'm').

northeast and southwest directions. Higher concentrations of all metals were found abundantly along this corridor and nearby these coal beds.

Conclusion

Based on many studies showing uptake of a great number of elements by lichens including those elements emitted by coal-fired power plants, it is suggested that lichens could be utilized as air pollution monitors around such stations.

The use of lichens as biomonitors for air pollution offers means for achieving preliminary estimations about the extent of such pollution, the location and identification of the pollution sources and also a method for the comprehensive mapping of the pollutant in an area.

In the present study, epiphytic lichen was used as a biomonitor of air pollution to determine the environmental impact of a coal-fired power plant. The pollution maps were prepared using the concentration of all the metals in order to indicate the location of the more polluted and influenced areas. In general some metals such as As, Cr, Cu, Fe, Se, V and Zn concentrations found in lichen samples in this study were higher when compared with literature values. The areas which were polluted by these elements were mostly found in the vicinity of the coal-fired power plant, especially through the direction of dominant air current. We believe that this wide research that is conducted around a coal-fired power plant will set light to future researches on pollution.

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