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Analysis of mosses along Sarp-Samsun highway in Turkey

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Abstract

The elemental analysis of mosses along Sarp-Samsun highway in Turkey was determined using energy dispersive X-ray fluorescence method. A radioisotope excited X-ray fluorescence analysis using the method of multiple standard additions is applied for the elemental analysis of mosses. An annular 50 mCi ^{241}Am radioactive source and annular 50 mCi ^{55}Fe radioactive source were used for excitation of characteristic K X-rays. An Si(Li) detector which has a 147 eV full width at half maximum for 5.9 keV photons was used for intensity measurements. A qualitative analysis of spectral peaks showed that the samples contained phosphates, potassium, calcium, titanium, iron, strontium, tin and barium. Since this study is the elemental analysis along the highway, one can expect to detect Pb. Due to the detection limit of EDXRF, elements were analyzed with Atomic Absorption Spectroscopy (AAS) for Pb. Evaluation of these elements with their potential hazards for ecology and human is briefly discussed.

Keywords: Moss; EDXRF; AAS; Elemental analysis

1. Introduction

Atmospheric particulates have attracted a great environmental concern over the last few decades because of the evidence that this type of pollution can have severe long-term implications for respiratory illness in humans [1]. In particular, heavy metals adsorbed on ambient particles were found to cause damage to lung tissues [2]. Due to rapid urbanization and industrial development in recent years, atmospheric pollution has caused serious deterioration of the terrestrial environment in many countries. Thus, the monitoring of airborne metals in the urban environment has become an essential part of environmental planning and control programs in many parts of the world. Biomonitoring is a technique using organisms or biomaterials to obtain information on certain characteristics of the biosphere [3]. Mosses have been well studied as tools for the biomonitoring of the atmospheric pollution. Unlike higher plants, mosses have no root system or cuticle layer; hence, mineral adsorption occurs over their entire surface. Mineral uptakes from soil play a minor role and the adsorption of heavy metals is mainly derived from atmospheric flux on the surfaces of the moss. Therefore, mosses are excellent biomonitors for trace elements in air [4].

Mosses are used as sensitive bioindicators of heavy metal contamination. They accumulate large amounts of these elements in their tissues [5–7]. Mosses have several advantages as indicator organisms: (1) many species have a vast geographical distribution, and they grow abundantly in various natural habitats, even in industrial and urban agglomerations; (2) they have no epidermis or cuticule, therefore, their cell walls are easily penetrable for metal ions; (3) they have no organs for uptake of minerals from substrate, they obtain them mainly from precipitation; (4) some species have layer structure and annually produced organic matter forms distinct segments; (5) transport of minerals between segments is poor because of lack of vascular tissues; (6) mosses accumulate metals in a passive way, acting as ion exchangers; and (7) mosses show the concentrations of the most metals as a function of the amount of atmospheric deposition [8,9]. Efficient and flexible transport systems are an important part of the world's economy and thus, life quality. Nevertheless, road traffic is an important negative factor regarding air quality, noise and land consumption. Additionally, it poses a threat to plants animals and has direct and indirect consequences for human beings [10,11]. The number of licensed motor vehicles in Turkey has increased the last few decades

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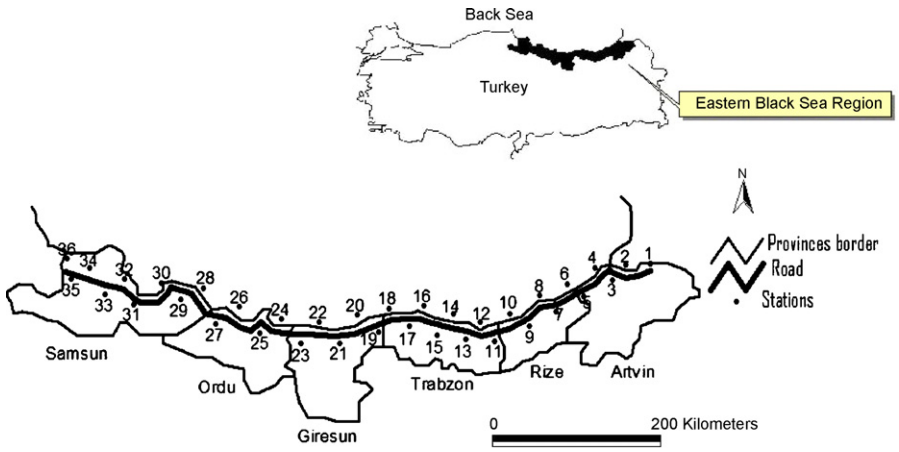

Fig. 1. Map of sampling area. (1) Hopa, (2) Arhavi, (3) Fındıklı, (4) Ardeşen, (5) Pazar, (6) Çayeli, (7) Rize, (8) Derepazarı, (9) İyidere, (10) Of, (11) Sürmene, (12) Araklı, (13) Arsin, (14) Yomra, (15) Trabzon, (16) Akçaabat, (17) Çarşıbaşı, (18) Vakfıkebir, (19) Beşikdüzü, (20) Eynesil, (21) Görele, (22) Tirebolu, (23) Espiye, (24) Keşap, (25) Giresun, (26) Bulancak, (27) Piraziz, (28) Gülyalı, (29) Ordu, (30) Perşembe, (31) Fatsa, (32) Ünye, (33) Terme, (34) Çarşamba, (35) Tekkeköy and (36) Samsun.

which is reflected by a similar annual increase of the average road performance. This increase shows a similar pattern as like in other most countries of the world.

For many years, lead (Pb) has been used to be the main indicator for ambient air pollution caused by traffic. For countries with smaller economies and thus less capacity for environmental protection, monitoring Pb emissions arised from traffic is still a matter of concern [12,13]. In 1990 lead-free gasoline was made compulsory in the United States of America and Canada. In 1993, Austria was the first European country with a similar legislation and other states followed this example [10]. Due to an increasing awareness of environmental pollution, the rates of Pb emissions and ambient air concentrations have been decreased dramatically in Western and Central Europe since the late 1970s [14].

It is observed that there has been a decreasing consumption rate of lead oil since 2001 compared to consumption rate of lead oil, lead-free oil and LPG in vehicles. In recent years, LPG is substituted for normal and lead oil. When the data published in

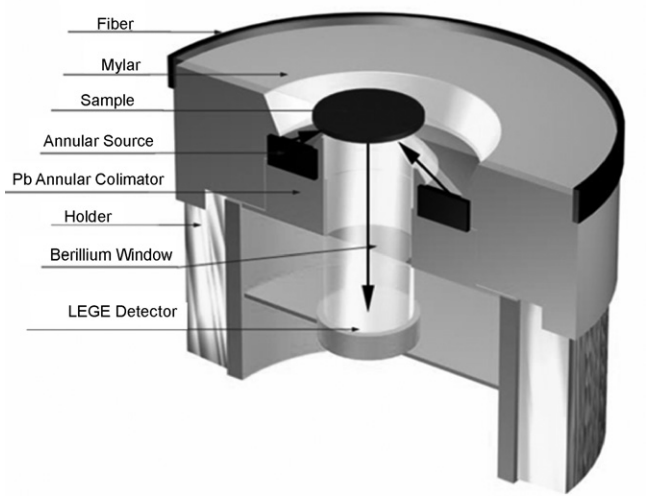

Fig. 2. Geometry of experimental set-up.

Table 1
Population distribution of the studying area

Code	City	Total	City center
1	Hopa	32,584	15,445
2	Arhavi	19,347	14,079
3	Fındıklı	16,740	11,043
4	Ardeşen	58,499	45,392
5	Pazar	32,215	14,682
6	Çayeli	51,816	22,546
7	Merkez	127,320	78,144
8	Derepazarı.	10,239	6,172
9	İyidere	10,074	5,466
10	Of	78,560	25,478
11	Sürmene	42,256	17,063
12	Araklı	62,139	22,506
13	Arsin	35,863	13,038
14	Yomra.	39,736	13,346
15	Merkez	283,233	214,949
16	Akçaabat	120,693	39,102
17	Çarşıbaşı	17,456	8,532
18	Vakfıkebir.	53,227	33,394
19	Beşikdüzü	47,331	29,766
20	Eynesil	21,110	10,667
21	Görele	52,420	27,214
22	Tirebolu	36,947	16,112
23	Espiye	30,567	12,990
24	Keşap	22,468	9,475
25	Merkez	112,501	83,636
26	Bulancak	59,841	32,182
27	Piraziz	17,901	9,416
28	Gülyalı	10,566	5,245
29	Merkez	150,586	112,525
30	Perşembe	37,512	10,804
31	Fatsa	120,774	63,721
32	Ünye	126,124	61,552
33	Terme	82,608	25,052
34	Çarşamba	131,194	49,189
35	Tekkeköy	50,476	15,071
36	Samsun	437,189	363,180

Table 2
Site description of the stations in along Sarp-Samsun highway

Sample no.	Species of moss	Average vehicle at 2004	Location
1	*Calliergonella cuspidata* (Hedw.) Loeske		Hopa
2	*Brachythecium albicans* (Hedw.) B.S.G.	1,844	Arhavi-Hopa
3	*Plagiothecium succulentum* (Wils.) Lindb.		Arhavi-Hopa
4	*Homalothecium sericeum* (Hedw.) B.S.G.		Arhavi-Hopa
5	*Hypnum cupressiforme* Hedw.		Arhavi-Hopa
6	*Pleurozium schreberi* (Brid.) Mitt.		Arhavi
7	*P. schreberi* (Brid.) Mitt.	3,402	Arhavi-Fındıklı
8	*Scleropodium purum* (Hedw.) Limpr		Fındıklı-Ardesen
9	*H. sericeum* (Hedw.) B.S.G.		Ardesen
10	*Eurhyncnium striatum* (Hedw.) Schimp.		Ardesen-Pazar
11	*Leptodictyum riparium* (Hedw.) Warnst.		Pazar
12	*Eurhyncnium hians* (Hedw.) Lac.		Pazar-Çayeli
13	*H. sericeum* (Hedw.) B.S.G.		Pazar-Çayeli
14	*E. striatum* (Hedw.) Schimp.	6,350	Rize-Çayeli
15	*H. cupressiforme* Hedw.	21,816	Rize
16	*E. striatum* (Hedw.) Schimp.		Rize-Derepazarı
17	*H. sericeum* (Hedw.) B.S.G.		Rize-Derepazarı
18	*Hypnum resupinatum* Tayl.		Rize-Derepazarı
19	*H. sericeum* (Hedw.) B.S.G.		Derepazarı-İyidere
20	*Amblystegium varium* (Hedw.) Lindb.		Of-İyidere
21	*C. cuspidata* (Hedw.) Loeske		Of
22	*Tortella fragilis* (Hook.&Wils.) Limpr.		Of
23	*H. sericeum* (Hedw.) B.S.G.	10,015	Of-Sürmene
24	*E. striatum* (Hedw.) Schimp.		Sürmene
25	*H. sericeum* (Hedw.) B.S.G.		Sürmene-Araklı
26	*H. cupressiforme* Hedw.		Araklı-Sürmene
27	*P. schreberi* (Brid.) Mitt.		Araklı
28	*E. striatum* (Hedw.) Schimp.		Araklı
29	*H. cupressiforme* Hedw.	9,647	Araklı-Arsin
30	*E. striatum* (Hedw.) Schimp.		Arsin
31	*H. cupressiforme* Hedw.		Arsin-Yomra
32	*H. sericeum* (Hedw.) B.S.G.		Arsin-Yomra
33	*H. sericeum* (Hedw.) B.S.G.		Trabzon-Yomra
34	*B. albicans* (Hedw.) B.S.G.		Yomra-Trabzon
35	*Ctenidium molluscum* (Hedw.) Mitt.		Trabzon-Yomra
36	*C. cuspidate* (Hedw.) Loeske	42,284	Trabzon
37	*H. cupressiforme* Hedw.	25,618	Trabzon-Akçaabat
38	*Rhynchostegium murale* (Hedw.) B.S.G.		Akçaabat
39	*Bryum capillare* Hedw.	7,547	Akçaabat-Çarşıbaşı
40	*E. striatum* (Hedw.) Schimp.		Akçaabat-Çarşıbaşı
41	*A. varium* (Hedw.) Lindb.		Çarşıbaşı
42	*H. resupinatum* Tayl.		Vakfıkebir
43	*B. albicans* (Hedw.) B.S.G.		Beşikdüzü
44	*E. striatum* (Hedw.) Schimp.		Beşikdüzü-Eynesil
45	*H. cupressiforme* Hedw.	7,355	Eynesil-Görele
46	*Rhytidiadelphus squarrosus* (Hedw.) Warnst.		Görele
47	*H. cupressiforme* Hedw.	8,420	Tirebolu-Görele
48	*H. cupressiforme* Hedw.		Tirebolu
49	*Thuidium tamariscinum* (Hedw.) B.S.G.		Espiye-Keşap
50	*A. varium* (Hedw.) Lindb.		Giresun-Keşap
51	*H. sericeum* (Hedw.) B.S.G.	6,350	Giresun-Keşap
52	*E. striatum* (Hedw.) Schimp.	18,514	Giresun
53	*S. purum* (Hedw.) Limpr.	11,155	Giresun-Bulancak
54	*P. succulentum* (Wils.) Lindb.		Giresun-Bulancak
55	*Leucodon sciuroides* (Hedw.) Schwaegr.		Bulancak
56	*S. purum* (Hedw.) Limpr.		Bulancak-Piraziz
57	*S. purum* (Hedw.) Limpr.		Piraziz-Gülyalı
58	*H. sericeum* (Hedw.) B.S.G.	6,800	Ordu-Gülyalı
59	*C. molluscum* (Hedw.) Mitt.		Ordu
60	*H. cupressiforme* Hedw.		Ordu-Perşembe
61	*Eurhyncnium striatulum* (spruce) B.S.G.	7,183	Perşembe-Fatsa
62	*C. molluscum* (Hedw.) Mitt.		Perşembe-Fatsa
63	*Brachythecium mildeanum* (Schimp.) Milde		Fatsa
64	*C. molluscum* (Hedw.) Mitt.	7,623	Fatsa-Ünye

Table 2 (*Continued*)

Sample no.	Species of moss	Average vehicle at 2004	Location
65	*C. molluscum* (Hedw.) Mitt.	7,949	Ünye
66	*H. sericeum* (Hedw.) B.S.G.		Terme
67	*L. sciuroides* (Hedw.) Schwaegr.	8,424	Terme-Çarşamba
68	*B. albicans* (Hedw.) B.S.G.		Çarşamba
69	*B. mildeanum* (Schimp.) Milde	13,478	Çarşamba-Tekkeköy
70	*P. schreberi* (Brid.) Mitt.		Çarşamba-Tekkeköy
71	*A. varium* (Hedw.) Lindb.		Samsun-Tekkeköy
72	*E. striatum* (Hedw.) Schimp.	43,177	Samsun
73	*H. cupressiforme* Hedw.		Samsun
74	*T. fragilis* (Hook.&Wils.) Limpr.		Samsun-Kavak

2003 is investigated, lead oil, LPG and lead-free oil have consumption rates of 25, 36 and 39%, respectively, in consumption distribution of oil and oil equivalent LPG. It means that there are still lead oil-dependent vehicles in the country [15].

The aims of this study are (1) to identify heavy metals and other elements that can be attributed predominantly to road traffic sources, (2) to find typical spatial patterns of road traffic-related element deposition, and (3) to discuss factors influencing these patterns. In addition this is the first study that has been done in this region.

2. Materials and methods

2.1. Method

Quantitative determination of elements is an important task in industrial, chemical, environmental, mineralogical, physical, medical science and in other fields. There are many elemental analysis techniques such as atomic absorption spectrometry, neutron activation analysis and X-ray fluorescence (XRF). Energy dispersive X-ray fluorescence (EDXRF) offers several unique advantages over other analytical methods [16].

It allows simultaneous detection and determination of several elements; it is sensitive and reproducible as well. Sample preparation is usually simple and fast. Also, the equipment cost is much cheaper than the conventional wavelength X-ray fluorescence techniques, especially if a radioisotope is used instead of an X-ray tube for excitation. The EDXRF method gives also a possibility of trace analysis of biological and geological samples. In recent years, EDXRF method has been used for elemental analysis by several authors [17–20].

Quantitative analysis for the elements was carried out using the standard addition method. The method involves the addition of known quantities of the analyte to the specimen. If analyte is presented at low levels and no suitable standards are available, standard addition may prove to be an alternative, especially if the analyst is interested in only one analyte element. Certain amounts of the element to be analyzed are added to samples.

In order to determine the detection limit of EDXRF for Pb we used the reference material which was prepared by International Atomic Energy Agency. Characteristic X-ray peak intensities for Pb was obtained through spectrum analysis of the reference material. Sensitivity of this element was calculated by using

$$C_i = \frac{I_i}{S_i} \tag{1}$$

where C_i is the concentration (mg kg^{-1}), I_i the characteristic X-ray intensity (cps), and S_i is the elemental sensitivity (cps mg^{-1} kg) for the element i. The detection limit was calculated by

$$\mathrm{DL}_i = \frac{3}{S_i}\sqrt{\frac{I_i\,(\mathrm{BG})}{t}} \tag{2}$$

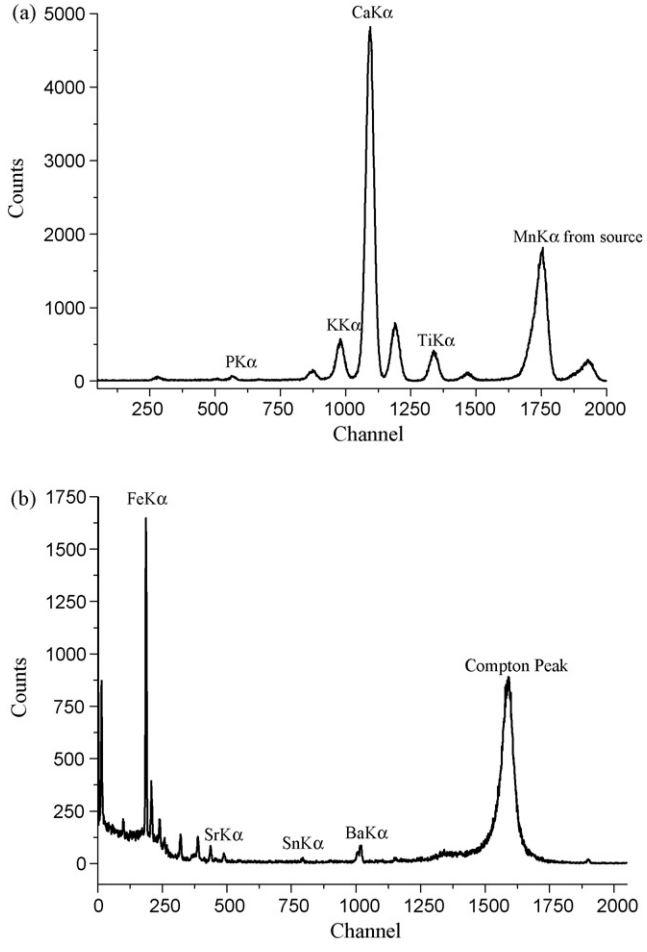

Fig. 3. A typical K X-ray spectrum of samples excited by (a) ^{55}Fe and (b) ^{241}Am radioactive source.

Table 3
Element concentrations in the samples collected (mg/g)

Sample no.	P	K	Ca	Ti	Fe	Sr	Sn	Ba	Pb
1	ND	8.31	20.96	6.90	33.50	0.17	0.03	0.21	0.01
2	12.97	5.85	22.79	5.04	26.00	0.11	0.03	0.17	0.02
3	15.06	8.79	23.40	7.09	28.00	0.14	0.03	0.38	0.04
4	19.09	5.74	47.64	7.57	38.90	0.29	ND	0.42	0.04
5	ND	ND	15.36	1.51	34.30	0.26	ND	0.41	0.03
6	44.68	8.94	87.51	9.79	35.30	0.29	0.03	0.41	0.01
7	38.07	7.81	66.02	12.30	47.60	0.39	0.02	0.64	0.02
8	ND	9.13	02.66	6.06	29.70	0.13	ND	0.43	0.07
9	ND	8.84	23.99	6.16	43.20	0.35	0.04	0.49	0.08
10	ND	9.97	72.23	17.40	55.30	0.32	ND	0.56	0.05
11	14.07	9.85	25.14	21.80	104.00	0.24	0.03	0.52	0.05
12	ND	7.65	58.96	6.97	24.50	0.19	0.02	0.38	0.05
13	16.17	6.74	25.58	3.89	13.10	0.11	0.04	0.11	0.01
14	ND	12.40	55.88	13.00	41.80	0.11	0.03	0.42	0.04
15	ND	9.57	68.83	11.30	42.50	0.34	ND	0.56	0.05
16	13.21	7.50	27.30	6.07	26.50	0.12	0.03	0.21	0.03
17	44.67	11.30	89.85	13.10	44.20	0.35	0.03	0.51	0.05
18	18.14	7.67	29.64	2.69	10.10	0.11	0.03	0.10	0.05
19	56.57	9.49	83.16	10.50	34.60	0.27	0.03	0.39	0.05
20	10.55	3.52	17.22	2.42	7.79	0.02	0.02	0.08	0.03
21	46.5	10.70	81.96	12.40	39.20	0.32	ND	0.43	0.04
22	52.66	11.20	86.91	15.00	42.20	0.40	0.02	0.58	0.03
23	33.92	9.39	51.13	9.76	37.10	0.19	0.04	0.52	0.04
24	13.20	6.71	26.03	10.20	45.10	0.20	0.03	0.22	0.03
25	28.57	12.30	52.69	11.90	36.60	0.24	0.04	0.91	0.05
26	25.5	12.10	50.82	12.20	38.40	0.24	0.03	0.77	0.03
27	12.91	9.05	19.89	6.58	25.20	0.12	0.03	0.40	0.05
28	22.21	9.43	42.04	15.60	72.40	0.28	0.07	0.52	0.02
29	30.49	6.42	48.14	8.09	41.60	0.14	0.04	0.24	0.03
30	14.69	6.09	26.25	13.70	49.00	0.11	0.03	0.46	0.02
31	15.16	8.69	26.64	12.30	59.90	0.21	0.03	0.28	0.03
32	53.01	11.40	84.52	13.90	41.50	0.32	0.02	0.50	0.03
33	18.23	9.19	37.86	12.50	72.80	0.22	0.04	0.47	0.05
34	28.57	8.17	53.25	10.60	35.10	0.19	0.04	0.46	0.05
35	21.33	9.81	36.16	11.40	65.00	0.18	0.04	0.40	0.03
36	16.22	7.70	25.44	6.04	23.20	0.10	0.04	0.25	0.04
37	12.26	4.70	19.00	1.83	6.15	0.07	0.03	0.09	0.03
38	18.98	7.46	29.52	4.62	24.90	0.13	0.03	0.08	0.06
39	17.95	3.51	24.96	2.75	08.34	0.05	0.03	0.11	0.06
40	03.75	4.53	20.23	6.72	15.60	0.08	0.02	0.16	0.04
41	08.15	3.45	14.57	2.39	7.66	0.03	0.03	0.05	0.04
42	27.11	6.85	54.20	12.10	28.90	0.17	ND	0.35	0.02
43	17.04	7.50	32.54	12.80	46.60	0.15	0.02	0.47	0.03
44	15.43	6.54	28.42	5.08	25.90	0.11	0.03	0.16	0.04
45	15.79	7.56	27.21	6.34	45.80	0.17	0.02	0.52	0.04
46	15.54	5.05	30.65	14.10	47.10	0.16	0.03	0.38	0.02
47	15.73	4.26	33.25	9.33	37.00	0.13	0.03	0.31	0.04
48	25.8	4.93	44.05	9.29	35.90	0.11	0.03	0.23	0.03
49	30.01	6.12	48.72	10.70	29.00	0.21	0.02	0.42	0.07
50	17.01	4.93	32.75	11.30	44.40	0.14	0.03	0.28	0.05
51	17.49	4.96	31.72	10.90	38.40	0.11	0.04	0.36	0.02
52	12.39	5.27	22.29	10.30	47.90	0.17	0.02	0.53	0.02
53	14.42	6.41	34.84	13.40	35.80	0.11	0.04	0.27	0.03
54	17.57	5.29	30.12	11.70	47.50	0.14	0.02	0.33	0.04
55	15.49	5.89	30.20	13.80	47.50	0.14	0.03	0.31	0.04
56	14.90	5.78	27.94	17.80	53.80	0.19	0.04	0.49	0.02
57	13.64	7.09	22.44	13.10	42.00	0.12	0.01	0.32	0.02
58	08.92	8.76	29.16	15.90	49.70	0.15	0.03	0.63	0.06
59	16.26	7.27	32.81	13.20	51.60	0.16	0.03	0.57	0.04
60	17.21	7.92	31.89	15.10	52.60	0.19	0.02	0.54	0.01
61	09.82	8.98	25.35	7.59	23.20	0.10	0.03	0.29	0.04
62	17.14	5.24	31.54	10.92	39.50	1.60	0.03	0.35	0.03
63	19.95	6.70	36.72	17.80	50.30	0.28	0.04	0.66	0.03
64	16.71	5.32	31.60	11.00	40.20	0.14	0.04	0.33	0.04

Table 3 (*Continued*)

Sample no.	P	K	Ca	Ti	Fe	Sr	Sn	Ba	Pb
65	20.46	4.54	33.65	11.00	40.80	0.14	0.04	0.31	0.03
66	17.31	5.82	29.67	16.00	49.80	0.18	0.03	0.54	0.04
67	13.47	5.66	20.88	12.50	42.80	0.12	0.03	0.49	0.04
68	19.77	6.50	29.64	13.80	46.10	0.15	0.04	0.36	0.05
69	07.56	5.77	13.80	33.00	62.80	0.47	0.03	1.10	0.02
70	11.97	5.23	23.17	13.60	42.40	0.13	0.03	0.29	0.03
71	16.86	6.32	32.49	12.70	6.860	0.18	0.03	0.39	0.08
72	22.00	8.23	31.00	16.80	53.20	0.17	0.03	0.62	0.10
73	17.02	5.12	31.38	13.30	47.30	0.14	0.03	0.42	0.07
74	ND	13.60	15.50	1.85	53.50	ND	0.10	0.88	0.07

Table 4
Description of the samples names and associated concentrations (mg/g)

Sample name	P	K	Ca	Ti	Fe	Sr	Sn	Ba	Pb
E. striatulum (spruce) B.S.G.	ND	8.31	20.96	6.91	33.47	0.17	0.03	0.21	0.01
H. cupressiforme Hedw.	16.56	8.09	33.61	9.73	40.66	0.16	0.04	0.52	0.02
S. purum (Hedw.) Limpr.	10.57	6.47	20.18	5.71	19.13	0.09	0.03	0.26	0.04
C. molluscum (Hedw.) Mitt.	34.02	9.21	67.42	10.84	39.77	0.32	0.02	0.48	0.04
H. sericeum (Hedw.) B.S.G.	17.15	6.29	34.28	10.06	36.83	0.15	0.03	0.31	0.03
B. mildeanum (Schimp.) Milde	22.33	10.62	81.04	15.24	49.71	0.34	0.01	0.53	0.01
E. striatum (Hedw.) Schimp.	18.53	7.14	31.72	13.61	50.82	0.17	0.03	0.41	0.02
B. albicans (Hedw.) B.S.G.	17.72	6.45	40.92	9.34	35.07	0.16	0.03	0.38	0.07
L. sciuroides (Hedw.) Schwaegr.	8.05	9.55	40.73	8.43	27.42	0.11	0.35	0.26	0.08
R. squarrosus (Hedw.) Warnst.	25.50	12.08	50.82	12.15	38.41	0.24	0.03	0.77	0.05
B. capillare Hedw.	22.21	9.43	42.04	15.64	72.39	0.28	0.07	0.52	0.05
R. murale (Hedw.) B.S.G.	30.49	6.42	48.14	8.09	41.61	0.14	0.04	0.24	0.05
P. succulentum (Wils.) Lindb.	14.69	6.09	26.25	13.73	49.04	0.11	0.03	0.46	0.01
C. cuspidata (Hedw.) Loeske	21.49	7.79	38.64	13.51	52.76	0.23	0.04	0.52	0.04
A. varium (Hedw.) Lindb.	17.98	7.01	32.51	13.47	53.42	0.17	0.03	0.48	0.05
P. schreberi (Brid.) Mitt.	13.65	4.84	20.99	3.25	11.33	0.06	0.03	0.12	0.03
E. hians (Hedw.) Lac.	27.11	6.85	54.21	12.07	28.93	0.17	ND	0.35	0.05
L. riparium (Hedw.) Warnst.	15.79	7.56	27.21	6.34	45.84	0.17	0.02	0.52	0.05
T. fragilis (Hook.&Wils.) Limpr.	17.21	5.81	31.31	12.18	27.21	0.16	0.03	0.36	0.05
T. tamariscinum (Hedw.) B.S.G.	13.64	7.09	22.44	13.05	42.04	0.12	0.01	0.32	0.03
H. resupinatum Tayl.	15.82	6.83	31.38	12.91	46.81	0.16	0.03	0.43	0.04
Average	19.03	7.62	37.94	10.77	40.13	0.18	0.05	0.40	0.04
Range	8.05–34.02	4.84–12.08	20.18–67.42	3.25–15.64	11.33–72.39	0.11–0.34	0.01–0.35	0.12–0.77	0.01–0.08

where DL_i is the detection limit (mg/kg), I_i (BG) the background intensity (cps) under element I peak, and t is the counting time (s). Detection limit for Pb was calculated to be 5 mg kg^{-1}.

2.2. Sampling and preparation

Moss samples were collected from 36 centers and 33 center intervals along Sarp-Samsun highway located in the Eastern Black Sea of Turkey (Fig. 1). All samples were dried in a Heraeus furnace and then ground in a spex mill. To reduce particle size effect, the powder obtained was sieved using a 400-mesh sieve and then stirred for 25 min to obtain a well-mixed sample. Forty milligrams of this powder was pressed in 13 mm diameter.

2.3. Excitation and spectral analysis

Samples positioned in Fig. 2 were irradiated by 59.5 keV photons emitted by an annular 50 mCi ^{241}Am radioactive source for iron, strontium, tin and barium determination and irradiated by 5.9 keV photons emitted by an annular 50 mCi ^{55}Fe radioactive source for phosphorus, potassium, calcium and titanium. A PGT Si(Li) detector having 147 eV full width at half maximum (FWHM) for 5.9 keV was used for the experiment. Two thousand and forty-eight channels of a multi-channel analyzer were employed in data acquisition. In qualitative analysis, char-

Table 5
Samples collected from the control region

Species of mosses	Locations
H. cupressiforme Hedw.	Giresun Kümbet high plateau
H. sericeum (Hedw.) B.S.G.	Giresun Kümbet high plateau
S. purum (Hedw.) Limpr	Artvin Hatila valley national park
S. purum (Hedw.) Limpr	Giresun Kümbet high plateau
H. cupressiforme Hedw.	Artvin Hatila valley national park
H. sericeum (Hedw.) B.S.G.	Artvin Hatila valley national park
H. cupressiforme Hedw. soil	Sürmene
H. sericeum (Hedw.) soil	Çayeli-Pazar

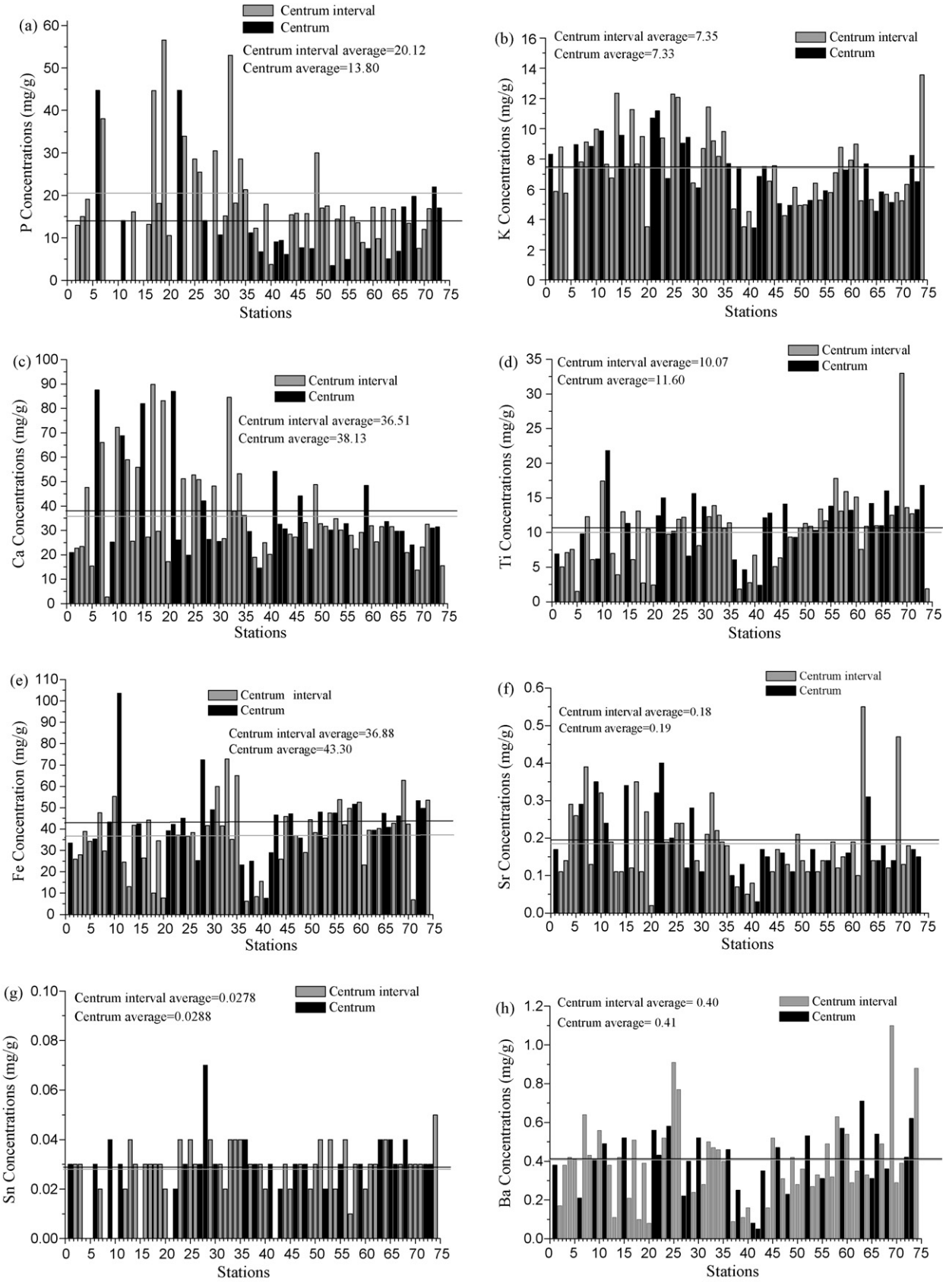

Fig. 4. Concentration profiles of samples for (a) P, (b) K, (c) Ca, (d) Ti, (e) Fe, (f) Sr, (g) Sn, (h) Ba and (i) Pb.

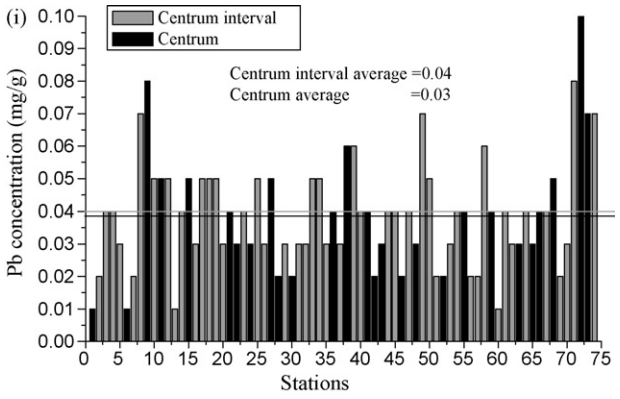

Fig. 4. (*Continued*).

acteristic X-rays emitted by excited atoms of the sample were registered for 2000 s (Tables 1 and 2).

Qualitative analysis of spectral peaks showed that the samples contained phosphorus, potassium, calcium, titanium, iron, strontium, tin and barium. In Fig. 3(a) and (b), representative spectrums of the elements excited by ^{55}Fe and ^{241}Am radioactive sources are shown, respectively.

Since this study is the elemental analysis along the highway, one can expect to detect Pb. But Pb was not observed with EDXRF because of the detection limit of the system. This is why we analyzed the samples with Atomic Absorption Spectroscopy (AAS) for Pb and added the results to Table 3. The detailed description of the AAS is given elsewhere [21].

3. Results and discussion

Heavy metals are emitted to the environment from different sources such as transportation, industrial activities, fossil fuels, agriculture, urbanization and other human activities.

The concentrations of nine elements (P, K, Ca, Ti, Fe, Sr, Sn, Ba and Pb) in moss samples are shown in Table 3 and Fig. 3(a)–(h). The average concentrations of elements collected from centrums are relatively higher (except P in Fig. 3(a)) than those collected from centrum intervals. It could be attributed to the urbanization and hence industrial activities. On the other hand, the presence of P in a special place is related to the geological formation (Fig. 4).

The species names and associated element concentrations are given in Table 4. As can be seen, while *Rhytidiadelphus squarrosus*, *Brachythecium mildeanum*, *Bryum capillare*, *Leucodon sciuroides*, and *Eurhyncnium striatum* have the highest concentration values of Ba and K, Ca and Sr, Ti and Fe, and Sn and P; *Pleurozium schreberi*, *L. sciuroides*, *Scleropodium purum* and *Thuidium tamariscinum* have lowest values of [K, Ti, Fe, Ba], [P and Sr], Ca and Sn, respectively. It is also observed that *L. sciuroides* (Hedw.) Schwaegr has highest Pb concentration.

A typical X-ray spectrum of the moss samples excited by ^{55}Fe and ^{241}Am radioactive sources are shown in Fig. 3(a) and (b). In elemental analysis using X-ray fluorescence technique, matrix effects are known to distort the linearity of "photo peak area versus concentration" graphs for analyses [22].

To minimize or to eliminate matrix effects we proceeded as follows:

(i) The Kα net peak areas for iron, strontium, tin and barium obtained from sample spectra were normalized by dividing them by Compton net peak areas. The Kα net peak areas for phosphates, potassium, calcium and titanium obtained from sample spectra were normalized by dividing them by Mn Kα peak areas.
(ii) To obtain an ideal grain size for the samples the ground material was sieved using a 400-mesh sieve.

Ba and Ca were classified as an important component in brakes [23,24]. Ca is predominantly an indicator for soil dust, as Ca is a frequent component of grit used on many roads during winter. Fe and Sn are heavy metals. While P, K, Ca, Ti, Fe and Ba are present in the earth crust naturally, Sr and Sn are not.

The main sources of lead are the combustion of leaded fuel, waste incineration and industry. Lead pollution is correlated with urbanization and density of population. Lead is known to induce reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults [25]. However not much Pb concentration has been detected in the samples collected from the study area.

Names and concentrations of elements in the samples collected from the control region are shown in Tables 5 and 6. No P and Sr elements have been detected in these samples. But in two soil samples Cu and Y have been detected. It has been observed that the concentrations of the elements in moss samples collected from the control region are much lower that those collected from the measurement site.

Higher or lower levels of the other elements were detected, in moss samples, when compared to substrate concentrations. These differing levels are directly relatable to morphological

Table 6
Elements concentrations in the control region samples (mg/g)

Sample name	K	Ca	Ti	Fe	Cu	Y	Sn	Ba
H. cupressiforme Hedw.	3.74	9.82	0.30	8.86	ND	ND	ND	0.09
H. sericeum (Hedw.) B.S.G.	3.74	7.51	0.30	8.33	ND	ND	ND	0.12
S. purum (Hedw.) Limpr.	3.13	8.12	0.40	9.12	ND	ND	ND	0.11
S. purum (Hedw.) Limpr.	3.45	9.34	0.35	8.46	ND	ND	ND	0.10
H. cupressiforme Hedw.	2.17	10.96	0.37	9.44	ND	ND	0.32	0.15
H. sericeum (Hedw.) B.S.G.	4.15	9.78	0.27	8.30	ND	ND	0.02	0.06
H. cupressiforme Hedw. soil	9.01	16.55	2.06	50.97	8.06	0.95	0.33	10.70
H. sericeum (Hedw.) B.S.G. soil	1.86	44.37	1.37	38.33	3.92	0.34	0.32	3.95

and anatomical features of moss, such as metal-absorbing abilities, surface area, large intercellular space, high cell membrane permeability, pH, additives, elemental concentrations in the atmosphere, humidity, direction of dominating wind and other climatic conditions have various effects on metal concentration in moss.

In our measurements maximum relative errors due to the counting system were of the order ∼0.5–5%. Errors originating from sample weighing, source intensity and system geometry were about 4%. The combined relative error in our results was accordingly of the order of 8%.

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