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Determination of Some Elements in Moss Samples from North Eastern Anatolia, Turkey

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Nine moss species were collected from high-density traffic roads and near the copper and zinc mine in Çayeli, Turkey. Eleven elements (K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb) were analyzed using AAS and EDXRF. The metal concentrations in moss samples were found to be 4057-30064, 7275-31658, 313-7595, 25.3-101.6, 121-1252, 18446-65851, 5.3-14.3, 12.4-60.0, 17.4-1442.5, 90-2175 and 15.5-87.5, mg/kg for potassium, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc and lead, respectively.

Key Words: Atmospheric heavy metal, moss, AAS, EDXRF, Çayeli, Sürmene, Turkey.

INTRODUCTION

Heavy metals constitute the most dangerous group of anthropogenic environmental pollutants due to their potential toxicity and their persistence[1,2]. Accumulation of heavy metals causes chronic damage to ecosystems and must be carefully monitored taking into account uptake, movement and effects of the contaminants on both the environment and its biota[3]. Industrial heavy metal pollutant is a serious environmental problem all over the world in recent years. There has been a rapid growth in pollution in Turkey and other developing countries. Roadside soil and plants are receiving considerable amounts of toxic metals, especially from automobile emission and transported toxic materials[4,5].

Determination of the concentrations of heavy metals in the environment is an important part of understanding biogeochemical process and gauging ecosystem health[6]. Effects of environmental pollutants can be well estimated by using bioindicators. These living organisms reflect the state of the environment and are

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suitable for indicating pollution because of their occurrence, absence or presence, frequency, distribution, abundance, vitality, reactions and responses change under certain environmental conditions[7].

The moss monitoring technique, first introduced in Scandinavia, has shown to be very suitable for studying atmospheric deposition of heavy metals and other elements as well[8,9]. Mosses have been used extensively since the late 1960's for assessing atmospheric heavy metal loadings[10]. Mosses are particularly effective biomonitors of atmospheric heavy metal contamination because of their bioaccumulative properties. These plant groups are amenable to biomonitoring because they are widespread, easy to handle and they lack a cuticle and root systems thus reflecting directly atmospheric heavy metal deposition[11,12].

A broad variety of analytical techniques have been used to determine trace and essential elements in mosses *i.e.*, atomic absorption spectrometry with flame (FAAS) and graphic furnace, inductively coupled plasma optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS), electrochemical methods and radioanalytical methods[13].

In this study, the levels of trace metals and essential metals were determined by EDXRF and AAS methods in moss samples collected from polluted (Çayeli, Rize) and unpolluted locations (Sürmene, Trabzon), north eastern, Anatolia, Turkey.

EXPERIMENTAL

Sampling: A total nine moss species were collected from high-density traffic roads and near the copper and zinc mine in Çayeli, Rize, north eastern, Anatolia, Turkey. Control samples were collected from Çamburnu, Trabzon. Samples were stored in polyethylene bottles until analysis. All reagents were of analytical reagent grade unless otherwise stated. Double deionizer water was used for all dilutions. HNO_3, H_2O_2 and HF were of suprapure quality (Merck).

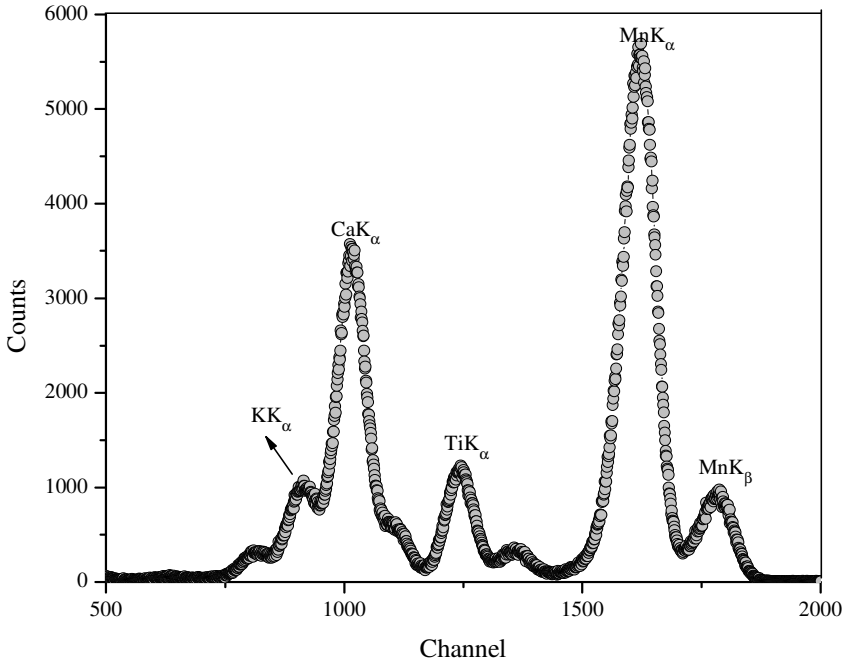
Analytical procedure for AAS: The samples were dried at 105 ºC for 24 h. Dried samples were homogenized. Milestone Ethos D microwave closed system was used in this study. 0.25 g of sample was digested with 6 mL of HNO_3 (65 %), 2 mL of H_2O_2 (30 %) and 1 mL HF (39 %) in microwave digestion system for 27 min and diluted to 25 mL with deionizer water. A blank digest was carried out in the same way (digestion conditions for microwave system were applied as 6 min for 250 W, 6 min for 400W, 6 min for 650 W, 6 min for 250 W, vent: 3 min, respectively).

Unicam Model AA-929 model atomic absorption spectrometer was used in this study for the elemental analysis. Cr, Mn, Ni, Pb, Cd, Cu, Co and Zn were analyzed with flame atomic absorption spectrometry (FAAS). Arsenic and Hg were determined with hydride generation system and cool vapour system (Unicam VP vapour system combined with FAAS). Concentration of elements in samples was determined using a single element hollow-cathode lamps and air/acetylene burner head. N_2O/acetylene-burner used for chromium.

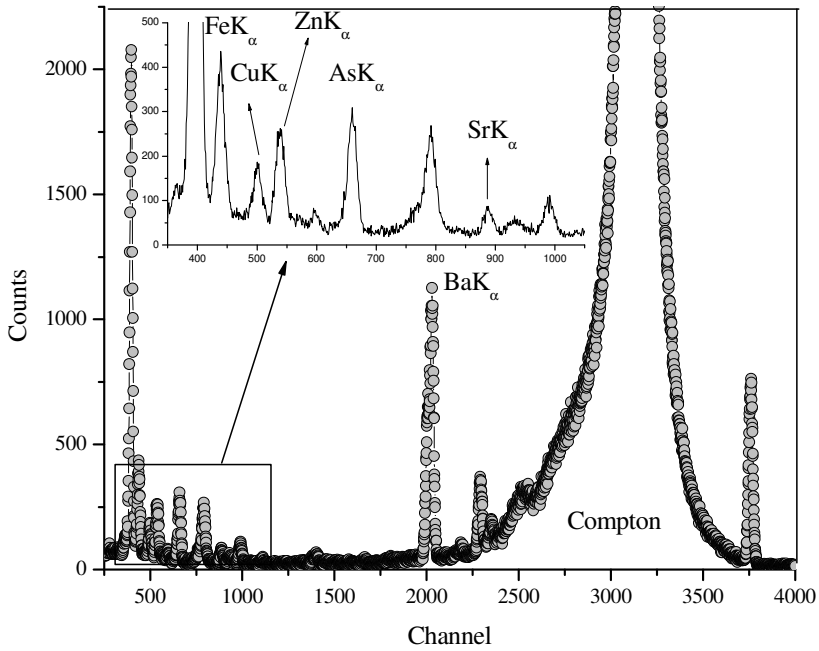
Analytical Procedure for EDXRF: Samples were dried in a Heraeus furnace and then ground in a spex mill. To reduce particle size effects, the powder obtained were sieved using a 400 mesh sieve and then stirred for 20 min to obtain a well-mixed sample. 100 mg of this powder was pressed 13 mm diameter.

Samples were positioned according to the geometry. 1.85 GBq ^{55}Fe and ^{241}Am radioactive sources excited by 5.96 and 59.54 keV, respectively, photon energies were used for direct excitation. The samples were analyzed in the form of pellets to obtain their characteristic X-ray spectra by using a collimated Ultra-LEGe detector having a thickness of 5 mm and an energy resolution of 150 eV at 5.96 keV. The output from the preamplifier, with a pulse pile-up rejection capability, was fed to a multi-channel analyzer interfaced with a personal computer provided with suitable software for data acquisition and peak analysis. Spectra were analyzed using the Genie 2000 program and net peak areas were determined using the Origin 7.0 software program. Each sample was irradiated for a time interval ranging 2000 to 5000 s. Typical spectra of moss samples are shown in Fig. 1.

Quantitative analysis for these elements was carried out using the method of multiple standard additions. In this method, certain amounts of the element to be analyzed, called analyte are added to samples. This method was explained in previous paper[14]. In order to minimize the absorption effect, the AK_α/MnK_α intensity ratio was used instead of AK_α intensity obtained from ^{55}Fe (A = K, Ca and Ti). In addition, the K_α peak areas obtained from the sample spectra using ^{241}Am radioactive sources were normalized by dividing them by Compton peak areas.



(a)



(b)

Fig. 1. Typical spectra of sample recorded with Ultra-lege detector using (a) ^{55}Fe and (b) ^{241}Am-radioisotopes

RESULTS AND DISCUSSION

All metal concentrations were determined on a dry weight basis. The recovery values were nearly quantitative (≥ 95 %) for chosen digestion method. The relative standard deviations were less than 10 % for all elements. The results of AAS and EDXRF are same. The mean concentrations of the eleven elements analyzed (K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb) with AAS and EDXRF in moss samples are given in Table-1. The metal concentrations in moss samples were found to be 4057-30064, 7275-31658, 313-7595, 25.3-101.6, 121-1252, 18446-65851, 5.3-14.3, 12.4-60.0, 17.4-1442.5, 90-2175 and 15.5-87.5, mg/kg for potassium, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc and lead, respectively.

Maximum concentrations were found at the sampling sites surrounding industrial zones (copper and zinc mine in Çayeli, Rize) and on the traffic roadside. Minimum metal levels were detected unpolluted regions (Çamburnu, Trabzon.). The concentration of trace metals in the samples is depended on moss species. For example, the high metal accumulation levels in the species were found in (*Polytrichum commune* - Çayeli-Rize) for Cu, Zn and Pb, (*Thuidium tamariscinum*- Çayeli-Rize) for Cr and Ni, *Brachythecium rutabulum* (Sürmene-Trabzon) for Ti and Co, *Dicranum polysetum* (Çayeli-Rize) for Fe, *Brachythecium rutabulum* (Çayeli-Rize) for Mn, *Tortula muralis* (Sürmene-Trabzon) for Ca, respectively.

TABLE-1
METAL CONCENTRATION IN MOSS SAMPLES DETERMINED WITH EDXRF AND AAS ANALYSIS (mg/kg)

Samples	Location	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb
Eurhychium pulchellum	Rize-Çayeli	6825	31213	392	34.0	717	34857	10.0	25.0	835.85	1268	31.0
Eurhychium pulchellum	Trabzon-Sürmene	11095	7275	3362	44.2	686	16521	7.4	28.5	17.5	109	15.5
Dicranum polysetum	Rize-Çayeli	10089	12081	1016	62.3	131	65851	ND	39.5	712.0	1585	117.2
Dicranum polysetum	Trabzon-Sürmene	2988	18281	313	43.3	172	16247	5.3	16.1	108.0	157	34.3
Leucobryum glaucum	Rize-Çayeli	7993	11432	1603	71.4	121	40252	ND	53.8	93.3	182	39.5
Leucobryum glaucum	Trabzon-Sürmene	6943	21680	607	46.8	304	20852	ND	25.3	34.3	135	25.1
Polytrichum commune	Rize-Çayeli	7666	14694	2554	37.9	166	38524	ND	ND	1406.1	2113	60.8
Polytrichum commune	Trabzon-Sürmene	22283	9639	1078	42.5	490	52088	7.9	30.0	17.4	90	16.7
Atrichum undulatum	Rize-Çayeli	11935	9945	1719	35.0	356	41272	9.3	16.5	41.2	261	ND
Atrichum undulatum	Trabzon-Sürmene	10562	8595	1203	48.8	425	36946	9.0	19.9	29.9	104	ND
Fissidens adianthoides	Rize-Çayeli	21546	20557	1749	25.3	1142	51519	7.9	17.3	389.4	746	29.1
Fissidens adianthoides	Trabzon-Sürmene	6913	24544	1111	41.5	574	31485	8.8	27.0	54.5	204	27.7
Thuidium tamariscinum	Rize-Çayeli	11957	18686	1070	86.8	749	42207	ND	34.5	828.7	1655	80.5
Thuidium tamariscinum	Trabzon-Sürmene	13490	21715	884	63.9	725	53325	11.0	30.0	95.2	238	41.9
Brachythecium rutabulum	Rize-Çayeli	7807	29597	1203	32.6	1252	54683	8.9	12.4	750.1	1345	67.1
Brachythecium rutabulum	Trabzon-Sürmene	10704	16408	7595	60.4	1050	24544	14.3	25.6	21.8	164	37.6
Tortula muralis	Rize-Çayeli	12821	20101	1206	35.7	233	62542	ND	ND	595.2	1047	37.7
Tortula muralis	Trabzon-Sürmene	1858	31658	1535	41.7	849	18446	13.9	ND	76.7	138	23.8

Iron is a vital constituent of plant and animal life and appears in hemoglobin. The lowest and highest iron concentrations were found to be 18446 mg/kg in *Tortula muralis* (Sürmene-Trabzon) and 65851 mg/kg in *Dicranum polysetum* (Çayeli-Rize), respectively. These values have been reported as 240-6761 and 1057-3504 μg/g in the literatures for different moss species[7,9]. A potential source of high iron level may be connected with the copper and zinc mine. Besides, soil in the sampling area may be rich with respect to iron metal.

The average manganese concentration was 121-1252 mg/kg in the samples. These values are in agreement with reported data from literature[5]. Present results were higher than those reported earlier[3,12]. The lowest and highest manganese values were observed in *Leucobryum glaucum* (Çayeli-Rize) and *Brachythecium rutabulum* (Çayeli-Rize) species, respectively.

Average potassium concentration ranged from 4057 to 30064 mg/kg in moss samples. Potassium value is almost four times higher than *Eurhynchium pulchellum* (Çayeli-Rize). Potassium values are the highest than Popescue *et al.*[12] values as max. 414 mg/kg. Potassium is never found free in nature. But is obtained by electrolysis of the chloride or hydroxide, potassium is an essential constituent for plant growth and is found in most soils. Toxicity limits of manganese for plants are high (400-1000 μg/g). Present values are on the toxicity limits.

The calcium levels in moss samples were found in the range of 78-824 mg/kg. Potassium is the second high concentration values after iron in moss samples. Calcium is a major element for fresh waters and is found in every terrestrial area in the world. It is essential for the life of plants and animals for presenting of calcium element in the animal skeleton, in tooth, in the egg's shell. The literature values for calcium were reported as 12340-18647 μg/g, 78-824 mg/kg, respectively[9,12].

The maximum copper, zinc and lead concentrations were found in *Thuidium tamariscinum* (Çayeli-Rize). This species may be a good indicator for copper, zinc and lead. Copper average levels were found as 17.4 and 1442.5 μg/g in *Polytrichum commune* (Sürmene-Trabzon) and *Brachythecium rutabulum* (Çayeli-Rize). Copper average values are not agreement with literature values as 3.3-29.1 and 0.01-32.00 μg/g, respectively[3,15]. Mean zinc concentration was between 90 and 1655 mg/kg in *Polytrichum commune* (Sürmene-Trabzon), *Thuidium tamariscinum* (Çayeli-Rize) species. Zinc levels in all moss samples were found to be higher than those of earlier[7,9,16]. The maximum lead concentration was found as 80.5 mg/kg in *Thuidium tamariscinum* (Çayeli-Rize). Control samples contained 15.5 mg/kg lead in *Eurhynchium pulchellum* (Sürmene-Trabzon). The adding of lead to the petrol increases the concentration of lead. In literature, Figueira *et al.*[17] have been reported 22.80 μg/g lead in moss as biomonitors in Portugal.

The maximum titanium and cobalt were found in *Brachythecium rutabulum* (Sürmene-Trabzon). Mean Ti concentrations ranged from 313 to 7595 mg/kg. Anicic *et al.*[9] have determined trace metal levels in moss samples and their values for Ti changed from 137 to 539 μg/g. Koz *et al.*[18] value for Ti (1.51-33.00 mg/g) is the

lowest than the present work. Concentrations of Co in the moss samples were between 5.3-14.3 mg/kg. Fernandez and Carballeria[3] value for Co was 0.1-2.5 µg/g. This work value is not agreement with literature value. The high Cr and Ni accumulation levels in the moss species were found in *Thuidium tamariscinum* (Çayeli-Rize) and *Leucobryum glaucum* (Çayeli-Rize), respectively. Chromium contents in the moss samples ranged from 25.3-86.8 mg/kg. Chromium values have been reported as 0-7.33 and 4.5-9.2 µg/g, respectively for different moss species[1,6]. Nickel concentrations were found as 12.4 mg/kg in *Brachythecium rutabulum* (Çayeli-Rize) and 53.8 mg/kg in *Leucobryum glaucum* (Çayeli-Rize). In present studies, nickel average values are lower than literature values[16].

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