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Determination of Heavy Metal Concentration of Mosses in Degirmendere Valley of Trabzon Province of Turkey

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The aim of this study is to determine environmental pollution in degirmendere Valley on the basis of Cu, Cd, Pb, Zn, Mn, Fe, Cr and Ni concentrations in Mosses. The metal ions concentrations were determined in polluted and unpolluted species and soils collected from a wide range of sites with different degrees of metal pollution (Akoluk, Deliklitas, Hacimehmet district) and from control site (Çamburnu-Sürmene). Eight elements were analyzed using atomic absorption spectrometry (AAS). All the elements that measured were found to be at high levels in samples collected from polluted areas including coal mining and crushing and screening plants.

Key Words: Heavy metal, mosses, AAS, Degirmendere valley, Trabzon, Turkey.

INTRODUCTION

Trace metal levels are important for human health. Metals like iron, copper, zinc and manganese are essential metals since they have an important role in biological systems, whereas lead and cadmium are non-essential metals and are toxic even traces[1]. The essential metals can also produce toxic effects when the metal intake is excessively elevated. According to the report by food and ingredients expert committees of FAO/WHO, a healthy person can consume 3.5 mg lead and 0.525 mg cadmium in a week[2,3].

There has been a rapid growth in pollution in developing countries. 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 environmental and its biota[4]. Industrial heavy metal pollution is a serious environmental problem all over the world in recent years. Heavy metals enter into the environment mainly *via* three routes: (I) deposition of atmospheric particulates, (II) disposal of metal enriched sewage sludge sewage effluents and (III) by products from metal mining processes[5]. The moss monitoring technique, first introduced in Scandinavia, has shown to be suitable for studying atmospheric deposition of heavy metals and other elements as well[6].

Mosses can indicate the presence of elements and their concentration gradients. The use of bryophytes constitutes an effective method in air pollution monitoring for many reasons: (I) many species are widely distributed and grow in a range of habitats. (II) Bryophytes are small and easy to handle. (III) Most of them are evergreen and can be surveyed all year round. (IV) Bryophytes lack a cuticle and a root system and obtain nutrients as particulates and in solution directly from atmospheric deposition. They have good bioaccumulation ability, particularly for heavy metals, where metal concentrations reflect deposition without the complication of additional uptake *via* a root system. (V) Comparisons of fresh samples with herbarium specimens enable retrospective analysis of metal pollution. (VI) The ability of bryophytes to accumulate elements in high concentrations aids chemical analyses of the tissues and may facilitate the detection of elements present in very low concentrations in the environment. (VII) The annual growth increment is usually easier to detect in mosses than lichens and mosses are often believed more desirable for temporal studies[7].

A number 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 radio analytical methods. In this study, the levels of trace metals and essential metals were determined by AAS method in moss samples.

There are six coal mining and crushing and screening plants along the Degirmendere stream in Degirmendere valley of Trabzon. Coal getting to Trabzon *via* ships from Russia is processed and stored in this establishment.

While the action is maintained, it emits fume to the along the valley and smothers the environment. Furthermore these foundations are to be in residential and agricultural areas. The pollution can also be seen with naked eyes easily.

EXPERIMENTAL

Sampling: Twenty six moss samples and four soil samples were collected from Degirmendere Valley near the coal mining and crushing and screening plants and control site (Çamburnu-Sürmene) in Trabzon on 27.08.2009. Moss species were identified and stored in polyethylene bags until analysis (Table-1).

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 400 W, 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. Cu, Cd, Pb, Zn, Mn, Fe, Cr and Ni were analyzed with flame atomic absorption spectrometry (FAAS). Arsenic and mercury were determined with hydride generation system and col 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.

RESULTS AND DISCUSSION

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

Trace metal concentrations were determined on dry weight as µg/g. The relative standard deviations were less than 10 % for all elements. *t*-Test was used in this study ($p \leq 0.05$).

The mean concentrations of the 8 elements were analyzed with AAS in moss and soil samples. Heavy metal concentrations of moss and soil samples are presented in Tables 2 and 3. The results obtained show that samples contain Cu, Cd, Pb, Zn, Mn, Fe, Cr and Ni. The data show that iron is the highest concentrated metal and is followed by cadmium, manganese, zinc, copper, lead. (Tables 2 and 3). These results are in agreement with reported papers[8-10].

Maximum concentrations were found at the sampling sites surrounding coal mining and crushing and screening plants in Degirmendere valley (Akoluk, Hacimehmet and Deliklitas districts). 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 *Eurhynchium pulchellum* (Akoluk, Degirmendere Valley) for Fe, Cd, Mn and Cu (Fig. 1), *Phylaisia polyantha* (Akoluk, Degirmendere Valley) for Fe, Cd, Zn and Cu (Fig. 2), *Eurhynchium striatum* (Deliklitas, Degirmendere Valley) for Fe, Cd, Zn and Cu (Fig. 3), *Hypnum resupinatum* (Akoluk, Degirmendere Valley) for Fe, Cd, Mn and Pb (Fig. 4), *Oxyrrhynchium speciosum* (Akoluk, Degirmendere Valley) for Fe, Cd, Mn and Cd (Fig. 5), *Oxyrrhynchium hians* (Deliklitas, Degirmendere Valley) for Fe, Cd, Zn and PB (Fig. 6), respectively.

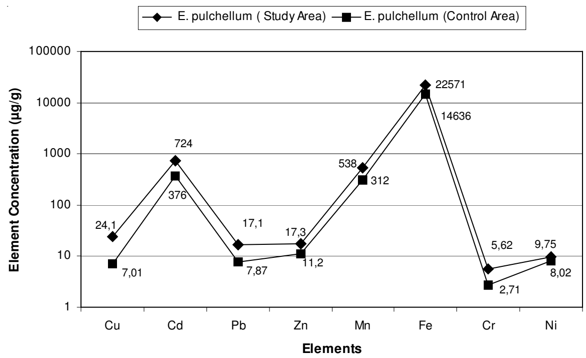

Fig. 1. The concentrations of metal ions present in *Eurhynchium pulchellum* in Akoluk district of Degirmendere Valley of Trabzon (control area: Sürmene-Çamburnu district of Trabzon province)

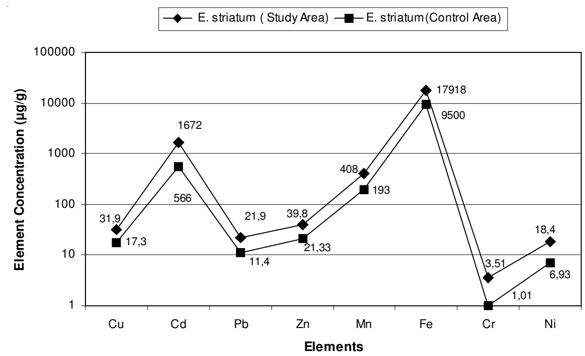

Fig. 2. The concentrations of metal ions present in *Pylaisia polyantha* in Akoluk disrict of Degirmendere valley of Trabzon (Control area: Sürmene-Çamburnu district of Trabzon province)

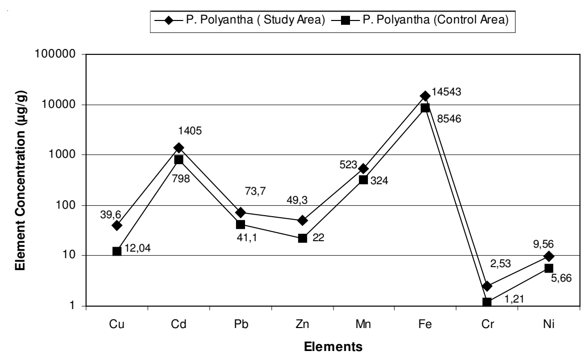

Fig. 3. The concentrations of metal ions present in *Eurhynchium striatum* in Deliklitas district of Degirmendere valley of Trabzon (Control area: Sürmene-Çamburnu district of Trabzon province)

TABLE-1
SITE DESCRIPTION OF STATIONS IN DEGIRMENDERE VALLEY OF TRABZON

Study area	Sites	Locations	Altitude (m)
Degirmendere valley	Akoluk (AK) (Polluted site)	40º 56' 18.53" N 39º 44' 05.79" E	74
Degirmendere valley	Deliklitas (DT) (Polluted site)	40º 58' 58.62" N 39º 44' 56.18" E	30
Degirmendere valley	Hacimehmet (HM) (Polluted site)	40º 56' 27.75" N 39º 44' 13.32" E	76
Sürmene district	Çamburnu (CB) (Control site)	40º 55' 27.75" N 40º12' 46.36" E	50

TABLE-2
CONCENTRATIONS (μG/G) OF TRACE METALS IN INVESTIGATED MOSSES SPECIES. HM: HACIMEHMET, SC: SÜRMENE-ÇAMBURNU, AK: AKOLUK, DT: DELIKLITAS, BDL: BELOW DETECTION LIMIT

Samples	Location	Cu	Cd	Pb	Zn	Mn	Fe	Cr	Ni
Calliergonella cuspidata	HM	16.5±1.1	BDL	10.0±1.0	15.8±1.1	378±27	11843±876	1.11±0.1	10.2±0.7
Calliergonella cuspidata	SC	12.4±1.2	BDL	6.1±0.5	11.7±1.0	77.2±6.9	5312.8±6.8	0.77±0.1	7.7±0.5
Hypnum resupinatum	HM	20.9±1.7	BDL	13.2±1.1	16.21±0.4	509±34	20136±1232	0.30±0.02	6.59±0.6
Hypnum resupinatum	SC	5.1±0.3	0.3±0.02	11.2±0.9	16.01±1.4	192.7±13.2	8909.8±8.1	0.29±0.02	4.1±0.33
Oxyrrhynchium speciosum	HM	20.7±1.9	15.9±1.1	15.4±1.4	29.5±2.1	337±33	12154±687	BDL	3.63±0.2
Oxyrrhynchium speciosum	SC	11.4±1.1	0.9±0.06	7.5±0.5	20.50±1.5	192.7±13.2	1024.45±9.8	BDL	2.76±0.1
Homalothecium sericeum	HM	7.71±0.5	16.3±1.3	15.8±1.2	11.1±1.0	152±12	5556.4±345	BDL	2.10±0.1
Homalothecium sericeum	SC	3.6±0.3	9.77±0.7	8.85±0.73	7.9±0.5	87.03±6.04	2800.7±16.7	BDL	1.1±0.09
Kindbergia praelonga	HM	21.5±2.1	256±22	17.4±1.5	24.3±2.4	408±35	11711±234	0.31±0.01	3.63±0.1
Kindbergia praelonga	SC	6.9±0.3	124.2±9.9	7.5±0.5	17.4±1.6	126±11.3	7662±7.6	0.09±0.01	1.97±0.1
Brachythecium rivulare	HM	16.7±1.2	176±14	27.3±2.1	6.48±0.5	372±32	12564±546	1.88±0.1	5.28±0.4
Brachythecium rivulare	SC	8.16±0.5	82.2±6.7	13.6±1.2	4.92±0.5	102.2±9.1	4379±276	0.7±0.1	2.0±0.1
Didymodon tophaceus	HM	12.8±1.1	421±36	15.6±1.4	17.0±1.3	339±25	10708±786	BDL	5.26±0.3
Didymodon tophaceus	SC	5.56±0.6	201±18	7.9±0.5	6.89±0.4	111.3±9.3	3365±34.3	BDL	3.34±0.2
Hypnum cupressiforme	AK	36.6±1.9	660±45	94±7.2	67.2±5.7	304±24	8392.0±568	4.19±0.2	8.39±0.7
Hypnum cupressiforme	SC	14.4±1.6	198±18	46±4.1	23.4±2.5	106±9.97	1995±19.5	1.78±0.1	3.6±0.4
Pylaisia polyantha	AK	39.6±3.2	1405±123	73.7±5.7	49.3±3.6	523±45	14543±1287	2.53±0.1	9.56±0.8
Pylaisia polyantha	SC	12.04±1.2	798±81	41.1±4.01	22±1.5	324±32	8546±850	1.21±0.1	5.66±0.5
Hypnum resupinatum	AK	39.1±3.2	723±45	54.5±4.3	39.2±2.9	269±17	7974.6±567	1.82±0.1	9.74±0.8
Hypnum resupinatum	SC	21.1±2	376±32	31.2±2.3	21.01±1.5	176±15	4370±450	1.1±0.1	6.89±0.5
Oxyrrhynchium speciosum	AK	18.1±1.1	914±78	11.9±1.1	27.1±2.4	353±24	15842±795	1.89±0.1	3.70±0.6
Oxyrrhynchium speciosum	SC	11.2±1.1	797±80	7.9±0.5	15.6±1.5	112±9	11071±222	1.1±0.1	1.89±0.1
Eurhynchium pulchellum	AK	24.1±2.1	724±56	17.1±1.3	17.3±1.6	538±45	22571±1564	5.62±0.4	9.75±0.7
Eurhynchium pulchellum	SC	7.01±0.4	376±32	7.87±0.6	11.2±0.9	312±25	14636±980	2.71±0.2	8.02±0.5
Brachythecium glareosum	AK	19.9±1.7	330±26	16.9±1.2	26.8±1.5	330±27	13999±1222	1.05±0.1	6.58±0.5
Brachythecium glareosum	SC	12.45±1.1	176±14	7.5±0.5	17.5±1.5	112.2±9.2	12456±540	1.01±0.1	5.43±0.2
Oxyrrhynchium speciosum	DT	20.4±1.9	757±57	12.0±1.0	38.0±2.8	349±25	12038±965	1.90±0.1	2.12±0.1
Oxyrrhynchium speciosum	SC	14.3±1.1	561±45	6.55±0.4	21.4±1.5	312±25	11045±221	1.20±0.1	1.76±0.1
Eurhynchium pulchellum	DT	21.2±1.5	337±25	19.3±1.4	37.8±2.5	451±35	16032±983	1.86±0.1	5.22±0.4
Eurhynchium pulchellum	SC	17.3±1.0	178±15	11.8±1.1	27.2±2.5	355±25	12950±560	0.94±0.1	3.76±0.2
Oxyrrhynchium hians	DT	22.0±1.7	804±56	13.3±1.1	15.8±1.1	484±34	17505±1232	2.58±0.2	9.76±0.8
Oxyrrhynchium hians	SC	9.6±0.5	276±25.6	6.94±0.5	6.77±0.5	176±1.8	7654±743	1.01±0.1	4.6±0.4
Eurhynchium striatum	DT	31.9±2.8	1672±143	21.9±1.9	39.8±2.8	408±34	17918±1345	3.51±0.2	18.4±1.2
Eurhynchium striatum	SC	17.3±1.5	566±58	11.4±1.1	21.33±1.9	193±22	9500±783	1.01±0.2	6.93±0.5
Rhynchostegium confertum	DT	18.5±1.3	736±56	7.81±0.6	15.3±1.3	375±24	15517±1211	0.31±0.02	8.33±0.8
Rhynchostegium confertum	SC	11.4±0.9	456±44	3.78±0.2	7.99±0.6	171±15	590±61	0.01±0.01	3.27±0.2

TABLE-3
CONCENTRATIONS (μg/g) OF TRACE METALS IN INVESTIGATED SOIL SAMPLES

Samples	Location	Cu	Cd	Pb	Zn	Mn	Fe	Cr	Ni
Soil	HM	45.3 ± 3.8	333 ± 23	26.7 ± 2.1	33.0 ± 3.0	844 ± 56	33447 ± 2345	3.37 ± 0.2	14.5 ± 1.1
Soil	SC	32 ± 2.6	201 ± 18	13.4 ± 1.1	21 ± 0.2	566 ± 38	21561 ± 1436	3.05 ± 0.2	12.6 ± 1.1
Soil	AK	31.4 ± 2.1	418 ± 34	25.1 ± 2.1	51.3 ± 4.6	743 ± 45	24144 ± 1343	6.51 ± 0.4	16.3 ± 1.2
Soil	SC	27.2 ± 1.9	376 ± 22	21.5 ± 1.9	44.6 ± 4.5	592 ± 32	19776 ± 930	5.34 ± 0.3	11.2 ± 0.9
Soil	DT	21.7 ± 1.8	1916 ± 121	13.4 ± 1.1	1.89 ± 0.1	325 ± 23	10698 ± 987	1.07 ± 0.1	12.8 ± 1.1
Soil	SC	17.4 ± 1.2	1566 ± 90	9.06 ± 0.5	1.1 ± 0.1	276 ± 25.6	8878 ± 873	0.9±0.1	9.3±0.6

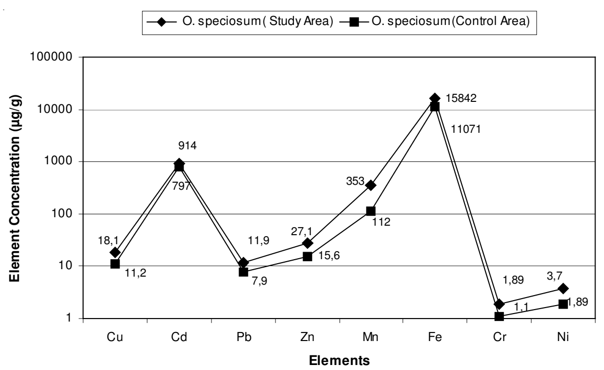

Fig. 4. The concentrations of metal ions present in *Hypnum resupinatum* in Akoluk district of Degirmendere valley of Trabzon (Control area: Sürmene-Çamburnu district of Trabzon province)

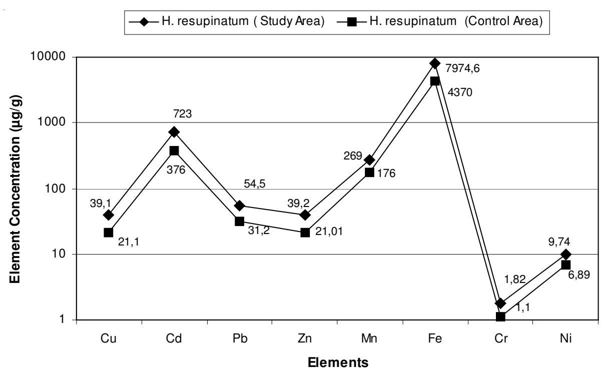

Fig. 5. The concentrations of metal ions present in *Oxyrrhynchium speciosum* in akoluk district of Degirmendere valley of Trabzon (Control area: Sürmene-Çamburnu district of Trabzon province)

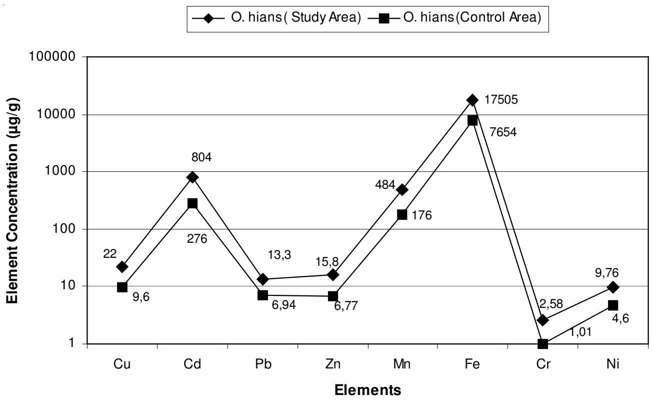

Fig. 6. The concentrations of metal ions present in *Oxyrrhynchium hians* in Deliklitas district of Degirmendere valley of Trabzon (Control area: Sürmene-Çamburnu district of Trabzon province)

The highest concentrations were found as iron metal in all the samples. The heavy metal is a vital constituent of plant and animal life and appears in hemoglobin. The lowest and highest iron concentrations were found to be 1024.45 µg/g in *Oxyrrhynchium speciosum* (Sürmene-Çamburnu) and 22572 µg/g *Eurhynchium pulchellum* (Akoluk, Degirmendere), respectively. These values have been reported as 240-6761 and 1057-3504 µg/g in the literature[11,12] for different moss species. Sürmene-Çamburnu district (control site) is average but Akoluk and other polluted regions (Hacimehmet and Deliklitas districts) are higher than average in literature. Furthermore, iron is high value in soil samples in all sites (Table-2). A potential source of high iron level may be connected with coal mining and crushing and screening plants and control sites. Besides, soil in the sampling area may be rich with respect to iron metal.

The average manganese concentration was 77.2-355 µg/g in control sites, 152-538 µg/g in Degirmendere Valley (Akoluk, Hacimehmet, Deliklitas regions). These values are in agreement with reported data from literature[7-9]. The lowest and highest manganese values were observed in Calliergonella cuspidata (Sürmene, Çamburnu) and *Eurhynchium pulchellum* (Akoluk, Degirmendere Valley) species, respectively. Toxicity limits of manganese for plants are high (400-1000 µg/g). Present values are on average (Table-2).

Average copper concentration ranged from 3.6-39.6 µg/g in moss samples. The lowest and highest copper values were found to be 3.6 µg/g in *Homalothecium sericeum* (Sürmene, Çamburnu) and 39.6 µg/g in *Phylaisia polyantha* (Akoluk, Degirmendere Valley), respectively. The average values of copper are similar with literature[4,13] value as 3.3-29.1 and 0.01-32.00 µg/g, respectively (Table-2).

Cadmium is the second high concentration values after iron in all samples. Zing levels were found as 4.92 µg/g in *Brachythecium rivulare* (Sürmene, Çamburnu) and 49.3 µg/g in *Phylaisia polyantha* (Akoluk, Degirmendere Valley) (Table-2).

The minimum and maximum lead concentrations were found as 6.1 µg/g in *Calliergonella cuspidata* (Sürmene Çarburnu), as 94 µg/g in *Hypnum cupressiforme* (Akoluk, degirmendere Valley), respectively. The addition of lead to the petrol increases the concentration of lead. Vargha *et al.*[14] have been reported 22.80 µg/g lead moss as biomonitors in Portugal. The lead level of the present study is different literature. Çamburnu region of Sürmene has low density traffic than Degirmendre Valley. Depending on this result, the lead concentration is high in density in Degirmendere Valley (Table-2). Consequently, it has been found a correlation between element concentration of study areas and control area.

Conclusion

The heavy metal analysis along the Degirmendere valley of Trabzon in Turkey was carried using mosses and soils. This valley is an industrial area of Trabzon, including coal mining and crushing plants, automobile industry. Copper, Cd, Pb, Zn, Mn, Fe, Cr and Ni elements were observed in the samples studied. Trace metal concentrations in mosses and soil emitted from the coal mining and crushing and screening plant have been polluting the Degirmendere Valley of Trabzon. Generally, the concentrations of trace metals increased in moss samples collected from polluted areas. Mosses is used as biomonitors from structural characteristics, such as *Hypnum cupressiforme*, *Hypnum resupinatum*,*Calliergonella cuspidate*, *Eurhynchium pulchellum*, *Eurhynchium striatum*. Further researches are required to determine the trace metal pollution trends in Degirmendere Valley of Trabzon.

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