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Determination of Trace Elements in Some Moss Samples by Atomic Absorption Spectrometry

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In the present work, the trace metal levels in moss samples were determined. Six species of moss samples were collected from near the Artvin motorway in Turkey. Fe, Cu, Mn, Zn, Pb and Cd in the samples were analyzed using flame and graphite furnace atomic absorption spectrometry after microwave digestion. The metal concentrations in samples were found to be 1076.0-2137.0, 13.3-28.6, 107.7-375.6, 86.8-134.1, 8.3-27.6 and 0.2-1.3 µg/g for iron, copper, manganese, zinc, lead and cadmium, respectively.

Key Words: Trace metals, Biomonitor, Moss samples, Atomic absorption spectrometry.

INTRODUCTION

Trace metal levels are important for human health. Metals like iron, copper, zinc and manganese are essential metals since they play an important role in biological systems, whereas lead and cadmium are non-essential metals and are toxic even in traces[1,2]. 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[3,4]. Mosses have been used as biomonitors of atmospheric heavy metal pollutants[5-9]. Determination of trace metals in moss samples will be contributed to the solution of environmental pollution in region.

In this study, trace metal levels of moss samples collected from polluted and unpolluted locations in Artvin, Turkey were determined by flame atomic absorption spectrometry. Lower concentrations are determined using graphite furnace atomic absorption spectrometry.

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EXPERIMENTAL

Samples were collected from near the Artvin motorway (5 and 150 meters away), Turkey in 2006. Control samples were collected from uncontaminated locations (Hatila Vadisi). The samples were dried at 105 ºC for 24 h. Dried samples were homogenized using agate homogenizer and stored in pre-cleaned polyethylene bottles until analysis.

All reagents were of analytical reagent grade. Double deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} resistivity) was used for all dilutions. HNO_3 and H_2O_2 were of suprapur quality (E. Merck). The element standard solutions used for calibration were produced by diluting a stock solution of 1000 mg/L of the given element supplied by Sigma and Aldrich. Matrix modifiers as $NH_4H_2PO_4$, Pd and $Mg(NO_3)_2$ were purchased from Sigma.

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 %) and 1 mL of H_2O_2 (30 %) in microwave digestion system for 23 min and diluted to 25 mL with deionized water. A blank digest was carried out in the same way. Digestion conditions for microwave system were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min, respectively.

A Perkin Elmer Analyst 700 model AAS with deuterium background corrector was used in this study. Lead and cadmium in samples were determined by HGA graphite furnace using argon as inert gas. Other measurements were carried out in an air/acetylene flame.

RESULTS AND DISCUSSION

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 ($p < 0.05$).

The mean concentrations of metals (Fe, Cu, Mn, Zn, Pb and Cd) in moss samples are given in Table-1. The data show that iron has the highest concentration and followed by manganese, zinc, copper, lead and cadmium. These results are in agreement with those reported earlier[1,2,10]. The concentration of trace metals in the samples is depended on moss species.

The lowest and highest iron concentrations were found to be 1076.0 μg/g in *Bryum mildeanum* Jun. and 2137.4 μg/g in *Eurhynchium striatulum* (Spruce) B.S.G., respectively. These values have been reported as 443-3494 μg/g in the literature for different moss species[11]. Iron concentrations were found lower than other reported data[2].

TABLE-1
CONCENTRATIONS (μg/g) OF TRACE METALS IN INVESTIGATED MOSSES SPECIES

Moss species	Area	Fe	Cu	Mn	Zn	Pb	Cd
Hypnum cupressiforme	Polluted	1343.3 ± 10.6	13.3 ± 1.2	203.0 ± 18.2	94.4 ± 4.5	23.6 ± 1.8	1.3 ± 0.10
	Unpolluted	712.8 ± 6.8	5.1 ± 0.3	84.2 ± 5.9	36.2 ± 2.2	17.4 ± 1.6	0.3 ± 0.02
Bryum mildeanum	Polluted	1076.0 ± 9.9	28.6 ± 1.5	192.7 ± 13.2	63.6 ± 3.4	27.6 ± 2.1	1.0 ± 0.10
	Unpolluted	618.3 ± 3.7	11.4 ± 1.1	101.4 ± 8.7	55.0 ± 4.3	6.1 ± 0.5	0.4 ± 0.02
Homalothecium sericeum	Polluted	1800.7 ± 16.7	19.8 ± 1.2	338.2 ± 21.4	107.0 ± 9.3	8.3 ± 0.6	0.9 ± 0.06
	Unpolluted	890.8 ± 8.1	6.9 ± 0.3	146.1 ± 13.8	43.8 ± 2.4	3.5 ± 0.3	BDL
Barbula ungiculata	Polluted	1227.9 ± 21.8	21.1 ± 1.6	107.7 ± 10.4	86.8 ± 5.9	13.9 ± 1.4	0.4 ± 0.01
	Unpolluted	523.6 ± 2.6	14.1 ± 1.1	39.6 ± 2.9	71.2 ± 6.9	6.2 ± 0.4	BDL
Amblystegium varium	Polluted	1950.7 ± 20.2	15.1 ± 0.6	217.4 ± 14.3	134.1 ± 11.5	9.2 ± 0.8	0.2 ± 0.02
	Unpolluted	1480.9 ± 9.3	4.7 ± 0.5	98.1 ± 7.8	77.2 ± 5.8	5.7 ± 0.6	BDL
Eurhynchium striatulum	Polluted	2137.4 ± 18.3	16.5 ± 0.9	375.6 ± 30.5	111.6 ± 9.5	21.4 ± 0.1	1.2 ± 0.10
	Unpolluted	1318.4 ± 8.7	5.3 ± 0.3	144.4 ± 11.7	36.5 ± 2.2	7.5 ± 0.5	0.7 ± 0.05

BDL = Below detection limit

The average copper concentration was 13.3-28.6 μg/g in the samples. These values are in agreement with reported data from literature[2,12,13]. The present results were higher than those reported earlier[14-16]. The lowest and highest copper values were observed in *Hypnum cupressiforme* Hedw. and *Bryum mildeanum* Jun. species, respectively.

Mean manganese concentration ranged from 107.7 to 375.6 μg/g in moss samples. Manganese value is almost three times higher than the control samples. Manganese values were reported higher by Sari *et al.*[2] value as 329.2 to 806.0 μg/g and lower by Mendil *et al.*[13] value as 63.7-188.0 μg/g.

Zinc levels were found as 86.8 and 134.1 μg/g in *Barbula unguiculata* Hedw. and *Amblystegium varium* (Hedw.) Lindb. Zinc average values are in good agreement with literature values as 86.69, 86 μg/g and 84.4, respectively[2,12,17].

The maximum lead concentration was found as 27.6 μg/g. The addition of lead to the petrol increases the concentration of lead. In literature, Figueira *et al.*[8] have been reported 22.80 μg/g lead in moss as biomonitors in Portugal. The lead level of the present study is similar to Figueira *et al.*[8], but present value is lower than reported by Culicov *et al.*[17] value as 46 μg/g.

Mean cadmium concentration was between 0.2 and 1.3 μg/g in *Amblystegium varium* Hedw. Lindb., *Hypnum cupressiforme* Hedw. species. Cadmium levels in all moss samples were found to be higher than those of earlier[9,10,12].

A linear regression correlation test was performed to investigate correlations between metal concentrations. The values of correlation coefficients between metal concentrations are given in Table-2. There is a good correlation between manganese-iron (r = 0.824), zinc-iron (r = 0.862), zinc-manganese (r = 0.653), lead-copper (r = 0.522), cadmium-lead (r = 0.791) and cadmium-manganese (r = 0.704). The other correlations between metals were not significant. There were positive correlations of copper-iron, manganese-copper, zinc-copper, lead-zinc, lead-manganese, lead-iron, cadmium-zinc, cadmium-copper and cadmium-iron with corresponding r values of 0.226, 0.412, 0.379, 0.102, 0353, 0.204. 0.366, 0.479 and 0.451, respectively.

TABLE-2
CORRELATION BETWEEN METAL CONCENTRATIONS

	Fe	Cu	Mn	Zn	Pb	Cd
Fe	1.000					
Cu	0.226	1.000				
Mn	0.824	0.412	1.000			
Zn	0.862	0.379	0.653	1.000		
Pb	0.204	0.522	0.353	0.102	1.000	
Cd	0.451	0.479	0.704	0.366	0.791	1.000

Conclusion

Generally, the concentrations of trace metals increased in moss samples collected from polluted areas. Some species can be used as a biomonitor for regional studies of atmospheric trace metal deposition such as *Bryum mildeanum* for copper, *Amblystegium varium* (Hedw.) Lindb. for manganese, *Hypnum cupressiforme* for cadmium.

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