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Heavy metals in some moss species found around Camlihemsin district of Rize, Turkey

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Abstract

In recent years, environmental safety associated with heavy metal levels of a tourism area and its surrounding areas has been one of the basic security for tourists health. Various methods have been used for measuring concentrations of heavy metal levels in these areas. Biomonitoring organisms such as mosses provide quantitative information on the quality of the environment around them, and they respond to pollution by altering their physiology or their ability to accumulate heavy metals. The aim of this study is to assess the concentration of aluminum, manganese, iron, nickel, copper, and zinc levels in five different moss species collected around Camlihemsin district of Rize, by using Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometry. The average concentrations of heavy metals in moss samples were found ranged from 3.8-8.3% for aluminum, 0.1-0.47% for manganese, 2.3-3.8% for iron, 38.8-74.2 ppm for nickel, 92.1-495.3 ppm for copper, 187.3-334 ppm for zinc. This study has shown that Abietinella abietina, Hypnum cupressiforme, Plagiomnium undulate, Rhytidium rugosum, and Thuidium tamariscinum samples were used to assess the potential contamination of Al, Mn, Fe, Ni, Cu, and Zn contamination in the region and made important contributions toward the understanding of Al, Mn, Fe, Ni, Cu, and Zn baseline data can be used for identification of changes in the levels of these heavy metals in the studied area.

Keywords: Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometry, heavy metals, moss, biomonitor, environment.

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1. Introduction

Heavy metals have high density or high relative atomic weight at least five times greater than water. Heavy metals are found naturally in the earth, and they are persistent in all parts of the environment. Heavy metals are dangerous as they tend to bio-accumulate in small quantities, certain heavy metals such as iron, cobalt, copper, manganese, and zinc are nutritionally essential for a healthy life but they become toxic when they are not metabolized by the body. Small amount of Ni is needed by the human body to produce red blood cells. Other heavy metals such as mercury, plutonium, and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation in the organism can cause serious illness. Some metals such as Cd, Cr, and Ni are highly toxic even in trace amounts (Agarwala, Kumar & Sharma, 1961; Bisht & Agarwala, 1982).

Every year, millions of tones of heavy metals are emitted in the air, both from natural sources and especially from anthropogenic sources. Common sources of heavy metals are mining, industrial wastes, fertilisers and vehicle emissions (Harvey, Handley & Taylor, 2015).

In recent years, high vehicle emissions was one of the important heavy metal pollution sources in tourism areas and its surrounding areas. As a consequence, various methods have been used for measuring concentrations of heavy metals in these areas.

The high cost of instrumental recording of pollutants and the difficulties of extending sampling in time and space makes indirect methods, such as the analysis of suitable bioindicators, very appropriate for large scale air pollution monitoring (Bargagli, Brown & Nelli, 1995).

The term bioindicator is used to refer to an organism, or a part of it that depicts the occurrence of pollutants on the basis of specific symptoms, reactions, morphological changes or concentrations. Bioindicator generally refers to all organisms that provide information on the environment or the quality of environmental changes (Poikolainen, 2004).

Biomonitoring with mosses is based on the fact that terrestrial carpet - forming species obtain most of their nutrients directly from wet and dry deposition, they clearly reflect the atmospheric deposition, especially well suited to heavy metal pollution on a larger time scale (Ceburnis, Sakalys, Valiulis & Kvietkus, 2000).

In this study investigates that the concentration of aluminum, manganese, iron, nickel, copper, and zinc levels in five different moss species (*Abietinella abietina, Hypnum cupressiforme, Plagiomnium undulate, Rhytidium rugosum, and Thuidium tamariscinum*) collected around Camlihemsin district of Rize, Turkey, by using Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometry.

2. Materials and Methods

2.1. Study Area

Camlihemsin is a district of Rize province in Black Sea Region of Turkey. This is a hill area surrounded by very high mountains that poke up into the clouds, and water by the river and other streams running down the Black Sea. It rains here all year round, temperatures drop to minus 7°C in winter and reach 25°C in summer. People in Camlihemsin live from forestry, beekeeping, or herding animals on the mountainside. Zilkale is one of the most important structures in Camlihemsin district. This castle is built at an altitude of 1130 m at the edge of a cliff overlooking the Firtina Creek southeast of it. In recent years, this region has begun the attract tourists came there by car and busses.

2.2. Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometry

Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometry is a quantitative determination of elements in a sample, independent of their chemical form. It is built on the fact that elements that are irradiated with high energetic X-ray have a certain probability of emitting characteristic X-rays, the

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energies of which are unique for each element (Wobrauschek, Streli & Lindgren, 2010). In the energy dispersive (ED) systems, the emitted X-rays are detected via their energies. Resolution of EDXRF systems is dependent upon the detector, and typically ranges from 150 eV- 600 eV. The principal advantages of EDXRF systems are their simplicity, fast operation, lack of moving parts, and high source efficiency. Energy dispersive X-ray Fluorescence (EDXRF) is the best choice for the analysis of elements from Beryllium (Be) to Uranium (U) in the concentration range from 100% down to the sub-ppm-level (Report of a Workshop, 1998).

2.3. Sample Preperation

Samples were dried out in an oven $\leq 60^{\circ}$ until constant mass was obtained. To be ready for EDXRF analysis, moss samples were ground to $\leq 710 \mu$ m. Grinding for 30 s resulted in a uniform grain size of approximately 500 μ m. Two grams of the fine ground sample and 0.5 g of the boric acid (H₃BO₃) were mixed. The mixture was thoroughly ground and pressed to form a pellet of 25 mm diameter, using a hydraulic press. The prepared samples were analysed using the Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometry available at Central Research Laboratory, Recep Tayyip Erdogan University.

3. Results and Discussion

The heavy metal concentrations in various moss samples are found in Table 1. Average concentrations of heavy metals in moss samples were found ranged from 3.8-8.3% for aluminum, 0.1-0.47% for manganese, 2.3-3.8% for iron, 38.8-74.2 ppm for nickel, 92.1-495.3 ppm for copper, 187.3-334 ppm for zinc. This study has shown that *Abietinella abietina, Hypnum cupressiforme, Plagiomnium undulate, Rhytidium rugosum, and Thuidium tamariscinum* samples were used to assess the potential contamination of Al, Mn, Fe, Ni, Cu, and Zn contamination in the region and made important contributions toward the understanding of Al, Mn, Fe, Ni, Cu, and Zn baseline data can be used for identification of changes in the levels of these heavy metals in the studied area.

Sample	Moss Species	Al	Mn	Fe	Ni	Cu	Zn	
Moss1	Abietinella abietina	8.2	0.47	3.8	50.3	105.9	232.8	
Moss2	Rhytidium rugosum	4.3	0.36	2.3	45.1	92.1	283.1	
Moss3	Hypnum cupressiforme	3.8	0.10	2.9	74.2	127.9	305.0	
Moss4	Plagiomnium undulatum	5.1	0.40	3.5	38.8	495.3	187.3	
Moss5	Thuidium tamariscinum	8.3	0.17	3.3	43.0	107.7	334.0	

Table 1. The heavy metal concentrations in various moss samples collected around Camlihemsin(Al, Mn, Fe: % dw., Ni, Cu,Zn: ppm dw.)

4. Conclusion

This study has shown the concentrations of aluminum, manganese, iron, nickel, copper, and zinc levels in five different moss species (*Abietinella abietina, Hypnum cupressiforme, Plagiomnium undulate, Rhytidium rugosum, and Thuidium tamariscinum*) collected around Camlihemsin district of Rize province. These moss samples were used to assess the potential contamination of Al, Mn, Fe, Ni, Cu, and Zn in the region. As a result of heavy metals analysis performed in moss samples by using EDXRF spectrometry, it was concluded that *Hypnum cupressiforme, Abietinella abietina, Rhytidium rugosum, Plagiomnium undulatum, Thuidium tamariscinum* were utilized as biomonitors for identification of Al, Mn, Fe, Ni, Cu, and Zn levels in the studied area. This study has made important contributions toward the understanding of aluminum, manganese, iron, nickel, copper, and zinc levels

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and obtained baseline data can be used for identification of changes in the levels of heavy metals in the studied area.

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