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Assessment of Metal Levels in Biotic and Abiotic Materials from Giresun **Forests**

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The study investigated the metal levels in biotic and abiotic materials from Giresun forests. While soil and water samples were selected as abiotic materials, leaves and moss were selected as biotic materials in forest. These selected materials were sampled from six stations. All samples were analyzed three times for arsenic, iron, chromium, copper, manganese, nickel, lead and zinc by ICP-Received : 23/08/2020 OES. A logarithmic transformation was done on the data to improve normality. One way ANOVA Accepted : 21/10/2020 and Duncan's multiple range tests were performed to test the differences among metal levels of stations. The differences among metal levels in stations were statistically significant (p<0.05). Metal levels from forests were assessed for environmental health.

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Giresun Ormanlarından Biyotik ve Abiyotik Materyallerde Metal Düzeylerinin Değerlendirilmesi

MAKALE BİLGİSİ	ÖZ							
Araştırma Makalesi	Bu çalışmada Giresun ormanlarından biyotik ve abiyotik materyallerdeki metal düzeyleri araştırılmıştır. Abiyotik mateyaller olarak toprak ve su örnekleri, biyotik materyaller olarak ise yaprak ve vosun numuneleri secilmiştir. Tüm bu secilen numunelerin örneklemeleri altı iştaşvondan							
Geliş : 23/08/2020 Kabul : 21/10/2020	yapılmıştır. Örneklenen numuneler ICP-OES cihazında arsenic, krom, demir, bakır, manganez, ni kurşun ve çinko içerikleri bakımından üçer kez analiz edilmiştir. Normalliği iyileştirmek için ver logaritmik dönüşüme tabi tutulmuştur. İstasyonların metal seviyeleri arasındaki farklılıkları test etr için tek yönlü varyans analizi ve Duncan çoklu karşılaştırma testi uygulanmıştır. İstasyonlardaki m							
Anahtar Kelimeler: Giresun Ormanları Ağır Metaller Yosun Yaprak Toprak	seviyeleri arasındakı farklılıklar ıstatıstıksel olarak anlamlı bulunmuştur. Ormanlardakı metal seviyeleri çevre sağlığı açısından değerlendirilmiştir.							
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Introduction

Forest ecosystems have many benefits, only some of which are; they are a source of oxygen, a source of food and shelter for all living things, especially humans, clean the air, water and soil, make it rain, fight wind and flood. That's why forest ecosystems have become the focus of scientific studies. The vital activities of living things in forests, for example, living things in aquatic ecosystems and pollutants in forest ecosystems, have attracted the attention of scientists for hundreds of years. It is precisely for these reasons that forest ecosystems have been the subject of research by many scientists (Tyler, 1984; Rademacher, 2001; Jamnická et al., 2013; Türkmen et. al., 2018; Emin et.al., 2019; Mutlu, 2019; Utermann et al., 2019). The input of heavy metals to forest ecosystems is usually controlled by atmospheric deposition. Over large parts of northern Europe heavy metals are deposited in "wet" form with rain or snow. However, coniferous forests act as giant filters and receive more dry deposition per unit area than open land or water surfaces. When a forest ecosystem receives "additional" deposition close to an emission source, these relative differences between compartments increase. Heavy metals are primarily concentrated in mosses and lichens and to some extent in vascular plants of the forest floor. However, the highest levels are found in the organic layer (litter and humus) of the topsoil (Tyler, 1984). The aim of study was to analyze the metal levels in biotic and abiotic materials such as soil. water, leaves and moss from Giresun forests, and to assess for environmental health.

Materials and Method

Soil, water, leaf and moss samples were collected from six stations in Giresun forests, Black Sea Region, Turkey (The number of samples collected and analyzed from each stations were three). Sampling stations and coordinates were given in Tables 1. Collected soil, leaf and moss samples were dried at 105°C for 24 h. Dried samples were homogenized and stored in polyethylene bottles until analysis. All the plastic and glassware were cleaned by soaking, with contact, overnight in a 10% nitric acid solution and then rinsed with deionized water. One gram of sample was digested with 6 ml of nitric acid, 2 ml of hydrogen peroxide in a microwave digestion system. After cooling, the residue was transferred to 10 ml volumetric flasks and diluted to level with deionized water. Water samples were collected from a depth of 0.5-1.0 m in 1 liter polyethylene bottles, which had previously had been washed with detergent, deionized water, 2 M concentrated nitric acid, deionized water again and finally medium water. Then were acidified with 0.5 ml high-purity concentrated HNO3 (Merck), brought to laboratory by placing on ice. Before analysis, the samples were filtered through a 0.45 µm filter. Sample blanks were prepared in the laboratory in a similar manner to the field samples. Calibration standards were prepared from a multi-element standard (Merck, Darmstadt, Germany). A Dorm-4 certified fish protein (Ontario, Canada) was used as the calibration verification standard. All samples were analyzed three times for As, Cr, Pb, Cu, Mn, Ni, Fe, and Zn by ICP-OES. A logarithmic transformation was done on the data to improve normality. One way ANOVA and Duncan's multiple range tests were performed to test the differences among metal levels in stations. Possibilities less than 0.05 were considered statistically significant (P<0.05).

Table 1 Sampling Stations and Coordinates

Stations	Coordinates			
Cımbırtlı, Orman İşletme (CM)	40° 35' N, 38° 27' E			
Aymaç Yolu, Kümbet Altı (AY)	40° 33' N, 38° 26' E			
Uzundere (UZ)	40° 32' N, 38° 24' E			
Tamdere (TM)	40° 30' N, 38° 21' E			
Kulakkaya Altı (KL)	40° 41' N, 38° 20' E			
Boğazoba (BG)	40° 37' N, 38° 20' E			

Results and Discussion

Concentrations of eight elements in the soil, leaf and moss samples according to stations from were presented in Table 2. The differences among stations and materials were statistically significant (P<0.05). Iron had the highest level all materials and stations. Generally, heavy metal levels in soil were more than leaf and moss materials. The lowest arsenic level was 0.11 in station TM (leaf), while the highest was 8.01 in station KL (soil) as mg kg⁻¹. Minimum level for chrome was 0.04 in station UZ (leaf), while maximum was 4.36 in station AY (soil). Lead had the lowest (0.03 in leaf) and highest levels (10.7 in soil) in station KL. While copper level was minimum with 0.42 in leaf for BG station, maximum level was in station TM with 44.5 for soil. Manganese had the lowest level with 144 mg kg⁻¹ in leaf for AY station, on the other hand maximum level was 650 in soil for CM station. Nickel and iron showed the highest contents in AY station for soil samples. Zinc had the lowest level with 6.02 for leaf in station BG, while it showed the highest level with 62.1 for soil in CM station. Heavy metal levels in some mosses species collected around thermic power stations in Mugla province were reported as follows; Cd 0.09-0.61, Pb 1.40-115, Cu 11.9-35.4, Ni 11.2-285 and Zn 40.7-160 mg/kg⁻¹ (Tonguç 1998). Heavy metal concentrastions in mosses that grow in the MATV, Mexico were declered Cr 8.4-47.0, Cd <0.1-7.3, Zn 64.7-428, Pb <0.5-140 mg/kg⁻¹ (Macedo-Miranda et al., 2016). TomaĐevic et al. (In another study, heavy metal levels in some indigenous mosses from Southwest China cities were reported Cu 57.5, Zn 159, Fe 5621, Mn 137, Ni 13.8, Pb 35, Cd 1.21 and Cr 16.9 mg/kg⁻¹ (Chen et al., 2010).

Concentrations of eight elements in water samples according to stations were presented in Table 3. The differences among stations were statistically significant (P<0.05). While iron had the highest levels in CM, AY and KL stations, nickel showed the highest levels in UZ, TM and BG stations. The lowest and highest concentrations in water samples were measured as arsenic 0.77-2.64, chrome 1.17-7.55, lead 0.46-2.33, copper 2.50-36.7, manganese 21.7-35.2, zinc 3.33-16.6, nickel 14.3-84.0, iron 47.6-104.5 respectively. In a study conducted in Gölbaşi Lake, concentrations were reported as Cr 9.31, Cu 22.9, Fe 1837, Mn 73.5, Ni 13.2, Pb 5.21 and Zn 53.2 μ g/l (Türkmen and Ciminli, 2011).

Table 2 Heavy Metals in Soil, Leaf and Moss Materials

ST	MT	Heavy Metals, Mean±SE (mg kg ⁻¹)							
		As	Cr	Pb	Cu	Mn	Zn	Ni	Fe
СМ	Soil	2.95±0.14 ^e	4.20±0.12e	6.48 ± 0.94^{e}	28.9 ± 1.68^{f}	650±13.61	62.1±2.161	14.2±0.82 ^{cd}	12412 ± 3096^{bc}
	Leaf	$0.29{\pm}0.04^{abc}$	$0.15{\pm}0.02^{a}$	$0.20{\pm}0.02^{a}$	$2.19{\pm}0.18^{ab}$	148 ± 5.53^{a}	18.5±1.39 ^{bcde}	5.63 ± 0.72^{ab}	162 ± 5.17^{a}
	Moss	$0.81 \pm 0.08^{\circ}$	$0.86{\pm}0.34^{ab}$	3.47 ± 0.13^{cd}	7.96 ± 0.61^{b}	355±1.92e	25.9 ± 0.30^{e}	2.02 ± 0.64^{a}	3322±155 ^a
	Soil	2.22 ± 0.06^{d}	4.36±0.63 ^e	8.26 ± 0.15^{f}	$26.2{\pm}0.18^{de}$	408 ± 2.76^{f}	57.2 ± 0.82^{hi}	28.9 ± 0.18^{f}	16849±130°
AY	Leaf	$0.76 \pm 0.06^{\circ}$	0.15 ± 0.11^{a}	$0.90{\pm}0.03^{ab}$	1.67 ± 0.21^{ab}	$144{\pm}1.08^{a}$	13.3±0.88 ^{abcd}	$5.24{\pm}0.26^{ab}$	451±9.83ª
	Moss	$0.61{\pm}0.05^{abc}$	1.26±0.21 ^{abc}	$3.74{\pm}0.08^{d}$	$2.24{\pm}0.60^{ab}$	$304{\pm}8.89^{cde}$	23.0±4.09 ^{cde}	$1.13{\pm}0.44^{a}$	3712±100 ^a
UZ	Soil	3.11±0.28 ^e	3.42 ± 0.45^{de}	$10.4{\pm}0.25^{g}$	32.9 ± 4.88^{f}	154 ± 5.50^{a}	43.6 ± 6.26^{fg}	19.1±4.51 ^e	9372±1882 ^b
	Leaf	$0.41{\pm}0.02^{abc}$	$0.04{\pm}0.00^{a}$	$0.25{\pm}0.03^{a}$	$2.63{\pm}0.65^{ab}$	165 ± 5.40^{ab}	5.44 ± 0.32^{a}	$4.44{\pm}0.18^{ab}$	155±12.9 ^a
	Moss	0.67 ± 0.08^{bc}	1.63 ± 0.20^{bc}	4.07 ± 0.44^{d}	$1.73{\pm}0.49^{ab}$	$311{\pm}23.7^{cde}$	19.9±1.92 ^{bcde}	$2.32{\pm}0.39^{a}$	1736±203ª
ТМ	Soil	$0.13{\pm}0.04^{a}$	$0.17{\pm}0.01^{a}$	$0.28{\pm}0.02^{a}$	$44.5 {\pm} 1.01^{g}$	$324{\pm}4.80^{cde}$	48.3 ± 1.39^{gh}	20.5 ± 0.49^{e}	9936±193 ^b
	Leaf	0.11 ± 0.04^{a}	0.15±0.01a	$0.24{\pm}0.02^{a}$	$0.46{\pm}0.11^{a}$	212 ± 4.89^{b}	$4.40{\pm}0.28^{a}$	5.67±1.68 ^{ab}	126 ± 4.48^{a}
	Moss	$0.56{\pm}0.05^{abc}$	1.29±0.26 ^{abc}	$9.82{\pm}0.05^{\text{g}}$	$2.27{\pm}0.17^{ab}$	$326{\pm}6.00^{cde}$	23.2±0.91 ^{de}	2.72 ± 0.40^{ab}	2789±160 ^a
KL	Soil	8.01 ± 0.20^{f}	2.22 ± 0.14^{cd}	10.7 ± 0.27^{g}	19.7±0.85 ^{cd}	558 ± 11.9^{h}	42.3 ± 0.82^{fg}	$8.96{\pm}0.65^{bc}$	16580±249°
	Leaf	0.15 ± 0.04^{ab}	0.49 ± 0.11^{ab}	$0.03{\pm}0.02^{a}$	$2.82{\pm}0.63^{ab}$	275±5.79°	$4.35{\pm}0.57^{a}$	5.04 ± 0.53^{ab}	71.6 ± 7.78^{a}
	Moss	0.41 ± 0.04^{abc}	0.66 ± 0.13^{ab}	2.31 ± 0.06^{bc}	$0.93{\pm}0.43^{a}$	478 ± 8.13^{g}	11.7 ± 0.62^{ab}	5.23±0.78 ^{ab}	1040 ± 30.4^{a}
BG	Soil	2.01 ± 0.03^{d}	1.63 ± 0.27^{bc}	$10.1{\pm}0.08^{\text{g}}$	$17.1 \pm 0.72^{\circ}$	331 ± 1.80^{de}	37.2 ± 0.63^{f}	18.1 ± 0.16^{e}	8580±112 ^b
	Leaf	0.14 ± 0.04^{ab}	$0.33{\pm}0.10^{a}$	$0.10{\pm}0.03^{a}$	$0.42{\pm}0.08^{a}$	355±20.8e	6.02 ± 0.86^{a}	6.79 ± 0.27^{ab}	76.7±9.92ª
	Moss	0.60 ± 0.07^{abc}	0.62±0.08 ^{ab}	2.96±0.08 ^{cd}	$0.44{\pm}0.29^{a}$	302±5.34 ^{cd}	12.4±0.39 ^{abc}	3.92±0.63 ^{ab}	1442 ± 55.6^{a}

*ST: Stations, MT: Materials, SE: Standard Error, **Vertically, letters *a*, *b* and *c* show statistically significant differences among stations and materials (P<0.05).

Table 3 Heavy Metal Levels in Water Samples (Mean \pm SE)

ST	Metals (µg/l)							
	As	Cr	Pb	Cu	Mn	Zn	Ni	Fe
СМ	0.77 ± 0.00^{a}	7.55 ± 0.04^{d}	0.75 ± 0.04^{b}	$2.50{\pm}0.46^{a}$	21.7±2.03 ^a	14.3 ± 0.32^{d}	21.7±2.03ª	104.5±4.66°
AY	1.37 ± 0.05^{bc}	3.01 ± 0.06^{bc}	1.77±0.05°	37.4 ± 4.64^{b}	25.0±2.31ª	3.33±0.31ª	47.8 ± 4.05^{b}	53.5 ± 3.18^{a}
UZ	$2.63{\pm}0.04^{d}$	3.95±0.05°	1.89±0.01°	$4.33{\pm}0.32^{a}$	$34.0{\pm}2.08^{a}$	$13.4{\pm}0.07^{d}$	83.9 ± 1.74^{d}	47.6 ± 0.34^{a}
TM	1.55±0.05°	2.27 ± 0.64^{ab}	2.33 ± 0.11^{d}	36.7 ± 5.24^{b}	22.1 ± 3.78^{a}	$10.8 \pm 0.10^{\circ}$	65.7±2.14°	53.7±0.41 ^a
KL	$2.64{\pm}0.08^{d}$	1.17 ± 0.04^{a}	$0.46{\pm}0.00^{a}$	29.3 ± 8.95^{b}	25.3 ± 7.84^{a}	16.6±0.49e	14.3 ± 0.69^{a}	75.5±0.71 ^b
BG	1.23 ± 0.07^{b}	7.15 ± 0.09^{d}	$0.66{\pm}0.02^{ab}$	20.1 ± 5.77^{ab}	35.2±11.4 ^a	7.51 ± 0.18^{b}	84.0 ± 1.33^{d}	48.1 ± 0.74^{a}

*ST: Stations, SE: Standard Error, **Vertically, letters a, b and c show statistically significant differences among stations and materials (P<0.05).

In another study conducted on the Asi River, heavy metal were reported as Cd 0.99, Cr 29.2, Cu 26.6, Fe 1714, Mn 114.5, Ni 60.3, Pb 6.23 and Zn 154.4 μ g/l (Türkmen and Çalışkan, 2011). On the other hand, in a study conducted in Dil stream, concentrations were reported as Cd 8, Cr 42, Cu 37, Fe 4030, Pb 120 and Zn 700 μ g/l (Pekey et al., 2004).

Conclusion

The results of the present study supply valuable information about metal contents in soil, leaf, moss and water samples in Giresun forests from Black Sea Region, Turkey, and indirectly indicate the environmental contamination of the region. Moreover, these results can also be used to understand the chemical quality of these forests and to evaluate the possible risk associated with environmental contamination and health. Statistically significant differences were observed in the mean metal values obtained from investigated materials. According to these results it may be concluded that metal levels in these materials may not a problem on the health of these forests. However, in the future, heavy metals in the examined materials in this study can pose a possible risk for these forests, if anthropogenic practices in the surrounding the region are not controlled. So, these results should be confirmed occasionally by conducting more detailed studies in this area to update our knowledge of metal contaminants in the forests.

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