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Determination of Seasonal Variation of Air Pollution in Rize Province by Using a Type of Biomonitor Moss Hypnum

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Abstract: In this study, in order to determine the variation of seasonal air pollution levels in Rize province, Hypnum c. samples placed in the moss bags were placed into 12 stations during 4 seasons. Hypnum c. samples not placed in stations was defined as a control sample and was used to compare Cr, Fe, Ni, Cu, Pb and Al concentrations in the stations. Cr, Fe, Ni, Cu, Pb and Al concentrations of Hypnum c. samples, in control samples and the stations, were determined by using EDXRF Spectrometer. The average concentrations of Cr, Fe, Ni, Cu, Pb and Al in the stations were found as 9.5 µg.g-1, 2370 µg.g-1, 5.4 µg.g-1, 15.9 µg.g-1, 5.3 µg.g-1 and 3712 µg.g-1, respectively. These values were compared with the results obtained from other studies for determining heavy metal levels in samples of mosses, in Turkey. It was found that the average Al value in this study was higher than the average Al value obtained from national studies and average Cr, Fe, Ni, Cu and Pb values were lower than the average Cr, Fe, Ni, Cu and Pb values obtained from national studies. In addition, the average metal values obtained from this study were compared with the permissible metal limits for plants. The average Ni, Cu and Pb values were found lower than permissible values for plants and Cr, Fe and Al values were found higher than the permissible values for plants. Kruskal Wallis H test was used to determine if there was a difference in terms of the amounts of Cr, Fe, Ni, Cu, Pb and Al between the control sample and stations and between stations and seasons. According to the test results, there was no statistically significant difference in terms of Cr, Fe, Ni, Cu, Pb and Al concentrations between control samples and stations. Even though the total amount of Cr, Ni and Cu in the stations were seasonally different, these values did not make a statistically significant difference. According to the results of KWH test, total Fe amount in stations was found highest in Spring, lowest in Autumn, total Al amount was found highest in Spring, lowest in Summer, total Pb amount was found highest in Winter and lowest in Autumn and total Fe, Al and Pb levels showed statistically significant difference in terms of seasons.

Rize İlindeki Hava Kirliliğinin Mevsimsel Değişiminin Bir Biyomonitor Karayosunu Türü Olan Hypnum cupressiforme Kullanılarak Belirlenmesi

Anahtar Kelimeler
Rize,
karayosunu,
Hypnum,
kirlilik,
EDXRF

Özet: Bu çalışmada, Rize ilindeki mevsimsel hava kirliliği seviyesinin değişimini belirlemek amacıyla, 4 mevsim boyunca 12 istasyona karayosunu çantalarına yerleştirilen Hypnum c. numuneleri konuldu. İstasyonlara yerleştirilmeyen Hypnum c. örnekleri kontrol numunesi olarak tanımlandı ve istasyonlardaki Cr, Fe, Ni, Cu, Pb ve Al konsantrasyonlarının karşılaştırılması için kullanıldı. Kontrol numunesi ve istasyonlardaki Hypnum c. örneklerindeki Cr, Fe, Ni, Cu, Pb ve Al konsantrasyonları EDXRF Spektrometresi kullanılarak tespit edildi. İstasyonlardaki ortalama Cr, Fe, Ni, Cu, Pb ve Al konsantrasyonları sırasıyla 9.5 µg.g-1, 2370 µg.g-1, 5.4 µg.g-1, 15.9 µg.g-1, 5.3 µg.g-1 ve 3712 µg.g-1 olarak bulundu. Bu değerler Türkiye'de karayosunu örneklerindeki metal seviyelerinin belirlenmesi için yapılan çalışmalardan elde edilen sonuçlarla kıyaslandı. Bu çalışmadaki ortalama Al değerinin ulusal çalışmalardan elde edilen ortalama Al değerinden yüksek olduğu ve ortalama Cr, Fe, Ni, Cu ve Pb değerlerinin ulusal çalışmalardan elde edilen ortalama Cr, Fe, Ni, Cu ve Pb değerlerinden düşük olduğu bulundu. Bu çalışmadan elde edilen ortalama metal değerleri, bitkiler için izin verilen metal limitleri ile karşılaştırıldı. Ortalama Ni, Cu ve Pb değerleri bitkilerde izin verilen değerlerden düşük ve Cr, Fe ve Al değerleri bitkilerde izin verilen değerlerden yüksek bulundu. Kontrol numunesi ve istasyonlar arasında ve istasyonlardaki numunelerin mevsimler arasında Cr, Fe, Ni, Cu, Pb ve Al miktarları bakımından farklılık gösterip göstermediğini belirlemek için Kruskal Wallis H testi kullanıldı. Test sonuçlarına göre kontrol numunesi ve istasyonlardaki Cr, Fe, Ni, Cu, Pb ve Al konsantrasyonları bakımından istatistiksel olarak anlamlı bir farka rastlanmadı. İstasyonlardaki toplam Cr, Ni ve Cu miktarları mevsimsel olarak farklı değerlere sahip olsalar bile bu değerler istatistiksel olarak anlamlı bir fark oluşturmadı. KWH testi sonucuçlarına göre istasyonlardaki toplam Fe miktarı en yüksek İlkbahar, en düşük Sonbahar, toplam Al miktarı en yüksek İlkbahar en düşük Yaz, toplam Pb miktarı en yüksek Kış, en düşük Sonbahar mevsiminde bulundu ve toplam Fe, Al ve Pb miktarları mevsimler açısından istatistiki olarak anlamlı bir farklılaşma gösterdiği tespit edildi.

1.Introduction

Air pollution is an important environmental problem that concerns countries, cities and all settlement areas. Air pollutants can be spread to the air from fertilizers used in agricultural activities, wastes in industrial and production facilities, exhaust fumes in traffic, fossil fuels used in heating and through transport of chemicals in garbages by winds.

One of the most important pollutants in the air is heavy metals. Heavy metals consist of metals such as chromium (Cr), iron (Fe), nickel (Ni), copper (Cu), lead (Pb) and aluminum (Al). While some of these metals are necessary for human, animal and plant health, some of these may cause harmful effects when they exceed limit values.

In recent years, intensive attention has been paid to the problems of heavy metal pollution in the air of settlement areas. Various electronic devices have been developed to measure the amount of heavy metals in the air. Besides, biomonitor organisms such as mosses are used in biomonitoring studies because they can accumulate heavy metals and allow for seasonal measurements.

The mosses don't contain xylem and phloem tissues and accumulate water and dissolved organic matter directly in their body. For this reason, mosses are used as biomonitor organisms in environments where they develop naturally or in transplants [1,2,3,4]. In particular, in cities where the mosses are rare or not present, the moss bag technique was developed to measure air pollution [5].

Nylon mesh filters are generally used in the moss bag technique. The mosses are placed in the filters and hung on the stations where heavy metal pollution is desired to be measured.

The aim of this study is to determine seasonal variation of air pollution in Rize Province by using a type of biomonitor moss Hypnum cupressiforme.

2.Materials and Method

In this study, plenty of Hypnum cupressiforme samples were collected around Kaçkar Mountains National Parks where the population, traffic and industrialization are few. The collected Hypnum cupressiforme samples were brought to the laboratory, placed on a plastic covers, divided into equal units, cleaned of polluting materials such as sand, dust and soil. 2 grams of samples were taken from each unit and approximately 70 samples of 140 grams were prepared. Some of these samples were separated as control samples to compare the pollution of moss bags placed to the stations. The other samples were placed in the plastic boxes (moss bags) with a diameter of 15 cm and a depth of 8 cm with the help of nylon nets spaced 1 cm apart.

Prepared moss bags were placed to the stations showed in Table 1 and Figure 1, between 2015 and 2016 years, for three months and for four seasons. Station numbers S1, S2, S3, S4, S5, S6, S7, S8, S9, S10, S11 and S12 were belongs to Hopa-Sarp Black Sea Coastal Road Crossroad-1, Crossroad-2, Crossroad-3, Crossroad-4, Crossroad-5, Tevfik İleri Street-1, Tevfik

İleri Street-2, Meydan Street, Sendika Street, Adliye Street-1, Adliye Street-2, Atmeydani Street Dosma Vocational School of Technical Sciences which were in Rize city, respectively. The metal levels of the Hypnum cupressiforme samples which not placed in any stations, and separated as control samples were defined as the control value (Scontrol) and used to compare the pollution levels of moss in the moss bags at the stations.

S1, S2, S3, S4 and S5 were the stations on the Hopa-Sarp Black Sea Coastal Road Crossroad that passes through the Central district of Rize. The purpose of choosing these stations is that this crossroad is the crossing point of the vehicles coming from east, west and south to Rize province. In addition, this crossroad is on the transit route of buses and minibuses, where people living in the city use their cars a lot.

S6, S7 and S8 stations were close to shopping centers and markets. The purpose of selecting these stations is to compare whether there is a difference about air pollution between these stations where people perform some of their shopping and the stations where traffic is more intense.

S9, S10 and S11 stations were close to Rize city square, a primary school, a high school and a library. The purpose of selecting these stations is to determine whether vehicles and buildings passing around the square contribute to pollution at these stations.

The S12 station was located a few km from Rize city center. The S12 station was close to a primary school and one of the Vocational School where the Recep Tayyip Erdogan University has the highest number of students. The purpose of selecting this station is to compare the pollution caused by traffic and buildings around these schools with other stations.

In Table 1, the codes started with 1S, 2S, 3S and 4S were defined as the stations for the samples in summer, autumn, winter and spring, respectively.

Table 1. Information about stations

Stations				
1S	2S	3S	4S	Coordinates
1S1	2S1	3S1	4S1	41°01'33.9"N; 40°31'14.7"E
1S2	2S2	3S2	4S2	41°01'36.2"N; 40°31'15.7"E
1S3	2S3	3S3	4S3	41°01'38.0"N; 40°31'14.1"E
1S4	2S4	3S4	4S4	41°01'37.7"N; 40°31'07.8"E
1S5	2S5	3S5	4S5	41°01'34.5"N; 40°31'08.9"E
1S6	2S6	3S6	4S6	41°01'30.2"N; 40°31'12.0"E
1S7	2S7	3S7	4S7	41°01'28.2"N; 40°31'11.1"E
1S8	2S8	3S8	4S8	41°01'27.2"N; 40°31'10.3"E
1S9	2S9	3S9	4S9	41°01'35.5"N; 40°30'57.5"E
1S10	2S10	3S10	4S10	41°01'34.5"N; 40°30'56.1"E
1S11	2S11	3S11	4S11	41°01'34.5"N; 40°30'56.7"E
1S12	2S12	3S12	4S12	41°00'58.8"N; 40°30'38.8"E
Scont	Scont	Scont	Scont	40°57'32.6"N; 40°57'46.6"E

1S:Summer, 2S: Autumn, 3S: Winter, 4S: Spring

Figure 1. Study area and the stations

Moss bags, which were kept for three months, were taken from the stations and brought to the laboratory. They were cleaned from polluting materials and dried in an oven at 105oC for 24 hours. Branches of dried samples were picked up, weighed 10 grams, placed in the grinding mill and pulverized. 2 g of the powdered samples were mixed with 0.5 g of boric acid. In order to analyze heavy metals of the moss samples on the EDXRF spectrometer (Epsilon 5, PANanalytical), pressure was applied on the hydraulic press machine for 20 s to pellets.

The IAEA-336 Lichen reference material [6] was used to verify the measurement results of the EDXRF instrument. The data for the reference material were shown in Table 2.

Table 2. Measured and reference values of IAEA-336(µgg-1)

Metals	Measured value	Reference value
Cr	1.1	0.89-1.23
Fe	415.8	380-480
Ni	-	-
Pb	4.8	4.3-5.5
Al	597.3	570-790

3.Results

The results of the heavy metal levels (Cr, Fe, Ni, Cu, Pb and Al) in the moss bags for 4 seasons were shown in Table 3-6. Table 7 shows the minimum, maximum and average heavy metal concentrations in all samples in the stations and the control sample.

In Table 3, the highest Cr, Ni, Cu, Fe, Pb and Al concentrations in first season (summer) samples were found as 37.6 µg.g-1, 14.1 µg.g-1, 49.4 µg.g-1 (1S11), 3100 µg.g-1 (1S7), 9.8 µg.g-1 (1S10) and 5325 µg.g-1 (1S4). In the same samples, the average Cr, Fe, Ni, Cu, Pb and Al concentrations were determined as 12.4 µg.g-1, 2043 µg.g-1, 6.2 µg.g-1, 18.1 µg.g-1, 5.1 µg.g-1 and 2870 µg.g-1, respectively.

Table 3. Heavy metal concentrations in first season samples (μg.g-1)

	Cr	Fe	Ni	Cu	Pb	Al
1S1	8.3	967	3.5	7.4	4.2	1366
1S2	7.4	2213	5.8	15.4	4.5	2297
1S3	7.4	1961	5.1	15.1	5.5	2348
1S4	5.2	1152	2.6	10.6	2.2	5325
1S5	29.6	2321	10.4	33.3	6.0	4260
1S6	8.5	2018	5.2	17.7	4.6	1943
1S7	9.1	3100	4.9	16.4	4.6	3371
1S8	7.6	2808	5.2	14.1	4.0	3592
1S9	11.5	1940	6.8	13.8	4.6	1920
1S10	7.0	2106	5.2	13.8	9.8	2875
1S11	37.6	1852	14.1	49.4	6.8	2634
1S12	9.1	2088	6.0	10.1	4.1	2511
Scont	8.4	2185	5.8	14.8	5.4	3234

In Table 4, the highest Cr, Ni, Cu, Pb, Fe and Al concentrations in second season (autumn) samples were found as 11.6 μg.g-1, 6.8 μg.g-1 (2S7), 20.0 μg.g-1, 5.2 μg.g-1 (2S76), 2562 μg.g-1 (2S2) and 3568 μg.g-1 (2S1). In the same samples, the average Cr, Fe, Ni, Cu, Pb and Al concentrations were determined as 7.7 μg.g-1, 1975 μg.g-1, 4.9 μg.g-1, 15.4 μg.g-1, 4.3 μg.g-1 and 2826 μg.g-1, respectively. Metal levels at stations 2S9 and 2S10 could not be detected.
In Table 5, the highest Fe, Cu, Pb, Cr, Ni and Al concentrations in third season (winter) samples were found as 3592 μg.g-1, 22.4 μg.g-1, 8.5 μg.g-1 (3S1), 14.8 μg.g-1 (3S10), 6.7 μg.g-1 (3S9, 3S10) and 7156 μg.g-1 (3S5). In the same samples, the average Cr, Fe, Ni, Cu, Pb and Al concentrations were determined as 9.8 μg.g-1, 2582 μg.g-1, 5.1 μg.g-1, 15.5 μg.g-1, 6.6 μg.g-1 and 4304 μg.g-1. Metal levels at stations 3S8 could not be detected.

Table 4. Heavy metal concentrations in second season samples (μg.g-1)

	Cr	Fe	Ni	Cu	Pb	Al
2S1	6.6	1731	4.2	17.9	3.6	3568
2S2	6.0	2562	5.5	12.9	4.9	2800
2S3	6.4	1911	4.5	13.8	4.3	2871
2S4	6.6	2094	4.4	15.6	4.0	3266
2S5	4.4	1146	2.2	13.1	2.7	2700
2S6	10.2	2506	6.3	20.0	5.2	3013
2S7	11.6	2299	6.8	15.3	4.5	2972
2S8	9.3	1888	5.2	15.3	4.4	2143
2S9	nd	nd	nd	nd	nd	nd
2S10	nd	nd	nd	nd	nd	nd
2S11	7.2	1618	5.1	18.0	4.9	1700
2S12	8.8	2003	5.2	12.1	4.5	3227
Scont	8.4	2185	5.8	14.8	5.4	3234

Table 5. Heavy metal concentrations in third season samples (μg.g-1)

	Cr	Fe	Ni	Cu	Pb	Al
3S1	12.4	3592	5.2	22.4	8.5	6344
3S2	10.5	2656	5.4	17.7	8.4	4586
3S3	8.1	2227	5.0	14.4	7.4	3840
3S4	10.5	2877	6.1	21.0	8.0	4695
3S5	8.4	3224	3.7	16.5	6.2	7156
3S6	6.6	1398	3.7	12.8	2.7	1492
3S7	6.6	1554	4.3	10.2	8.2	2024
3S8	nd	nd	nd	nd	nd	nd
3S9	12.8	2987	6.7	12	6.2	5660
3S10	14.8	3014	6.7	17	5.3	4694
3S11	8.6	2563	5.1	16	6.2	3380
3S12	9.0	2312	4.2	11	5.1	3480
Scont	8.4	2185	5.8	14.8	5.4	3234

In Table 5, the highest Fe, Cu, Pb, Cr, Ni and Al concentrations in third season (winter) samples were found as 3592 μg.g-1, 22.4 μg.g-1, 8.5 μg.g-1 (3S1), 14.8 μg.g-1 (3S10), 6.7 μg.g-1 (3S9, 3S10) and 7156 μg.g-1 (3S5). In the same samples, the average Cr, Fe, Ni, Cu, Pb and Al concentrations were determined as 9.8 μg.g-1, 2582 μg.g-1, 5.1 μg.g-1, 15.5 μg.g-1, 6.6 μg.g-1 and 4304 μg.g-1. Metal levels at stations 3S8 could not be detected.

Table 6. Heavy metal concentrations in fourth season samples (μg.g-1)

	Cr	Fe	Ni	Cu	Pb	Al
4S1	8.4	2932	5.6	18.8	5.2	4080
4S2	6.7	2453	10.7	14.1	5.4	3765
4S3	6.4	3168	3.6	17.6	4.6	5932
4S4	7.8	3172	4.9	18.4	5.5	5185
4S5	5.7	3781	7.2	24.0	10.2	6077
4S6	5.9	3240	3.6	13.8	5.6	5420
4S7	8.4	3338	4.1	9.6	2.7	5564
4S8	10.5	2276	4.9	15.9	6.9	4576
4S9	7.8	1535	4.3	9.2	3.8	2775
4S10	6.5	2709	3.6	9.6	4.6	4319
4S11	7.0	2210	5.2	12.1	4.8	3846
4S12	16	3784	7.6	11.9	5.5	6671
Scont	8.4	2185	5.8	14.8	5.4	3234

In Table 6, the highest Cr, Fe, Al, Cu, Pb and Ni concentrations in fourth season (spring) samples were found as 16.0 μg.g-1, 3784 μg.g-1, 6671 μg.g-1 (4S12), 24.0 μg.g-1, 10.2 μg.g-1 (4S5) and 10.7 μg.g-1 (4S2). In the same samples, the average Cr, Fe, Ni, Cu, Pb and Al concentrations were determined as 8.1 μg.g-1, 2883 μg.g-1, 5.4 μg.g-1, 14.6 μg.g-1, 5.4 μg.g-1 and 4850 μg.g-1, respectively.

Table 7. Minimum, maximum and average heavy metal concentrations in all samples (μg.g-1)

	Cr	Fe	Ni	Cu	Pb	Al
min	4.4	967	2.2	7.4	2.2	1366
max	37.6	3784	14.1	49.4	10.2	7156
average	9.5	2370	5.4	15.9	5.3	3712
Scont	8.4	2185	5.8	14.8	5.4	3234

4. Discussion

In this study that aims to determine the seasonal variation of air pollution in Rize province by using Hypnum cupressiforme which is a type of biomonitor moss, moss bags were placed to the 12 stations in the city center of Rize for 3 months during 4 seasons and heavy metal levels were determined. The average values obtained from this study were compared with the heavy metal levels of control sample and the heavy metal levels of the other studies about heavy metal levels detected in moss samples in Turkey showed in Table 8.

Table 8. Studies about heavy metal levels in moss samples in Turkey (µg.g-1)

	Cr	Fe	Ni	Cu	Pb	Al
Çatalagzi [7]	4.81	2530	6.6	3.3	21.1	-
Düzce [8]	2.67	2003	2.1	9.2	27.6	-
Eregli [9]	5.1	3360	5.0	3.8	24.4	-
İstanbul [10]	14.6	5.93	12.1	24.8	50.1	14.6
Blacksea [11]	60.6	-	18.8	293	39.8	-
Sakarya [12]	9.7	2917	10.9	25.4	14.7	4194
Trakya [13]	21.7	6000	-	-	-	-
Zonguldak [14]	4.3	3771	6.6	13.6	15.3	-
İstanbul [15]	11.2	3100	8.0	27.2	-	-
average	14.9	2960	8.7	50.0	27.5	2104
Present study	9.5	2370	5.4	15.9	5.3	3712

When taking into account Table 7 and Table 8 Cr concentration was found as 8.4 µg.g-1 in the control sample and the average Cr concentration in the stations was detected as 9.5 µg.g-1. This average Cr value in this study was above the recommended Cr concentration (2 µg.g-1) for the plants [16] and was below the average Cr concentration value obtained from other studies in Turkey (14.9 µg.g-1).

The Fe concentration was found as 2185 µg.g-1 in the control sample. The average Fe concentration in the stations was detected as 2370 µg.g-1. The average Fe level in this study was found above the recommended limit (200 µg.g-1) for the plants [17,18] and was below the average Fe concentration value obtained from studies in Turkey (2960 µg.g-1).

The recommended amount of Ni for plants is given as 10 µg.g-1 [19,20]. In this study, the average Ni value was found as 5.4 µg.g-1 in stations and 5.8 µg.g-1 in control sample. These values are both below the recommended Ni concentration for the plants and the average Ni concentration is obtained from Turkey (8.7 µg.g-1).

In this study, Cu concentration was found in the range of 7.4-49.4 µg.g-1 in stations, and 4.8 µg.g-1 was detected in the control sample. While recommended Cu value in plants is given as 30 µg.g-1 [19,20], in this study, the average Cu value was obtained as 15.9 µg.g-1. This value is both below the recommended Cu concentration for the plants and the average Cu concentration of studies in Table 8 (50 µg.g-1).

In this study, Pb concentration was found as 5.4 µg.g-1 in the control sample and the highest Pb concentration in the stations was detected as 10.2 µg.g-1. The permissible limit of Pb in plants is given as 10 µg.g-1 [16,21]. In this study, the average Pb value was found as 5.3 µg.g-1. This value is both below the recommended concentration for the plants and the average Pb concentration in Table 8 (27.5 µg.g-1).

In this study, Al value was obtained as 3284 µg.g-1 in control sample and average Al value found as 3715 µg.g-1 in stations. This values is higher than the permissible level for Al in plants (160 µg.g-1) [22,23]. In addition, Al value in present study is above than the average value of the Al concentration obtained from the study about moss in Turkey (2104 µg.g-1).

Kruskal Wallis H test was performed to determine whether there was a significant difference about Cr, Fe, Ni, Cu, Pb and Al metals in the stations according to the control sample and performed to determine whether the total Cr, Fe, Ni, Cu, Pb and Al concentrations in the stations had a significant difference in terms of four seasons. The data obtained from the results of the Kruskal Wallis H tests were shown in Table 9 and Table 10. In Table 9; S1, S2, S3, S4, S5 stations are the first group, S6, S7, S8 stations are the second group, S9, S10, S11 stations are the third group, S12 station is the fourth group and Scontrol was defined as the fifth group.

When Table 9 is examined, according to Kruskal Wallis H test results, in the stations Cr amount is the highest in 3rd group (X=34.38) and the lowest in 5th group (X=18.48), Fe amount is the highest in 4th group (X=25.25) and the lowest in 5th group (X=19.00), Ni amount is the highest in 3rd group (X=33.50) and the lowest in 2nd group (X=20.32), Cu amount is the highest in 3rd group (X=28.38) and the lowest in 4th group (X=8.38), Pb amount is the highest in 3rd group (X=28.50) and the lowest in 4th group (X=19.25) and Al amount is the highest in 1st group (X=27.05) and the lowest in 5th group (X=19.55). The difference of Cr, Fe, Ni, Cu, Pb and Al levels between the control sample and other groups do not have a statistically significant difference (p>.05).

In Table 10, according to Kruskal Wallis H test results, in the spring season, the total Cr, Ni and Cu levels of the stations are at the lowest level (X=18.25, 21.29, 20.71) and the total Cr, Ni and Cu levels of the stations in summer season are the highest level (X=29.18, 26.29, 24.70). The Table 10 shows that the total amount of Cr, Ni and Cu in the stations increased from spring to summer and from autumn to winter and decreased from winter to spring. In terms of Cr, Ni and Cu levels in the stations, there is no statistically significant difference between spring and summer seasons (p>.05).

According to Table 10, obtained Kruskal Wallis H test results show that the amount of Fe in the stations is significantly difference in terms of seasons (p<.01). The total Fe amount of the stations in the spring season is at the highest level compared to other seasons (X=32.17). In spite of this, Fe amount of the stations is the lowest level in the autumn compared to other seasons (X=14.70). In terms of spring and autumn seasons, the total amount of Fe in the stations showed statistically significant difference. This finding shows that the total amount of Fe in the stations decreased significantly from spring to summer and from summer to autumn, and increased from autumn to winter and spring.

Table 9. Kruskal Wallis H test results of Cr, Fe, Ni, Cu, Pb and Al values in the stations according to the control sample

Metal	G	N	X	sd	χ2	p	dif.
Cr	G1	20	25.09	4	6.39	.17	-
	G2	11	25.50				
	G3	10	34.38				
	G4	4	27.25				
	G5	1	18.48				
Fe	G1	20	24.45	4	.77	.94	-
	G2	11	24.18				
	G3	10	20.60				
	G4	4	25.25				
	G5	1	19.00				
Ni	G1	20	21.73	4	3.00	.55	-
	G2	11	20.32				
	G3	10	33.50				
	G4	4	27.50				
	G5	1	28.63				
Cu	G1	20	23.00	4	8.15	.08	-
	G2	11	22.55				
	G3	10	28.38				
	G4	4	8.38				
	G5	1	20.90				
Pb	G1	20	24.60	4	2.17	.70	-
	G2	11	19.50				
	G3	10	28.50				
	G4	4	19.25				
	G5	1	26.75				
Al	G1	20	27.05	4	2.87	.57	-
	G2	11	20.00				
	G3	10	20.70				
	G4	4	24.50				
	G5	1	19.55				

p>.05; 1. Group: Crossroad-1, Crossroad-2, Crossroad-3, Crossroad-4, Crossroad-5; 2. Group: Tevfik İleri Street -1, Tevfik İleri Street -2, Meydan Street; 3. Group: Sendika Street., Adliye Street.-1, Street-2; 4. Group: DVSTC; 5. Group: Control Sample (Scontrol); G: Group no, N: number of samples, X: mean ranks, sd: standard deviation, dif: difference

In Table 10, according to the results of Kruskal Wallis H test, the amount of Pb in stations shows a significant difference in terms of seasons (p<.01). The total Pb amount of the stations in the winter is highest compared to other seasons (X=33.09). However, in the autumn season, the Pb amount of the stations is the lowest level in comparison to other seasons (X=13.70). In terms of winter and autumn seasons, the total amount of Pb in the stations has a statistically significant difference. In addition, between the summer and winter seasons Pb amount is significantly different, also. These results indicate that the total Pb amount decreased from winter to autumn, from spring to summer and from summer to autumn and increased in winter season.

As Table 10 is examined, according to Kruskal Wallis H test results, Al level in stations shows a significant difference in terms of seasons (p<.01). When compared to other seasons, the total amount of Al of the stations, is highest level in the spring (X=33.25) and is the lowest level in summer season (X=14.75). In terms of spring and autumn seasons, the total amount of Al in the stations showed statistically significant differences. In addition, the amount of Al is significantly different between spring and summer seasons. The results in Table 10 indicate that the total amount of Al decreased from spring to summer and from summer to autumn and the total amount of Al in the stations increased from autumn to winter.

Table 10. Kruskal Wallis H test results of total Cr, Fe, Ni, Cu, Pb and Al values of the stations in terms of seasons

Metal	G	N	X	sd	χ2	p	dif.
Cr	Summer	12	29.18	3	5.79	.122	-
	Autumn	10	18.45				
	Winter	11	25.88				
	Spring	12	18.25				
Fe	Summer	12	16.75	3	13.7	.003 **	1S-4S, 2S-4S
	Autumn	10	14.70				
	Winter	11	27.36				
	Spring	12	32.17				
Ni	Summer	12	26.29	3	1.06	.786	-
	Autumn	10	22.00				
	Winter	11	22.18				
	Spring	12	21.29				
Cu	Summer	12	24.70	3	.67	.880	-
	Autumn	10	22.58				
	Winter	11	24.41				
	Spring	12	20.71				
Pb	Summer	12	19.96	3	12.3	.006 **	2S-3S, 1S-3S
	Autumn	10	13.70				
	Winter	11	33.09				
	Spring	12	24.54				
Al	Summer	12	14.75	3	17.5	.001 **	1S-4S, 2S-4S
	Autumn	10	14.90				
	Winter	11	28.18				
	Spring	12	33.25				

p>.05, **p<.01, **p<.01, 1S:Summer, 2S: Autumn, 3S: Winter, 4S: Spring, N: number of samples, X: mean ranks, sd: standard deviation, dif: difference

5. Conclusions

In this study, Cr, Fe, Ni, Cu, Pb and Al concentration in the control sample were found as 8.4 µg.g-1, 2185 µg.g-1, 5.8 µg.g-1, 14.8 µg.g-1, 5.44 µg.g-1 and 3234 µg.g-1, respectively. The average Cr, Fe, Ni, Cu, Pb and Al concentrations in the stations were found to be 9.5 µg.g-1, 2370 µg.g-1, 5.4 µg.g-1, 15.9 µg.g-1, 5.3 µg.g-1 and 3712 µg.g-1, respectively. The average Cr, Fe and Al values in the stations are higher than the permissible values for plants. Ni, Cu and Pb values are lower than permissible values for plants. Except Al, the detected average Cr, Fe, Ni, Cu and Pb concentrations in stations are found lower than the average value obtained from some studies that determine the levels of heavy metal in moss samples in Turkey.

In this study, Kruskal Wallis H test was used to determine whether there was a significant difference for Cr ,Fe, Ni, Cu, Pb and Al levels between the stations and the control sample. According to the test results it was no found statistically significant difference in terms of Cr, Fe, Ni, Cu, Pb and Al amounts between the stations and the control sample.

Kruskal Wallis H test was used to determine if there was a statistically significant difference in terms of total Cr, Fe, Ni, Cu, Pb and Al in the stations, also. According to the test results, it was determined that the total amount of Cr, Ni and Cu in the stations in terms of seasons did not have a statistically significant difference even if they had different values.

The highest total amount of Fe and Al in the stations was found in the spring season and the highest total amount of Pb was found in the winter season. The lowest total amount of Fe and Pb in the stations was determined in autumn and the lowest total amount of Al was determined in summer season. The increased of total Fe and Al in the spring season and the increased of total Pb in the winter season, showed a statistically significant difference, according to the results of Kruskal Wallis H test.

The data obtained from this study is comparable with the data obtained from other studies. With the data of this study, a basic data were formed for the analyzes of the same or different stations in the following years. As a result of this data, it was concluded that Hypnum cupressiforme is a useful biomonitor organism that can be used in heavy metal accumulation and determination studies.

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