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Records of metals in bryophytes emitted from ash clouds of thermal power plants: A case study of Orhaneli, Bursa, Türkiye

Termik santrallerin kül bulutlarından salınan metallerin bryofitlerdeki kayıtları: Orhaneli, Bursa, Türkiye Örneği

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A B S T R A C T / Ö Z

Most of the world's energy production still comes from fossil fuels such as coal and lignite. Thermal power plants that produce energy using these resources have the potential to cause serious damage to the environment due to the heavy metals and other pollutants they release into the atmosphere. This study investigates the accumulation of heavy metals in fly ash clouds from a thermal power plant in Orhaneli, Bursa in the tissues of *Hypnum cupressiforme Hedw. and Homalothecium sericeum (Hedw.) Schimp.* Within the scope of the study, ICP-OES analyses were performed on moss and rock samples taken from five different sampling sites around the thermal power plant. Bioconcentration Factor (BCF) was calculated based on Pb, Cr, Cd, Ni, Ni, Co, Cu, Hg and As concentrations. The results showed that there was no accumulation of Hg and As, bioaccumulation for Cd, Fe and Cu was observed in only one station, but the average BCF values for these metals were below 1. In contrast, the BCF levels of Cr and Pb were found to be quite high, with mean values of 60.26 and 1.54, respectively. These results suggest that mosses can be used as effective biological indicators for heavy metal accumulation. It is also emphasized that regular monitoring of air quality and mitigation of environmental risks are vital for the health of the inhabitants of the region.

Dünya enerji üretiminin hala büyük bir kısmı kömür ve linyit gibi fosil yakıtlardan sağlanmaktadır. Bu kaynakları kullanarak enerji üreten termik santraller, atmosfere saldıkları ağır metaller ve diğer kirleticiler nedeniyle çevreye ciddi zarar verme potansiyeline sahiptir. Bu çalışma, Bursa Orhaneli'ndeki bir termik santralden kaynaklanan uçucu kül bulutlarındaki ağır metallerin Hypnum cupressiforme Hedw. ve Homalothecium sericeum (Hedw.) Schimp. türü karayosunlarının dokularında birikimini incelemektedir. Araştırma kapsamında, termik santral çevresinde belirlenen beş farklı örnekleme sahasından alınan karayosunu ve kaya örnekleri üzerinde ICP-OES analizleri gerçekleştirilmiştir. Pb, Cr, Cd, Ni, Co, Cu, Hg ve As konsantrasyonlarına dayanarak Biyokonsantrasyon Faktörü (BCF) hesaplanmıştır. Bulgular, Hg ve As birikiminin olmadığını, Cd, Fe ve Cu için biyoakümülasyonun yalnızca bir istasyonda gözlemlendiğini, ancak bu metallerin ortalama BCF değerlerinin 1'in altında kaldığını göstermiştir. Buna karşın, Cr ve Pb'nin BCF seviyeleri oldukça yüksek bulunmuş ve ortalama değerleri sırasıyla 60,26 ve 1,54 olarak tespit edilmiştir. Bu sonuçlar, karayosunlarının ağır metal birikimi için etkili biyolojik indikatörler olarak kullanılabileceğini göstermektedir. Ayrıca, bölgede yaşayanların sağlığı için hava kalitesinin düzenli izlenmesinin ve çevresel risklerin azaltılmasının hayati önem taşıdığı vurgulanmaktadır.

1. Introduction

Türkiye meets a significant portion of its energy needs from lignite-based thermal power plants. According to the 2022 data from the Turkish Statistical Institute (TUIK, 2024), the distribution of electricity production in Türkiye by energy sources is as follows: coal (34.6%), natural gas (22.2%), hydroelectric (20.6%), wind (10.8%), solar (4.7%), geothermal energy (3.3%), and other sources (3.7%). Additionally, thermal power plants consume 61.9% of the hard coal and 84.2% of the lignite used in Türkiye (TUIK, 2022).

Despite their role in energy production, thermal power plants are major sources of environmental pollution. They are one of the three main contributors to air pollution, alongside residential and vehicular emissions (Elkoca, 2003). Fly and bottom ashes from lignite and coal combustion contain toxic elements like Pb, Zn, Cd, Ni and Co, posing disposal challenges due to heavy metal residues (Baba & Kaya, 2004). Ineffective filtration and leakage can lead to increased environmental pollution (Baba, 2000; Ölgen & Gür, 2012). Predicting and controlling environmental impacts are further complicated by changing dispersion patterns influenced by wind and other meteorological factors.

Mosses accumulate most heavy metals in their tissues and have several advantages as indicator organisms. They have a wide geographical distribution and thrive in various natural habitats, including industrial and urban centers, though in lesser abundance in cleaner regions. Due to the absence of a cuticle and epidermis, their cell walls easily absorb metal ions. Lacking organs for mineral uptake from the substrate, mosses accumulate minerals through precipitation. The poor transport of minerals between organ structures is due to the lack of vascular tissue, and metal accumulation and ion exchange in mosses occur passively. Mosses demonstrate the accumulation of most metals as a function of atmospheric deposition amounts (Yayıntas & Yayıntas, 2001).

Biomonitoring, which uses biological organisms to evaluate environmental quality, is a widely used method in environmental monitoring (Tuncel & Yenisoy-Karataş, 2003). Bryophytes are particularly effective for this purpose due to their cost-effectiveness, ease of sampling, and widespread distribution (Grodzińska & Szarek-Łukaszewska, 2001; Wolterbeek, 2002). They accumulate pollutants passively, lacking a root system and a protective cortex layer (Berg & Steinnes, 1997; Rühling & Tyler, 1973). Studies have used bryophytes as bioindicators to measure metal concentrations and compare uptake values among different species (Bačeva et al., 2012; Berg et al., 1995; Macedo-Miranda et al., 2016; Maxhuni et al., 2016; Olajire, 1998; Türkan et al., 1995; Zechmeister, 1998).

Bryophytes obtain nutrients from rain and sediments, absorbing metals from the substrate (Sabovljević et al., 2020). Many studies have documented heavy metal transfer from substrates to moss (Jiang et al., 2018; Macedo-Miranda et al., 2016; Świsłowski, 2024; Varela et al., 2015). In Türkiye, bryophytes have been used in biomonitoring studies around industrial areas, including thermal power plants, iron and steel facilities, mining areas, and roadsides with heavy traffic (Batan et al., 2021; Doğrul, 2007; Haktanır et al., 2010; Ören et al., 2021; Tonguç, 1998; Uğuz, 2007; Uyar et al., 2005). This study focuses on the Orhaneli Thermal Power Plant (OTPP) in Bursa province, with an installed capacity of 210 MW. Previous research has shown significant respiratory function decline in individuals living near the OTPP (Pala et al., 2012). However, biomonitoring studies around OTPP are limited, with only one study using lichens (Gür, 2006). This study aims to determine heavy metal concentrations in bryophyte tissues around OTPP.

2. Materials and Methods

2.1. Study Area

Orhaneli is a district in the Bursa province, located in the Orhaneli Stream valley, east of Bursa city center in the Marmara Region of Turkey. The Orhaneli Thermal Power Plant (OTPP), subject of this research, is 47 km from Bursa and 17 km from Orhaneli. The area features undulating plateaus at elevations between 450-1000 meters, predominantly used for agriculture, including sunflower, wheat, and fruit cultivation (Erginal et al., 2008).

The study area is under the influence of Mediterranean climate represented by the letters Csa according to Köppen-Geiger climate classification. The average annual temperature is 12.8C and the total annual precipitation is 674 mm (Taşoğlu et al., 2024). According to the global wind atlas (Atlas, 2021), the dominant wind direction in the region is in the NW-SE direction (Fig.1). The region's main lithology comprises ophiolites (Sarıfakıoğlu et al., 2009; Uysal et al., 2015).

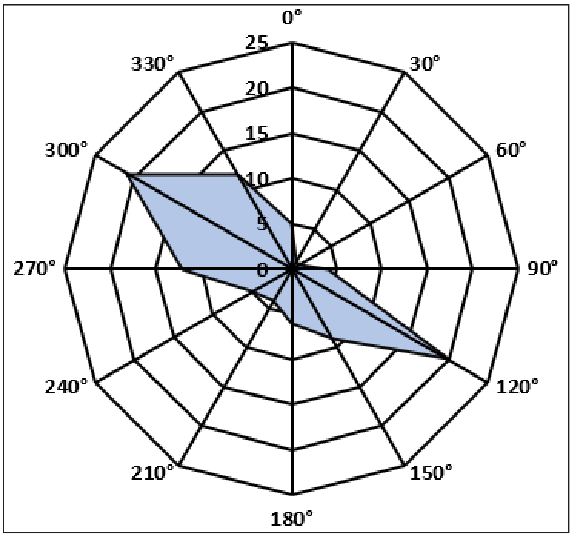

Figure 1. Annual average wind frequency (%) in the study area

2.2. Sampling and Analysis

The selection of bioindicator species in heavy metal research is critical due to their absorption properties (Lippo et al., 1995). To ensure consistency in absorption abilities and avoid data discrepancies, common pleurocarpic moss species *(Hypnum cupressiforme and Homalothecium sericeum)* were selected for this study. Moss and rock samples were collected from five different stations around the OTPP on 20 November 2022 (Figure 1). A total of 10 samples, one moss and one rock, were collec-

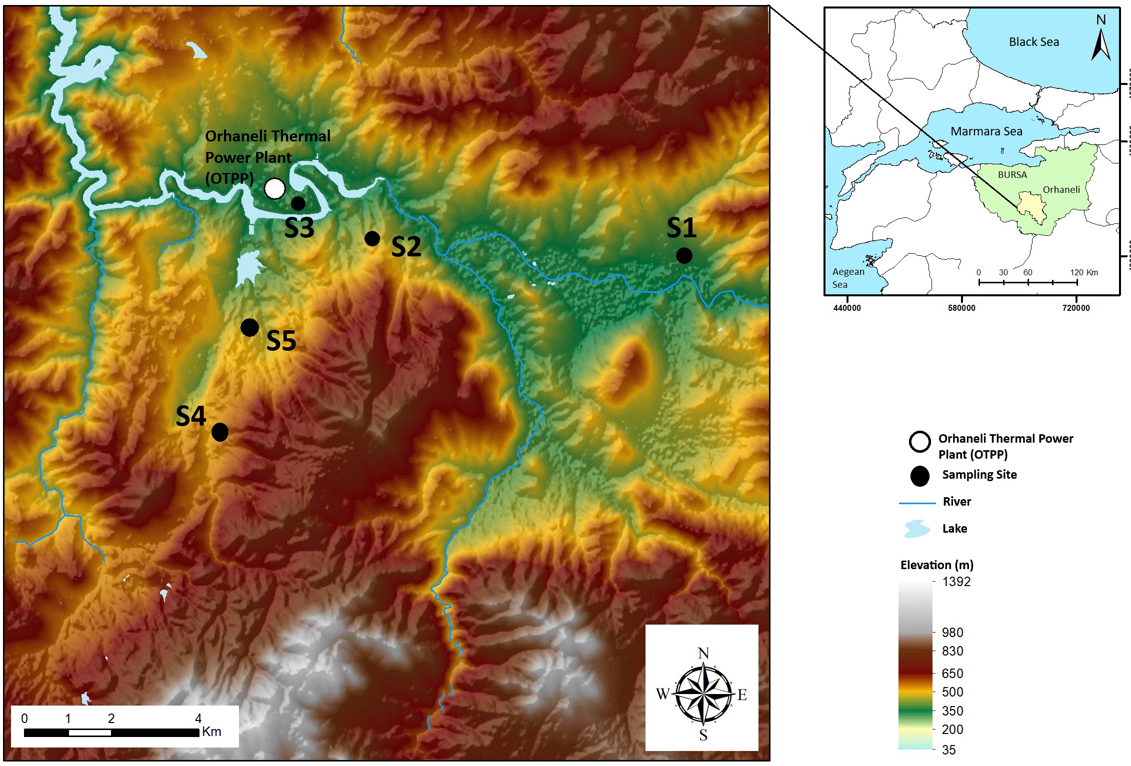

Figure 2. Location map of the study area (a) and sampling sites (S1-S5) on the digital elevation model (b).

ted from each station. The distribution of moss species according to the stations is as follows: *Homalothecium sericeum* was collected from S1 and S2, *Hypnum cupressiforme* from S3, S4 and S5.

Specimens were identified primarily using related literature (Kürschner & Frey, 2020; Smith, 2004) by Özlem Tonguc Yayıntas. The bryophyte species were stored in the geography laboratory at the Faculty of Education, Çanakkale 18 Mart University. Metal analyses of the dried samples were conducted using ICP-OES to determine the concentrations of Pb, Cr, Cd, Ni, Co, Fe, Cu, Hg, and As. Elemental analyses were performed at the Scientific and Technological Application and Research Center of Burdur Mehmet Akif Ersoy University using a Perkin Elmer ICP-OES Optima 8000, Milestone Stard-D device. Sample preparation involved using 0.5 g of sample with 5 mL of 65% HNO_3 and 3 mL of 40% HF, following the microwave program milestone application note HPR-EN-22. The program included heating to 100 °C over 15 minutes, maintaining this temperature for 15 minutes, followed by the drying process.

To accurately determine the source of heavy metals accumulated in the bryophytes, whether atmospheric or substrate-based, it is essential to calculate the background value. Elemental analysis was therefore conducted on the rocks to which the bryophytes adhere. This is particularly important because the Orhaneli basin is rich in chrome ores and lignite mines (Borchert & Uzkut, 1967; Sarıfakıoğlu et al., 2009; Uysal et al., 2015).

The relationship between the elemental components of rocks, which influence the nutrient uptake process of bryophytes, and the elemental components of bryophytes was determined through bioconcentration factor (BCF) calculations. BCF expresses the ratio of metal concentration in the plant to that in the sediment. A high BCF value indicates the plant's ability to concentrate metals in its tissues (Phetsombat et al., 2006; Zhang et al., 2009). A BCF value of 1 confirms the bioaccumulation of heavy metals in the sample (Cadar et al., 2019; Sekabira et al., 2011). The BCF is calculated using the following formula:

(heavy metal in moss)/(heavy metal in rock)

Bioconcentration values were evaluated against the limit values specified by USEPA and NIOSH (Table 1).

3. Results and Discussion

3.1. Metals in the Host Rock and Moss Samples

Table 2 shows that rocks generally exhibit high iron content. Fe is the predominant metal in all samples, with a maximum concentration reaching 1.4%. Cr has a maximum concentration of 40 ppm across all samples, while Cd reaches up to 2.5 ppm. Cu was undetected in one sample and ranged from 1 to 4.8 ppm in others.

Table 1. Maximum acceptable heavy metal limits in air based on USEPA (2024, 2006 & 1987) and NIOSH (2007).

Metal	Limit Value (ug/m3)	Reference
Cr	0.018	USEPA*, 2024
Cu	100	NIOSH**, 2007
Fe	10.000	NIOSH, 2007
Pb	0.5	USEPA, 2006
Cd	0.006	USEPA***, 1987

*USEPA: U.S. Environmental Protection Agency **NIOSH: National Institute for Occupational Safety & Health
***Concentration for the situation where 1 in 100,000 people are at risk of cancer

Table 2. Concentrations of heavy metals in rock samples (mg/kg).

Sampling Site	Pb	Cr	Cd	Fe	Cu
S1	-	40.038	2.588	13.101.923	3.087
S2	0.664	0.192	0.119	22.13	1.440
S3	-	3.124	2.313	14.409.259	3.831
S4	-	0.137	0.321	7.463	4.846
S5	-	2.27	2.413	2.409.615	-

(-) not detected

Table 3. Concentrations of heavy metals in Moss samples (mg/kg)

Sampling Site	Pb	Cr	Cd	Ni	Co	Fe	Cu	Hg	As
S1 (Hs)	1.458	19.396	-	-	-	-	-	-	-
S2 (Hs)	0.426	26.140	0.040	-	-	30.304	2.098	-	-
S3 (Hc)	3.823	28.168	-	-	-	1488	0.242	-	-
S4 (Hc)	-	19.919	1.019	-	-	-	-	-	-
S5 (Hc)	1.812	23.428	-	-	-	1615.686	-	-	-

Although the fly ashes of a thermal power plant was found to be enriched in Ni as well as Hg and As (Esenlik et al., 2006), and soils have high amounts of As, Cd, Co and Ni in excess of the limit values due to mining activities (Menteşe & Böbrek, 2020). When Table 3, which presents the ICP-OES results of our moss samples, is examined, none of the moss samples analyzed contained detectable levels of Ni, Co, Hg, or As, in contrast to previous studies conducted around termal power plants elsewhere (C´ujic´ et al., 2014; Sabovljevic et al., 2007; Uyar et al., 2007). Cd concentrations in two samples remained below 2.1 ppm. Cr was the only metal detected in all samples, with concentrations ranging from 19 to 28 ppm (mean: 23.4 ppm). Pb, absent in one sample, ranged from 0.4 ppm to 3.8 ppm in the remaining four samples. Fe was detected in three samples, with a maximum concentration of 0.16%.

3.1. Bioconcentration Factor (BCF) Calculations

ICP-OES data revealed a significant difference between metal distributions obtained from bedrock samples and those obtained directly from bryophyte. BCF values indicate metal accumulation of more or less anthropogenic origin in all samples. The most striking point here is the enrichment in Pb values in bryophytes, except for one example. As can be seen in Table 4, values greater than 1 in dark color indicate toxic metal enrichment. As a result of BCF values, the elements are in descending order of; Cr (145.39) > Pb (3.823) > Cd (3.17) > Cu (1.45) > Fe (1.36).

When Pb concentrations are examined, it is seen that the limit values accepted by USEPA (2006) are exceeded in S1, S3 and S5. Station 2 gives a result close to the limit values. It was found to be approximately 8 times higher than the threshold value specified in USEPA (2006) in the sample 1 km away from the thermal power plant.

Considering USEPA (2024), Cr also exceeded the specified limit values at all stations. A positive relationship was determined between the distance of the stations to the thermal power plant and the chromium concentration obtained from bryophyte. BCF calculation displayed that all stations except S1 station were exposed to high levels of atmospheric Cr accumulation. Cr concentrations at stations S2 and S4 were found to be significantly above the threshold value specified in USEPA (2024) excessively. While it was found very close to the acceptable value at station no. S1, the values were also found to be very high at stations no. S3 and S5. Except for one sample (S1), the values found in all stations exceed the values of Cr in the bedrock beneath the moss, indicating that Cr is of anthropogenic origin, probably originating from the power plant.

Cd accumulation was determined in two of the samples. Only in S4, 3 times more Cd accumulation than that determined in the bedrock was determined in the bryophyte. According to USEPA (1987), this value is extremely high. The iron distribution in the studied samples presents interesting differences. Despite the Fe content determined in all rock samples, Fe was not determined in 2 bryophyte samples, and an approximately 1.5-fold increase in iron was determined in only one station (S2). The same increase is also valid for Cu at a similar rate and at the same station considering NIOSH (2007).

When comparing the BCF values for Pb and Cr in this study with those from previous research on thermal power plants in Turkey, Cr was found to be significantly higher than in other plants, whereas Pb was lower (Fig. 2).

This discrepancy in Cr levels may be attributed to the rich chrome ores reported near the power plant; however, the ICP-OES technique revealed that the accumulation in some stations had an atmospheric origin (Table 3). The current study reports Cr and Pb values of 3.823 and 28.168, respectively. In contrast, Tonguç (1998) reported higher values for both Cr (51.9) and Pb (12.04). Ugur et al. (2004) also observed elevated Pb values

Table 4. Bioconcentration values obtained from multi-element analysis results obtained from moss and the bedrock samples.

Sampling Site	Pb_{Bc}	Cr_{Bc}	Cd_{Bc}	Fe_{Bc}	Cu_{Bc}
S1	**1,458**	0,48	-	-	-
S2	0,64	**136,145**	0,33	**1,36**	**1,45**
S3	**3,823**	**9,01**	-	0.10	0,29
S4	-	**145,39**	**3,17**	--	-
S5	**1,812**	**10,31**	-	0,67	-
Average	**1.54**	**60.26**	0.7	0.42	0.34

*Bold and higher than 1 numbers show anthropogenic pollution

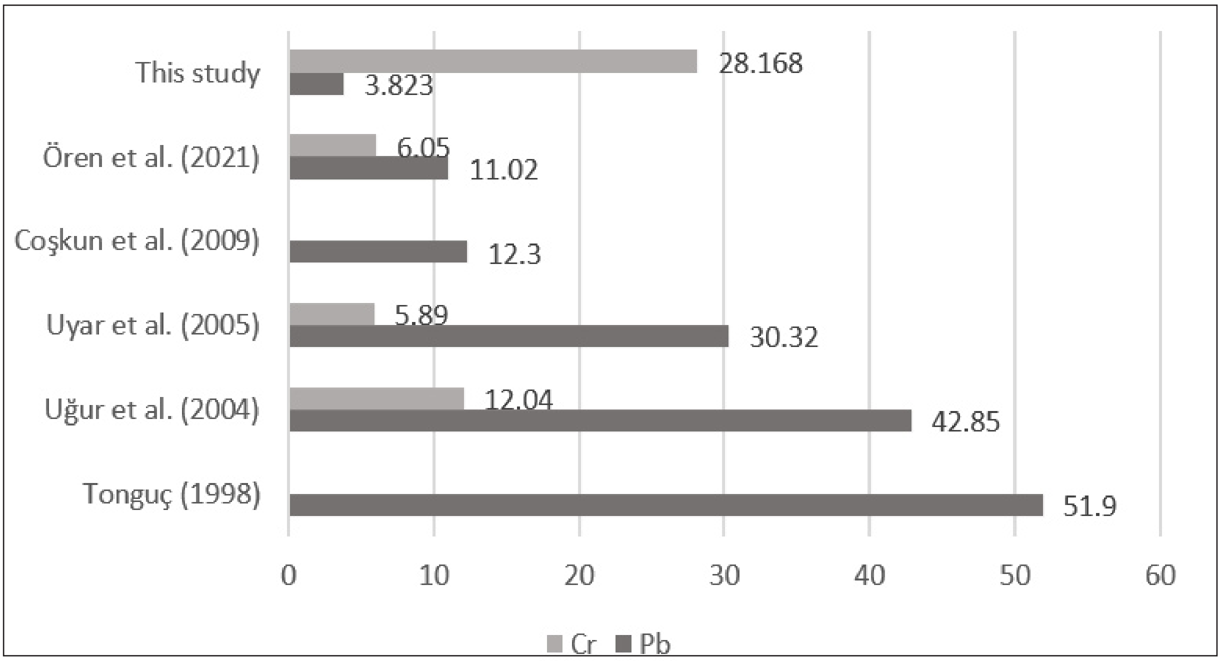

Figure 2. Comparison of Cr and Pb enrichment with previous studies (values are ppm).

(42.85) and a Cr value of 12.04. Uyar et al. (2005) recorded Pb at 30.32 and Cr at 5.89, which is higher for Cr but lower for Pb compared to the current study. Coskun et al. (2009) found moderate levels of Cr (12.3) and Pb (11.02), while Ören et al. (2021) reported Cr at 6.05 and Pb at 11.02, showing higher Cr but lower Pb than the current study. Overall, this study presents the highest Pb value, but a relatively low Cr value compared to previous findings.

4.Conclusion

Mosses and lichens are widely used in biomonitoring of atmospheric pollution. Unlike higher plants, mosses and lichens do not have root systems and cuticle layers. Therefore, they absorb minerals with their entire surface. Mosses have been used to determine atmospheric heavy metal deposition for more than 50 years. BCF calculations from bryophyte and substrate rock revealed an excessive accumulation of Cr and Pb. The bryophytes at some stations are more enriched in Fe, Cd, and Cu than their substrates. The high Pb and Cr values found in bryophytes prove that bryophytes serve as good archive storage and show how effectively the power plant enriches heavy metal pollution in the environment. It is a serious warning that excessive exposure to these heavy metals may threaten the sustainability of the entire ecosystem and living creatures, as well as harm nature and human health.

Conflict of Interest: There is no conflict of interest in the study.

Author Contribution: This study was prepared within the scope of TÜBİTAK 2209-A Project. S.Y., S.N.A. and A.E.E. contributed to the fieldwork, sampling and analysis processes, and Ö.Y. contributed to the method and material design. All authors contributed jointly to the writing process.

Ethics Committee Approval: Ethics Committee Approval is not required for this study.

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