



Moss as a passive biomonitoring tool for the atmospheric deposition and spatial distribution pattern of toxic metals in an industrial city

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Received: 11 January 2024 / Accepted: 30 April 2024 / Published online: 6 May 2024
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Abstract Anthropogenic pollution impacts human and environmental health, climate change, and air quality. Karabük, an industrial area from the Black Sea Region in northern Türkiye, is vulnerable to environmental pollution, particularly soil and air. In this research on methodological aspects, we analyzed the concentrations of six potential toxic metals in the atmospheric deposition of the city using the passive method of moss biomonitoring. The ground-growing terrestrial moss, *Hypnum cupressiforme* Hedw., was collected during the dry season of August 2023 at 20 urban points. The concentrations of Cr, Cu, Cd, Ni, Pb, and Co were determined in mosses by the ICP-MS method. Descriptive statistical analysis was employed to evaluate the status and variance in the spatial

distribution of the studied metals, and multivariate analysis, Pearson correlation, and cluster analysis were used to investigate the associations of elements and discuss the most probable sources of these elements in the study area. Cd and Co showed positive and significant inter-element correlations ($r > 0.938$), representing an anthropogenic association mostly present in the air particles emitted from several metal plants. The results showed substantial impacts from local industry, manufactured activity, and soil dust emissions. Steel and iron smelter plants and cement factories are the biggest emitters of trace metals in the Karabük area and the primary sources of Cr, Cd, Ni, and Co deposition.

Keywords Air pollution · Biological indicator · Bioaccumulation · Urban air quality · Urban industry

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Introduction

Monitoring environmental accumulation in industrial cities is a critical issue in terms of quality of life, and it is a vital issue that directs urban soil use interventions. Air pollution, one of the urban problems, is a severe public health risk factor that can have consequences up to and including death (Boogaard et al., 2019; Juginović et al., 2021). Trace elements are broadly diffused in the surrounding environment (Oduro et al., 2023). Their combination with diverse natural ingredients harms the biosphere from stationary and traffic-related mobility pathways

(Capozzi et al., 2017; Kelepertzis et al., 2020). Since 1980, the deterioration of air quality has accelerated due to the rapid increase in industrial/traffic emissions and the increase in atmospheric pollutant levels due to unplanned urbanization (Asamoah et al., 2023; Banerjee et al., 2021; Bargagli et al., 2019). From a biogeochemical perspective, within the air quality under the influence of various anthropogenic, natural, organic, or inorganic pollutants, potentially toxic metals have come to the forefront, posing a potential danger to human and environmental health via variability sources (Fuller et al., 2022; Nieder & Benbi, 2023). Nowadays, steps have been taken to improve air quality worldwide under the emergency action plan of governments and authorities. The increase in mortality and morbidity rates as a result of long-term exposure to air pollutants, especially in those living close to industrial zones (Rajak & Chattopadhyay, 2020; Świsłowski & Rajfur, 2023), in high-traffic areas or areas with poor ventilation due to topography, is significant by atmospheric wet and dry deposition (Isinkaralar et al., 2023; Shabanda et al., 2019). The impact of anthropogenic pollutants is not only to reduce air quality but also to trigger climate change, with negative consequences for biodiversity and human well-being (Ayanlade et al., 2020; Potapowicz et al., 2019).

Trace elements, particularly toxic metals emitted by various industrial facilities (Coker et al., 2023) and vehicular emissions (Konadu et al., 2023), are recognized as very harmful because of their high persistence in the atmospheric environment (Mondal & Singh, 2021; Wiklund et al., 2020). The incomplete combustion of fuels releases soot in the form of ultrafine particles that penetrate the respiratory organs and cause various diseases. Toxic metals such as Zn, Pb, Cu, Hg, Cd, and Cr, which are fuel contributors, are dispersed into the ambient atmosphere through combustion (George et al., 2020; Wang et al., 2020). Heavy metals are non-biodegradable and persistent toxic pollutants that are persistent and transferred from one trophic level to another through biomagnification. Atmospheric excessive concentrations of toxic elements in different forms adversely influence human health and certain constituents of the natural environment (Ali et al., 2019; Rahman & Singh, 2019). Tracking potentially harmful air pollutants is essential in understanding their spatial variations and elaborating actions planned to reduce their adverse effects (Ferreira et al., 2024; Jeong et al., 2019).

Air pollution can be assessed by using many techniques and methods. The biomonitoring technique is the most popular and widely used, in which mosses are often used as the most suitable bioindicator in urban areas (Cecconi et al., 2019). The types of environmental pollution and their chemical properties significantly impact environmental conditions, and their presence varies depending on pollution status. Widespread availability and the ability to withstand environmental conditions are critical characteristics sought in species used to investigate atmospheric deposition of potentially toxic metals (Vithanage et al., 2022). While many researchers use different species, the most common are self-growing and landscape types (Fernández et al., 2015; Rota et al., 2018). Passive biomonitoring is based on the fact that moss species, especially carpet-forming moss species, take up nutrients directly from atmospheric deposition and less from substrate soils (Słonina et al., 2021). One of the four moss species proposed in the biomonitoring protocol of the European Moss: 2015 Survey is *Hypnum cupressiforme* (Hypnum Moss), which is commonly distributed in Türkiye and used for air quality monitoring (EN 16414:2014, 2014). Using a single species to assess local climate and air quality effectively evaluates and interprets the results obtained for different regions (Bargagli, 2016; Isinkaralar & Isinkaralar, 2023; Qarri et al., 2019). Atmospheric heavy metal accumulation is correlated with ambient conditions (topography, transport, and deposition of air dust), meteorological conditions (wind speed, particle size, air temperature, and humidity), and uptake capability by species (Di Palma et al., 2016; Mahapatra et al., 2019).

Using mosses to project the scale and orientation of heavy metal contamination is a leading bioindicator of air quality in urban pollution (Ávila-Pérez et al., 2019; Rajfur et al., 2023). For most of these studies, the highest concentrations of the metals in natural mosses are detected in the immediate proximity of sources and decrease with distance from the source until background levels are achieved (Allajbeu et al., 2017; Cowden & Aherne, 2019a, 2019b). Potential toxic metal pollution in the working environment is generally the result of industrial and traffic emissions. A dense human population and various anthropogenic sources of pollutants characterize the Karabük area. The objective of this study is to assess (i) the pollution level and distribution of toxic metals in atmospheric

deposition under the influence of anthropogenic emissions from local industrial processes and traffic in the Karabük region; (ii) report temporal trends of Cr, Cu, Cd, Ni, Pb, and Co amount in mosses; and (iii) categorize data and define the possible origins of elements and their accumulation pathways.

Literature review

In the biomonitoring study, several types of bioindicators of atmospheric metal deposition have been used to assess the territory worldwide (Coskun et al., 2011; Schröder & Nickel, 2019). The variability of these species depends on their different amounts and absorption capacities, type of climate, topographic structure, and purpose of use (such as landscaping, ornamental, or recreation) (Akbay et al., 2023; Allajbeu et al., 2016; Foan et al., 2015; Motyka et al., 2020). The use of land-grown algae has been widely investigated by many researchers, revealing the increasing interest of the scientific community (Barandovski et al., 2012; Kapusta & Godzik, 2020; Kempter et al., 2017). Carpet-forming moss species have been shown to have several advantages as bioindicators compared to higher plants. Terrestrial mosses, generally used easily in all climatic regions, have simple leaves and rhizoids that fix them to the lower layers and easily take in elements from the atmosphere (Jiang et al., 2018; Varela et al., 2013). Therefore, it is very easily exposed to changes in the atmosphere. These species can be considered the most straightforward and cheapest of the methods used to monitor changes in the atmosphere. *Sphagnum papillosum* in Salo and Mäkinen (2014), *P. purum* (Hewd.) M. Fleisch. in Ares et al. (2015), *Pleurozium schreberi* in Vergel et al. (2019), and *Sphagnum fallax*, *Pleurozium schreberi*, and *Dicranum polysetum* in Świsłowski et al. (2022) have been used in their studies to monitor the distribution of atmospheric precipitation due to their availability in all seasons. In recent years, many academic researchers in different countries have carried out studies to monitor the situation in areas with high levels of environmental pollutants (toxic metals), and its source was defined by Bonanno et al. (2012), Boquete et al. (2013), and Boev et al. (2022). Biomonitoring can enable high-density sampling at nearly all required spatial and temporal extents at low cost and allow quantification of a broad

range of contaminants (Tabors et al., 2023; Urošević et al., 2023).

Moreover, considering moss' age and growth intervals, periodic atmospheric metal accumulation has revealed the environmental problem with an excellent data source in domestic regions. The number of mosses as indicators of potentially toxic metal has successfully shown the accumulation level of multiple elements simultaneously and in processing long-distance transport data (Chaligava et al., 2021; Stafilov et al., 2023). A comparison of studies in the literature makes it easier to evaluate the differences in the absorption capacities of the same species and the accumulation in the environment in Table 1.

The current literature review shows that moss biomonitoring is widely used for assessment atmospheric metal deposition. The network between identifying potentially toxic metal sources and relation is strong in Fig. 1. Therefore, biomonitoring was chosen to indicate atmospheric dry and wet deposition.

Materials and methods

The steps needed in sampling include a guide that will reveal sampling issues. We outline a framework to define the necessary considerations for sampling moss as an air quality indicator in Fig. 2. In particular, a potential starting point for source assessment, as well as collection from relevant sampling sites, inspection, chemical, and distributional analysis, is examined in this biomonitoring study. Research is utilizing moss biomonitoring trace metal bioaccumulation and evaluating the formation of relatively high concentrations of selected elements that may constitute high pollution or ecological risk. The first stage consists of data collection, the second stage is analysis, and the last consists of spatial and statistical analysis results.

Study area

Karabük is located in the Western Black Sea region with an area of 4145 km² and an altitude of 354 m. The population of 248,014 is concentrated in the flat terrain in the central part by 2019. On the other hand, it is an important industrial, urban, and agricultural area. Various inorganic and organic pollutants are emitted into the atmosphere from industrial

Table 1 Past studies implementing atmospheric metal deposition

Authors	Details of the study site	Climate condition	Research method	Regulatory monitoring	Strengths and limitations
Gerdol et al. (2014)	An industrial area (chemical plants, etc.) in the municipality of Ferrara-Northern Italy	Temperate sub-continental, MAT: 13.2 °C MAR: 650 mm, PW: westerly	<i>Tortula muralis</i> Hedw., 10×10 km ² area following the guidelines of ANPA (2001), 23 elements	Point sources: (i) car repair and paint shops, (ii) domestic heating plants, (iii) agricultural practices and vehicle traffic, (iv) both in the local road network and a motorway located relatively close to the city center	A higher contribution of oxidized N species to atmospheric N influx
Vuković et al. (2015)	Belgrade urban area, elevation: 70–250 m; traffic is regarded as the primary contributor	NA	<i>Sphagnum girgensohnii</i> Russow and <i>H. cupressiforme</i> Hedw., 109 sampling sites, 800×800 m ² with a sampling site in the center of each square, 12 elements	Urban central, suburban, industrial, and green zones	Obvious differences between urban land use classes with high, medium, and low levels of pollution were observed by both species
Yan et al. (2016)	Wuxi, China	Typical subtropical monsoon climate, MAT: 15.6 °C, MAR: 1095.1 mm	<i>Haplocladium microphyllum</i> and <i>H. angustifolium</i> , 49 sites, 10×10 km ² grids from each grid point, 6 elements	Domestic industrial activities and traffic emissions	Atmospheric deposition on mosses is mainly attributed to domestic industrial activities and traffic emissions
Lequy et al. (2017)	Distributed over France	NA	<i>Hylocomium splendens</i> (Hedw.) Schimp., <i>Hypnum cupressiforme</i> Hedw., <i>Pseudocleropodium purum</i> (Hedw.) M. Fleisch., <i>Pleurozium schreberi</i> (Brid.) Mitt., and <i>Thuidium tamariscinum</i> (Hedw.) Schimp., 449 sites, 6 elements	To identify key determinants of their spatial distribution	No sufficient atmospheric deposition data was available
Kosior et al. (2018)	Upper Silesia, the most urbanized region of Poland	NA	<i>Hylocomium splendens</i> (Hedw.) Schimp., the base from 50 m × 50 m squares, while within a 30×30 m ² area five sub-samples, 11 elements	Largest urban and industrial areas	Findings indicate that air quality in industrial, urban, and rural areas is mainly affected by the impact of local emissions

Table 1 (continued)

Authors	Details of the study site	Climate condition	Research method	Regulatory monitoring	Strengths and limitations
Bidwell et al. (2019)	Western Washington, USA	NA	<i>Isoetium stoloniferum</i> Bridel and <i>Kindbergia praelonga</i> (Hedw.) Ochyra., 273 moss samples, 12 elements	Intensive urban sites	A comparative index of metal deposition and as a screening tool to assess areas of metal pollution
Hristozova et al. (2020)	A substantial portion of the territory of Bulgaria	Summers are hot and dry, temperate continental, and transition to subtropical and Mediterranean to the south	<i>Hypnum cupressiforme</i> Hedw., and <i>Pleurozium schreberi</i> (Brid.) Mitt., 115 sites, 34 elements, 5–10 subsamples within a 50×50 m ² area	Lead–zinc plant, tailings and quarries, road construction and increased traffic, coal combustion and copper ore mining, and border crossing points	Major anthropogenic factors affecting the ecological situation, road construction, and related traffic pollution
Hussain and Hoque (2022)	Golaghat and Tezpur (roadside and residential), Numaligarh and Guwahati (roadside, residential, and industrial) in Brahmaputra valley, India	Golaghat, Tezpur, and Guwahati have subtropical highlands, a subtropical climatic zone, and a humid subtropical climate (MAR: 172.2 cm)	<i>Atrichum angustatum</i> , 99 samples investigated for 10 elements	Residential and urban/commercial spots, coal burning, vehicular emission, biomass burning, road dust, and crustal dust	Influenced anthropogenic inputs, atmospheric derivation, and long-range transport of pollutants

*MAT mean annual temperature, **MAR mean annual rainfall, ***PW prevailing winds, NA not applicable

establishments and dense urban areas, affecting the region's environmental quality. The industrial zone, which includes a steel complex and some other factories, was built in the 1970s of the last century. Today, a metal processing plant, recycling and production of plastic materials, various polyester and chemical factories, and a factory for aluminum smelting and production operate in the industrial zone. Karabük's climate is characterized by dry, rainy summers and cold winters with little rainfall. The annual temperature is 13.6 °C with an average annual precipitation of 487.5 mm, and the wind direction is southwest.

The description of the sampling points in Table 2 shows the emission diversification used to define and the distribution of measurement stations in the study area, which is presented in Fig. 3.

Sampling methods

This study used *Hypnum cupressiforme* Hedw. moss, which is prevalent across the study area. Moss samples were gathered and washed with distilled water in August 2023 following the ICP Vegetation protocol and the European Program for Biomonitoring sampling strategy of Heavy Metal Atmospheric Deposition (ICP Vegetation, 2020). EN 16414–2014 European standards were implemented for sampling from main roads, buildings, rural roads, and single houses, mostly in open spaces. Five subsamples were taken in a 50 m×50 m area at each sampling site, and composite samples were created from these. Using a moss clone for biomonitoring of pollutants offers some benefits, particularly the repeatability in physical attributes. A coupled plasma mass spectrometer (Agilent, 7800) was employed to define the elemental composition of the moss samples (ICP-MS), digested 0.3–0.5 g of moss samples in PTEF digestion dishes (DAP 60) using analytical grade reagents: 6 mL 67% HNO₃ (trace purity, Merck, Germany) and 1 mL 30% H₂O₂ (trace purity, Merck, Germany) and Speed-wave Xpert, Berghof Microwave Digestion System, implementing a four-step digestion program. Samples digested quantitatively were transferred into 50-mL calibrated vials, then filled to 50 mL with 2% HNO₃.

The quality control was conducted by concurrently analyzing the plant reference material (IAEA 336) and blank solutions with the moss samples. The recovery of the examined elements was controlled by the standard addition method. We achieved good

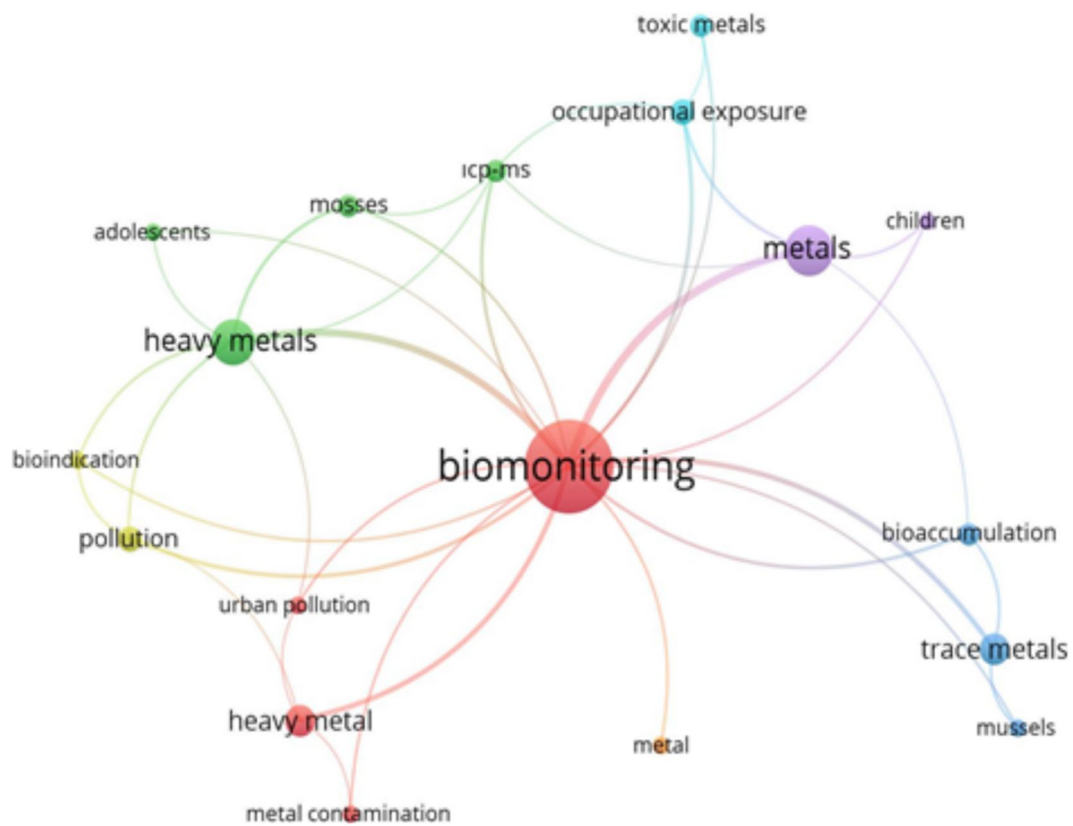
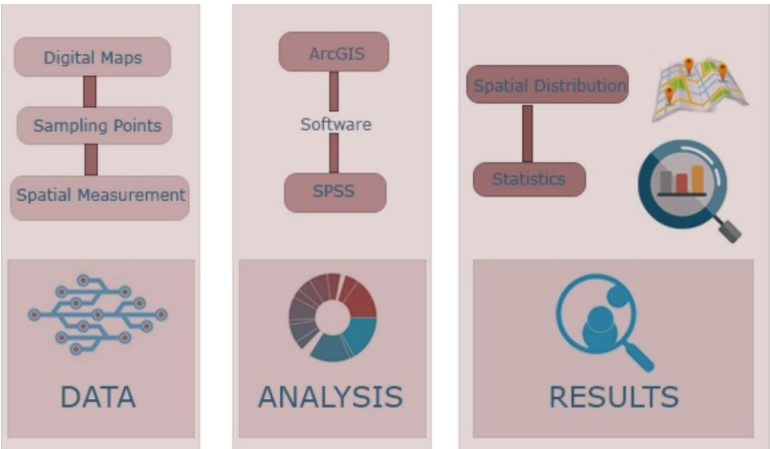


Fig. 1 Link-based visualization of the network, including street dust via Vosviewer software bibliographic analysis

Fig. 2 Framework of study



recoveries for the elements analyzed with three replicates and 60 samples in total (98.5% and 105.2%). The comparison of the declared concentrations with the analyzed concentrations of the IAEA 336 reference material showed satisfactory accuracy in the analysis.

Bioaccumulation factor

The bioaccumulation factor (BCF) is the ratio of the moss concentration to the soil concentration. It was important and derived from the metal concentration

Table 2 Characteristics of the sampling points

Sampling points	Position type	Proximity to emission
1	Out of city	None of them, agricultural
2	Out of city	Near the shopping mall, low T-RA
3	The main road to the city	Low T-RA
4	Residential area	Middle T-RA
5	Residential area	Middle T-RA and low I
6	Multiple intersections	Middle T-RA
7	Main street-1	Middle T-RA and low I
8	Main street-2	Middle T-RA and low I
9	Main street-3	Middle T-RA and low I
10	Main street-4	High T-RA, low I and traffic lights
11	City center-1	High T-RA, traffic lights, commercial areas
12	City center-2	High T-RA, commercial areas, dense zone
13	City center-3	Middle T-RA, commercial areas, middle-dense zone
14	City center-4	Middle T-RA, commercial areas, middle-dense zone
15	Main road-1	Middle T-RA, iron and steel industry area
16	Main road-1	Low T-RA, iron-steel industry area
17	Main road-2	Low T-RA, iron-steel industry area
18	Main road-3	Iron-steel industry area
19	Main road-4	Iron-steel industry area
20	Main road-5	Iron-steel industry area

Traffic (T), industry (I), residential area (RA)

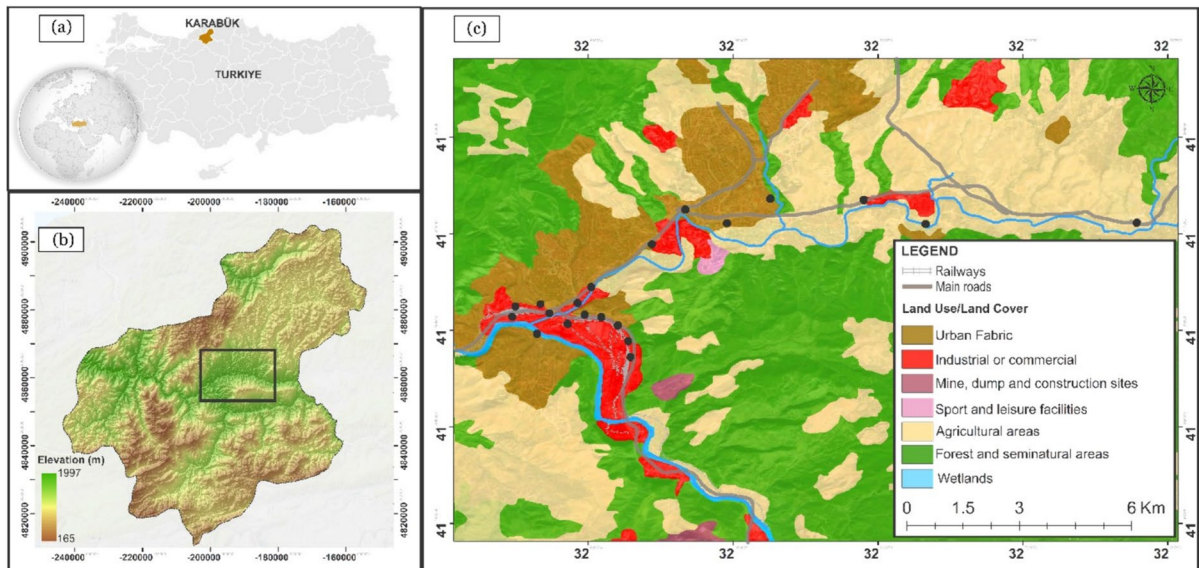


Fig. 3 Maps of **a** Karabük City in Türkiye, **b** an elevation map of Karabük, and **c** sampling points in Karabük City

ratio of the plant to the soil, which was calculated using Eq. (1) (Ren et al., 2021).

$$BCF : \frac{C_{biomass}}{C_{soil}} \quad (1)$$

where $C_{biomass}$ and C_{soil} were the concentrations of trace metals in moss and in soil, respectively. Where $BCF \leq 1$, it means that the moss can only accumulate elements but cannot deposit them; where $BCF > 1$, it implies that the moss can accumulate metals.

Spatial and statistical analysis

Quantification of toxic metals and related descriptive statistics were performed with Microsoft Excel. The normal distribution of ANOVA residuals was examined and applied using the normality of probability distributions test by Kolmogorov–Smirnov and Shapiro–Wilk since even after Lilliefors correction and cluster analysis using SPSS 23.0 software. Both tests were conducted for moss samples to investigate differences between each other and between the natural area and industrial sites.

In this study, the inverse distance weighted (IDW) method is used to interpolate ArcGIS and multivariate interpolation based on Tobler's first law. The uncertain value at point S_o , $Z(S_o)$ is computed according to the following Eq. (2).

$$Z(S_o) : \sum_{f=1}^n W_f Z(S_i) \quad (2)$$

Here n denotes the monitoring station, $Z(S_i)$ is the value at the sampled S_i points, and W_i is the weight of S_i ; d_i is the horizontal distance between the interpolation points and the points observed, and k is the power of the distance in Eq. (3).

$$W_f : \frac{1/d_i^k}{(\sum_{i=1}^n 1/d_i^k)} i : 1, 2, 3, 4, \dots \dots n, \quad (3)$$

The average values of Cr, Cu, Cd, Ni, Pb, and Co were used for unknown points using values from a scattered set of known points. The IDW method integrates ArcGIS with multivariate statistical analysis. In order to examine the spatial distribution characteristics of Cr, Cu, Cd, Ni, Pb, Ni, Pb, and Co in mosses in Karabük Province and the factors affecting their contents, Kriging spatial optimal unbiased interpolation was conducted with ArcGIS 10.2 program.

Results and discussion

Table 3 provides statistical data (mean and standard deviation, median, coefficient of variation, minimum and maximum concentrations in mg/kg d.m. (dry mass), and skewness and kurtosis for the six elements detected by ICP/MS in 60 moss samples in this study). The normality tests of Kolmogorov–Smirnov and Shapiro–Wilk were performed for the statistical analyses of physicochemical characteristics (data not presented) of trace metals in Table 4. While the highest values were acquired in Pb (153.25 mg/kg d.m.), Ni (149.33 mg/kg d.m.), and Cr (127 mg/kg d.m.), the lowest values were obtained in Co (0.09 mg/kg d.m.) and Cd (0.19 mg/kg d.m.).

The abundance of elements in current moss is evaluated by their mean concentrations, which follow the order $Cd < Co < Cu < Cr < Pb < Ni$. The abundance of elements in current moss, evaluated by moss median concentrations, is similar to the other investigations by Mentese et al. (2021). This indicates the presence of dust mineral particles in the atmospheric deposition of the study area and enrichment for Ni and Pb in the current moss.

Table 3 The results of descriptive statistical analysis of all components

Variable	^a Mean	StDev	^a Median	CV%	^a Min	^a Max	Skewness	Kurtosis	<i>p</i> value
Cr	30.61	30.98	18.17	101.21	0.14	127.00	1.19	0.78	8*
Cu	8.80	9.86	3.53	112.13	0.46	55.00	2.13	6.83	2.55*
Cd	2.27	1.25	2.14	55.16	0.19	5.60	0.75	0.17	0.32*
Ni	50.00	42.45	45.00	84.90	2.89	149.33	0.76	−0.31	10.97*
Pb	34.63	35.60	19.59	102.80	0.32	153.25	1.08	0.69	9.20*
Co	4.20	4.20	2.51	102.24	0.09	22.01	1.85	4.32	1.11*

^aIn mg/kg d.m.; in brackets: median concentration of each element measured in national scale

* $p > 0.05$

Table 4 The normality of all components in the moss using Kolmogorov–Smirnov and Shapiro–Wilk tests

	Kolmogorov–Smirnov Level of significance	Shapiro–Wilk Level of significance	df
Cr	0.175	0.856	60
Cu	0.228	0.754*	60
Cd	0.101*	0.950	60
Ni	0.142	0.895	60
Pb	0.179	0.859	60
Co	0.169	0.814	60

df degrees of freedom

*This is a lower bound of the true significance

°Lilliefors Significance Correction

Figure 4 depicts the Boxplot diagram and graphically shows the numerical data's level, spread, and skewness groups through the first and third quartiles (Q1 and Q3). It can be noticed that elements of anthropogenic origin such as Cr, Cu, Cd, Ni, Pb, and Co contained in the available moss reveal relatively high concentration values, indicating a high impact from the operation of the iron smelter and other industrial activities and related industrial dumpsites, which leads to a continuous increase in the concentration of these elements in the study area. Various research in several conditions have compared the species including *Hylocomium* (Barkan & Lyanguzova, 2018; Rivera et al., 2011), *Pleurozium* (Cowden & Aherne, 2019a, 2019b; Michel et al., 2024), and *Hypnum* (Adžemović et al., 2023; Gómez-Arroyo et al., 2021),

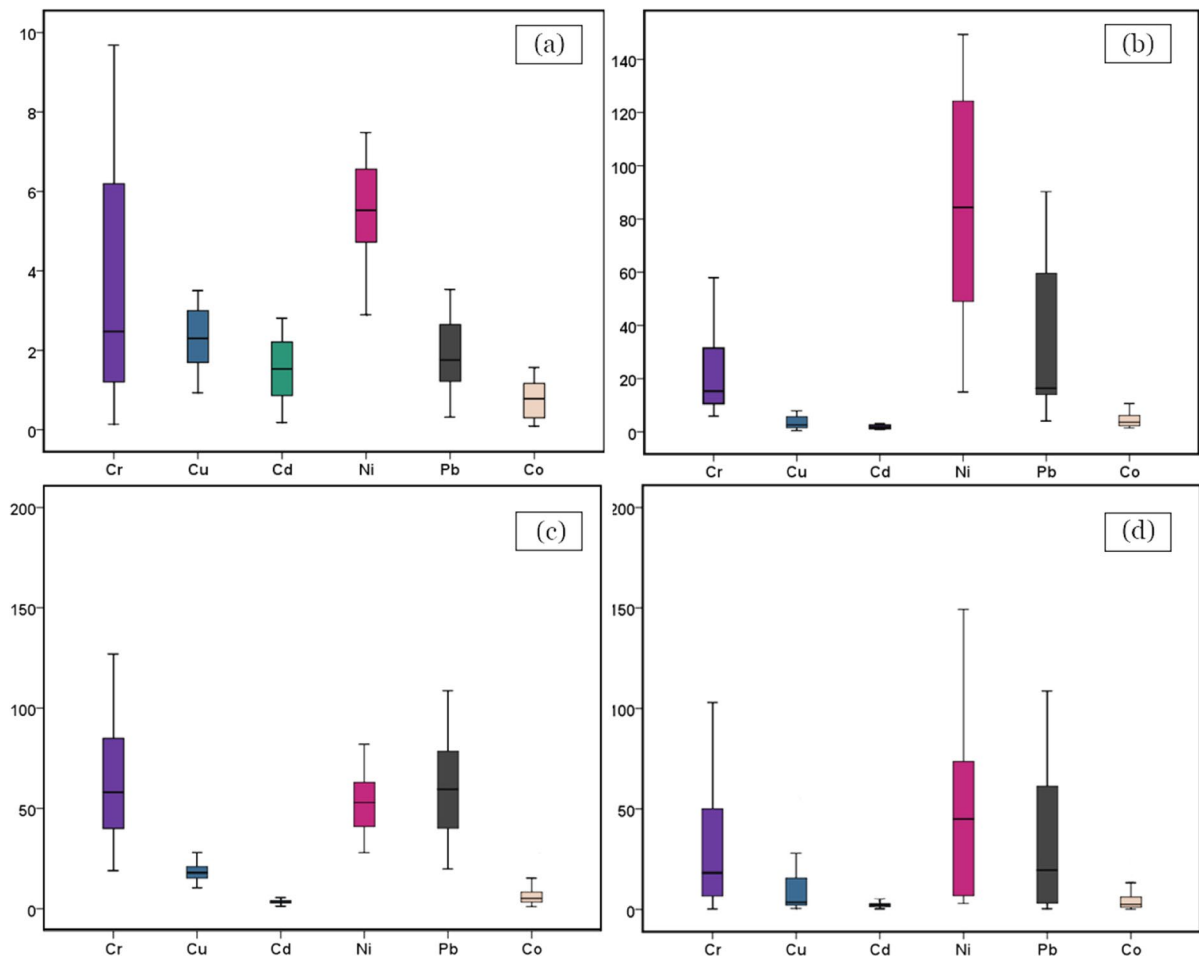


Fig. 4 Boxplot diagrams of elements present in sampling locations of **a** out of city, **b** residential area-main street, **c** city center, and **d** main road

which also contain different quantities of trace metals by Nguyen Viet et al. (2010) and Xiao et al. (2021). Only Cd showed moderate variability ($CV\% < 75\%$), indicating they are relatively stable in the study area. The other elements, Cr, Cu, Ni, Pb, and Co, showed high variation ($CV\%$) between 84.90 and 112.13, indicating relatively high fluctuation of these elements in the study area.

Many studies worldwide have proven that mosses reflect atmospheric metal deposition (Isinkaralar et al., 2024a, b). Maxhuni et al. (2016) investigated that *Pseudocleropodium purum* and *Hypnum cupressiforme* were analyzed as carpet-forming mosses for atmospheric metal deposition in Kosovo. Most elements follow lognormal distribution except Ni and Cd, which showed atmospheric metal deposition from windblown soil dust. Also, they reported that anthropogenic factors and lithogenic origin played a vital role. Mao et al. (2022) examined three types of native mosses for monitoring atmospheric 12 heavy metals pollution in Xichang. Their result defines trace metal accumulation via atmospheric deposition in selected species. The presence of trace metals in the zones is related to anthropogenic emissions from the metal processing industry in the selected points. Sergeeva et al. (2021) analyzed elements for environmental pollution in Donetsk, Ukraine, which is used to benefit from *Ceratodon purpureus* (Hedw.) Brid and *Brachythecium campestre* (Müll.Hal.) as terrestrial moss. The element absorption capacity of two different species was examined, and it was observed that they retained different amounts due to tailings and mine activities. Vergel et al. (2022) studied moss *Pleurozium schreberi* biomonitoring for 35 elements in the Moscow, Vladimir, and Yaroslavl regions where air pollution sources were identified, including industrial activity and thermal power plants. They found that the most polluted zone was the Moscow region.

Table 5 presents the Pearson correlation between the pairs of elements, and cluster analysis was used to explore the association between elements and identify their probable sources in current moss samples.

The dendrogram produced by the cluster analysis is shown in Fig. 5, and the spatial distribution maps in Fig. 6 show the distribution of elements over the monitoring sites. Four dependent clusters linked to each other with various degrees of similarity were obtained for the cluster analysis. One geogenic and three anthropogenic relationships were identified among the elements based on the correlations between the elements and the apparent degree of similarity across clusters.

The elements of the first cluster refer to the presence of potentially harmful and anthropogenic elements (Cd, Co, and Cu) in the samples, which showed very high and significant inter-element correlations and are assumed to come from atmospheric dust particle emission. Agnan et al. (2015) reported that moss morphology supports high particle retention capacities and carries large amounts of strongly retained particles on their surface, which contain atmospheric pollutants. The second cluster combined the Cr, Pb, and Ni into a single cluster, which showed moderate to high and significant inter-element correlations primarily generated from local and long-range transport of pollutants. This cluster exhibits a high similarity, which has revealed strong and significant correlations, primarily derived from the local iron, nickel, and iron-steel industries within this study area. It indicates a geogenic and anthropogenic origin of metals that show the spatial distribution of elements that support it in spatial distribution characteristics (Istanbullu et al., 2023).

The BCFs were calculated from the concentrations of metals in soils and mosses. The BCF values of Cr, Cu, Cd, Ni, Pb, and Co in the samples ranged from 0.08–1.53, 0.23–3.50, 0.71–4.29, 0.130–4.42,

Table 5 Correlogram of pairwise Pearson correlations between metals

	Cr	Cu	Cd	Ni	Pb	Co
Cr	1.000					
Cu	0.610**	1.000				
Cd	0.396**	0.815**	1.000			
Ni	0.457**	0.237*	0.155	1.000		
Pb	0.752**	0.598**	0.333*	0.603**	1.000	
Co	0.464**	0.815**	0.938**	0.241*	0.353**	1.000

* and ** show statistically significant correlation levels (p : 0.05 and 0.01) for two-tailed

Fig. 5 The dendrogram of potential harmful elements by Ward's method

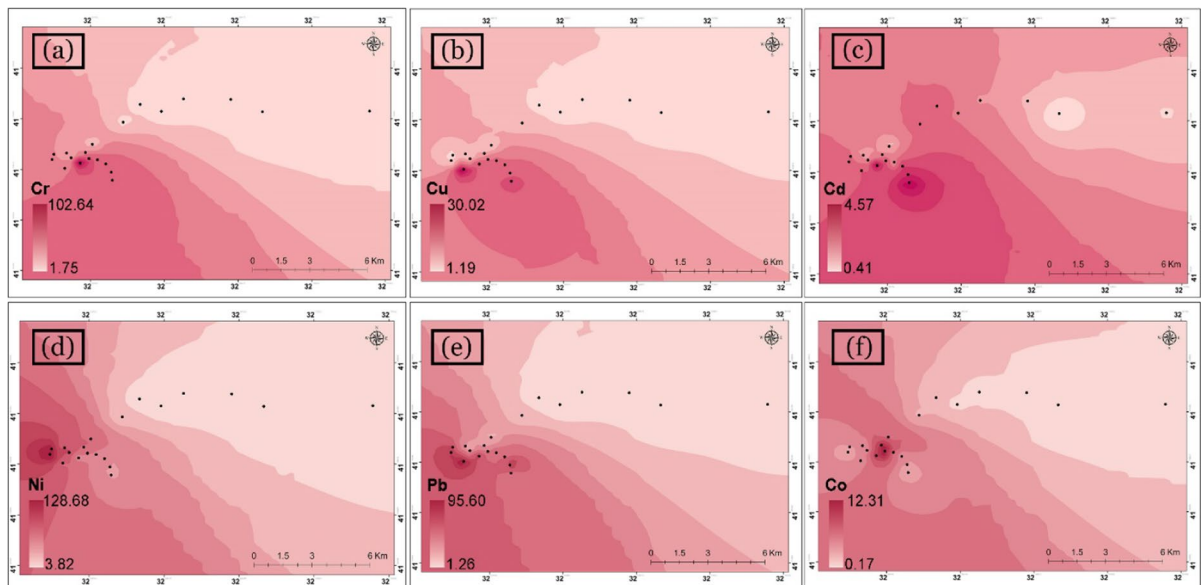
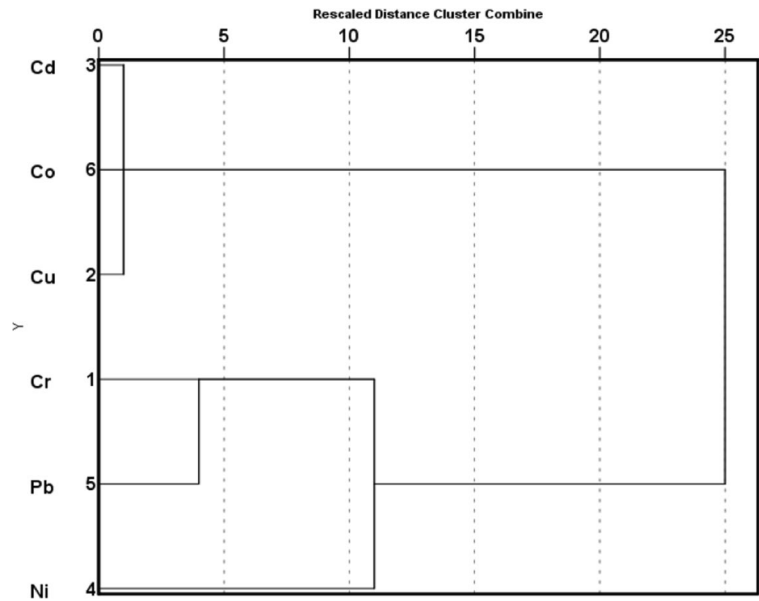


Fig. 6 The distribution pattern of **a** Cr, **b** Cu, **c** Cd, **d** Ni, **e** Pb, and **f** Co (mg/kg d.m.) over monitoring stations

0.13–1.81, and 0.390–1.57, respectively. For each trace metal which have values indicate partial pollution, different spatial and temporal distributions and their distribution characteristics are given in Fig. 6.

The distribution modeling demonstrated that where metallurgical smelters exist, Cr, Cu, Cd, Pb, Ni, and Co have similar distribution patterns. The Cd level is higher than other elements in the measurement from

out-of-city areas near the main roads and shopping malls. Some studies show that transportation and agricultural production are the main sources of Cd levels (Zhang et al., 2023). Most of the Cd in Karabük is weakly contaminated in the city center. Most of the iron and steel industry's Cr, Co, Cd, and Cu are mildly polluted. Relatively concentrated Pb and Ni pollution areas in the center are mostly near traffic

routes. Cr contamination was broadly unenriched, with the main enrichment areas being vehicles and industry. Chen et al. (2013) pointed out Cr concentration with industrial development in Xi'an city, the capital of Shaanxi province. Du and Lu (2022) emphasize the effect of industrial activities on the increase of Cu and Cr content. Ni was concentrated mainly near highly populated areas, where only mild contamination was seen. Also, Ni concentration is remarkable among the pollution resulting from urban center land use. Pb levels were higher along traffic routes. Cr, Co, Cd, and Cu were concentrated primarily in industrial areas, and industrial pollution was markedly increased. Spatial accumulation of Cd concentration stands out along the industrial corridor.

Conclusion

Monitoring environmental pollution in industrial cities is a critical issue for public health, and its interpretation based on urban land use is essential for urban planning. This study involved a useful tool for assessing the air quality of Karabük by using moss biomonitoring and trace metal atmospheric deposition. It is known that the city is growing in a northern direction, and new development areas are planned in this region. In order to reduce exposure to heavy metals resulting from urban land use, investments in the east and south directions, where accumulations are concentrated, should be limited, and it is especially appropriate to plan the built areas in the northeast direction by synthesizing them with other settlement suitability analyzes within the framework of these analyses. Data on six elements were determined in 20 streets with high-density levels of traffic and industrial activities, and this research revealed selected trace metal (Cr, Cu, Cd, Ni, Pb, and Co) pollution levels in Karabük City. High concentrations of trace metals are found close to the emission sources from local industry, indicating that point emission is vital to the air quality of the study area. The long-term operation of metal processing and its supporting industry, iron, steel, and derivative factories are the primary sources affecting this area's environment and human health. It is pointed out as a hotspot area (represented local pollution area), affected mainly by anthropogenic emissions from industry in this area. Potential toxic metals were identified as anthropogenic elements, and their

origin revealed relatively high concentration values, indicating a high impact from the operation of the local industry, like metal processing and other industrial activities and the respective industrial dumps that led to a continuous increase of these elements in the study area. Cr, Cu, Cd, Ni, Pb, and Co show higher median concentrations than the respective values estimated nationally in Karabük and revealed high variation ($CV\% > 75\%$), indicating relatively high fluctuations over the study area. Metal processing can cause severe degradation to the ecosystem, evidenced by the high concentration of potentially toxic elements in plant organisms in the mosses of the study area. The historical deposit emissions of Cr, Cu, Cd, Ni, Pb, and Co from the metal processing industry, cement production, and steam production in the Karabük area pose crucial problems that require strong actions to improve technology for reducing emissions into the atmosphere and industrial waste.

Author contribution Oznur Isinkaralar: conceptualization; methodology; validation; formal analysis; visualization; investigation; data curation; writing—original draft; writing—reviewing and editing. Paweł Świsłowski: data curation, writing—reviewing and editing. Kaan Isinkaralar: validation; formal analysis; investigation; data curation; writing—original draft; writing—reviewing and editing. Małgorzata Rajfur: data curation, writing—reviewing and editing.

Data availability No datasets were generated or analysed during the current study.

Declarations

Ethics approval All authors have read, understood, and have complied as applicable with the statement on “Ethical responsibilities of Authors” as found in the Instructions for Authors.

Consent to participate Not applicable.

Consent to publish Not applicable.

Competing interests The authors declare no competing interests.

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