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# Determination And Statistical Analysis of Atmospheric Deposition of Heavy Metals In Kosovo. A Moss Survey

**Flamur Sopaj**
University of Prishtina
**Trajče Stafilov**
Ss Cyril and Methodius University
**Robert Šajn**
Geological Survey of Slovenia
**Krste Taševi**
State Phytosanitary Laboratory
**Musaj Paçarizi** (musaj.pacarizi@uni-pr.edu)
University of Prishtina https://orcid.org/0000-0002-1097-6619

**Research Article**

**Keywords:** heavy, metals, samples, industrial, pollution

**Posted Date:** October 12th, 2021

**DOI:** https://doi.org/10.21203/rs.3.rs-839800/v2

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## Abstract

Atmospheric deposition of heavy metals on the territory of Kosovo was studied using the already widely used technique of mosses as biomonitors. This method is very convenient as it uses natural samples and thus avoids many difficulties associated with artificial samplers. Eight heavy metals (Al, Cd, Cr, Cu, Fe, Ni, Pb, and Zn) were determined in 45 moss samples. Statistical analysis was performed to better present and explain the data. High concentrations of Pb, Zn, Cd, and Ni were found near industrial sites and in more densely populated areas. Principal component analysis (PCA) identified more polluted sites such as Zveqan, Stanterg, Prapashticë, Siboc, and Lupç. It was also found that Pb, Zn, Cd, Cr, and Ni are the heavy metals that affect these polluted sites the most. High contents of Cd were found in Kaçanik and Paldemicë, Te Kalaja, Çikatovë, and Shalc, all sampling points found around industrial sights. The contamination factor (CF) and the polluted load index (PLI) were calculated. CF showed that only Cu, and Zn, had no or almost no contamination levels over the range of moss samples, while Cd and mainly Pb gave extremely high values for CF, indicating extreme contamination levels. The pollution load index also showed that only a few samples were slightly polluted, while most samples showed considerable and very high pollution levels.


## Introduction

Industrialisation and development, as necessary as they are, bring difficulties along. One of the worst consequences of industrialisation is producing many waste materials, which are frequently harmful to the environment. Chemical pollutants generated from many industrial processes and other human activities are spread in waters, soil, and air, depending on their chemical-physical properties and the nature of the industry. Air pollution is a very serious issue, and it has been reported continuously worldwide (Webb et al. 1992; Rocher et al. 2004; Soltanali et al. 2008; Silva et al. 2014; Li et al. 2017; Zhu et al. 2018; Ribeiro et al. 2019; McDonnell et al. 2020). Of course, Kosovo makes no exception regarding air pollution (Arditsoglou and Samara 2005; Kabashi et al. 2011; Zeneli et al. 2011).

Among air pollutants, heavy metals are widespread in every inhabited area and not inhabited remote ones (Kord et al. 2010; Thöni et al. 2011; Vianna et al. 2011; Silva et al. 2014; Abuduwailil et al. 2015). They can harm human health in various ways once entering the organism (Järup 2003; Kampa and Castanas 2008; Kelly and Fussell 2011). Heavy metals can be inhaled with air (Järup 2003; MacNee and Donaldson 2003) or ingested with food, such as vegetables which have been exposed to polluted air or water during their development (Pandey and Sharma 2002; Khan et al. 2015; Shahid et al. 2017). Adverse effects have also been reported on plants and animals (Pandey and Sharma 2002; Reis et al. 2010; Khan et al. 2015). Therefore, it is necessary to continuously measure the levels of heavy metals in the air so that appropriate actions can be initiated when they are beyond tolerated values.

Heavy metals are introduced into the atmosphere in various ways. Globally, they can rise into the atmosphere from wind-blown dust, aerosols formed at the sea surface, forest fires, volcanoes, and biological processes such as methylation (Duce et al. 1975; Lantzy and Mackenzie 1979; Thayer and Brinckman 1982; Nriagu 1989). The anthropogenic origin of metals in the atmosphere is also significant and has continuously impacted living organisms. Metal production involves several sub-processes, such as digging, transporting and crushing of the minerals, grinding, and concentration processes followed by extraction methods of metals from ores. During each stage, dust and gasses can be released into the atmosphere. Thus, many reports have emerged indicating that the mining and ore processing industry contributes to the atmospheric pollution with heavy metals (Lantzy and Mackenzie 1979; Walsh et al. 1979; Thayer and Brinckman 1982; Romo-Kröger et al. 1994; Mansha et al. 2012). Other sources of anthropogenic pollution are traffic, waste incineration, oil, fuel, and coal combustion (Trindade et al. 1981; Pacyna et al. 2007; Xia and Gao 2011; Suvarapu and Baek 2017).

The monitoring of metals atmospheric deposition traditionally is performed by collectors spread throughout the area intended to be monitored. Despite the advantages this approach has, there are also drawbacks to be considered. Collectors have to be built, transported and maintained. This makes it complicated to operate and expensive compared to some naturally grounded methods, such as moss survey (Schröder and Nickel 2019). Mosses grow naturally, and it is easier to cover more areas with a higher density of sampling points with less cost (Harmens et al., 2010). They are currently widely used in the monitoring of atmospheric heavy metals deposition because of their characteristic structure. Their cuticle being very thin enables good permeability towards atmospheric gaseous, metals, water, and other chemical species along with it (Roberts et al. 2012; Mahapatra et al., 2019). The absence of real roots essentially restricts the absorption of the nutrient to substrates they grow on (Mahapatra et al., 2019). They also contain various organic molecules, acting as complexing agents and ion exchange sites that can retain metals in the plant tissues (Wells and Brown 1990; Azuma et al. 2000; Klavina et al. 2015). These facts have made mosses a very suitable mean for air pollution investigation (Steinnes et al. 1994; Zechmeister 1998; Rühling and Tyler 2004; Harmens et al. 2010; Qarri et al. 2014; Barandovski et al. 2015; Macedo-Miranda et al. 2016; Lazo et al. 2018; Stafilov et al. 2018; Schröder and Nickel 2019).

This work aims to estimate the atmospheric deposition of most commonly expected heavy metals in Kosovo using mosses as bioindicators. It also intends to find patterns of the data distribution in order to locate the main sources of pollution through statistical analysis. The moss collection in Kosovo for heavy metals atmospheric deposition analysis was first performed in 2010 (Maxhuni et al., 2016). Nine metals were investigated: Cd, Cr, Cu, Fe, Hg, Ni, Mn, Pb, and Zn, in 25 sampling points. It was found that the concentrations of metals reached pollution levels with variation throughout the area studied. In this survey, 45 samples were collected over the whole territory of Kosovo, evenly spread to the possible maximum allowed by moss presence. The concentration of Al, Cd, Cr, Cu, Fe, Ni, Pb, and Zn, as more commonly expected, heavy metals were determined in moss samples. The data obtained were processed by statistical analysis to identify polluted sites and pollution sources and estimate the level of contamination.

## Materials And Methods

# Study area

Kosovo is situated in the centre of the Balkan Peninsula with geographical coordinates between longitudes 41° 50' 58" and 43° 15' 42" and between the latitudes 20° 01' 30" and 21° 48' 02". It has a surface area of 10,900 $km^2$ with an average altitude of about 800 m above sea level. It is characterised by a complex geologic setting and high mineral activity of Pb-Zn, Cu, Ni, and Cr throughout the territory. The total estimated land is 858,063 ha, and about 63.3 % is agricultural land area, and 35 % is forest area. The geology of Kosovo is complex, with formations created at different intervals of a geological timeline (Fig. 1). Metamorphic, flysch, carbonate rocks and clastic sediments appear to cover most of the area. Then, there are deluvial/proluvial sediments mostly in the west, South and to the east of the territory, magmatic rocks mostly are found in the North and the east and magmatic rocks mostly in the north and north/east. There are also alluvial sediments that lie along the river basins, such as Drin, Sitnica and Morava rivers.

## Sampling

Moss samples were collected during the dry season of summer, August to September 2019. In total 45 samples were collected in the whole territory of Kosovo (Fig. 2 and Table 1). The sampling procedure followed the Monitoring Manual of "International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops, 2020. Three types of mosses were collected: *Homalothecium sericeum* (Hedw.) Schimp. 1851, *Hypnum cupressiforme* Hedwig. 1801, and *Pseudoscleropodium purum* (Hedw.) M.Fleisch. Three to ten (mostly over five) samples were collected at each sampling site in an area of (50 x 50) m. The collected mosses were put in paper bags of 1 L, which were stored for 5–7 days at ambient temperature (20–25°C) before cleaning. Moss samples were taken at least 100 m away from small roads and over 300 m away from main roads, villages and industries. All samples were collected from ground soil, avoiding rocks, sometimes from rotten branches or tree trunks, in open fields with low shrubs or without shrubs. In forest areas, open gaps of at least 10 m diameter were chosen for mosses sampling, and at least a 3 m distance from the nearest tree canopy drip was always respected.

Table 1
Number of sampling site location, location, and elevation (m)

| No | Location | Elevation | No | Location | Elevation |
|---|---|---|---|---|---|
| 1 | Kukljan | 1200 | 24 | Kamenicë | 543 |
| 2 | Zym | 634 | 25 | Te Kalaja | 1050 |
| 3 | Korishë | 595 | 26 | Vasilevë | 706 |
| 4 | Shterpc | 936 | 27 | Çikatovë | 680 |
| 5 | Paldenicë | 619 | 28 | Siboc | 581 |
| 6 | Kaçanik | 573 | 29 | Makoc | 737 |
| 7 | Zhub | 473 | 30 | Prapashticë | 990 |
| 8 | Hoqë | 492 | 31 | Trude | 736 |
| 9 | Reqan | 479 | 32 | Istog | 568 |
| 10 | Ilirias-Greme | 616 | 33 | Izbicë | 736 |
| 11 | Zhegër | 574 | 34 | Shalc | 674 |
| 12 | Petrovë | 715 | 35 | Klinë e eperme | 677 |
| 13 | Junik | 770 | 36 | Studime e eperme | 651 |
| 14 | Mrasor | 485 | 37 | Lupç | 640 |
| 15 | Banjë | 583 | 38 | Herticë | 845 |
| 16 | Gadime | 687 | 39 | Kçiqi madh | 666 |
| 17 | Bresalc | 705 | 40 | Çabër | 703 |
| 18 | Pejë | 650 | 41 | Zveqan | 677 |
| 19 | Jabllanicë | 656 | 42 | StarTerg | 691 |
| 20 | Zabërgj | 530 | 43 | Vidishiq-Bare | 1065 |
| 21 | Llapushnik | 717 | 44 | Revuq | 798 |
| 22 | Harilaq | 770 | 45 | Cerajë | 573 |
| 23 | Janjevë | 850 | | | |

# Digestion

Interfering materials such as other herbs, leaves, twigs, and vegetation parts were carefully removed to leave a clean moss mass. After this, mosses were hand-ground using gloves and dried at 40°C for 48 h. Samples were digested in a microwave system by the wet digestion method. 0.5 g of sample were put in the Teflon tube, where 7 ml of nitric acid and 2.5 ml of hydrogen peroxide were added. The mixture was left to react for 10 minutes to give some time reactions to take place and some gases to release so that less pressure would develop in the Teflon tube during microwave digestion. Then Teflon tubes were put in the microwave system with a program: 5 min up to 170°C, hold time of 10 min at 170°C, 1 min up to 200°C, hold time of 15 min at 200°C, 1 min down to 50°C, hold time of 23 min at 50°C. After digestion, the obtained solutions were filtered in 25 mL Teflon flasks and the rest of the vessel was filled with redistilled water, in which chemical analysis was performed.

# Instrumentation

All reagents used in this work were analytical grade or better: nitric acid, trace pure (Merck, Germany) and hydrogen peroxide, p.a. (Merck, Germany). For glassware washing and other tools used for the preparation of samples, redistilled water was always used, and solutions prepared. Standard solutions of metals were prepared by dilution of 1000 mg/L solutions (11355-ICP multi–Element Standard).

Inductively coupled plasma—atomic emission spectrometry (ICP-AES) was used to determine the following elements: Al, Cr, Cu, Fe, and Zn (Varian, model 715ES). The QC/QA of the applied technique was performed by the standard addition method, and it was found that the recovery for the investigated elements ranges from 98.5–101.2%. Quality control was also ensured by typical moss reference materials M2 and M3, prepared for the European Moss Survey (Steinnes et al. 1997b). The measured concentrations were in good agreement with the recommended values, Table 2.

Table 2
Found and certified content of Al, Cd, Cr, Cu, Fe, Ni, Pb and Zn in referent moss samples M2 and M3 (Steinnes et al. 1997b)

| | M2 | | M3 | |
|---|---|---|---|---|
| Element | Found | Certified | Found | Certified |
| Al | 167 ± 3 | 178 ± 15 | 178 ± 5 | 169 ± 10 |
| Cd | 0.43 ± 0.03 | 0.45 ± 0.019 | 0.177 ± 0.02 | 0.106 ± 0.005 |
| Cr | 0.96 ± 0.06 | 0.97 ± 0.17 | 1.50 ± 0.08 | 0.67 ± 0.19 |
| Cu | 59.2 ± 2.8 | 68.7 ± 2.5 | 4.58 ± 0.14 | 3.76 ± 0.23 |
| Fe | 262 ± 14 | 262 ± 35 | 192 ± 12 | 138 ± 12 |
| Ni | 14.7 ± 0.6 | 16.3 ± 0.9 | 1.14 ± 0.08 | 0.95 ± 0.08 |
| Pb | 5.67 ± 0.52 | 6.37 ± 0.43 | 3.63 ± 0.39 | 3.33 ± 0.25 |
| Zn | 32.5 ± 0.9 | 36.1 ± 1.2 | 26.2 ± 0.78 | 25.4 ± 1.1 |

To determine Cd, Ni, and Pb, the isotopes $^{60}$Ni, $^{114}$Cd, and $^{206}$Pb, $^{207}$Pb, $^{208}$Pb, inductively coupled plasma-mass spectrometry, ICP-MS (Plasma Quant ICP-MS, Analytic Jena, Germany) was used. External calibration was performed by measuring standard solutions of these elements at 0.5, 1, 2, 5, 10 and 100 µg/L concentrations for following isotopes $^{114}$Cd, and Pb ($^{206}$Pb, $^{207}$Pb, $^{208}$Pb). No internal standards were used. Detector attenuation mode was used to cover a wide range of linearity without collision gas. For the problematic isotopes such as $^{60}$Ni, He was used as collision gas. $^{60}$Ni was determinate by external calibration in the range of 1, 5, 10, 50, 100 and 500 µg/L. The instrument software automatically calculated the limit of detection and quantification (Aspect MS 4.3, 2017). Standard solutions were inserted into the sample sequence at every 20 samples to verify sensitivity and repeatability. The recoveries of these elements were 82.1–105.1%.

# Statistical analysis

Distribution maps of elements and basic and multivariate statistical analyses were performed on the data obtained from the chemical analysis of mosses samples. Statistica 13 software package (StatSoft, Inc., Tulsa, OK, USA), whereas the data visualisation was performed employing several software packages: Statistica 13 (StatSoft, Inc., Tuls, OK, USA), QGIS and Surfer 17 (Golden Software, Inc., Golden, CO, USA). Some of the fundamental statistical quantities calculated were the mean, median, minimum, maximum, tenth percentile, ninetieth percentile, standard deviation, coefficient of variation, standard deviation (standard error), MAD (median absolute deviation), skewness, kurtosis. Pearson correlation coefficients were calculated for all the elements concentration in samples, and values 0.30 and higher were considered significant. Principal component analysis was performed to reveal the possible polluted sites, and sampling sites were plotted in two principal components graphs.

# Pollution indices

Contamination factor (CF) (Fernández and Carballeira 2001) and pollution load index (PLI) were calculated (Tomlinson et al. 1980), for pollution level evaluation. The formula for calculation of CF used to evaluate the pollution of a single heavy metal in the mosses samples is:

$$CF = \frac{C^{i}_{sample}}{C^{i}_{reference}}$$

Where CF is the contamination factor for heavy metal; $C^{i}_{sample}$ is the measured value of the heavy metal in mosses; $C^{i}_{reference}$ the median of the heavy metal in Norway mosses samples in this study. CF values are categorized as follows (Fernández and Carballeira 2001): CF < 1 – no contamination, 1 ≤ CF ≤ 2 – suspected contamination, 2 ≤ CF ≤ 3.5 – slightly contaminated, and 3.5 ≤ CF ≤ 8 – moderate, 8 ≤ CF ≤ 27 severe, and CF > 27 extreme contamination factor.

The pollution load index of one sampling site is calculated as the n-th root of the product of n CFs of the metals (Tomlinson et al. 1980):

$$PLI_{site} = \sqrt[n]{CF_1 x CF_2 x \ldots CF_n}$$

Whereas the PLI of the entire area (in this case, the territory of Kosovo) is calculated as per the following formula:

$$PLI_{zone} = \sqrt[n]{site_1 x site_2 x \ldots site_n}$$

Where *site* is sampling site and *n* is the number of sampling sites. The obtained PLI values are categorized as follows (Zhang et al. 2011): PLI = 0 background concentration, 0 < PLI ≤ 1 unpolluted, 1 < PLI ≤ 2 moderately to unpolluted, 2 < PLI ≤ 3 moderately polluted, 3 < PLI ≤ 4 moderately to highly polluted, 4 < PLI ≤ 5 highly polluted, and PLI > 5 very highly polluted.

# Results And Discussion

The determination of eight heavy metals was performed in 45 moss samples collected throughout the Kosovo territory (Fig. 2). To better present and understand the concentrations which resulted from the chemical analysis, the crude data were processed by statistical methods. In Table 3, descriptive statistics quantities are presented. In the table, high concentrations of Al and Fe stand out of all heavy metals studied in this work. High concentrations of these heavy metals are always expected as they are the prevailing heavy metals of the earth's crust. Zn and Pb also occur in high concentrations. The order of median concentration of the analysed metals is, Al > Fe > Zn > Pb > Cu > Cr > Ni > Cd. A striking difference between the maximum concentration and the 90th percentile can be observed for Ni and Pb. Although the maximum concentrations of these two elements are very high – 79 mg/kg for Ni and 38 mg/kg for Pb - their 90th percentiles are only 6.1 mg/kg and 10 mg/kg correspondingly. A big difference between the maximum concentration of 150 mg/kg and the P90 49 mg/kg was also found of Zn. The big difference between these two statistical quantities indicates different zones over the study area with the presence of particular heavy metals, which can also mean a presence of pollution. The high skewness and kurtosis values indicate that the distribution of concentrations of heavy metals in moss samples is not normal. Except for Pb and Ni, the concentration distributions of all other heavy metals fit more closely the lognormal distribution. Pb and Ni also have a high coefficient of variation, most probably arising from the artificial introduction of these two elements in the environment.

Table 3
Descriptive statistic of measurements for moss samples (in mg/kg)

| Element | X | Md | Min | Max | P10 | P90 | S | CV | $S_X$ | MAD | A | E |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al[a] | 1100 | 890 | 480 | 2700 | 600 | 1900 | 520 | 48 | 77 | 230 | 1.32 | 1.26 |
| Cd[b] | 0.48 | 0.36 | 0.16 | 2.1 | 0.23 | 0.80 | 0.38 | 78 | 0.056 | 0.11 | 2.59 | 7.69 |
| Cr[a] | 3.1 | 2.6 | 0.93 | 10.1 | 1.5 | 5.5 | 1.8 | 58 | 0.27 | 1.0 | 1.64 | 3.90 |
| Cu[a] | 3.9 | 3.9 | 2.6 | 8.1 | 2.9 | 4.6 | 0.94 | 24 | 0.14 | 0.52 | 2.14 | 8.00 |
| Fe[a] | 920 | 820 | 430 | 2000 | 530 | 1400 | 390 | 42 | 58 | 200 | 1.09 | 0.47 |
| Ni[b] | 4.4 | 1.7 | 0.46 | 79 | 0.82 | 6.1 | 12 | 270 | 1.8 | 0.75 | 5.98 | 37.83 |
| Pb[b] | 6.6 | 7.3 | 0.58 | 38 | 0.63 | 10 | 6.0 | 90 | 0.89 | 2.5 | 3.24 | 16.78 |
| Zn[a] | 36 | 31 | 20 | 150 | 23 | 49 | 21 | 58 | 3.1 | 5.2 | 3.97 | 18.82 |

X - arithmetical mean, Md - median, Min - minimum, Max - maximum, P10–10 percentile, P90–90 percentile, S - standard deviation, $S_X$ - standard error of mean, CV - coefficient of variation, MAD—median absolute deviation, A -skewness, E - kurtosis, a - Determined by ICP-AES, b - Determined by ICP-MS.

# Spatial distribution

Spatial distribution maps of studied heavy metals are presented in Fig. 3. Al and Fe show very similar distribution patterns. Their highest concentrations are found in the east of Kosovo as well as around the centre. The maximum concentration of these two metals is found in Siboc municipality of Obiliq, 2700 mg/kg for Al and 2000 mg/kg for Fe. High concentrations of Al and Fe are expected as they are the most abundant metals naturally present in the soil, reaching mosses under wind and precipitation. However, the anthropogenic origin cannot be entirely excluded (Ötvös et al., 2003). The maximum Fe concentration in the present moss survey (2000 mg/kg) is lower than that of the 2010 survey, which was 3082 mg/kg, but the median is higher, 820 mg/kg vs 288 mg/kg (Maxhuni et al. 2016). Noteworthy is that the difference between the present heavy metals concentration in mosses and that of the 2010 survey cannot be taken as entirely valid as the sampling locations are not the same, and the number of sampling points is more significant in the present study. This should be considered every time the 2010 survey is referred to in this work. As can be seen in the distribution map, the lowest concentration of both elements is primarily found in the South and the most North of the sampling area. Both metals are primarily present in the districts of Prishtina and Gjilani. Geologically they are mainly present in the areas of clastites of Neogene-Paleogene and flysch of Mesozoic, where they occur in fine soil particles owing to rock weathering under atmospheric conditions and geological processes, whereby transferred in moss by wind and precipitations.

Zinc, lead, and copper come next as the most concentrated heavy metals in mosses samples in the territory of Kosovo. All three are found around pollution sources, such as lead and zinc Trepça mines and ore processing units, ferronickel smelter in Drenas, the coal power plant in Obiliq, and the cement production plant Hani i

Elezit. The elements in the just mentioned areas are clearly of anthropogenic origin. Zn is found at highest concentrations in the North of Kosovo at sampling points Zveqan 86 mg/kg and Stanterg 146 mg/kg, then in Çikatovë 64 mg/kg and Shalc 61 mg/kg. All those points in the district of Mitrovica where Zn concentration is the highest are shown in Fig. 3. The median of Zn is lower than in the 2010 survey; the maximum is around twice as high. The median and max of Pb are slightly lower than in 2010, whereas the median of Cu is higher and the maximum lower than in 2010. The median concentration of Zn and Pb are higher than in Albania, North Macedonia and Norway, except for Zn, which median is the same as in Norway (Steinnes et al. 2016; Lazo et al. 2018; Stafilov et al. 2018).

On the contrary, the median concentration of Cu was lower than in the countries mentioned above. The highest concentration of Zn corresponds with the geologic formation of the Magmatic rocks of Neogene-Paleogene, which are located around the same sampling sites. Lead is more present in the North, South-West, and the South-East, with concentrations lower than Zn and more heterogeneously distributed. Districts with the highest concentration of Pb are Mitrovica and Prizren, whereas according to geological composition, Pb reaches the highest concentrations in Magmatic rocks of Paleogene-Neogene. Pb shows a similar pattern to Zn because of the Lead/Zinc mines and smelter in Mitrovica, the primary source of these two heavy metals. Relatively high concentrations of Pb were found in the district of Prizren (7.9–10.08 mg/kg), although there is no industry involving Pb particularly. In this regard, it can be said that, apart from the traffic emissions coming from the roads and the highway, which pass just beside or join in the Prizren city, long-range atmospheric transport may also contribute to the overall Pb concentration in moss samples (Steinnes et al. 1997a; Steinnes 2001). Cu is mostly present From the North to the South in the districts of Mitrovica, Prishtina, Prizren, and Gjilan. Its highest concentration is found at the sampling site in Shalc, which is 8 mg/kg. Cu concentrations are lower than Zn and Pb, whereas they are more evenly spread than Pb. The districts with the highest concentrations lie in geologic formations where Cu concentration is also high. Because geologic areas where Cu concentration is higher do not always correspond with pollution sources, it may be thought that Cu occurs in mosses due to natural processes. Exceptionally high concentrations of these heavy metals in the North have also been reported for soil samples (Šajn et al. 2013; Kerolli-Mustafa et al. 2015b; Kastrati et al. 2021), which partly explains their concentration in mosses. Fine dust particles contaminated with heavy metals can become airborne during dry seasons and spread by the wind in larger areas. But emissions during the processing can also be spread and settle over a vast territory under gravity or by precipitations.

Chromium and nickel have a spatial distribution somewhat similar. Their highest concentrations appear in the west, centre and the east of the sampling area. The highest concentrations of Cr are those in sampling points Prapashticë 10 mg/kg, Reqan 6.6 mg/kg, and Lupç 5.9 mg/kg. Cr and Ni medians are only slightly smaller than the 2010 survey in Kosovo. In contrast, medians of these two heavy metals are lower than those of Albania and North Macedonia but higher than Norway (always surveys of 2015). Prishtina is the district where Cr is at the highest concentration, followed by Prizren, and Peja. Geological formations that contain mostly Cr are clastic sediments of Neogene-Paleogene, whereas it is found at the lowest concentrations in carbonate and metamorphic formations of Paleozoic. Ni represents an outstanding peak in sampling point Harilaq 79 mg/kg, then in Llapushnik 19.8 mg/kg, and Çikataovë 11.6 mg/kg. These high concentrations compared to other samples are expected as the three sampling points are located just close to the Ferro-Nickel facilities and are a result of direct pollution. Ni is most present in samples of the District of Prishtina, whereas Magmatic rocks of Mesozoic are the geologic areas where it is present mostly, with a very high difference compared to other geologic formations. The three sampling points with peak Ni concentration also fall in the areas of Mesozoic rocks, but outstandingly higher concentrations than in other Mesozoic rocks areas indicate the presence of pollution.

Cadmium is the heavy metal with the lowest concentration in mosses samples in the territory of Kosovo. Cd concentrations are the highest in sampling points Stanterg 2 mg/kg and Zveqan 1.7 mg/kg, Siboc 1.15 mg/kg, Te Kalaja 1 mg/kg, Kaçanik 0.8 mg/kg. All these sampling points correspond to sites where pollution is expected because of industrial activities. Cd median is greater than that of the 2010 survey in Kosovo, as well as it is greater than the medians found in Albania, North Macedonia, and Norway (2015 surveys). Districts with the highest concentrations of Cd are Mitrovica and Gjilani. In contrast, according to geological formations, it is Magmatic rocks of Paleogene-Neogene the formation with the highest concentration, and Carbonates of Paleozoic come second.

# Multivariate analysis

Multivariate statistical analyses were carried out to identify the pollution or geogenic origin of heavy metals studied. In Table 4, Pearson correlation coefficients are given for each combination of elements, where six significant correlations can be seen, all with a p-value under 0.05. The strongest correlation for Al and Fe with a value of 0.936 was observed, then Zn and Cd with 0.858. Strong correlation coefficients showed the pairs Fe – Cr (0.751) and Al - Cr (0.656), whereas there was only one moderate correlation Pb – Cd (0.437). Other correlations were weak or very weak.

Table 4

Pearson correlation coefficients between element concentrations in mosses in Kosovo

| Elements | Al | Cd | Cr | Cu | Fe | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| Al | 1.000 | | | | | | | |
| Cd | -0.068 | 1.000 | | | | | | |
| Cr | 0.656 | -0.146 | 1.000 | | | | | |
| Cu | 0.035 | 0.173 | 0.027 | 1.000 | | | | |
| Fe | 0.936 | -0.094 | 0.751 | 0.037 | 1.000 | | | |
| Ni | -0.059 | -0.086 | 0.193 | -0.155 | 0.203 | 1.000 | | |
| Pb | 0.069 | 0.437 | -0.092 | 0.037 | 0.018 | -0.174 | 1.000 | |
| Zn | -0.075 | 0.858 | -0.069 | 0.213 | -0.048 | -0.035 | 0.351 | 1.000 |

Principal component analysis (PCA) was performed to identify possible patterns of heavy metals distribution in mosses samples and potentially polluted areas and pollution sources. The results obtained are shown in Fig. 4. The PCA analysis produced two principal components (PCs); the first PC accounted for 33.42% of the total variance and the second PC for 26.81% of it. Sampling sites could be visualised in the plot of scores of PC1 and PC2. In the PCs score plot can be easily noticed the two sampling sites, Zveqan and Stanterg, which score highly on PC2 and on PC1 almost just as well. Shalc score is also relatively high in PC2. This result can be explained by the loading plot of the variables shown just under the samples plot. It can be seen that Zn, Cd, and Pb also load highly on PC2 and to some value on PC1 also, and the direction of the vectors in PCs loading plot are similar, as it is the placement of the sampling points Zveqan and Stanerg in the PCs score plot.

Similarly, can be argued for Shalc. The angle between Zn, Pb, and Cd vectors is also tiny, particularly for Zn and Cd, which indicates a high correlation between these heavy metals. Cu vector is shorter but still considerably in a slight angle with the Zn, Cd, and Pb vectors, meaning that it is correlated with these metals and related with the sampling points Zveqan, Stanterg, and Shalc. A high correlation of these elements and the vectors' directions show that Stanterg and Zveqan have high scores primarily due to these elements' high presence in that area. This is a consequence of the Trepça mining and ore enrichment processes and mineral tailing dump just in the South of Mitrovica city (Šajn et al. 2013; Kerolli-Mustafa et al. 2015a). To a lesser extent sampling point, Vidishiq-Bare was also influenced by those four elements, but more significantly by Cd and Zn, as their vectors' directions are slightly closer to this point. The provenance of these heavy metals in this area is from Trepça's facilities, as it is located just a few kilometres in the North.

As the variables loading plot shows, all the sampling sites in the fourth quadrant of the sampling points PCA plot (Fig. 4) are mainly influenced by heavy metals of geogenic origin. Sampling point Siboc (28) scored highly in both PCs, and Prapashticë, Lupç, and Reqan scored highly on PC1. The high scores of these sampling sites can be explained by high values of the variables Al, Fe, and Cr. Although Al, Fe, and Cr are mostly of geogenic origin, their exceptionally high concentrations in the moss sample of Siboc reveal the atmospheric pollution effect of coal digging and burning in electricity plants in Obiliq. A high concentration of Pb was also found in Siboc (12.5 mg/kg), and this site is among those with the highest Cu concentration too (4.5 mg/kg). This can explain the fact that Siboc tends slightly to the left closer to Cu and Pb vectors, which reveals the contribution of these two elements in its score. Thus, an overlap of polluted air currents emerging from Mitrovica (Trepça plant) and Obiliq (electricity power plant) is expected in this sampling point and almost all along the Kosovo basin. Cr, not being a crustal element but present in this group of elements, also may be an indicator of the pollution effect of electricity plants.

Moreover, Cr was found at relatively high concentrations in the fly ash of lignite used to power the electricity plant (Kittner et al., 2018). However, Cr content in most of the moss samples is probably of geogenic origin. They are not close to industrialised sites, such as Prapashticë and Reqan, where the highest concentration is. Harilaq scores relatively high in PC1 and PC2 primarily due to the high presence of Ni, and it reflects the atmospheric deposition of dust emitted majorly by the ferronickel mine in Magure, which is located just nearby, and probably also the geochemical composition of the surface soil of the area. As indicated by the direction of Ni vector, Izbicë, Janjevë, Llapushnik are also influenced by Ni, which can be transported there by winds from the ferronickel plant in Drenas and mine in Golesh. As can be seen in the variables loading plot, Cu, and mostly Ni do not show a significant correlation between them or any of the two already discussed groups. The score plot of the sampling points also indicates that most of them score around the origin or in the upper left quadrant of the PCs axes, which means that most of the samples are not strongly influenced by the variables under consideration.

# Pollution indices

To further estimate the atmospheric pollution level, the values of CF and PLI were calculated and are presented in Table 5. According to Fernandez's categorisation of the CF values (Fernández and Carballeira 2001), most of the CF of Cu also do not exceed 1 as well as those for Zn, except for Zn in sampling points Çikatovë with a CF = 2.1 which corresponds to slightly contaminated, and Zveqan CF = 2.8 and Stanterg CF = 4.7 as moderately contaminated. Ni shows variable CF values, among those four sampling sites correspond to moderate contamination, two severe and one has extreme contamination factor. Severe CF was found in Llapushnik and Çikatovë, whereas extreme CF resulted in Harilaq. In the case of Al and Fe all sampling sites lie in the moderate contamination category or lower. Cr has three sampling sites with severe CF and one with extreme contamination. Cd CF values are the highest for 10 moss samples and fall in the extreme contamination category. All moss samples with high CF are located near industrial facilities discussed previously, except Kukljan where no industrial activities are performed. The CF value of this site is in the lower limit of the severe category (8.9). The highest CF appears to be for Pb. Most of the sampling sites fall in the extreme contamination factor with values over 100, and the rest of the samples correspond to the severe contamination category.

**Table 5** Contamination factor (CF) values for heavy metals measured in 45 moss samples

(in mg/kg)

| Sampling site | Al | Cd | Cr | Cu | Fe | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| *1* | 1.5 | 8.9 | 3.1 | 1.1 | 1.9 | 1.1 | 158.0 | 0.9 |
| *2* | 1.7 | 3.9 | 3.3 | 1.1 | 2.1 | 1.0 | 179.0 | 0.9 |
| *3* | 1.0 | 4.5 | 2.2 | 0.9 | 1.4 | 0.7 | 180.7 | 1.1 |
| *4* | 1.2 | 8.9 | 1.3 | 1.0 | 1.5 | 0.4 | 11.9 | 0.9 |
| *5* | 3.1 | 7.7 | 4.0 | 0.8 | 3.5 | 1.0 | 206.6 | 0.7 |
| *6* | 2.5 | 10.0 | 4.0 | 1.0 | 3.0 | 0.8 | 145.9 | 0.9 |
| *7* | 1.7 | 5.1 | 5.1 | 0.6 | 2.3 | 4.9 | 201.7 | 1.1 |
| *8* | 3.3 | 3.4 | 6.1 | 1.0 | 3.5 | 1.5 | 196.2 | 0.9 |
| *9* | 4.0 | 4.9 | 9.4 | 1.1 | 4.6 | 2.8 | 25.5 | 0.9 |
| *10* | 2.8 | 4.0 | 3.2 | 1.1 | 3.6 | 1.0 | 173.7 | 1.1 |
| *11* | 1.3 | 2.9 | 1.8 | 0.8 | 1.9 | 0.7 | 139.2 | 0.8 |
| *12* | 2.6 | 5.9 | 2.1 | 0.8 | 2.9 | 3.3 | 58.6 | 0.9 |
| *13* | 1.3 | 2.8 | 7.3 | 0.7 | 2.2 | 7.2 | 11.8 | 0.7 |
| *14* | 1.8 | 2.9 | 4.9 | 0.7 | 2.7 | 5.5 | 192.6 | 0.8 |
| *15* | 1.5 | 3.6 | 2.6 | 0.9 | 1.9 | 1.0 | 170.7 | 0.9 |
| *16* | 1.6 | 5.1 | 2.6 | 0.7 | 2.1 | 1.0 | 185.1 | 0.7 |
| *17* | 3.2 | 3.3 | 5.0 | 0.9 | 4.4 | 0.8 | 137.1 | 0.8 |
| *18* | 2.0 | 4.5 | 4.8 | 0.8 | 2.8 | 3.4 | 147.6 | 0.8 |
| *19* | 2.1 | 5.6 | 3.8 | 0.9 | 2.5 | 2.3 | 12.5 | 0.9 |
| *20* | 1.6 | 3.7 | 2.9 | 0.7 | 2.0 | 1.5 | 166.1 | 1.0 |
| *21* | 1.5 | 4.6 | 6.8 | 1.1 | 2.6 | 18.0 | 33.6 | 1.0 |
| *22* | 2.0 | 4.0 | 5.7 | 0.7 | 4.5 | 72.2 | 36.3 | 1.0 |
| *23* | 2.6 | 3.9 | 5.1 | 1.0 | 3.2 | 1.8 | 75.6 | 1.3 |
| *24* | 4.1 | 4.8 | 6.2 | 0.9 | 5.2 | 1.8 | 181.4 | 1.2 |
| *25* | 1.3 | 12.3 | 1.7 | 1.0 | 1.7 | 0.5 | 45.8 | 1.3 |
| *26* | 1.9 | 5.9 | 3.0 | 0.9 | 2.7 | 2.7 | 54.3 | 1.2 |
| *27* | 2.4 | 9.6 | 8.5 | 1.1 | 4.0 | 10.5 | 53.0 | 2.1 |
| *28* | 6.0 | 14.4 | 7.9 | 1.1 | 6.5 | 2.1 | 249.5 | 1.6 |
| *29* | 1.5 | 2.0 | 2.8 | 0.9 | 2.2 | 1.1 | 11.6 | 0.8 |
| *30* | 4.5 | 5.2 | 14.4 | 0.8 | 5.6 | 3.6 | 150.0 | 1.1 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *31* | 1.9 | 2.2 | 2.8 | 0.9 | 2.6 | 1.1 | 12.0 | 0.8 |
| *32* | 1.9 | 3.2 | 2.6 | 0.8 | 2.1 | 0.8 | 12.9 | 0.8 |
| *33* | 3.6 | 2.8 | 6.7 | 0.8 | 3.6 | 1.7 | 111.2 | 0.7 |
| *34* | 1.9 | 10.0 | 5.4 | 1.9 | 2.9 | 2.2 | 87.5 | 2.0 |
| *35* | 4.5 | 3.1 | 4.8 | 0.8 | 4.7 | 1.3 | 183.5 | 0.9 |
| *36* | 2.3 | 3.4 | 2.3 | 0.8 | 2.8 | 0.7 | 138.3 | 0.8 |
| *37* | 4.1 | 2.1 | 8.4 | 0.8 | 5.8 | 2.6 | 147.4 | 1.0 |
| *38* | 3.9 | 3.0 | 4.8 | 1.1 | 4.6 | 1.7 | 152.9 | 1.2 |
| *39* | 1.7 | 8.8 | 2.5 | 0.9 | 2.2 | 1.1 | 27.2 | 1.4 |
| *40* | 1.2 | 3.2 | 2.1 | 0.8 | 1.6 | 2.9 | 161.6 | 1.1 |
| *41* | 1.4 | 20.9 | 2.1 | 1.0 | 2.0 | 0.9 | 760.3 | 2.8 |
| *42* | 1.6 | 25.7 | 2.3 | 0.8 | 2.0 | 1.1 | 177.8 | 4.7 |
| *43* | 1.2 | 6.0 | 2.2 | 1.4 | 1.7 | 0.9 | 245.5 | 1.3 |
| *44* | 1.8 | 3.4 | 5.3 | 0.6 | 2.4 | 2.5 | 141.4 | 1.0 |
| *45* | 1.8 | 4.9 | 3.2 | 1.0 | 2.4 | 1.4 | 31.8 | 1.2 |

The $PLI_{Site}$ values for eight heavy metals throughout the sampling area, and then only for four of them, are shown in Fig. 5. According to Zhang (Zhang et al. 2011) PLI categorisation, none of the moss sampling sites falls in the unpolluted category site (Fig. 5a). Four samples fall in the unpolluted to moderately category, 13 are moderately polluted, 17 are moderate to highly contaminated, eight correspond with the highly polluted type, and very highly polluted are three of them. The $PLI_{zone}$ for the whole territory of Kosovo when all eight elements were included in the calculation was 3.4, which corresponds to the moderately to highly polluted category. However, when only Cd, Cr, Ni, and Pb were included in PLI calculation, three sampling sites were put in the moderately polluted category. Only one in moderate to highly polluted, three in highly polluted, and 38 samples correspond to the highly polluted type (Fig. 5b). The $PLI_{zone}$ of the entire study area now is 7.4, which is just within the threshold of the very highly polluted category.

# Conclusion

The estimation of atmospheric deposition of heavy metals in the territory of Kosovo was performed using mosses as bioindicators. The concentrations measured in mosses samples vary greatly between heavy metals and the single metals in different sampling sites. Exceptionally high concentrations of Zn and Pb were found around the Trepça mining area of Mitrovica. However, both these heavy metals are present in considerably high concentrations in most of the studied areas, including locations where no great pollution sources exist. For this reason, more studies are required to establish if long-range transport from known pollution sources is the main contributor to the content of these heavy metals in mosses or if the geochemical composition of the soil is more significant. Ni, Cr, and Cd also showed spikes of concentrations around industrial sites. Principal component analysis revealed polluted areas such as Zveqan (41) Stanterg (42) polluted with Zn, Cd, and Pb. Then Siboc (28), Reqan (9), Prapashticë (30), and Lupç (37), with high contents of Al, Fe, and Cr, and the rest of the samples which were more similarly affected by the metals und consideration. Harilaq (22) was found to be polluted majorly with Ni. Based on distribution maps and the PCA analysis, the most significant sources of heavy metal pollution appear to be: Trepça mining and ore processing facilities in Mitrovica, Artana, and Kishnica, then ferronickel smelter in Drenas and mine in Golesh, thermoelectric power plant in Obiliq, and cement production plant in Hani i Elezit. Urban areas such as Prishtina city also contribute to pollution from heavy traffic, coal combustion for house heating and various local businesses.

According to CF values, only Cu and Zn in most sampling sites are not present at concentration when contamination is to be considered. All other heavy metals are found in some contamination category. CF shows that Pb content in mosses is not only in a very extreme contamination category, but extremely high compared to the begging limit of this category which is 27. $PLI_{site}$ values in none of the samples correspond to the unpolluted class when all the heavy metals are taken in the calculation. Its values increase even more when only Cd, Cr, Ni, and Pb are included in the analysis. Thirty-eight (38) sites of the sampling area fall in the highest pollution category for these four heavy metals.

# Declarations

### Acknowledgement

We want to thank the Kosovo Agency for Environment Protection and Mr Afrim Berisha for collaborating on this research project.

**Funding**: The authors have no relevant financial or non-financial interests to disclose.

**Conflicts of interest/Competing interests**: the authors have no conflicts of interest to declare anything relevant to the content of this article.

**Availability of data and material**: all data generated or analysed during this study are included in this published article.

**Code availability**: not applicable.

**Authors' contributions**: Conceptualization: [Musaj Paçarizi, Trajče Stafilov], Methodology: [Trajče Stafilov, Musaj Paçarizi, Flamur Sopaj, Krste Tašev]; Formal analysis and investigation: [Flamur Sopaj, Musaj Paçarizi, Robert Šajn]; Writing - original draft preparation: [Flamur Sopaj]; Writing - review and editing: [Trajče Stafilov, Robert Šajn, Musaj Paçarizi].

# References

1. Abuduwailil J, Zhaoyong Z, Fengqing J (2015) Evaluation of the pollution and human health risks posed by heavy metals in the atmospheric dust in Ebinur Basin in Northwest China. Environ Sci Pollut Res 22:14018–14031. https://doi.org/10.1007/s11356-015-4625-1

2. Arditsoglou A, Samara C (2005) Levels of total suspended particulate matter and major trace elements in Kosovo: A source identification and apportionment study. Chemosphere 59:669–678. https://doi.org/10.1016/j.chemosphere.2004.10.056
3. Azuma M, Obayashi A, Kondoh M et al (2000) Removal of cadmium ion by the moss Pohlia flexuosa. Elsevier Masson SAS
4. Barandovski L, Frontasyeva MV, Stafilov T et al (2015) Multi-element atmospheric deposition in Macedonia studied by the moss biomonitoring technique. Environ Sci Pollut Res 22:16077–16097. https://doi.org/10.1007/s11356-015-4787-x
5. Duce RA, Hoffman GL, Zoller WH (1975) Atmospheric trace metals at remote northern and southern hemisphere sites: Pollution or natural? Science 187:59–61. https://doi.org/10.1126/science.187.4171.59
6. Fernández JA, Carballeira A (2001) Evaluation of contamination, by different elements, in terrestrial mosses. Arch Environ Contam Toxicol 40:461–468. https://doi.org/10.1007/s002440010198
7. Harmens H, Norris DA, Steinnes E et al (2010) Mosses as biomonitors of atmospheric heavy metal deposition: Spatial patterns and temporal trends in Europe. Environ Pollut 158:3144–3156. https://doi.org/10.1016/j.envpol.2010.06.039
8. Järup L (2003) Hazards of heavy metal contamination. Br Med Bull 68:167–182. https://doi.org/10.1093/bmb/ldg032
9. Kabashi S, Bekteshi S, Jonuzaj A, Zidanšek A (2011) Dynamic modeling of air pollution and acid rain from energy system and transport in Kosovo. Proc 24th Int Conf Effic Cost. Optim Simul Environ Impact Energy Syst ECOS 2011 2012:2803–2823. https://doi.org/10.4236/ojap.2012.13011
10. Kampa M, Castanas E (2008) Human health effects of air pollution. Environ Pollut 151:362–367. https://doi.org/10.1016/j.envpol.2007.06.012
11. Kastrati G, Paçarizi M, Sopaj F et al (2021) Investigation of concentration and distribution of elements in three environmental compartments in the region of mitrovica, kosovo: Soil, honey and bee pollen. Int J Environ Res Public Health 18:1–17. https://doi.org/10.3390/ijerph18052269
12. Kelly FJ, Fussell JC (2011) Air pollution and airway disease. Clin Exp Allergy 41:1059–1071. https://doi.org/10.1111/j.1365-2222.2011.03776.x
13. Kerolli-Mustafa M, Ćurković L, Fajković H, Rončević S (2015a) Ecological risk assessment of jarosite waste disposal. Croat Chem Acta. https://doi.org/10.5562/cca2554
14. Kerolli-Mustafa M, Fajković H, Rončević S, Ćurković L (2015b) Assessment of metal risks from different depths of jarosite tailing waste of Trepça Zinc Industry, Kosovo based on BCR procedure. J Geochemical Explor 148:161–168. https://doi.org/10.1016/j.gexplo.2014.09.001
15. Khan A, Khan S, Khan MA et al (2015) The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: a review. Environ Sci Pollut Res 22:13772–13799. https://doi.org/10.1007/s11356-015-4881-0
16. Kittner N, Fadadu RP, Buckley HL et al (2018) Trace Metal Content of Coal Exacerbates Air-Pollution-Related Health Risks: The Case of Lignite Coal in Kosovo. Environ Sci Technol 52:2359–2367. https://doi.org/10.1021/acs.est.7b04254

17. Klavina L, Springe G, Nikolajeva V et al (2015) Chemical composition analysis, antimicrobial activity and cytotoxicity screening of moss extracts (Moss Phytochemistry). Molecules 20:17221–17243. https://doi.org/10.3390/molecules200917221
18. Kord B, Mataji A, Babaie S (2010) Pine (Pinus Eldarica Medw.) needles as indicator for heavy metals pollution. Int J Environ Sci Technol 7:79–84. https://doi.org/10.1007/BF03326119
19. Lantzy RJ, Mackenzie FT (1979) Atmospheric trace metals: global cycles and assessment of man's impact. Geochim Cosmochim Acta 43:511–525. https://doi.org/10.1016/0016-7037(79)90162-5
20. Lazo P, Stafilov T, Qarri F et al (2019) Spatial distribution and temporal trend of airborne trace metal deposition in Albania studied by moss biomonitoring. Ecol Indic 101:1007–1017. https://doi.org/10.1016/j.ecolind.2018.11.053
21. Lazo P, Steinnes E, Qarri F et al (2018) Origin and spatial distribution of metals in moss samples in Albania: A hotspot of heavy metal contamination in Europe. Chemosphere 190:337–349. https://doi.org/10.1016/j.chemosphere.2017.09.132
22. Li J, Xue Q, Fang L, Poon CS (2017) Characteristics and metal leachability of incinerated sewage sludge ash and air pollution control residues from Hong Kong evaluated by different methods. Waste Manag 64:161–170. https://doi.org/10.1016/j.wasman.2017.03.033
23. Macedo-Miranda G, Avila-Pérez P, Gil-Vargas P et al (2016) Accumulation of heavy metals in mosses: a biomonitoring study. Springerplus 5:. https://doi.org/10.1186/s40064-016-2524-7
24. MacNee W, Donaldson K (2003) Mechanism of lung injury caused by PM10 and ultrafine particles with special reference to COPD. Eur Respir Journal Suppl 21:47–51. https://doi.org/10.1183/09031936.03.00403203
25. Mahapatra B, Dhal NK, Dash AK et al (2019) Perspective of mitigating atmospheric heavy metal pollution: using mosses as biomonitoring and indicator organism. Environ Sci Pollut Res 26:29620–29638. https://doi.org/10.1007/s11356-019-06270-z
26. Mansha M, Ghauri B, Rahman S, Amman A (2012) Characterisation and source apportionment of ambient air particulate matter (PM2.5) in Karachi. Sci Total Environ 425:176–183. https://doi.org/10.1016/j.scitotenv.2011.10.056
27. Maxhuni A, Lazo P, Kane S et al (2016) First survey of atmospheric heavy metal deposition in Kosovo using moss biomonitoring. Environ Sci Pollut Res 23:744–755. https://doi.org/10.1007/s11356-015-5257-1
28. McDonnell TC, Reinds GJ, Wamelink GWW et al (2020) Threshold effects of air pollution and climate change on understory plant communities at forested sites in the eastern United States. Environ Pollut 262:114351. https://doi.org/10.1016/j.envpol.2020.114351
29. Nriagu JO (1989) A global assessment of natural sources of atmospheric trace metals. Nature 338:47–49
30. Ötvös E, Pázmándi T, Tuba Z (2003) First national survey of atmospheric heavy metal deposition in Hungary by the analysis of mosses. Sci Total Environ 309:151–160. https://doi.org/10.1016/S0048-9697(02)00681-2
31. Pacyna EG, Pacyna JM, Fudala J et al (2007) Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. Atmos Environ 41:8557–8566.

https://doi.org/10.1016/j.atmosenv.2007.07.040

32. Pandey N, Sharma CP (2002) Effect of heavy metals Co2+, Ni2 + and Cd2 + on growth and metabolism of cabbage. Plant Sci 163:753–758. https://doi.org/10.1016/S0168-9452(02)00210-8
33. Qarri F, Lazo P, Stafilov T et al (2014) Multi-elements atmospheric deposition study in Albania. Environ Sci Pollut Res 21:2506–2518. https://doi.org/10.1007/s11356-013-2091-1
34. Reis LSL, de S, Pardo, Camargos PE, Oba AS E (2010) Mineral element and heavy metal poisoning in animals. J Med Med Sci 1:560–579
35. Ribeiro AG, Downward GS, Freitas CU de et al (2019) Incidence and mortality for respiratory cancer and traffic-related air pollution in São Paulo, Brazil. Environ Res 170:243–251. https://doi.org/10.1016/j.envres.2018.12.034
36. Roberts AW, Roberts EM, Haigler CH (2012) Moss cell walls: Structure and biosynthesis. Front Plant Sci 3:1–7. https://doi.org/10.3389/fpls.2012.00166
37. Rocher V, Azimi S, Gasperi J et al (2004) Hydrocarbons and metals in atmospheric deposition and roof runoff in central Paris. Water Air Soil Pollut 159:67–86. https://doi.org/10.1023/B:WATE.0000049165.12410.98
38. Romo-Kröger CM, Morales JR, Dinator MI et al (1994) Heavy metals in the atmosphere coming from a copper smelter in Chile. Atmos Environ 28:705–711. https://doi.org/10.1016/1352-2310(94)90047-7
39. Rühling Å, Tyler G (2004) Changes in the atmospheric deposition of minor and rare elements between 1975 and 2000 in south Sweden, as measured by moss analysis. Environ Pollut 131:417–423. https://doi.org/10.1016/j.envpol.2004.03.005
40. Šajn R, Aliu M, Stafilov T, Alijagić J (2013) Heavy metal contamination of topsoil around a lead and zinc smelter in Kosovska Mitrovica/Mitrovicë, Kosovo/Kosovë. J Geochemical Explor 134:1–16. https://doi.org/10.1016/j.gexplo.2013.06.018
41. Schröder W, Nickel S (2019) Spatial structures of heavy metals and nitrogen accumulation in moss specimens sampled between 1990 and 2015 throughout Germany. Environ Sci Eur 31:1–15. https://doi.org/10.1186/s12302-019-0216-y
42. Shahid M, Dumat C, Khalid S et al (2017) Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake. J Hazard Mater 325:36–58. https://doi.org/10.1016/j.jhazmat.2016.11.063
43. Silva LT, Pinho JL, Nurusman H (2014) Traffic air pollution monitoring based on an air–water pollutants deposition device. Int J Environ Sci Technol 11:2307–2318. https://doi.org/10.1007/s13762-014-0625-9
44. Soltanali S, Shams Hagani Z, Pazouki Yaftabadi M (2008) Economic evaluation for air pollution control technologies selection in power plants processes. Int J Environ Sci Technol 5:555–564. https://doi.org/10.1007/BF03326053
45. Stafilov T, Šajn R, Barandovski L et al (2018) Moss biomonitoring of atmospheric deposition study of minor and trace elements in Macedonia. Air Qual Atmos Heal 11:137–152. https://doi.org/10.1007/s11869-017-0529-1
46. Steinnes E (2001) Metal contamination of the natural environment in Norway from long range atmospheric transport. Water Air Soil Pollut 1:449–460

47. Steinnes E, Allen RO, Petersen HM et al (1997a) Evidence of large scale heavy-metal contamination of natural surface soils in Norway from long-range atmospheric transport. Sci Total Environ 205:255–266. https://doi.org/10.1016/S0048-9697(97)00209-X
48. Steinnes E, Hanssen JE, Rambæk JP, Vogt NSB (1994) Atmospheric deposition of trace elements in Norway: Temporal and spatial trends studied by moss analysis. Water Air Soil Pollut 74:121–140. https://doi.org/10.1007/BF01257151
49. Steinnes E, Rühling Å, Lippo H, Mäkinen A (1997b) Reference materials for large-scale metal deposition surveys. Accredit Qual Assur 2:243–249. https://doi.org/10.1007/s007690050141
50. Steinnes E, Uggerud HT, Pfaffhuber KA, Torunn B (2016) Atmospheric deposition of heavy metals in Norway. 1–57
51. Suvarapu LN, Baek SO (2017) Determination of heavy metals in the ambient atmosphere: A review. Toxicol Ind Health 33:79–96. https://doi.org/10.1177/0748233716654827
52. Thayer JS, Brinckman FE (1982) The Biological Methylation of Metals and Metalloids
53. Thöni L, Yurukova L, Bergamini A et al (2011) Temporal trends and spatial patterns of heavy metal concentrations in mosses in Bulgaria and Switzerland: 1990–2005. Atmos Environ 45:1899–1912. https://doi.org/10.1016/j.atmosenv.2011.01.039
54. Tomlinson DL, Wilson JG, Harris CR, Jeffrey DW (1980) Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgoländer Meeresuntersuchungen 33:566–575. https://doi.org/10.1007/BF02414780
55. Trindade HA, Pfeiffer WC, Londres H, Costa-Ribeiro CL (1981) Atmospheric Concentration of Metals and Total Suspended Particulates in Rio de Janeiro. Environ Sci Technol 15:84–89. https://doi.org/10.1021/es00083a008
56. Vianna NA, Gonçalves D, Brandão F et al (2011) Assessment of heavy metals in the particulate matter of two Brazilian metropolitan areas by using Tillandsia usneoides as atmospheric biomonitor. Environ Sci Pollut Res 18:416–427. https://doi.org/10.1007/s11356-010-0387-y
57. Walsh PR, Duce RA, Fasching JL (1979) Considerations of the Enrichment, Sources, and Flux of Arsenic in the Troposphere. J Geophys Res 84:1719–1726. https://doi.org/10.1029/jc084ic04p01719
58. Webb AH, Bawden RJ, Busby AK, Hopkins JN (1992) Studies on the effects of air pollution on limestone degradation in Great Britain. Atmos Environ Part B Urban Atmos 26:165–181. https://doi.org/10.1016/0957-1272(92)90020-S
59. WELLS JM, BROWN DH (1990) Ionic control of intracellular and extracellular Cd uptake by the moss Rhytidiadelphus squarrosus (Hedw.) Warnst. New Phytol 116:541–553. https://doi.org/10.1111/j.1469-8137.1990.tb00538.x
60. Xia L, Gao Y (2011) Characterisation of trace elements in PM2.5 aerosols in the vicinity of highways in northeast New Jersey in the U.S. East coast. Atmos Pollut Res 2:34–44. https://doi.org/10.5094/APR.2011.005
61. Zechmeister HG (1998) Annual growth of four pleurocarpous moss species and their applicability for biomonitoring heavy metals. Environ Monit Assess 52:441–451. https://doi.org/10.1023/A:1005843032625

62. Zeneli L, Daci N, Paçarizi H, Daci-Ajvazi M (2011) Impact of environmental pollution on human health of the population which lives nearby Kosovo thermopower plants. Indoor Built Environ 20:479–482. https://doi.org/10.1177/1420326X11409471
63. Zhang C, Qiao Q, Piper JDA, Huang B (2011) Assessment of heavy metal pollution from a Fe-smelting plant in urban river sediments using environmental magnetic and geochemical methods. Environ Pollut 159:3057–3070. https://doi.org/10.1016/j.envpol.2011.04.006
64. Zhu Q, Liu Y, Jia R et al (2018) A numerical simulation study on the impact of smoke aerosols from Russian forest fires on the air pollution over Asia. Atmos Environ 182:263–274. https://doi.org/10.1016/j.atmosenv.2018.03.052

# Figures

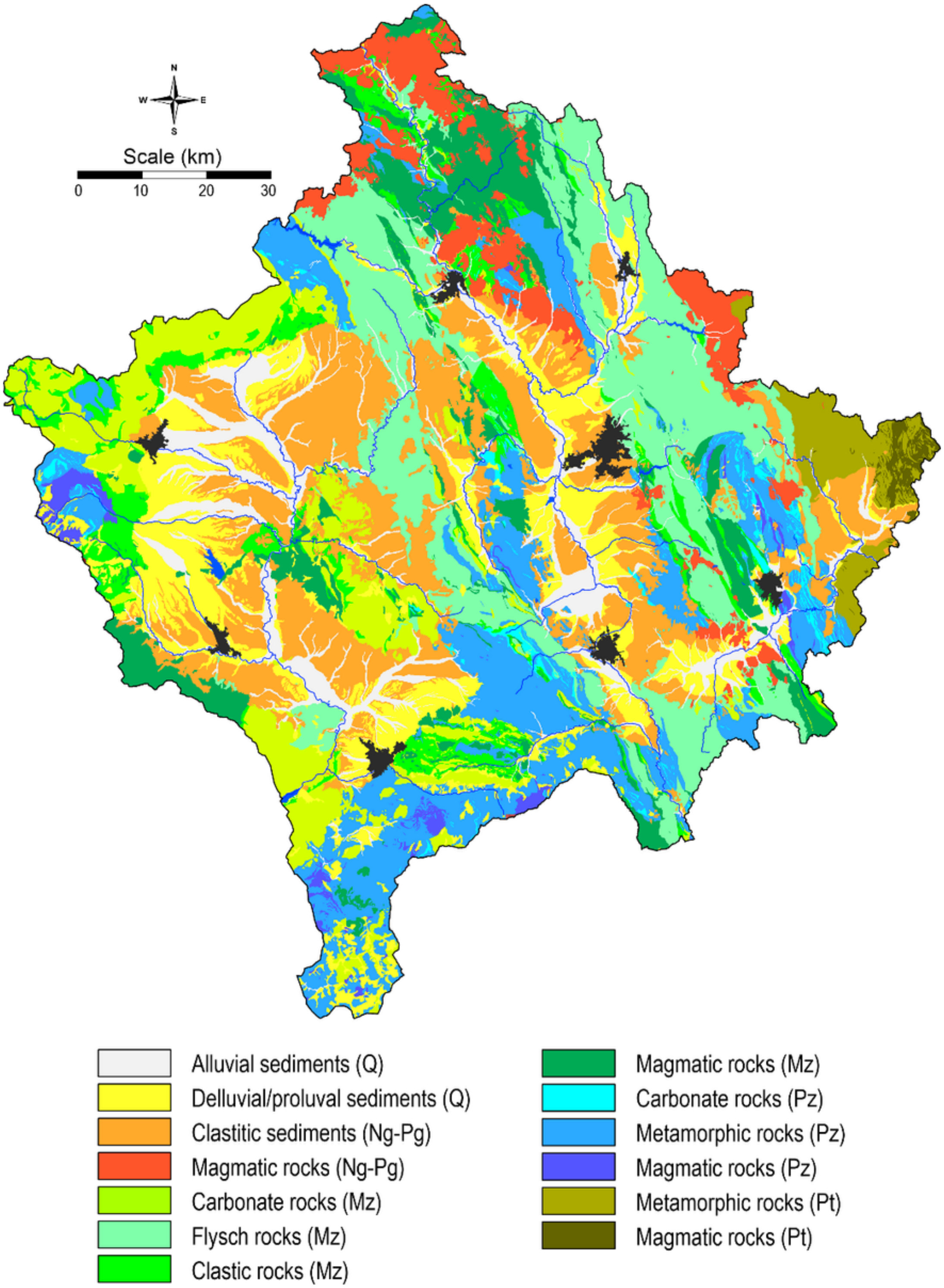



**Figure 1**

Map of the geological formations of Kosovo

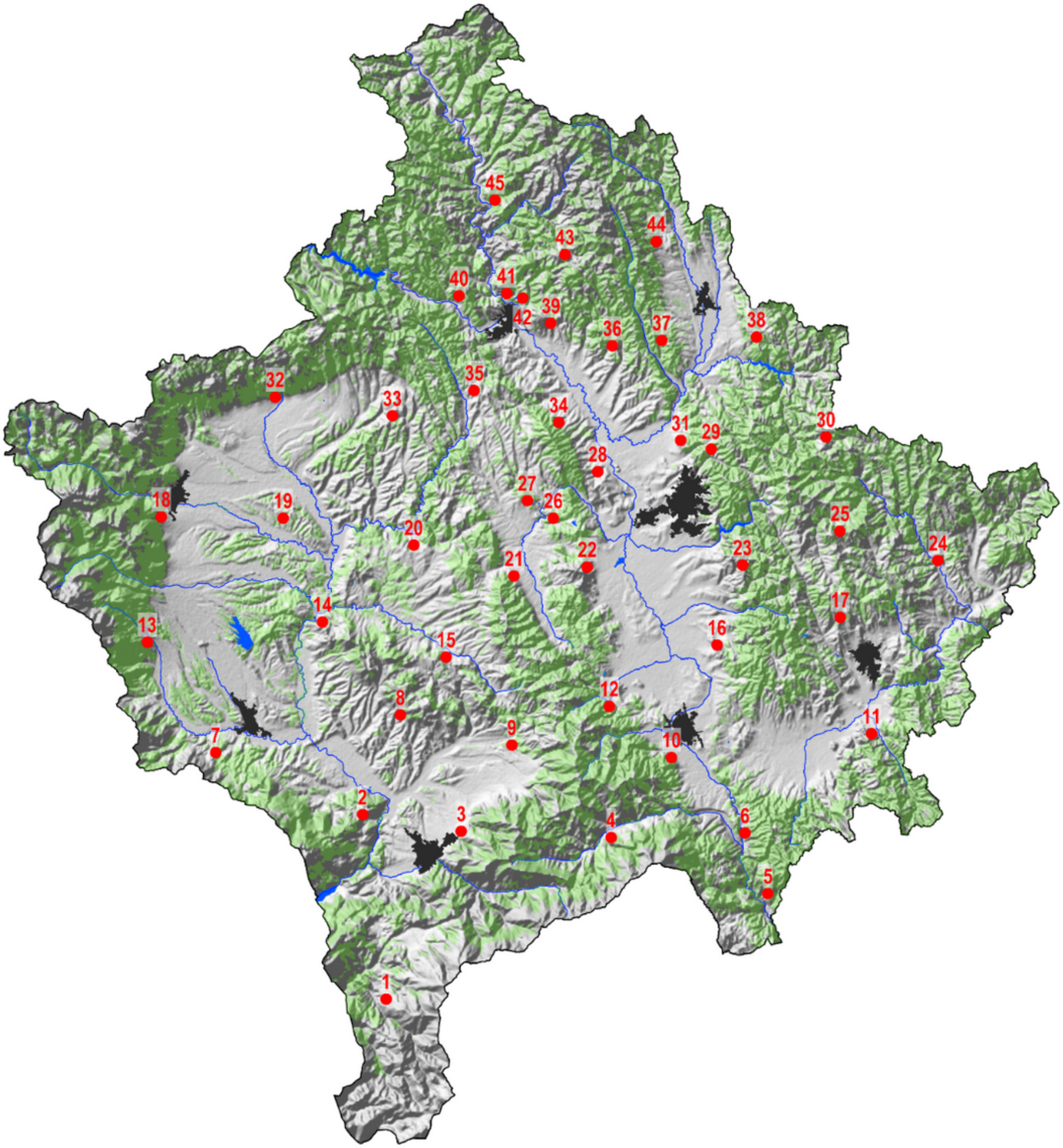
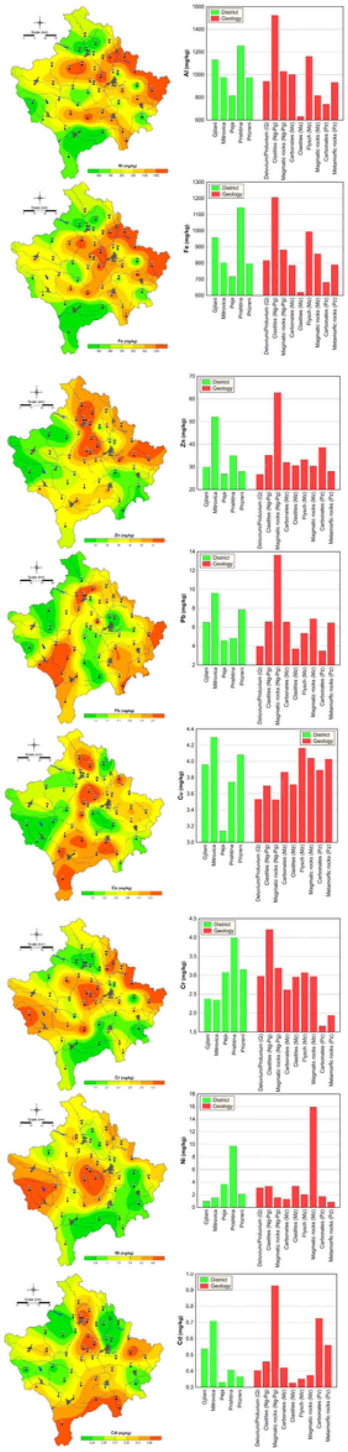


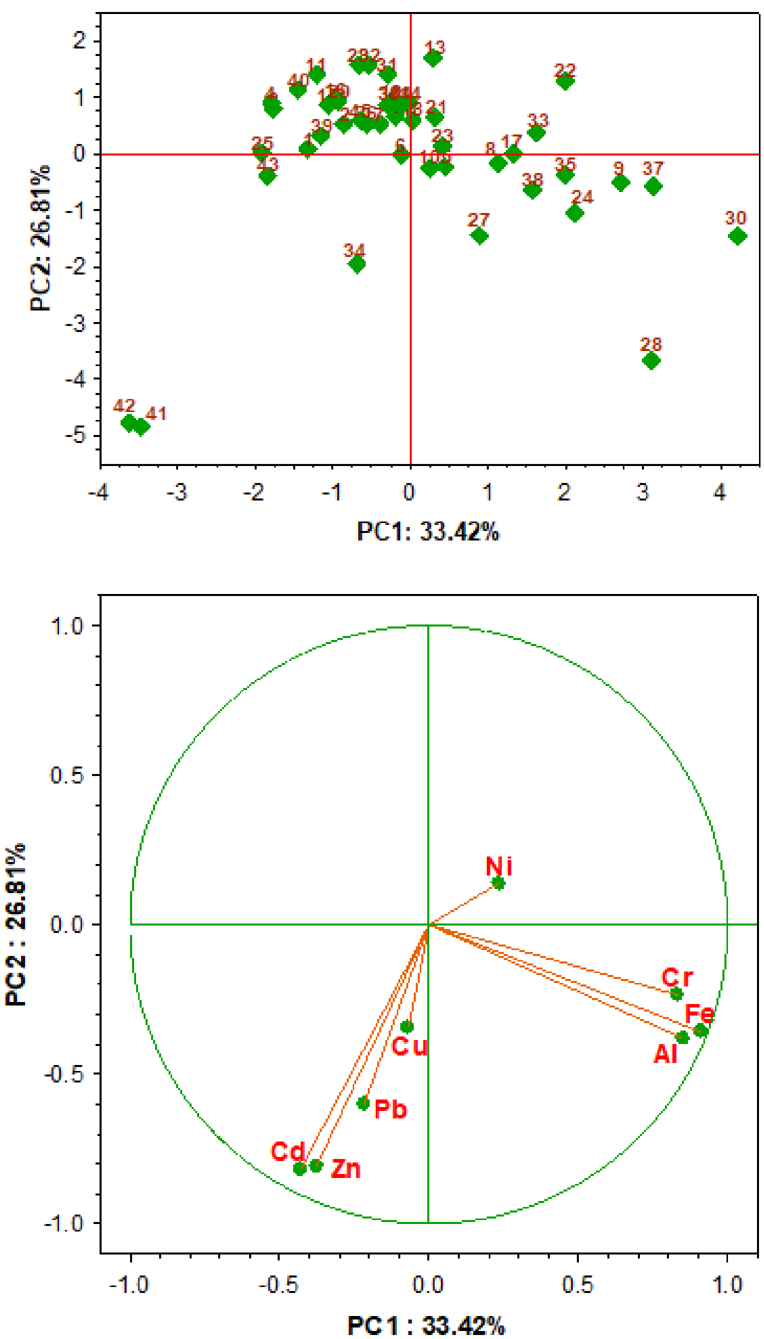

**Figure 2**

Map of the distribution of sampling points of mosses



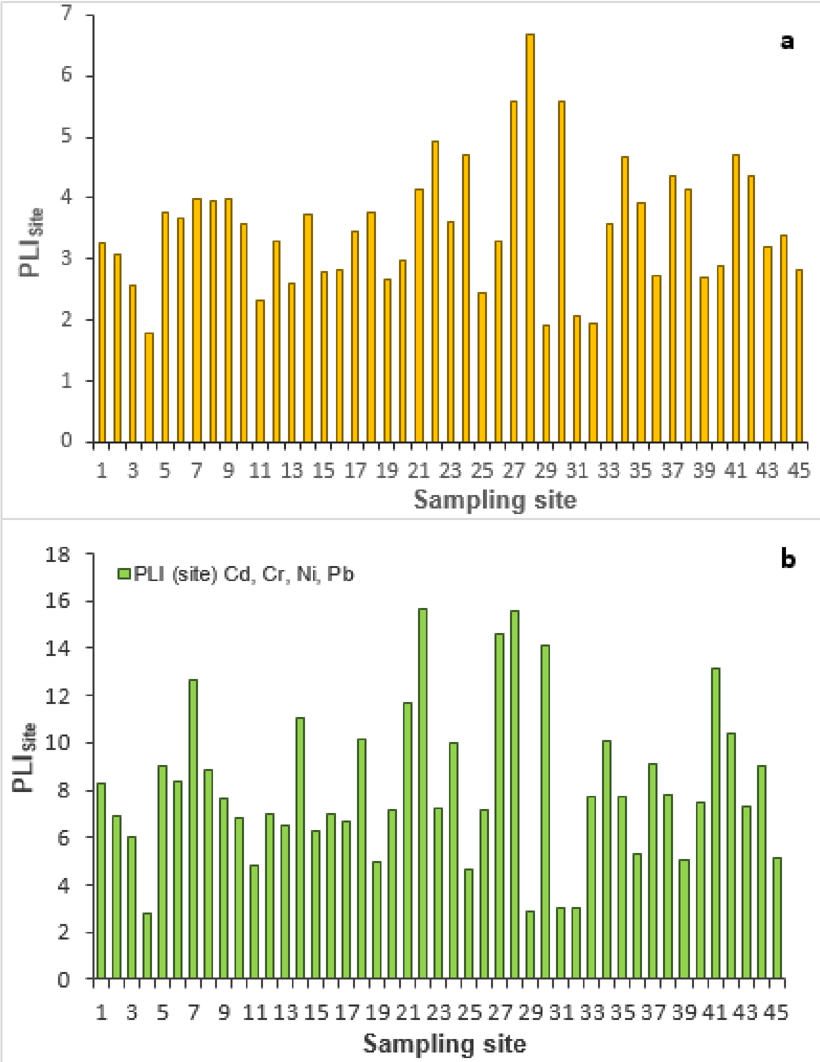
## Figure 3

Distribution of the concentration of heavy metals in mg/kg in the study area




## Figure 4

Multivariate principal component analysis of eight heavy metals for 45 moss sampling sites




## Figure 5

Pollution load index calculated for eight heavy metals a), and b) for Cd, Cr, Ni, and Pb