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Bioconcentration capacity of moss *Leskea angustata* Tayl., for heavy metals and its application in the atmospheric biomonitoring of a metropolitan area

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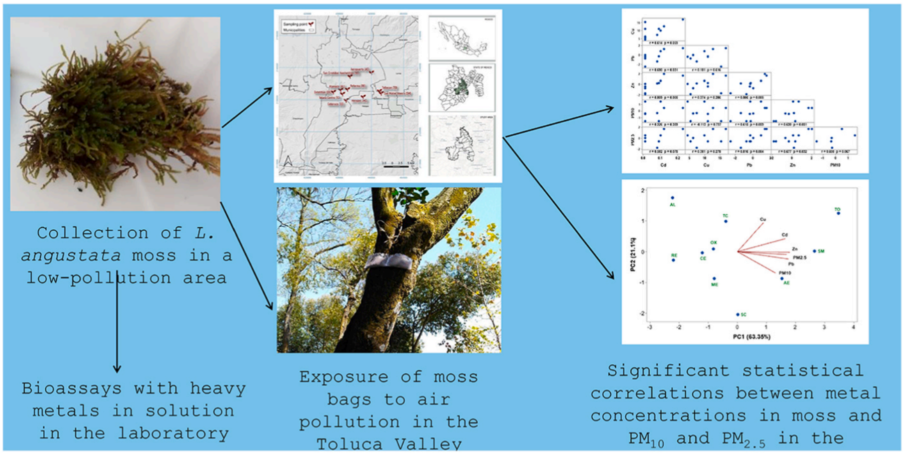
HIGHLIGHTS

- Native moss proved to have great qualities for atmospheric biomonitoring.
- Significant correlations between metals in moss and particulate matter.
- Strong association between anthropogenic activities and heavy metals in moss.
- Forest vegetation appears to act as a barrier to retain airborne particulate matter.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the bioconcentration capacity of heavy metals Cd, Cu, Pb and Zn in the moss *Leskea angustata* Tayl., exposed under laboratory conditions was evaluated, and subsequently the usefulness of moss for the heavy metals' biomonitoring associated with suspended particulate matter in air of the Toluca Valley Metropolitan Area was determined by means of the moss bag technique. To achieve the aims, bioassays were carried out in the laboratory with the moss, the exposure for a period of 6 months of the moss bags in the sites of the Automatic Atmospheric Monitoring Network of the Government of the State of Mexico and their subsequent analysis through of elemental and structural characterization techniques. The results of the bioassays on the moss *L. angustata*, demonstrate that this moss has adequate bioconcentration capabilities to be used as a biomonitor of heavy metals in polluted areas. The structural characterization of the moss *L. angustata*, shows that this moss has

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good adsorption characteristics (presence of functional groups, surface area of 19.87 $m^2\ g^{-1}$, average pore diameter equal to 2.86 nm and a total pore volume of 0.014218 $cm^3\ g^{-1}$). The significant correlations between Cd–Zn–Pb and between Pb and Zn with $PM_{2.5}$, as well as a strong correlation between Pb and Zn with PM_{10}, allow us to establish that these three metals have their main origin in the domestic combustion of wood and liquid petroleum gas (LP gas), as well as emissions from agricultural burning in the study area. Cu has a different origin than other metals and PM_{10} and $PM_{2.5}$. The findings demonstrate a strong association between anthropogenic activities - such as domestic wood and LP gas combustion, agricultural burning emissions, vehicular emissions, tire wear, and industrial activities - and the detection, entrapment, and accumulation of several heavy metals by *L. angustata* moss.

1. Introduction

Air pollution has become a growing concern in recent years, especially in developing countries due to increased urbanization and industrialization. The World Health Organization (WHO) recognizes air quality as a major environmental health risk, with people having little control over their exposure (Salo et al., 2016). The primary contributors to air pollution are anthropogenic sources, particularly heavy traffic, and industrial activity (Salo and Makinen, 2014). Combustion processes result in the high emission of airborne pollutants, including particulate matter (PM) (Vuković et al., 2015). PM consists of minerals from various sources, organic compounds, and heavy metals (Sýkorová et al., 2016).

Heavy metals pose a significant threat to environmental and human health (Loomis et al., 2013). Once introduced into the environment, they are challenging to eliminate and tend to accumulate in the tissues of plants and other organisms through food chains (Stanković et al., 2018). The presence of heavy metals like Pb, Cd, Cu, Ni, and Zn is largely attributed to vehicular traffic and its emissions (Iodice et al., 2016). Biomonitors have frequently been used to evaluate air pollution levels caused by metals emissions (Aboal et al., 2010; Capozzi et al., 2016a). To evaluate the extent of atmospheric metal contamination, biomonitors are frequently employed in both urban and industrial regions. Mosses were among the first biomonitors used to monitor air pollution in Europe, particularly in industrial areas (Carballeira et al., 2008; Gallego-Cartagena et al., 2021). This is due to their ectohydral characteristics, which enables them to reflect the chemical composition of the surrounding atmosphere, as they directly obtain most of their elements and nutrients from atmospheric deposition (Ilieva-Makulec et al., 2021). The biomonitoring technique consists of utilizing air pollution-resistant organisms with the capability to accumulate pollutants in tissues (Gerdol et al., 2014).

Native mosses have been successfully utilized as biomonitors of heavy metal atmospheric deposition (Harmens et al., 2015). These organisms acquire nutrients directly from precipitation and dry deposition, possess a substantial surface area exposed to the atmosphere, and possess a high capacity to accumulate elements in high concentrations (Caballero-Segura et al., 2014). In addition, since phyllidia in mosses have a monostratified layer of cells, these are exposed on their two surfaces (axial and abaxial) for nutrient capture (Varela et al., 2023). Metals absorbed by moss may be trapped as particles in the surface layer, dissolved in liquids or solids surrounding cells (intercellular fraction), interchangeably bound in the cell wall and outer surface of the plasma membrane (extracellular fraction - ion exchange), or transported into cells and maintained in soluble or insoluble forms (intracellular fraction) (Stanković et al., 2018). The presence of heavy metals in moss leads to the formation of free radicals, which causes oxidate stress. Oxidative stress involves increased production of reactive oxygen species (ROS), which can overwhelm cells' inherent antioxidant defenses and cause cellular damage or death (Ali et al., 2013). Although certain heavy metals, such as Cu, are necessary for moss growth, an excess of these vital ions or exposure to non-nutritional ions can lead to harm (Lazo et al., 2013).

In urban areas, where naturally occurring mosses are often scarce or absent, biomonitoring assesses urban air pollution using the 'moss bag technique', a method developed for this purpose (Aničić et al., 2009; Capozzi et al., 2016b). This method offers significant benefits, including the ability to standardize every process step (from selecting species to post-exposure treatments), independence from moss's natural abundance in the monitored site, knowledge of the initial concentrations of the elements under review, and flexibility in choosing exposure duration (Arndt and Friedrich, 2018; Di Palma et al., 2016). Studies by Ares et al. (2012, 2015), Capozzi et al. (2016b), Iodice et al. (2016) and Capozzi et al. (2017) have demonstrated that the moss bag's sorption of contaminants is primarily impacted by the moss density within the bag and the connection between the moss weight and bag surface. Additionally, the researchers concluded that a decrease in moss density leads to an increase in metal uptake, while variations in metal sorption result from the mode of deposition (dry, wet, or hidden) and exhibit greater homogeneity as exposure time increases. Nonetheless, when exposed to pollution, mosses may require shorter exposure periods. Quantitative comparison of metal adsorption in mosses with other natural organic and inorganic materials has demonstrated that mosses are among the most efficient natural adsorbents for heavy metals (González and Pokrovsky, 2014). On the other hand, the complex relationship between metal concentrations in moss tissues and atmospheric deposition has led to a general lack of significant correlations between these two matrices, precluding the use of moss data to reliably estimate absolute rates of heavy metal deposition (Boquete et al., 2020).

The Toluca Valley Metropolitan Area (TVMA), is situated in central Mexico, covering a territorial area of 2410.5 km^2, and comprising of 16 conurbated municipalities. The process of metropolization for the TVMA began in the 1960s, because of the industrialization of the Toluca-Lerma corridor. By the 1980's, it was considered a semi-diversified metropolis, and over the following decade, it became established in the tertiary sector. The TVMA is the fifth most populous metropolis in the country, with a current population of 2,202,886 inhabitants. This represents 13.1% of the total population of the State of Mexico. The area boasts an average annual growth rate of 1.9% and an average urban density of 64.4 inhabitants/ha. Due to the high altitude, averaging 2600 m above sea level, combustion processes are less efficient, resulting in increased pollutant generation despite the use of new generation engines in vehicles (GEM, 2018).

According to World Health Organization (WHO) data from 2016, 91% of the global population resided in areas where $PM_{2.5}$ concentrations surpassed the WHO Air Quality Guide's recommended limit of 10 $mg\ m^{-3}$ for human health (Gallego-Cartagena et al., 2021; World Health Organization, 2016). According to the Management Program to Improve Air Quality in the State of Mexico (GEM, 2018), all air quality monitoring stations in the TVMA failed to meet the particulate matter limits in the last 10 years. In fact, more than 50% of the year days, there is poor air quality relative to PM_{10} (which means concentrations between 76 and 214 $\mu g\ m^{-3}$) and $PM_{2.5}$ (which means concentrations between 45.1 and 97.4 $\mu g\ m^{-3}$). Regarding ozone, about 35% of the days of the year, there is poor air quality due to this pollutant. In 2017, TVMA had 0 days with good air quality (which means concentrations of $PM_{10} > 40\ \mu g\ m^{-3}$ and $PM_{2.5} > 12\ \mu g\ m^{-3}$), according to the evaluation based on the Metropolitan Air Quality Index.

The aim of the study was to assess the bioconcentration capacity of heavy metals Cd, Cu, Pb and Zn in the moss *L. angustata*, exposed under laboratory conditions and subsequently determine by the technique of moss bags, the usefulness of the moss for biomonitoring of heavy metals associated with airborne particulate matter in the TVMA.

2. Materials and methods

2.1. Sampling of moss L. angustata

Samples of L. *angustata*, an epiphytic moss, were collected from the Miguel Hidalgo y Costilla "La Marquesa" Insurgent National Park situated on the Mexico-Toluca highway, at 32 km from the city of Toluca, with geographical coordinates of 19°17′48.26'' N, 99°21′55.15'' W. The samples were solely collected based on objective criteria. Most of the region is covered by *Abies religiosa* forests (oyamel), with *Pinus hartwegii* forests (pine) interspersed in higher areas, along with grasslands. The region's climate is semi-cold and subhumid, with harsh winter frosts and an average height of 2700 m a.s.l. The area was selected to acquire mosses that represented the contamination background level, given its distance from urban centers. The sampling procedure was carried out in the rainy season (August–September), taking care to avoid as much as reasonably possible the loss of material during the removal of tree bark and contamination by other moss species. A total of 15 trees higher than 1.5 m above the ground were sampled. The moss specimen was collected using a plastic spatula and carefully stored in polythene bags for transportation. The specimen was gathered with the tree's bark to ensure its proper preservation. In the laboratory, the moss samples were placed on plastic trays for cleaning. The area was extensively cleaned using plastic tweezers to remove all soil residues, insects, and non-study-species gametophytes from the mosses. The flora of Mexican mosses (Sharp et al., 1994) and the Mosses manual of the Valley of Mexico (Cárdenas and Delgadillo, 2009) at the Faculty of Sciences of the Autonomous University of the State of Mexico (UAEMex) were consulted for species identification. The sanitized moss was stored in sealed plastic containers and watered every other day by gently sprinkling water on top. The containers were positioned near a shut window in the lab to preserve the moss.

L. angustata moss is a species of moss native to Mexico, terrestrial, epiphytic and thaloid growth form. The moss is dark green in color and has narrow, pointed phyllids. It grows in dense clumps in moist, shady soils, such as in forests and ravines, and it has been reported in parks and urban areas of Mexico City and the TVMA (Zepeda-Gómez et al., 2014). *L. angustata*, grows on trees, about 3000–3200 m.a.s.l., Mexico City, and State of Mexico, reported from Jalisco Mexico, Colombia, Ecuador, Peru and Venezuela (Sharp et al., 1994).

2.2. Preparation of metal solutions

Solutions of Cd, Cu, Pb and Zn were prepared to study under laboratory conditions, the bioconcentration of these metals in moss exposed to different concentrations in solution. The reagents used were SPEX CertiPrep. 60 mL of each concentration of the selected metals were prepared as follows: Pb at 10, 20 and 40 mg L^{-1}, Cu at 35, 55 and 75 mg L^{-1}, Zn at 5, 25 and 45 mg L^{-1} and Cd at 0.5, 1 and 10 mg L^{-1}. As reported by Xu et al. (2011), low, medium-high and a blank solution were used.

2.3. Bioassays in moss

Three g of moss was placed in plastic boxes. The bioassays were performed in triplicate for each concentration level and for each of the metals studied. Three unexposed moss samples (control) were used as quality control. Moss was exposed for 30 days (Basile et al., 2012; Koz and Cevik, 2014) to 2 mL of solution every 24 h, which were added by direct spraying of the solution on the moss (Koz and Cevik, 2014; Smolyakov et al., 2017). The mosses were stored for 30 days in a climatic chamber with temperature of 13–20 °C (night/day cycle), 70% constant RH, and 16 h light/8 h dark photoperiod (Basile et al., 2012). Unexposed and exposed moss was removed from the bark of the tree with plastic tongs and placed in plastic trays to dry on a stove at 40 °C for 24 h. The dried moss was ground in an agate mortar, until obtaining a mesh size 50 (pore diameter of 0.050 mm). The ground moss was placed in clean glass jars (cleaned for 6 h in 10% nitric acid and subsequently rinsed with running and deionized water) until quantification of metals by Atomic Absorption Spectrophotometry (AAS).

2.4. Use of moss bags in the TVMA

Commercial polyester tulle (4 mm mesh) of white color was used to make the moss bags. The dimensions of the rectangular flat bags were 15 x 10 cm. They were washed with deionized water and dried on absorbent paper for 2 h at room temperature. The moss was devitalized by heating, applying a drying ramp in an oven Binder FD 56UL with the following temperatures: 50, 80 and 100 °C, each maintained for 8 h and continuously. Approximately 2.5 g of moss were weighed, taking as reference the values reported by Capozzi et al. (2016b), the bags were closed, sewed with nylon thread, and placed in plastic containers.

In this study, 10 sampling sites were selected, distributed in the TVMA and coinciding with the sites of the automatic atmospheric monitoring network of the Ministry of Environment of the State of Mexico. Fig. 1 shows the location of the monitoring sites where moss bags were placed at a height of 4 m (Capozzi et al., 2016b) and according to the prevailing wind direction (southeast to northwest) (GEM, 2007). The sampling sites were Alameda Park (AL), Metepec (ME), Ceboruco (CB), Oxtotitlán (OX), San Cristóbal Huichotitlán (SC), Aeropuerto (AE), San Mateo Atenco (SM), and Toluca Centro (CE). Table 1 shows the geographic coordinates of each of the sampling sites used in this work.

Three moss bags containing the native *L. angustata* moss were exposed in each site to air pollution for a period of 6 months. At the end of the exposure period, the moss bags were removed from each of the monitoring sites and taken to the laboratory, where each of the moss bags was opened, the moss removed, and placed on plastic trays to dry at room temperature for 3 days. The dried moss was ground in an agate mortar, sieved to 50 mesh, and stored in pre-labeled glass vials for further analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

2.5. Analysis of heavy metals in moss by AAS

Zero-point twenty-five g of each moss sample was weighed and placed in an OMNI PLUS XP-1500 Teflon vessel to which 2 mL of ultrapure water, 5 mL of HNO_3 (Baker, Instra grade) and 1 mL of HF (Baker, Ultrapure grade) were added. The vessels containing the samples were placed in a CEM microwave oven, model Mars X 907600, XM3047 series for digestion.

The digestion process was carried out in two stages using the "OMNI Moss - XP 1500″ method. In step 1, a temperature of 187 °C and a pressure of 240 psi were reached for 30 min, with a hold time of 20 min. In Step 2, the presence of residual HF in the samples was neutralized with 15 mL of 4% H_3BO_3 solution added to each vessel. Then, the Neutra-Omni-XP1500 method was used, increasing the temperature to 170 °C, which was maintained for 10 min, followed by the cooling phase. The digested samples were decanted into polyethylene containers and kept refrigerated until analysis.

Quantification of metals was performed in an atomic absorption spectrophotometer (PerkinElmer, model 3110) according to NMX-AA-051-SCFI-2001. Hollow cathode lamps (PerkinElmer or GBC) were used for each metal, and the wavelengths were 228.7 nm for Cd, 213.9 nm for Zn, 324.7 nm for Cu, and 216.9 nm for Pb. To evaluate the accuracy and repeatability of the analytical methods, each sample was prepared in triplicate. A certified reference standard, IAEA-336 lichen certified reference material, was used for quality control.

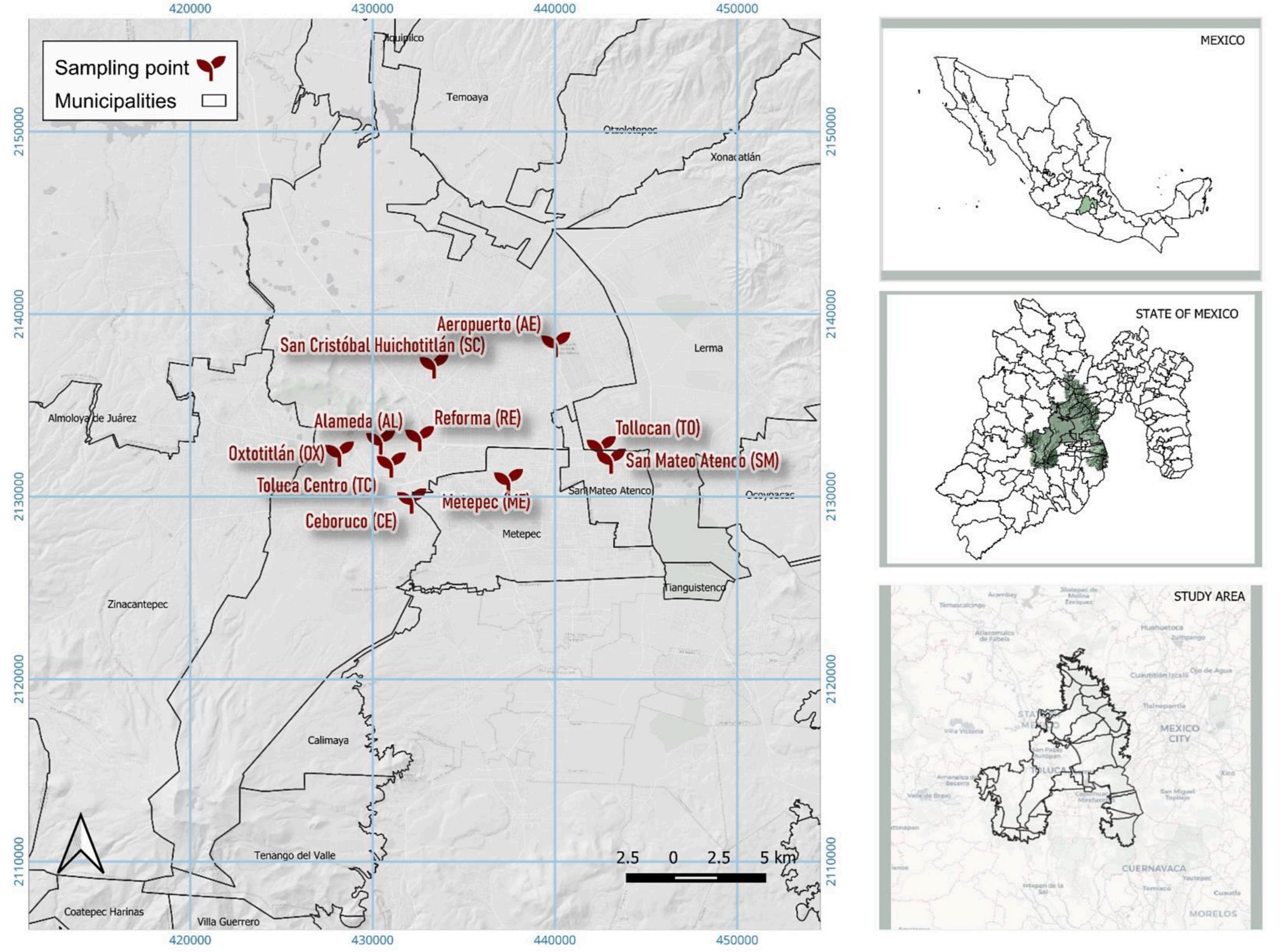

Fig. 1. Location of monitoring sites on TVMA.

Table 1
Location of monitoring sites used in this study.

Site	Geographical Location
1. Aeropuerto (AE)	19°20′16.76’’ N, 99°34′14.52’’ W
2. Alameda (AL)	19°17′22.36’’ N, 99°39′43.03’’ W
3. Ceboruco (CE)	19°15′37.10’’ N, 99°38′44.60’’ W
4. Metepec (ME)	19°16′12.70’’ N, 99°35′42.70’’ W
5. Oxtotitlán (OX)	19°17′0.40’’ N, 99°41′00.56’’ W
6. Reforma (RE)	19°17′28.41″ N, 99°38′29.79’’ W
7. Tollocan (TO)	19°17′11.53’’ N, 99°32′48.65’’ W
8. San Cristóbal Huichotitlán (SC)	19°19′38.00’’ N, 99°38′03.44’’ W
9. San Mateo Atenco (SM)	19°16′49.50’’ N, 99°32′30.00’’ W
10. Toluca centro (TC)	19°16′41.1’’ N, 99°39′23.10’’ W

2.6. Analysis of heavy metals in moss by ICP-MS

The digestion of the samples was carried out by placing 350 mg of moss in Teflon vessels, adding 5 mL of HNO_3 suprapur and 0.4 mL of HF suprapur (Chevallier et al., 2015). The digestion was carried out in two stages in a microwave digestion and extraction system MARS 6, One Touch Technology. In the first stage, digestion was performed at 200 °C (285–290 psia) for 15 min, then the same temperature was maintained for another 10 min to ensure complete degradation of organic matter. At the end of the cooling phase, the samples were placed in plastic volumetric flasks (50 mL), taking care not to spill a drop of the solution obtained. 2 mL of supersaturated H_3BO_3 was added and Ge was used as an internal standard, for which a concentration of 10 μg/L was added to each sample. Samples were measured with ultrapure water and vortexed before analysis. Sample reading was performed on an ICP-MS 7700, Agilent Technologies, G3281A. For quality control of the analyses, IAEA-336 lichen certified reference material was analyzed under the same conditions as the samples.

2.7. Fourier Transform Infrared Spectroscopy (FTIR) and B.E.T. Analysis

The characterization of the moss was carried out through Fourier Transform Infrared Spectroscopy to determine the functional groups that are part of the moss *L. angustata* and that may be related to the metal adsorption process. The characterization of the moss biomass was carried out using a VARIAN 640-IR FTIR instrument, AGILENT brand, MID-IR configuration. The specific surface area and pore size were determined by the B.E.T. technique using a BELSORP-max model surface area and pore volume measuring instrument BELJAPAN. The Belprep Vac II degasser with a pore distribution range of 0.01 $m^2\ g^{-1}$ was also used. 0.0345 g samples (dried for 2 weeks at room temperature) were degassed under vacuum for 5 h at 60 °C. The analysis was then performed, and the surface area and pore volume values were obtained. Adsorption/desorption curves were determined at 22 h and 45 °C.

Sample weight: 0.0345 g, standard volume: 27.659 cm^3, dead volume: 26.449 cm^3, equilibrium time: 0 s, adsorbate N_2 (Nitrogen gas, purity ≥99.999%), instrument temperature 0 °C, adsorption temperature 77 K, saturated vapor pressure 77.439 kPa and adsorption cross-sectional area 0.162 nm^2 were the operating conditions of the B.E.T. analyzer and equipment.

2.8. Net enrichment and Relative Accumulation Factor

To evaluate the content of the elements in the moss, the net enrichment (NE) was determined, which is defined as the difference between the moss concentrations at the end of the exposure period and the moss concentrations at the beginning of the exposure period (Ares et al., 2012; García-Seoane et al., 2023). For bioassays, the bioconcentration factor (BF) was obtained by dividing the moss concentration at the end of the exposure period by the concentration to which the moss was exposed. The ratio of the concentration of each heavy metal in the exposed samples to the control samples (exposed-to-control ratio, EC ratio) was used to evaluate the bioconcentration rates of the moss samples (Frati et al., 2005). EC ratio values were interpreted using the scale of accumulation/loss scale proposed by Frati et al. (2005). In addition, the Relative Accumulation Factor (RAF) was determined for moss bags, based on the moss concentration of each element after exposure ($C_{exposed}$) reduced by and then divided by the element concentration before exposure ($C_{initial}$) (Vuković et al., 2015).

$$\mathrm{RAF} = \frac{Cexposed - Cinitial}{Cinitial}$$

2.9. Statistical analysis of the data

Means, standard deviations and confidence limits were obtained. The normality of the data was determined by Ryan Joiner and Shapiro-Wilk tests, non-normal data were normalized by means of the Johnson transformation and treated by the Pearson correlation to determine possible associations between metals in moss and between metals and PM_{10} and $PM_{2.5}$ data obtained from the Automatic Atmospheric Monitoring Network of the Ministry of the Environment of the State of Mexico for the same exposure period (six months). Subsequently, the single factor ANOVA test was used to detect significant differences between initial and final concentrations and between different study sites, and multivariate analysis and principal component analysis (PCA) were used to identify the most important variables contributing to the variability of the data. Statistical tests were performed using Minitab® 21.4.1. All statistical tests were performed at the 95% confidence level.

3. Results and discussion

3.1. Bioassays in moss

The results of the analysis of the IAEA-336 lichen reference material by AAS, showed recovery percentages of 99% for Cd, 98.2% for Cu, 96.6% for Pb and 98.9% for Zn, indicating that the technique is reliable for the analyses performed in this work. Table 2 shows the results of metal concentrations, net enrichments, EC ratio and bioconcentration factors in moss exposed to different metals concentrations in the bioassay. Metal concentrations of Cd, Cu, Pb and Zn in moss exposed samples were always statistically higher ($p < 0.05$) than in control samples. In terms of total metal concentration, the order of concentration present in moss was Zn > Cu > Pb > Cd, but when net enrichments are considered, the order changes to Cu > Pb > Zn > Cd.

Net enrichment values increased as the concentration of the metal to which the moss was exposed increased. However, this increase is not proportional to the increase in the concentration of the metals used in the bioassay, as can be seen from the bioconcentration factors.

The EC ratios of the total concentrations indicated a strong bioconcentration for all metals, regardless of the amount of metal supplied. Furthermore, it can be observed that the order of the EC ratio was Cd > Cu > Pb > Zn, which in some way reflects the preference, affinity, or bioconcentration capacity of the metal by the moss. The same order of the EC ratio was obtained by Basile et al. (2012), which supports the affinity in the bioconcentration capacity of mosses for the metals studied in solution.

A higher bioconcentration factor for the 4 metals was observed in the first concentration to which the moss was exposed, and this bioconcentration factor decreased as the exposed concentration increased. This is a clear indication that the moss quickly incorporates the metal and subsequently reaches a saturation point or the detoxification mechanisms begin to act, such as the induction of Glutathione (GSH), which reduces its incorporation into the exposed organism (Bellini et al., 2023). Only for samples exposed with Pb and Zn, the bioconcentration factor reflected the order of magnitude of the metals supplied, both at the two highest concentrations.

Different bioconcentration levels under similar conditions may be caused by metal-specific transport mechanisms, probably involving specific membrane transport proteins (Vázquez et al., 2000). This is probably true for Cu and Zn, as they are important essential micronutrients for moss, but not for Cd and Pb. This is confirmed also by the fact that in samples supplied with Pb, the bioconcentration reflected the order of magnitude of the metals supplied, suggesting that their transport is not specifically regulated.

According to Koz and Cevik (2014), the size of phyllid surfaces is a

Table 2
Results of metal concentration (mg kg^{-1} d.w., ± standard deviations), net enrichments, EC ratio and bioconcentration factors of moss bioassays.

Sample	Metal concentration	Net enrichment	EC ratio	Bioconcentration factor	Average Bioconcentration Factor
Control	0.82 ± 0.35	–		–	–
Cd-0.5 mg L^{-1}	9.78 ± 0.99*	8.96 ± 0.96	11.9	17.9	11.0
Cd-1mg L^{-1}	13.06 ± 1.21*	12.24 ± 1.12	15.9	12.2	
Cd-10 mg L^{-1}	28.30 ± 2.09*	27.48 ± 1.95	34.5	2.8	
Control	28.7 ± 2.4	–		–	–
Cu-35 mg L^{-1}	309.3 ± 13.1*	280.7 ± 12.6	10.8	8.0	6.3
Cu-55 mg L^{-1}	366.4 ± 9.3*	337.7 ± 8.7	12.8	6.1	
Cu-75 mg L^{-1}	393.9 ± 11.5*	365.2 ± 9.9	13.7	4.9	
Control	19.3 ± 3.1	–		–	–
Pb-10 mg L^{-1}	100.1 ± 5.7*	80.8 ± 5.0	5.2	8.1	6.2
Pb-20 mg L^{-1}	128.1 ± 9.2*	108.8 ± 8.3	6.6	5.4	
Pb-40 mg L^{-1}	223.6 ± 15.7*	204.3 ± 14.1	11.6	5.1	
Control	98.5 ± 5.3	–		–	–
Zn-5mg L^{-1}	155.4 ± 8.2*	56.9 ± 6.6	1.6	11.4	8.7
Zn-25 mg L^{-1}	288.6 ± 17.1*	190.1 ± 10.0	2.9	7.6	
Zn-45 mg L^{-1}	415.5 ± 14.7*	317.0 ± 7.1	4.2	7.0	

* Significant statistical differences between the moss exposed and the control ($p < 0.05$).

crucial factor in the concentration variations among moss species. In the case of *L. angustata*, Robinson (1959) reported an average phyllid width of 0.6–0.8 mm. When comparing the results obtained by Koz and Cevik (2014) for phyllid bioconcentration, where they used 6 species of moss with different phyllid lengths; *Thuidium tamariscinum* with a phyllid length of 1.15–1.4 mm, *Homalothecium sericeum* with a phyllid length of 1.32–4 mm, *Eurhynchium striatulum* with a phyllid length of 0.97–1.87 mm, *Pleurozium schreberi* with a phyllid length of 1.4–2.6 mm, *Hypnum cupressiforme* with a phyllid length of 0.93–2 mm *and Eurhynchium striatum* with a phyllid length of 2.1 at 3.25 mm, it can be observed that although the moss *L. angustata* has the shortest phyllid length (0.6–0.8 mm) it presents greater net enrichments and bioconcentration factors than the other 6 species examined. This could be attributed to the method of administration of the solutions in both studies (gaseous atomization versus liquid atomization) and the different exposure durations (10 days of exposure versus 30 days of exposure). So greater efforts should be made to standardize the study of the bioconcentration capacities of heavy metals in mosses in order to make comparisons and determine those mosses that may have the best capabilities to be used as indicators of air pollution caused by airborne particulate matter.

Based on the aforementioned results, it is evident that the moss *L. angustata* possesses sufficient bioconcentration capabilities to serve as a biomonitor for heavy metal pollution in urban and industrial settings.

3.2. *Results of moss characterization using FTIR and B.E.T*

In order to better understand the adsorption mechanisms involved in the uptake of metals in moss, a FTIR analysis was carried out. Fig. 2 shows the results of the FTIR analysis in the moss *L. angustata*, where the bands originated by the functional groups present in moss compounds can be observed, such as the band at ∼3700–∼3000 cm^{-1} corresponding to O–H and N–H bonds (symmetric and asymmetric stretch) of carbohydrates and proteins, as well as the water molecule (Hu et al., 2011). Following bands were also observed at 2840 cm^{-1} and 2912 cm^{-1} corresponding to the C–H (stretch) from polysaccharides, lipids, and carbohydrate bonds, which are very common in moss cells (Świsłowski et al., 2022). Similarly, bands were found at 2280 cm^{-1} and 2125 cm^{-1} corresponding to the group N=C=O and N=C=S that have been reported in cruciferous vegetables (Palliyaguru et al., 2018, Merck, 2023), at 1630 cm^{-1} with the group C=O and N–H (Merck, 2023), at 1230 cm^{-1} which could be attributed to the presence of amide (C–N stretch) belonging from proteins and glycoproteins (Świsłowski et al., 2022), and 1030 cm^{-1}, indicating an elongation of the group of C–O–C (stretch) from oligosaccharides, glycoproteins, and carbohydrates. (Hou et al., 2005).

Furthermore, identical bands with slight variations were detected in *P. schreberi, D. polysetum, and S. fallax* mosses (Świsłowski et al., 2022), as well as in 16 species of the genera *Pohlia, Bryum, Mnium, Plagiomniuma*, and *Trachycystis* (Cao et al., 2014), and in Romanian peat moss (Bulgariu et al., 2009) where it was observed that heavy metal adsorption significantly affects the O–H/N–H band. The decrease in the intensity of this peak suggests that bound O–H functional groups and amide fractions may play a crucial role in metal ion sorption. Furthermore, the intensity of the C]O and N–H bands displays a decrease after adsorption, indicating the participation of the C]O and N–H groups in the conjugation of metal cations (Bulgariu et al., 2009; Świsłowski et al., 2022).

The process of heavy metal accumulation in mosses primarily occurs through ion exchange and on the surface (Świsłowski et al., 2022). De-esterified galacturonic acids are the main compounds responsible for cation exchange in mosses, although phenolic, amino, silicic, and sulfate ester compounds are also involved to a lesser extent (Varela et al., 2023). When methyl groups are removed from these acids, they generate negatively charged functional groups (–OH–, –COOH–) that can serve as binding sites for elements in cationic form. This process determines the cation exchange capacity in mosses (Carballeira et al., 2008). Additionally, it has been reported that most of the adsorption and accumulation of heavy metals in mosses is related to cell wall pectins. Metal cations can bind to the surface layers of the cell wall through cation exchange. Carboxylates and phosphorylates have been reported as the major binding site for metal complexation on the surface of mosses (González and Pokrovsky, 2014). Various substances such as cellulose and glycoproteins are part of the cell wall of mosses and have been reported to be involved in metal adsorption (Nag and Biswas, 2021). Therefore, based on the analysis of the above, it seems likely that the surface layers of mosses are responsible for the adsorption of metals, wherein, differences in the composition of the cell wall of mosses may influence the adsorption of metals (Balabanova et al., 2021).

The adsorption-desorption isotherm of *L. angustata* moss is shown in Fig. 3a, which corresponds to type IV, and is characteristic of mesoporous solids. Additionally, it has a surface area of 19.87 m^2 g^{-1}, which, as compared to other similar materials such as lichen that has a surface area of 0.0442 and 0.0542 m^2 g^{-1}, the hollow *Sphagnum* moss that have a surface area of 0.0176, 0.0265, 0.0287 and 0.167 m^2 g^{-1} and the mound *Sphagnum* moss, which has an surface area of 0.0406, 0.0958, 0.108 and 0.202 m^2 g^{-1} (Cazaurang et al., 2023), it can be observed that

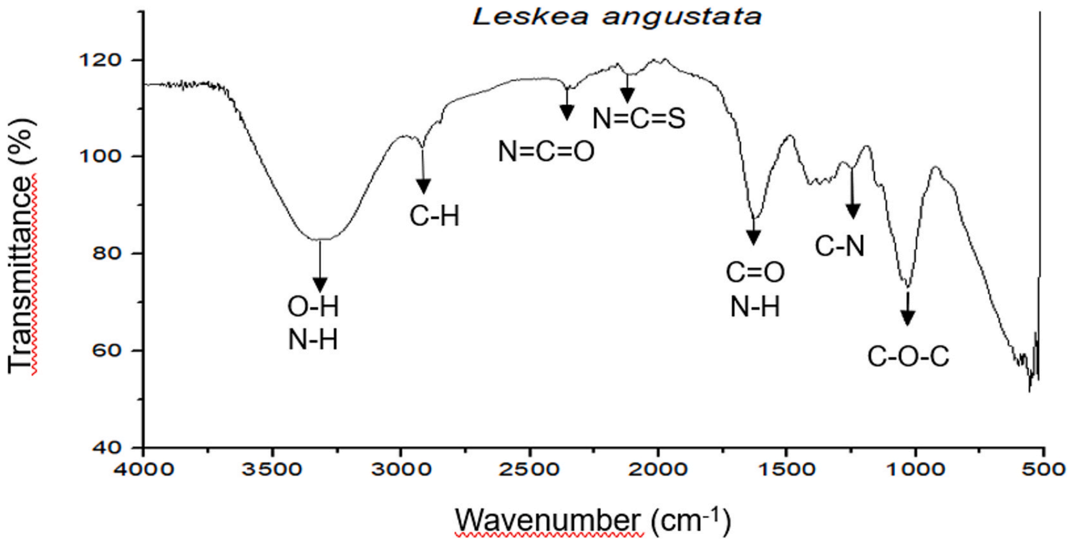

Fig. 2. FTIR spectrum of the moss *L. angustata*.

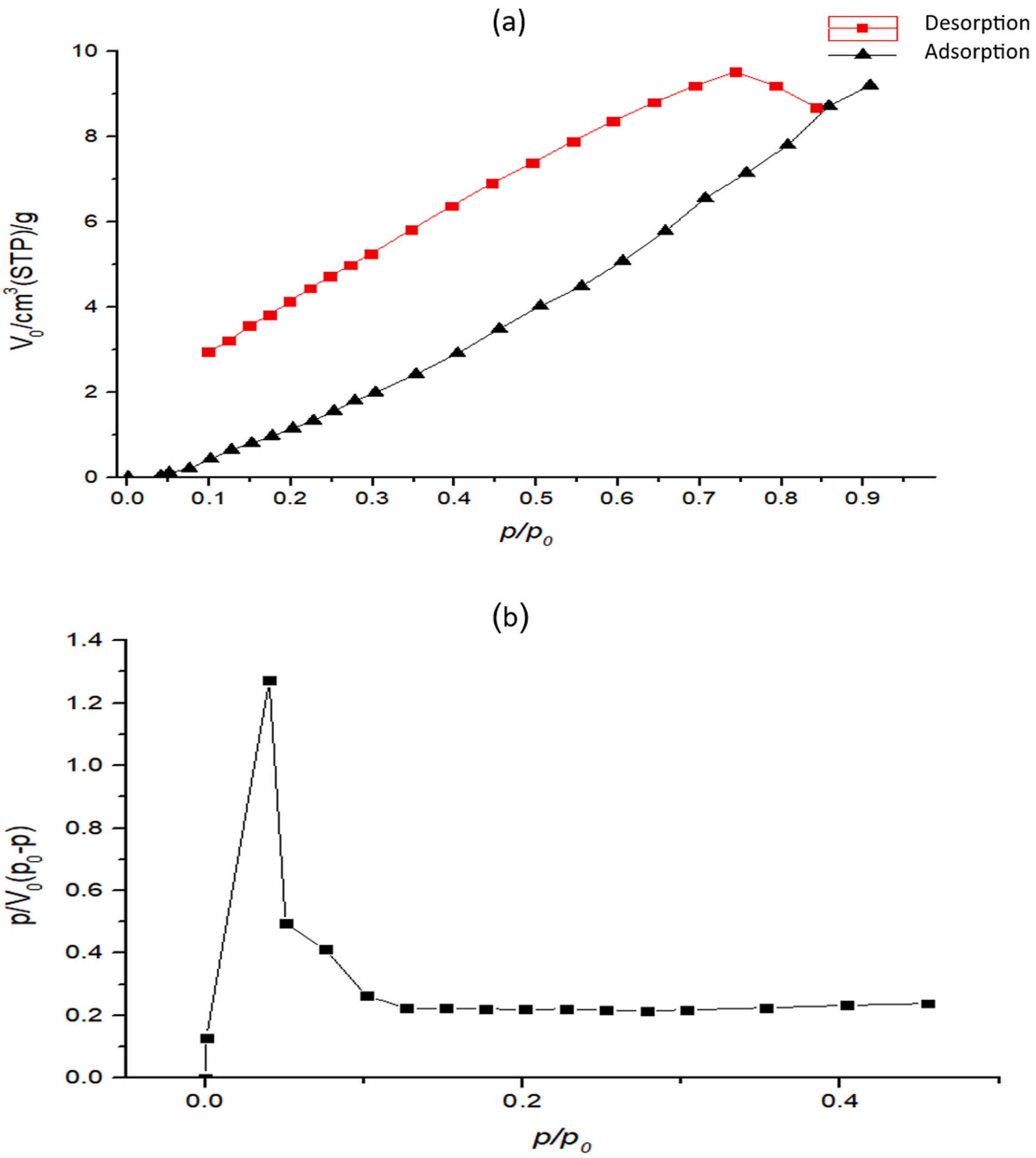

Fig. 3. (a) N_2 adsorption-desorption isotherm in the moss *L. angustata*. (b) BET model applied to the N_2 adsorption isotherm in the moss *L. angustata*.

the surface area is larger. This characteristic is related to its potential ability to absorb heavy metals and other environmental pollutants (Bulgariu et al., 2009). Fig. 3b shows the application of the BET model to the N_2 adsorption isotherm in the moss *L. angustata*, where a linear trend and uniform surface area can be observed. The analysis of pore diameter and volume plays an important role in the adsorption process. The values obtained by the BET analysis show that the moss *L. angustata*, contains mesopores (2–50 nm) since it has an average pore diameter of 2.86 nm and a total pore volume of 0.014218 cm^3 g^{-1}. The high specific surface area of mosses also provides a high capacity to retain particles, where surface characteristics, thickness, and phyllids architecture determine the extent up to which the particles are trapped (Real et al., 2021). Koz and Cevik (2014) demonstrated through a study of lead adsorption capacity, that there is a positive correlation between the adsorption capacities and the leaf areas of moss species. They concluded that surface area has an important effect on the adsorption process and that these organisms can be used to monitor heavy metal pollution in urban environments.

Based on the characterization results presented, it is possible to conclude that *L. angustata*, an epiphytic moss, exhibits favorable adsorption properties that can qualify it as a biomonitor for heavy metal pollution linked to airborne particulate matter in urban environments.

3.3. *Use of moss bag in the TVMA*

The results of the analysis of the reference material IAEA-336 Lichen by ICP-MS, showed recovery percentages of 95.9% for Cd, 96.1% for Cu, 97.1% for Pb and 96.3% for Zn respectively, which indicates that the technique is reliable for the analysis of moss bags carried out in this work.

Table 3 displays the net enrichments acquired from the moss bags at the 10 TVMA monitoring locations. The results show that Zn presents the highest average net enrichment (857.4 mg kg^{-1}), followed by Pb (32.27 mg kg^{-1}), Cu (10.08 mg kg^{-1}) and finally Cd (0.07 mg kg^{-1}). Regarding the monitoring sites, the sites present the following average net enrichment: 9-SM (707.6 mg kg^{-1}) > 7-TO (557.6 mg kg^{-1}) > 1-AE (262.7 mg kg^{-1}) > 10-TC (188.4 mg kg^{-1}) > 3-CE (170.9 mg kg^{-1}) > 8-SC (155.5 mg kg^{-1}) > 5-OX (105.4 mg kg^{-1}) > 4-ME (76.8 mg kg^{-1}) > 2-AL (16.6 mg kg^{-1}) > 6-RE (8.1 mg kg^{-1}). Likewise, it is possible to observe that the highest net enrichments of Cd are presented in the 7-TO site (0.23 mg kg^{-1}), of Cu in the 7-TO sites (17.01 mg kg^{-1}), 2-AL (15.46 mg kg^{-1}) and 9-SM (12.74 mg kg^{-1}) of Pb in the 7-TO site (92.11 mg kg^{-1}), 9-SM (77.84 mg kg^{-1}), and 1-AE (49.08 mg kg^{-1}) and of Zn at sites 9-SM (2739.5 mg kg^{-1}), 7-TO (2121.2 mg kg^{-1}), and 1-AE (991.5 mg kg^{-1}). The data shown above indicates that the areas with the most significant concerns regarding pollution due to heavy metals in the TVMA are 9-SM, 7-TO, and 1-AE. These areas are identified by high vehicular traffic and proximity to industrial areas, and in the case of zone 1-AE, the international airport of the Toluca city (Avila-Pérez et al., 2019; Macedo-Miranda et al., 2016). Otherwise, the sites with the lowest net enrichments and therefore with the least problems of pollution by heavy metals associated with airborne particulate matter in the TVMA are sites 4-ME, 2-AL, and 6-RE. These sites are characterized by being located within parks of the municipalities of Metepec and Toluca and by the presence of wooded vegetation, which, according to Abhijith and Kumar, 2020, Salazar-Rojas et al. (2023); Zhou et al. (2023), function as a barrier to the retention of airborne particulate matter, which may be the main reason why these sites have the lowest concentrations of metals in this study. During the 6-month period of exposure to moss bags, the mean net enrichments of Cd, Cu, Pb, and Zn in the moss species *L. angustata*, were in the range of other urban sites (Gallego-Cartagena et al., 2021; Vuković et al., 2016).

The RAF is shown in Table 4, where Zn is the metal that most bioaccumulates with an average factor of 9.3, which indicates that it increases on average up to 9.3 times the initial concentration in moss prior to the exposure period. It is followed by Pb with a RAF of 2.4, followed by Cu (0.7) and Cd (0.1). In relation to the different monitoring sites, the sites with the highest average RAF are 9-SM with 9.1, 7-TO with 7.8, and 1-AE with 3.8 and those with the lowest average RAF are 4-Me with 1.3, 2-AL with 0.5 and 6-RE with 0.4. Individually, the RAF of Zn stands out at sites 9-SM (29.6), 7-TO (22.9), and 1-AE (10.7), and Pb at sites 7-TO (6.9), 9-SM (5.8) and 1-AE (3.7). The RAF values in this work are at levels similar to those reported by Vuković et al. (2015), Vuković et al. (2016) and Ilieva-Makulec et al. (2021) for mosses in urban areas and above those reported by Aničić et al. (2017) for a botanical garden in Belgrade, Serbia. Therefore, the moss *L. angustata* proves to have the necessary accumulation capabilities to be used in heavy metal monitoring in urban areas.

Table 3
Net enrichments for moss bags exposed over a 6-month period in the TVMA. Concentrations in mg kg^{-1} d.w., ± standard deviations.

Site	Cd	Cu	Pb	Zn	Mean
1. AE	0.1 ± 0.05	9.92 ± 0.98	49.08 ± 5.81	991.5 ± 70.0	**262.7**
2. AL	<LOD[a]	15.46 ± 1.99	7.01 ± 0.93	44.0 ± 6.5	**16.6**
3. CE	0.08 ± 0.03	7.42 ± 0.80	9.54 ± 1.06	666.5 ± 85.0	**170.9**
4. ME	<LOD[a]	6.23 ± 0.75	22.59 ± 2.79	278.4 ± 9.1	**76.8**
5. OX	<LOD[a]	11.06 ± 0.96	16.71 ± 0.20	393.7 ± 52.2	**105.4**
6. RE	<LOD[a]	5.42 ± 0.78	12.87 ± 1.61	14.1 ± 3.2	**8.1**
7. TO	0.23 ± 0.05	17.01 ± 1.35	92.11 ± 8.0	2121.2 ± 152.5	**557.6**
8. SC	<LOD[a]	4.41 ± 0.71	17.04 ± 1.87	600.4 ± 42.4	**155.5**
9. SM	0.12 ± 0.04	12.74 ± 0.15	77.84 ± 6.32	2739.5 ± 110.0	**707.6**
10. TC	0.09 ± 0.04	11.1 ± 0.62	17.9 ± 1.97	724.5 ± 62.4	**188.4**
Mean	**0.07**[a]	**10.08**	**32.27**	**857.4**	

LOD = 0.01 mg kg^{-1}

[a] The value of LOD = 0.01 was used to calculate the mean of each site and cadmium.

Table 4
Relative accumulation factors (RAF) for moss bags exposed over a 6-month period in the TVMA.

Site	RAF Cd	RAF Cu	RAF Pb	RAF Zn	Mean
1. AE	0.2	0.6	3.7	10.7	**3.8**
2. AL	–	1.0	0.5	0.5	**0.5**[a]
3. CE	0.1	0.5	0.7	7.2	**2.1**
4. ME	–	0.4	1.7	3.0	**1.3**[a]
5. OX	–	0.7	1.3	4.3	**1.6**[a]
6. RE	–	0.4	1.0	0.2	**0.4**[a]
7. TO	0.4	1.1	6.9	22.9	**7.8**
8. SC	–	0.3	1.3	6.5	**2.0**[a]
9. SM	0.2	0.8	5.8	29.6	**9.1**
10. TC	0.1	0.7	1.3	7.8	**2.5**
Mean	**0.1**[a]	**0.7**	**2.4**	**9.3**	

[a] The mean was calculated based on the 4 metals and the 10 sites.

The data underwent a normality test using the Ryan-Joiner and Shapiro-Wilk methods, revealing that Cd and Cu followed a normal distribution. In contrast, Pb and Zn had a non-normal distribution. Consequently, to enable corresponding statistical analyses, the data for Pb and Zn underwent a transformation via the Johnson method.

Metal concentrations of Cd, Cu, Pb, and Zn in moss exposed samples were always statistically higher ($p < 0.05$) than in moss unexposed samples. The results of the one-way ANOVA show that there are statistically significant differences ($p < 0.05$) between the mean concentrations of Pb, Cd, and Zn with those of Cu.

Fig. 4a shows the results of Pearson's correlations with the data of Cd, Cu, normalized Pb and normalized Zn, where there are statistically significant correlations between Cd–Pb (0.68, $p < 0.05$), Cd–Zn (0.81, $p < 0.05$) and Pb–Zn (0.81, $p < 0.05$), which may indicate a common natural or anthropogenic origin. Fig. 4b shows the results of Pearson's correlations with the data of Cd, Cu, normalized Pb, normalized Zn, normalized PM$_{10}$ and normalized PM$_{2.5}$ (provided by the Ministry of Environment of the State of Mexico). In addition to the aforementioned correlations between Cd, Pb, and Zn, there are statistically significant correlations between Pb and PM$_{2.5}$ (0.82, $p < 0.05$) and Zn-PM$_{2.5}$ (0.68, $p < 0.05$) were observed, as well as strong correlations between Pb-PM$_{10}$ (0.62, $p = 0.059$) and Zn-PM$_{10}$ (0.63, 0.051), which, although it does not reach the statistical significance level of 95%, the p-value remains very close to the required limit level of statistical significance at 95%.

Fig. 5a presents the dendrogram generated by conducting multivariate analysis on cluster variables that included Cd, Cu, normalized Pb, and normalized Zn data. The dendrogram displays three clusters, namely C1, C2, and C3. The C1 cluster is comprised of Cd and Zn, which are highly correlated at 90.44%. The C2 cluster is formed by Pb, with a strong correlation of 83.99% with Cd and Zn in C1. Lastly, the C3 cluster includes Cu, which has a correlation coefficient of 59.09% with C1 (Cd and Zn) and C2 (Pb). The study's findings revealed that the heavy metals examined derive from a minimum of three distinct pollution sources. Specifically, copper emerges from a separate pollution source and/or is impacted by different factors than the other metals. Conversely, cadmium and zinc share a common pollution source and/or are influenced by similar factors. Lastly, lead shares a pollution source and/or is influenced by similar factors as cadmium and zinc, while also possessing its own distinct source of contamination (Xiao et al., 2021). Fig. 5b

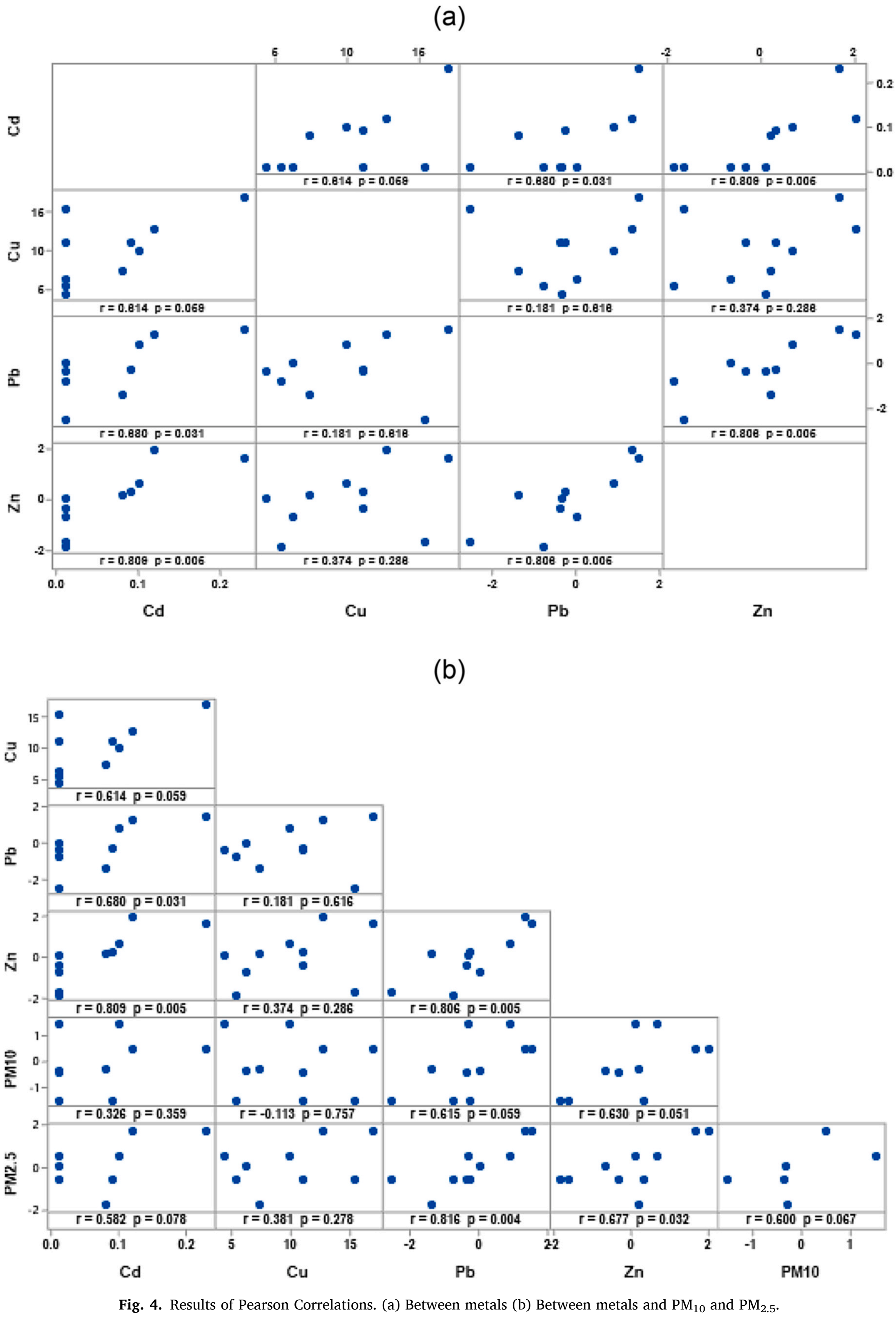

Fig. 4. Results of Pearson Correlations. (a) Between metals (b) Between metals and PM_{10} and $PM_{2.5}$.

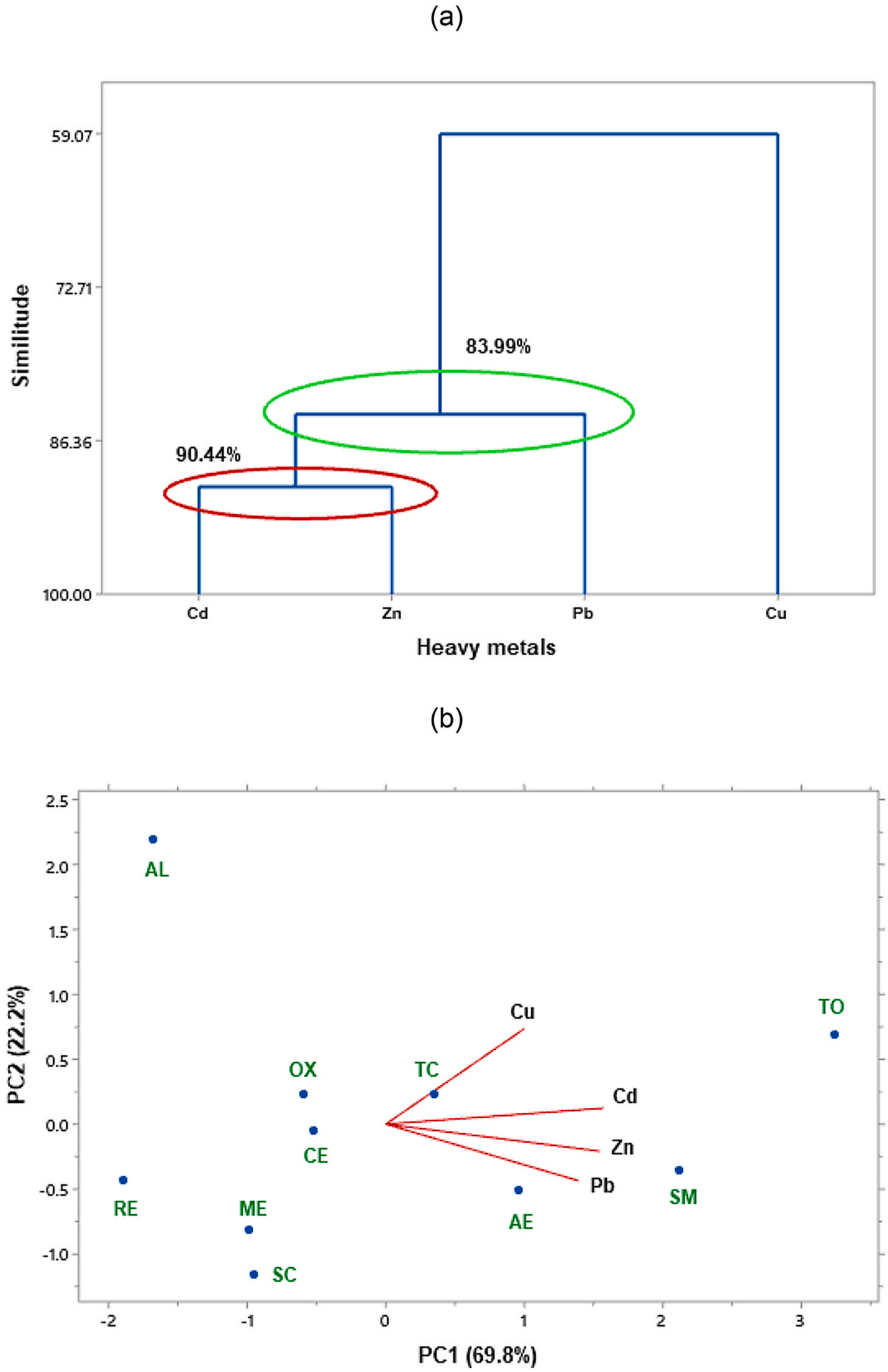

Fig. 5. (a) Dendrogram obtained by HCA, using the distance of the correlation coefficients. (b) Biplot of heavy metals and sampling sites obtained with the moss bags of *L. angustata* by PCA.

shows the biplot of heavy metals and sampling sites obtained by PCA, in the case of heavy metals there are also two trends. The first trend is related to the loads of Cd, Zn, and Pb, which explains 69.8% of the total variance. The second trend is linked to the loads of Cu (mainly) and Cd (marginally), with a total variance of 22.2%. In the case of sampling sites, the scoring plot shows that the sampling sites 1-EA, 7-TO, 9-SM and 10-TC are correlated with a higher metal concentration and a greater impact due to the associated anthropogenic activities. These results confirm the observations obtained from the analysis of clusters, where it is evident that Cd, Zn and Pb can share the same origin, while Cu comes from a different source than the rest of the metals.

Fig. 6a shows the dendrogram resulting from the multivariate analysis, analysis of cluster variables, of the Cd, Cu, normalized Pb, normalized Zn, normalized PM_{10} and normalized $PM_{2.5}$ data. The dendrogram shows three principal clusters C1, C2, and C3. The C1 is formed by Cd and Zn, which has a similarity or correlation coefficient of 80.89%. C2 is formed by Pb and $PM_{2.5}$, which has a correlation coefficient of 81.63%. Finally, C3 is formed by Pb and $PM_{2.5}$ with PM_{10} which are correlated at a level of 60%. These results indicate that Pb, $PM_{2.5}$ and PM_{10} come from a common source of pollution and/or are influenced by

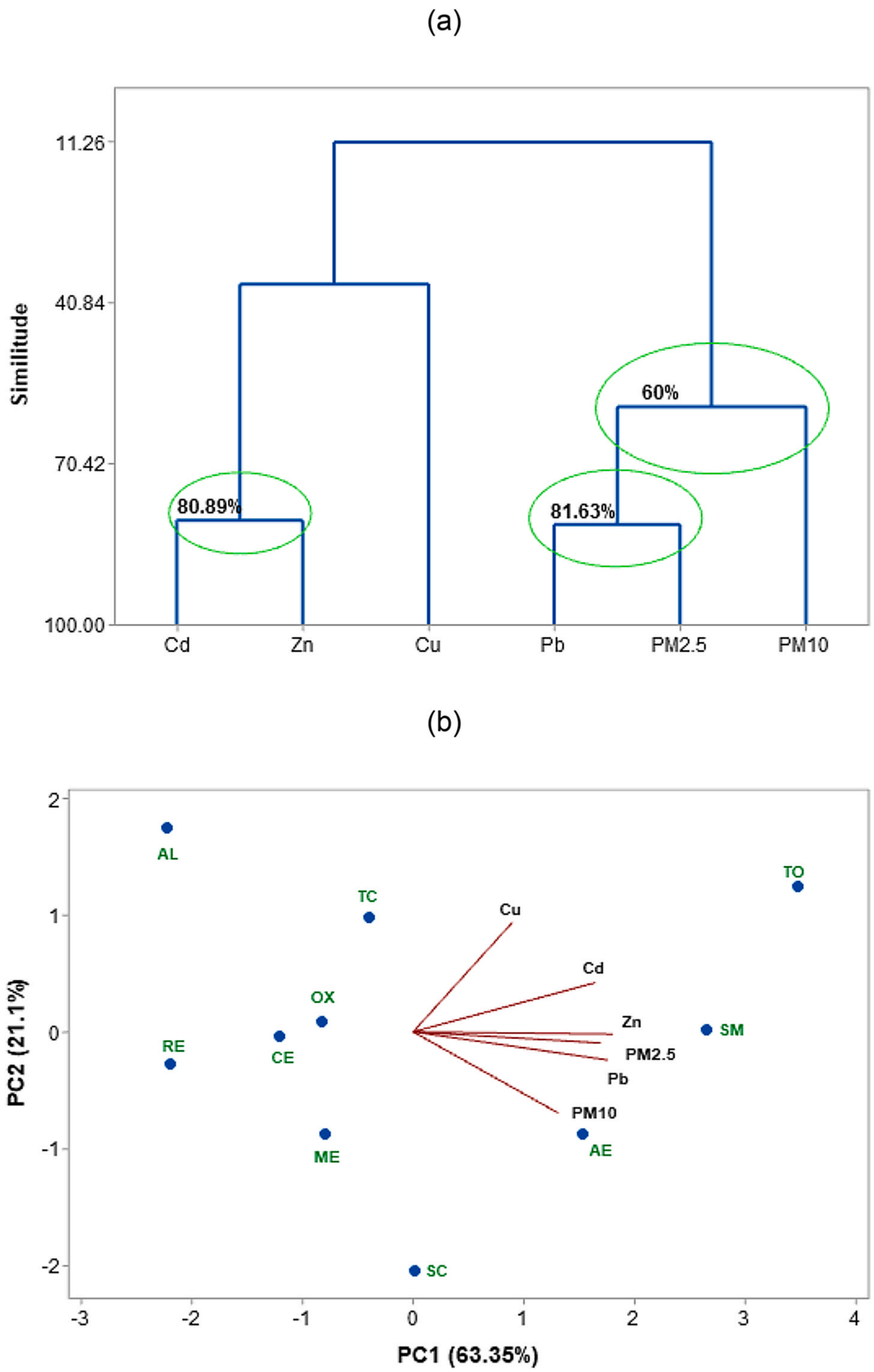

Fig. 6. (a) Dendrogram obtained by HCA, using the distance of the correlation coefficients, and including heavy metals, PM_{10} and $PM_{2.5}$. (b) Biplot of heavy metals, PM_{10}, $PM_{2.5}$ and sampling sites obtained with the moss bags of *L. angustata* by PCA.

similar factors. Fig. 6b shows the biplot of heavy metals, PM_{10}, $PM_{2.5}$ and the sampling sites obtained by PCA. The first component or trend explains 63.3% of the total variance. This trend is linked to the loads of Zn, Pb, $PM_{2.5}$, Cd and PM_{10}. The second trend (PC2) is related to the Cu (mainly) and Cd (minority) loadings, with a total variance of 21.1%. Likewise, it can be observed that the monitoring sites that correlate with the distribution of heavy metals, $PM_{2.5}$, and PM_{10} and that can be inferred to have the greatest impact due to anthropogenic activities are the same sites already shown in Fig. 5b and discussed above. The results obtained confirm that Zn, Pb, $PM_{2.5}$, and Cd share one or more origins or are influenced by similar factors, that PM_{10} also shares a similar origin with Pb and Zn, while Cu has a completely different origin from the others.

The transport sector is the primary contributor to air pollution in urban areas. It releases suspended particulate matter containing toxic elements, which are often concentrated in major roads, junctions, and bus stations. These pollutants have been linked to various severe health effects (Vuković et al., 2016). The foremost anthropogenic sources of airborne particulate matter comprise industrial and livestock processes, domestic fuel usage, residential heating, mining activities, forest fires, fossil fuel combustion, and vehicular traffic (Gallego-Cartagena et al., 2021; Haikerwal et al., 2015; Lelieveld et al., 2015). According to Vuković et al. (2015), in numerous countries with moderate to continental climates, fossil fuel and wood combustion processes are exceedingly intense for residential heating purposes, employing oil, gas, or coal combustion to produce heat. This combustion process results in the emission of high quantities of airborne pollutants, such as particulate matter, that are associated with trace elements. Additionally, thermal inversion processes, low air dispersion due to stagnant atmospheric conditions and low temperatures cause increased concentrations of air pollutants, especially PM_{10} and $PM_{2.5}$ (Perišić et al. 2014; Samara et al. 2014). Some cities are highly polluted with Mn, Pb, Zn, and Hg, emitted from the cement industry and metallurgical operations in this area, as well as moderately polluted, due to the vehicular emissions and city dust (Lazo et al., 2013). The presence of Cu and Zn has been linked to local industrial activities. In the case of Cu, it is used in the production and commercialization of petroleum and hydrocarbons, to modified tars and carbon black oil (Freije, 2015; Gallego-Cartagena et al., 2021; Qing et al., 2015). In the case of Zn, it has been closely related to ZnO particles, which are widely used as an additive coating for steel ting (Ma et al., 2018, Gallego-Cartagena et al., 2021). Accumulation of Zn is also caused by a zinc refining and smelting plant, as a large proportion of zinc is used to galvanize metals such as Fe to prevent corrosion (Frati et al., 2005). Zn has been reported to be one of the tracers of non-exhaust gas traffic emissions, because Zn emissions from tire wear have been shown to be approximately 1000 and 500 times greater than those of Pb and Cu, respectively (Napier et al., 2008). Lead has also been associated with vehicular traffic. It has been observed that Pb contamination still characterizes roads with heavy traffic because of street dust resuspension. In fact, it is well known that the deposition of Pb is mainly incorporated into street dust and in sites with an active dust resuspension, Pb can also be associated with coarse particles (Frati et al., 2005). Pb has been linked to emissions from coal burning, emissions from smelting industries, lead-based paints, lead-acid batteries, and municipal solid waste incineration (Gallego-Cartagena et al., 2021; Khan et al., 2012; Sun et al., 2017; Wu et al., 2012). Wei et al. (2022) demonstrated that the influence of key environmental factors such as elements transported by the airborne dust carried by winds may be related to the presence of statistically significant correlations between elements in *Dicranum angustum* moss in the Arctic and that the presence of Cd, Zn, and Pb in moss tissues is mainly due to industrial and anthropogenic sources.

According to the Emissions Inventory of the State of Mexico (GEM, 2018), domestic combustion is the largest emitter of PM_{10} (34%) and $PM_{2.5}$ (42%) particles in the TVMA. This is due to the high consumption of firewood and LP gas as fuel. In second place is agricultural burning with 20% of emissions for PM_{10} and 24% of emissions for $PM_{2.5}$, because, like firewood, the burning of biomass from agricultural waste emits high amounts of soot particles due to incomplete combustion. Likewise, the important participation of brick factories in both types of particles (7–8%); the unpaved roads also contribute to PM_{10} emissions and buses in $PM_{2.5}$. In this work, significant correlations were found between Cd–Zn–Pb and between Pb and Zn with $PM_{2.5}$, as well as a strong correlation between Pb and Zn with PM_{10}, which allows us to establish that these three metals have their main origin in the domestic combustion of wood and LP gas, as well as emissions from agricultural burning. This is consistent with what has been established by other authors, where PM_{10} and $PM_{2.5}$ emissions are associated with domestic fuel use, agriculture and forest fires, wood combustion processes, and the burning of fossil fuels (Haikerwal et al., 2015; Perišić et al. 2014; Samara et al. 2014).

The statistical results demonstrate that Cd, Pb, and Zn may originate from vehicular emissions, tire wear, and industrial activities. This is because the monitoring sites with the highest concentrations of these metals (9-SM, 7-TO, and 1-AE) are situated in areas with high volumes of vehicular traffic (121,000 average daily annualized vehicular traffic) near the Toluca-Lerma industrial zone and in the direction of the prevailing winds, which are SE-NW (Avila-Pérez et al., 2019; GEM, 2018). Additional sources, such as the combustion of food, paper, plastics, textiles, and rubber foundries, as well as wood and metal melting, emissions from the plastics, textile, and metalworking industries, and the resuspension and redeposition of old Pb from leaded gasoline, may contribute to the presence of Pb in the atmosphere of the TVMA (Chrastný et al., 2018; Yao et al., 2015). Crustal dust is a significant constituent of road dust, and the increase in heavy metals in moss due to road dust is mainly influenced by wind-induced resuspension and vehicle activities, including traffic volume (Vuković et al., 2015). As such, it is possible that some of the metal concentrations examined in this study may have originated from natural sources.

Cu has a different origin than the other metals and PM_{10} and $PM_{2.5}$, so it is likely that agricultural and livestock activities in the region may contribute to the enrichment of this metal (Mirzaei Aminiyan et al., 2018), because fertilizers and pesticides have been described as an important source of Cu (McBride and Spiers, 2001; Pan et al. 2016). Therefore, the intensive use of pesticides and fertilizers used on crops in agricultural and livestock areas can transfer Cu through runoff, and this metal is likely to be resuspended and deposited by the wind in the TVMA. Additionally, Cu can be related to the activities of the automotive, glass, paints, and electroplating industries located in the Toluca-Lerma industrial sector (Avila-Pérez et al., 2019).

Varela et al. (2023) have demonstrated the existence of cuticles, epidermis, and rhizoids in mosses. Consequently, moss cells are not directly exposed to pollutants deposited from the atmosphere and can not only obtain water and nutrients (and, potentially, pollutants) from the atmosphere, as is often assumed. Therefore, the absorption (and loss) of pollutants depends both on the type of cuticle, epidermis, and phyllids characteristics. The role of these moss structures in pollutant uptake processes and the effect on the results of biomonitoring studies are unknown. Therefore, greater efforts are needed on this issue.

4. Conclusions

The results of the bioassays on the moss *L. angustata*, demonstrate that this moss has adequate accumulation capabilities to be used as a biomonitor of heavy metals in polluted areas. The preference, affinity, or accumulation capacity of the metal by the moss was Cd > Cu > Pb > Zn. The characterization of the moss *L. angustata*, using FTIR and B.E.T. shows that this moss has good adsorption characteristics (presence of functional groups, surface area of 19.87 $m^2 g^{-1}$, average pore diameter equal to 2.86 nm and a total pore volume of 0.014218 $cm^3 g^{-1}$) to be used as a biomonitor of heavy metal pollution associated with airborne particulate matter from urban areas. The sites 9-SM, 7-TO, and 1-AE exhibit the most significant pollution issues linked to heavy metals in the TVMA. These sites are defined by heavy vehicular traffic, proximity to industrial areas, and their location near the international airport in Toluca city. Sites 4-ME, 2-AL and 6-RE have the least heavy metal pollution problems in the TVMA and are characterized by being sites located within parks in the municipalities of Metepec and Toluca with the forest vegetation present, which may act as a barrier for retaining particulate matter in the air. Cd, Pb, Zn and $PM_{2.5}$ share one or more origins or are influenced by similar factors, while PM_{10} also shares a similar origin with Pb and Zn, and that Cu has a completely different origin from the others. The significant correlations between Cd–Zn–Pb and between Pb and Zn with $PM_{2.5}$, as well as a strong correlation between Pb and Zn with PM_{10}, allow us to establish that these three metals have their main origin in the domestic combustion of wood and LP gas, as well as emissions from agricultural burning. Cd, Pb and Zn may have alternative origins, such as vehicular emissions, tire wear, and industrial activities, because the monitoring sites that have the highest levels of these metals are in areas with high vehicular traffic and close to the Toluca-Lerma industrial zone, as well as in the direction of the prevailing winds. However, it cannot be ruled out that a portion of the concentration of the metals studied in this work comes from natural sources. Cu has a different origin than other metals and PM_{10} and $PM_{2.5}$, so it is likely that fertilizers and pesticides can contribute to the enrichment of this metal and may be related to the activities of the automotive, glass, paints and electroplating industries located in the Toluca-Lerma industrial sector. The studied moss species, *L. angustata*, demonstrated effectiveness as a heavy metal monitor in the TVMA, presenting results comparable to other urban moss species. The findings demonstrate a strong association between anthropogenic activities - such as domestic wood and LP gas combustion, agricultural burning emissions, vehicular emissions, tire wear, and industrial activities - and the detection, entrapment, and accumulation of several heavy metals by *L. angustata* moss.

CRediT authorship contribution statement

M.G. Macedo-Miranda: Writing – original draft, Resources, Funding acquisition, Conceptualization. **C.E. Barrera-Díaz:** Writing – review & editing, Resources, Formal analysis. **P. Avila-Pérez:** Writing – review & editing, Writing – original draft, Resources, Funding acquisition, Formal analysis, Data curation, Conceptualization. **E. López-Solórzano:** Writing – original draft, Investigation, Data curation. **H.B. Ortiz-Oliveros:** Validation, Software, Investigation, Formal analysis. **R.E. Zavala-Arce:** Methodology, Investigation, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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