1916 - 2026

An Acad Bras Cienc (2026) 98(Suppl. 1): e20250560 DOI 10.1590/0001-3765202620250560
Anais da Academia Brasileira de Ciências | *Annals of the Brazilian Academy of Sciences*
Printed ISSN 0001-3765 I Online ISSN 1678-2690
www.scielo.br/aabc | www.fb.com/aabcjournal

GEOSCIENCES

Assessing trace metal concentration in urban soils: a study of urban parks and unforested urban areas

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Abstract: Urban soils act as long-term reservoirs for trace metals, yet how soil physicochemical properties and anthropogenic pressure interact over time remains poorly understood in medium-sized cities of the Global South. This study evaluates the spatiotemporal dynamics and ecological risks of Ba, Cu, Zn, Pb, Cr, Ni, Mo, Co, and Cd in urban topsoils, through a 33-week monitoring campaign. Linear Mixed Models (LMM) and Positive Matrix Factorization (PMF) were combined to identify retention controls and source contributions. No significant temporal variability was observed ($p > 0.05$), confirming soil as a stationary reservoir, whereas marked spatial heterogeneity occurred ($p < 0.001$), driven by localized soil properties. LMM results highlighted soil organic matter (SOM) as a key enhancer of Cu ($\beta = 6.15$) and Zn ($\beta = 17.9$) retention, while pH exerted a strong negative control on Pb mobility ($\beta = -23.9 \times 10^{4}$). PMF identified three major contributors: geogenic sources (35.9%), industrial/traffic emissions (32.4%), and mixed anthropogenic-lithogenic inputs (30.7%). Although metal concentrations remained below intervention thresholds, localized Cd-driven ecological risks persist in densely populated areas. This study highlights that vegetation and SOM function as vital geochemical sinks for metal immobilization, offering effective pathways for sustainable urban risk mitigation.

Key words: trace metals, urban soil, urban parks, urban pollution.

INTRODUCTION

Soil pollution originates from both geogenic and anthropogenic sources. While natural processes have historically influenced soil composition, human activities, especially over the past few centuries, have significantly intensified the exposure to pollutants (Bussian & Eugenio 2021, Dror et al. 2021). This issue is especially pronounced in developing countries, where unplanned urban growth, industrialization, and increasing traffic have exacerbated pollution by trace metals (Kabir et al. 2012, Bussian & Eugenio 2021, Chand et al. 2024).

Urban soil contamination arises from diverse sources, including transportation (e.g., vehicle emissions, wear and tear of parts), industrial activities such as metallurgy, electronics manufacturing, and steel production (Binner et al. 2023, Cheng et al. 2014, Modabberi et al. 2018, Wei & Yang 2010), civil construction, metal structure weathering, waste incineration, and legacy pollution (Donado et al. 2021, Sager 2020). Trace metals are primarily released into the atmosphere and subsequently removed through various deposition processes, including

dry and wet deposition (Albanese & Cichella 2012, Wong et al. 2006). Adsorbed or bound to particles, these elements are transported over long distances by wind and rain, ultimately depositing in water bodies or soil (Connan et al. 2013, Werkenthin et al. 2014). Pollutants are transported via water through road runoff, surface infiltration, and eventual groundwater movement (Binner et al. 2023). As a result, urban soils serve as stationary reservoirs for pollutants, some with half-lives extending to hundreds of years (Albanese & Cichella 2012).

The retention of trace metals in soils is influenced by physicochemical properties such as pH, cation exchange capacity, clay content, and soil organic matter content (Gu & Gao 2018, Kowalska et al. 2018, Lehmann & Stahr 2007). Vegetation cover also plays a vital role by intercepting pollutants and acting as a barrier against urban pollution (Nowak et al. 2006, Gredilla et al. 2017, Selmi et al. 2016). However, the spatial variability of soil contamination is influenced by proximity to pollution sources, land use patterns, and historical development (Albanese & Cichella 2012, Liu et al. 2020, Luo et al. 2012, Pouyat et al. 2015, Tume et al. 2014, 2018, Guo et al. 2023). For instance, urban parks near roads exhibited elevated levels of Cu, Pb, and Zn, due to vehicular traffic, while those close to chemical and cement industry facilities showed higher concentrations of Pb and Cd (Kuzmanoski et al. 2014, Gredilla et al. 2017, Cui et al. 2011).

Trace metals, when present in elevated concentrations, can become toxic and pose significant risks to human health. In urban environments, exposure to these elements occurs primarily through ingestion, inhalation, and dermal contact, particularly in settings such as urban parks (Gredilla et al. 2017, Sager 2020, Vasenev et al. 2018, Xia et al. 2011). This exposure has been associated with a wide range of health issues, including respiratory damage (Madrid et al. 2002, Manta et al. 2002), neurological disorders, cardiovascular diseases, cancer, and, in severe cases, mortality (Li et al. 2014, Sapcanin et al. 2017, He et al. 2013, Pecina et al. 2021). Given these risks, assessing the level of trace metal pollution in urban soil and understanding its potential risks to the environment is essential. Among the various methods utilized in recent years for evaluating soil pollution, the use of geochemical indicators normalized to the background levels has emerged as a reliable approach for assessing and comparing environmental quality (Hosseini & Sobhanardakani 2024). Additionally, to identify and categorize the sources of trace metals pollution in urban soil, models such as Positive Matrix Factorization have been successfully applied (Li et al. 2023, Huang et al. 2022, Jiang et al. 2021, Guan et al. 2018, Fei et al. 2020).

Despite the significant environmental and health risks posed by urban soil pollution, research on this topic remains limited, particularly in urban parks in developing regions. Compared to agricultural and industrial zones, urban parks have unique properties that influence pollution dynamics but are often understudied. Most previous studies have focused on pollution sources or health impacts, but few have simultaneously examined the role of vegetation in modifying soil properties alongside multi-index risk assessments and source apportionment modeling in urban soils (Shen et al. 2024, Madrid et al. 2002, Setälä et al. 2017, Xing & Brimblecombe 2019, Gredilla et al. 2017).

We hypothesize that vegetation in urban parks enhances the soil's capacity to retain trace metal contaminants by modifying its physicochemical properties. To test this hypothesis, we aim to: (1) compare contamination levels of urban topsoil from vegetated and non-vegetated urban areas; (2) assess how soil

characteristics (pH, cation exchange capacity, clay content, and organic matter) influence metal adsorption; (3) quantify ecological risks using multiple geochemical indices (e.g., geoaccumulation index, enrichment factor, contamination factor, pollution load index and potential ecological risk index); (4) apply Linear Mixed Models to account for variability across sampling sites and evaluate differences in soil contamination and properties; and (5) apply Positive Matrix Factorization (PMF) to distinguish between anthropogenic and geogenic sources of contamination.

MATERIALS AND METHODS

Study area and sampling sites

Limeira is a city located 154 km northwest of São Paulo State's capital, with an estimated population of 310,783 (IBGE 2022). Its economy is supported by diverse industrial sectors, including metallurgy and nonmetallic mineral products, alongside agriculture (particularly citrus, sugarcane, and cellulose production), and the manufacture of semiprecious jewelry (Baeninger et al. 2012). The city hosts a vehicular fleet of approximately 228,677 units, including 134,757 cars and 4,996 trucks (IBGE 2022). According to Köppen climate classification, Limeira has a humid subtropical climate with dry winters and hot, humid summers (Cwa) (Alvares et al. 2013). Limeira is underlain by sedimentary and magmatic rocks of the Paraná Basin, including siltstones, sandstones, and shales of the Itararé Group, as well as diabase sills associated with the Serra Geral Formation (Fúlfaro 1971, Lino & Perinotto 2007, Zaine 1994).

Soil samples were obtained from four urban sites: two urban parks (*Bosque Prefeita Maria Thereza* Park and *Cidade de Limeira* Park), one university campus (School of Technology), and one schoolyard (Prada School). All sampling locations are situated within the urban perimeter of Limeira (Figure 1). These locations were purposely selected to contrast vegetated and built environments while remaining under comparable atmospheric influence. Bosque and Limeira Parks have dense canopy cover, persistent leaf litter, and minimally disturbed soil profiles, whereas the School and University Campus show limited vegetation, extensive pavement, and heavy traffic. The main physical attributes for each site are presented in Table I.

Sampling methods and preparation

We collected topsoil samples (0-5 cm depth) during weekly sampling campaigns conducted between September 2019 and March 2020, resulting in a total of 132 samples over 33 weeks. The sampling strategy was designed as a monitoring effort to assess potential temporal variations in urban soil properties, particularly in relation to trace metal concentrations. Weekly sampling allowed us to capture possible changes driven by environmental conditions, anthropogenic inputs, or seasonal dynamics. At each site, a composite sample was obtained by thoroughly mixing five subsamples collected from the corners and center of a 1 m^2 area using an acrylic shovel. Soil pH was measured directly using a Soil pH tester Grolin (accuracy ± 0.2 pH). After manually removing coarse-grained particles and vegetation, the samples were packed in polyethylene bags and transported to the laboratory. To minimize the risk of cross-contamination, we used individual acrylic shovels at each sampling site. Following each sampling procedure, all shovels were cleaned by immersion in 10% nitric acid for at least 24 hours. In the laboratory, the soil samples were oven-dried at 40°C for at least 24 hours, sieved with 2 mm nylon sieve mesh, and pulverized in a mortar grinder (Pulverizette 2 Fritsch) with an agate (SiO_2) for 5 minutes. The samples

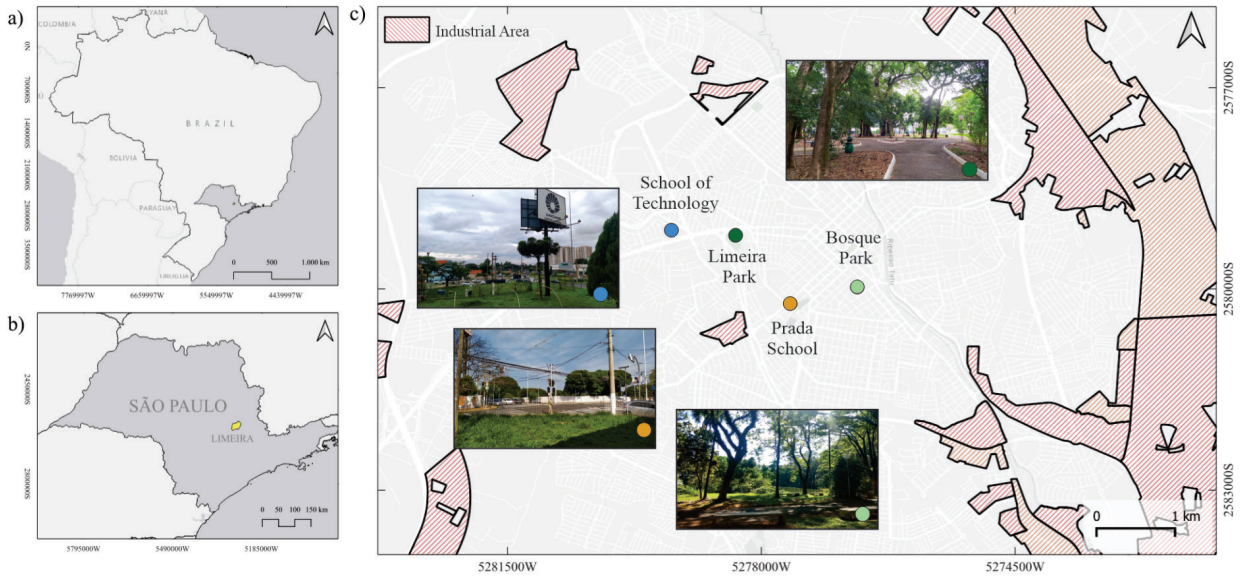


Figure 1. Location of sampling sites included in this study. a) Map of Brazil; b) State of São Paulo and Limeira City location; c) Detailed sampling points in urban parks and unforested areas.

were subsequently sieved through 0.074 mm nylon sieve mesh before being stored in acrylic containers for analysis.

Analytical methods

The concentrations of major and trace elements in the soil samples were determined according to EPA Method 3051a (EPA 2007), which employs microwave-assisted acid digestion of soil and sediments for trace metals quantification. A 0.5 g sample was added to Teflon tubes along with 9 ml of concentrated nitric acid and 3 ml of concentrated hydrochloric acid, and then digested in a closed-vessel microwave digestion system (Ethos Advanced Microwave Digestion System) for 50 minutes. During the digestion process, the ramp rate of temperature increased to 180°C over the first 15 minutes and was maintained at this temperature for an additional 10 minutes. During the final 25 minutes, the samples were allowed to cool to room temperature. After digestion, the samples were centrifuged at 3,500 rpm for 10 minutes, and the resulting supernatant was subsequently removed. The samples were then diluted to a final volume of 50 ml with ultrapure water. To ensure the reliability of the analytical results, blank samples prepared with deionized water underwent the same digestion process as part of quality control procedures.

Analysis of Cd, Cu, Fe, and Pb in the digested samples was performed by FAAS (Varian Spectra AA-220 model) using an air-acetylene flame. The samples were also analyzed for Al, Ba, Ca, Co, Cr, K, Mg, Mn, Mo, Na, Ni, and V by ICP OES (Agilent 5100 model). Details of the operational conditions and the limitations of detection and quantitation are provided in Appendix I. To ensure reproducibility and quality control, the analysis sequence consisted of calibration of standards, method blanks, and certified material references. FAAS validation utilized the National Institute of Standards & Technology (NIST) certified reference material 2709a (San Joaquin Soil), whereas ICP OES validation employed NIST-certified reference material 1648 (Urban Dust) (Table II). Once validated, FAAS was used for the

Table I. Characteristics of the sampling sites.

Name	Localization	Land use	Traffic intensity	Area (m²)	Ground cover	Location description
Bosque Park	22° 34' 10.38" S 47° 24' 7.11" W	Urban Park	Low	20,000	Dense tree cover and thick litter	Located in a residential district, this park features native vegetation, river springs, and recreational spaces.
School of Technology	22° 33' 43.81" S 47° 25' 21.33" W	University Campus	High	55	Sparse trees and grass	Located in a commercial district adjacent to a high-traffic road.
Limeira Park	22° 33' 45.01" S 47° 24' 58.77" W	Urban Park	High	96,000	Dense trees cover and thick litter	Situated in a commercial area near a major road, the park offers native trees and recreational and equestrian facilities.
Prada School	22° 34' 15.62" S 47° 24' 35.14" W	Schoolyard	High	33	Sparse trees and grass	The school is in a commercial district adjacent to a busy arterial road.

determination of Cd, Cu, Fe, and Pb, whereas the remaining elements were quantified by ICP OES.

Regarding the physicochemical properties of the soil, we assessed the cation exchange capacity (CEC), soil organic matter (SOM) content, and particle size distribution. The CEC was determined through extraction using a barium chloride solution (Gillman 1979, Gillman & Sumpter 1986). The SOM content was estimated by the Walkley-Black method (Camargo et al. 2009). CEC and SOM measurements were conducted by the Unithal Laboratory (Campinas, Brazil) and were certified under ISO 17025. Particle-size distribution was determined on bulk soil fraction following the Brazilian technical standard (ABNT 2016). Soil texture was classified according to the Brazilian system of Lemos & Santos (1996). For international comparison, approximate equivalents of the USDA soil textural classes (USDA 2017) are provided.

The distribution and homogeneity of the soil sample data were evaluated using the Shapiro-Wilk test for normality in Jamovi 2.4.14, adopting a significance level of $p < 0.05$. Given that samples were repeatedly collected from the same locations over time, thereby violating the independence assumption of traditional ANOVA, Linear Mixed-Effects Models (LMMs) were employed. These models were also implemented in Jamovi and accounted for temporal dependence by incorporating random intercepts for each week, ensuring robust comparisons among sampling sites. Model parameters were estimated using Restricted Maximum Likelihood (REML), and the significance of the fixed effect was evaluated at $p < 0.05$. Post-hoc comparisons between sites were conducted using Tukey-adjusted contrasts, also adopting a significance threshold of $p < 0.05$.

Pollution and ecological risk indices

To evaluate pollution levels of urban soils, we calculated the geoaccumulation index (I_{geo}), enrichment factor (*EF*), contamination factor (*CF*), pollution load index (*PLI*), index of ecological risk (E_r), and potential ecological risk index (*RI*) (Müller 1969, Hakanson 1980).

Table II. Comparison between measured and certified values of reference materials (NIST 2709a and NIST 1648) analyzed by FAAS and ICP OES.

Certified materials	Element	Certified value ± SD ($mg.kg^{-1}$)	Average measure value ± SD ($mg.kg^{-1}$)	Recovery (%)
San Joaquin Soil (NIST 2709a)	Cd	0.380 ± 0.010	0.430 ±0.200	113
	Cu	34.6 ± 0.700	36.1 ± 3.48	104
	Fe	$3.50\times10^{4} \pm 1.10\times10^{3}$	$2.46\times10^{4} \pm 770$	70.2
	Pb	18.9 ± 0.500	19.5 ± 2.16	103
Urban Dust (NIST 1648)	Al	$3.43\times10^{4} \pm 1.30\times10^{3}$	$1.50\times10^{4} \pm 372$	43.7
	Ca	$5.84\times10^{4} \pm 1.90\times10^{3}$	$5.78\times10^{4} \pm 1.04\times10^{3}$	98.9
	Cd	73.7 ± 2.30	93.0 ± 3.20	126
	Cu	610 ± 70.0	647 ± 15.0	106
	Fe	$3.92\times10^{4} \pm 2.10\times10^{3}$	$2.65\times10^{4} \pm 951$	67.6
	K	$1.06\times10^{4} \pm 500$	$6.90\times10^{3} \pm 155$	65.3
	Mg	$8.13\times10^{3}\pm120$	$7.14\times10^{3} \pm 332$	87.8
	Mn	790 ± 44.0	843 ± 26.0	107
	Na	$4.24\times10^{3} \pm 60.0$	$3.00\times10^{3}\pm135$	70.8
	Pb	$6.55\times10^{3}\pm$	$6.44\times10^{3} \pm 213$	98.3
	Zn	$4.80\times10^{3} \pm 270$	$5.16\times10^{3} \pm 137$	108

The I_{geo} assesses the pollution level of individual metals in the soil by comparing current concentration to geochemical background levels (Różański et al. 2018, Müller 1969). It is calculated using Eq. 1, where *Cn* represents the current concentration in the soil and *Bn* corresponds to its background value. The geoaccumulation index is classified as: unpolluted $\left(I_{geo} < 0\right)$, unpolluted to moderately polluted $\left(0 < I_{geo} < 1\right)$, moderately polluted $\left(1 < I_{geo} < 2\right)$, moderately to strongly polluted $\left(2 < I_{geo} < 3\right)$, highly polluted $\left(3 < I_{geo} < 4\right)$, highly to extremely polluted $\left(4 < I_{geo} < 5\right)$, and extremely polluted $\left(I_{geo} > 5\right)$ (Müller 1969).

$$I_{geo} = \log_2(Cn/1.5*Bn) \quad \text{(Eq. 1)}$$

The *EF* quantifies the enrichment of an element in soil relative to its natural abundance and allows distinguish anthropogenic influence (Bern et al. 2019). It is calculated using Eq. 2, where $(Cn/Cb)_{sample}$ is the ratio between the concentration of element n and the reference element in the sample, and $(Cn/Cb)_{background}$ is the same ratio in the geochemical background. The enrichment factor is categorized as: minimal enrichment ($EF < 2$), moderate ($2 \leq EF < 5$), significant ($5 \leq EF < 20$), very high ($20 \leq EF < 40$), and extremely high enrichment ($EF > 40$), (Sutherland 2000, Hakanson 1980).

$$EF = (Cn/Cb)_{sample}/(Cn/Cb)_{background} \text{ (Eq. 2)}$$

The *CF* expresses the ratio between the metal concentration in the soil (*Cm*) and its background value (*Cb*) (Eq. 3) (Silva et al. 2021, Hakanson 1980). The contamination factor is classified as: low ($CF < 1$), medium ($1 < CF < 3$), high ($3 < CF < 6$), extremely contamination ($CF > 6$) (Hakanson 1980).

$$CF = Cm / Cb \quad \text{(Eq. 3)}$$

The *PLI* is a tool used to assess the overall pollution status of a site, calculated as the geometric mean of *CF* values (Eq. 4) (Silva et al. 2021, Tomlinson et al. 1980). It is categorized as: low pollution (*PLI* < 1), moderate pollution (1 < *PLI* < 3), and high pollution (*PLI* > 3) (Chen et al. 2005).

$$PLI = (CF1 * CF2 * ... * CFn)^{1/n} \quad \text{(Eq. 4)}$$

The *RI* is used to evaluate the potential ecological risk posed by the soil and to determine the extent of heavy metal contamination, considering both their concentration and toxicity (Qing et al. 2015, Wu et al. 2015). *RI* is calculated using Eq. 5, where E_r^i is the degree of ecological risk of a single element and *Tr* is the toxic response factor. *Tr* for the metals are Cd=30, Cr=2, Cu=5, Ni=5, Pb=5 and Zn=1 (Hakanson 1980, Zgłobicki et al. 2018).

The degree of ecological risk is classified as: low ($E_r < 40$), moderate ($40 < E_r < 80$), considerable ($80 < E_r < 160$), high ($60 < E_r < 320$) and very high potential ($E_r > 320$) (Hakanson 1980, Pecina et al. 2021). Similarly, *RI* is interpreted as: low (*RI* < 150), moderate (150 < *RI* < 300), considerable (300 < *RI* < 600), and very high ecological risk (*RI* > 600) (Hakanson 1980, Pecina et al. 2021).

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} Tr_i * CF \quad \text{(Eq. 5)}$$

Positive Matrix Factorization Model

The Positive Matrix Factorization (PMF) receptor model uses multivariate data analysis and factor analysis to identify and categorize pollution sources. It is particularly effective for determining the origins of pollutants in urban soils (Li et al. 2023, Huang et al. 2022, Jiang et al. 2021, Guan et al. 2018, Fei et al. 2020). In PMF, the concentration matrix *X* is decomposed into two matrices: factor contributions (*g*) and factor profiles (*f*) (Norris et al. 2014). Using a least-squares fitting approach, the model reduces data dimensionality into *p* latent factors (Hopke 2000, Paatero & Tapper 1994), as shown in Eq. 6 (Hopke 2000).

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad \text{(Eq. 6)}$$

The PMF model estimates the matrices *g* and *f* by minimizing the objective function *Q*, which accounts for the uncertainties u_{ij} of each data point (Eq. 7).

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{m} [(x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}) / u_{ij}]^2 \quad \text{(Eq. 7)}$$

Uncertainty estimates (u_{ij}) were calculated according to EPA (2014), based on analyte concentration (*c*) and the limit of detection (*LOD*). For values below or equal to the *LOD*, uncertainty was estimated using Eq. 8; for values above the *LOD*, Eq. 9 was applied, with a fixed error fraction of 10%. *LOD* values used are provided in Table SII.

$$For\ c \leq LOD,\ u_{ij} = 5/6\ x\ LOD \quad \text{(Eq. 8)}$$

$$For\ c > LOD,\ u_{ij} = \sqrt{(\varphi * c)^2 + (LOD * 0{,}5)^2} \quad \text{(Eq. 9)}$$

where *i* is the number of samples; *j* is the number of chemical species; *p* is the number of factors; *f* is the number of profiles; *g* is the contribution of each factor to individual samples; *e* is the residual number of species; *u* is the estimated uncertainty; and *LOD* is the limit of detection of the analytical method.

RESULTS AND DISCUSSION

Soil characteristics and metal adsorption

Soil characteristics, including particle size distribution, textural classification, cation exchange capacity (CEC), soil organic matter (SOM), and pH, are detailed in Table III, which presents the mean values across all samples.

Table III. Particle size distribution, cation exchange capacity (CEC), organic matter (OM), textural class, and pH of urban soils.

Local	Sand (%)	Silt (%)	Clay (%)	Textural class	CEC ($cmol.kg^{-1}$)	SOM (%)	pH in situ
Bosque Park	28.0	22.0	50.0	Clay	6.27	4.80	6.38 ± 0.81
School of Technology	42.0	28.0	30.0	Clay Loam	7.12	5.80	5.17 ± 0.63
Limeira Park	40.0	12.0	48.0	Clay	9.71	4.60	6.46 ± 0.64
Prada School	72.0	12.0	16.0	Sandy Loam	4.51	2.40	5.62 ± 0.60

These physicochemical properties are critical for understanding metal-soil interactions and adsorption capacity (Denaix et al. 2001, Kabata-Pendias & Pendias 2001). To investigate these relationships while accounting for spatial dependence, we applied LMMs to a subset of 33 samples. The models incorporated clay content, SOM, and pH as fixed effects, with random intercepts by sampling site to account for intra-site dependencies. Each metal (Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, and Zn) was analyzed independently.

A strong positive correlation in all sites was observed between clay content and CEC (Pearson's $r > 0.70$, $p < 0.05$), consistent with clay's colloidal properties and its characteristically large surface area and permanent negative charge (Alloway 2013, Lepsch 2010, Setälä et al. 2017). Due to high multicollinearity between CEC and clay, we excluded CEC from the final models to ensure robust parameter estimation.

Soil pH is a critical factor influencing the solubility and mobility of trace metals (Brady & Weil 2013). Hydrogen ions (H^+) strongly interact with negatively charged soil surfaces, displacing most cations, including trace metals (Alloway 2013, Brady & Weil 2013, Pagnanelli et al. 2003). The optimal pH range for trace element adsorption is generally considered to be 5.7 to 7 (Adriano 2001, Kabata-Pendias 2011). Accordingly, all study sites exhibited favorable conditions for adsorption. Metals such as Ni, Zn, Cu, Cd, Co, and Pb demonstrate enhanced adsorption capacity under alkaline conditions (Adriano 2001). For Pb, pH emerged as the sole significant predictor of Pb concentrations ($\beta = -2.39 \times 10^4$, $p < 0.01$), suggesting that acidic soil conditions increase its mobility. SOM, CEC, and clay content exhibited no detectable effects ($p > 0.45$), suggesting that Pb adsorption in this system is predominantly governed by pH-dependent mechanisms, such as precipitation or binding to oxide surfaces (Figure S1). The absence of a significant correlation between soil pH and other metals observed in this study aligns with findings from previous findings, which attribute such variations to human-induced modifications in soil dynamics, including alkalization and oxidation in urban environments (Setälä et al. 2017, Manta et al. 2002, Ribeiro et al. 2012).

Besides soil pH, SOM is also important in determining the retention capacity of soils (Lair et al. 2007). SOM was a significant positive predictor of Cu ($\beta = 6.15$, $p < 0.05$) and Zn ($\beta = 17.9$, $p < 0.01$) (Figure S2-S3). Furthermore, SOM is 10.8 and 8.20 times more effective than mineral matter as a sorbent for Zn and Cu, respectively (Lair et al. 2007). Clay content was positively associated with Ni ($\beta = 0.174$, $p < 0.05$) and Cu ($\beta = 2.15$, $p < 0.01$) concentrations, but negatively

correlated with Ba (β=-1.57, p < 0.01) and Zn (β=-1.69, p<0.01). Clay-rich soil has been associated with elevated metal concentrations in numerous urban parks (Ljung et al. 2006, Huang et al. 2021, Zhaoyong et al. 2018). Similarly, dos Santos et al. (2017) found that clay-rich soils exhibited higher concentrations of Pb and Zn compared to sandy soils under identical anthropogenic influences in *Todos os Santos Bay* (Brazil).

Bosque Park and Limeira Park exhibited superior adsorption capacities, attributed to their relatively high clay content (50% and 48%, respectively) and SOM content (> 4.5%). These properties contributed to elevated CEC values (> 6 $cmol.kg^{-1}$) at both locations, facilitating metal retention, particularly for elements such as Zn and Cu. The high SOM content in these parks was further supported by the presence of humus derived from leaf litter and roots, underscoring the critical role of vegetation in trace metal retention in urban environments (Setälä et al. 2017, Acosta et al. 2014). Humus compounds contain functional groups, such as carboxyl and phenolic hydroxyl groups, that are primary contributors to the soil's total negative charge (Acosta et al. 2014). At the School of Technology site, the high CEC was attributed to both the clay content and the presence of grasses, which enhanced SOM accumulation (Acosta et al. 2014). In contrast, Prada School, characterized by sandy soil (16% clay content) and low SOM content, showed the lowest CEC among all sites.

Quantitative analysis and contamination level

Table IV displays the means, medians, minimums, maximums, coefficients of variation, and standard deviations for Al, Fe, Ca, K, Mg, Mn, Na, P Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, and Zn. Elements with more than 50% of values below *LOD* were excluded. For representative concentration levels, we used average values. Additionally, we assessed statistically significant differences among the four sites using LMMs followed by Tukey's post-hoc tests.

Figure 2 displays violin plots of selected trace metals alongside the Brazilian reference limits for Ba, Cd, Co, Cr, Cu, Ni, Pb, and Zn (CETESB 2014) (Table SIII). According to this guideline, Quality Reference Values (QRVs) represent permissible concentrations in uncontaminated soil, corresponding to natural background levels; Prevention Values (PVs) indicate levels above which soil quality may deteriorate; and Intervention Values (IVs) indicate concentrations that pose direct or indirect risks to human health, applicable across various land-use scenarios. While international guidelines (e.g., U.S. EPA, Dutch guidelines) offer useful frameworks, accurate soil quality assessments require locally derived indices. These indices account for regional background levels and specific physical, chemical, and geological characteristics (Penteado et al. 2022). Tailoring assessments to the local context prevents misinterpretation of pollution levels and ensures more reliable evaluations of soil quality.

Major elements, predominantly inherited from the parent material, constitute the baseline chemical composition of tropical soil. Geological surveys indicate that the study area is dominated by red latosols (Oxisols) developed from siltstones and sandstones of the *Tatuí* Formation (Paraná Basin) (Santos et al. 2011). These soils are typically deep, clay-rich, and highly weathered, with lowCEC, elevated Fe_2O_3 and Al_2O_3 content, and generally low natural fertility (IAC 2014, Ferreira et al. 1999).

The geochemical profiles are consistent with lithogenic control, with Al and Fe dominating across all sites, reflecting inheritance from the parent material. Elevated Al and Fe concentrations are widely reported in Brazilian urban soils developed under acidic tropical

Table IV. Major and minor elements contents (mg.kg^{-1}) in urban soil.

Local		Major element content								Minor element content									
		Al	Fe	Ca	K	Mg	Mn	Na	P	Ba	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
Bosque Park	Mean	9.36×10^4	5.49×10^4	1.39×10^3	1.46×10^3	47.8	429	114	508	45.8	*	1.20	60.2	119	1.42	22.0	22.8	343	82.7
	Median	9.46×10^4	5.49×10^4	1.33×10^3	5.14×10^4	46.5	417	73.0	500	43.1	*	1.70	60.5	123	1.29	21.9	21.7	352	81.4
	Min.	7.02×10^4	4.17×10^4	644	872	60.5	303	35.0	347	28.7	*	0.030	50.9	81.4	0.25	16.1	14.9	261	58.0
	Max.	1.12×10^5	6.19×10^4	2.42×10^3	3.47×10^3	114	765	437	759	71.7	*	3.52	67.0	157	3.91	28.1	30.0	428	99.3
	CV	11.9	8.53	35.3	31.6	27.7	17.3	90.4	20.1	34.4	*	44.2	7.16	15.4	54.9	15.2	23.5	10.9	12.1
	SD	1.11×10^4	4.68×10^3	489	462	13.2	74.0	103	102	15.7	*	0.530	4.31	18.4	0.780	3.35	5.36	37.2	10.0
School of Technology	Mean	6.82×10^4	3.44×10^4	1.58×10^3	1.52×10^3	82.7	517	70.0	416	76.8	0.540	0.630	43.3	48.3	3.08	15.6	48.5	130	142
	Median	6.86×10^4	3.18×10^4	1.63×10^3	1.55×10^3	83.2	525	69.0	424	77.7	0.490	0.490	43.4	48.1	2.99	16.2	48.0	132	147
	Min.	5.40×10^4	2.55×10^4	1.21×10^3	1.12×10^3	69.7	399	49.0	249	60.4	0.120	0.020	34.8	32.7	1.60	12.6	30.6	105	85.1
	Max.	8.96×10^4	4.55×10^4	1.89×10^3	2.90×10^3	96.9	653	113	565	101	1.31	1.60	56.3	64.0	4.40	19.8	64.0	167	183
	CV	12.0	17.9	11.3	12.6	8.97	13.0	21.4	14.4	10.8	24.1	14.3	11.4	14.8	27.9	12.2	15.7	11.6	17.1
	SD	8.16×10^3	6.17×10^3	178	192	7.42	67.0	15.0	60.0	8.28	0.130	0.090	4.95	7.13	0.860	1.90	7.59	15.1	24.3
Limeira Park	Mean	8.75×10^4	3.31×10^4	1.51×10^3	4.06×10^3	90.9	297	118	446	95.1	0.810	0.800	43.6	38.8	1.46	14.8	32.9	120	97.7
	Median	8.88×10^4	3.26×10^4	1.48×10^3	4.01×10^3	90.2	297	118	435	96.1	0.880	0.600	43.4	37.9	1.65	14.9	32.9	119	94.8
	Min.	5.73×10^4	2.51×10^4	1.07×10^3	2.71×10^3	51.1	249	68.0	335	64.5	0.400	0.010	36.4	32.7	0.700	12.5	22.9	104	757
	Max.	1.06×10^5	5.19×10^4	2.07×10^3	2.71×10^3	137	416	167	615	121	1.12	2.20	49.8	46.8	2.50	17.4	53.1	135	131
	CV	11.2	19.1	15.9	15.5	16.9	12.3	22.9	15.3	18.0	8.64	5.00	9.60	11.3	34.9	8.65	21.1	5.30	14.5
	SD	9.82×10^3	6.32×10^3	240	627	15.4	36.6	27.0	68.0	17.1	0.070	0.04	4.18	4.40	0.510	1.28	6.93	6.35	14.7
Prada School	Mean	8.15×10^4	2.66×10^4	3.48×10^3	3.18×10^3	85.3	283	132	467	103	0.800	0.880	44.9	29.4	1.82	11.1	27.5	98.1	103
	Median	8.28×10^4	2.57×10^4	3.39×10^3	3.07×10^3	84.0	265	129	456	103	0.680	0.850	43.6	27.7	1.81	11.0	27.2	95.0	98.5
	Min.	6.73×10^4	1.63×10^4	1.67×10^3	1.81×10^3	60.5	248	76.0	318	80.9	0.370	0.040	32.5	18.8	1.47	8.10	22.0	72.6	73.8
	Max.	1.15×10^5	3.70×10^4	5.00×10^3	5.20×10^3	114	355	221	709	143	1.66	1.61	62.9	43.9	2.32	15.0	35.6	138	143
	CV	9.91	21.5	23.0	22.9	15.5	17.3	28.8	19.3	14.5	15.0	61.4	15.5	22.2	15.4	15.5	16.2	14.5	18.6
	SD	8.08×10^3	5.72×10^3	800	727	13.2	49.0	38.0	90.0	15.0	0.120	0.540	6.94	6.52	0.280	1.72	4.46	14.2	19.2

(CV = coefficient of variation (%); SD = standard deviation; *More than 50% of results below detection limit (LOD)).

and subtropical conditions, which are typically rich in iron oxides (Paula et al. 2025, Huang et al. 2020, Furquim & Almeida 2021). Bosque Park shows the highest mean Al and Fe contents (Al = 9.36×10^4 mg.kg^{-1}; Fe = 5.49×10^4 mg.kg^{-1}), supporting its characterization as the least anthropogenically disturbed site and the one with the strongest lithological influence. In contrast, macronutrients such as Ca, K, Mg, and Na are generally depleted in highly weathered tropical soils (Ferreira et al. 1999). However, Ca and K enrichment at Prada School and Limeira Park suggests localized urban inputs, likely associated with construction materials and fertilizer use (Sager 2020, Deshani Igalavithana et al. 2017).

Although trace elements may still reflect geological inheritance, their spatial patterns are more strongly modulated by anthropogenic activities. The descending order of trace element concentrations (mg.kg^{-1}) differed across sites: Cu > Ba > Zn > Cr > Pb > Ni > Mo > Co at Bosque Park and Zn > Ba > Cr > Cu > Pb > Ni > Mo > Co > Cd at Limeira Park. At the School of Technology,

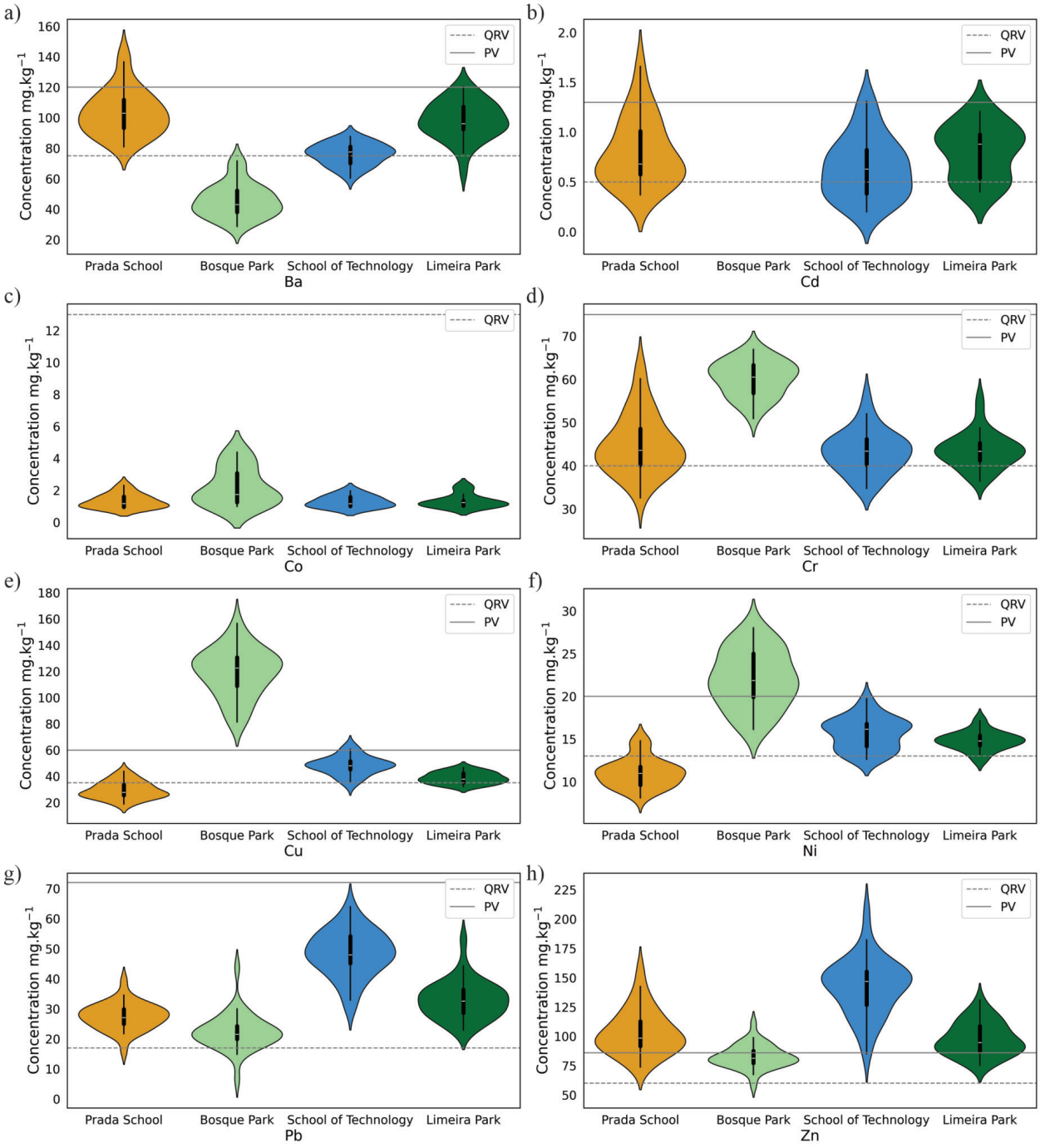


Figure 2. Violin plots showing the distribution of Ba, Cd, Co, Cr, Cu, Ni, Pb, and Zn concentrations in topsoil samples. Dotted lines indicate QRV (Reference Quality Value) and PV (Prevention Value) thresholds. a) Ba; b) Cd; c) Co; d) Cr; e) Cu; f) Ni; g) Pb; and h) Zn.

the order was Zn > Ba > Pb > Cu > Cr > Ni > Mo > Co > Cd, and at the Prada School, it was Zn > Ba > Cr > Cu > Pb > Ni > Mo > Co > Cd. Although anthropogenic contributions were evident at all sites, concentrations predominantly remained below the PVs, except for Cu and Ni at Bosque Park and Zn at all sites. None of the sites exceeded IVs. Furthermore, no statistically

significant temporal variations were detected. Nonetheless, descriptive analyses, including violin plots and coefficients of variation (CV), revealed some degree of variability over time for certain elements commonly associated with anthropogenic sources, such as Cu, Pb, and Zn. Notably, Pb and Cu exhibited CVs greater than 16% across all sites, with Cu reaching 22% at the Prada School.

Bosque Park exhibited significantly higher Cu concentrations compared to all other sites. Linear Mixed Models indicated significantly lower Cu concentrations at School of Technology ($\beta = -2.12\times10^4$ mg.kg^{-1}, p <.001), Limeira Park ($\beta = -2.07\times10^4$ mg.kg^{-1}, p < .001), and Prada School ($\beta = -2.75\times10^4$ mg.kg^{-1}, p < .001), using Bosque Park as the reference category (Appendix I). Given Bosque Park's distance from high-traffic areas, the elevated Cu levels may originate from the natural soil parent material. Previous studies report Cu concentrations in São Paulo soils ranging from 3 to 393 mg.kg^{-1} (Casarini et al. 2001). Supporting this hypothesis, Bosque Park also showed significantly (p < .001) higher concentrations of Co, Cr, and Fe - elements typically associated with geogenic sources (Binner et al. 2023, Manta et al. 2002, Moreno-Alvarez et al. 2020). Fixed effects estimate for these elements were consistently elevated (e.g., $\beta > 3.68\times10^4$ mg.kg^{-1} for Fe and $\beta = 48.0$ mg.kg^{-1}for Cr at Bosque Park).

Alternatively, Cu contamination may be linked to anthropogenic sources, potentially introduced via seasonal flooding from a local spring. Local studies have reported anomalous concentrations of Fe, Cr, Ni, and Cu in river sediments, attributed to jewelry industries and unregulated industrial discharges (Moreira & Fazza 2008, Vilela et al. 2013). Additional Cu sources may include plumbing corrosion (Sutherland 2000) and degradation of park infrastructure, including deteriorating wall coatings (Huang et al. 2023). Historical use of copper-based pesticides and fungicides (Huang et al. 2022, Cai et al. 2015) may also have contributed to Cu accumulation. Moreover, Cu concentrations in the park (119 mg.kg^{-1}) fall within the range reported for Brazilian urban ecological parks (84–205 mg.kg^{-1}), indicating that Cu enrichment is a recurrent feature in urban green areas (Paula et al. 2025).

Several factors influence urban soil contamination levels, including proximity to pollutant sources and the presence of vegetation (Luo et al. 2012, Rodríguez-Oroz et al. 2018, Tume et al. 2018, Gredilla et al. 2017, Han et al. 2020). For instance, although the School of Technology and Limeira Park are located approximately 2 km apart and are exposed to similar pollution sources, significant differences (p < .001) were observed in Ba, Pb, and Zn concentrations according to Tukey's post hoc test. School of Technology had 22.5 mg.kg^{-1} lower Ba concentrations than Limeira Park, and 15.5 mg.kg^{-1} and 44.7 mg.kg^{-1} higher Pb and Zn concentrations, respectively. A similar pattern was observed when comparing Prada School and Bosque Park. Tukey's post hoc test showed that Bosque Park had 57.5 mg.kg^{-1}, 5.19 mg.kg^{-1}, and 20.7 mg.kg^{-1} lower Ba, Pb, and Zn concentration, respectively, than Prada School. These contrasts suggest that local factors (e.g., vegetation cover and soil properties) may override broader spatial trends.

Vegetation, particularly large trees, efficiently intercepts polluting particles and particulate matter, acting as a physical barrier to atmospheric pollutants (Nowak et al. 2006, Gredilla et al. 2017, Liu et al. 2020). Complex vegetated surfaces enhance atmospheric deposition, whereas smooth, vegetation-free surfaces favor particle escape and resuspension (Seinfeld & Pandis 2006). In Brazilian urban parks, the input of organic matter derived from

grasses and trees was shown to be essential for increasing carbon contents in surface soil layers, reinforcing the role of urban green spaces as active geochemical sinks (Costa & Furquim 2025). As a result, trace element deposition is reflected in plant concentrations, with dry deposition rates up to 10–30 times higher on rough vegetated surfaces than on smooth materials such as glass or cement (Berthelsen et al. 1995, Roupsard et al. 2013).

To contextualize the degree of contamination, observed concentrations were compared with those reported in other urban soil studies (Table SIV). Overall, metal levels were lower than those documented for highly urbanized metropolises such as Mexico City (Rodríguez-Salazar et al. 2011) and high-traffic corridors in Brazilian cities (Ribeiro et al. 2012, Canteras et al. 2019, Figueiredo et al. 2009, 2011), where Zn and Ba often exceed 300 $mg{\cdot}kg^{-1}$. However, Cu and Zn concentrations exceeded those reported for Brazilian urban parks influenced by vehicular and industrial emissions (Gredilla et al. 2017, Paula et al. 2025) and were comparable to levels in Chinese metropolises (Cheng et al. 2014). Lead concentrations at the School of Technology were similar to those observed at a Brazilian university campus (Bourotte et al. 2019). Overall, these results place Limeira within an intermediate contamination range, characteristic of medium-sized cities where vehicular traffic and urban infrastructure are moderate but pervasive pollution sources.

Pollution index and ecological risk assessment

To evaluate the impact of anthropogenic activities on the environmental risk posed by heavy metals in the soil within the study area, I_{geo}, *EF*, *CF* and *RI* indices were calculated (Figure 3). For a representative classification of these indices, mean concentrations of the measured elements were used, while Al was used as the reference element for *EF* calculations. Aluminum was selected due to its geochemical stability, low anthropogenic mobility, and conservative behavior in highly weathered tropical soils (Sposito 2008, Fontes et al. 2001). This approach is widely adopted in soil contamination studies (Loska et al. 2004, Thiombane et al. 2019, Uduma & Jimoh 2014).

Brazilian soil reference values (BRVs) proposed by Fadigas et al. (2006) were adopted as the geochemical background. These values were derived from minimally disturbed Brazilian soils using multivariate grouping (silt, clay, CEC, Fe, and Mn), combined with upper-quartile statistic. This approach provides a more realistic baseline than global reference values (de Mattos et al. 2018, Juchen et al. 2014), such as the upper continental crust, which often overestimates natural metal contents (Matschullat et al. 2000, Reimann & De Caritat 2005). Soil from Prada School were classified as Group 4, with background values ($mg.kg^{-1}$): Cr (35), Co (10), Ni (17), Cu (12), Zn (35), Cd (0.1), and Pb (18). The parks and the School of Technology were classified as Group 1 with background values ($mg.kg^{-1}$): Cr (55), Co (20), Ni (35), Cu (119), Zn (79), Cd (10), and Pb (19).

The geoaccumulation index for all elements indicated conditions ranging from unpolluted to moderately polluted ($I_{geo} < 1$). Pb and Zn showed the highest enrichment, with peak values approaching 1.0 at Limeira Park and Prada School. The average Pb value (0.40) was comparable to those reported for peri-urban agricultural areas in China (Xu et al. 2025). Similarly, in an industrial area in Chile, Pb an Zn also showed I_{geo} values bellow 1 (Salmanighabeshi et al. 2015). In contrast, Co and Ni predominantly remained within the unpolluted class, with Co values consistently near zero and Ni remaining below the enrichment threshold in nearly half of the samples. Comparable results have been

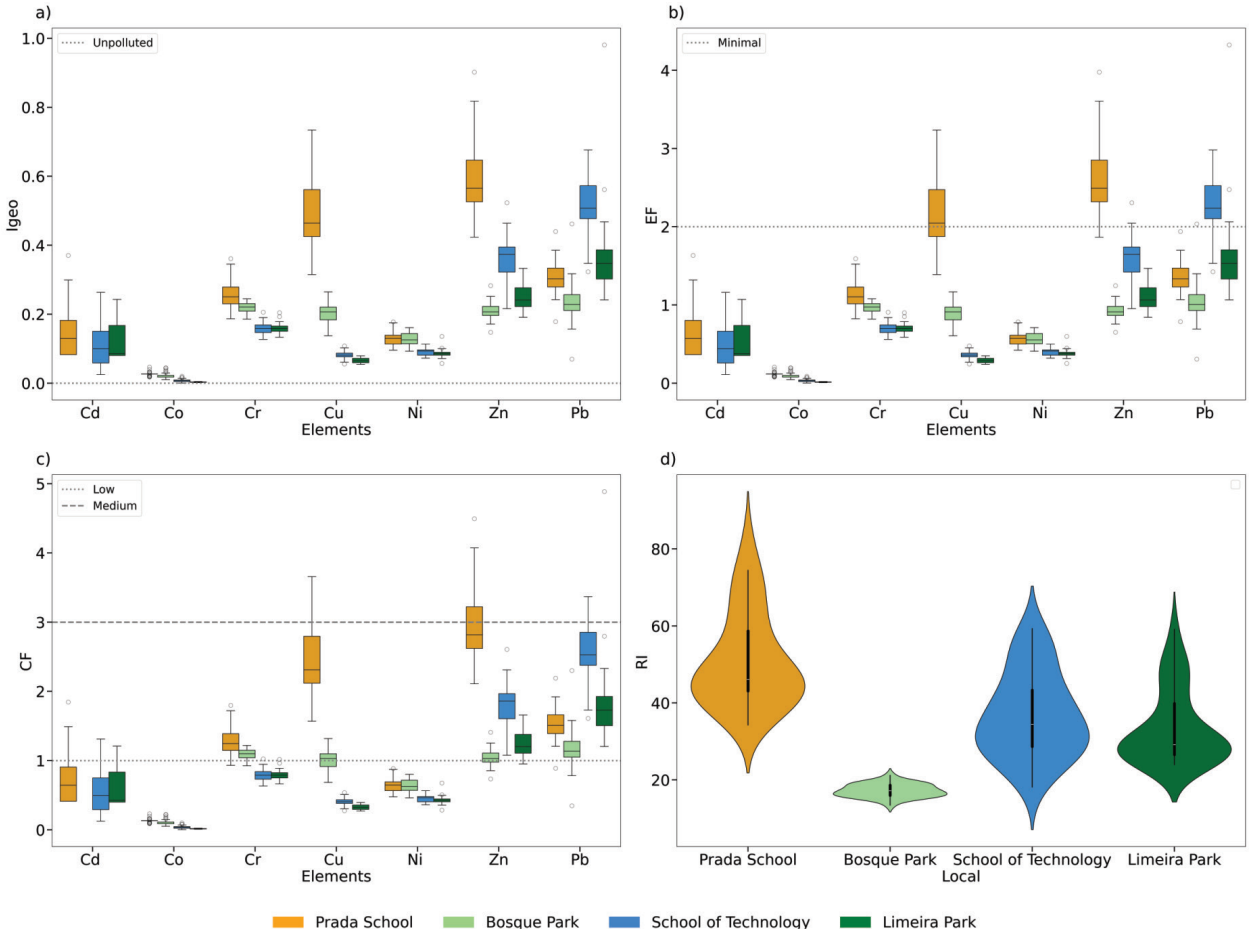


Figure 3. Geochemical indices highlighting contamination patterns across sites. a) Geoaccumulation Index (I_{geo}); Enrichment Factor (*EF*); c) Contamination Factor (*CF*); d) Potential Ecological Risk Index (*RI*).

reported for urban parks in Brazil and China, where Ni levels were classified as unpolluted in most samples (Huang et al. 2021, Paula et al. 2025).

EF results indicated minor enrichment for most elements (*EF* < 2). The highest EF values for Zn (3.98) and Cu (3.24) were observed at Prada School, and for Zn at Limeira Park (4.33), reaching moderate enrichment. In general, *EF* values < 1.5 indicate predominantly geogenic sources, whereas values *EF* > 1.5 suggest notable anthropogenic contributions (Li et al. 2015, Jiang et al. 2021). Based on this criterion, anthropogenic influence was inferred mainly for Cu, Zn, and Pb at all sites. Overall, samples exceeding *EF* > 1.5 accounted for 23% of Cu, 42% of Zn, and 45% of Pb, indicating widespread enrichment of these elements within the study area. At the School of Technology, more than 70% of Zn and Pb values were associated with anthropogenic sources. In contrast, Co, Cr, and Ni consistently showed *EF* values < 1.5 across all sites, supporting a predominantly geogenic origin. These findings are consistent with results from urban garden soils in Hungary, where Ni, Cr, and Co showed no enrichment, while Zn and Pb were enriched in soils located close to roads (Szolnoki et al. 2013).

CF results corroborated these patterns, with Zn and Pb consistently showing moderate contamination values (1 < *CF* > 3) across all sites, accounting for 90% and 80% of the Pb

and Zn values, respectively, while Co, Cd and Cr predominantly exhibited low contamination (*CF* < 1) in more than 85% of the samples. *PLI* indicated overall low pollution levels of Cd, Cr, Cu, Ni, Pb and Zn across all study locations, with over 90% of samples presenting *PLI* < 1. Among the sites, Prada School showed the highest mean value (0.96). *PLI* values in the parks were comparable to those reported for Brazilian urban parks, ranging from 0.40 to 0.70 (Paula et al. 2025).

Ecological risk assessment indicated predominantly low to moderate risk across all sites. Bosque Park and Limeira Park showed the lowest overall ecological risk, with 100% of samples classified as low risk (Table V). The school sites exhibited similar patterns, with up to 81% of samples classified as low risk. However, comparatively higher *RI*values were observed at these locations, mainly associated with Cd and Pb enrichment, which together accounted for more than 80% of the total *RI*. Although Pb and Zn presented relatively higher *CF* values, their individual E_r^i values remained low due to their low toxicity response coefficients (*Tr* ≤ 5) (Hakanson 1980). In contrast, moderate *CF* values for Cd, combined with its high toxicity coefficient (*Tr*=30) (Hakanson 1980), made Cd the main contributor to relatively elevated E_r^i values

Table V. Potential ecological risk index (E_r^i) for Cd, Cr, Cu, Ni, Zn, and Pb. Values are presented as mean, median, minimum (Min.), maximum (Max.), and standard deviation (SD).

Local		Cd	Cr	Cu	Ni	Zn	Pb
Prada School	Mean	22.5	2.57	12.3	3.26	2.96	7.63
	Median	19.7	2.49	11.6	3.23	2.82	7.54
	Min.	12.3	1.86	7.84	2.38	2.11	4.44
	Max.	55.3	3.60	18.3	4.42	4.49	11.0
	SD	11.6	0.396	2.72	0.506	0.550	1.24
Bosque Park	Mean	*	2.19	5.01	3.15	1.05	5.87
	Median	*	2.20	5.15	3.12	1.03	5.68
	Min.	*	1.85	3.42	2.30	0.735	1.74
	Max.	*	2.44	6.59	4.01	1.41	11.5
	SD	*	0.145	0.772	0.478	0.127	1.58
School of Technology	Mean	16.3	1.58	2.03	2.24	1.80	12.8
	Median	14.8	1.58	2.02	2.31	1.86	12.6
	Min.	3.71	1.26	1.37	1.80	1.08	8.04
	Max.	39.3	2.05	2.69	2.82	2.61	16.8
	SD	10.2	0.180	0.30	0.271	0.307	2.00
Limeira Park	Mean	17.7	1.58	1.64	2.15	1.24	9.16
	Median	12.8	1.58	1.61	2.13	1.20	8.65
	Min.	12.0	1.33	1.35	1.42	0.952	6.02
	Max.	36.3	2.03	1.97	3.38	1.66	24.4
	SD	7.84	0.152	0.184	0.312	0.179	3.24

***More than 50% of results below the detection limit (LOD).**

at Prada School, the School of Technology, and Limeira Park.

Cadmium is a known carcinogen that disrupts calcium metabolism and impairs the reproductive and respiratory systems (Genchi et al. 2020, Olajide-Kayode et al. 2023). In comparison with other urban soil studies, the E_r^{Cd} values obtained in this study were lower than those reported near a municipal solid waste facility in Nigeria (Kolawole et al. 2023) and in Chinese cities, where 33% of urban soils were classified as presenting high potential ecological risk (Pecina et al. 2021).

An exception was identified at Bosque Park, where moderate *CF* and *EF* values for Cu locally resulted in moderate ecological risk, identifying Cu as the main risk driver at this site despite its lower inherent toxicity. Nevertheless, Cu mobility and bioavailability are strongly influenced by soil properties, increasing mainly under conditions of low CEC, low SOM, and acidic pH (Huang et al. 2020, Rosen & Chen 2018, Wang et al. 2023, Paula et al. 2025). As these conditions are less pronounced at Bosque Park, the Cu-related risk is likely spatially limited and of lower ecological concern when compared to the Cd-driven risk observed at the other locations.

Sources appointment

A PMF model was applied to identify the main sources of Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, and Zn in the study area. Using EPA PMF 5.0, factor solutions ranging from two to six were tested, with 20 runs performed to compare the Q_{robust}/Q_{true} values. A three-factor model was identified as the most suitable. Elements contributing more than 40% to each factor were considered representative (Figure S4). Factor contributions were calculated as the arithmetic means of individual element contributions within each factor. The relative contributions of Factors 1, 2, and 3 were 32.4%, 35.9%, and 30.7%, respectively. Factor profiles and site-specific contributions are shown in Figure 4.

Factor 1 was dominated by Cd (100%), Mo (69.5%), Pb (50.8%), and Zn (42.5%), with Cd identified as the most critical contaminant due to its high toxicity and ecological risks. Cadmium is commonly associated with industrial activities such as electroplating, alloy processing, and metallurgical operations (Ajmone-Marsan & Biasioli 2010, Zhao et al. 2020, Guan et al. 2019, Huang et al. 2023), as well as the application of fertilizers and pesticides in urban green areas (Suciu et al. 2022, Huang et al. 2022).

In the study area, the proximity of semiprecious jewelry industries likely represents a major source of Cd, Pb, and Zn emissions (Vilela et al. 2013), together with legacy inputs from agricultural amendments historically applied during the establishment and maintenance of urban parks (Huang et al. 2022, Cai et al. 2015). These combined industrial and historical inputs are consistent with the widespread occurrence of Cd, Pb, and Zn across the sampling sites, suggesting that windborne dispersion from industrial and traffic-related sources plays a key role in soil contamination (Lee et al. 2007).

Lead and Zn enrichment further supports this interpretation, as both elements are strongly linked to anthropogenic sources (Díaz Rizo et al. 2013, Tume et al. 2018). Zinc primarily originates from engine additives, tire wear, and galvanized urban infrastructure, whereas Pb is associated with industrial emissions, battery and paint production, and traffic-related source (Donado et al. 2021, Figueiredo et al. 2019, Mielke et al. 2008, Sutherland 2000). Despite the ban of tetraethyl lead in Brazilian gasoline in 1999, Pb persists in urban soils due to historical vehicular emissions and legacy contamination (Furquim &

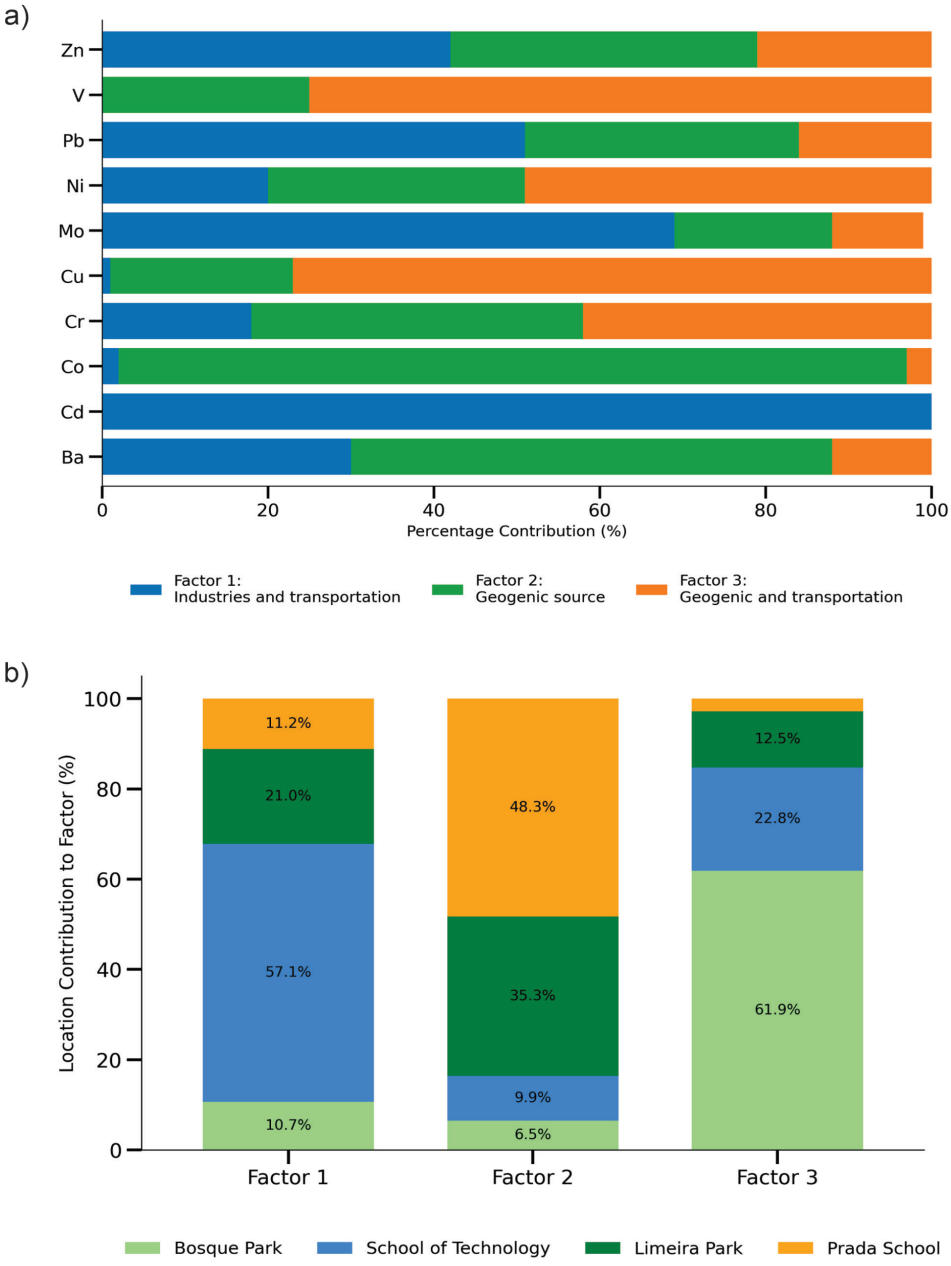


Figure 4. Main results of the Positive Matrix Factorization (PMF) analysis. a) Percentage contribution of each trace metal to the identified source factors. Three main source profiles were resolved: industrial and traffic-related sources (Factor 1), geogenic sources (Factor 2), and mixed geogenic and traffic-related sources (Factor 3). b) Relative contribution of each sampling site (Bosque Park, School of Technology, Limeira Park, and Prada School) to the three PMF factors.

Almeida 2021, Filippelli et al. 2012, Mielke et al. 2008, Gredilla et al. 2017).

Accordingly, Factor 1 is interpreted as representing predominantly industrial and transportation-related sources, with its spatial distribution reinforcing this conclusion. The highest contribution at the School of Technology (57.1%) reflects the influence of heavy traffic and nearby industrial activities, identifying this area as the main anthropogenic hotspot, whereas the contribution of urban parks (31.7%) indicates a secondary but relevant influence of diffuse, legacy anthropogenic inputs.

Factor 2 was dominated by Co (94.8%), Ba (57.5%), and Cr (40.0%) and is interpreted as representing geogenic sources. Cobalt and Cr are widely recognized as elements largely controlled by natural soil composition and parent material, particularly in tropical soils (Ihl et al. 2015, Liu et al. 2020, Moreno-Alvarez et al. 2020, Bourotte

et al. 2019, Tume et al. 2019). Although Ba may originate from anthropogenic activities such as brake pad wear and metallurgical processes (Apeagyei et al. 2011, da Silva et al. 2020), it is also a common constituent of soil parent materials (Davis et al. 2009, Aelion et al. 2012).

In the present study, Ba background concentration is 75 $mg.kg^{-1}$, and measured concentrations range from 45 to 103 $mg.kg^{-1}$, remaining close to or only slightly above the local background. This range falls well within the broad natural variability reported for soils in São Paulo State (<5 - 223 $mg.kg^{-1}$) (Casarini et al. 2001). The absence of pronounced enrichment relative to background values, combined with the strong association of Ba with Co and Cr in the PMF loadings and with geochemical indices indicating low anthropogenic influence, supports the interpretation that Ba in this factor is predominantly of geogenic origin. Accordingly, Factor 2 reflects natural soil composition.

Spatially, the Prada School site exhibited the highest contribution of Factor 2 (48.3%), indicating a predominance of natural inputs and a reduced role as a sink for atmospheric pollutants, likely related to local soil properties that limit metal retention. In contrast, the contribution observed at Bosque Park (35.3%) suggests a strong influence of soil parent material on Co, Ba, and Cr concentrations.

Factor 3 was characterized by high loadings of Cu (77.0%), V (75.0%), Ni (49.5%), and Cr (42.2%). Nickel and Cr are commonly associated with parent material and background soil composition (Qing et al. 2015, Manta et al. 2002), while Cu may derive from both natural sources and anthropogenic activities (Rehman et al. 2019). In urban environments, Cu is linked to vehicle braking systems, automotive components, lubricants, and fossil fuel combustion (Iijima et al. 2007, Wei & Yang 2010, Cheng et al. 2014, Lu et al. 2010). In addition, Cu, V, and Ni have been reported as constituents of particulate matter derived from fossil fuel emissions and waste incineration, contributing to diffuse atmospheric deposition in urban soil (Hernandez & Rodriguez 2012).

Within the study area, Cu exhibits pollution indices indicative of anthropogenic influence across all sites, whereas Ni and Cr remain closely associated with geogenic background levels. Vanadium concentrations, except at Bosque Park, fall within the broad natural variability reported for soils of São Paulo State (75^{th} percentile = 274 $mg.kg^{-1}$), further supporting a predominantly natural control for this element. Spatially, Factor 3 showed a strong influence at Bosque Park (61.9%), where pollution indices suggest limited industrial impact and a stronger control by natural background and diffuse traffic-related sources. This indicates that metal accumulation at this site is qualitatively less severe than at the School of Technology (22.8%), where industrial inputs dominate. Therefore, Factor 3 represents a mixed source dominated by natural background, with secondary contributions from diffuse traffic-related emissions.

CONCLUSIONS

This study demonstrates that trace metal distributions in the urban soils of Limeira are primarily controlled by intrinsic soil physicochemical properties rather than by proximity to emission sources. LMMs confirmed the absence of significant temporal variability ($p > 0.05$), reinforcing the role of urban soils as stationary reservoirs, while revealing marked spatial heterogeneity driven by local soil characteristics.

SOM and clay content emerged as the main factors enhancing the retention of Cu and Zn, with SOM showing strong positive effects ($\beta = 6.15$ for Cu and $\beta = 17.9$ for Zn). In contrast, Pb mobility

was predominantly governed by pH-dependent processes, with lower pH values increasing its potential mobility. These results highlight the importance of soil properties in regulating metal behavior in urban environments. Source apportionment using PMF identified three major contributors to soil metal loads: geogenic sources (35.9%), industrial and traffic-related emissions (32.4%), and mixed anthropogenic–lithogenic inputs (30.7%). This distribution indicates that diffuse anthropogenic inputs are overlaid on a strong natural background, even in areas distant from major industrial facilities.

Vegetated sites exhibited enhanced metal retention associated with higher SOM content, likely derived from litter input and root turnover. While this pattern suggests an indirect role of vegetation in promoting metal immobilization through soil property modification, direct plant uptake was not evaluated in this study and should be addressed in future research. Although metal concentrations remained below regulatory intervention thresholds, ecological risk assessment revealed localized and site-specific Cd-driven ecological risks, restricted to a limited number of samples, particularly in less vegetated and more anthropogenically influenced sites. These findings underscore the need for targeted monitoring strategies that consider both soil properties and land-use characteristics in medium-sized urban centers.

Acknowledgments

This study was partially funded by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) – Finance Code 001. The authors are grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the financial support (Grant Number: 426074/2018-1), Fundo de apoio ao ensino, pesquisa e extensão (FAEPEX) - Grants No: 4. We also thank the Espaço da Escrita – Pró-Reitoria de Pesquisa – UNICAMP - for the language services provided.

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SUPPLEMENTARY MATERIAL

Figures S1-S4.
Tables SI-SIV.

Appendix I. Assessing trace metal concentration in urban soils: a study of urban parks and unforested urban areas

1) Operational conditions

The FAAS analyses were conducted using a Varian Spectra AA-220 model using an air-acetylene flame. Calibration curves were constructed using multi-element standard solutions. The ICP OES analysis was performed using an Agilent 5100 model. Details of the operational conditions are provided in Table SI.

2) Limitations of detection and quantitation

The limits of detection and quantitation for the soil samples were calculated using Eq. S1 and Eq. S2, respectively. In these equations, *LOD* represents the limit of detection, SD_{blank} represents the blank standard deviation, *b*

denotes the slope of the analyte calibration line and *LOQ* indicates the limit of quantitation. The detailed results for *LOD* and *LOQ* obtained through FAAS and ICP OES analysis are provided in Table SII.

$$LOD = \frac{SD_{blank} \times 3}{b} \quad \text{(Eq. S1)}$$

$$LOQ = \frac{SD_{blank} \times 10}{b} \quad \text{(Eq. S2)}$$

3) Soil guiding values

QRV represents the maximum allowable concentration in clean soil, PV indicates levels above which soil quality may deteriorate, and IV signifies concentrations posing direct and indirect risks to human health across various land uses. Table SIII presents reference values for Ba, Cd, Pb, Co, Cr, Cu, Ni, Mo, and Zn in the state of São Paulo soils (CETESB 2014).

4) Linear Mixed Model (LMMs)

To assess statistically significant differences in metal concentrations across the four study sites, we performed Linear Mixed Models (LMMs) using Jamovi (v2.3.28) (Jamovi 2023). LMMs were used both to evaluate metal concentrations among sites and to investigate the influence of soil properties on metal accumulation.

4.1) Site Comparison Models

Bosque Park was designated as the reference category due to its minimal anthropogenic influence. The LMMs accounted for nested structure of the data (repeated measurements over sampling weeks) and temporal variability (unmeasured week-to-week fluctuations, e.g., weather conditions and sampling variability). The model specifications were: i) Dependent variables: Al, Ba, Cd, Co, Cr, Cu, Fe, Mo, Pb, Zn concentrations; ii) Fixed effect: Site (categorical: Prada School, Bosque Park, School of Technology, Limeira Park), and iii) Random effect: Intercept grouped by sampling week.

Model validation was performed through Q-Q plots (to assess normality) and residual vs. fitted values plots (to check for homoscedasticity). When the site effect was significant ($p < 0.05$), pairwise comparisons were conducted using Tukey's post-hoc tests.

4.2) Soil Property Models

To evaluate the influence of soil characteristics on metal concentrations independently of site location, LMM were also constructed with the following specifications: i) Dependent variables: Metal concentrations (as above); ii) Fixed effects: Soil properties (clay content, SOM, pH; all continuous variables); iii) Random effect: Intercept grouped by site. As with the site comparison models, validation included inspection of residuals (Figures S1-3).

5) Quantitative analysis and contamination level

Table SIV compares trace metal concentrations in urban soils from Limeira with those reported for urban environments in Latin America and other global metropolitan areas.

6) Positive Matrix Factorization (PMF)

Pollution source diagram of the Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V and Zn resulted in PMF analysis. (Figure S4). For each factor, elements contributing more than 40% were considered representative and are highlighted above the green line.

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How to cite

PENTEADO PB, NOGAROTTO DC, COSTA BES, ALVES VN, OLIVEIRA BFF, POZZA SA & CANTERAS FB. 2026. Assessing trace metal concentration in urban soils: a study of urban parks and unforested urban areas. An Acad Bras Cienc 98: e20250560. DOI 10.1590/0001-3765202620250560.

Manuscript received on May 20, 2025;
accepted for publication on February 21, 2026

Author contributions

Priscila Bassi Penteado: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Original Draft. Danilo Covaes Nogarotto: Formal analysis. Bruno Elias dos Santos Costa: Resources and Investigation. Vanessa Nunes Alves: Resources, Investigation. Bruna Fernanda Faria Oliveira: Resources and Investigation. Simone Andrea Pozza: Conceptualization, Methodology, Resources and Writing – Review & Editing, Supervision. Felippe Benavente Canteras: Conceptualization, Methodology, Resources, Investigation, Writing – Review & Editing, Supervision, Project administration, and Funding acquisition.

Handling editor

Luiz Drude Lacerda

Data availability

The datasets generated and analyzed during the current study are available in the Mendeley Data repository: https://data.mendeley.com/datasets/3tb6yz52mx/1.

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