

## Temporal analysis of pollutant metals in trees of three parks in Mexico City's Metropolitan Area

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High concentrations of atmospheric pollutants, resulting from anthropogenic activities, cause direct precipitation of metals and metalloids on soil and vegetation surfaces. Urban trees can be used as passive monitors of particulate pollutants. This study aimed to evaluate the distribution of heavy metals and metalloids, namely iron (Fe), copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), boron (B), and arsenic (As), in the soil and roots and foliage of *Pinus greggii* at three parks with different atmospheric pollution levels: San Juan de Aragón (SJA – high pollution level); Sierra de Guadalupe State Park (GUAD – medium level); and Viveros de Coyoacán Park (COY – low level). The highest concentrations of metals and metalloids in the soil were observed at the surface layer (0-10 cm), except for As, which was higher at the 10-20 cm layer. According to Official Mexican Standard NOM-147-SEMARNAT/SSA1-2004, the analyzed soils did not show excessive contamination. However, a super accumulation of metals and metalloids was identified in fine roots of *P. greggii*; for example, Cd (3.90 ppm) exceeded the limits or requirements for the plant at COY, indicating contamination in roots. The highest foliage concentrations for B, Cu, and Fe were found at SJA, whereas those for As and Pb were at GUAD. A remarkable variation in foliage accumulation of metals and metalloids was recorded throughout the year at all sites, with peak values for external surface concentrations in the spring and for intracellular concentrations in the winter, indicating movement of metals through the soil and tree components. The results confirm that urban trees are useful bio-indicators of pollution accumulation and dynamics in the soil-plant system.

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### Introduction

The increase in atmospheric and soil pollutants is associated with urbanization, energy use, and infrastructure demands in large cities. Although some pollutants, such as heavy metals, are naturally present, their concentration increases due to the influence of anthropogenic sources; for example, the overuse of fossil-fuel powered vehicles can lead to the deposition of metals, such as Cd, Mn, Cu, Mo, As, Sb, Zn, Pd, Pt, and Rh onto the soil surface after rainfall (Luo et al. 2019). As a result, urban environments generally have higher concentrations of heavy metals, threatening the health and stability of urban forests (Covarrubias & Peña 2017).

Urban trees serve as important passive monitors of air quality by tracking the distribution of particulate pollutants over time and space. They accomplish this by bioaccumulating them in different components such as foliage, bark, and roots, thus providing information on pollutant levels at a specific location (El-Khatib et al. 2019). Trees are considered biomarkers of metal contamination in soil and atmosphere due to their long-term presence in the same location (Cindoruk et al. 2020), allowing bidirectional fluxes of heavy metals through their roots in the soil-plant-atmosphere system (Saladin 2015).

Heavy metal pollution, reduced atmospheric humidity, and increased temperature, together with a higher presence of pests and diseases, can cause a remarkable decline and deterioration in the health of urban forests (Ledesma 2014). For instance, high concentrations of heavy metals inhibit seed germination, as well as seedling growth and development (Kraner & Colville 2011). On the other hand, pollutants can influence the biochemical and physiological processes by damaging cell membranes, reducing transpiration, and impeding protein synthesis (Roy et al. 2024). In the Valley of Mexico's Metropolitan Area (VMMA, hereafter), poor seasonal air quality is exacerbated by the high population density, high concentration of industries and vehicles, and recent heat waves affecting the atmosphere chemistry. This is evident in areas of high pollution (hot-spots) where levels exceed permissible limits defined by different standards (Cruz-Huerta et al. 2024). As a result, air quality has deteriorated, threatening the health of urban forests in the region and creating an ecological problem that needs to be monitored and addressed (Molina et al. 2019).

In recent decades, different studies have been carried out using trees as bioindicators of heavy metal pollution, mainly using foliage as an indicator of contamination

(Chen et al. 2022). However, no study has been conducted in parks within the VMMA to comprehensively evaluate pollutant metal contamination in components such as foliage, roots, and soil, which would allow for a more complete understanding of the impact of contaminants on urban trees. This study aimed to evaluate the distribution of heavy metals and metalloids (iron (Fe), copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), boron (B), and arsenic (As)) in the soil and across different tree components (roots and foliage). The analysis was performed along an atmospheric pollution gradient observed for  $\text{NO}_x$ ,  $\text{PM}_{10}$ , and  $\text{PM}_{2.5}$  (Cruz-Huerta et al. 2024), which is latitudinally distributed from the north of Mexico City (Sierra de Guadalupe) to the center (Aragón Forest) and south (Viveros de Coyoacán). The hypothesis to be tested was that the concentration of heavy metal and metalloid in different tree components (foliage, roots) and soils are interrelated and reflects the existing atmospheric pollution gradients, which are related to the current conditions of vehicular traffic and industrial activities at each site.

## Materials and methods

### Study area and species studied

The study was conducted in three parks located in Mexico City's Metropolitan Area (Fig. 1), San Juan de Aragón Park – SJA, Sierra de Guadalupe State Park – GUAD, and Viveros de Coyoacán National Park – COY. San Juan de Aragón Park is one of the most relevant public green areas in the east of Mexico City, located in the division of Gustavo A. Madero ( $19^\circ 27' 32'' \text{ N}$ ,  $99^\circ 04'$

$17'' \text{ W}$ ) at an elevation of 2240 m a.s.l.; the park encompasses an area of 162.03 ha, of which 70.94% is covered by trees (114.96 ha), with species of the genera *Hesperocyparis*, *Eucalyptus*, *Fraxinus* and *Pinus* (Mijangos et al. 2014). Sierra de Guadalupe State Park covers 5293.40 ha in the northern Valley of Mexico's Metropolitan Area ( $19^\circ 37' 20'' \text{ N}$ ,  $99^\circ 03' 20'' \text{ W}$ ), with a mean elevation of 2600 m a.s.l. This park has a mean annual temperature of  $16.7^\circ \text{ C}$  with a total annual precipitation of 700 mm. The main plant communities are oak forest, xeric scrub, grassland, and induced forest of *Pinus greggii*, *Schinus molle*, and *Eucalyptus* sp. Viveros de Coyoacán National Park is located in Coyoacán, Mexico City ( $19^\circ 21' 14'' \text{ N}$ ,  $99^\circ 10' 19'' \text{ W}$ ), at an elevation of 2240 m a.s.l., with an area of 42 ha (CDMX 2016). The representative species are *Alnus acuminata* Kunth, *Casuarina cunninghamiana*, *Hesperocyparis lusitanica*, *Eucalyptus globulus*, *Fraxinus uhdei*, *Pinus strobiformes* Ehrenb., *Pinus greggii*, *Pinus oocarpa*, and *Ulmus parvifolia* (Muñoz et al. 2022). The selected sites reflect an atmospheric pollution gradient defined by  $\text{NO}_x$ ,  $\text{PM}_{10}$ , and  $\text{PM}_{2.5}$  in the high (SJA), medium (GUAD), and low (COY) order (Cruz-Huerta et al. 2024).

*Pinus greggii* was used as a common indicator species at the three sampling sites. The species is endemic to Mexico and is naturally distributed in isolated populations of the Sierra Madre Oriental in the states of Puebla, Hidalgo, Veracruz, Querétaro, San Luis Potosí, Coahuila, and Nuevo León (Márquez-Ramírez et al. 2022). It was introduced to the study sites (SJA, GUAD, and COY) through reforestation efforts,

considering its ability to withstand limited ecological conditions such as low moisture and eroded soils.

### Soil sample collection

The study started in September 2022, when the first foliage samples were collected and the traps were placed to obtain root samples. Two composite soil samples were collected at each study site. To evaluate the content of chemical elements in the soil at different depths, soil samples were taken at 0-10 and 10-20 cm soil depth at four points, where the root traps were placed (Austruy et al. 2019).

Each composite sample consisted of 1.5 kg of soil placed in a Ziploc-type bag, identified with the place of origin, date, and depth, and transported to the lab. Here, the soil samples were dried in plastic trays, spreading the soil to create a layer  $\leq 2.5$  cm thick, and maintained at a temperature below  $35^\circ \text{ C}$  and relative humidity between 30% and 70%, according to NOM-021-REC-NAT (2000). The dried soil was sieved using a 10 mm mesh.

### Soil chemical analysis

The analytical procedures to determine the presence of pollutant elements in the soil samples were carried out at INIFAP's National Laboratory for Water, Soil, Plant and Atmosphere Analysis, in Gómez Palacio, Durango, following the NOM-021-REC-NAT-2000 standard. The AS-14 analytical method was used for boron (B), arsenic (As), cadmium (Cd), copper (Cu), iron (Fe), zinc (Zn), and lead (Pb). This method is primarily associated with its capacity to dissolve or extract various chemical forms of these metals present in the soil. For soil analysis, a 10-g extract of sieved soil was combined with 20 ml of DTPA (Diethylene triamine penta-acetic acid) to quantify Fe, Cu, Zn, Pb, and Cd. B was determined using the AS-15 method, which employs azomethine-H as a reagent to form a colored complex of boric acid in an aqueous medium. B extraction was performed with a 1.0 M calcium chloride solution and 15 g of soil. Metal concentration in the extracts was determined using the colorimetric method in hot water proposed by John et al. (1975).

Arsenic analysis was carried out using a palladium-magnesium matrix modifier (Palazón et al. 2015), following the atomization program recommended in the EPA 206.2 methodology (EPA 1978b).

### Root sampling

To sample fine roots, we used cylindrical traps of  $12 \times 30$  cm (diameter  $\times$  height), with a total volume of  $3392 \text{ cm}^3$ , made with 5 mm steel mesh and 2 mm shade mesh. These traps were placed no more than 1.0 m from the trunk of the sampled tree, at a depth of 30 cm. Four traps were installed at each site during the first week of September 2022 (autumn), when the first foliage sample was taken. The traps were

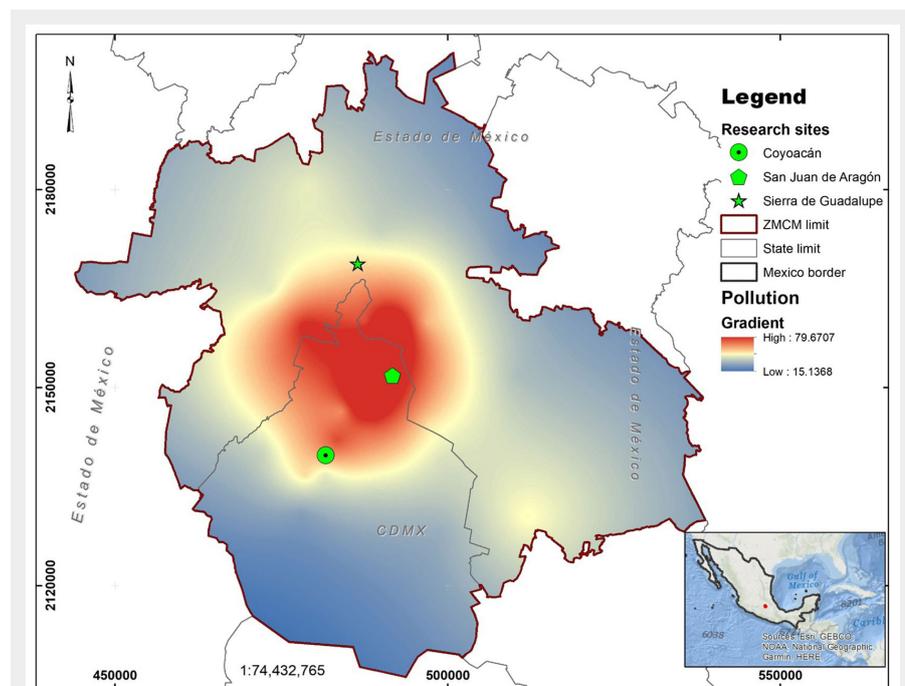


Fig. 1 - Map of the location of study sites and pollution gradient of the VMMA, according to Cruz-Huerta et al. (2024). The gradient represents the annual average concentration of  $\text{NO}_x$  (ppb).

filled with sieved soil from the same site to facilitate the removal of the new roots inside the trap.

The traps were removed eleven months later in summer using a hand shovel and knife (last week of July 2023). A composite sample containing both the soil and the fine roots of *Pinus greggi* was collected from the four traps at each site. The soil was then removed and the roots were washed with tap water and rinsed with distilled water. The root samples were oven-dried at 75 °C until constant weight at the Colegio de Postgraduados' Plant Breeding Lab.

**Foliage sampling**

To evaluate the changes in environmental pollutants throughout the year, we conducted four foliage samplings, one for each season: autumn (September 2022), winter (January 2023), spring (March 2023), and summer (July 2023). We selected 10 healthy trees showing no visible damage and representative of the ecological conditions of the site at each park. From each tree, 150 g of foliage of the last growth cycle was collected from the upper, middle, and lower parts of the crown at each sampling season. Subsequently, a composite sample of the foliage from the 10 trees was obtained and labeled for subsequent laboratory analysis.

Two subsamples were obtained from the composite sample of fresh foliage per site, one with washing (WW) and the other without washing (NW). The first subsample was used to determine the intracellular content of contaminants, by washing the foliage with tap water twice and once with distilled water; the second subsample was used to determine the total concentration of pollutants, including those accumulated on the foliage surface. The foliage was dried in a FELISA-brand oven at the Colegio de Postgraduados' Plant Breeding Lab at 75 °C for three days or until constant weight. The foliage was then ground to a particle size of < 0.5 mm.

**Chemical analysis of foliage and roots**

Heavy metals, metalloids, and other elements were analyzed at INIFAP's National Lab for Water, Soil, Plant, and Atmosphere Analysis in Gómez Palacio, Durango. Fe, Cu,

and Zn were quantified by direct aspiration in an air-acetylene flame in a Perkin Elmer AAnalyst700® atomic absorption spectrometer. In the case of Pb and Cd, the digestates were analyzed using the graphite furnace technique, employing a phosphate-based matrix modifier as cited in the EPA 213.2 and EPA 239.2 methodology, following the recommended atomization ramps (EPA 1978a, EPA 1978c).

For the analysis of B, a 0.5 g sample of plant tissue was used for digestion with an acid mixture of nitric acid and perchloric acid at a 3:2 ratio, respectively, at a temperature of 240 °C until the samples were almost dry. Once the digestion was completed, approximately 3 ml of distilled water was added to re-suspend and dissolve formed salts; this volume was transferred to a 15 ml Falcon tube, rinsing the digestion flask twice more until reaching a 10 ml capacity in the tube. The samples were analyzed by an atomic absorption spectrometer. The As analysis was performed using a palladium-magnesium matrix modifier (Palazón et al. 2015), following the atomization program recommended in the EPA 206.2 methodology (EPA 1978b) by atomic absorption spectrometry with the graphite furnace technique.

The Miller & Miller (2002) method was used to calculate detection and quantification limits. Precision and percent error were estimated by processing and analyzing duplicates of control samples with each batch of samples. Recovery evaluation was done by synthetically adding samples and measuring the amount recovered in each addition (Tab. 1).

The surface concentration of elements in the foliage was determined using the following equation (eqn. 1)

$$Sc = Tc - Ic \tag{1}$$

where Sc is the surface concentration, Tc is the total concentration (unwashed foliage), and Ic is the internal concentration (washed foliage).

**Statistical analysis**

Shapiro-Wilk tests were conducted using R software for each element analyzed across three components (soil, roots, and foliage) to assess the normality of the data

distribution (R Core Team 2024). None of the concentrations of metals and metalloids in the soil samples followed a normal distribution. In contrast, the data for the roots and foliage showed no significant deviation from normality ( $\alpha = 0.05$ ), with the exception of cadmium (Cd) in the roots. We assessed differences between sites (SJA, GUAD, COY), soil sample depths, treatments (WW, NW), and seasonal variations in foliage samples. For data that followed a normal distribution, we utilized ANOVA, while we applied the Kruskal-Wallis test when data exhibited significant departures from normality (Van 2010). Whenever significant differences were detected, a post-hoc comparison was performed using the Dunn test and the Bonferroni adjustment for multiple comparisons.

**Results and discussion**

**Heavy metal concentration in the soil**

No significant difference was found between sites for pollutant metal concentrations in the soil ( $p < 0.05$ ). The highest concentrations of the chemical elements were found in the surface layer (0-10 cm), which agrees with the results by Acosta et al. (2015). These authors argue that metals are neither biodegradable nor leached; therefore, the highest metal content is found in the surface layer of the soil, since the organic horizon in this layer has a greater capacity for heavy metal binding. Nonetheless, arsenic (As) showed higher concentrations in the lower layer (10-20 cm – Tab. 2), which might be due to differences in the mobility of the elements. Arsenic can be transported through the soil in solution or as a solid, depending on its chemical form (Mejía et al. 2014). The primary sources of As pollution in urban areas are attributed to anthropogenic causes, such as coal burning and industrial emissions (Li et al. 2020).

Although the differences between the study sites were not significant, we found that the highest values of B (7.32 ppm) and Zn (25.15 ppm) were recorded at the SJA site, while those of Fe (202.94 ppm), Pb (37.99 ppm) and Cu (8.08 ppm) were found at COY, and those of As (2.83 ppm) at GUAD. However, the concentrations of heavy metals at the sampled sites were rel-

**Tab. 1** - Chemometric criteria obtained in developing the procedures in the instrumentation used for the analyses. (ODL): Optimal detection limit; (OQL): Optimal quantifiable limit; (AAS): Atomic Absorption Spectrometry; (GF): Graphite furnace technique.

Element	Units	Correlation	Equation	ODL	OQL	Linear Range	Precision	% Error	% Recovery	Technique
Copper	ppm	0.9996	Y = 0.0077 + 0.0495·X	0.11	0.32	0.32 - 8	98.3	1.70	> 96.0	AAS
Iron	ppm	0.9985	Y = 0.0108 + 0.0244·X	0.38	1.14	1.14 - 16	96.9	3.10	> 96.0	AAS
Zinc	ppm	0.9977	Y = 0.0224 + 0.1629·X	0.10	0.29	0.29 - 3.2	96.1	3.90	> 96.0	AAS
Nickel	ppm	0.9997	Y = 0.4167 + 34.6505·X	0.02	0.05	0.05 - 1.6	98.6	1.40	> 96.0	AAS
Arsenic	ppb	0.9992	Y = 0.0248 + 0.0026·X	5.43	16.3	16.3 - 320	98	2.00	> 96.0	GF
Lead	ppb	0.9987	Y = 0.0168 + 0.0058·X	1.44	4.31	4.31 - 64	97.1	2.90	> 97.0	GF
Cadmium	ppb	0.9956	Y = 0.0205 + 0.0693·X	0.33	0.99	0.99 - 8	94.6	5.40	> 95.0	GF

**Tab. 2** - Average concentration (ppm) of heavy metals at two soil depths in three urban parks in Mexico City. (<DL): Concentrations below the detection limit for the element; (SJA): San Juan de Aragón Park; (GUAD): Sierra de Guadalupe State Park; (COY): Viveros de Coyoacán National Park.

Element (ppm)	SJA		GUAD		COY	
	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm
Copper (Cu)	5.15	4.16	2.57	1.59	8.08	5.38
Zinc (Zn)	25.15	8.82	14.18	2.4	22.72	1.15
Lead (Pb)	16.78	11.06	9.56	4.85	37.99	9.28
Cadmium (Cd)	<DL	<DL	<DL	<DL	<DL	<DL
Arsenic (As)	2.21	2.74	2.59	2.83	0.98	1.23
Boron (B)	7.32	6.26	3.97	3.2	3.2	1.55
Iron (F)	79.3	66.1	165.98	130.11	202.94	103.96

**Tab. 3** - Average concentration (ppm) of heavy metals in fine roots of trees in three urban parks in the Valley of Mexico's Metropolitan Area. Values are expressed as mean  $\pm$  standard error. (<DL): Concentrations below the detection limit for the element; (SJA): San Juan de Aragón Park; (GUAD): Sierra de Guadalupe State Park; (COY): Viveros de Coyoacán National Park.

Element (ppm)	SJA	GUAD	COY
Copper (Cu)	10.49 $\pm$ 0.12	21.96 $\pm$ 0.10	20.85 $\pm$ 0.26
Zinc (Zn)	57.40 $\pm$ 0.35	298.98 $\pm$ 0.13	972.58 $\pm$ 0.11
Lead (Pb)	<DL	13.86 $\pm$ 0.09	45.44 $\pm$ 0.07
Cadmium (Cd)	<DL	2.97 $\pm$ 0.12	3.90 $\pm$ 0.04
Arsenic (As)	3.62 $\pm$ 0.01	4.03 $\pm$ 0.02	2.61 $\pm$ 0.003
Boron (Cd)	111.33 $\pm$ 0.27	74.56 $\pm$ 0.26	53.70 $\pm$ 0.23
Iron (Fe)	198.48 $\pm$ 0.30	7431.69 $\pm$ 0.60	7574.41 $\pm$ 0.60

detection limit (Tab. 3). The highest concentration of B was recorded in SJA (111.33 ppm), and that of As in GUAD (4.03 ppm). The above results indicate that the fine roots of plants play a crucial role in heavy metal absorption because roots aggregate soil particles and can bind heavy metals (Brunner et al. 2008). Significant differences between sites are likely related to the various industrial activities, vehicular traffic, soil structure, and management in each area (Song et al. 2024). For example, the As concentrations in GUAD could be associated with the impact of specific industries established around the area and the dense vehicular traffic (Rojas 2013).

#### Heavy metal concentrations in foliage

A significant difference ( $p < 0.05$ ) between sites was found in As, B, Fe, and Zn concentrations in the foliage. Fig. 2 shows the mean annual concentrations at the three parks. The SJA trees had the highest total concentration of As, B, Cu, and Fe, while the GUAD trees had the highest concentration of Cd and Pb. This agrees with the atmospheric pollution gradient reported by Cruz-Huerta et al. (2024), indicating that the SJA park has the highest atmospheric pollution and GUAD has medium-level of PM<sub>10</sub>, PM<sub>2.5</sub>, NO<sub>x</sub> and O<sub>3</sub>. However, by analyzing the distribution of pollutant metals in the foliage, we found that sampled trees at GUAD and COY accumulated As in a greater proportion on the surface of foliage (NW). In contrast, in SJA 79.24% of the total concentration of metals was found at the intracellular level (VW). The elements B, Cu, and Zn presented a similar trend, with a higher concentration at the intracellular level, as well as Pb in SJA and COY (65.6% in both sites). On the other hand, Fe accumulation was higher on the surface of foliage at all the three sites, with values between 62% and 69%.

Likewise, a significant difference ( $p < 0.05$ ) in As, B, Cd, Cu, and Zn concentrations was found between seasons (Tab. 4), which implies that total concentrations in foliage changed seasonally over the year. However, the seasonal dynamics of total

atively low, according to the maximum allowable limits outlined in the Official Mexican Standard NOM-147-SEMARNAT/SSA1-2004, which sets criteria for determining remediation concentrations of arsenic in contaminated soils (22 mg kg<sup>-1</sup>), cadmium (Cd) levels in disturbed soils (37 mg kg<sup>-1</sup>) and undisturbed soils (0.422 mg kg<sup>-1</sup>), and lead (Pb - 400 mg kg<sup>-1</sup>). Therefore, it can be concluded that the contamination by heavy metals and metalloids in the soil of these urban parks is not excessive.

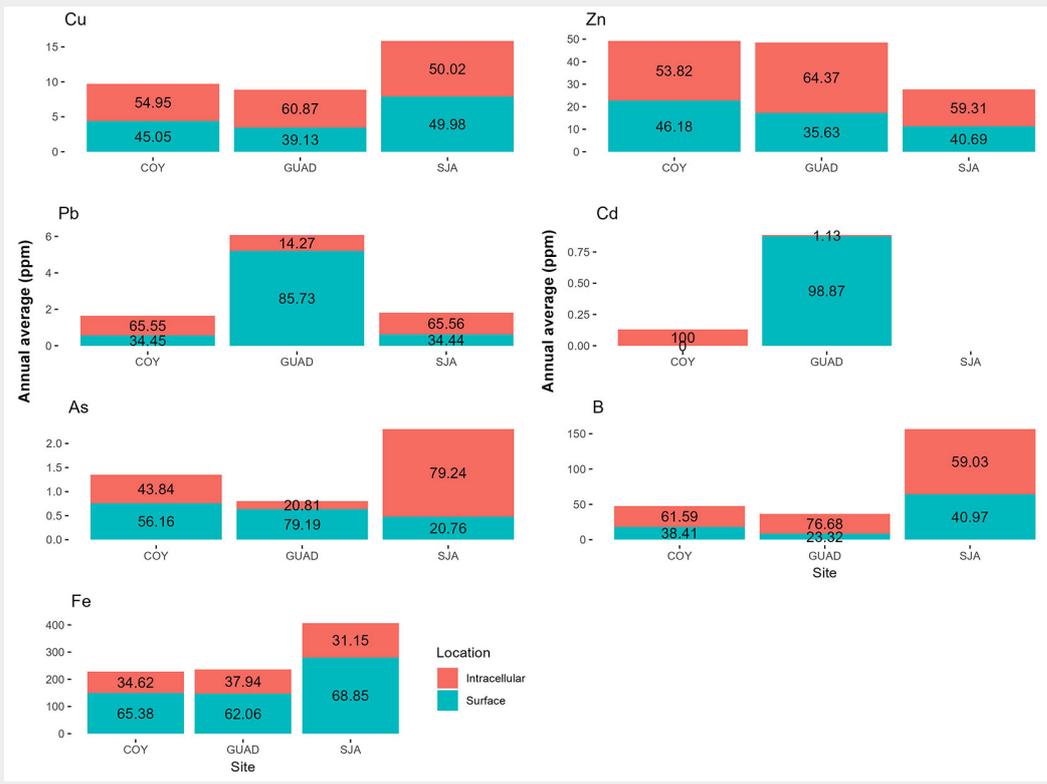
#### Heavy metal concentration in fine roots

Significant differences between sites were found in the concentration of metals in fine roots ( $p < 0.05$ ). The highest concentrations of Pb (45.44 ppm), Cd (3.90 ppm), Fe (7574.41 ppm), and Zn (972.58 ppm) were found in COY. This finding likely relates to the use of treated water for irrigation in the park, which adds fine sediments, increases cation exchange capacity (CEC), and enhances the ability to adsorb heavy metals (García-Carrillo et al. 2020). In SJA, Pb and Cd had concentrations below the

**Tab. 4** - Results of the Dunn test by metal analyzed for foliage. (I): Winter; (P): Spring; (O): Autumn; (V): Summer; (W): washing; (NW): No washing; (SJA): San Juan de Aragón Park; (GUAD): Sierra de Guadalupe State Park; (COY): Viveros de Coyoacán National Park; (<DL): Concentrations below the detection limit for the element; (\*): P<sub>adj</sub>  $\leq$  0.05.

Variable	Comparison	Copper (Cu)	Zinc (Zn)	Lead (Pb)	Cadmium (Cd)	Arsenic (As)	Boron (B)	Iron (Fe)
Site	COY- GUAD	0.87	1	0.41	0.67	1	1	1
	COY - SJA	0.48	0.0008*	1	0.91	0.007*	0.0022*	0.04*
	GUAD - SJA	0.38	0.001*	0.80	0.11	0.0002*	0.000067*	0.23
Seasons	I - O	1.4e-04*	0.09	0.08	0.0027*	1.5e-07*	1	1
	I - P	1.5e-04*	1	1	<DL	1	0.0005*	1
	O - P	1	0.04*	0.23	<DL	1.3e-05*	0.01*	1
	I - V	7.7e-05*	0.91	<DL	<DL	0.99	0.15	0.74
	O - V	1	0.96	<DL	<DL	1.3e-04*	0.41	0.80
	P - V	1	0.45	<DL	<DL	1	0.58	0.37

**Fig. 2** - Average annual concentration of contaminants in the foliage of *Pinus greggii* separated by location (intracellular and surface). Numbers indicate the percentage concerning total concentration at each site. San Juan de Aragón Park (SJA), Sierra de Guadalupe State Park (GUAD), and Viveros de Coyoacán Park (COY).



foliage concentration differed among chemical elements. For example, the total concentration of As and B showed significant differences across all seasons, whereas Cu showed significant differences in the spring, summer, and autumn. Cd only differed between winter and autumn, and Zn only in autumn. Regarding the sampling sites, we found significant differences in As, B, and Zn foliage concentrations between COY and SJA as well as between GUAD and SJA. This is likely related to particle dispersion in the environment, which is affected by vehicular traffic and meteorological factors, e.g., wind direction, solar radiation, temperature, and precipitation at each site (Rahim et al. 2021).

**Seasonal trend of pollutant concentration on foliage surface**

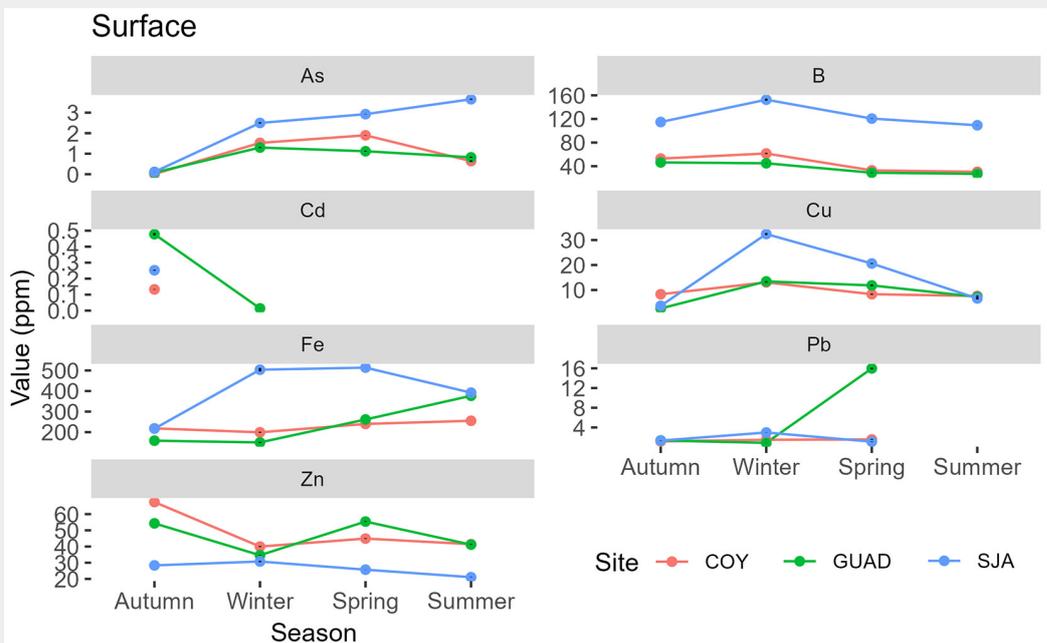
The seasonal variation of surface concentrations of metals and metalloids showed a maximum peak in the spring season at the three sites (Fig. 3). This can be explained by the meteorological conditions in study area during the March-May period, which is characterized by increased temperature, higher radiation, pollutant formation, and

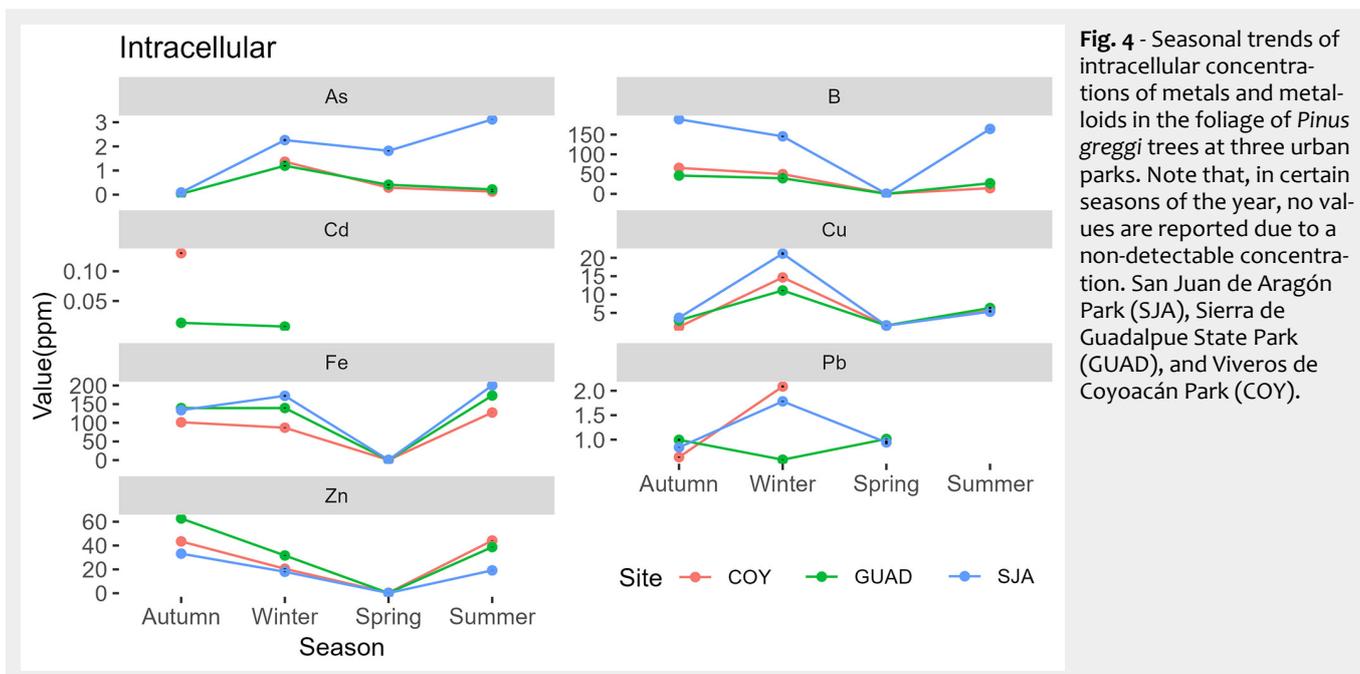
low percentage of relative humidity. These factors foster the deposition of heavy metals (Fe, Al, Pb, Zn, Ti, Mn, Cu, V, Ni, and Cr) on the surface of the *P. greggii* needles (ProAire 2021). Additionally, tree phenology is another important aspect to consider since the needles elongate during these months, thus increasing the particle deposition area.

Exceeding allowable limits of heavy metal concentration in the foliage can harm plants; for instance, cadmium (Cd) is toxic to most plants, with normal concentrations in foliage tissues ranging from 0.05 to 0.2

**Fig. 3** - Seasonal trends for metals and metalloids concentration on the foliage surface of *Pinus greggii* trees at three urban parks.

Note that, in certain seasons of the year, no values are reported due to a non-detectable concentration. San Juan de Aragón Park (SJA), Sierra de Guadalupe State Park (GUAD), and Viveros de Coyoacán Park (COY).





**Fig. 4** - Seasonal trends of intracellular concentrations of metals and metalloids in the foliage of *Pinus greggii* trees at three urban parks. Note that, in certain seasons of the year, no values are reported due to a non-detectable concentration. San Juan de Aragón Park (SJA), Sierra de Guadalupe State Park (GUAD), and Viveros de Coyoacán Park (COY).

mg kg<sup>-1</sup> (He et al. 2015). The Cd detected on the foliage in GUAD (1.29 ppm) threatens tree health as it exceeds the limits in intracellular tissues of the plant. In addition, Cd has rapid environmental mobility and high toxicity to living organisms at low concentrations (Hernández et al. 2019). Furthermore, the three study sites exceed the Fe concentration limits, ranging from 101 to 200 mg kg<sup>-1</sup> (Alcalá et al. 2009), with the highest concentrations recorded in spring (GUAD: 513.41 ppm; SJA: 261.09 ppm; and COY: 239.62 ppm). This could damage cell membranes and other cell components, causing oxidative stress, reduced growth, and, ultimately, the death of tree root cells (Harish et al. 2023).

The surface concentration of metals and metalloids (Cd, Cu, Pb, As, and Fe) in foliage decreased in autumn and winter; this is likely due to the rainy season that begins in early June and ends in late October, favoring the washing of foliage and the removal of surface pollutants (ProAire 2021).

#### Seasonal trends of pollutant concentration in the foliage

The maximum peaks of As, Cu and Pb occurred in winter and the lowest values for As, B, Cu, Fe, Zn in spring-summer (Fig. 4). The observed increase in metal absorption occurred after the rainy season (summer and autumn), which facilitated the movement of metals and metalloids into the soil through both wet and dry deposition, making them available for plant absorption through roots and leaves (Zeiner & Juranović Cindrić 2021). The highest concentrations of arsenic (As) were recorded in summer at the SJA site (3.12 ppm) and in spring at the COY site (1.89 ppm). These concentrations exceed the threshold for plants to benefit from arsenic, which is set at above 1.0 mg kg<sup>-1</sup> (Adriano 2001a). According to Mishra et al. (2017), arsenic primarily accu-

mulates in small amounts in the cell nucleus, interfering with nucleic acid synthesis and impairing pigment biosynthesis. Cadmium presented high concentrations at intracellular level in COY (0.13 ppm), considering that normal concentrations in foliage tissues range between 0.05 and 0.2 mg kg<sup>-1</sup> (He et al. 2015). On the other hand, the highest Cu value at intracellular level occurred in SJA (21.15 ppm), exceeding the typical threshold of Cu in foliage (5-30 mg kg<sup>-1</sup> - Adriano 2001b), probably related to vehicular traffic, specifically through the wear of brake linings (Straffellini et al. 2015).

#### Soil, roots, and foliage relationship in heavy metal concentrations

Metals and metalloids accumulation in soil, root, and foliage components showed a large variation. Fine roots accumulated 50%-100% at GUAD and COY sites, compared to soil and foliage. This result aligns with the findings of Kataweteetham et al. (2020), who indicate that fine roots accumulate more heavy metals and metalloids than other components. The accumulation in fine roots occurs because the cell walls effectively immobilize heavy metals. Additionally, tree roots often form mutualistic associations with ectomycorrhizal fungi, which can accumulate these elements in their cell walls and vacuoles, resulting in increased concentrations (Cejpková et al. 2016).

Metals and metalloids at intracellular and surface levels in *Pinus greggii* showed different seasonal trends throughout the year. For example, Pb, Zn, Cu, and Fe presented their maximum peaks at the surface level (NW) in spring and their lowest values at the intracellular level (WW). In contrast, the highest concentrations of metals and metalloids at the intracellular level occurred in winter, while concentrations at

the surface level decreased. When comparing this information with soil accumulation, it is evident that the concentrations in soils are lower than those in foliage during spring. However, they are similar to the intracellular foliage concentrations observed during winter. This may be linked to the mobility of heavy metals through the plant, that begins with dry deposition on foliage surface during the spring. Later, during the rainy season, the foliage is washed, causing the metals to be deposited in the soil and either retained in the soil or absorbed by the roots. Metal absorption occurs through the epidermal cells of the root cortex, passing through the endodermis and into the parenchyma cells, where the metals are stored before entering the xylem's conductive elements (Song et al. 2017). As a result, higher intracellular concentrations in the foliage are observed in autumn and winter, as metals are transported and accumulated when the foliage matures and ages.

#### Conclusions

The accumulation of heavy metals and metalloids in the soil of three urban parks in Mexico City was higher in the surface soil (0-10 cm), with the exception of arsenic which had the highest concentrations in the 10-20 cm layer, indicating soil internal transport. No park exceeded the allowable threshold for metals and metalloids in urban soils, although SJA had higher concentrations of most elements analyzed. The accumulation of metals and metalloids in fine roots was detected at all three sites, having COY and GUAD the highest concentrations. Although in SJA the metal concentrations in roots were lower, they were higher than those in the surface soil layer of the three sites. Concentrations higher than the permissible limits were found in *Pinus greggii* foliage for B, Cu, Fe, and Cd,

showing significant differences between sites at the intracellular and surface level. The concentrations of the studied elements in foliage (intracellular and surface) showed significant differences at the seasonal level, suggesting internal movement of metals and metalloids in trees. The results also showed that the SJA and GUAD sites had the highest concentration of heavy metals and metalloids in foliage, which agrees with the pollution gradients determined by  $\text{NO}_x$ ,  $\text{PM}_{10}$ , and  $\text{PM}_{2.5}$ .

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