Research article

Assessment of metals in PM$_{10}$ filters and *Araucaria heterophylla* needles in two areas of Quito, Ecuador

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**A R T I C L E  I N F O**

**Keywords:** Metals; Ecuador; Pollution; Quito

**A B S T R A C T**

The reliability of *Araucaria heterophylla* needles as a biomonitor was evaluated by analyzing the concentration of metals in PM$_{10}$ filters and in *Araucaria heterophylla* needles. The sampling campaign was carried out at two sites in the city of Quito, Ecuador, in 2017–2019. Concentrations of Cr, Cu, K, Mn, Pb, Zn, Ca, Fe, Al and Mg were determined in PM$_{10}$ filters and in *Araucaria heterophylla* needles using an Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). The annual mean concentrations of PM$_{10}$ ranged between 24.9 and 26.3 μg m$^{-3}$, exceeding the limit established by the World Health Organization (20 μg m$^{-3}$). Statistical analyses, performed for the PM$_{10}$ filters, showed that dust resuspension and anthropogenic activities were important sources for PM$_{10}$ emissions in the city. Metals related to natural emissions (Ca, Mg, K, Al and Fe) dominated in both types of samples, while the minor metals were those related to anthropogenic emissions (Zn, Cu, Cr and Pb). The former were positively associated with the needle samples, while the latter were associated with PM$_{10}$ filters. This work not only improved scientific knowledge on the concentrations of PM$_{10}$ and metals in the Andean city of Quito, but also greatly contributed to the progress of research on the use of *Araucaria heterophylla* needles as a biomonitor.

1. Introduction

Air pollution is a global problem that has adverse effects on ecosystems and living organisms. One of the main pollutants of concern is particulate matter (PM), due to its adverse effects on human health. The PM$_{10}$ fraction (particles with aerodynamic diameter less or equal to 10 μm) and especially the PM$_{2.5}$ fraction (particles with aerodynamic diameter less or equal to 2.5 μm) are the main cause of such effects. PM can penetrate deeply into human lungs and cause cardiovascular, respiratory and neurodegenerative disorders (Boda et al., 2020; Burnett et al., 2014; Costa et al., 2020; Middleton et al., 2008). Metals are considered one of the most challenging and toxic elements present in PM because they cannot degrade biologically or chemically and they tend to bioaccumulate (Chen et al., 2013; Li et al., 2015).

The investigation of chemical PM composition is essential to identify possible sources of pollutant emission and understand the toxicological effects. High-volume air samplers are a conventional monitoring technique, which allow to collect PM on a filter and perform the chemical analysis later (González et al., 2018; Ramírez et al., 2019). On the other hand, the use of plants to identify changes in environmental quality is an ideal low-cost alternative (Avila et al., 2019; Illi et al., 2017; Solgi et al., 2020; Türkylmaz et al., 2018a). The ability of plants to assimilate trace metals from the surrounding atmosphere and bioaccumulate them in their tissues has made plants the most suitable biological air monitors (Sevik et al., 2019; Türkylmaz et al., 2018b). Specifically, trees have received increasing attention, as they are long-lived species widely distributed in urban areas. Thus, they can provide comprehensive information on temporal and spatial scales (Darley, 2012; Sawidis et al., 2011). Furthermore, due to their size and persistence, trees have an outstanding adaptability and a greater accumulation of xenobiotics (Alatou and Sahli, 2019).

Monitoring and biomonitoring techniques can be used individually or they can be combined to analyze the concentration of metals in an area (Monaci et al., 2000; De Paula et al., 2015). Monaci et al. (2000) quantified various metals present in PM$_{10}$ filters collected from 1995 to 1997 and in *Quercus ilex* leaves collected in 1997. The study (Monaci et al., 2000) was carried out along a busy road and in a park in Florence.
(Italy). Both materials (filters and plants) indicated that Ba and Zn were reliable tracers for vehicle traffic emissions, instead of Pb. On the other hand, De Paula et al. (2015) quantified various metals present in the hemiepiphyte herb *Struthanthus flexicaulis* and compared the concentrations with those found in PM$_{2.5}$ filters. The study was carried out in urban, industrial and rural areas of Rio de Janeiro, Brazil. In general, the concentration of metals measured in the biomonitor was higher than those in the PM$_{2.5}$ filters. Anthropogenic sources were identified using both types of samples, supporting the use of *S. flexicaulis* as a biomonitor.

Nevertheless, there are very few studies that address the relationship between metals accumulated in filters and plants, especially in conifer needles. Previous studies indicate that the use of conifers can be more effective in monitoring the concentration of metals than broad-leaved trees, mainly because the needles have additional resin channels that facilitate the capture of metals (Brown et al., 2017; Chen et al., 2017). *Araucaria heterophylla* is a conifer species of interest. However, the studies on its use as a biomonitor have been limited to the analysis of the air pollution tolerance index (APTI) (Anake et al., 2018, 2019). Whereas, its ability to accumulate metals is scarcely studied. In a previous work of the group (Alexandrino et al., 2020a), the *Araucaria heterophylla* was used for the first time to assess the presence of metals in areas with different vehicular traffic intensity. The samples were collected from a number of sites with high, moderate and low vehicular traffic intensity, showing that *Araucaria heterophylla* needles are suitable for monitoring metals associated with road traffic emissions. However, the comparison of the concentration of metals found in the needles of this conifer species with those found in PM filters is not yet available to date. Therefore, the aim of this work was to assess the reliability of *Araucaria heterophylla* needles as a biomonitor by analyzing the concentration of several metals in PM$_{10}$ filters and in *Araucaria heterophylla* needles in two areas in the Andean city Quito, Ecuador.

2. Materials and methods

2.1. Study area and sampling site

Quito, the capital of Ecuador, covers a surface of about 372.4 km$^2$ and is at an altitude of approximately 2850 m above sea level (m.a.s.l.) (Figure 1). The city has a population density of 7347.1 inhabitants km$^{-2}$, and is the hub of the Metropolitan District of Quito (DMQ) that extends over an area of 4235 km$^2$ with approximately 2.2 million inhabitants. Quito has a mean precipitation value of 1204 mm, concentrated mainly in the rainy period (September–May). The accelerated development and population growth of the city have brought deterioration of the air quality. Hence, an air quality monitoring network was installed in 2003 in the city. The main source of air pollution in Quito is road-traffic (Herrera et al., 2016). Moreover, the city also has industries located mainly in surrounding areas that also contribute to air pollution (Zalakeviciute et al., 2020a).

The investigation was carried out using high-volume samplers installed in two sites of the atmospheric monitoring network of Quito: Belisario (S1, 78°29’45.1"W, 0°11’04.7"S) and Los Chillos (S2, 78°27’19.5"W, 0°17’48.8"S) (Figure 1). Belisario is an urban area with a high vehicular traffic according to the Google Maps Traffic application and a real traffic sampling using the QGis software (Alexandrino et al., 2020b; Zalakeviciute et al., 2020b). On the other hand, Los Chillos is considered a suburban area influenced by industry activities (Cevallos et al., 2017; Zalakeviciute et al., 2020a).

2.2. Sampling and chemical analysis

The procedure followed to collect and determine the concentration of metals in PM$_{10}$ filters and needles was explained in detail previously (Alexandrino et al., 2020a; Zalakeviciute et al., 2020a). Briefly, the PM$_{10}$ samples were collected twice a month between January 2017 and
needles, respectively. The digestion was carried out at 200°C for 45 min. The extracts were filtered and diluted with ultrapure water to a final volume of 50 ml for the PM10 filters and needles. The digestion was repeated using plastic gloves to avoid any contamination. The collected samples were stored in zip-lock bags and kept at 4°C until analysis. Part of the samples was subjected to the same chemical procedure as the sampled needles. The digestions were carried out at 200°C for 45 min.

On the other hand, a single Araucaria heterophylla tree was identified close to each monitoring station (see Figure 1), at a maximum distance of 260 m. Approximately 8 g of Araucaria heterophylla needles were collected and chemically analyzed once a month during August, September and November 2019 at both sites. The needles were sampled in the directions of the four cardinal points, at a height of about 2.5 m from the ground using plastic gloves to avoid any contamination. The collected samples were stored in clean zip-lock bags, wrapped in aluminum foil, transported to the laboratory and stored at 4°C until analysis. Part of the samples was used to determine the water content and another faction was used for chemical analysis. Samples were only collected when no precipitation was recorded at least 5 days before sampling, in order to avoid the loss of information caused by the washing effect.

The methods by Zalakeviciute et al. (2020a) and Alexandrino et al. (2020a) were used to obtain the chemical composition of PM10 filters and needles, respectively. Briefly, 16 cm³ of loaded filter or 0.5 g of fresh needle sample was digested (microwave digestion system MARS 6 - CEM Corporation) with 10 ml of concentrated HNO₃ or with 7 ml of concentrated HNO₃, 2 ml of H₂O₂ and 1 ml of ultrapure water, for the filters and needles, respectively. The digestion was carried out at 200°C for 45 min. The extracts were filtered and diluted with ultrapure water to a final volume of 50 ml for the filters, and 25 ml for the needles. The diluted solutions were analyzed for concentrations of Cr, Cu, K, Mn, Pb, Zn, Ca, Fe, Al and Mg using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Thermo Scientific iCAP 7000 Series). The extraction efficiencies were determined using the certified reference materials NIST1648a - Urban particulate matter and NIST SRM 1575a - Trace elements in Pine Needles, as explained previously (Alexandrino et al., 2020a; Zalakeviciute et al., 2020a). Moreover, blank filters were subjected to the same chemical procedure as the sampled filters in order to determine the limit of detection (LOD) and quantification (LOQ) for each element (see Zalakeviciute et al. (2020a) for details).

Additionally, the water content in the needles was determined to express the results in a dry weight basis (µg g⁻¹ DW). This allows comparing the concentration of metals found in this work with those reported in the literature. The process consisted of drying, in triplicate, 2.5 g of fresh material at a constant temperature of 75°C until verifying that a constant weight was reached. The mean water content in the samples was 57.50 ± 3.37% (mean value ± standard deviation).

### Statistical analyses

Univariate, bivariate and multivariate statistical analyses were performed on the datasets (Taheri Shahraijy and Sodoudi, 2016) in order to identify the emission sources and to assess the relationship between the metals found in the PM10 filters and needles. An Exploratory Data Analysis (EDA) was performed on the datasets for the PM10 filters and the Araucaria heterophylla needles. The EDA was performed for univariate and bivariate cases. Univariate analysis allowed expressing the results as the mean value ± standard deviation for each concentration of metal. The bivariate analysis performed was namely a Pearson’s correlation for every pair of variables with their respective significance test. A one-way analysis of variance (ANOVA) was performed together with a pairwise comparison of means by a post-hoc Tukey’s test whenever significant differences were indicated by the ANOVA between sampling years (PM10 filters) or monitoring stations (PM10 filters and needles). The ANOVA assumptions were verified by a Shapiro-Wilk normality test, as well as by inspection of residual vs. fitted values plot. Moreover, a Principal Component Analysis (PCA) was performed on the metal data of the PM10 filters to identify the potential sources of pollution that affect the study areas and evaluate their contribution (Braga et al., 2004). PCA is the most widely used multivariate statistical analysis technique in atmospheric sciences (Calessio et al., 2012). This technique seeks to reduce the size of the data set but preserves the initial information by grouping the variables that have similar characteristics into the same component (Wannaz et al., 2013), which may indicate a common source (Abril et al., 2014a; Wannaz et al., 2012).

Additionally, a PCA was performed using the metal data of the PM10 filters and needles as classification criteria in order to assess the relationship between both samples. PCA was used to highlight how strongly each characteristic (vector) influence the principal components, in order to identify the importance and relation of the measured variables (concentration of metals) according to the data of the materials (PM10 filters and needles). All statistics were performed using R language.

### Results and discussion

#### 3.1. PM10 filters

Figure 2 shows the annual variation of the concentration of PM10 for both study sites. It is observed that the limit value for the daily

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**Table 1. Equipment for the measurement of meteorological parameters.**

| Meteorological parameter | Equipment |
|--------------------------|-----------|
| Precipitation            | Rain Fall sensor model 382 (Met One Instruments) |
| Relative humidity        | Hygro-ThermoTransmitter-compact model 1.1005.54.161 (Thies Clima) |
| Pressure                 | PTB101B Barometric Pressure Sensor (Vaisala) |
| Temperature              | Hygro-ThermoTransmitter-compact model 1.1005.54.161 (Thies Clima) |
| Wind speed               | 010C Wind Speed Sensor (Met One Instruments) |

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concentration of PM$_{10}$ established by The World Health Organization (50 μg m$^{-3}$; WHO, 2005), the European Union (50 μg m$^{-3}$; European Commission, 2019) and the Ecuador Standards Air Quality (100 μg m$^{-3}$; TULS, 2015) is not exceeded at the urban site S1. However, the WHO and the European Union standards were exceeded on two days (01/01/2017 and 22/09/2017) at the suburban site S2.

A separate statistical analysis was performed for each year in order to provide more complete information on compliance with the guidelines-based annual concentration limit values, as well as to provide information on the variation in the concentration of PM$_{10}$ between years and monitoring stations. Table 2 shows the mean values and standard deviation (SD) of the concentrations of PM$_{10}$ (μg m$^{-3}$) found in the filters for each sampling year in both sites. The $p$-values for the ANOVA test between years and monitoring stations are also shown. It is observed that the mean annual concentration of PM$_{10}$ is in the range of 24.9–26.3 μg m$^{-3}$. Thus, the WHO mean annual limit value (20 μg m$^{-3}$) is exceeded in both years (WHO, 2005). However, these concentrations are below the mean annual limit established by the Ecuadorian Standards for Air Quality (50 μg m$^{-3}$) (TULS, 2015) and the European Union (40 μg m$^{-3}$) (European Commission, 2019). The annual mean concentration was higher in 2018 than in 2017 at both sites, with a higher concentration at site S2 than at site S1. However, no significant difference is observed between years or monitoring stations.

Table 3 shows the mean value and standard deviation of the concentration of metals (μg m$^{-3}$) found in the filters analyzed in 2017 and 2018, in the two study sites. The $p$-values for the ANOVA test between years and monitoring stations are also shown. It is observed that the major metals found in both stations are Ca (6.6–8.7 μg m$^{-3}$), Al (0.4–2.6 μg m$^{-3}$), Mg (1.6–2.0 μg m$^{-3}$), K (0.4–0.8 μg m$^{-3}$) and Fe (0.4–0.6 μg m$^{-3}$), which is in line with previous works (Celis et al., 2004; Loyola et al., 2012; Monaci et al., 2000; Vargas et al., 2012). These metals are major components of crustal materials and soil, thus they are typically related to natural origin, such as dust resuspension (Arditsoglou and Samara, 2005; Loyola et al., 2009, 2012). On the other hand, mean concentration of the minor metals Cr, Cu, Pb, Zn and Mn were found in the range of 0.009–0.2 μg m$^{-3}$. These metals are typically related to anthropogenic emissions (Loyola et al., 2012; Pacyna and Pacyna, 2001), although Cu and Zn are also micronutrients which are essential for life but are toxics at high concentrations (Gandois and Probst, 2012).

Statistically significant difference between years, in both sites, was only observed for the concentrations of Mn and Al, for which the mean concentrations were higher in 2018 than in 2017. Moreover, there is also a significant difference in the concentration of Zn at site S1 between years, with 2017 being the year with the highest concentration. A significant difference is also observed in the concentration of Ca, K, Ca, Fe and Mg at site S2 between years, with the highest concentration of Cu in 2017, while the mean concentrations of K, Ca, Fe and Mg were higher in 2018 than in 2017. In summary, it is noticed that the concentrations of the metals mainly associated with soil dust (K, Ca, Mg, Fe and Al) were higher in 2018, while the concentrations of the metals mainly associated with anthropogenic emissions (Zn and Cu) were higher in 2017. These variations may have been due to different factors, such as irregularity of the behavior of emission sources, like vehicular sources and power plants, and to meteorological parameters, as mentioned in previous

| Site | 2017 | 2018 | ANOVA between years |
|------|------|------|---------------------|
| S1   |      |      |                     |
| Cr   |      |      |                     |
| Cu   |      |      |                     |
| K    |      |      |                     |
| Mn   |      |      |                     |
| Pb   |      |      |                     |
| Zn   |      |      |                     |
| Fe   |      |      |                     |
| Mg   |      |      |                     |
| Al   |      |      |                     |
| ANOVA between stations | 0.7 | 1.0 |                     |

| Site | 2017 | 2018 | ANOVA between stations |
|------|------|------|------------------------|
| S1   |      |      |                        |
| Cr   |      |      |                        |
| Cu   |      |      |                        |
| K    |      |      |                        |
| Mn   |      |      |                        |
| Pb   |      |      |                        |
| Zn   |      |      |                        |
| Fe   |      |      |                        |
| Mg   |      |      |                        |
| Al   |      |      |                        |
| ANOVA between stations | 0.7 | 1.0 |                        |

Table 3. Concentration of metals (mean ± SD) found in the extract of the PM$_{10}$ filters at sites S1 and S2 in 2017 and 2018. Unit: (μg m$^{-3}$). $p$-values for the ANOVA test between years and monitoring stations.
works (Braga et al., 2005; Manalis et al., 2005; Ramírez et al., 2018; Sanchez-Ccoyllo and Andrade, 2002).

In order to evaluate the effect of meteorological parameters on the metal composition of PM, Table 4 shows the mean and standard deviation of precipitation, relative humidity, pressure, temperature and wind speed during the samplings in 2017 and 2018. It is observed that wind speed was lower in 2018 than in 2017, which indicates that the increase in the concentration of metals associated with soil dust in 2018 may be due to the absence of wind that causes these metals to accumulate in the ambient air. On the other hand, the higher relative humidity in 2017 compared to 2018, can causes worsened combustion efficiency (Zalakevicuiu et al., 2018), and thus a greater emission of metals associated with anthropogenic activities occurs in 2017.

Regarding the differences between sites, statistically significant differences are found in 2017 for Cu (p = 0.06) and Mn (p = 0.04), with the mean concentrations of these metals being higher at site S2 and at site S1, respectively. Cu is associated with sources like brake linings (Hjortenkranst et al., 2006), and metallurgical industry (López et al., 2011). Mn, in addition to being associated with natural soil source (Bilos et al., 2001; Thorpe and Harrison, 2008), is also associated with components of steel and alloys used in the automotive industry (Fujinara et al., 2011). Table 5 compares the concentration of the metals found in Quito with those found in other Latin American cities (Buenos Aires – Argentina, Sao Paulo – Brazil, Cunha – Brazil, Chillan – Chile, Santiago – Chile, Bogota – Colombia). The concentration of Cr found in Quito is 10 times higher than that reported in Bogota, but 10 times lower that reported in Santiago. Mn, Pb and Zn follow the same pattern: the concentrations of these metals are around 10 times lower in Quito than in Santiago. The concentrations of Cu and Al in Quito are similar to those found in Chillan and Santiago, and also Buenos Aires and Bogota in the case of Al, but much higher than the concentrations found in the other cities. Lower concentration of Fe is found in Quito compared to Buenos Aires, Chillan and Bogota, but higher than the ones reported in Sao Paulo. The concentration of Fe in Quito is similar to Santiago and Bogota, and higher than Chillan. Ca is the element which appears to be enriched in Quito compared to other world cities, and is similar to the Ca concentration in Santiago. It could be due to the composition of the carbonaceous soil-source material of this city.

Finally, to identify possible sources of pollution in both sites, Pearson and PCA tests were performed using the PM10 filter data. Table 6 shows the Pearson correlation coefficients for the metals found in the PM10 filters in both sites. At site S1, high correlations were found for the following metal groups: (i) Ca, Mg, Fe, Al and Mn; (ii) Cr, Cu, K and Zn; and (iii) Pb, K and Mn. The first group is clearly derived from natural

### Table 4. Meteorological parameters values (mean ± SD) during the samplings in 2017 and 2018 at sites S1 and S2.

| Site   | Precipitation (mm) | Relative humidity (%) | Pressure (mmHg) | Temperature (°C) | Wind speed (m s⁻¹) |
|--------|--------------------|-----------------------|-----------------|------------------|--------------------|
|        | 2017               | 2018                  | 2017            | 2018             | 2017               |
|        | 2017               | 2018                  | 2017            | 2018             | 2017               |
| S1     | 3.4 ± 7.3          | 2.6 ± 5.7             | 67.6 ± 13.3     | 65 ± 14.5        | 726 ± 0.7          |
|        | 2017               | 2018                  | 2017            | 2018             | 2017               |
|        | 2017               | 2018                  | 2017            | 2018             | 2017               |
| S2     | 1 ± 3              | 2.7 ± 5.8             | 69.2 ± 11.4     | 67.3 ± 11        | 759 ± 0.7          |
|        | 2017               | 2018                  | 2017            | 2018             | 2017               |
|        | 2017               | 2018                  | 2017            | 2018             | 2017               |

### Table 5. Comparison of the concentrations of metals found in PM₁₀ filters in Quito and in other Latin American cities. PW: present work. *nd not detected.

| City (Country) | Concentration (ng m⁻³) | Reference          |
|---------------|------------------------|--------------------|
|               | Cr                     | Cu                 | K             | Mn   | Pb   | Zn   | Ca   | Fe   | Al   | Mg   |
| Quito (Ecuador) | 8.5-95 | 88-200 | 410-820 | 32-56 | 19-45 | 71-120 | 6550-8690 | 360-550 | 380-2600 | 1560-2120 | PW |
| Buenos Aires (Argentina) | - | 17.2-30.0 | - | 16.0-24.9 | 14.2-52.0 | 46.8-109 | 1029-1419 | 672-1215 | 763-1133 | - | Reich et al. (2009) |
| Sao Paulo (Brazil) | - | 29.3 | - | 18.90 | 16.6 | 118 | - | 97-0 | 54.3 | - | Marie Bourotte et al. (2011) |
| Cunha (Brazil) | - | 4 | - | 7.70 | 13.2 | 221 | - | nd* | 39.6 | - | Marie Bourotte et al. (2011) |
| Chillan (Chile) | - | 180 | 1910 | 40 | 20 | 300 | 1610 | 2110 | 1410 | 290 | Cels et al. (2004) |
| Santiago (Chile) | 240-920 | 80-320 | - | 60-110 | 80-960 | 450-1080 | 6909-11230 | - | 2620-3820 | 1300-3940 | Richter et al. (2007) |
| Bogota (Colombia) | 7 | 13-28 | 236-262 | 5-20 | 128 | 37-194 | 1082-1534 | 663-1068 | 898-1107 | 1050-1380 | Vargas et al. (2012) |

### Table 6. Pearson analysis for metals found in PM₁₀ filters at sites S1 (bold) and S2 (normal).

| Mg   | Fe   | Al   | Cr   | Zn   | Ca   | Mn   | K    | Pb   |
|------|------|------|------|------|------|------|------|------|
| Ca   | 0.9*** | 0.5** | 0.6** | 0.06 | -0.1 | 0.2 | 0.6*** | 0.2 | 0.1 |
| Mg   | 1    | 0.5* | 0.7*** | 0.02 | -0.2 | 0.3 | 0.8*** | 0.3 | 0.3 |
| Fe   | 1    | 0.6*** | 0.04 | -0.3 | 0.07 | 0.3 | -0.01 | 0.02 |
| Al   | 1    | -0.2 | -0.2 | 0.3 | 0.7*** | 0.1 | 0.4* |
| Cr   | 1    | 0.2 | 0.5* | 0.3 | 0.6** | 0.3 | 0.5* |
| Zn   | 1    | 0.6** | 0.3 | 0.3 | 0.4* |
| Cu   | 1    | 0.8*** | -0.1 | -0.3 | 0.4* |
| Mn   | 1    | 0.4* | 0.8*** | 0.3 | 0.3 |
| K    | 1    | 0.6** | 0.3 | 0.3 |
ANOVA test between monitoring stations.

On the other hand, the high correlation of Fe and Al with the crustal elements Ca (0.5 for Fe and 0.6 for Al) and Mg (0.5 for Fe and 0.7 for Al) (Table 6), and their presence in the component loaded with the anthropogenic elements (Cr, Cu, Zn and Pb, Table 7), can suggest that Fe and Al may also have additional source different than the dust resuspension, specifically, vehicle traffic. In fact, these metals have been associated with components of steel and alloys used in the automotive industry (Fujiwara et al., 2011). Moreover, Fe has been found in high concentration in car brake linings, car brake dust and in the exhaust of diesel and gasoline engines, while Al has been identified in relatively high concentration in motor exhaust (Loyola et al., 2012).

At site S2, high correlations were found for the following metal groups: (i) Ca, Mg, Fe, Al, Mn and K; (ii) K and Zn; and (iii) Pb and Cr (Table 6). As in the case of the site S1, the first group is crustal elements, identifying a soil dust source, while the other two groups can be associated with anthropogenic emissions. Similar results were observed with the PCA (Table 7). Two dimensions accounting for a total of 66.4% of the data variability were identified for site S2. Dimension 1, which accounts for the 49.1% of the total variance, presents high loads for K, Mn, Ca, Fe, Al and Mg. Dimension 2 presents high loads for Cr, Cu, Pb and Zn, which are associated with industrial and road traffic emissions. Emissions of Cr, Cu, Pb and Zn, with respect to industrial activities, could be related to chemical industries (Wannaz et al., 2012), cement plants (Ogunkunle and Fatoba 2014; Wannaz et al., 2012), metallurgical industries (Quitiero et al., 2004) and manufacturing processes of power transformers (Bermúdez et al., 2009). Unlike at the urban site S1, Fe and Al seems to come mainly from resuspension of dust, due to the tight correlation with crustal elements (Table 6) and its presence in the same dimension (Table 7).

### 3.2. *Araucaria heterophylla* needles

Table 8 shows the mean and standard deviation of the concentration of metals found in the *Araucaria heterophylla* needles. It is observed that, in both areas, the metals with the highest mean concentration are Ca (27627 μg g⁻¹ DW (S1); 18236 μg g⁻¹ DW (S2)), Mg (3999 μg g⁻¹ DW (S1); 4093 μg g⁻¹ DW (S2)), K (3212 μg g⁻¹ DW (S1); 3032 μg g⁻¹ DW (S2)), Al (996 μg g⁻¹ DW (S1); 642 μg g⁻¹ DW (S2)), Fe (734 μg g⁻¹ DW (S1); 278 μg g⁻¹ DW (S2)) and Mn (382 μg g⁻¹ DW (S1); 136 μg g⁻¹ DW (S2)). The highest concentrations were also observed for Ca, Mg, K and Al in the PM₁₀ filters (see Table 3). Similar sequence for metal accumulation was also obtained in works using biomonitors such as mosses (Lazo et al., 2019; Staffilove et al., 2018; Steinnes et al., 2016), pine needles (Brown et al., 2017) and lichen (Bergamaschi et al., 2007). Ca, Mg and K are macronutrients considered essential for plant metabolism and therefore are part of the tissue composition (Fernández and Carballé, 2000). On the other hand, Al, Fe and Mn are considered geological elements but are also related to components used in the automotive industry (Fujiwara et al., 2011). Zn, Cu, Cr and Pb are other minor metals found in the *Araucaria heterophylla* needles, with concentrations ranging from 0.6 to 48.3 μg g⁻¹ DW. These results indicate that *Araucaria heterophylla* needles are suitable for biomonitoring because they tend to accumulate metals and the needles indicate similar differences with PM₁₀ in quantitative relationships in the two study areas (Tables 3 and 8).

### Table 7. Factor loading for metals in PM₁₀ filters at sites S1 (bold) and S2 (normal).

| Metal | Dim. 1 | Dim. 2 |
|-------|--------|--------|
| Cr    | 0.02   | 0.6    |
| Cu    | 0.3    | 0.03   |
| K     | 0.4    | 0.08   |
| Mn    | 0.04   | 0.02   |
| Pb    | 0.2    | 0.02   |
| Zn    | 0.1    | 0.06   |
| Ca    | 0.3    | 0.09   |
| Fe    | 0.2    | 0.4    |
| Al    | 0.4    | 0.1    |
| Mg    | 0.4    | 0.01   |

### Table 8. Concentration of metals (mean ± SD) found in the *Araucaria heterophylla* needles collected near to the monitoring stations. Unit: (μg g⁻¹ DW), p-values for the ANOVA test between monitoring stations.

| Site (n = 3) | Cr   | Cu   | K     | Mn   | Pb   | Zn   | Ca   | Fe   | Al   | Mg   |
|-------------|------|------|-------|------|------|------|------|------|------|------|
| S1 (n = 3)  | 3.6 ± 0.1 | 12.2 ± 3.5 | 3212 ± 1459 | 382 ± 208 | 3.0 ± 2.1 | 48.3 ± 17.1 | 27627 ± 2501 | 734 ± 211 | 996 ± 793 | 3999 ± 409 |
| S2 (n = 3)  | 0.6 ± 0.3 | 3.3 ± 1.4 | 3032 ± 1312 | 136 ± 23.9 | 1.2 ± 0.2 | 17.5 ± 2.8 | 18236 ± 1825 | 278 ± 91.9 | 642 ± 505 | 4093 ± 214 |

ANOVA between stations: 0.008** 0.02 * 0.9 0.1 0.2 0.03 * 0.006 * 0.03 * 0.6 0.7

** 0.001 < p < 0.01; * 0.01 < p < 0.05.
The mean concentrations of Cr, Cu, Zn, Fe and Ca show statistically significant differences between monitoring stations, with S1 being the site with the highest concentration of these metals (Table 8). As mentioned above, Cr, Cu and Zn are largely associated with traffic emissions (Al-Alawi and Mandiwana, 2007; Solgi et al., 2020). Thus, the higher concentration of these metals at site S1 could be due to higher traffic flux than at site S2. On the other hand, the higher concentrations of Fe and Ca at site S1, compared to site S2, could be related to the natural composition of the plant and to the soil resuspension (Abril et al., 2014b).

The concentration of Cr, Cu, Mn, Pb, Zn and Fe found in the present work was compared with data from studies carried out in other cities of the world (Table 9). Data for K, Ca, Al and Mg were not included because there were no values for these elements in the other studies. Because there is no information in literature on the detection of metals in the air filtering events in Quito throughout the year, the lower concentration of anthropogenic metals in the 

### Table 9. Comparison of the concentrations of Cr, Cu, Mn, Pb, Zn and Fe found in the Araucaria heterophylla needle samples and in other cities of the world. Different plant species are included. Unit: (mg g⁻¹ DW). PW: present work.

| City/Country and plant species | Cr   | Cu  | Mn  | Pb   | Zn   | Fe   | Reference               |
|-------------------------------|------|-----|-----|------|------|------|-------------------------|
| Quito - Ecuador              |      |     |     |      |      |      | Araucaria heterophylla   |
| Cordoba - Argentina           |      |     |     |      |      |      | Tillandsia capillaris    |
| Lithuania                     |      |     |     |      |      |      | Picea abies needles      |
| Lithuania                     |      |     |     |      |      |      | Juniperus communis       |
| Lithuania                     |      |     |     |      |      |      | Moss                     |
| Amman - Jordan                |      |     |     |      |      |      | Pinus halepensis L.      |
| Turkey                        |      |     |     |      |      |      | Pinus brutia needles     |
| São Paulo - Brazil            |      |     |     |      |      |      | Tillandsia usneoides     |

### Table 10. Concentration of metals (mean value ± SD) found in PM₁₀ filters and in Araucaria heterophylla needles. Unit: mg kg⁻¹.

| Site and materials | Cr     | Cu     | K      | Mn      | Pb      | Zn      | Ca      | Fe       | Al       | Mg       |
|--------------------|--------|--------|--------|---------|---------|---------|---------|----------|----------|----------|
| PM₁₀ filter S1     | 13.2 ± 48.6 | 27.6 ± 22.6 | 208 ± 155 | 13.8 ± 5 | 7.8 ± 8.3 | 26.6 ± 25.3 | 2301 ± 693 | 139 ± 50.1 | 440 ± 509 | 554 ± 218 |
| Araucaria heterophylla | 1.6 ± 0.5 | 5.5 ± 1.3 | 1434 ± 564 | 175 ± 102 | 1.4 ± 1 | 21.9 ± 8 | 12571 ± 1688 | 332 ± 92.1 | 456 ± 374 | 1812 ± 175 |
| PM₁₀ filter S2     | 2.6 ± 2 | 40.1 ± 44.3 | 182 ± 98.4 | 13.1 ± 5.7 | 7.7 ± 8.6 | 29.2 ± 26.1 | 2117 ± 617 | 130 ± 67.5 | 463 ± 517 | 516 ± 204 |
| Araucaria heterophylla | 0.3 ± 0.2 | 1.6 ± 0.6 | 1442 ± 603 | 65.5 ± 13 | 0.5 ± 0.7 | 8.8 ± 0.5 | 8723 ± 694 | 132 ± 41.4 | 305 ± 236 | 1961 ± 128 |

### 3.3. Comparison between the concentration of metals in PM₁₀ filters and Araucaria heterophylla needles

Table 10 shows the mean concentration, in mg kg⁻¹, of the metals found in PM₁₀ filters and Araucaria heterophylla needles. It is observed that, in both areas, the concentrations of crustal materials and soil (K, Ca, Mg, Mn and Fe) were higher in the plant material than in the PM₁₀ filters, while the concentrations of anthropogenic metals Cr, Cu, Pb and Zn were higher in the PM₁₀ filters. Additionally, a PCA analysis was carried out using the data for metals (PM₁₀ filters and Araucaria heterophylla needles) as classification criteria, to have a clear view of the metals that are more associated with each material (Table 11, Figure 3). A positive association is observed between the needles and K, Ca, Mg, Mn, Fe and, to a lesser extent, Al, while Cr, Cu, Pb and Zn are associated with PM₁₀ filters (see Figure 3). This result is opposite to that observed in the work of De Paula et al. (2015) where, in general, the concentration of the metals measured in the Struthanthus flexicaulis leaves were higher than those found in the PM filters. This was attributed to the fact that the recollection of PM filters was over a 24-h period, while leaves present a long-term effect. However, in the present work, taking into account frequent high precipitation events in Quito throughout the year, the lower concentration of anthropogenic metals in the Araucaria heterophylla needles could be mainly due to a wash effect of the rain that contribute to eliminate metals retained in the wax layer (Çelik et al., 2005; Al-Alawi and Mandiwana, 2007).
Solgi et al., 2020; De Nicola et al., 2008). Roberts (1972) indicated that the retention of pollutants in plant leaves depends largely upon the physical, rather than the chemical, state of the pollutant and the physical form of the vegetation, and the wash effect is different depending on the plant species (Little, 1973; Moraghan, 1991; Rossini and Valdés, 2004).

We are aware of the limitation of the present study related to the analysis of the effect of rain on the removal of metals from the needles. However, we are confident that the dataset available here can give preliminary results of this effect. Therefore, Figure 4 shows, as an example, the concentration of Cr, Cu, Pb and Zn in the Araucaria heterophylla needles and the precipitation level in sampling months (August, September and November 2019) at site S1. It is observed that the concentration of the metals decrease in the months with highest precipitation levels (September and November). In this way, the Araucaria heterophylla needles could be a good biomonitor, but it must be taken into account that the samples must be collected in a period when it does not rain to obtain more reliable results of the metals accumulated in the plant.

4. Conclusions

The concentrations of different metals were investigated in PM$_{10}$ filters and Araucaria heterophylla needles at two sites in the city of Quito, Ecuador. There is a clear significant contribution of dust resuspension and anthropogenic activities to particulate matter presence in both sites. Ca, Mg, K, Al and Fe were the major metals found in PM$_{10}$ filters and Araucaria heterophylla needles. At the urban site S1, Fe and Al were found to have an additional source different to the resuspension of dust, specifically vehicular contributions. Minor metals found in both materials were Zn, Cu, Cr and Pb, which are associated with anthropogenic activities. Araucaria needles showed higher concentration of Cr, Cu, Zn, Fe and Ca at site S1 compared to the suburban site S2. This could be due to higher traffic flux in that area. The concentrations of crustal materials and soil (K, Ca, Mg, Mn and Fe) were higher in the Araucaria heterophylla needles than in the PM$_{10}$ filters, while the concentrations of the anthropogenic metals Cr, Cu, Pb and Zn were higher in the PM$_{10}$ filter. In fact, a PCA analysis showed a positive association between the needles and K, Ca, Mg, Mn, Fe and, to a lesser extent, Al, while Cr Cu, Pb and Zn were associated with PM$_{10}$ filters. The lower concentration of anthropogenic metals in the Araucaria heterophylla needles than in the PM$_{10}$ filters was attributed to a wash effect of the rain that contributed to eliminate metals retained in the wax layer. Based on the results obtained...
in this work, *Araucaria heterophylla* needles are suitable for biomonitoring because they tend to accumulate metals and the needles indicate similar differences with PM$_{2.5}$ in quantitative relationships. However, the samples should be taken in a period when it does not rain, to obtain more reliable results on the ability to accumulate metals.

**Declarations**

**Author contribution statement**

K. Alexandrino: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

T. Mancheno: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

R. Zalakeviciute and M. González-Rodríguez: Contributed reagents, materials, analysis tools or data.

**Funding statement**

This work was supported by Universidad de Las Américas (Grant numbers: AMB.KAF.19.04 and AMB.RZ.19.01), Quito, Ecuador.

**Data availability statement**

Data will be made available on request.

**Declaration of interests statement**

The authors declare no conflict of interest.

**Additional information**

No additional information is available for this paper.

**Acknowledgements**

Authors express their gratitude to the Environment Ministry (MAE) by providing the permission to collect the vegetable species samples (authorization number 013-2019-IC-FLO-DPAPCH-MA). We thank Maria Genoveva Granda for laboratory assistance.

**References**

Abril, G.A., Mannen, E.D., Mateos, A.C., Invernizzi, R., Pisk, R., Piknata, M., 2014a. Characterization of atmospheric emission sources of heavy metals and trace elements through a local-scale monitoring network using *T. capillaris*. Ecol. Indic. 40, 153–161.

Abril, G.A., Mannen, E.D., Mateos, A.C., Piknata, M.L., 2014b. Biomonitoring of airborne particulate matter emitted from a cement plant and comparison with dispersion modelling results. Atmos. Environ. 82, 154–163.

Adachi, K., Taisinho, Y., 2004. Characterization of heavy metal particles embedded in tire dust. Environ. Int. 30, 1009–1017.

Al-Alawi, M.M., Mandiwna, K.L., 2007. The use of Aleppo pine needles as a bio-monitor of heavy metals in the atmosphere. J. Hazard Mater. 148, 43–46.

Alatou, H., Sahli, L., 2019. Using tree leaves and barks collected from contaminated and uncontaminated areas as indicators of air metallic pollution. Int. J. Phytoremediation 21, 985–997.

Alexandrino, K., Viteri, F., Bybacezyk, Y., Guevara Andino, J.E., Zalakeviciute, R., 2020a. Biomonitoring of metal deposition: comparison with mosses and precipitation, role of the canopy. Atmos. Environ. 34, 4265–4271.

Celik, A., Kartal, A.A., Akdogan, A., Kaska, Y., 2005. Determining the heavy metal pollution in Denizli (Turkey) by using *Robinia pseudo-acacia*. L. Int. J. Phytoremediation 8, 105–112.

Celik, J.E., Morales, J.R., Zaror, C.A., Inuzuma, J.C., 2004. A study of the particulate matter PM$_{10}$ composition in the atmosphere of Chillana, Chile. Chemosphere 54, 541–550.

Cervolos, V., Blaz, V., Siroes, C., 2017. Particulate matter air pollution from the city of Quito, Ecuador, activates inflammatory signaling pathways in vitro. Innate Immun. 23, 392–400.

Chen, Y., Hu, W., Huang, B., Weindorf, D.C., Rajan, N., Liu, X., Niedermann, S., 2013. Accumulation and health risk of heavy metals in vegetables from harmful and organic vegetable production systems of China. Environ. Sci. 98, 324–330.

Chen, L., Liu, C., Zhang, L., Zou, R., Zhang, Z., 2017. Variation in tree species ability to capture and retain airborne fine particulate matter (PM 2.5 ). Nat. Sci. Rep. 7, 5034.

Costa, L.G., Cole, T.B., Dao, K., Chang, Y.-C., Coburn, J., Garrick, J.M., 2020. Effects of air pollution on the nervous system and its possible role in neurodevelopmental and neurodegenerative disorders. Pharmacol. Ther. 210, 107523.

Darley, E., 2012. Use of plants for air pollution monitoring. J. Air Pollut. Control Assoc. 10, 98–199.

De Nicola, F., Maisto, G., Prati, M.V., Alfani, A., 2008. Leaf accumulation of trace metals in urban areas with different vehicular traffic intensity. Chemosphere 69, 448–457.

De Paula, P.H.M., Mateus, V.L., Ararite, D.R., Duque, C.B., Saint-Pierre, T.D., Gioda, A., 2015. Biomonitoring of metals for air pollution assessment using a hemiepiphyte *Tillandsia capillaris*. J. Environ. Sci. 89, 823–832.

DeSouza, F.A., Carvalho, C., 2007. Contribution of atmospheric metallic pollution in the metropolitan region of Sao Paulo, Brazil, employing *Tillandsia caerulea* L. as biomonitor. Environ. Pollut. 145, 279–292.

Fujivara, F., Jimenes Rebagliati, R., Dawidowski, L., Gomez, D., Polla, G., Pereyra, V., Smichovsk, P., 2011. Spatial and chemical patterns of size fractionated road dust collected in a megacity. Atmos. Environ. 45, 1497–1505.

Gandio, L., Probst, A., 2012. Localisation and mobility of trace metal in silver fir needles. Chemosphere 87, 29–34.

González, L., Longoria, F., Sánchez, M., Levy, C., Acuta, K., Kharissov, B., Alfaro, J., 2018. Seasonal variation and chemical composition of particulate matter: a study by
