Biomonitring of metal levels in urban areas with different vehicular traffic intensity by using *Araucaria heterophylla* needles

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**ABSTRACT**

For the first time, *Araucaria heterophylla* needles were used as a biomonitor to assess the concentration of metals in urban areas. The samples were collected in the Andean city Quito, in Ecuador, from sites with high, moderate and low vehicular traffic intensity. Then, the concentrations of Ca, K, Mg, Fe, Al, Ba, Zn, Cu, Cr, Pb and Co were measured by using an Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Source apportionment was studied employing Principal Component (PCA) and Pearson analyses. Ca, K, and Mg were identified to come from natural sources, showing the highest levels. On the other hand, Mn, Fe and Al were related to both natural and road traffic emissions, while Ba, Zn, Cu, Cr, Pb and Co were only related to road traffic emissions. The decelerating activities were identified as the main source for vehicle non-exhaust emissions in the area of study. Areas with the highest vulnerability in metal emissions from vehicular traffic in the city of Quito were also identified through Geographic Information System. Alarming concentrations of traffic-related metals near a pediatric hospital were revealed. It was observed that streets located near a green area such as urban park, even with high or moderate traffic intensity, may experience reduced concentrations of pollutants. This work showed that *Araucaria heterophylla* needles are suitable for monitoring metals associated with road traffic emissions in areas with different vehicular traffic intensity.

**1. Introduction**

Air pollution is an increasing problem in cities of many countries, and motorized fleet emissions are one of the main sources of pollutants in urban areas. Particulate matter (PM) is among these pollutants. PM may contain toxic materials that endanger the health of the population, such as metals (e.g. Zeng et al., 2016). Metals particle emissions, related to road traffic, can occur through different pathways, such as combustion of fuel and oil, corrosion of metallic parts, tailpipe exhaust, tire wear, lubricants, brake wear and particle resuspension from the road surface (Charron et al., 2018; Karagulian et al., 2015; Pernigotti et al., 2016; Thorpe and Harrison, 2008).

Among metals related to road traffic, Cu, Fe, Ba, Sb, Cd, Pb, Zn, Cr and Ni can be mentioned. Brake wear emissions have been identified to contain significant amounts of Cu, Fe, Ba, Sb and Mn (Adachi and Tainosho, 2004; Hildemann et al., 1991; Hjortenkrans et al., 2006; Iijima et al., 2007; Lough et al., 2005; Monaci et al., 2000; Thorpe and Harrison, 2008; Sternbeck et al., 2002). Cd, Pb and Zn are used in tire manufacture (Ball et al., 1991; Hjortenkrans et al., 2006; Monaci et al., 2000; Thorpe and Harrison, 2008). Cr and Ni have been identified to be associated with fossil fuel and petrochemical products (Huffman and Wener, 2001; Manno et al., 2006; Yatkin and Bayram, 2008). Furthermore, Cr has also been associated with yellow road markings and stainless steel in traffic environments (e.g. Murakam et al., 2007). On the other hand, some metals, typically known as geogenics, such as Ca, K, Mg, Al, Fe and Mn, have been identified to also be correlated with traffic markers (Charron et al., 2018; Hildemann et al., 1991; Kennedy and Gadd, 2003; Monaci et al., 2000). Even Ca and Mg have been reported in literature to be found in common engine oil as detergent additives (Monaci et al., 2000) and in the composition of tire tread and tire dust (Adachi and Tainosho, 2004).

Metals can be present in different matrices, such as, airborne...
particulates, vegetation, river sediments, road dust, soils, etc. (Fujiiwara et al., 2011). In this sense, different vegetation species have been used as biomonitors to help provide information on the environmental quality (Alatou and Sahli, 2019; Baldantoni et al., 2014; Illi et al., 2017; Jouraeva et al., 2002; Kularatne and de Freitas, 2013; Lazo et al., 2019; Mansour, 2014; Monaci et al., 2000; Sevik et al., 2019; Wannaz et al., 2006), and even to assess the variation of chemical element concentration due to the density of vehicular traffic (Guidotti et al., 2009; Huang et al., 2019; Mateos et al., 2018; Rodriguez et al., 2010; Sevik et al., 2019; Turkyilmaz et al., 2018a; Turkyilmaz et al., 2018b). The airborne metals can precipitate directly on plants and ground surfaces, can be deposited on these surfaces through the transport of rainwater after accumulating in the atmosphere, or can be absorbed through the roots (Gunawardena et al., 2013; Shahid et al., 2016). Many studies that address the concentration of chemical elements in soils, plants and water showed to be higher near roads than further away from them (Duruihe et al., 2007; Khalid et al., 2018; Lu et al., 2014; Wawer et al., 2015).

Biomonitors are a low cost alternative to analyze air quality and obtain information related to the population’s exposure to air pollutants, and in this way it allows to evaluate many different sampling sites simultaneously (Capozzi et al., 2016; Giampaoli et al., 2016). However, plant species used as biomonitors is an important factor controlling the deposition of pollutants on the foliage of plants (Carreras et al., 2009; Fellet et al., 2016; Piccardo et al., 2005; Ratola et al., 2011).

Persistent vascular plants, such as conifer needles, has been suggested for monitoring pollutants, like metals (Brown et al., 2017; Ceburnis and Steiness, 2000; Gandois and Probst, 2012; Luo et al., 2014; Migaszewski et al., 2002; Sun et al., 2011; Tang et al., 2014). One of the advantages of using conifers is their ability to accumulate traffic-related metals that cause air pollution throughout the year, and thus are good indicators for year-round pollution (Turkyilmaz et al., 2018c). Moreover, it has been shown that the accumulation of pollutants, like metals, by conifers, is higher than broadleaf species (Beckett et al., 1998; Chen et al., 2017; Freer-Smith et al., 2005), although their leaves do not have trichomes or rough surfaces. Mechanism of accumulation of conifers is not entirely understood. However, an explanation for these results could be the following: (i) the long and narrow needles can be hit more easily by airborne particles than larger and flat leaves, which have thicker boundary layers (Bertolotti and Gialanella, 2014; Säbe et al., 2012); (ii) the additional resin channels in conifers allow the uptake of metals thus they can be more effective in accumulating elements related to broadleaf species (Guardo et al., 2003); (iii) the capacity of conifers to acidify soil solutions is higher than deciduous trees, which may increase metal solubility near their roots and enhance uptake (Andersen et al., 2004).

Among conifer species, pine trees have been the most widely studied as biomonitors (Aboal et al., 2004; Al-Alawi and Mandiwana, 2007; Kord et al., 2010; Lehndorff and Schwark, 2010). However, further studies of other conifer species is necessary because the availability of pine trees may be limited in some areas and also because the ability to accumulate metals of conifer species has been shown to differ. For example, Turkyilmaz et al., 2018c studied the accumulation of metals (Fe, Co, Ni, Cu, Zn, Cd, Hg and Pb) in the needles of different conifer species, specifically Pinus nigra, Pinus sylvestris, Abies bormülleriana and Picea pungens. The results indicate that there were significant differences between species in terms of metal accumulation. Abies bormülleriana showed to be particularly useful as a biomonitor since the accumulation for most of the metals analyzed was greater in this conifer species. In this sense, more conifer species need to be investigated, and thus expand the range of vegetation species studied as biomonitors.

In this way, the aim of this study was to evaluate the potential use of Araucaria heterophylla needles to determine the incidence of metals in areas with different vehicular traffic intensity in one of the highest capital cities in the world, Quito, Ecuador. This species was selected because its high dispersion in the study area and because, to our knowledge, its capacity to accumulate metals has not yet been evaluated. However, the sensitiveness to contamination of this species, and thus the potential as biomonitor, has been assessed by air pollution tolerance index (APTI) (Anake et al., 2018; Anake et al., 2019). APTI is an index that shows capability of a plant to tolerate air pollution based on variation in biochemical parameters (chlorophyll content, ascorbic acid content, relative water content and pH of leaf extract). High APTI value shows that the plant has tolerance to air pollution and can be used to withstand pollution. On the other hand, low APTI value shows that the plant has less tolerance and is therefore classified as sensitive and can be used to indicate levels of air pollution (Hamal and Chettri, 2017; Singh and Rao, 1983).

In this way, this work contributes: (i) to expanding the range of vegetation species studied as biomonitors; (ii) to the knowledge of the capacity of Araucaria heterophylla to accumulate metals; (iii) to the knowledge of the metals that are associated with road traffic; and (iv) to a better understanding of the air quality and health implications in an Andean city suffering from air pollution problems.

2. Material and methods

2.1. Plant species used as biomonitor

Araucaria heterophylla was used to assess the presence of metals in areas with different vehicular traffic intensity. This conifer species was selected as its capacity to accumulate metals has not yet been evaluated. The conifer genus Araucaria (Araucariaceae) comprises 20 species mostly distributed in the Southern Hemisphere (Gondwana origin) and is considered an early divergent lineage that predates the Late Cretaceous (Sequeira and Farrrell, 2001; Kranitz et al., 2014). Most of the Araucaria species are endemic to New Caledonia, New Zealand, New Guinea and Australia and just two species, Araucaria angustifolia (Bertol.) Kuntze and Araucaria araucana (Molina) K. Koch, are endemic to South America (Escapa and Catalano, 2013). In Ecuador, the genus is represented by the species Araucaria angustifolia and Araucaria heterophylla (Salish.) Franco, both introduced from the southern portion of South America. The genus is characterized by dioecious trees with massive erect stems reaching up to 80 m height with branches regularly arranged in whorls. The juvenile leaves loosely imbricate, thin, needle-like and spirally arranged; the adult leaves usually scale-like or sometimes needle-like, spirally arranged, closely imbricate, flattened, sometimes lanceolate and sharp-pointed and persistent.

2.2. Study area and sampling

The study has been carried out in Quito, located in the north of Ecuador (Fig. 2) with an elevation of about 2850 m.a.s.l, which makes it one of the highest capital city in the world. This city has an area of 372.39 km² and a population density of 7347.1 inh/km². The population size is about 2700 million inhabitants (INEC, 2011). Despite its high elevation, Quito has a spring-like climate for most of the year, due to its location on the equator. The average annual temperature varies from 7 to 22 °C. Precipitation in dry period (June–August) does not exceed 70 mm/month, while in rainy period (September–May) the average precipitation is around 123 mm/month. The growth and development of the city, as well as, the explosive growth of the vehicle fleet, have generated a level of traffic congestion that is considered one of the main problems of the city (Herrera et al., 2016). In this sense, several areas of the city have a very intense traffic load, mainly in the north part (Vega and Parrá, 2014), some of them near to schools and hospitals. The number of vehicles registered in the city is around 465,000 and the number of daily car trips on public and private transport in 2014 was 2,800,000 and 1,050,000, respectively (Herrera et al., 2016).

Araucaria heterophylla needle samples were collected from areas in the central-north part of the city classified as high, moderate and low.
traffic intensity, based on Google Maps Traffic. In the typical traffic scale of Google Maps Traffic, less congested streets are represented by green color, and the color is changing in the traffic-light scale from orange to red and dark red, as traffic gets worse. In the present study, streets classified as low traffic intensity were considered those in green color in rush hour, while streets classified as moderate and high traffic intensity were considered those in orange and red color, respectively. See Fig. 1 for an example of the Google Maps Traffic for a typical Tuesday rush hour (18:10) for three representative study sites. A recent study performed in Quito validates the quality or application to the real traffic velocities. It confirmed that the velocity of traffic significantly decreases as the spectrum moves towards the red colors of traffic (Zalakevičiūtė et al., 2020). Thus, the selection of the study sites in the present work is supported by the choice of the areas with different street types and a dominated traffic color.

Both high (n = 7) and moderate (n = 7) traffic areas include the presence of urban transportation buses and private cars. However, the former could be classified as congested, with constant acceleration and breaking, while the second one could be classified as slow. The low traffic areas (n = 5) are those where vehicular traffic is scarce and is mainly due to circulation of private cars. Based on a previous study performed by our research group, in a central area of Quito (Zalakevičiūtė et al., 2019a; Zalakevičiūtė et al., 2019b), during rush hour in a small residential street (low traffic intensity) and in a main avenue (high traffic intensity), the number of heavy vehicles (e.g., bus, truck, mini bus) could range from 10 to 170 per hour, while the number of light vehicles could range from about 300 to 1300 per hour, respectively. These statistics are representative in the traffic classification of the present work.

Furthermore, some Araucaria heterophylla needles were collected in a background site (an area near the study site with a lesser impact of pollution) and considered as reference sample for comparison purpose. A total of 20 sampling sites were selected and their distribution is shown in Fig. 2, along with a colorimetric description of their vehicular traffic levels. A more detailed description of the sampling sites can be seen in Table S1.

At each sampling site, approximately 8 g of Araucaria heterophylla needles were collected simultaneously in May 2019 from trees located just in front of the road (around 5 m of distance between the tree and the road). The needles were collected from outer branches at 2 m height above ground. Needles with a similar position in the crown, and at different orientations in respect to the cardinal point (i.e., North, South, East and West), and with no unusual aspect (e.g. yellow color), were removed whole using plastic gloves to avoid any risk of sample contamination. Samples obtained from the different orientations were mixed to obtain one bulk sample. Sampling was only done if there had been no rain during the previous six days in order to avoid the rain wash effect. The collected samples were placed in a clean polyethylene bag, wrapped in aluminum foil, transported to the laboratory and conserved at 4 °C in the dark until analysis. Part of the sample was prepared for metal determination and another part was separated to determine water content.

2.3. Quantification of chemical elements

For the determination of metals, 0.5 g of fresh needles of Araucaria heterophylla were digested with 7 mL of HNO₃, 2 mL of H₂O₂ and 1 mL of H₂O at 200 °C during 45 min in a microwave digester (MARS 6 – CEM Corporation). Then, the samples were filtered and the volume was adjusted to 25 mL with Milli-Q water. The content of the metals Ca, K, Mg, Mn, Fe, Al, Ba, Zn, Cu, Cr, Pb and Co, in the digestion solutions, was analyzed by an Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Thermo Scientific iCAP 7000 Series). The calibration of the instrument was done by external standard solutions ranging from 0.001 mg/L to 100 mg/L.

2.4. Quality control of analyses

Digestion blank (i.e. digestion solution without plant material) was analyzed following the same procedure used for the needles in order to check for contamination. To ensure quality control, all samples, including blanks, were analyzed in triplicate. Relative Standard Deviation (RSD) values were below 20%. In addition, the accuracy of the measurements was confirmed by the observation of the linearity of the calibration curve and through the extraction efficiencies by applying the same extraction and quantification procedures as for the samples, to the certified reference material NIST SRM 1575a – Trace elements in Pine Needles. The recoveries obtained were in the range of 43.41%–111.01%, which are detailed in Table S2. In general, the recoveries were good, which indicates that the adopted digestion procedure was adequate to the samples of Araucaria needles. The lowest recovery values were registered for Pb (53.77%) and Co (43.41%). This could be due to the dilution volume which could be lower in order to adjust the analytical signal to acceptable levels. The concentrations of Pb and Co measured in this work were considered cautiously due to the low percentage of recovery. The limits of detection (LOD) were calculated as 3 times the standard deviation of 10 blanks measurements divided by the slope of the analytical curve. The limits of quantification (LOQ) were calculated similarly but multiplying the standard deviation by 10. The values of LOD and LOQ ranged from 2.58x10⁻⁷ μg g⁻¹ to 0.0088 μg g⁻¹ and from 8.59x10⁻⁷ μg g⁻¹ to 0.029 μg g⁻¹, respectively (see Table S2 for details).

2.5. Water content of the samples

In order to express the results in a dry weight basis (μg g⁻¹ DW), the water content of the needles, for each site, was determined by drying in triplicate 2 g of fresh material at 70 ± 2 °C until reaching a constant weight. In this way, the different water content of the needles in the sites is counterbalanced. The average water content obtained was 57.75 ± 5.42%, similar to the values obtained by Amigo et al. (2011) and Ratola et al. (2006), in pine needles.

2.6. Statistical analysis and Geographic information system

A Principal Component Analysis (PCA) was performed, in order to analyze the distribution and contribution of the chemical elements
3. Results and discussion

3.1. Metal concentrations in the samples

Table 1 shows the mean concentrations, and standard deviations, of the elements quantified in Araucaria heterophylla needles for different vehicular traffic intensity and for the reference site. Moreover, Fig. 3 shows the biplot based on the first two principal components, which explain around 80% of the variability, of the PCA analysis. Finally, and in order to complement the observations from Table 1 and Fig. 3, Table 2 shows the Pearson analysis.

Comparing the concentration of metals recorded in the urban areas with those of the reference site (Table 1), it is observed that concentrations are higher in the urban areas, except for Mg. The ratio between the mean concentration of the metals in the sample and in the reference site allows us to deduce the highest accumulation of metals. In this way, Cr (4.45) and Mn (4.32) show a higher accumulation. High accumulation for Cr was also observed in works carried out using pine needles in Iran (Kord et al., 2010) and Pseudovernoria furfuracea lichen in Italy (Guidotti et al., 2009).

On the other hand, Table 1 indicates that the metals found with the highest values of average concentrations, for any vehicular traffic intensity, are the geological elements Ca, K and Mg, which are also macronutrients of the plants (Maathuis, 2009). This is in line with the results of studies on metal deposition using different plant species, such as moss (Lazo et al., 2019) Tillandsia usneoides (Figueiredo et al., 2007), pine needles (Brown et al., 2017), Abies fabri (Sun et al., 2011), Rhododendron williamsianum (Sun et al., 2011) and lichens (Bergamaschi et al., 2007; Frati et al., 2005). Fig. 3 shows that there is no direct association of these metals with the vehicular traffic intensity, which means that they are associated with natural emissions rather than with road traffic emissions. This conclusion can be supported by Table 2 where no significant correlation between Ca, K and Mg, and metals typically related to road traffic (see below), was observed.

It is worth mentioning that, in a previous study on the chemical characterization of PM10 in the city of Quito (Zalakeviciute et al., 2019a; Zalakeviciute et al., 2019b), very high concentrations of metals related to natural sources, such as Ca and Mg were identified. This was attributed to several factors, such as the weather conditions that influence the resuspension of dust in the city, as well as the chemical composition of the soil and human activities like constructions.

In general, the concentration of Mn, Fe, Al, Ba, Zn, Cu, Cr, Pb and Co increases with the traffic intensity (Table 1). This is consistent with previous studies reported in literature (e.g. Rodriguez et al., 2010; Sevik et al., 2019; Turkyilmaz et al., 2018a). To the best of our knowledge, the variation of the concentration of Ba with traffic levels, using biomonitors, is poorly investigated. However, it is important to study this metal, because brake wear has been identified as a major source of
emission of Ba (Adachi and Tainosho, 2004; Iijima et al., 2007; Lough et al., 2005; Sternbeck et al., 2002; Thorpe and Harrison, 2008; Zechmeister et al., 2006).

The increase in the levels of Mn, Fe, Al, Ba, Zn, Cu, Cr, Pb and Co with the increase of traffic intensity could indicate that these metals are related to the vehicle emissions. Although Mn, Fe, and Al are typical geological elements, they are also components of steel and alloys widely used by the automotive industry (Fujiwara et al., 2011). In this way, Mn, Fe and Al can be attributed to the contribution of a natural input and to different automotive parts.

In fact, Fe, Al, Ba, Zn, Cu, Cr, Pb and Co show a positive association with the high vehicular traffic intensity (Fig. 3), with a strong confidence level indicated by the large magnitude of the eigenvectors, which confirms that they are traffic-related metals. Moreover, Table 2 shows a significant correlation between these metals, which suggests the same source of emission. Although the association of Mn with the high vehicular traffic intensity is not so strong (Fig. 3), the Pearson analysis (Table 2) shows a significant correlation ($p < 0.01$) between Mn and traffic-related metals, such as Fe, Al, Ba, Zn, Cu and Co, which indicate that Mn could be associated with traffic emissions, as well. In the work carried out by Charron et al. (2018), on the identification and quantification of particulate tracers of exhaust and non-exhaust vehicle emissions, Mn was strongly correlated with traffic markers. Moreover, in the work performed in Florencia using Quercus ilex leaves (Monaci et al., 2000), Mn was identified as a main metal pollutant emitted by vehicles. In fact, Mn has been found in brake material and brake dust (Lawrence et al., 2013), as well as in tire wear debris (Thorpe and Harrison, 2008).

In this way, the pollution level of traffic-related metals in high, moderate and low traffic intensity is as follow:

- Mn > Fe > Al > Ba > Zn > Cu > Cr > Pb > Co;
- Mn > Al > Fe > Mn > Ba > Zn > Cu > Cr > Pb > Co;
- Mn > Al > Fe > Ba > Zn > Cu > Cr > Co > Pb (Table 1), respectively.

However, among traffic-related metals, and not associated as typical geological elements (i.e., Ba, Zn, Cu, Cr, Pb and Co), Ba was found to be the most abundant followed by Zn and Cu, which is consistent with works carried out in tunnels (Lawrence et al., 2013; Pant et al., 2017) and using biomonitor, such as moss (Lazo et al., 2019), Cinnamomum zeylanicum (De la Cruz et al., 2019), Struthanthus flexicaulis (De Paula et al., 2015), pine needles (Brown et al., 2017) and Rhododendron williamsianum (Sun et al., 2011).

It is reported that the main non-exhaust vehicle source of Ba is brake dust emissions (Adachi and Tainosho, 2004; Iijima et al., 2007; Lough et al., 2005; Sternbeck et al., 2002; Thorpe and Harrison, 2008), due to the addition of BaSO$_4$ to increase the density of the brake pad (Švabenská et al., 2015; Kubilé et al., 2017; ORNL, 2001). The mean

### Table 1

Mean concentration (± standard deviation) of the metals quantified in the *Araucaria heterophylla* needles in areas with different vehicular traffic intensity in the city of Quito. Unit: µg g$^{-1}$ DW.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Vehicular traffic intensity</th>
<th>Reference site</th>
<th>[Sample]/[Reference site] ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High (n = 7)</td>
<td>Moderate (n = 7)</td>
<td>Low (n = 5)</td>
</tr>
<tr>
<td>Ca</td>
<td>24966.76 ± 8750.82</td>
<td>24742.86 ± 9041.22</td>
<td>24925.19 ± 10691.80</td>
</tr>
<tr>
<td>K</td>
<td>6028.36 ± 1394.47</td>
<td>11417.20 ± 4388.53</td>
<td>8484.26 ± 3274.02</td>
</tr>
<tr>
<td>Mg</td>
<td>3283.60 ± 1187.16</td>
<td>3290.95 ± 456.69</td>
<td>3373.83 ± 1292.70</td>
</tr>
<tr>
<td>Mn</td>
<td>1250.95 ± 1012.31</td>
<td>224.49 ± 89.36</td>
<td>692.71 ± 670.33</td>
</tr>
<tr>
<td>Fe</td>
<td>1084.92 ± 907.32</td>
<td>646.25 ± 314.55</td>
<td>424.50 ± 168.26</td>
</tr>
<tr>
<td>Al</td>
<td>936.01 ± 585.67</td>
<td>732.34 ± 313.43</td>
<td>350.92 ± 217.35</td>
</tr>
<tr>
<td>Ba</td>
<td>203.81 ± 155.72</td>
<td>112.00 ± 72.82</td>
<td>111.56 ± 45.23</td>
</tr>
<tr>
<td>Zn</td>
<td>60.43 ± 38.27</td>
<td>42.58 ± 18.49</td>
<td>28.52 ± 12.50</td>
</tr>
<tr>
<td>Cu</td>
<td>19.12 ± 15.98</td>
<td>8.86 ± 6.31</td>
<td>4.38 ± 2.30</td>
</tr>
<tr>
<td>Cr</td>
<td>7.16 ± 4.96</td>
<td>3.75 ± 1.95</td>
<td>1.90 ± 1.36</td>
</tr>
<tr>
<td>Pb</td>
<td>3.22 ± 2.00</td>
<td>1.32 ± 0.85</td>
<td>0.18 ± 0.15</td>
</tr>
<tr>
<td>Co</td>
<td>0.74 ± 0.43</td>
<td>0.54 ± 0.14</td>
<td>0.48 ± 0.06</td>
</tr>
</tbody>
</table>

**Fig. 3.** Principal Component Analysis (PCA) for metal concentrations found in *Araucaria heterophylla* needles, considering traffic intensity (high, moderate and low) as supplementary variables to interpret the results.
concentration of Ba found in this work (111.56–203.81 µg g⁻¹ DW) is higher than the levels found in other research works using, for example, fir leaves (8.721 µg g⁻¹ DW) (Sun et al., 2011), Rhododendron leaves (77.92 µg g⁻¹ DW) (Sun et al., 2011) and moss (18.20 µg g⁻¹ DW) (Lazo et al., 2019).

On the other hand, the high contribution of traffic to the increased levels of Zn, has been reported in previous biomonitoring studies using for example, Tillandsia capillaris (Lazo et al., 2019), Tillandsia usneoides (Figueiredo et al., 2007), Graminaceae (Viard et al., 2004), Cupressus sempervirens, Ligustrum ovalifolium and Euonymus japonicus (Mansour, 2014). The main non-exhaust vehicle source for Zn has been reported to be tire wear (Fujiwara et al., 2011; Hjortenkrans et al., 2006; Hjortenkrans, 2008; Lawrence et al., 2013; Suzuki et al., 2009; Thorpe and Harrison, 2008), due to the addition of mainly ZnO to activate vulcanization process and increase durability and high heat conductivity to the tire (Adachi and Tainosho, 2004; Hjortenkrans et al., 2006; Hjortenkrans, 2008; ORNL, 2001). The average concentrations found in the present work (from 4.38 µg g⁻¹ to 19.12 µg g⁻¹ DW) are higher than those reported in other investigations using Tillandsia capillaris (2.39 µg g⁻¹–14.69 µg g⁻¹ DW) (Abril et al., 2014a; Abril et al., 2014b; Pignata et al., 2002; Wannaz et al., 2006), lichens (3.60 µg g⁻¹–9.27 µg g⁻¹ DW) (Minganti et al., 2003), Cupressus sempervirens (3.56 µg g⁻¹ DW), Ligustrum ovalifolium (7.09 µg g⁻¹ DW) and Euonymus japonicus leaves (4.72 µg g⁻¹ DW) (Mansour, 2014).

On the other hand, in general, the metal found with the lowest concentration was Co (0.48–0.74 µg g⁻¹ DW), which is in line with other investigations using plant species to detect metals in areas with different vehicular traffic intensity (Rodriguez et al., 2010). A possibly source of this metal from traffic is the resuspended road dust (Huang et al., 2019; López et al., 2011; Zechmeister et al., 2006).

It is worth mentioning the presence of lead in the needle samples (Table 1). Leaded petrol has been banned in Ecuador since 2000. However, due to the long-residence time of Pb in urban soils, the contamination of this heavy metal can still be identified, mainly in high traffic areas (Monaci et al., 2000) due to the resuspension of road dust (Lough et al., 2005). Moreover, brake wear has been considered as one of the main sources of this metal in the urban environment (Fujiwara et al., 2011). In the present work, Pb was detected in the concentration range of 0.18–3.22 µg g⁻¹ DW, and it is 2.44 and 17.89 times higher in areas of high vehicular traffic intensity than in areas of moderate and low vehicular traffic intensity, respectively. The relationship between traffic intensity and the level of Pb has been reported previously in the literature (Chung and Li, 2001; Viard et al., 2004). The Pb level found in this work is higher than that found in studies using T. capillaris (0.52 µg g⁻¹ DW 1.02) (Wannaz et al., 2006), T. permutata (0.53 µg g⁻¹ DW) (Wannaz et al., 2006) and Cinnamomum zeylanicum (0.29 µg g⁻¹ DW) (De la Cruz et al., 2019).

Significant correlations (p < 0.05) between traffic intensity, and the respective concentrations of Cu, Pb and Zn, are observed (Table 2). As Cu is thought to derive from brake linings, and Pb and Zn from tire (e.g. Sternbeck et al., 2002), the decelerating activities are probably the main source for vehicle non-exhaust emissions in the city of Quito. In fact, the city of Quito has an elongated shape, stretching from North to South, and a complex terrain, which makes mobility difficult and increase the use of brake. This, together with the fact that there is traffic lights and roundabouts very close to each other, the decelerating activities are promoted, which contributes to the deterioration of air quality.

### Table 2

Pearson correlation for the metals measured in the city of Quito using Araucaria heterophylla needles.

<table>
<thead>
<tr>
<th>Traffic intensity</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Zn</th>
<th>Ba</th>
<th>Pb</th>
<th>Fe</th>
<th>Al</th>
<th>Mn</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
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</thead>
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<td>Traffic intensity</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Traffic intensity</td>
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<td>0.34</td>
<td>0.52</td>
<td>0.52</td>
<td>0.46</td>
<td>0.36</td>
<td>0.74</td>
<td>0.44</td>
<td>0.38</td>
<td>0.33</td>
<td>0</td>
<td>−0.31</td>
</tr>
<tr>
<td>Co</td>
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<td>0.82*</td>
<td>0.89*</td>
<td>0.92*</td>
<td>0.76*</td>
<td>0.87*</td>
<td>0.89*</td>
<td>0.90*</td>
<td>0.77*</td>
<td>0.41</td>
<td>−0.24</td>
<td>0.22</td>
</tr>
<tr>
<td>Cr</td>
<td>1</td>
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<td>0.95*</td>
<td>0.92*</td>
<td>0.88*</td>
<td>0.98*</td>
<td>0.79*</td>
<td>0.53</td>
<td>0.29</td>
<td>−0.31</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
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<td>0.87*</td>
<td>0.96*</td>
<td>0.95*</td>
<td>0.88*</td>
<td>0.73*</td>
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<td>0.37</td>
<td>0.19</td>
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<tr>
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<td>0.9*</td>
<td>0.95*</td>
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<td>0.66*</td>
<td>0.33</td>
<td>0.38</td>
<td>0.35</td>
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<tr>
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<td>0.77*</td>
<td>0.67*</td>
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<td>0.43</td>
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<td>0.73*</td>
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<td>−0.31</td>
<td>0.30</td>
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<tr>
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<td>0.65*</td>
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<td>0.36</td>
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<tr>
<td>Al</td>
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<td>−0.21</td>
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<tr>
<td>Ca</td>
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<td>0.32</td>
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<tr>
<td>K</td>
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</table>

* p < 0.01 by Pearson’s rank correlation.

** p < 0.05 by Pearson’s rank correlation.
concentrations are mainly observed in the southern area. In fact, Fig. 6 shows that the main concentration of metals linked with traffic emissions is higher at sites H4 and H5. This is especially alarming at site H5, where the Baca Ortiz pediatric hospital is located. This is a dense vehicular traffic area, with a high flux of diesel-powered buses that emit great amounts of particulate matter, easily identifiable from black exhaust clouds. Anthropogenic metals are associated with such particles emitted by buses (Colman et al., 2018; López et al., 2011; Thomas and Morawska, 2002), which means that sick children are in a constant exposure to pollutants harmful to their health. Moreover, it is well reported that children are known to be more vulnerable to the adverse health effects of air pollution due to their higher minute ventilation and immature immune system (Buká et al., 2006).

It is worth mentioning that Fig. 6 highlights that the average concentration of traffic-related metals is sometimes higher in areas with moderate or even low traffic intensity than in areas with high traffic. This could be attributed to the fact that the intensity of traffic is not the only controlling parameter of the traffic-related metal concentrations. Location of the measurement point can also play an important role. For instance, the highest values for the average concentration of traffic-related metals, in the low traffic intensity category, are identified to be in L1 and L2 (see Fig. 6). This is because these points are close to the high traffic intensity areas H1, H2, H3 and H7 (Fig. 5). On the other hand, the lowest values for the average concentration of traffic-related metals in the low traffic intensity category are observed in L4 and L5 (see Fig. 6), and this could be due to their approximation to the Metropolitan Park, one of the main parks in the city (Figs. 5 and S1). It is reported in literature that the urban parks play an important role in the reduction of the concentration of particulate pollution (Hernandez et al., 2019; Cohen et al., 2014). This proximity to the park also affects M5, M6 and even H6 that, although they are areas with moderate and high traffic intensity, the concentration of the traffic-related metals is low (Figs. 5, 6 and S1). Finally, M2 shows the highest average concentration of traffic-related metals in the medium traffic intensity category (Fig. 5), which may be due to its proximity to points H4 and H5 (Fig. 5). These points are located in an area with a high flux of diesel-powered buses, emitting great amounts of particulate matter, and with the closely packed tall buildings, restricting the natural ventilation of pollutants. As a result, pollutants are trapped in the lower region, consequently, increasing their concentrations (Ahmand et al., 2005; Yuan et al., 2014).

These observations may indicate that even streets with high or moderate traffic intensity can experience reduced concentrations of pollutants if located near a green area such as urban park, as well as building configurations can influence the concentration of pollutants. These findings also suggest that using plants as biomonitor, a greatly improved spatial understanding of pollution levels in an urban area can be achieved. In spite of a low temporal resolution, this approach reports significantly denser street-level information compared to an air quality network, which might only have one monitoring station for a whole study area (Zalakeviciute et al., 2020). Therefore, the biomonitoring using plants may help identify areas in the city with high levels of risk of toxic metals.

4. Conclusions

In this work, the use of Araucaria heterophylla needles as biomonitor was analyzed for the first time. Specifically, the association of different metals (Ca, K, Mg, Mn, Fe, Al, Ba, Zn, Cu, Cr, Pb and Co) with the vehicular traffic intensity was studied. The concentration of Mn, Fe, Al, Ba, Zn, Cu, Cr, Pb and Co increases with the traffic intensity, while there is no relationship between the level of Ca, K and Mg and the vehicular traffic intensity. Principal Component (PCA) and Pearson analyses suggest that Ca, K and Mg are related to natural emissions; Mn, Fe and Al are related to both natural and road traffic emissions; and Ba, Zn, Cu, Cr, Pb and Co are only related to road traffic emissions. Among traffic-related metals, and not associated as typical geological elements (i.e., Ba, Zn, Cu, Cr, Pb and Co), Ba was found to be the most abundant followed by Zn and Cu, for any traffic intensity.

The spatial distribution patterns of the metals show that Ca and Mg present higher values in the northern and central areas, while the distribution pattern of K show higher values mainly in the northern part of the study area. This because the further north of the city, the drier it is, which contributes to increase the soil particle resuspension, and due to the burning of biomass in the northern part. Hot-spots of elevated concentrations of traffic-related metals are mainly observed in the southern area where there is a pediatric hospital. This allows us to warn about the potential risk for children. Since this is an area with a high
Fig. 5. Distribution patterns of the concentrations (µg g$^{-1}$ DW) of the traffic-related metals (Mn, Fe, Al, Ba, Zn, Cu, Cr, Pb and Co) in Araucaria heterophylla needles in the study area. H – High (black markers), M – Moderate (grey markers), L – Low (white markers) vehicular traffic intensity.
Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecolind.2020.106701.

References


