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Spatial-temporal variability of metal pollution across an industrial district, evidencing the environmental inequality in São Paulo☆

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A B S T R A C T

Although air pollution decreased in some cities that shifted from an industrial to a service-based economy, and vehicular emission regulation became more restrictive, it is still a major risk factor for mortality worldwide. In central São Paulo, Brazil, air quality monitoring stations and tree-ring analyses revealed a decreasing trend in the concentrations of particulate matter and metals. Such trends, however, may not be observed in industrial districts located in the urban periphery, where the usual mobile sources may be combined with local stationary sources. To evaluate environmental pollution in an industrial district in southeastern São Paulo, we assessed its spatial variability, by measuring magnetic properties and concentrations of Al, Ba, Ca, Cl, Cu, Fe, K, Mg, Mn, P, S, Sr, Zn in the bark of 62 trees, and its temporal trends, by measuring Cd, Cu, Ni, Pb, V, Zn in tree rings of three trees. Source apportionment analysis based on tree barks revealed two clusters with high concentrations of metals, one related to vehicular and industrial emissions (Al, Ba, Cu, Fe, Zn) in the east side of the industrial cluster, and the other related to soil resuspension (Cu, Zn, Mn) in its west side. These patterns are also supported by the magnetic properties of bark associated with iron oxides and titanium-iron alloy concentrations. Dendrochemical analyses revealed that only the concentrations of Pb consistently decreased over the last four decades. The concentrations of Cd, Cu, Ni, V, and Zn did not significantly decrease over time, in contrast with their negative trends previously reported in central São Paulo. This combined biomonitoring approach revealed spatial clusters of metal concentration in the vicinity of this industrial cluster and showed that the local population has not benefited from the decreasing polluting metal concentrations in the last decades.

1. Introduction

According to the World Health Organization (Health Effects Institute, 2019), 90% of the world's population breathes polluted air that exceeds the established limits, which makes air pollution the fifth major risk factor of mortality worldwide (Health Effects

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Institute, 2019). In many cities, the source of air pollution is changing as the urban economy is rapidly shifting from an industrial-based to a service-based economy (Kellerman, 2005; Hermelin, 2007). Regulation of vehicular emissions also became gradually more restrictive over the years, significantly affecting pollution in most urban locations (Sawyer, 2010).

The Metropolitan Area of São Paulo, Brazil, is the fifth largest urban conglomerate in the world with more than 22 million inhabitants (UN, 2018). It is an example of a metropolitan area that faced important transformations in the last decades with a clear de-industrialization and an increasing regulation of vehicular emissions supported by technological advances (Monteiro and Lima, 2017; Salvo et al., 2017). These changes resulted in a reduction of the exposure to some pollutants in the cities over the years (e.g. Zheng et al., 2018; Locosselli et al., 2018). Nevertheless, vehicular emission is still one of the most important sources of air pollution in São Paulo (Moreira et al., 2016) as in many other cities of the World (Maykut et al., 2003; Querol et al., 2007; Sawyer, 2010; Andrade et al., 2012, Cheng et al., 2016). This predominance of vehicular emissions can change in large industrial districts in the urban periphery, where more vulnerable populations may be exposed to additional sources of air pollution (Querol et al., 2007; Anguelovski, 2013).

Such low-income areas (Anguelovski, 2013) may also lack a comprehensive set of air quality monitoring stations, if any, required to support appropriate public-health policies. In many cases, however, these regions have a sufficient number of trees (Silva et al., 2019) that may be used for biomonitoring purposes. The chemical composition of tree bark and its magnetic properties have been used to assess the spatial variability of certain pollutants such as trace metals and persistent organic pollutants, to name but a few (Guéguen et al., 2012; Moreira et al., 2016; Chrabaszcz and Mróz, 2017; Hofman et al., 2017; Brignole et al., 2018). Some tree species may also produce visible tree rings that can be used to evaluate long-term trends in environmental pollution (e.g., Mihaljevic et al., 2008; Dinis et al., 2016, Turkyilma et al., 2018). Despite the reported limitations of dendrochemical records, mainly due to the radial transport of trace-elements in the wood (Lepp, 1975; Smith and Shortle, 1996; Scharnweber et al., 2016), some studies showed their potential to evaluate historical trends of urban pollution (e.g. Ragsdale and Berish, 1988, Tommasini et al., 2000; Beramendi-Orosco et al., 2013; Geraldo et al., 2014; Locosselli et al., 2018). Studies involving the combination of tree barks and tree rings are rare in the biomonitoring literature. This approach represents a unique opportunity to assess spatial-temporal variation in the exposure to environmental pollution, especially where only a small number of air quality stations is available (Odabasi et al., 2015).

To assess the environmental pollution variability around a large industrial cluster in the periphery of the Metropolitan Area of São Paulo, we evaluated patterns of spatial variability of metal concentrations in the bark of trees as well as of temporal trends of metals in tree rings. We considered the following hypotheses: I) there are clusters of metal concentrations in the bark of the trees located in the vicinity of the industrial cluster, II) the observed decreasing trend of metal concentration from mobile sources in the central Metropolitan Area of São Paulo is not observed in the rings of trees sampled in the vicinity of this local stationary source (Fig. 1).

2. Material and methods

2.1. Sampling site and tree species

Sampling was conducted in the industrial district of Capuava in the southeastern border of the Metropolitan Area of São Paulo, Brazil (Fig. 1, 23° 38′S and 46° 28′W, 700 m a.s.l.). This district is characterized by a large industrial conglomerate that comprises fertilizer, cement and petrochemical plants. This industrial cluster started its activities in the mid 1950's (Deimling and Triches, 2015), leading to the rapid growth of the population density around the complex. The petrochemical complex reached relatively high levels of production, processing about 54,000 barrels of oil per day (Deimling and Triches, 2015).

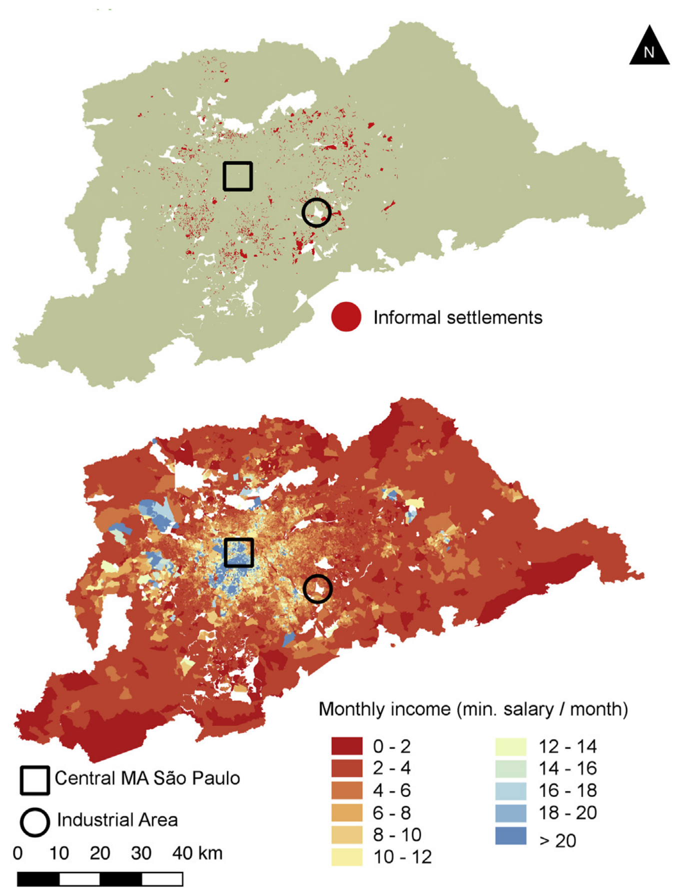

Fig. 1. Maps of the Metropolitan Area of São Paulo with the distribution of informal settlements and of monthly income (Data: CEM, 2019), with the sampling site from Locosselli et al. (2018) and Moreira et al. (2016, 2018) represented by a square, and the industrial area of the present study represented by a circle.

We sampled trees of the species *Tipuana tipu* (Benth.) Kuntze and *Poicianella pluviosa* (DC.) L.P. Queiroz (Leguminosae) (Fig. 2) in the vicinity of the industrial cluster. The bark of these tree species is known to produce reliable information on the spatial variability of airborne metal concentrations (Moreira et al., 2018). *Tipuana tipu* is also known to produce clear semi-ring porous tree rings delimited by a marginal parenchyma band (Locosselli et al., 2019), with a great dendrochemical potential for pollution evaluation (Hagemeyer, 2000; Locosselli et al., 2018).

2.2. Sampling design

We sampled 62 trees (41 trees of *T. tipu* and 21 of *P. pluviosa*), in the dry season of 2016. The sampling design was based on the previously modeled distribution of PM_{10} emitted by the industrial cluster (Fig. 2), via AERMOD implementation that includes the wind direction as an input variable (more details can be obtained from Locosselli et al., 2019). We sampled two species in this study

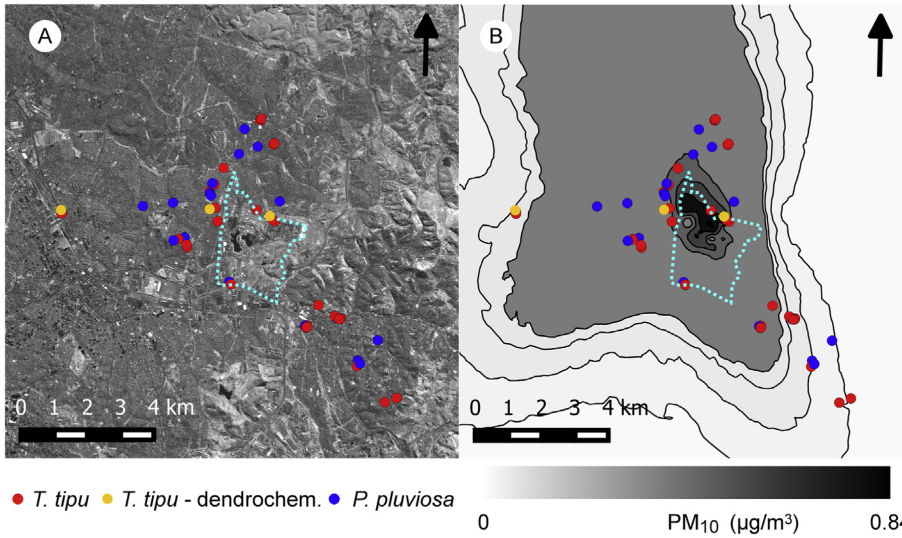

Fig. 2. Spatial distribution of the sampled trees of *Tipuana tipu* (red and orange) and *Poincianella pluviosa* (blue) around an industrial district in the Metropolitan Area of São Paulo, Brazil. The industrial cluster, including a petrochemical complex, is represented by the dashed line. All trees were used for the analysis of the chemical composition of the bark. Trees of *T. tipu* used for dendrochemical analysis are highlighted in orange. A) Satellite image (CBERS 4) of the sampling site. B) Modeled distribution of PM_{10} from the industrial cluster emission (modified from Locosselli et al., 2019). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

because of the heterogeneous distribution of their individuals in the region. The combination of both species is not to be considered an issue given that both are equally reliable for biomonitoring purposes (Moreira et al., 2018). Furthermore, the sampled trees are evenly distributed across the sampling design (Fig. S1). We carefully chose trees with no external sign of injury or decay and recorded their diameter at breast height, tree height and geographical position.

Using titanium knives, we collected four 8 cm × 8 cm samples of the bark of each specimen, at 1.3 m from topsoil, following the cardinal directions to avoid bias related to wind direction and the presence of obstacles around the trees. Samples were carefully brushed using a white toothbrush to remove insects, packed in paper envelopes and stored in desiccators. In addition, we sampled two to three cores of three *T. tipu* tree at breast height using 5 mm increment borers. All samples were fixed in wood supports in the field for protection. We polished the sample surface using aluminum oxide sandpapers to avoid contamination (Locosselli et al., 2018). All tree rings were dated using standard dendrochronological methods (see Locosselli et al., 2019 for further details). Three trees were chosen in an east-west transect along a gradient of exposure to the modeled PM_{10} plume. We sampled a tree at 5600m from the industrial cluster, and another two adjacent to the cluster, one in the east side and the other one in the west side (Fig. 2).

2.3. Chemical composition of the bark

We grated the outermost 3 mm of the bark, where the concentration of elements of interest is usually higher (Chiarantini et al., 2016), using a titanium tool (Wolterbeek and Bode, 1995). Samples were ground to powder using a micro-mill with agate mortar (Fritsch Pulverisette 0, Fritsch GmbH, Idar-Oberstein, DE). The ground barks were then used to produce double layer pellets composed of 0.5 g of bark powder and 1 g of boric acid, in a press under 3.9 ton/cm^2.

We analyzed the chemical composition of the barks using an X-ray fluorescence spectrometer – XRF (EDX 700 - HS, Shimadzu Corp., Kyoto, Japan). The bark composition is proportional to the emitted fluorescence X-rays wavelength and energy (van Grieken and Markowicz, 2002), so this approach allows the simultaneous evaluation of the concentration of Al, Ba, Ca, Cl, Cu, Fe, K, Mg, Mn, P, S, Sr, and Zn. These elements comprise a mixture of vehicular and industrial emissions (Moreira et al., 2016; Austruy et al., 2019; Miller et al., 2019). We used the following parameters: time (240 s), target (Rh, 5–50 kV _ 1–1000 A) and Si (Li) detector in a vacuum atmosphere, and Peach Leaves #1547 as a certified reference material (Table S1, National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA).

In addition to the EDXRF measurements, we also considered magnetic parameters commonly employed in magnetic environment studies as a proxy for air pollution (Hofman et al., 2017). The following parameters were considered: initial magnetic susceptibility (Sus) and Anhysteretic Remanent Magnetization (ARM). The Sus measures the easiness to induce an internal magnetic field in the sample using an external field. The ARM measures the magnetization of the sample after a demagnetization by an alternate field superposed by a constant low “bias” field. We analyzed Sus with MKF1–FA Multifunction Kappabridge (Agico) susceptibilimeter with an alternate magnetic field of 200 A/m with 976 Hz, and we analyzed ARM with SQUID (super quantum interference design) magnetometer model RAPID (2G-Enterprises) with a 100 mT alternate magnetic field and a bias field of 0.01 mT. These parameters are associated with different behavior in the soil material and in the anthropogenic emissions.

2.4. Chemical composition of the tree rings

We evaluated the content of Cd, Cu, Ni, Pb, V, Zn and C in the tree rings of *T. tipu* using a high-resolution laser ablation system (New Wave UP-213, with a Nd:YAG 213 nm laser source) coupled to a quadrupole-based ICP-MS (PerkinElmer ELAN DRC-e) in a class 10,000 clean room. Operational conditions of the ICP-MS were optimized daily, using a solution of Mg, In, Be, Ce and U, for checking the production of mono charged ion and the production of oxide and doubly charged species Pessôa et al., 2017. Analyses were only conducted after background signal stabilization. Argon was used as the carrier gas and the chamber was purged for 10 s for cleanup after each analysis. Ablation conditions were the same as in

Locosselli et al. (2018) for comparison purposes and are described in Table S2.

We used the line scan mode to produce a continuous signal of the ablated transect. We chose Cd, Cu, Ni, Pb, Zn because they are related to vehicular emissions (Moreira et al., 2016). The analyses of these elements also allow the comparison of temporal trends from this industrial district with the trends observed in the central region of the Metropolitan Area of São Paulo (Locosselli et al., 2019). In addition, we analyzed V that is specifically related to oil processing in petrochemical plants (Querol et al., 2007). The differences in the analyzed elements by XRF and LA-ICP-MS only mirror the intrinsic detection characteristics of each method. We used the ^{13}C as internal standard for all ions (Chacón-Madrid and Arruda, 2018) to account for variations in the ablation and to normalize the mass spectrometry signals, using the argon signal as a blank. The results are presented as the intensity ratio between the concentration of the analyzed element and the internal standard (^{13}C).

Since the size of the ablation cell is limited, we produced 2 mm height sections of each sample that were subsequently segmented in about 40 mm long segments, always at tree-ring limits. We performed the analyses in transects along the sample segments using a 110 μm laser beam. We obtained between 2300 and 4700 measurements from each radii, representing an average 106 measurements per tree ring.

2.5. Statistical analyses

In order to identify the generating sources of the chemical elements measured in the tree barks, a factor analysis was performed via Principal Components with Varimax rotation based on a robust correlation matrix composed by Spearman's correlation coefficients between element concentrations (Johnson and Wichern, 2007). The spatial distribution of the values of each factor score and the barks magnetic variables were evaluated independently by building interpolated maps in QGIS using the Inverse Distance Weighting (IDW) method QGIS Development Team, 2019. The interpretation of the interpolated maps is robust considering the small area of the study site with respect to that of other studies (e.g. Guéguen et al., 2012), especially if the interpretation of the maps is focused on the vicinity of the sampled trees.

For the dendrochemical analysis, we used the same methods as in Locosselli et al. (2018) to allow a proper comparison between the trends found in the central region of the Metropolitan Area of São Paulo and in this industrial district. Given the high spatial resolution of the laser ablation system, we were able to obtain the chemical composition of different cell-types in the wood along the sampling transect in the tree rings. We evaluated the third quartile of the distribution of the intensity ratio values of each trace element within each tree ring. This quartile corresponds to higher values of the intensity ratio associated with the presence of vessels (Locosselli et al., 2018). The measured intensity ratio in the vessels, in turn, is a better record of the trends of the trace elements found in the environment (refer to Locosselli et al., 2018 for further details).

The median intensity ratio was not used because it may represent a mixture of values from some vessels, fibers and parenchyma cells. The latter is recognized as the main path for radial transport of trace elements and other substances in the wood (Lepp, 1975; Lukaszewski et al., 1993), and is likely the main source of noise in dendrochemical records. We also removed intensity ratio outliers of some tree rings. Trends in the three sampled trees were then evaluated together for each measured element using linear mixed-effects models to account for individual variation and possible dependence of the tree rings measurements. The only element for which we evaluated the individual trends was Vanadium because it is known to be associated with oil refining. The conditional independence of the within tree measurements in the linear fits were checked by plotting the residuals and using Durbin-Watson's test. All analyses were performed in R (R Core Team, 2018) using the packages "nlme" (Pinheiro et al., 2020) and "lmtest" (Zeileis and Horthon, 2002).

3. Results

The concentration of Al, Ba, Ca, Cl, Cu, Fe, K, Mg, Mn, P, S, Sr, Zn presented substantial variation in the bark of the sampled trees (Table 1). We combined the variability of these elements using a factor analysis. We chose to analyze from factor one to factor five according to the percentage of explained variability of the concentration of the elements in the sampled barks (Table 2, Fig. S2). Together, these five factors account for 86.70% of the data variability, ranging from 30.20% explained by factor one to 10.50% explained by factor 5 (Table 2). The loadings of each element measured in the bark of the sampled trees are shown in Table 2. Most of these elements contribute to a single factor, while only Cu and Zn contribute to two factors, namely, factors 1 and 3.

The values of each factor and of the magnetic variables were then used to build interpolated maps of their distribution in the bark of the sampled trees. By evaluating only the grids under the influence of the sampled trees, it is possible to observe that factor 1 presents higher values in trees located mainly in the east side of the industrial cluster, but also in its south and south east sides (Fig. 3). Factor 2 presents lower values towards the east and west side of the industrial cluster. Factor 3 presents lower values towards east and west sides of the industrial cluster, with hotspots that are located towards the east and south of it. Factor 4 presents higher values in the east and west sides of the industrial cluster, while factor 5 presents higher values in the east side, and lower values in the west side of the industrial cluster. Considering only the magnetic properties of the tree barks, ARM is high towards the southeast side of the industrial cluster, while Sus is high towards the west side of it. Because the sampled trees of both species, are evenly distributed in the region (Fig. S1), these trends are not species dependent.

In addition to the spatial variability of the concentrations of the chemical elements measured in the tree barks, the dendrochemical analyses revealed temporal trends in the trace elements measured in the tree rings (Table 3). The composition of Pb in the tree rings of all sampled trees analyzed together showed a consistent decreasing trend over the last decades in the sampling site, while no temporal

Table 1
Descriptive statistics of the concentrations of chemical elements in the bark (mg/kg), and their magnetic properties including Sus ($g^{\wedge -1}$) and ARM (emu), of the sampled trees of *Tipuana tipu* and *Poincianella pluviosa* in an industrial district in the Metropolitan Area of São Paulo.

Variable	Mean	Std	Max	Min
Al	760.11	1192.30	6767.15	67.06
Ba	444.80	563.74	2606.40	12.70
Ca	33683.00	8303.15	51408.00	13998.00
Cl	251.71	434.66	3461.55	65.83
Cu	7.07	7.00	55.57	3.91
Fe	1204.00	1396.32	7009.17	96.69
K	1288.70	848.42	4910.00	487.50
Mg	1434.80	930.32	4282.50	252.50
Mn	109.03	164.67	1265.27	15.80
P	841.20	251.57	2380.00	417.50
S	2435.00	695.03	4245.00	1270.00
Sr	125.51	42.06	300.77	45.20
Zn	167.93	229.87	1739.56	16.66
Sus	$2.23\ 10^{-5}$	$3.70\ 10^{-5}$	$2.22\ 10^{-4}$	$-8.75\ 10^{-7}$
ARM	$1.95\ 10^{-5}$	$4.13\ 10^{-5}$	$2.94\ 10^{-4}$	$-1.53\ 10^{-7}$

Table 2
Loading values of the factor analysis using both the chemical composition and the magnetic properties of the samples of tree barks. Loading values higher than 0.5 are highlighted in bold. Variance and percentage of explained variance (%) are also provided for each Factor.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
Al	**0.93**	0.21	−0.11	0.10	−0.20	0.97
Ba	**0.92**	0.16	−0.21	0.14	−0.14	0.95
Fe	**0.93**	0.20	−0.16	0.07	−0.20	0.97
Cu	**0.55**	0.19	**−0.59**	0.27	0.05	0.76
Zn	**0.70**	0.21	**−0.53**	0.20	0.14	0.89
Cl	0.19	**0.86**	−0.04	0.10	−0.02	0.79
Mg	0.11	**0.85**	−0.29	0.04	−0.19	0.86
S	0.20	**0.90**	−0.03	0.05	0.10	0.87
Mn	0.20	0.10	**−0.89**	−0.10	−0.24	0.90
Ca	−0.40	−0.43	0.10	**−0.57**	0.47	0.90
P	−0.27	−0.14	0.04	**−0.80**	−0.15	0.76
Sr	0.40	0.28	−0.42	**−0.53**	0.32	0.80
K	0.22	0.03	−0.12	−0.05	**−0.89**	0.87
Variance	3.93	2.76	1.79	1.42	1.36	11.27
%	30.20	21.20	13.80	10.90	10.50	86.70

Table 3
Estimated coefficients, standard errors and p-values of the mixed-effects linear models with both specimen and year as random effects.

Variable		Coefficient	Std	p-value
Cd	Intercept	$4.68\ 10^{-3}$	$5.61\ 10^{-3}$	0.41
	Year	$-1.66\ 10^{-6}$	$2.80\ 10^{-6}$	0.55
Cu	Intercept	$-9.62\ 10^{-2}$	$3.17\ 10^{-1}$	0.76
	Year	$7.70\ 10^{-5}$	$1.59\ 10^{-4}$	0.63
Ni	Intercept	$-6.24\ 10^{-2}$	$7.07\ 10^{-2}$	0.38
	Year	$3.49\ 10^{-5}$	$3.53\ 10^{-5}$	0.33
Pb	Intercept	5.52	$7.03\ 10^{-1}$	<0.0001
	Year	$-2.71\ 10^{-3}$	$3.51\ 10^{-4}$	<0.0001
V	Intercept	$1.09\ 10^{-2}$	$1.09\ 10^{-2}$	0.32
	Year	$-3.93\ 10^{-6}$	$5.50\ 10^{-6}$	0.48
Zn	Intercept	$-8.25\ 10^{-1}$	1.15	0.48
	Year	$4.72\ 10^{-4}$	$5.76\ 10^{-4}$	0.41

trends were observed for Cu, Ni, Zn and V. The individual analysis for V (Fig. 4) showed a significant positive trend throughout the decades in the tree that is located in the west side of the oil refinery where most of the chimneys are concentrated. These trends were not observed in the tree located in the east side of the oil refinery or in the tree located at a distance of 5600 m from it. Overall, the residuals of the individual linear fits for the concentrations of V and the results of Durbin-Watson's test do not suggest that the model assumptions were violated (Fig. S3).

4. Discussion

In this study, for the first time in Brazil, we used a combined biomonitoring approach using tree barks and tree rings to evaluate the spatial/temporal variability of metal pollution in the vicinity of

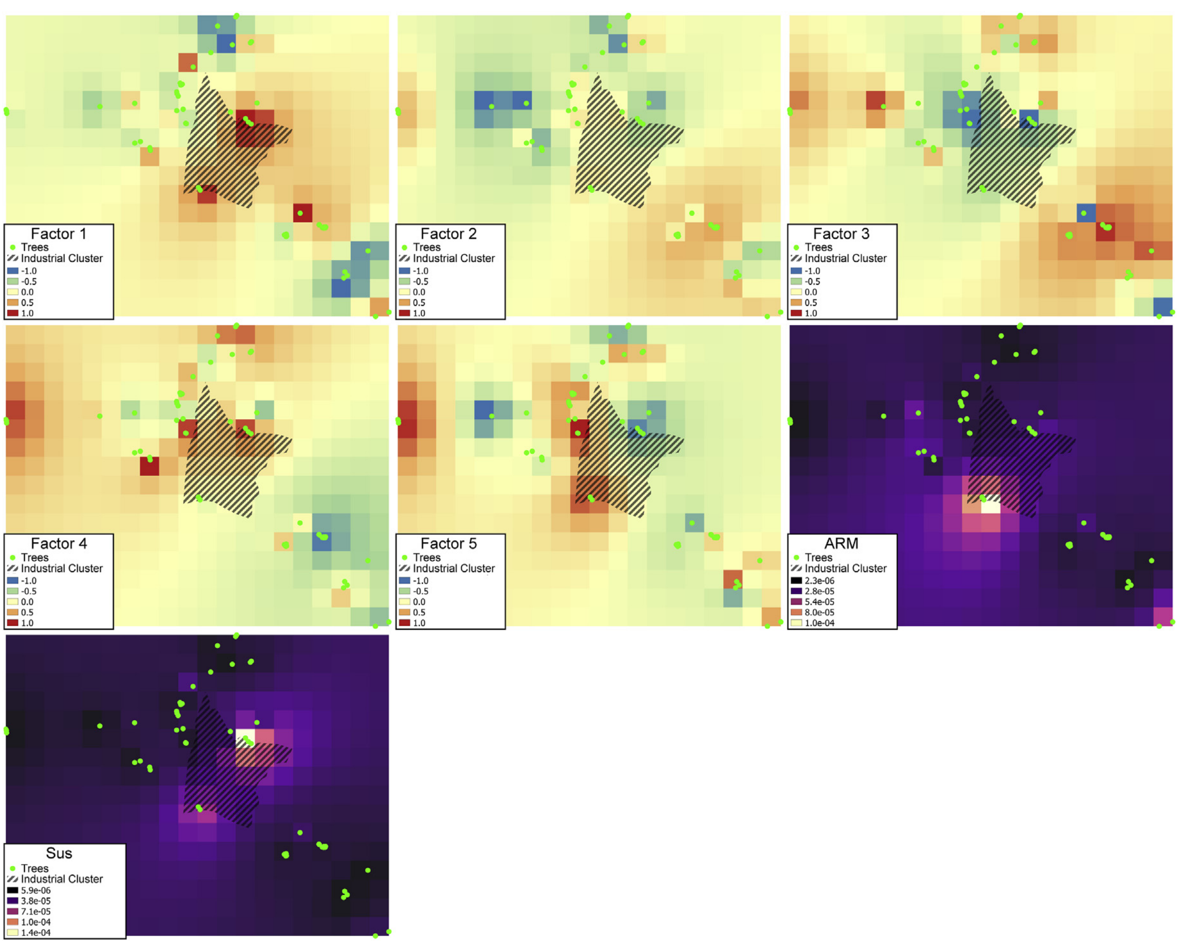

Fig. 3. Distribution maps of the Factor Analysis scores from the elemental composition of bark and the distribution maps of the magnetic properties of the bark of the sampled trees (green dots) around the industrial cluster (shaded area). Background color represent the Inverse Distance Weighting interpolation of each Factor score, which is standardized for the Factor 1 to 5. Pixel size: 500 × 500 m. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

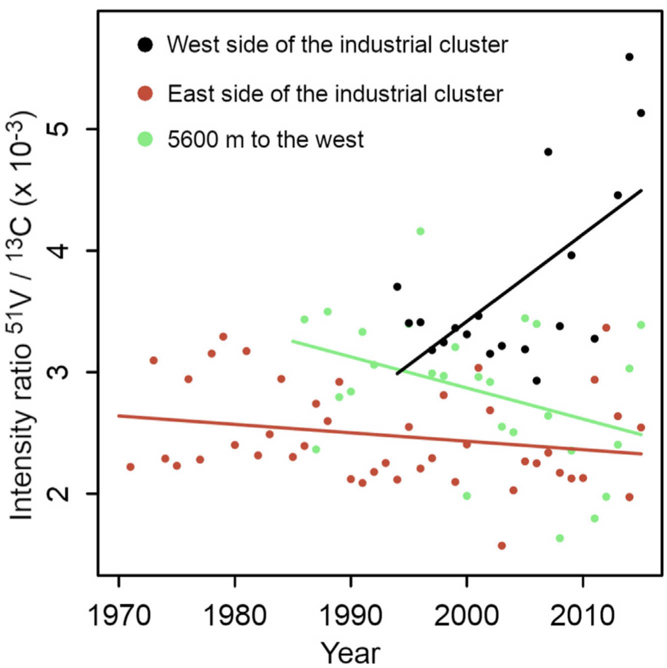

Fig. 4. Trends of vanadium intensity ratio measured in the tree rings of *Tipuana tipu* trees in the vicinity of an industrial cluster. Trees were sampled in the west side of the cluster close to the main chimneys (black, $R^2 = 0.40$, $p = 0.004$), in the east side of the cluster (red, $R^2 = 0.05$, $p = 0.15$), and at 5600 m to the west of the industrial cluster (green, $R^2 = 0.15$, $p = 0.05$). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

a stationary source. In our study, an additional feature was obtained by combining the concentrations of the measured elements in the bark of trees with their magnetic properties. This approach allows assessing the presence of groups of elements in extremely low concentrations that cannot be detected using more conventional techniques, such as the EDXRF. The measured magnetic parameters are useful for differentiating iron oxides and other magnetic material as titanium-iron alloys (Evans and Heller, 2003; Maher and Thompson, 1999).

The results of the factor analysis and magnetic properties of barks suggest that factor 1 (related to Al, Ba, Cu, Fe, Zn) and Sus are mainly associated with soil resuspension and vehicular emissions, similarly to what was observed in Central São Paulo (Moreira et al., 2016). Their highest values were observed in the east side of the industrial cluster. Factor 2 is related to S and Cl, which are overall evenly distributed in the area with no significant hotspots. This suggests that the source of these elements is likely more diffuse (Masri et al., 2015) and could not be determined by this study. Nonetheless, it is interesting to note that these two elements were not part of the same factor in Central São Paulo, and their combined variance may be related to the activities undertaken in this industrial district. Factor 3 is related to industrial and vehicular emissions, as well as ARM, in which the combination Cu, Zn, and mainly Mn, is comparatively high in the west side of the industrial cluster. This hotspot is consistent with the predominant southeastern wind direction and, consequently, with the estimated concentrations of emitted PM_{10} in this area (Fig. 2b, Locosselli et al., 2019). This is also the place where chimneys are concentrated in the industrial cluster (Fig. 2). The fourth and fifth factors are related to exposure to biomass burning from biofuel (Andrade et al., 2012) and/or fertilizer production which is consistent with the presence of a fertilizer plant in the industrial complex.

The distributions of factor 1 and ARM, or of factor 3 and Sus, in the bark of the sampled trees show that the population living closer to the industrial cluster may be under higher exposure to metal pollution. Differently from the central Metropolitan Area of São Paulo, and from other cities where the population is mainly exposed to light-duty vehicular emissions (Moreira et al., 2018), people living in this industrial district may face a mixed exposure to industrial and vehicular emissions. The latter may also have a different composition as industries are generally supplied by heavy-duty vehicles (Almeida et al., 2014).

Temporal trends of metal concentrations in the tree rings also suggest that exposure in this industrial district is different from that of the central Metropolitan Area of São Paulo. This central area has experienced a decreasing trend in the concentration of some pollutants as measured by air quality stations (CETESB, 2017) and tree rings (Geraldo et al., 2014; Locosselli et al., 2018, Table 4), a conclusion that is also observed in other cities worldwide (e.g. Zheng et al., 2018). The observed decreasing trends in central São Paulo is only observed for Pb in the present study site. This result is consistent with the phase out of Pb starting in the late 1980’s in Brazil (Paoliello and Capitani, 2007). For all other elements, the observed decreasing trend in the central Metropolitan Area of São Paulo is not replicated in this industrial district.

Among all elements measured in the tree rings, vanadium is the one known to be associated with oil refining activities (Querol et al., 2007). The concentration of this element presented increasing trends in the tree rings of the tree located in the west side of the industrial cluster (Fig. 3). Although this trend was observed in a single tree, it is in accordance with the results of factor 3 and ARM and of the modeled PM_{10} (Locosselli et al., 2019) that jointly point out to an emission hotspot in the east side of the industrial cluster. In addition, the expected decreasing trend in Pb observed in all sampled trees enhances our confidence that this is not a spurious result. Overall, the presence of the industrial clusters may expose the population to two distinct sources of pollution, one related to the traffic of heavy-duty vehicles that supply that cluster, and the other, related to the industrial activities per se (Almeida et al., 2014).

Pollution trends revealed by biomonitoring studies in the Metropolitan Area of São Paulo highlight the environmental inequality found in many large cities around the world (Viel et al., 2011; Zwickl et al., 2014). Many countries are striving to reduce environmental pollution because of its effects on citizens’ health (Kuklinska et al., 2015). However, the results of such efforts may not benefit the entire population, as some may still be affected by potentially polluting activities (Zwickl et al., 2014). The industrial emissions from this specific location have already been associated with clusters of autoimmune thyroid disease (Camargo et al., 2006; Freitas et al., 2010) and primary hypothyroidism (Zaccarelli-Marino et al., 2019), similarly to other industrial regions in the world (Benvenga et al., 2016). Since these industrial complexes are usually located at the periphery of the cities, the low-income and most vulnerable population bears the burden of the pollution exposure (Viel et al., 2011; Slovic et al., 2019). These evidences call for coordinated governmental actions to reduce emissions in peripheral locations, through more restrictive regulations and urban planning, in order to reduce environmental inequalities in the large cities.

5. Conclusions

This study brings new insights about the distribution of air pollution in the vicinity of stationary sources in a city. As a result of this and previous studies, large-scale exposure patterns to environmental pollution are emerging. The decreasing trends of metal concentrations in the tree rings observed in the central Metropolitan Area of São Paulo were replicated only for Pb in the trees

Table 4
Comparison of the temporal trends of metal concentration in the tree rings of *Tipuana tipu* sampled in the Metropolitan Area of São Paulo (MASP), based on the results of different studies. ↑ increasing trend, ↓ decreasing trend, - stable trend (no significant increase or decrease), x not analyzed. * in the west side of the industrial cluster.

Location in the MASP	Study	Method	Cd	Cu	Ni	Pb	V	Zn	Cr
Central	Geraldo et al. (2014)	X-ray fluorescence	x	x	↓	↓	x	x	↓
Central	Locosselli et al. (2018)	LA-ICP-MS	↓	↓	↓	↓	x	↓	x
Peripheral industrial district	The present study	LA-ICP-MS	–	–	–	↓	↑*	–	x

sampled in the vicinity of the industrial cluster. Vanadium, a key target element in oil processing, increases in a tree sampled in the west side of the industrial cluster. This result is in accordance with the spatial patterns obtained from elements and magnetic properties measured in tree barks that reveal a stronger influence of the industrial emissions in the west side of the industrial cluster. In summary, this study suggests that the population living in this more peripherical industrial district may not entirely benefit from the policies for emission reduction observed in the central region of São Paulo.

Main finding

Decreasing trends of metal pollution are not observed in the vicinity of an oil refinery in the periphery of the Metropolitan Area of São Paulo.

Declaration of competing interest

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

CRediT authorship contribution statement

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.114583.

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