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Biomonitoring as a Nature-Based Solution to Assess Atmospheric Pollution and Impacts on Public Health

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Abstract
The control of air pollution remains a challenge to the planning of cities and fossil fuel burning is the main cause of air degradation. Particulate matter (PM) is the contaminant commonly used as an indicator of pollution, but environmental agencies may face difficulties in operating surveillance networks due to the lack of resources and infrastructure. As an alternative to conventional networks, scientific studies have pointed out that nature itself can contribute to the diagnosis and reduction of air pollution. Nature-based solutions (NbS) are proposals that use natural processes and structures to meet different environmental challenges. In this study, biomonitoring with *Tillandsia usneoides* was applied as a NbS tool to evaluate air quality in an important port urban area in the city of Guarujá, Brazil, affected by industrial and vehicular emissions. It was observed that cadmium mass fractions were at least forty times higher than the control area with one-month exposition.

Keywords Air pollution · Nature-based solution · Biomonitoring · *Tillandsia usneoides* · ET AAS · Cadmium

Urbanization modifies land planning and dynamics, directly interfering in the resilience of cities to environmental disasters (Braga 2012). One of the consequences of rapid urban growth is the need to travel longer distances to obtain basic services, a fact that favors the increase of vehicle fleet for cargo transport (Aguiléra and Mignot 2004).

Among environmental problems, air pollution remains a challenge to be transposed. More than the industrial, the emissions from vehicles are recognized as the main source of atmospheric degradation (Castro 2013). Heavy-duty vehicles are the ones that contribute significantly to the enrichment of nitrogen oxides (NO_x) and particulate matter (PM) rich in toxic elements. The material emitted in exhaust pipes consists of a mixture of organic and inorganic chemicals in the form of gases, liquids and solid particles (Saldiva 2018; Khaefi et al. 2016; Kim et al. 2015).

In PM, trace elements with toxic potential, such as cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) may be present. Inhalation of such elements is strongly associated with respiratory and cardiovascular diseases (Nogueira 2006). PM is easily inhaled, so it can cause several public health problems (Rodriguez et al. 2010; Ferreira et al. 2017).

In the case of port cities, such as Santos and Guarujá in São Paulo State, Brazil, which include the facilities of the Port of Santos, the largest in Latin America, impacts of anthropic activities are more pronounced. In these cities, it is often observed more intense vehicular movement than the

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observed in more populous cities. In port areas, economic development is determined by the intensification of activities and negotiations in cargo terminals, causing a significant increase in the vehicle fleet, mainly of trucks, which congest commercial centers and residential neighborhoods. The adverse effects of port activities are mainly verified in the quality of life of the population (Souza 2006).

There is no doubt about the role of the activities of the Port of Santos in the seashore area of São Paulo State, transforming the former colonial region into an area of national prominence (Souza 2006). However, this immediate expansion culminated in a demand for the release of urban spaces, which for now are not suitable for port facilities, requiring interventions through engineering projects, to adapt to the premises of port legislations.

In this scenario, Guarujá was surprised by a logistics bottleneck in the production flow. The problem experienced by local residents implies several challenges to be addressed by the municipal management: the disruption of urban mobility in predominantly residential areas, the lack of fluidity in traffic, endangering the safety of the population, the significant emission of gases and PM from motor vehicles (with a predominance of cargo transport), resulting in increased air pollution, with potential adverse effects on public health.

Although the Environmental Company of the State of São Paulo (CETESB) inspects air quality, following the guidelines of State Decree No. 59,113/2013, through measurement parameters and techniques, this monitoring in Guarujá is recent. It started in 2016 and only includes one collection site, for measuring PM_{10} (CETESB 2017).

In the national scenario, Guarujá is certainly recognized for its tourist vocation, due to its natural beauty embedded in a dragon-shaped island, with an area of 143 km², housing 25 paradisiacal beaches. However, the significant participation of the Port of Santos, even if it directs substantial financial resources to the city, culminated in impacts on the territorial planning, due to truck congestion (Guarujá City Hall 2012).

Thus, urban planning needs to recognize the strong connection of inhabitants with nature, both associated with the demand for ecosystem services and environmental impacts (Elmqvist et al. 2013).

As an alternative to conventional air quality management stations, scientific studies have pointed out that nature itself can contribute to the diagnosis and reduction of air pollution (AMS 2019; Gopalakrishnan et al. 2019). Nature-based Solutions (NbS) are proposals inspired and supported by nature, which are characterized by cost-effectiveness. NbS proposals are multifunctional, economical and offer a wide range of benefits, ranging from environmental degradation control to improving public health (MEA 2005; IUCN 2012; Brazil 2016; Ferreira and Ribeiro 2020).

NbS including projects present innovative scientific strategies that do not necessarily involve cutting-edge technologies, to promote sustainable development. NbS considers issues about biodiversity and ecosystems in broader social agendas, such as socio-environmental conflicts and environmental justice, equal access to treated water and food security (Potschin et al. 2015). Thus, NbS measures integrate urban governance and local participation, resulting in additional benefits to the population, such as promotion of health and quality of life and enabling the local green economy (Kabisch et al. 2017; Frantzeskaki 2019).

Regarding biomonitoring, this is an efficient measure of NbS to evaluate contamination in urban areas from living organisms, called biomonitors of environmental quality (Markert et al. 2003, 2011). Biomonitoring with plants and the expansion of green infrastructure are examples of measures that use nature and allow the diagnosis and/or filtering of air pollutants.

The aim of this study is to assess the relationship between vehicular fleet and air pollution in the District of Vicente de Carvalho, Guarujá, a neighborhood at the left bank of the Port of Santos, where some chemical industries are also located. The information on air pollutants could advice the municipal managers in their decision-making. Therefore, for such purpose, a NbS protocol, based on biological monitoring was conducted for evaluating the impact of vehicular emissions to the air quality of the district.

Living organisms, such as plant leaves, lichens, mosses and trees are receptors of atmospheric contaminants (Norouzi et al. 2015; Cardoso-Gustavson et al. 2017; Moreira et al. 2016; Giampaoli et al. 2016; Ribeiro et al. 2017; Ferreira et al. 2017).

In the Vicente de Carvalho District, the bromeliad *Tillandsia usneoides* (Linnaeus, 1762) was used as a biomonitor. *T. usneoides* is an epiphyte species (aerial plant), which means that, with surface roots, it can only rely on tree trunks, to always reach the highest place, in an attempt to absorb all the nutrients, it needs from the atmosphere (Markert et al. 2003, 2011). As PM, *T. usneoides* also retains the pollutants that are present in the environment. Its growth is slow, and it does not present any contact with the soil; that is, in studies for the determination of chemical compounds, it is known that these come from the atmosphere (Cardoso-Gustavson et al. 2017; Giampaoli et al. 2016; Moreira et al. 2016; Ribeiro et al. 2017).

Materials and Methods

T. usneoides were obtained from a producer located in Cordeirópolis, an inner city of São Paulo State. The samples were acquired from a nursery garden named *Spagnhol Plantas Ornamentais*. The plants are cultivated in a space far from polluting activities; thus, the place could be considered a clean area. This nursery garden was also chosen because the producers have been providing *bromeliads* for others reliable studies conducted by the São Paulo Botanic Institute (Giampaoli et al. 2016, 2021).

With regard to the exposure time, periods often vary, depending on pollution intensity and monitoring purposes (Ratcliffe 1975; Calasans and Malm 1997; Martínez-Carrillo et al. 2010; Martínez-Reséndiz et al. 2015). Anyway, it is important to ensure that the biomarker retention capacity is not exceeded (Martin and Coughtrey 1982; Martínez-Reséndiz et al. 2015). Accordingly, it is possible to find studies where the exposure time varied from 5 days until 6 months (Calasans and Malm 1997; Martínez-Carrillo et al. 2010; Martínez-Reséndiz et al. 2015). The 2-month exposure period is the most used, since for some researchers, this time has been recognized as the saturation point for *T. usneoides* (Figueiredo et al. 2007; Cardoso-Gustavson et al. 2017). Therefore, considering the traits of Vicente de Carvalho District, regarding the intensity of vehicular emissions and the logistic of sampling by the Department of the Environment of Guarujá City (SEMAM), a 4 to 6-week period for exposure time was adopted, for the whole of 2019 and sample analyses are still in progress. In the case for the results herein presented, *T. usneoides* samples were exposed for two one-month periods: from January 16 and from February 14, 2019.

The distribution of the plants took place throughout the area of Vicente de Carvalho District, Guarujá city, totaling 43 sampling sites. At each sampling site one sample containing about 15 g of *T. usneoides* was inserted. Plants were arranged in tree branches, at approximately 3 m high. Each sampling site (Fig. 1) had its coordinates recorded by means of a GPS using the Mercartor Transverse Universal System (UTM). It should be noted that according to SEMAM, the congestion of trucks occurs daily, especially on Idalino Pines Street, Santos Dumont Avenue and Cônego Domênico Rangoni Highway. This highway is one of the largest in São Paulo State. It starts on the Imigrantes Highway; being about 30 km long and connecting Guarujá to the Rio-Santos highway, passing through the Cubatão city industrial hub. It is the main access to the left bank of the Port of Santos, located in Vicente de Carvalho. Idalino Pines Street is 1.5 km long. In it, is located the Ecopoint, a 70,000 m^2 area used as a stop site for vehicles to be washed and reload for new transport.

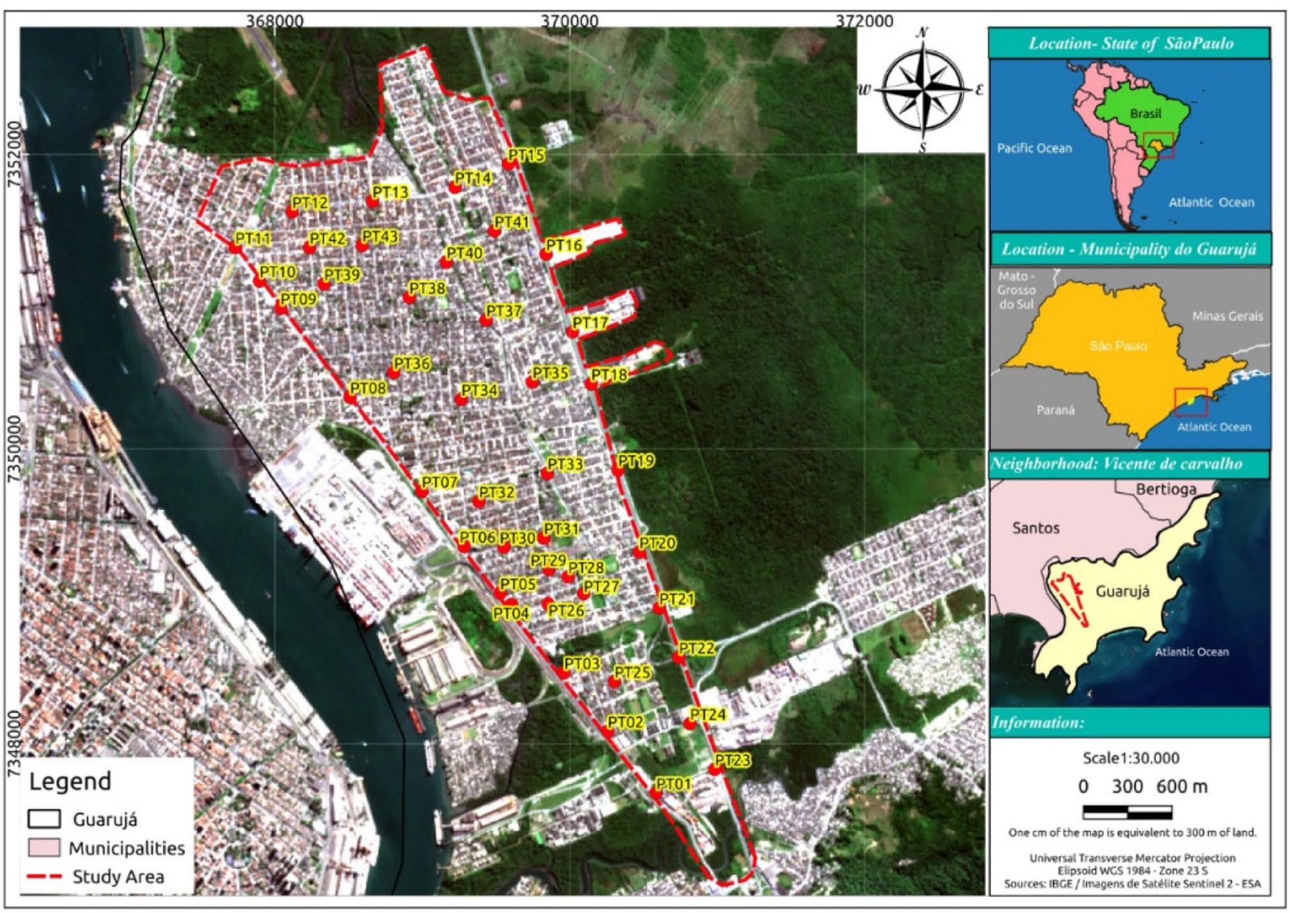

Fig. 1 Location of Vicente de Carvalho within Guarujá city and biomonitoring sites

Samples were collected and transported to the laboratory in paper bags to avoid cross contamination and to prevent extra humidity. They were not washed and were kept in a freezer until further manipulation. Then samples were freeze-dried and grinded in a cryogenic mill. Very homogeneous powder aliquots of 0.2–0.3 g were submitted to microwave assisted digestion using the *Plant Material* digestion program of the CEM MARS6 microwave oven, with addition of 7 mL concentrated HNO_3, 2 mL concentrated HF and 2 mL 30 % (v/v) H_2O_2. Only one aliquot was analyzed for each sample in this study but each aliquot was read twice in the spectrometer. The digestion program has three steps: ramp time, hold time and cooling time, with 20 min, 10 and 10 min periods, respectively. The maximum temperature of the program is 200°C while the microwave power is varied between 1030 and 1800 W in order to control sample temperature. Digests were diluted up to 15 mL with purified water (Milli-Q) and were analyzed by Electrothermal Atomic Absorption Spectrometry (ET AAS), using a Perkin Elmer AAnayst 800 spectrometer. For the calibration curve, 5 Cd standard solutions were used (0.7, 1.75, 3.5, 5,70 and 7.0 ng mL^{-1}) and the correlation coefficient for the minimum squares fit of the curve were higher than 0.9997, according to the spectrometer software. The limits of detection (L_D = 11.7 µg kg^{-1}) and of quantification (L_Q = 37.4 µg kg^{-1}) were estimated using the calibration curve and a series of readings of blank solutions, according to the equations described by Welz and Sperling (1999). For quality assurance control, the certified reference material INCT-MPH-2, *Mixed Polish Herbs*, and reagent blanks were analyzed on each sample batch (INCT 2020). Cd certified value for this referenced material is 199 ± 15 µg kg^{-1} (certified value ± U, $k=2$) and the obtained value for a series of measurements was 200 ± 16 µg kg^{-1} (mean value, standard deviation, $n=8$), representing a 100.5% recovery.

From the sample geographic coordinates, a spreadsheet was generated with nomenclature to identify each point and its respective Cd mass fraction, for each evaluated period. With the spreadsheet and using the software QGIS 3.10.12 (QGIS 2020), a shape file was generated on a Google Earth satellite image cartographic base, with the delimitation of the study site as initial support for the making of maps (Archela and Théry 2008). These maps were generated on a 1:30,000 scale, with a Universal Transverse Mercator (UTM) projection and SIRGAS 2000 Datum, respecting the current cartographic conventions. For better visualization of contaminant mass fractions, the inverse distance interpolation (IDW) technique was used, a resource available in QGis 3.10.12, which basically consists of estimating concentrations at unknown sites, based on values at known sites (Archela and Théry 2008; Almeida et al. 1997; Nogueira 2008).

Results and Discussion

Since the main goal of the study was to evaluate the potential relationship between heavy-duty vehicular emissions and air pollutants, preliminary mass fraction results in *T. usneoides* are presented, regarding the toxic element Cd. Although Cd is present in the chemical composition of gasoline, this element has been recognized as an important marker of emission diesel engines (Coufalík et al. 2019; Shukla et al. 2017).

Monthly data is important as meteorological parameters such as wind direction, relative humidity and temperature are quite dynamic. With the results obtained monthly, it will be possible to evaluate the influence of the climatic characteristics of dry and rainy periods on the accumulation of air pollutants. Future analyses will also include other potentially toxic elements associated with light vehicle emissions and industrial activities.

Despite of being transplanted to areas with intense anthropic activity, *T. usneoides* samples remained green and presented discrete growth for the 1-month exposure period. It indicates that plants maintained their physiological and metabolic characteristics to accumulate potentially toxic substances from the atmosphere, evidencing their ability to be used as a biomonitors (Nogueira 2006).

Table 1 presents Cd mass fractions determined for samples exposed in January and collected in February (2019) and exposed in February and collected in March (2019), and Cd mass fractions for the control site (Cordeirópolis). Results for the certified reference material INCT MPH-2 are also presented.

The results for the certified reference material were in good agreement with the certified value, proving the adequacy of the method used. Sample results presented a significant variation between the months of January and February. Of the total of 43 sampling points in January, only 11 of them had mass fractions above 100 µg kg^{-1}. The maximum mass fraction occurred in the sample exposed at the entrance to the Ecopoint (PT28). The other 10 points refer to samples exposed around it. Mass fraction values < 100 µg kg^{-1} were observed in the residential streets, at northernmost area. In these sites, Cd levels varied between 44 and 83 µg kg^{-1}. Although above those obtained for the control region (35.4 µg kg^{-1}), the data suggest that the contribution of heavy-duty vehicle emissions, in January, was in the same order of magnitude of urban areas, but where there is intensive greenery, such as Botanic Garden, a famous urban park located in Rio de Janeiro City, Brazil (Vianna et al. 2011). Table 2 presents the range of Cd concentration for *T. usneoides*, in other regions of Brazil.

For samples exposed in February, the behavior at most collection sites was consistent with locations with a

Table 1 Cd mass fraction (mean ± standard deviation; number of determinations; range and median, μg kg^{-1}) in *Tillandsia usneoides*, at different sites at Guarujá and at Cordeirópolis (control area) in different exposition periods, 2019, with indication of sites of Minimum and Maximum values

Sampling area	Month	Mean ± SD (n)	Median	Range	Extreme sites[b]	
					Min.	Max.
Vicente de Carvalho	January	121 ± 226 (43)	69	44–1501	PT42	PT28
	February	1075 ± 702 (43)	887	194–3012	PT37	PT29
Control Area	January	35.4 ± 2.3 (3)	35.0	33.3–37.9	–	–
	February	26.3 ± 5.8 (3)	27.4	20.0–31.4	–	–
MPH-2	-	200 ± 16 (8)	205	179–222	(199 ± 15)[a]	

[a](certified value ± U, *k* = 2); [b](sites PT28 and PT29 at Ecopoint; sites PT37 and PT42, at Northernmost area)

Table 2 Cd mass fraction (μg kg^{-1}) in *Tillandsia usneoides*, at highly urbanized areas in Brazil

Region	Site	Cd	Remark	References
São Paulo Metropolitan Region (SPMR)	Pinheiros District	270	Green zone	Nogueira (2006)
	Pinheiros Highway	1260	Heavy-duty vehicles	
	Santo André City	1340	Industrial area	
	São Caetano City	350	Industrial area	
	Mauá City	320	Industrial area	
Rio de Janeiro and Baixada Fluminense	Botanic Garden	70	Green zone	Vianna et al. (2011)
	Center	230	Vehicle emissions	
	Nova Iguaçu City	300	Industrial area	
	São Gonçalo City	300	Industrial area	
Salvador	Barra District	800	Vehicle emissions	
	Stella Mares District	300	Close to airport	

significant contribution of vehicular and industrial emissions. The median for the data set (43 samples) was around 887 μg kg^{-1}. The mass fraction observed for the sample exposed in PT28 remained close to 1500 μg kg^{-1}. The maximum concentration (3012 μg kg^{-1}) was observed in a sample exposed at the backwards of the Ecopoint.

The marked differences observed between the months of analysis suggest the influence of two important parameters: (i) the volume of rain and (ii) the intensity of the flow of cargo vehicles.

According to Brighigna et al. (1997), the ratio between the levels of chemical elements in external and internal leaves of *T. usneoides* decreases with rain. Although pollutants are retained in the plant trichomes, their mass fractions are diluted by rainwater. According to historical series (1980 to 2016) of meteorological data, made available by the *Weather Spark* website, January is usually the rainiest month in Guarujá, while February tends to decrease precipitation. In 2019, the same rain pattern was observed in these months. Regarding the flow of trucks, the movement of vehicles starts in February, with a peak in March (soybean distribution) and August (corn distribution). Therefore, the combination of the rainiest period, causing a wash effect on the plants, with the lowest truck traffic, resulting in potential lower exhaust emissions in January and the dispersion of pollutants resulted in lower Cd mass fractions for the first exposition period.

According to Table 2, Cd levels in previous studies indicated the level of industrial and vehicular contribution. Lower concentration values were observed in samples exposed in areas with significant tree densities. Samples from the Botanical Garden, for example, showed mass fractions in the same order of magnitude as several samples at Vicente de Carvalho, exhibited in January.

Also noteworthy are the samples from the Pinheiros Highway, in the São Paulo Rodoanel region, which connects the southern region of the country to the Port of Santos, causing truck movement to be intense on this area. Cd levels at the Pinheiros Highway are equivalent to those observed at the entrance of the Ecopoint, in Vicente de Carvalho. Values obtained for areas with industrial activities and predominant emissions from light vehicles agree with the Cd levels observed in the plants exposed in February/March.

The maps generated from Cd mass fractions on *T. usneoides* allow visualizing the regions with the highest concentrations (Fig. 2).

Although the minimum Cd mass fraction in Feb/Mar is 4.5 times higher than in Jan/Feb; as well as the maximum

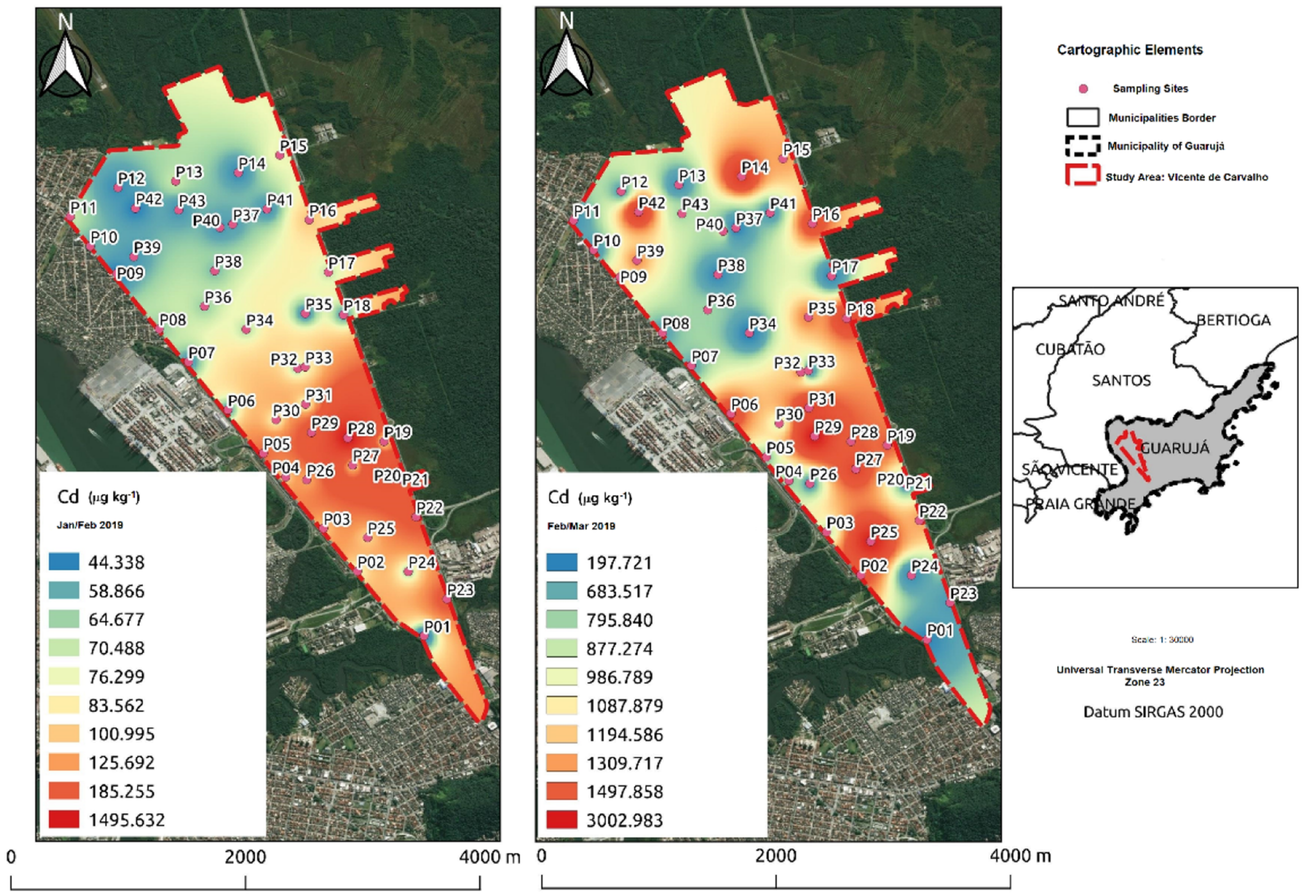

Fig. 2 Spatial distribution for Cd mass fractions at Vicente de Carvalho, Guarujá, in the period from January to March 2019

content found to be the double, there is a tendency for enrichment at the Ecopoint and its surroundings. As already informed, the highest Cd contents at the southernmost, in the residential area, is associated with the yard of trucks, where drivers wait for the turnout to clean off cargo residues, after transportation to the Port. Furthermore, at surrounding areas of Ecopoint, the traffic conditions are predominantly under stop and go style, which contribute for the enrichment of contaminants in the airborne and might explain the Cd contents observed in Fig. 2.

In the northernmost region, there are lower Cd mass fractions, with no anomalous points in Jan/Feb. However, in Feb/Mar, levels above 1000 µg kg^{-1} were observed (PT09; PT14; PT15; PT39; PT42). It is emphasized once again that the discrepancies between the Cd levels between the first sampling campaign and the second one must be due to the (higher) rainfall level and the decrease in heavy-duty fleet circulation in January.

Cadmium is normally present in the main environmental compartments (water, air, and soil). In PM, the element is presented mainly as cadmium oxide (CdO); although occurrences of Cd salts from incinerations are common (CETESB 2017). The main sources of this metal are associated with the burning of fossil fuels, production of iron and steel, mining, the plastics industry, the manufacture of batteries, waste from phosphate fertilizer industries, among others. The natural contribution has a volcanic origin (Page and Bingham 1973).

The most relevant route of human exposure is through food, with emphasis on seafood. The maximum allowed (direct) intake in drinking water is 5 µg L^{-1} according to Brazilian legislation (Brazil 2008).

Although the levels of Cd in Vicente de Carvalho exceed 5 µg kg^{-1}, it is necessary to make it clear that there is no direct relationship between the observed mass fractions, the inhalation of PM by the population and health effects (Ribeiro et al. 2017). In this sense, previous studies are again indicated (Table 2) that presented Cd mass fractions well above 5 µg kg^{-1}, but that do not necessarily indicate associated diseases. More rigorous environmental epidemiological studies, involving humans, are needed to assess dose effects (Ribeiro et al. 2017).

The use of biomonitoring, as a NbS tool to assess air quality in port areas has been shown to be adequate, since there is no representative management in Vicente de Carvalho.

Presented data are still incipient but reflected the trend of origin and dispersion of pollutants in the studied area. The retention of air pollutants by plants highlighted the importance of green infrastructure in continuous studies of air quality monitoring, with emphasis on the low cost of biomonitoring and the advantage of using NbS.

One of the fundamental needs of public environmental policies is the establishment of indicators that allow decision making. In this sense, it is expected that in the near future, an increase in public environmental projects that encourage NbS measures, will result in the growth of the so-called "green cities", with a focus on reducing the adverse effects of environmental pollution. However, more scientific evidence is needed so that, in fact, public managers can rely on NbS results for fomenting projects aimed at environmental quality.

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Declarations

Conflict of interest All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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