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Urban contamination sources in tunnel dusts from São Paulo city: Elemental and isotopic characterization

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HIGHLIGHTS

- Geochemical data and Pb and Zn isotopes were investigated in tunnel dusts of São Paulo megacity, Brazil.
- Pb and Zn isotopes suggested vehicular sources: fuel combustion for Pb and wear of tire and brakes for Zn.
- Traffic-related elements, such as Sb, Cu and Cd, are highly enriched, especially in the smaller size fractions.
- Scanning electron microscopy revealed the presence of tire like structures in the smallest grain size fractions of dusts.
- Multiple statistical approaches indicate geogenic sources for rare earth elements, U and Th.

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ABSTRACT

Elemental and isotopic composition of tunnel dusts collected from Jânio Quadros (JQ) and Maria Maluf (MM) tunnels in São Paulo city were analyzed aiming to determine the potential sources of trace elements in these environments. Sampling was performed in the summer and winter of 2017. Elemental mass fractions were determined by Instrumental Neutron Activation Analysis (INAA) and Graphite Furnace Electrothermal Atomic Absorption Spectrometry (GF-AAS) for 28 elements. Isotopic signatures of Pb and Zn were determined by Thermal Ionization Mass Spectrometry (TIMS) and Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS), respectively. The mean mass fractions of elements, such as Pb, Cd, Zn, Sb and Cu, were in general similar to the reported in the literature, in studies that demonstrated urban contamination by potentially toxic elements. Statistics demonstrated significant differences in mass fractions between the tunnels for most analyzed elements. Results showed that rare earth elements, U and Th, mostly associated with geogenic sources, presented higher concentrations in MM tunnels, while elements frequently related to vehicular emissions (Sb, Zn, Ba, Cu and Pb) presented mean mass fraction values higher in JQ tunnel, pointing to a more important contamination in JQ tunnel. No significant differences in the mass fractions between campaigns were observed, evidencing that tunnels are not much affected by external weather conditions. Pb isotopic analysis presented $^{206}Pb/^{207}Pb$ ratios between 1.1715 and 1.1791 and $^{208}Pb/^{206}Pb$ ratios between 2.0889 and 2.0961, which pointed out to a vehicular signature, related to tailpipe emissions. On the other hand, Zn isotope data also suggested a vehicular signature, but mostly related to the wear of tires and brakes. Grain size distribution analysis showed that the smallest fractions of dust contained, on average, about 10% of particulate matter of aerodynamic diameter smaller than 10 μm, fractions highly inhalable, what may be a concern to human health. Enrichment factors (EFs) showed that Cr, Zn, Cu, Cd, Pb and Sb are the most enriched elements, in both tunnels, but higher EFs were found for JQ tunnel. Principal Component Analysis revealed a profile for a crustal source, marked by U, Th and rare earth elements, whereas vehicular sources were characterized mostly by Pb, Ti and V from gasoline/diesel combustion; Pb and Ti from road paints; Sb, Ba and Zn from brakes, and Zn from wear of steel and tires. These results indicate an important anthropic impact in the tunnels and that vehicular traffic is the main source of potentially toxic elements.

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1. Introduction

São Paulo megacity is one of the most populated regions in the world, with about 20 million inhabitants in its metropolitan area (MASP), more than 8 million motor vehicles and intense traffic, mainly during peak hours. According to recent data gathered by the National Traffic Department (DENATRAN), those vehicles run on different main types of fuels: 47% are fueled with gasohol (a mixture of gasoline and ethanol – a sugarcane biofuel); 6% are fueled exclusively with hydrated ethanol; 5% are fueled exclusively with diesel; and 39% are flex-fuel vehicles, that can be fueled with both gasohol or hydrated ethanol, depending on the market offering and the current prices (DENATRAN, 2020).

Over the last four decades, industrial centers have moved from São Paulo to surrounding cities and then vehicle emissions became the main source of atmospheric pollution in the city (Andrade et al., 2017; Toledo and Nardocci, 2011). According to São Paulo State Environmental Protection Agency (CETESB), vehicles are responsible for the emission of several substances to the atmosphere, including both carbon monoxide and dioxide (CO and CO_2), hydrocarbons, nitrogen oxides (NO_x), sulfur dioxide (SO_2), methane (CH_4), nitrous oxide (N_2O), and particulate matter (PM). Specifically, the agency reported that, in 2016 only, about 1435 t of particulate matter of vehicular origin were emitted in MASP (CETESB, 2016).

In fact, when analyzing data collected at the air quality monitoring stations located near the main city avenues and high vehicular circulation spots, it was found that PM concentrations are frequently exceeding the state legal maximum concentration values allowed for inhalable particles (CET, 2017). This compromises the environment and poses risks to human health as well (Biasioli et al., 2006; Pope and Dockery, 2006), since PM is an important carrier of potentially toxic elements, such as lead, zinc, copper, arsenic and cadmium (Figueiredo et al., 2007). Studies carried out by researchers from the University of São Paulo Medical School demonstrated that these emissions are more toxic than the residues of the burning of biomass (Braga et al., 2001).

It is important to highlight that emissions derived from wear of vehicular components are constituted mostly of particulate matter. Bukowieki et al. (2010) estimated that non-exhaustion vehicular sources originate approximately 60% of all PM_{10} emitted in vehicular traffic. This indicates that non-exhaustion emissions can be as harmful as those originated in vehicular tailpipe emissions, as discussed by Amato et al. (2014).

Impacts are also observed in the effluents generated in the cleaning and maintenance of road tunnels. Runoff water from a tunnel in Norway showed the presence of potentially toxic elements in the effluent, such as Pb, Zn, Cd and Cu (Andersen and Vethe, 1994). Meland et al. (2010), studying another Norwegian tunnel, showed that the runoff water was highly polluted, containing polycyclic aromatic hydrocarbons (PAHs) and metallic elements. These results indicate that pollutants can be mobilized by aqueous medium and be concentrated in soils and underground waters, if incorrectly disposed.

Although controlled ambient conditions inside tunnels are not necessarily an accurate depiction of the vehicle traffic conditions and its consequences in the entirety of urban scenarios, performing analysis inside tunnels presents some advantages when identifying emissions from vehicles: (i) their inner portions are not directly affected by meteorological conditions or variations, such as rain or sunlight, which can induce transformations in the dust samples; (ii) the samples come almost solely from vehicular emission, reflecting realistic driving conditions and averaging a large number of vehicles simultaneously; (iii) sampling is representative of the burning of different fuels; and (iv) samples are generated at relatively constant parameters since driving conditions usually do not change drastically over time (Bardelli et al., 2011; Lawrence et al., 2016).

Tunnel dust sampling was applied in several studies worldwide (Alves et al., 2015; Handler et al., 2008; Hung-Lung and Yao-Sheng, 2009; Sternbeck et al., 2002), demonstrating enrichment of traffic related elements such as Cu, Zn, Cd, Sb, Ba and Pb, and increase in PM concentrations, in comparison to the background outside tunnels.

Tunnel studies were conducted in MASP as well. Sánchez-Ccoyllo et al. (2009) estimated PM emissions at Jânio Quadros and Maria Maluf tunnels, the same studied here. They demonstrated that diesel fueled vehicle emissions are four (PM_{10}) and six ($PM_{2.5}$) times higher, respectively, when compared to the emissions of ethanol or gasohol fueled vehicles. Also, important differences were found when comparing emissions sampled at weekdays and at weekends at Jânio Quadros (in the city) and Rodoanel (outside the city) tunnels, in São Paulo, supporting the statement that higher vehicle traffic leads to higher PM emissions and characterizing vehicles as important sources of PM in urban environments (Pérez-Martínez et al., 2014).

Despite of the impact of vehicular emissions on the environment and on public health system, especially in urban centers, there are still few studies about it in MASP or São Paulo city, and very few involving isotope characterization.

Relying on the fact that elements maintain the isotopic signatures of their sources, the characterization of the isotopic composition of elements is also being used to study the impacts of traffic emissions in the environment (Carrasco et al., 2018; Dong et al., 2017; Félix et al., 2015; Maréchal et al., 2000; Wen et al., 2015).

In São Paulo city, atmospheric particulate matter and anthropogenic materials, such as tires and cement, have been analyzed to stablish isotopic signatures for Zn, Pb and Cu, what made possible to discriminate specific source characterization for these elements (Babinski et al., 2003; Gioia et al., 2008, 2017; Souto-Oliveira et al, 2018, 2019). Isotopic analysis is a powerful tool to trace elements in the environmental reservoirs, supporting their use as fingerprints of pollutants. In this context, lead and zinc isotopes have been used to determine the sources of these elements in a great variety of environments worldwide.

There is very little information about metallic pollution in São Paulo city. This study aims to determine potentially toxic elements concentrations in tunnel dusts of this megacity, focusing on describing their possible sources, improving information about pollution or contamination of this urban environment.

2. Materials and methods

2.1. Site description

The dust samples were collected in three tunnels of São Paulo city: the President Jânio Quadros tunnel (JQ) and two tunnels of the Maria Maluf Road Complex (MM).

JQ tunnel is 1900 m long and is located at the southeastern region of the city, at 7.4 km from the city center. Its traffic is characterized by the circulation of light-duty vehicles only, with total weight less than 3500 kg, according to National Traffic Council (CONTRAN). MM tunnels are 1200 m long and are located at 8.7 km from the city center, at the western region of the São Paulo city. Each independent tunnel hole (one for each direction) has three traffic lanes and admit circulation of both light-duty (LDVs) and heavy-duty vehicles (HDVs), like trucks and buses.

2.2. Sampling and sample preparation

Dust samplings were held at two different sampling campaigns: the first in February (summer) and the second in July (winter) of 2017. The dusts were collected using plastic brushes and shovels, as described in Varrica et al. (2003) and Guney et al., (2010).

JQ tunnel lanes have their traffic direction inverted daily, and sampling occurred in its inner central portion, comprising the road pavement and the pedestrian sidewalk (~1 m elevation from the road surface), separately. At MM tunnels, sampling was performed at the entrance and exit portions of the tunnels, separately. This sampling comprised only the pedestrian sidewalk (also ~1 m elevation from the

road surface). At each sampling campaign, four samples from JQ tunnel (two from road pavement and two from pedestrian sidewalk) and four samples from MM tunnels (two from the entrance and two from the exit) were collected. All samplings were performed comprising an area of approximately 5 m^2, at each location.

Samples of approximately 100 g each were packaged into clean polyethylene bags and transported to the laboratory, at room temperature conditions. At laboratory, samples were individually oven dried, at 60 °C, for 24 h each, and manually sieved in stainless steel sieves into three different grain sizes: 2 mm, 150 μm and 63 μm, totalizing six subsamples (summer: 2 mm, 150 μm and 63 μm; and winter: 2 mm, 150 μm and 63 μm).

Grain size fractions coarser than 2 mm were discarded, since they were constituted mainly by small rocks and plant leaves. Dusts of grain sizes between 2 mm and 150 μm were manually ground in an agate mortar to obtain a homogeneous powder suitable for Instrumental Neutron Activation Analysis (INAA).

2.3. Elemental characterization

Determination of the mass fractions of chemical elements was performed by Instrumental Neutron Activation Analysis (INAA) and Graphite Furnace Electrothermal Atomic Absorption Spectrometry (GF-AAS).

2.3.1. INAA

Portions of 150 mg of all subsamples and of the certified reference materials (CRM) BE-N (SARM), granite GS-N (SARM) and BCR®-723 (IRMM), were accurately weighted in polyethylene bags, which were individually sealed and wrapped in aluminum foil. For the determination of the mass fractions of long half-lives elements, multiple sets of 15 envelopes were sealed into aluminum cylinders and sent into the IEA-R1 nuclear research reactor core, under a thermal neutron flux of approximately 5 10^{12} cm^{-2} s^{-1}, for 8 h (long-time irradiation).

Induced activity measures were performed in a gamma spectrometry system comprised by a solid state high-purity Ge detector (Canberra GX20190) and associated electronics. The first measures were taken seven days after irradiation and the second ones, two weeks after irradiation. All subsamples were analyzed in quadruplicates and measured separately for 1 h each in the same detection system.

Subsamples of grain size 63 μm were submitted to short-time irradiations, to determine the mass fractions of short half-lives elements. The preparation of these samples followed the same procedures described above. All samples, standards of known concentrations and portions of standard reference material SRM 2709a San Joaquin Soil (NIST) were irradiated for 20 s and the induced activities were measured 5 min and 1 h after the irradiation, for 5 min each, in the same detection system and geometry arrangements, in the presence of a radioactive source of ^{60}Co and ^{57}Co, for dead-time and pulse pile up correction.

Mass fractions of 25 elements (As, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Tb, Th, U, Yb, Zn, Ti and V) were then determined, based on comparative INAA method, in which the values of the detection coefficient, neutron flux, thermal neutron cross section, Avogadro's constant, isotopic abundance, half-lives and irradiation time are identical for samples and reference materials.

2.3.2. GF-AAS

For the determination of the mass fractions of Cu, Pb and Cd, portions of 50 mg of dust samples previously prepared and of CRM EnviroMAT SS-1 Soil (SCP Science) were weighted into Teflon tubes. Each tube received (step 1) 7 mL of a 3:1 mixture of HNO_3 (60%) and HF (40%), and 3 mL of H_2O_2 (30%). After gentle mixing, the tubes were closed and left at room temperature for 24 h. After that, to each tube were added (step 2) 2 mL of HNO_3 (60%) and 6 mL of HCl (60%). All reagents used were analytical grade.

All tubes were submitted to a microwave assisted acid digestion (MARS6, CEM) according to the following program: heating from room temperature to 180 °C (20 min), temperature maintenance (10 min), heating from 180 °C to 210 °C (20 min), temperature maintenance (10 min), and cooling (40 min). This program was executed twice for each set of samples.

After dissolution, each sample was filtered (Whatman qualitative filter paper) and diluted in Milli-Q ultra-pure water ($\rho = 18{,}2$ MΩ cm), as needed. Mass fractions of Cu, Pb and Cd were determined in a GF-AAS system (AAnalyst800, PerkinElmer), using $NH_4H_2PO_4$ (0.5% m v^{-1})/ $Mg(NO_3)_2$ (0.03% m v^{-1}) chemical modifier and Milli-Q water for further dilutions. Each sample was measured twice, at least.

Quality control of results obtained by both INAA and GF-AAS was made through z-score evaluation of the mean results obtained for the analyzed reference materials. In general, results were considered in good agreement with the certified values. Z-score values showed that the results were within 95% confidence level for almost all analyzed elements, except for Ca, K and Sc, which were, then, excluded from further statistical analysis.

2.4. Grain size analysis

Aiming to evaluate particle size distribution of collected tunnel dusts, the <63 μm grain size subsamples were analyzed by Laser Diffraction Spectrometry (CILAS diffractometer, model 1064). Particle size distribution was calculated using Fraunhofer method.

2.5. Morphology analysis

Morphology analysis was performed by Scanning Electron Microscopy (SEM) (HITACHI TM3000 Tabletop Microscope, 15 kV) for subsamples of grain sizes < 2 mm and <63 μm, to evaluate differences between the most different sets of subsamples. Also, Energy-Dispersive X-ray Spectroscopy (EDS) was applied to these samples to evaluate the composition of the visualized structures (software Quantax 70).

2.6. Isotopic characterization

Isotopic signatures of Pb and Zn were determined by Thermal Ionization Mass Spectrometry (TIMS) and Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS), respectively. All chemical procedures were conducted using ultrapure acids, in a clean room laboratory (class 10,000) and laminar flow hoods (class 100) at the Center of Geochronological Research, at University of São Paulo (USP).

As it was not expected a change in the isotopic ratios between different grain size fractions, portions of approximately 50 mg of total (non-sieved) samples were weighted in Teflon beakers and submitted to acid digestion and further separation of Pb and Zn by ion exchange chromatography, according to validated methodology described in Souto-Oliveira et al. (2019), and references therein.

2.7. Statistics

In order to identify differences in mass fractions and isotopic ratios between different tunnels, sampling campaigns, sampling sites and dust grain sizes, as well as to identity the possible origins of the elements in the analyzed environments, statistical analysis were applied to mass fraction data.

All results are related to a significance level of $\alpha = 0.05$, unless otherwise stated, and were obtained after analysis of outlier values (Grubbs test). For calculations and graphs, the following softwares were used: IBM SPSS version 22, XLSTAT 2018.5, PAST version 3, Excel 2016, Origin 2019b and Tableau 2020.1.

3. Results

3.1. Mass fractions

The mean mass fractions results obtained for the 28 analyzed elements, by both INAA and GF-AAS, are shown in the Supplementary Table S1. For INAA results, associated uncertainties were determined considering contributions from the mass fractions and counting statistics of both samples and reference materials, as described in Zahn et al. (2015). For GF-AAS results, uncertainties were determined considering contributions from sample weighting, diluted and certified standard solutions preparation, digested solutions volume, spectrometer readings, repeatability and calibration curve, according to Budiman et al. (2009) and Ellison et al. (2009).

Ranges of element distribution in different mass fractions (μg g^{-1}) for both tunnels are shown in Fig. 1. It can be observed that most elements presented similar distributions.

Comparing our results found for some of the main potentially toxic elements to results reported in other studies (Table 1), which analyzed tunnel dusts or road dusts, the mean mass fractions were, in general, similar.

3.2. Grain size analysis

Grain size distribution analysis showed that the smallest fractions of dust contained, on average, 6.4% (JQ) and 13.0% (MM) of particulate matter of aerodynamic diameter smaller than 10 μm. Also, about 1.8% (JQ) and 3.7% (MM) of these values corresponded to particulate matter of diameter smaller than 2.5 μm. It is possible that these percentages are even higher, since sampling was manual and thinner fractions may not have been collected efficiently. The reduced diameter of these particles facilitates its penetration into respiratory tract, increasing the risk of health-related conditions.

3.3. Morphology analysis

In general, visual aspect of thicker grain size dust samples were very alike; the same occurred when comparing the thinnest fractions.

In the <2 mm samples, clean and smooth surface structures could be seen, showing more regular cleavage sharp edges and scratches, without the presence of agglomerates (Fig. 2). According to results of EDS analysis, these structures can be described as silicates, more probably quartz.

The lighter and brighter structures usually present elements of higher atomic number, mostly Fe and Zr. It can be assumed that these bigger structures are natural, derived from geological matrix, or that they are small pieces of concrete, in which metals of both natural and anthropogenic origins may adhere.

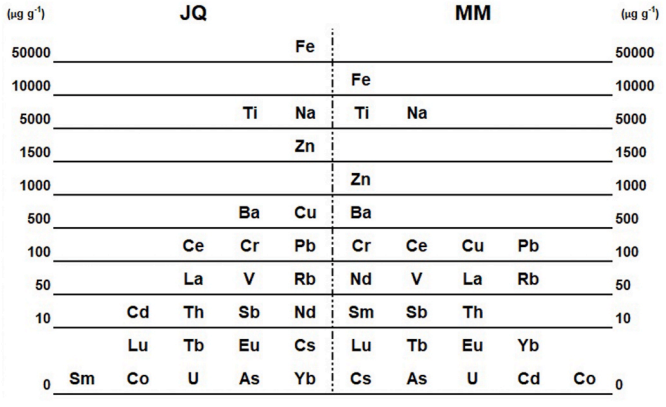

Fig. 1. Mean elemental mass fraction distribution for both tunnels.

In the <63 μm samples (Fig. 3), it is noticed the prevalence of darker, elongated and more granular structures, similar to those attributed to wear of tire in other studies (Adachi et al., 2005; Adachi and Tainosho, 2004; Oliveira and Bourotte, 2016).

These results were compared to data from similar studies found in literature, starting from 2000, which included samples related to vehicular emission, such as tunnel dusts, fuels, tires, road dust and particulate matter from industrial emissions from Cubatão area, the major industrial region located in southeastern coast of São Paulo state, 44 km far from São Paulo city.

3.4. Isotopic characterization

The $^{206}Pb/^{207}Pb$ isotopic ratios ranged from 1.1715 to 1.1791 and the $^{208}Pb/^{206}Pb$, from 2.0889 to 2.0961 (Table 2). Statistical analysis revealed no significant differences in results between tunnels or sampling campaigns. These results were compared to data from similar studies found in literature, starting from 2000, which included samples related to vehicular emission, such as tunnel dusts, fuels, tires, road dust and particulate matter from industrial emissions from Cubatão area, the major industrial region located in southeastern coast of São Paulo state, 44 km far from São Paulo city.

Fig. 4 shows a plot of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ isotopic ratios for all samples analyzed in this study and samples analyzed by Aily (2001); Gioia et al. (2008); and Souto-Oliveira (2017). These studies were the most important performed in São Paulo city focusing on local dusts and particulate matter, fuels and tires. The plot shows a very marked distinction between the isotopic ratios obtained for particulate matter from Cubatão industrial region, with more radiogenic signatures, vehicular emissions (fuel, road, dust and tire), and geogenic lead, represented by rocks and minerals sampled in USP site (Aily, 2001).

In general, Pb found in tunnel dust samples from JQ and MM tunnels are strongly related to vehicular emissions compared to any other source, since the isotopic ratios of these samples are closer to those obtained for gasoline, gasoline with additives, diesel, tire and road dust. All samples presented $^{206}Pb/^{207}Pb$ ratios between 1.17 and 1.18, which overlap the field of vehicular signatures, evidencing minor contributions of Cubatão and geogenic sources, which presented $^{206}Pb/^{207}Pb$ ratios close to 1.10 (Aily, 2001).

Although tetraethyl lead was removed from modern gasoline formulation, in a phase out process which started in the 1970s (and was concluded in 1989, in Brazil), Pb is found in gasoline and diesel, in a mean concentration of 1.6 μg g^{-1} (Aily, 2001; Souto-Oliveira, 2017). It is important to emphasize that, although Pb concentrations in gasoline are very low, the amount of Pb released to the environment can be very significant, due to the increasing number of vehicles in circulation in megacities.

Gioia et al. (2010) estimated that approximately 72% of Pb of vehicular origin found in atmospheric aerosol in São Paulo city could be derived from gasoline combustion, which is a very relevant contribution, in agreement with the dominant use of gasoline fueled vehicles in the city.

Results also suggest that tires are probably a source of Pb in the tunnels, since our dust samples have $^{206}Pb/^{207}Pb$ ratios that overlap isotope compositions reported for tires in the literature (Fig. 4). Lead derived from tire is released as a consequence of wear. Mean concentration of Pb in Brazilian tires is about 1.5 μg g^{-1} (Souto-Oliveira, 2017), markedly lower than those found for tire samples from London (11 μg g^{-1}) (Dong et al., 2017).

About the association between isotopic ratios of road dusts and the tunnel dusts analyzed in this study, it is important to highlight that soil resuspension contributes to recirculation of particulate matter emitted by vehicles after its deposition on the roads. According to CETESB, approximately 40% of all particulate matter in the atmosphere is derived from direct emissions of gasoline and diesel powered vehicles (CETESB, 2017a). So, road dust also contains particulate matter originated in

Table 1
Mass fractions (μg g^{-1}) of some potentially toxic elements: a comparison between this and other studies.

Reference	Country	Matrix	As	Ba	Cr	Co	Zn	Sb	Pb	Cd	Cu	V
Jiries (2003)	Jordan[a]	TD	–	–	28	–	333	–	1567	1.9	458	–
Ozaki et al. (2004)	Japan[c]	RD	2.4	–	–	–	–	1.4	–	–	–	–
Wang et al. (2006)	Taiwan[a]	TD	13	496	174	–	1290	13	220	–	163	67
Sysalova and Szakova (2006)	Czech Republic[a]	TD	25	–	182	–	1284	–	1762	2.0	–	–
Hjortenkrans et al. (2006)	Sweden[a]	RD	–	–	30	–	220	3.6	53	0.3	79	–
Duzgoren-Aydin et al. (2006)	China[a]	RD	–	356	79	13	586	–	240	2.4	176	23
		TD	–	853	85	8.7	1760	–	310	4.2	265	53
Spada et al. (2012)	USA[a]	TD	–	~300	~300	~30	~1150	~30	–	–	–	–
Valotto et al. (2015)	Italy[a;b]	RD	7.0	379	959	13	1495	51	678	2.7	1814	89
Valotto et al. (2018)	Italy[a;b]	RD	5.9	300	–	9.0	1700	21	102	1.2	295	–
This study	**Brazil[a]**	**TD – JQ**	**5.2**	**875**	**159**	**8.7**	**1891**	**36**	**269**	**9.5**	**998**	**60**
		TD – MM	**4.3**	**880**	**110**	**7.8**	**1066**	**14**	**105**	**5.4**	**240**	**74**

Note: TD: Tunnel dust /RD: Road dust /JQ: Jânio Quadros tunnel /MM: Maria Maluf tunnels /a: urban area /b: industrial area /c: countryside area.

vehicular emissions, which explains their similar Pb isotopic ratios.

Table 3 summarizes the results obtained in Zn isotopic analysis. A plot of $\delta^{66}Zn_{JMC}$ (‰) *versus* $^{206}Pb/^{207}Pb$ ratios for all samples analyzed in this study and samples analyzed in other studies (Dong et al., 2017; Gioia et al., 2008; Souto-Oliveira et al., 2018) is shown in Fig. 5. The $\delta^{66}Zn_{JMC}$ (‰) values varied from 0.13 to 0.26 (JQ tunnel) and from 0.08 to 0.17 (MM tunnel).

The $\delta^{66}Zn_{JMC}$ (‰) values are all positive indicating that Zn in sampled dusts are not derived from vehicular tailpipe emissions (Ochoa Gonzalez et al., 2016; Souto-Oliveira et al., 2018). According to data from Table 3, it can be noticed that samples from the exit portion of MM tunnels show a lighter Zn isotopic signature compared to samples from the entrance. Considering standard deviation associated with results, it is possible that these samples present some Zn contribution from tailpipe emissions, since their $\delta^{66}Zn_{JMC}$ (‰) values can be closer to zero.

Comparison of $\delta^{66}Zn_{JMC}$ values found in this study to those reported in literature for road dust, tires, brakes, atmospheric particulate matter (collected in tunnels and emitted in the industrial area of Cubatão) and gasoline burning, indicates that lighter isotopic signatures of Zn are verified in atmospheric particulate matter collected in tunnels ($-0.23 < \delta^{66}Zn_{JMC}$ (‰) < -0.06), collected in Cubatão area ($-0.59 < \delta^{66}Zn_{JMC}$ (‰) < -0.06) (Souto-Oliveira, 2017), and in gasoline burning ($-0.58 < \delta^{66}Zn_{JMC}$ (‰) < -0.18) (Gioia et al., 2008), which obtained the lowest values of $\delta^{66}Zn_{JMC}$ (‰).

However, values of $\delta^{66}Zn_{JMC}$ (‰) obtained in our dust samples are closer to those found, in the studies cited above, for tire, brakes and road dust (Fig. 6), indicating that these could be sources of Zn in these environments, in agreement to results reported in other studies (Almeida-Silva et al., 2011; Chellam et al., 2005; Dong et al., 2017; Hildemann et al., 1991; Lough et al., 2005; Ochoa Gonzalez et al., 2016; Spada et al., 2012; Sternbeck et al., 2002; Varrica et al., 2003).

Geogenic sources related to rocks, mineral dust and unpolluted soils from different places worldwide presented $\delta^{66}Zn_{JMC}$ values raging between −0.07 and + 0.5‰ (Schleicher et al., 2020). Isotopic signatures of geogenic Zn from São Paulo city was not assessed until now, which is an important target to be addressed in future studies.

3.5. Differences in mass fractions

Tests of normality (Shapiro-Wilk) showed that mass fractions values do not follow a Gaussian distribution for most of the elements, for both tunnels, indicating the use of non-parametric tests. In subsequent analysis, Mann-Whitney or Kruskal-Wallis/Dunn tests were used to identify significant differences between means, and correlations were expressed in terms of Spearman's rank correlation coefficients (r_s).

When comparing mass fractions between tunnels, for each analyzed element, statistically significant differences were found for 16 out of 25 elements: Ce, Cr, Cs, Eu, Fe, La, Lu, Nd, Rb, Sb, Sm, Tb, Yb, Zn, Cu and Pb. Results show that rare earth elements, U and Th, mostly associated with soil and other natural sources, presented higher concentrations in MM tunnels, while the opposite occurred to elements frequently related to vehicular emissions (Sb, Zn, Cu and Pb), that presented mean mass fraction values higher in JQ tunnel than in MM tunnels, pointing to a more important contamination in JQ tunnel.

This result can be attributed to the fact that JQ tunnel does not have a ventilation system and that it has more accentuated curves along its length, which may increase the usage of brakes and of particles released on its wear. In contrast, MM tunnels have a ventilation system and a straighter map design. These characteristics are believed to facilitate the dispersion of pollutants in MM tunnels.

Comparison of mean mass fractions between sampling campaigns showed statistically significant differences for only 2 elements (As and Na) in JQ tunnel and for 8 elements in MM tunnels (As, Ba, Cs, Eu, Th, Zn, Pb and V), evidencing that tunnels are indeed relatively closed environments that are not much affected by external weather conditions. Anyway, higher mass fractions were found mostly in winter, since winter is a more critical time of the year for pollutants dispersion (CETESB, 2017b).

Analyzing the differences in mean mass fractions between sampling sites (Mann-Whitney) for each tunnel, statistically significant differences were found for 14 elements (Cd, Ce, Co, Fe, La, Na, Nd, Pb, Sb, Sm, Tb, V, Yb and Zn) in JQ tunnel. For JQ tunnel, dusts sampled at the pedestrian sidewalk presented higher mass fractions for most of the traffic related elements (except for V) when compared to samples collected at the floor. In contrast, pedestrian sidewalk samples presented lower mass fractions for rare earth elements, U and Th, in comparison to floor samples.

These results can be explained since vehicular emissions are characterized by the emission of small and light particles, which can be more easily resuspended by vehicular traffic, accumulating in the sidewalk. Rare earth elements, U and Th presented higher mass fractions on the road pavement in this tunnel, pointing to a clear differentiation in the sources. These elements are mostly associated with geogenic sources, what may suggest a natural occurrence.

On the other hand, comparison of the mean mass fractions of dusts sampled at the entrance and exit portions of MM tunnels showed differences only for 4 elements (Fe, Pb, Rb and Ti). This is believed to happen since the entrance of the lanes of one traffic way is side by side with the exit of the lanes of the opposite traffic way, causing mutual influence between them. Therefore, differences found cannot be attributed to real differences between these sites.

Finally, comparison of mean mass fractions between grain sizes showed that statistically significant differences were found for almost all analyzed elements, exception made for Co, Fe and Pb (JQ) and As, Na and Pb (MM). Different grain sizes were compared at pairs – 2 mm/150 μm, 2 mm/63 μm, and 150 μm/63 μm – and the most pronounced differences were noticed for the pair 2 mm/63 μm, with higher concentrations found in the thinnest grain size dusts. This was an expected result, since the concentration of trace metals tends to increase as particle size decreases, due to the increase of superficial adsorption

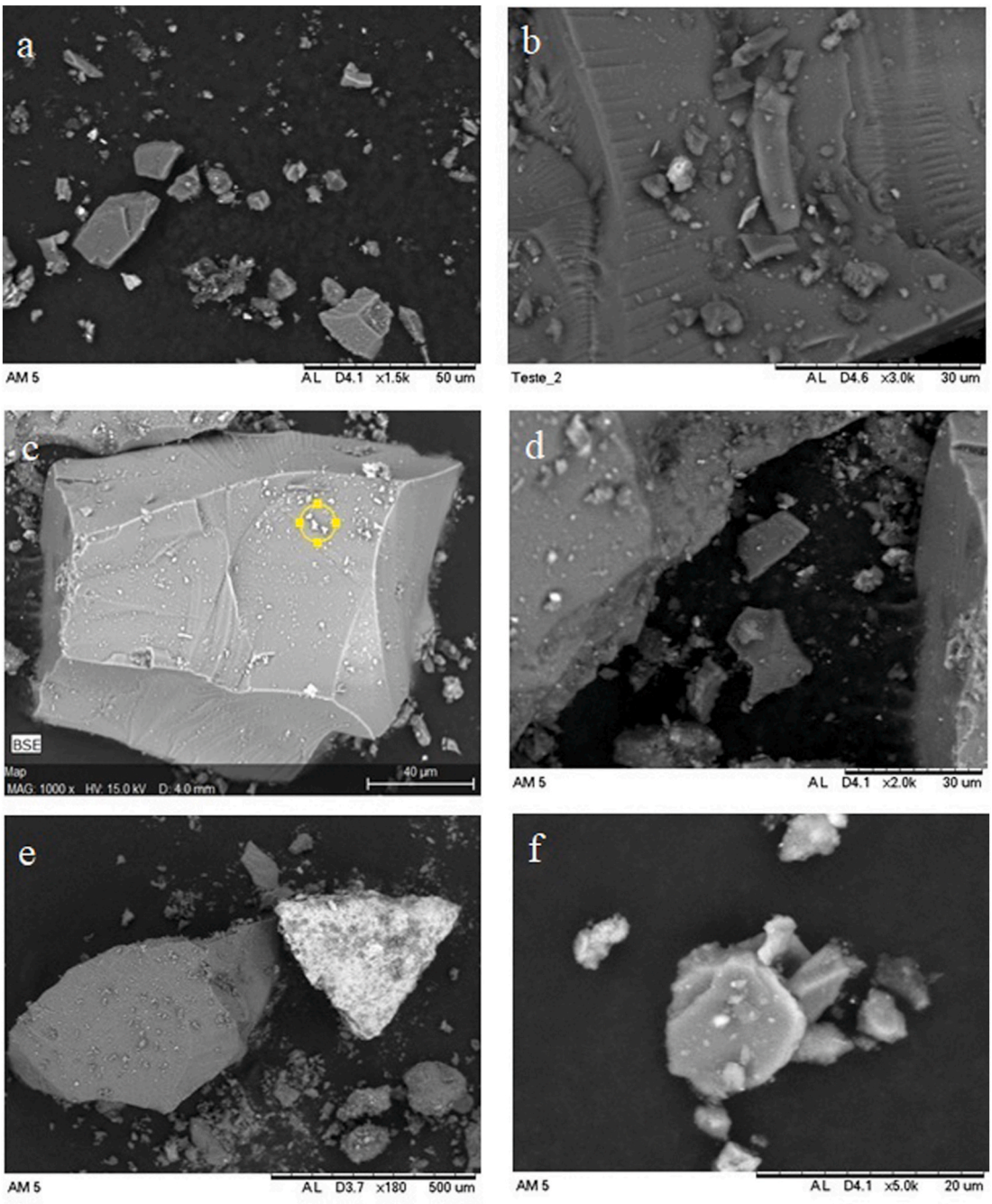

Fig. 2. Scanning Electron Microscopy images of <2 mm grain size dusts (JQ: a-d, MM: e-f) showing structures characterized by smoother surfaces, regular cleavage sharp edges and scratches.

(Daskalakis and O'Connor, 1995). All these results are summarized in Supplementary Fig. S1 to S4.

3.6. Enrichment factors and Cu/Sb ratios

Mass fractions determination alone is not sufficient to correctly evaluate the extent of contamination in different environments. Calculation of enrichment factors (EF) is a more precise way of estimating the anthropic contribution of chemical elements in environmental reservoirs. In this study, EFs were calculated for all analyzed elements, using mass fractions data obtained for the <63 µm grain size dusts, proven to be the most concentrated. The element Rb was used as normalizing element and the results were obtained in comparison to concentrations of Upper Continental Crust (UCC), described by Rudnick and Gao (2003) (exception made for Ti, which is not determined in this reference. It's EF was calculated based on UCC concentration values reported by Wedepohl, 1995). This element was chosen because it is one of the most used elements in enrichment factors determinations (Barbieri, 2016) and because it is a conservative element, which can be easily and accurately determined by INAA. Besides, Al and Fe, which are commonly used, can be originated in vehicles wearing processes. Results are shown in Table 4.

Using classification criteria described by Barbieri (2016), it can be seen that Cr, Zn, Cu, Cd, Pb and Sb are the most enriched elements, in both tunnels, but higher EFs were found for JQ tunnel. These results point to a significant anthropic contribution. Especially, these elements are frequently related to vehicular emissions in several studies (Dong et al., 2017; Ochoa Gonzalez et al., 2016; Souto-Oliveira, 2017;

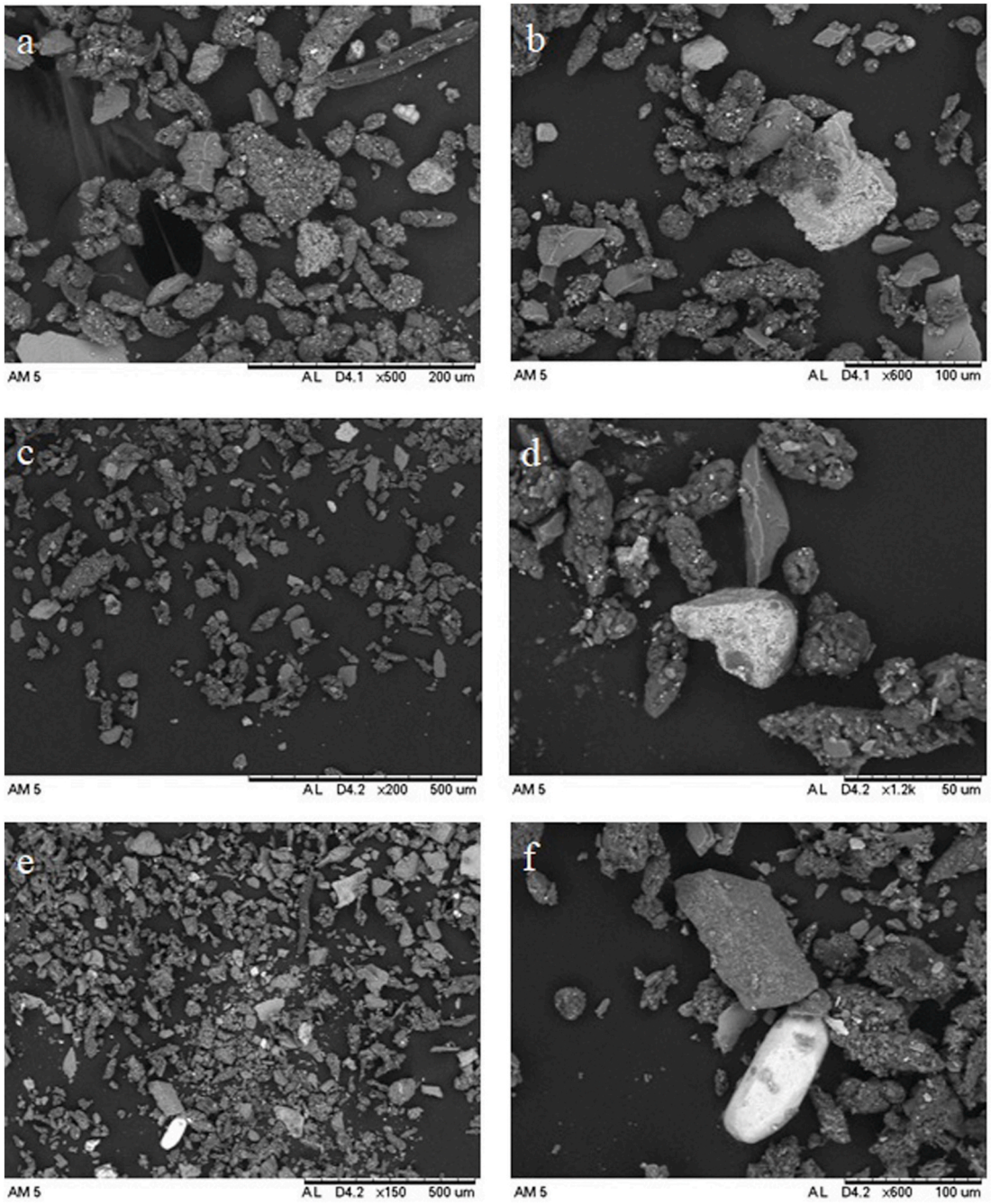

Fig. 3. Scanning Electron Microscopy images of <63 μm grain size dusts (JQ: a-d, MM: e-f) showing structures characterized by elongated dark granular surfaces, a characteristic of tire fragments. In f, a zircon can be seen.

Table 2
Mean isotopic ratios of Pb for non-sieved samples of dust from MM and JQ tunnels.

Tunnel	Site	$^{206}Pb/^{204}Pb$	2 sd	$^{207}Pb/^{204}Pb$	2 sd	$^{208}Pb/^{204}Pb$	2 sd	$^{206}Pb/^{207}Pb$	2 sd	$^{208}Pb/^{206}Pb$	2 sd
MM	Entrance	18.3914	0.0045	15.6182	0.0043	38.4604	0.0117	1.1773	0.0001	2.0913	0.0003
	Exit	18.4204	0.0056	15.6330	0.0056	38.4775	0.0162	1.1781	0.0001	2.0889	0.0004
JQ	PS	18.3108	0.0043	15.6174	0.0042	38.2522	0.0116	1.1722	0.0001	2.0891	0.0003
	RP	18.3556	0.0057	15.6116	0.0057	38.4737	0.0151	1.1756	0.0001	2.0961	0.0003

JQ = Jânio Quadros tunnel/MM – Maria Maluf tunnels.
Note: Isotopic ratios were corrected to mass fractionation of 0.12%/Da ($^{207}Pb/^{204}Pb$ ratio) and 0.13%/Da ($^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios).
2 sd - 2 σ standard deviations (n = 60)
Mean values of isotopic ratios of NBS-981 standard between January/2017 and December/2017:
value ± sd (1σ): $^{206}Pb/^{204}Pb = 16.893 \pm 0.006$; $^{207}Pb/^{204}Pb = 15.431 \pm 0.008$ e $^{208}Pb/^{204}Pb = 36.510 \pm 0.024$.
PS: Pedestrian sidewalk / RP: Road pavement

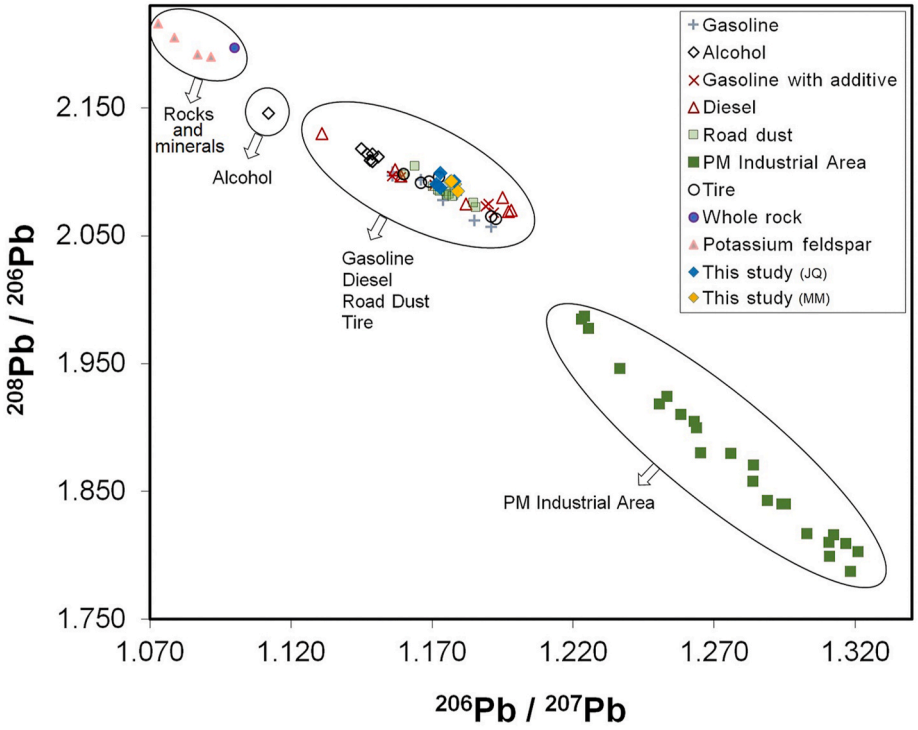

Fig. 4. Three-isotope plot ($^{208}Pb/^{206}Pb$ versus $^{206}Pb/^{207}Pb$) of main urban pollutant sources, showing contributions of vehicular traffic and of Cubatão industrial area. Additional data were obtained from Aily (2001); Gioia et al. (2008); Souto-Oliveira (2017).

Table 3
$\delta^{66}Zn_{JMC}$ (‰) mean values for non-sieved samples of dust from Maria Maluf and Jânio Quadros tunnels.

Tunnel	Site	$\delta^{66}Zn_{JMC}$ (‰)	2 sd
MM	Entrance	0.15	0.06
	Exit	0.10	0.07
JQ	Pedestrian sidewalk	0.14	0.03
	Road pavement	0.21	0.05

Souto-Oliveira et al., 2018; Valotto et al., 2015; Varrica et al, 2003, 2013).

Antimony presented enrichment that was classified as extremely high in almost all analyzed samples. It is an element frequently associated with wear of brakes and its components (Alves et al., 2015; Dong et al., 2017; Hjortenkrans et al., 2006; Ochoa Gonzalez et al., 2016; Ozaki et al., 2004; Sternbeck et al., 2002; Varrica et al, 2003, 2013). On average, this element showed the highest EF, followed by Cd, which presented EF classified as extremely high in all samples, from both tunnels. Cadmium can also be associated with wear of brakes. Another element frequently associated with wear of brakes is Cu. Copper presented significant enrichment particularly in JQ tunnel (EF_{av} JQ = 72 *versus* EF_{av} MM = 13), in which EFs were high or extremely high in all samples.

The same occurred for Zn. Lead showed to be the less enriched element (among traffic related elements), presenting significant enrichment for most samples and higher EFs in JQ tunnel as well. These higher enrichments in JQ tunnel, compared to MM tunnels, are believed to reflect the differences in ventilation systems, in engagement of brakes and in the road map design between the two tunnels, as cited previously.

Other elements, including rare earth elements, U and Th, exhibited moderate or deficient to minimal enrichment, which reflects the geologic background, rather than an anthropic contribution. Despite of having low EF values, Ti, significantly enriched in some samples, is a known component of road paints and brakes, which leaded us to attribute its presence to wear of paint and brakes, caused by weather and friction with vehicles during traffic.

In comparison, it can be noticed that the EFs obtained in this study for JQ and MM tunnels are similar or even lower than those found in other studies for some of the analyzed elements (Almeida-Silva et al., 2011; Alves et al., 2015; Dong et al., 2017; Rajaram et al., 2014). For Pb, results of EFs obtained for tunnel and road dusts in literature ranged between 5.1 and 100 (JQ_{av} = 14, MM_{av} = 5); for Cr, between 2 and 300 (JQ_{av} = 3, MM_{av} = 2); for Zn and Cu, between 3.3 and 100 (Zn JQ_{av} = 52, Zn MM_{av} = 24; Cu JQ_{av} = 72, Cu MM_{av} = 13); and for Sb, between 100 and 2000 (JQ_{av} = 214, MM_{av} = 52). In these studies, the enrichments were attributed, in general, to industrial and vehicular sources.

Analysis of brake pads, linings and other brake parts, as well of dusts released in its abrasion, showed the presence of particles containing Sb_2S_3, a compound employed as lubricant in substitution to asbestos in modern brakes (Iijima et al., 2007; Thorpe and Harrison, 2008). Especially in megacities, engagement of brakes is very frequent due to traffic congestion. Based on this, it is possible to verify if other traffic related elements are linked to a brake origin by means of a regression analysis related to Sb (Fig. 7), as suggested by Dong et al. (2017).

According to Fig. 7, values of determination coefficients (R^2) indicate good linear fit for the pairs Sb–Zn and Sb–Ba, for both tunnels, indicating that brakes can be a common source for these elements. Indeed, Ba is pointed as a tracer for wear of brakes in other studies (Dong et al., 2017; Valotto et al., 2015).

In JQ tunnel, Cd presented a moderate fit to linear model. Copper presented a poor fit, indicating that its presence in the analyzed dusts can be due to another source or even to brakes with different compositions: Cu is typically present in high quantities in low-metallic brakes, that are more commonly used for HDVs than in LDVs (Bukowiecki et al., 2009). In MM tunnels, Cd and Cu showed high R^2 values, indicating that brakes can be a source of these elements in these tunnels. This assumption is in agreement with other studies, which state that brakes are important diffusers of Cu in the environment (Hjortenkrans et al., 2007; Thorpe and Harrison, 2008). It is worth remembering that traffic, in MM tunnels, is characterized by the circulation of heavy-duty vehicles, like buses and trucks, that can undergo a more aggressive wear of

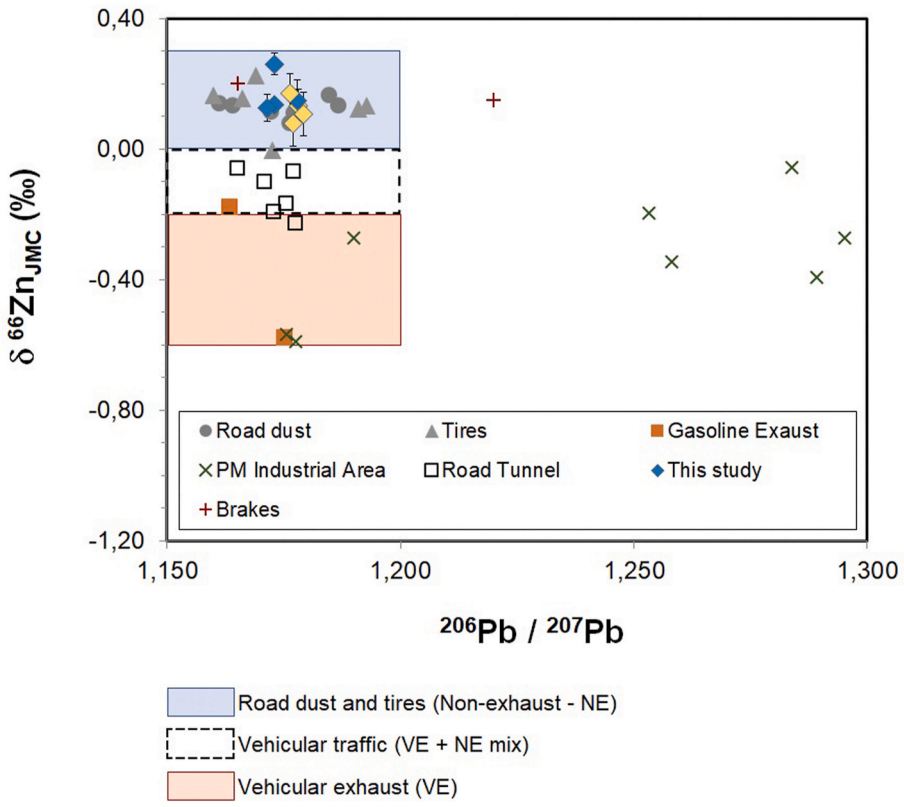

Fig. 5. Four-isotope plot ($\delta^{66}Zn_{JMC}$ (‰) versus $^{206}Pb/^{207}Pb$) of urban pollutant sources and aerosol from Cubatão industrial area. Red and blue fields represent the ranges defined for vehicular emission and road dust/tires, respectively, based on their isotopic signatures. Additional data were obtained from Dong et al. (2017); Gioia et al. (2008) and Souto-Oliveira (2018). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

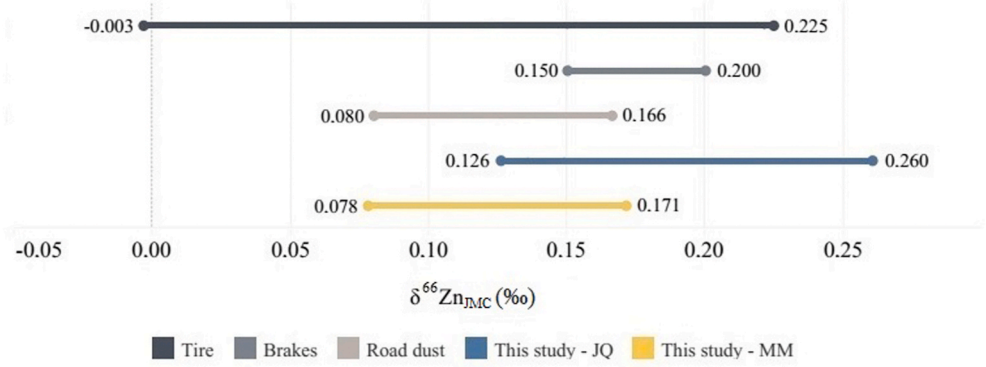

Fig. 6. Range of values of $\delta^{66}Zn_{JMC}$ found for samples of tire, brakes and road dusts in other studies (Dong et al., 2017; Gioia et al., 2008; Souto-Oliveira, 2018), and for tunnel dusts analyzed in this study. The overlapping bars are an indication that tire, brakes and road dusts are possible sources of Zn in the Jânio Quadros and Maria Maluf tunnels.

brakes, since they are heavier vehicles that have higher masses and linear momentum.

Ratios between mass fractions are also being used as a source signature for elements in the environment. In this study, Cu/Sb ratios were determined and compared to values found in literature (Adachi and Tainosho, 2004; Dong et al., 2017; Fabretti et al., 2009; Gietl et al., 2010; Hjortenkrans et al., 2007; Iijima et al., 2007; Lin et al., 2005; Sternbeck et al., 2002; Weckwerth, 2001).

The values most frequently found in these studies range between 4.6 and 9.1, while the values found in this study (mean ± sd) were 17.2 ± 1.7 (JQ) and 27.1 ± 18.7 (MM), values closer only to those found in Japan by Iijima et al. (2007) (18) and in United Kingdom by Dong et al. (2017) (28.7, on average). In studies performed in England and Kosovo, higher Cu/Sb ratios were also found (19.1 ± 7.0 and 34 ± 30, respectively). It should be noted that variation of the Cu/Sb ratio may be attributed to differences in the brake lining composition from a country/period to another. Nevertheless, higher values found in MM tunnels may indicate that traffic of heavy-duty vehicles can cause more wear of brakes, confirming our initial hypothesis. In addition, these higher values may indicate that there is another source of Cu in tunnels. These values may represent contributions from gasoline combustion and other fuels (Arditsoglou and Samara, 2005), and from metallurgical activities (Ochoa Gonzalez et al., 2016), respectively, plausible sources according to Nriagu and Pacyna (1988). In fact, fuel and gasoline combustion can be possible sources of Cu in the studied tunnels, where automobile sources are predominant.

3.7. Correlations

For JQ tunnel, element Sb is positively correlated to Zn ($r_s = 0.902$, p

Table 4
Enrichment factors (EF) for 22 analyzed elements.

Tunnel/Campaign	Site	Cr	Zn	Cu	Cd	Pb	Sb	Ba	V	As	Co	Th
MM/Winter	Entrance	1	25	11	83	7	51	2	1	0	1	1
MM/Winter	Exit	2	33	16	126	8	65	2	1	0	1	2
MM/Summer	Entrance	1	9	7	43	5	23	1	1	1	0	2
MM/Summer	Exit	2	27	17	139	1	71	2	1	3	1	2
JQ/Winter	RP	3	44	51	101	16	204	2	1	2	1	3
JQ/Winter	PS	3	75	111	541	19	323	3	1	2	1	2
JQ/Summer	RP	3	26	85	152	12	110	2	1	1	1	5
JQ/Summer	PS	2	64	39	363	10	218	2	1	1	1	1
Tunnel/Campaign	**Site**	**Nd**	**Sm**	**Eu**	**Tb**	**Yb**	**Lu**	**Cs**	**U**	**La**	**Ce**	**Ti***
MM/Winter	Entrance	2	3	2	2	1	2	1	1	2	2	2
MM/Summer	Exit	3	4	3	3	2	2	1	3	4	4	2
MM/Winter	Entrance	3	2	2	2	2	2	0	2	2	2	2
MM/Summer	Exit	4	4	3	2	3	3	1	3	4	4	3
JQ/Winter	RP	3	2	2	2	3	2	1	3	3	3	4
JQ/Summer	PS	4	3	2	2	4	3	1	4	4	3	6
JQ/Winter	RP	5	5	2	3	4	4	1	5	5	5	4
JQ/Summer	PS	1	1	1	0	1	1	1	2	1	2	2

Note: < 2 Deficiency to minimal enrichment, 2–5 Moderate enrichment, 5–20 Significant enrichment, 20–40 Very high enrichment, > 40 Extremely high enrichment, RP: Road pavement, PS: Pedestrian sidewalk, * Based on Upper Continental Crust concentration values reported by Wedepohl (1995).

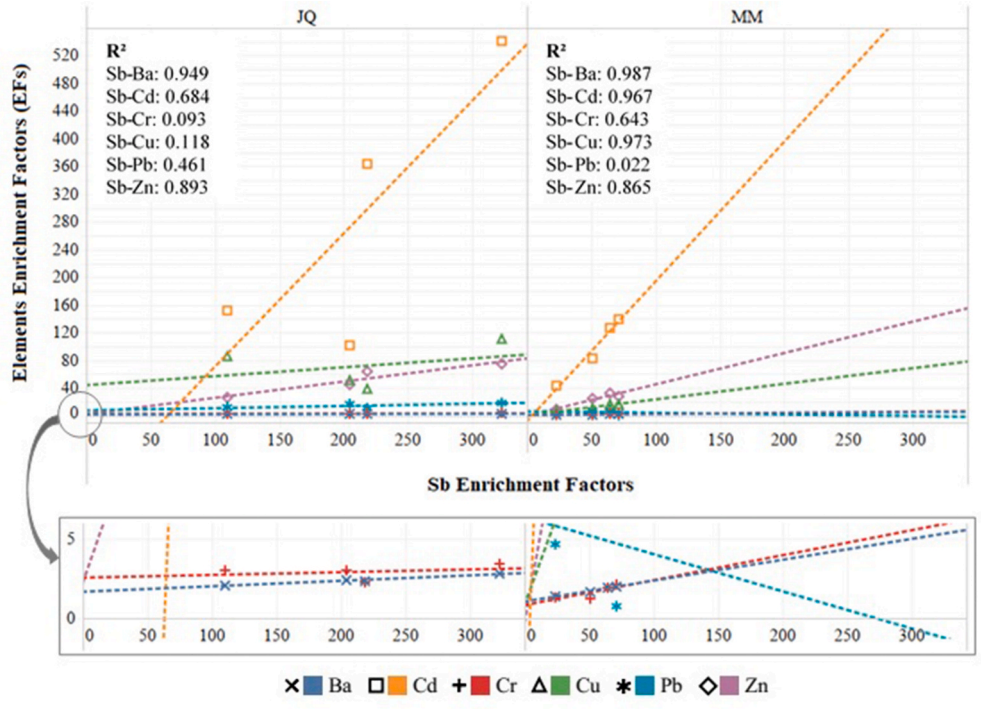

Fig. 7. Plots of enrichment factor values of Sb versus Enrichment Factor values of other traffic related elements. Detail shows the bottom region of the plots, highlighting Cr and Ba lines.

< 0.05) and Ba ($r_s = 0.791$, $p < 0.05$), indicating a common source for them, probably brakes (Chellam et al., 2005; Gietl et al., 2010; Thorpe and Harrison, 2008). Lead is correlated just to V ($r_s = 0.753$, $p < 0.05$), which can be associated with gasoline. Iron and Co are also correlated ($r_s = 0.855$, $p < 0.05$) – metallic alloys can be a possible source. Sodium is not correlated to any other element, which suggests a different and isolated source for Na in JQ tunnel.

For MM tunnels, besides the group formed by rare earth elements, U and Th, elements Fe, Ba, Co, Sb, Zn, Cu and Cd showed high correlations to each other, all higher than 0.7. The origin of these elements is assumed to be a mix between anthropic and natural contributions, since these elements also present high correlation values in relation to the former group. These results are summarized in Fig. 8.

It is worthy to highlight that La and Ce, besides of its natural origin, can also be originated in the wear of vehicle catalytic converters, which have these two elements in their composition, besides Pt and Pd, which were not analyzed in this study.

3.8. Principal Component Analysis

Principal Component Analysis (PCA) was applied to mass fraction data, for both tunnels, in order to identify or confirm identified groups of elements, indicative of a common source in these tunnels. PCA was calculated using correlation matrices and varimax rotation. For JQ tunnel, five components were extracted, and three for MM tunnels, according to Kaiser criterion. Kaiser-Meyer-Olkim measurement indicated good sampling adequacy, except for As, which was then excluded from further analysis. To analyze results, only loadings above 0.4 were considered.

For both tunnels, a component grouping elements related to natural/

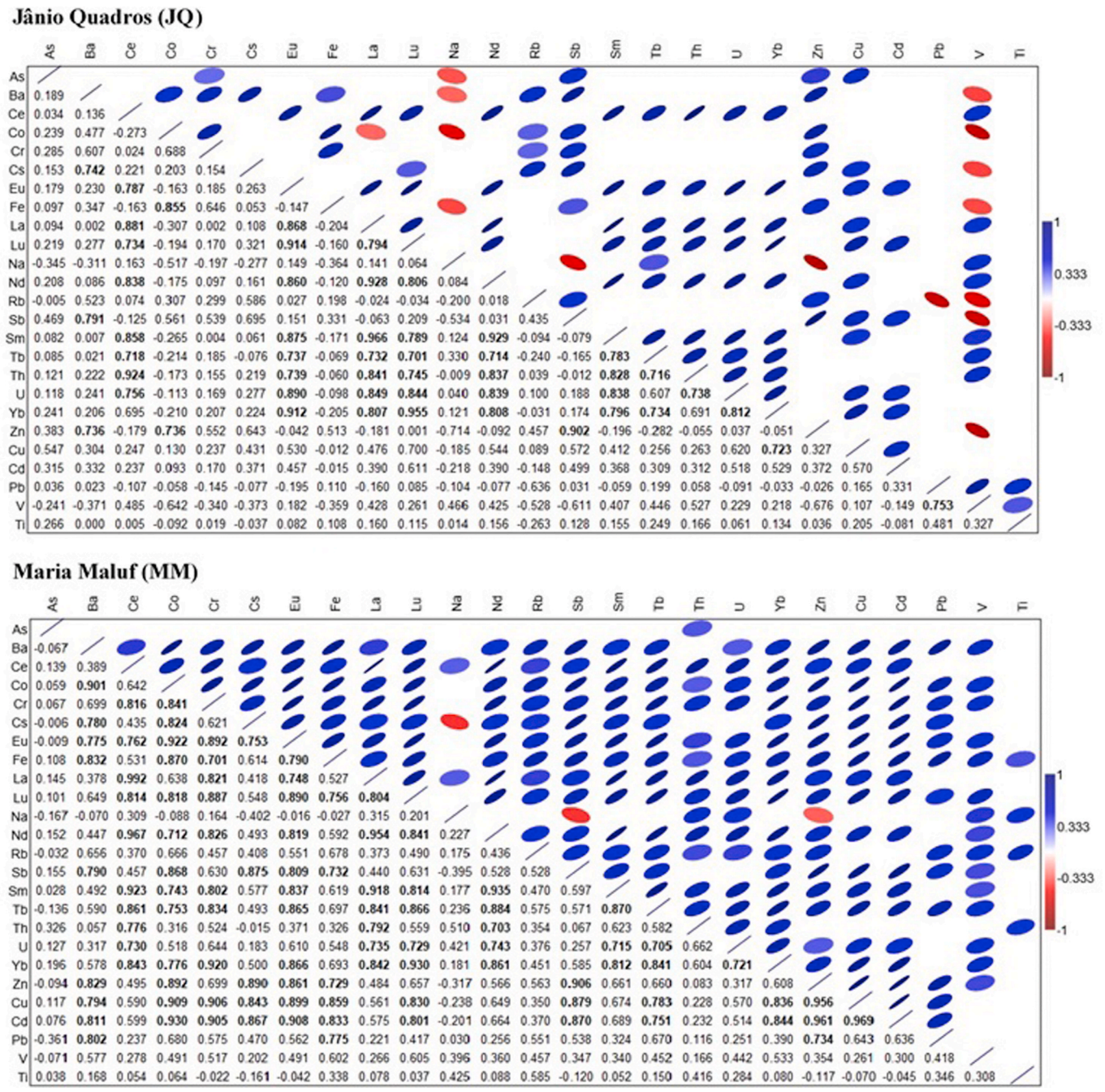

Fig. 8. Spearman's rank correlation coefficients (r_s) for pairs of elements, for Jânio Quadros and Maria Maluf tunnels. Ellipses show only statistically significant correlations. Correlations above 0.7 are highlighted. Ellipses eccentricities indicate the same as the color scale: the higher the eccentricity, the stronger the correlation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

geogenic sources was identified. It showed higher loadings for elements Ce, Eu, La, Lu, Nd, Sm, Tb, Th, U and Yb (JQ tunnel; 36.9% of variance) and Ce, Cr, Eu, La, Lu, Nd, Sm, Tb, Yb, Th and U (MM tunnels; 34.9% of variance). This component was named "Geogenic/Natural".

A second extracted component shows higher loadings for traffic related elements: Ba, Cs, Rb, Sb and Zn (JQ tunnel; 16.2% of variance) and Ba, Cd, Co, Cr, Cs, Cu, Eu, Fe, Sb and Zn (MM tunnels; 38.1% of variance). Table 5.

It is known that Ba, Sb and Zn are related to wear of brakes and that Zn is related to wear of tire as well, as previously discussed, which gives to this component a predominant vehicular characteristic (Chellam et al., 2005; Thorpe and Harrison, 2008; Valotto et al., 2015). Rubidium, Eu and Cs can indicate soil resuspension and Fe can be related to both sources. Thus, this component was named "Wear of tire and brake and soil resuspension".

The third extracted component also shows high loadings for traffic related elements: Pb, Ti and V (JQ tunnel; 9.3% of variance) and for Na, Rb, Pb, Ti and V (MM tunnels; 12.7% of variance). Lead, Ti and V are elements related to vehicular tailpipe emissions, associated with gasoline and/or diesel combustion (Alloway and Trevors, 2013; Andrade et al., 2012; Selim and Sparks, 2001). The presence of Pb and Ti can be attributed also to road paints (Adachi and Tainosho, 2004).

This component seems to be a mix of compounds originated in gasoline and diesel combustion (Pb, Ti and V) and in road surface abrasion (Pb, Rb and Ti). Sodium showed moderate correlation to Ti in correlation analysis ($r_s = 0.425$, $p < 0.05$), which can indicate soil resuspension

Table 5
Principal Component Analysis components loadings after Varimax rotation – Jânio Quadros and Maria Maluf.

	JQ					MM		
Element	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC1**	**PC2**	**PC3**
Ba	0.154	**0.792**	0.036	0.377	0.049	**0.856**	0.138	0.409
Ce	**0.918**	0.059	0.021	−0.120	−0.202	0.259	**0.944**	0.038
Co	−0.208	0.259	−0.117	**0.886**	0.105	**0.841**	0.438	0.237
Cr	0.183	0.209	−0.082	**0.831**	0.027	**0.602**	**0.709**	0.146
Cs	0.162	**0.917**	−0.061	−0.054	0.109	**0.902**	0.181	−0.113
Eu	**0.931**	0.075	−0.118	−0.016	0.194	**0.750**	**0.608**	0.116
Fe	−0.112	0.088	0.112	**0.908**	−0.102	**0.727**	0.340	0.485
La	**0.950**	−0.038	−0.006	−0.125	0.051	0.238	**0.946**	0.049
Lu	**0.869**	0.142	0.066	−0.068	0.373	0.531	**0.749**	0.199
Na	0.190	−0.426	−0.035	−0.378	−0.281	−0.499	0.445	**0.546**
Nd	**0.939**	0.022	0.045	−0.029	0.072	0.346	**0.902**	0.071
Rb	0.040	**0.687**	−0.503	0.138	−0.359	0.429	0.217	**0.685**
Sb	−0.013	**0.780**	0.002	0.386	0.430	**0.916**	0.212	0.002
Sm	**0.944**	−0.095	0.034	−0.071	0.062	0.428	**0.836**	0.061
Tb	**0.820**	−0.257	0.229	0.080	0.014	0.489	**0.744**	0.275
Th	**0.891**	0.113	0.208	0.011	−0.159	−0.167	**0.834**	0.285
U	**0.881**	0.143	−0.062	−0.010	0.233	0.129	**0.787**	0.306
Yb	**0.871**	0.064	−0.014	−0.055	0.358	0.485	**0.789**	0.158
Zn	−0.146	**0.738**	−0.035	**0.542**	0.276	**0.939**	0.248	0.055
Cu	0.464	0.352	0.134	0.037	**0.603**	**0.861**	0.437	0.014
Cd	0.360	0.212	0.052	0.067	**0.793**	**0.867**	0.434	0.028
Pb	−0.102	−0.094	**0.901**	−0.017	0.286	**0.668**	0.035	**0.552**
V	0.382	−0.402	**0.635**	−0.396	−0.178	0.290	0.245	**0.627**
Ti	0.117	0.074	**0.760**	0.059	−0.086	−0.167	0.045	**0.859**

Note: In general, for both tunnels, separated components presented higher loadings for: rare earth elements, U and Th, representing a natural/geogenic source; Ba, Cs, Rb, Sb; and Pb, traffic related elements and markers of soil resuspension; and V and Ti, indicating contributions from combustion of oil derived fuels and from road paints.

(Lawrence et al., 2013; Thorpe and Harrison, 2008). Another source of Na may be the burning of ethanol (Dancsak et al., 2014). This component, then, was named "Fuel burning and soil resuspension".

Two more components were extracted for JQ tunnel. The fourth component (13.6% of variance) shows higher loadings for elements Co, Cr and Fe, and a minor loading for Zn. These elements are characteristic of the composition and/or treatment of steel and another metal alloys, which can be coming from wear of vehicular components or from the wear of the metallic covering structures of JQ tunnel walls. Because of that, this component was named "Steel and metal alloys".

The fifth component (8.6% of variance) presented higher loadings for Cd and Cu, indicating a common source for these elements. It is known that Cu is a brake related element (Johansson et al., 2009; Straffelini et al., 2015; Thorpe and Harrison, 2008), but it didn't group with elements of the second component, contrary to what would be expected. So, Cd and Cu are believed to come from a vehicular source (probably brakes), since it is the predominant source in the studied environment, but it could not be fully identified. This component was named "Unidentified vehicular source".

Results of PCA confirmed the results obtained in isotopic characterization, correlation and EF analysis, increasing the confidence of the results. Combined conclusions about the elements and their sources, obtained from all analysis performed, are summarized in Table 6.

Table 6
Summary of elements and respective sources, according to analysis performed in this study.

Main sources	Elements
Gasoline/Diesel	Pb, Ti, V
Tire	Pb, Zn
Road paint	Pb, Ti
Brakes	Sb, Ba, Zn, Cu, Cd
Metallic structures	Fe, Co, Cr, Zn
Natural/Geogenic	U, Th, REEs, Rb, Cs

4. Conclusions

This study aimed to determine potentially toxic elements concentrations in tunnel dusts of São Paulo megacity, focusing on describing their possible sources. The analysis of elements such as Pb, Zn, Cu, Sb and Cd revealed an important accumulation of these elements in these environments, pointing to vehicular traffic related sources.

Statistical analysis of mass fraction results indicated significant differences in mean values between tunnels for most elements. JQ tunnel samples indicated more contamination, since presented higher means for traffic related and potentially toxic elements, while, in MM tunnel, the highest means were found for elements related to a natural/geogenic origin. The <63 μm grain size fractions presented the highest mean mass fraction values, for almost all analyzed elements.

Results of isotopic analysis, in comparison to results obtained from previous studies, associated Pb to the burning of gasoline and diesel and to wear of tire ($1.1715 < {}^{206}Pb/{}^{207}Pb < 1.1791$), and Zn to wear of brake and tire, as well ($0.08 < \delta^{66}Zn_{JMC}$ (‰) < 0.26).

Enrichment Factors evaluation indicated that traffic related elements are highly enriched inside the tunnels, especially Sb, Cu and Cd. Combined results of PCA and correlation analysis confirmed some previous results from isotopic characterization and indicated, for both tunnels, the presence of a natural source for some elements (rare earth elements, U and Th, mostly) and at least one anthropic source, traffic related as expected, comprising especially Sb, Zn, Ba, V and Pb. Lead, Ti and V are attributed to burning of fossil fuels; Pb and Ti to road paints; and Pb, alone, to tire wear. Antimony, Ba, Zn and Cu are probably derived from wear of brakes; and Zn, alone, also from wear of metallic structures and tires.

Scanning electron microscopy imaging revealed that the smallest fractions of dust samples presented elongated dark granular structures, compatible to tire fragments, in a comparative analysis with other studies found in literature, supporting results suggested by isotopic and statistical analysis.

These results indicate that the studied tunnels are negatively affected by anthropic activities, vehicular traffic being the main source of potentially toxic elements, which can be harmful to human health.

Vehicular emissions, in the last decades, are being targeted and are receiving attention in governmental emission control policies. However, these policies focus mostly on emissions derived from fuel combustion, disregarding contributions from non-exhaust sources, like the wear of road and vehicle components, which imposes practical limitations to the reduction of particulate matter concentrations in atmosphere.

It is important to highlight that the identified contamination is not restricted to tunnels, since, especially in megacities, vehicular traffic reaches almost the entirety of urban spaces.

CRediT authorship contribution statement

Renata Mendes Nory: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Ana Maria Graciano Figueiredo:** Conceptualization, Methodology, Investigation, Resources, Writing - review & editing. **Carlos Eduardo Souto-Oliveira:** Methodology, Validation, Formal analysis, Investigation, Writing - review & editing. **Marly Babinski:** Methodology, Resources, Supervision, Funding acquisition.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2021.118188.

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