Increase in the Platinum Group Elements content in road dust from São Paulo city, Brazil, due to exhaust emissions from vehicle catalytic converter, over a 10-year period

***Marcos, Hortellani M.A.*[*a] and Jorge, Sarkis J. E. S.*[a]**

1 *Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN), Av. Lineu Prestes, 2242, São*
2 *Paulo, SP 05508-000, Cidade Universitária, 05508-000 São Paulo-SP, Brazil*

*e mail: mahortel@ipen.br

http://orcid.org/0000-0003-3364-0648

Abstract

Platinum Group Elements (PGEs) are widely used as catalysts in vehicle emission reduction, and road dust is a primary receptor for PGE releases. However, the determination of PGEs in these samples by ICP-MS is affected by matrix interferences, and measurement and sampling uncertainties are often overlooked. This study presents the first PGEs measurements in road dust samples from São Paulo city avenues, including matrix separation and estimation of measurement uncertainty includes analytical and sampling uncertainties. Measurement uncertainties for PGEs ranged from 12.3% to 19.5%, and analytical uncertainty ranged from 2.25% to 5.64%. PGEs concentrations: Pt (2.6 - 227 ng g^{-1}), Pd (16.3 - 1875 ng g^{-1}), Rh (2.02 - 257 ng g^{-1}). Three methodologies were applied to evaluate the PGEs and other metals contamination in 54 road dust samples (< 100 μm fraction) collected in 2008, 2016 and 2018 at 18 sites with high (17 sites) and low (1 site) volumes of traffic. Metal pollution index (MPI), enrichment factor (EF) and statistical analyses. These evaluations suggested that PGEs and Mo contamination were originated from automobile exhaust emissions. Cu and Zn contamination seemed to have been caused by tires and brakes vehicular sources (non-exhaust emissions), but Ni and Pb contamination seemed from non-vehicular sources. Only rare earth elements are mostly associated with crustal source. The changes in PGE ratios stemmed from decreased Pt and increased Pd concentrations. A considerable portion of these metals in road dust is bioaccessible and poses health risks to the population near high-traffic density avenues, through ingestion, dermal contact, and inhalation pathways.

Keywords: Road dust, Platinum group elements, Metal contamination, Rare earth elements, matrix separation, ICP-MS, enrichment factor.

1. Introduction

São Paulo is the largest City in South America, with a population of 11.45 million in 2023 (IBGE-Population, 2023). In October 2008, the city reported 5.5 million vehicles, 7.8 million in October 2016 and 8.2 million in September 2018. About 70% of the total used catalytic converters (IBGE-Cities-Brazil, 2023).

The use of vehicle catalytic converters to reduce emissions of NOx, CO and hydrocarbons (HC) to below legislated limits in Brazil started in 1992-1993. But these catalytic converters went into effect in 1996 (Morcelli et al., 2005).

Canada, the United States and Japan have used the catalytic converters in car exhaust systems containing Pt, Pd and Rh, since 1976 (Barbante et al., 2001). In the European Union (EU), all new cars registered from January 1st, 1993, have been fitted with catalytic converters to reduce these emissions (Motelica-Heino et al., 2001).

The catalysts contribute to the improvement of air quality, but cause a significant increase of environmental contamination. The high temperatures, vibrations, abrasion and attrition bring about the release of PGEs (nanometer size range particles and associations with other metals as part of the coating to which they are connected in the converters) to the environment (Spada et al., 2012; Ravindra et al., 2004; Whiteley & Murray, 2003, 2005).

PGE proportions in catalytic converters vary globally and in different years, due to design and fuel differences. Road dusts are considered, the primary receptor for PGEs in urban environments (Spada et al., 2012). It is important to verify the different proportions of PGEs in São Paulo, Brazil, between 2008 and 2018, and comparison with other cities around the world.

Studies showed that the Pd is more soluble and bioavailable than Pt and Rh (Jarvis et al., 2001; and Moldovan et al., 2001). Platinum can enter the food chain by accumulation in plants (Verstraete et al., 1998).

It also describes, in broad term, that Pt (II), Pt (V) and Pd (II) have been found to be toxic on a cellular level comparable or even exceeding the toxic effects of Cd(II) and e Cr (VI) (Kalavrouziotis & Koukoulakis, 2009). On the other hands, the Rhodium plays no natural biological role and is harmless to humans (Birke et al., 2018).

A Daphnia toxicity test, used by (Zimmermann et al., 2017), showed that the PGEs toxicity to Daphnia magna decreased in the order Pd > Pt >> Rh with e.g. LC50(48 h) values of 14 mg/L for Pd, 157 mg/L for Pt and 56,800 mg/L for Rh.

PGEs levels in road dust samples from São Paulo city have not been determined yet. However, significant increases in PGE levels were observed in roadside soils from an important road in the State of São Paulo, attributed to catalytic converter exhausts (Morcelli et al., 2005). Additionally, urban soils collected next to seven main avenues with high traffic density in the metropolitan region of São Paulo also demonstrated a relationship between the PGEs and catalytic converter abrasion (Ribeiro et al., 2012).

PGEs determination in environmental samples by ICP-MS involves matrix interferences. Correct measurement requires removing interferences through anionic or cationic-exchange resin (Spada et al., 2012), Tellurium coprecipitation (Gomez et al., 2003), or mathematical correction (Moldovan et al., 1999). Ion-exchange removes interferences based on the highly stable anionic chloro-complexes of PGEs, separating matrix elements in stable cationic form or weaker anionic species (Kovacheva & Djingova, 2002). PGEs chloro-complexes are separated by elution on cationic exchangers, retaining other matrix elements (Lesniewska et al., 2006); or selectively retained on anion exchange, subsequently eluted (Hann et al., 2001; and Kanitsar et al., 2003).

Mathematical correction, on the other hand, is usually a tedious task since it requires determining and mathematically correcting all interfering species (Moldovan et al., 1999).

This study's objective was to investigate, for the first time, PGEs concentrations (Pt, Pd, Rh) in São Paulo city's road dust. A cation exchange resin was used for matrix separation, eliminating isotopic interferences in PGEs, and the other elements were examined without matrix separation. To increase confidence in the results and support informed decision-making regarding metallic pollution, estimations of measurement, analysis, and sampling uncertainties were conducted. The evaluation of metal pollution employed the metal pollution index (MPI), enrichment factor (EF), and statistical analyses to explore the impact of catalytic converters on PGEs and potential sources of other elements in road dust samples across three sampling campaigns.

2. Experimental

2.1. Study area and road dust sampling preparation

A total of 54 road dust samples were collected during three sampling campaigns to investigate variations in the concentration, ratio, and proportion of platinum, palladium, and rhodium. Specifically, 18 samples were collected during the dry winter period in July 2008 (1st sampling), another 18 samples were collected during the dry winter period in July 2016 (2nd sampling), and the remaining 18 samples were collected during the dry winter period in July 2018 (3rd sampling).

Figure 1 shows the locations of the road dust samples selected for this study, which were collected from ten avenues characterized by high traffic density, as well as one location with low traffic volumes known as IPEN-USP Parking, situated in São Paulo city.

Among these avenues, the Marginal Pinheiros and Marginal Tietê Avenues are adjacent to the city's two primary rivers, named Pinheiros and Tietê Rivers. These avenues are characterized by a consistently high speed of approximately 90 km/h and no traffic lights. According to a previous study on vehicle flow conducted by Ribeiro et al. (2012), in 1996, Marginal Tietê had an average of 400,000 vehicles per day, while Marginal Pinheiros had

around 300,000 vehicles per day. Another significant avenue in São Paulo is the 23 de Maio Avenue, which serves as a connection between the North and South regions of the city, with a steady speed ranging from 50 to 60 km/h and no traffic lights. The remaining avenues included in this study are also key roadways in São Paulo city, featuring traffic lights, high-density stop-and-go traffic patterns, and a speed limit of 50 km/h.

The samples were collected within areas measuring approximately 1-2 m² (0.3 x 3 or 5m), forming a rectangular grid. A plastic dustpan and brush were used to collect the samples from the gutters of streets and avenues. Subsequently, the samples were transferred to air-tight polyethylene bags for transportation to the laboratory, where they were stored at room temperature.

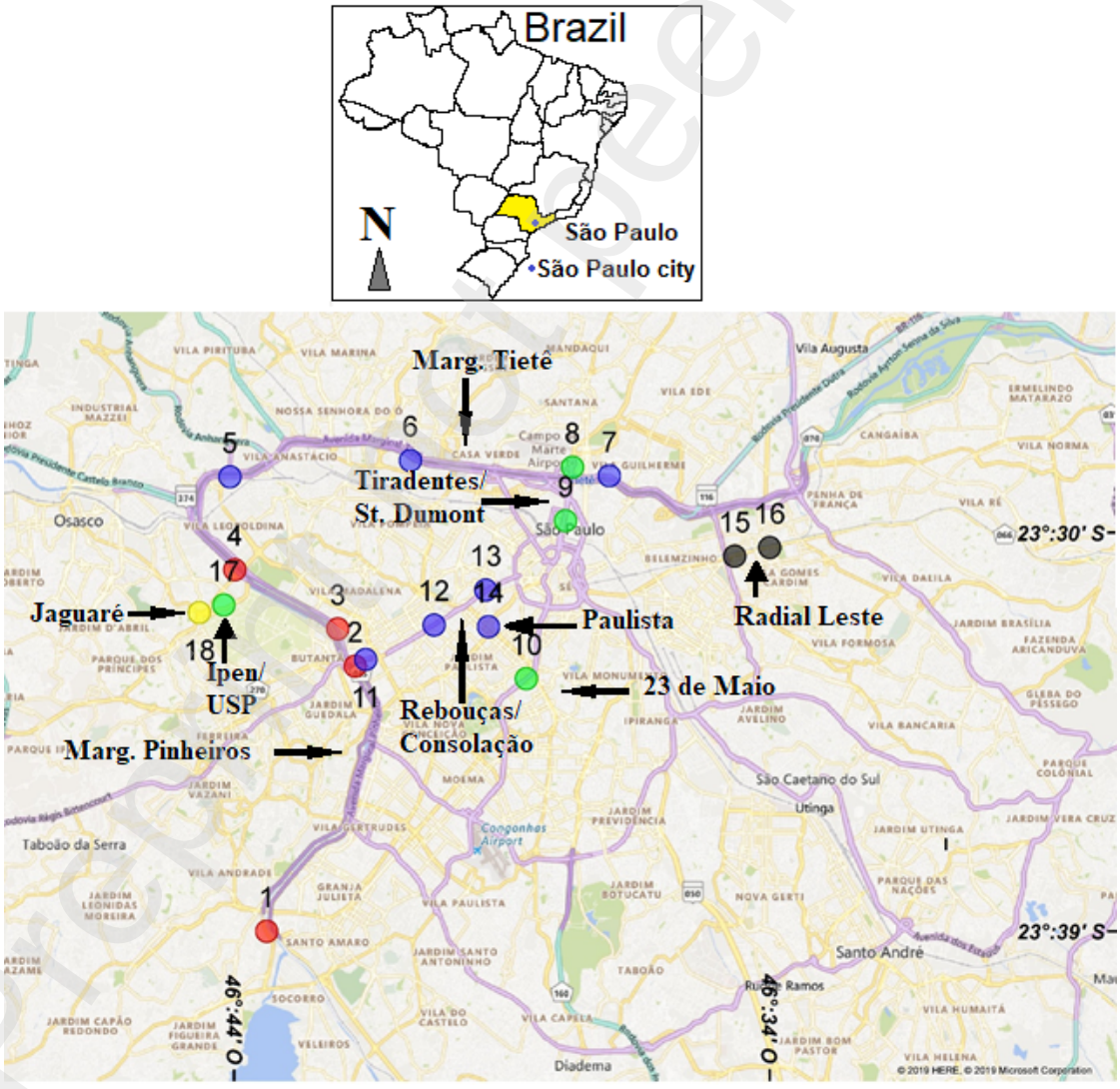


Fig. 1. Map of the study area and location of the sampling sites.

Prior to conducting the analysis, the samples were dried at 80 °C and sieved through meshes with sizes of 2 mm, 1 mm, 150 µm, and 100 µm. The fraction with a diameter smaller than 100 µm was repeatedly quartered until a sample weight of approximately 2 g was obtained. Subsequently, the sample was ground for 10 minutes in a 50 mL centrifuge tube using two plastic balls (Spex) to enhance homogeneity. It is important to note that this fraction, with a diameter smaller than 100 µm, can easily become airborne and inhaled during breathing (Ferreira-Baptista & De Miguel, 2005). This specific fraction was then used to determine the PGEs and other metals.

The samples collected in 2008 were archived and reanalyzed alongside the newly collected samples to ensure that any observed increases in PGEs were not due to changes in analytical methods.

2.2. Analytical methods

2.2.1. Sampling preparation by microwave digestion

The samples were digested using a procedure similar to Spada et al.(2012). Digestions of samples were performed in a programmable 1030 -1800 W microwave system (MARS 6, CEM Corp., Matthews, NC) using Xpress 55 mL Teflon vessels rated at 200 ºC. Conditions inside the vessels were monitored and controlled in every vessel with an infrared sensor. A known quantity (200 - 400 mg for road dust samples, < 100 µm fraction, and for certified material BCR 723, or 100 mg for certified material SRMs 2556 and 2557) was placed into a Teflon vessel, 8 mL of *acqua regia* was added and left for 5 min and loosely capped. The control points were 200 ºC and 300 psig with a ramp time of 20 min. and dwell time of 20 min.

After cooling, each vessel's content was transferred to a 50-mL centrifuge tube and the volume was increased to 20 mL for samples and BCR, and to 40 mL for SRMs by adding ultrapure water (Milli-Q).

After decanting or centrifuging the residues from the vial content, the digestion samples were divided into two parts: one for the determination of Pt, Pd, and Rh, and another for the analysis of the remaining elements (two sub-samples). To determine PGEs, a 10 mL aliquot was evaporated almost to dryness on a hot plate at approximately 80ºC in a 50 mL Teflon beaker. The resulting residues were dissolved in 2 mL of concentrated HCl and heated again until almost dry. This treatment was repeated twice more to adequately remove HNO3. The ultimate residue was dissolved in 10 mL of 0.5M HCl and then subjected to cation exchange elution.

2.2.2. Separation on cation-exchange resin

The interfering species were chemically removed by cation-exchange resin. Before each use, Dowex 50WX8, 200-400 mesh resin was cleaned using a procedure similar to (Spada et al., 2012). Each Poly-Prep column was prepared with 3.5 mL of cleaned resin in 0.5M HCl. The resin was first equilibrated with 10 mL of 0.5M HCl and the eluent was collected in a polyethylene tube used as the column background sample preparation. Then, this tube is replaced with a sample tube and 2 mL of sample in 0.5M HCl was added to the column. The eluent was collected at a flow of 0.2 mL min^{-1}. After the samples passed through the column, the resin was rinsed by adding 2 mL 0.5M HCl, collected in the same tube. Then, 0.5 ppb of In (internal standard) was added and the final volume was made up to 5 g, and the PGEs concentrations were determined by ICP-MS.

2.2.3. Nexion 300D-ICP-MS

A Nexion 300D ICP-Mass Instrument (Perkin Elmer) was used to determine PGEs. The isotopes ^{194}Pt, ^{195}Pt, ^{196}Pt, ^{104}Pd, ^{105}Pd and ^{103}Rh were used to PGEs quantification. The same results were obtained to the multi-isotopic elements Pt and Pd after removing the interfering species.

The rare earths elements analyses, Ce, La, Nd, Pr, Sm, Pb and Mo concentration were determined by ICP-MS, after 200 times dilution of sub-samples without ion-exchange separation.

A Nexion 300D ICP-MS daily optimization was performed using a 1µg L^{-1} NexIon Setup solution (PerkinElmer), consisting of Be, Ce, Fe, In, Li, Mg, Pb, and U in 1% HNO_3. Formation of oxides ($^{156}CeO^+$ / $^{140}Ce+ <= 0{,}035$) and doubly charged ions ($^{70}Ce^{++}$ / $^{140}Ce <= 0.035$) were minimized by adjusting the nebulizer gas flow. Auto lens voltage were adjusted to maximize ion transmission based on $^{9}Be > 3000$, $^{24}Mg > 20000$, $^{114}In > 50000$, and $^{238}U > 40000$ cps. Under typical operating conditions, sensitivities for ^{9}Be, ^{24}Mg, ^{115}In, and ^{238}U were approximately 9000, 70000, 70000, and 40100 cps, respectively. Calibration was performed with multi-element standards contained Pt, Pd and Rh and interfering elements (Y, Rb, Sr, Zr, Mo, Cd, Sn, Sb, Pb, and Hf) were also monitored. Cleaning procedures were used for Glass Nebulizer, Cyclonic Spray chamber, Quartz Ball Joint Injector, Nickel cones and Torch when ^{115}In sensitivity was decreased by ~25%.

2.2.4. Absorption Spectrometer

A fast sequential atomic absorption spectrometer Varian, model Spectr-AAS-220Fs was used to determine the Zn, Cu and Ni concentration in the remaining sub-samples without ion-exchange separation, using the flame mode, with deuterium lamp for background corrections. (Hortellani et al., 2013).

2.2.5. Reagents and materials

All reagents were of analytical grade, (HNO_3 sub boiling and HCl sub boiling). It was used high purity water, of 18 MΩ cm^{-1} resistivity via Synergy System by Millipore Corporation. The PGEs, rare earths elements and Mo stock solution (1000 mg L^{-1}) were acquired (Spex), the Cu, Ni, Pb, Zn stock solution (1000 mg L^{-1}) was acquired (Merck), a cation-exchange resin (Dowex 50WX8 200-400 mesh, Sigma–Aldrich, Saint Louis, MO)

were used to chemically separate. The resin was contained in 12 mL Poly-Prep chromatography columns (2 mL bed volume with 10 mL reservoir, Bio-Rad Laboratories Inc., Hercules, CA).

^{115}In was used as an internal standard for all determination to correct instrumental drift or non-spectral interferences because of their low abundance in road dust, similar atomic mass, and broadly similar chemical and physical properties to those of the PGEs.

The standard reference materials used consisted of BCR-723 (road dust; European Commission, Joint Research Centre; Institute for reference material and measurement-IRMM), "Used auto Catalyst" (SRM 2556 and SRM 2557), in powder form, NIST, with a certified content of Pt, Pd and Rh, and SRM 2709 San Joaquin Soil –NIST.

2.3. Quantification of uncertainties

Uncertainty in measurement can be estimated by two components: the uncertainty derived from sampling and the uncertainty derived from the analytical process. The measurement uncertainty (RSD) is given by Eq. (1)

$$S_{measurement}^2 = S_{sampling}^2 + S_{analytic}^2 \quad (1)$$

2.3.1. Analytical uncertainty

The analytical uncertainty was estimated using a modeling approach (Ramsey and Ellison, 2007). The sources of uncertainty were identified, quantified and combined according to Ellison et al. (2002).

2.3.2. Sampling uncertainty

The sampling uncertainty ($S_{sampling}$) was calculated by the relative standard derivation, RSD ($S_{measurement}$), for the steps in the single split design and relative range statistics (Magnusson et al. 2020). To use this single split design, six road dust samples (R1 to R6) were carried out in August 2018, at collection site - 13 (Consolação Avenue). The choice of the point was because it was one of the sites, previously sampled, with highest values of

PGEs. Each one of the six samples was considered a sampling target analyzed in duplicate (sample A and sample B) (Tessari-Zampieri et al., 2022) (see Supplementary Information for details). This single split design gives the measurement uncertainty (RSD).

Then, the sampling uncertainty $S_{sampling}$ can be calculated using Eq. (2), by rearranging Eq. 1,

$$S_{sampling} = \sqrt{S^2_{measurement} - S^2_{analytic}} \quad (2)$$

2.4. Assessment of PGEs contamination

Three approaches evaluated the PGEs, earth rare elements and Mo, Zn, Cu, Pb, and Ni results: the Metal Pollution Index (MPI), the Enrichment Factor (EF) and Statistics Analyses.

2.4.1. Metal Pollution Index

The metal pollution index (MPI) (Eq. (3) (Usero et al., 1996; Okafor & Opuene, 2007), was applied to compare the total content of PGEs (Pt, Pd and Rh) between the 18 points from the São Paulo city avenues.

$$MPI = (C_{Pt} \times C_{Pd} \times C_{Rh})^{1/3} \quad (3)$$

Where:

C_{Pt}= concentration value in ppb of the platinum.

C_{Pd}= concentration value in ppb of the palladium.

C_{Rh}= concentration value in ppb of the rodhium.

2.4.2. The Enrichment Factors

For the estimation of anthropogenic PGEs emissions in road dust samples, it was calculated the enrichment factor (EF) of Pd, Pt and Rh and the other elements with respect to Sm element's crustal concentrations, because Sm is a conservative element (Wedepohl, 1995).

EF is a useful tool proposed buy Buatmenard & Chesselet (1979) to differentiate the metals source between anthropogenic and crustal concentration.

238 The EF is calculated using Eq. (4):

239 $$\boldsymbol{EF} = \frac{(C_{PGE}/C_{Sm})_{road\ dust}}{(C_{PGE}/C_{Sm})_{crust}} \qquad \textbf{(4)}$$

240 Where C_{PGE}/C_{Sm} is the ratio of individual concentration of PGEs or other elements
241 whit Sm.

242 According to Sutherland (2000), *EF* < 2 minimal enrichment (indicative of no
243 pollution), EF=2 to 5 is moderate enrichment, EF = 5 to 20 is significant enrichment, EF =20
244 to 40 is very severe enrichment, and EF > 40 is extremely severe enrichment (indicative of
245 extreme pollution).

246 2.4.3. Statistical analyses

247 Statistical differences among the PGEs ratio in the road dust in three samplings were
248 determined with analysis of variance (ANOVA) and considered statistically significant at p-
249 values <0,05.

250 The box plot method was also used to better illustrate changes in the PGEs ratio
251 (Pt/Pd, Pt/Rh and Pd/Rh) at three sampling campaigns from 2008, 2016 and 2018, from
252 visual data exploration and outlier detection.

253 The ternary graph was used to compare the varying proportions of PGEs in road dust
254 samples collected during the three sample collections of this study with those from other
255 studies conducted in different countries. The ternary diagram comprises three sides that
256 correspond to Pt, Pd, and Rh concentrations, where the lines of the triangle represent
257 proportions ranging from 0% to 100%.

258 A correlation matrix of all studied variables was performed to identify any existing
259 relationships among the concentrations of the metals studied. Principal Component Analysis
260 (PCA) was applied to examine the various relationships between the variables. The cluster
261 analysis, commonly applied method to environmental evaluation, was used to identify and
262 study the interrelationships among variables and sites exhibiting similar patterns in terms of

PGEs concentrations. These statistical analyses were performed using Origin and IBM SPSS Statistics software for Windows.

3. Results and Discussion

3.1. Optimization of a cation-exchange column for PGEs separation from road dust matrix.

In order to confirm the immediate elution of PGEs, the standard solution containing 5 μg kg^{-1} of PGEs and interfering elements in similar concentrations as BCR 723 (road dust; certified Rh, Pd and Pt concentrations of 12.8, 6.1 and 81,3 μg kg^{-1} respectively) was prepared and its elution's behavior on Dowex resin was investigated by elution's curves. The simulated solution, 5 mL, was loaded on the columns and was eluted with 11mL 0.5M HCl. The aliquots (1 mL) were collected separately, 0.5 ppb of In (intern standard) was added to each fraction and the PGEs contents were analyzed by ICP-MS.

Effective separation of spectral interferences was demonstrated solely by analyzing the Pd concentration using the ^{105}Pd isotope. This interfering specie ($^{90}Zr^{16}O^{+}$), cause interference in ^{106}Pd and $^{92}Mo^{16}O^{+}$ cause interference in ^{108}Pd, (Gomez et al., 2000). However, the Pt isotopes and the monoisotopic Rh showed an effective separation of the interfering isotopes.

The elimination of spectral interferences was also monitored by the Mo interference caused in internal standard ^{115}In (^{115}Mo-O with abundance of 0.03%) which will be detected without saturation effects. Mo was present in high concentration compared to Pd. This value causes saturation of ICP-MS detector that presented a false low intensity to Mo.

This experiment aimed to determine the matrix separation efficiency of PGEs using the ICP-MS on cation-exchange resin procedure. For this purpose, 2 mL of the sample solution and 2 mL of 0.5 M HCl were used for rinsing to prevent Zr interference in ^{106}Pd and Mo interference in ^{108}Pd. Additionally, the ^{115}Mo-O interference in ^{115}In was also prevented

by using 2mL of sample and 2 mL of 0.5 M HCl for rinsing. Hence, Indium (In) proved to be a suitable internal standard for this procedure.

3.2. The recovery of the PGEs and other metals using four standard reference material

The method validation was performed by analyzing four certified references. Three materials to Pt, Pd, Rh, (SRM 2556 (1), SRM 2557(2) and BCR-723 (3)) and one material to Ce, La, Nd, Pr, Sm, Cu, Zn, Mo, Ni and Pb, (SRM 2709-San Joaquin soil-NIST (4)). In the SI section, a table shows the metals recovery for the four certified reference materials, the detection and determination limits for all metals established agree with INMETRO-2019.

The PGEs recovery was > 80%, an indicant of a satisfactory method. Except for elements Pt((3)-75%, Pd(3)-79%, Rh(3)-74%, in BCR-723. These results are in agreement with other studies. Reviewed Literature about the PGEs's contents in the reference material BCR-723 from 2001 to 2006 (Sutherland, 2007); showed Pd concentrations ranging from 4.2 to 7.9 μg kg^{-1} in the 95% confidence band. In this study it was found Pd concentrations = 4.8 ± 0.6 μg kg^{-1}. Another study conducted by Alsenz et al. (2009) reported that the Pd concentration in BCR-723 measurement after mercury co-precipitation by ID-ICP-MS using helium as the collision gas was 4.2±1.4 μg kg^{-1}, whereas the Pd concentration without helium as collision gas was 7.2±2.5 μg kg^{-1}. Due to the reduction of molecular interferences by Helium collision, the lower concentration range of 4.2±1.4 μg kg^{-1} Pd appears to be more likely, according to the authors' findings.

The recoveries of rare earth elements for SRM 2709-San Joaquin soil (4) were: La-76%, Ce-80 %, Nd-79%, Eu-89%, Sm-90% and the non-certified Pr-103%, in comparison to the findings reported by da Silva et al. (2016). Our results agree with da Silva et al.'s study and are in line with the validation data presented by method (USEPA 3051A). It is important to note that Method 3051A, although not fully decomposing the samples, achieved a nearly complete digestion, similar to our study's procedure.

The remaining metals recovery for SRM 2709 San Joaquin (4) soil was as follows: Mo-89%, Cu-104%, Zn-99%, Ni-91%, and Pb-84%. The detection limit for these metals was obtained based on the mean of determinations of the seven blank preparations ($\bar{X}$) plus "t" times the standard deviation determined by these seven blank preparations (LD = $\bar{X}$+ t*s*), where t = 3.143 (the value of "Student's" t for p = 0.05 and six degrees of freedom, n - 1). The determination limit was obtained using the equation (LQ = $\bar{X}$+ 5*s*) according to INMETRO-2019.

3.3. Uncertainty

The combined uncertainty of analytical results from this study were relatively tiny, 3.7% for Pd, 2.3% for Pt and 5.6% for Rh. The uncertainty associated with samples preparation ranged from 2 to 8 times higher than analytical uncertainty (2 times for Rh, 4 times for Pd and 8 times for Pt).

Table 1 shows the results of estimated uncertainties for PGEs in road dust samples and comparison between sampling uncertainty ($U_{sampling}$) in road dust (this work) and the results of Tessari-Zampieri et al. (2022) that determined PGEs in the fractions deposited on leaves of plants.

Table 1: Values of Uncertainties associated with the PGEs determinations in road dust (this study) and comparative values of $U_{sampling}$ in road dust whit $U_{sampling}$ in tree Branches (Tessari-Zampieri et al., 2022).

PGE	$u_{analisis\ combined\ standartb\ u\%}$	$u_{measurement}$ RSD%	*$U_{measurement}$	$u_{sampling}$	*$U_{sampling}$ This study Road dust	*$U_{sampling}$ tree branches (Tessari-Zampieri et al., 2022)
Pd	3.7	16.9	34	16.5	33	66
Pt	2.3	19.5	39	19.4	39	48
Rh	5.6	12.3	25	10.9	22	54

*The expanded uncertainty (U) was obtained multiplying the measurement ($u_{measurement}$) and sampling uncertainty ($u_{sampling}$) by 2 for a level of confidence of approximately 95 %

3.4. PGEs and other metals results

In the three sampling campaigns conducted in 2008, 2016, and 2018, concentrations of Pt, Pd, and Rh ranged from 2.6 to 227 ng g^{-1}, 16.3 to 1875 ng g^{-1}, and 2.0 to 257 ng g^{-1}, respectively. The mean Pt/Pd ratios were 0.29, 0.14, and 0.10, for 2008, 2016, and 2018, respectively. These results for 54 samples are present in Supplementary Information Section and suggest a gradual increase in the levels of palladium (Pd) in automotive catalysts over a 10-year period.

The concentrations of various metals, Mo, Ni, Pb, Cu, Zn, and rare earth elements also were determined and are present in Supplementary Information Section. Among these elements, only the rare earth elements appear to have originated primarily from crustal sources.

Thus, the ratios of lanthanides observed in the road dust samples from São Paulo city indicate a predominantly "natural" origin. The median values for the ratios of La/Ce, La/Pr, La/Nd, and La/Sm in this study were 0.5, 4.6, 1.26, and 7.5, respectively. These values closely resemble those found in the continental crust (0.5, 4.89, 1.28, and 6.9, respectively, according to (Wedepohl, 1995).

3.5. Assessment of the increase in Pd concentration

The recent increase in palladium (Pd) concentrations in automotive catalysts aligns with findings from two relevant studies. CETESB (2019) presented emissions data from 2006 to 2019, indicating a decreasing trend in pollutant emissions. Despite this reduction, air quality in major cities remains compromised, with elevated levels of ozone and particulate matter (PM) that pose risks to public health. Additionally, the rise in carbon dioxide emissions, primarily driven by the growing urban vehicle fleet, has contributed to global climate change. In the context of human health, Wiseman et al. (2018) investigated the bioaccessibility of platinum group elements (PGEs) in road dust samples using a simulated

lung fluid. Their results revealed that platinum exhibited the highest geomean % bioaccessibility (16%), followed by rhodium (14%), and palladium (3.4%).

Earlier research conducted by Moldovan et al. (2001) and Jarvis et al. (2001) has shown that palladium (Pd) is more soluble and bioavailable than platinum (Pt) and rhodium (Rh). Additionally, Zimmermann et al. (2017) discovered that the toxicity of Pd to Daphnia magna was roughly 11 times higher than that of Pt. These findings indicate that higher levels of Pd could present a greater risk to the environment.

3.6. Comparison with other studies

Palladium (Pd) concentrations in road dust samples have increased in the last 20 years, as seen in Table 2. In the 15 studies that have been examined, only the initial two studies conducted in Sweden 1998 by (Motelica-Heino et al., 2001) and Hawaii (2002) by (Sutherland et al., 2008), followed by a subsequent 2012 study conducted by Spada et al. (2012) on street dust samples from Houston, Texas, USA, have demonstrated Platinum (Pt) concentrations surpassing those of Palladium (Pd), indicated by a Pt/Pd ratio exceeding 1. Notably, the first study based on road dust samples collected in 1998 by (Motelica-Heino et al., 2001) exhibited a Pt/Pd ratio of 2.5 and a Rhodium (Rh) proportion of 25%, signifying characteristics consistent with the early catalysts employed in the automobile industry. The remaining studies, including the present investigation, exhibited Rh proportions ranging from 6% to 13%. Pt enrichment and Pd depletion were partially attributed to the relative predominance of diesel vehicles in Europe (Spada et.al. 2012)

The road dust samples collected in São Paulo in 2008 (fraction <100 μm) exhibited an average Pt/Pd ratio of 0.3, a value consistent with one of three prominent cities in the Pearl River Delta region of China, Guangzhou, where ten samples collected in 2008 exhibited a Pt/Pd ratio of 0.2 (QI et al., 2011) (Table 2). A similar Pt/Pd ratio of 0.3 was observed in a road dust sample (fraction <100 μm) obtained from Taiwan in 2012 (HSU et al., 2013).

However, a notable decrease in the average Pt/Pd ratio to 0.1 was observed in the road dust samples from São Paulo in 2016 and 2018. Notably, these results are consistent with a previous study conducted in Taiwan in 2012, where a sample exhibited a Pt/Pd ratio of 0.1 (Hsu et al., 2013). (Table 2), indicates a lower Pt content compared to the levels observed in 2008. Several factors can contribute to variations in Platinum Group Elements (PGEs) concentrations in road dust across different countries, including geographic, topographic, and climatic disparities, traffic patterns, vehicle characteristics, maintenance practices, catalytic converter designs, prevailing environmental regulations, and fuel types.

Table 2 also presents the Pt/Pd ratio (1.0) with consistent proportions of Pt and Pd (both at 45%) among the total Platinum Group Elements (PGEs) found in road dust samples collected in Perth, Australia, in 2002, by Whiteley and Murray (2003). Furthermore, other studies conducted in various locations provide additional Pt/Pd ratios ranging from 0.5 to 0.7: Guangzhou, China, in 2009 (0.7) by Zhong et al. (2012); Beijing, China, in 2010 (0.5) by Gao et al. (2012); Seoul and Newcastle, England, Europe, in 2014 (0.5) by Okorie et al. (2015); Houston, Texas, USA, in tunnel dust in 2012 (0.7) by (Spada et.al. 2012); and Toronto, Canada, in the inhalable fraction of road dust in 2015 (0.6) by Wiseman (2018). These findings indicate a recent increase in the usage of Pd compared to Pt in automotive catalysts.

404 **Table 2**. Comparative values of Pt, Pd and Rh in road dust in relation to this study

References	Sample Year	Sample location (samples numbers, fraction examined (µm))	*PGEs* (µg kg^{-1})			Pt/Pd	% Rh
			Pt	Pd	Rh		
(Motelica-Heino et al., 2001)	1998	(Goteborg, Sweden (n=1, < 63)	[c]195 ± 17	[c]68 ± 5	[c]90 ± 11	2.9	25
(Sutherland et al., 2008)	2002	Honolulu, Havaii (n=12, < 63)	[b]4.1 – 173.8 [c]51.8 ± 53	[b]1.7- 101 [c]29 ± 32	[b]0.24–15.8 [c]5.2 ± 5.1	1.8	6
(Whiteley & Murray, 2003)	2002	Perth, Australia (n=9, < 63)	[b] 53.8 – 419.4 [a]200	[b]58.2 – 440.5 [a]199	[b]8.8 – 91.4 [a]41	1.0	9
(Qi et al., 2011)	2007-2008	Shenzhen (n=13, <150)	[a]111.8	(a)154.0	(a) 29.6	0.7	10
		Guangzhou (n=10, < 150)	[a]23.4	[a]97.8	[a]6.9	0.2	5
		Hong Kong (n=12, <150)	[a]57	(a)75	(a)9.4	0.8	7
(Zhong et al., 2012)	2009	Guangzhou, China (n=35, <63)	[a]68	[a]93	[a]24	0.7	7
(Gao et al., 2012)	2010	Beijing, China(n=158, <63)	[b](9.4-182.9) [a]56.2	[b](17.4-458.8) [a]112.6	[b](4.0 – 68.0) [a]19.9	0.5	11
(Spada et al., 2012)	2012-streets	Houston, Texas (n=4, < 63)	[b]35 – 131	[b]10 – 88	[b]6 – 8	1.5 - 3	----
	2012-tunnel		[c]529 ± 130	[c]770 ± 208	[c]152 ± 52	0.7	11
(Hsu et al., 2013)	2012-AM-1	Taiwan (n=2, < 100)	[a]148	[a]485	[a]32.2	0.3	5
	2012-AM-2		[a]30.2	[a]381	[a]21.1	0.1	5
(Wiseman et al., 2018)	2015	Toronto, Canada (n=64, <10)	[a]31	[a]85	[a]11	0.6	9
(Okorie et al., 2015)	2014	New Castle, United Kingdom (n=9, < 250 µm)	[a]36	[a]80	[a]18	0.5	13
This study	2008	São Paulo, Brazil (n=18, < 100)	[b]5.5 – 171 [a]79	[b]16.3 – 1034 [a]268	[b]2.4 – 85 [a]39	0.3[a]	10
This study	2016	São Paulo, Brazil (n=18, < 100)	[b]2.6 – 191 [a]69	[b]22.5 – 1832 [a]505	[b]2.0 – 192 [a]59	0.18[a]	9
This study	2018	São Paulo, Brazil (n=18, < 100)	[b]2.8 – 227 [a]64	[b]2..3 – 1875 [a]640	[b]2.8 – 257 [a]73	0.10[a]	9

405 (means[a], range[b] and means ± SD[c])

406 ### 3.7. Three approaches are used to interpret the results.

407 #### 3.7.1. Metal pollution index

408 The Metal Pollution Index (MPI), as defined in equation 3, was used to assess the presence of PGEs
409 contamination in road dust over a specific time period. The results revealed a gradual escalation in PGEs
410 contamination, with the mean MPI values increasing from 90 in 2008 to 123 in 2016, and further to 143 in
411 2018. The most severe pollution levels (MPI > 300) were observed at point 12 in both the 2016 and 2018
412 samples, as well as at points 13 and 14 in 2016. These specific locations are situated near heavily congested
413 avenues with stop-and-go traffic, traffic lights, and a speed limit of 50 km/h.

414 In the 2018 sample collection, several other locations also displayed elevated PGE pollution indices
415 (MPI > 200), namely points 9, 10, 16, and 18. These locations also experience high levels of traffic. In
416 contrast, the lowest MPI (6, 5, and 6 in 2008, 2016, and 2018, respectively) was recorded at point 17
417 (Ipen/USP-Parking), which is characterized by low traffic volumes. Interestingly, point P-12 exhibited a
418 total PGE concentration (MPI) that was approximately 60 times higher than that of point P-17 (Ipen/USP-
419 Parking). Despite having the lowest MPI, indicating relatively low PGE contamination, point P-17 is still
420 influenced by the same anthropogenic vehicular sources as the other sampling locations.

421 These results align with the results reported by Wichmann et al. (2007), which identified higher
422 concentrations of PGEs in central and busy streets with stop-and-go traffic in Germany. The concentrations
423 were approximately 2.2 times higher compared to the central lanes of avenues where vehicles maintained a
424 constant speed of 50 km/h.

425 It was also observed by Merget and Rosner (2001) that automotive catalysts emit Pt under various
426 operating conditions, as studied using a dynamometer in different scenarios. In urban areas, where vehicle
427 speeds are lower and there is stop-and-go traffic, Pt emissions were measured at 60 ng km^{-1}, whereas at a
428 constant speed of 80 km h^{-1}, emissions were reduced to 20 ng km^{-1}.

429 #### 3.7.2. The Enrichment factor EF

430 The enrichment factor (EF) for individual PGEs (Pt, Pd, or Rh) and other metals present in road dust
431 was determined in relation to the crustal concentration of samarium (Sm), as described by equation 4. In this
432 study, samarium (Sm) was selected as the reference element due to its origin being indistinguishable from

433 the upper continental crust, and it exhibited a 90% recovery rate for certified reference materials. The
434 reference values used for the Earth's crust (WEDEPOHL, 1995) were as follows: 5.3 μg g^{-1} for Sm,
435 0.4 ng g^{-1} for Pt, 0.4 ng g^{-1} for Pd, and 0.06 ng g^{-1} for Rh.

436 Fig. 2a presents average EF for Pt and shows stability, with a small decrease from 142 in 2008 to 128
437 in 2016, followed by a slight increase to 148 in 2018. On the other hand, the average EF values for both Pd
438 (509, 942 and 1507) and Rh (487, 729 and 1119) showed an increase between 2008, 2016 and 2018,
439 respectively. These results indicate a consistent rise in Pd and Rh contents since 2008, likely attributed to the
440 increasing number of vehicles and changes in the proportion of PGEs used in automotive catalysts.

441 In contrast, Point 17 (IPEN parking) consistently exhibited the lowest EF levels throughout the three
442 sampling campaigns. However, despite being a relatively lower EF compared to other sites, there was a very
443 high enrichment for Pd (19, 51 and 30), a significant enrichment for Pt (7, 6 and 4) and a very high
444 enrichment for Rh (19, 31 and 25) between 2008, 2016 and 2018, respectively. These values exceed EF > 2,
445 which indicates a low pollution or non-polluted status. All the samples sites, except for site P-17, showed an
446 EF much higher than 40 for PGEs, indicating an extremely high enrichment of PGEs, based on the
447 categories proposed by SUTHERLAND (2000).

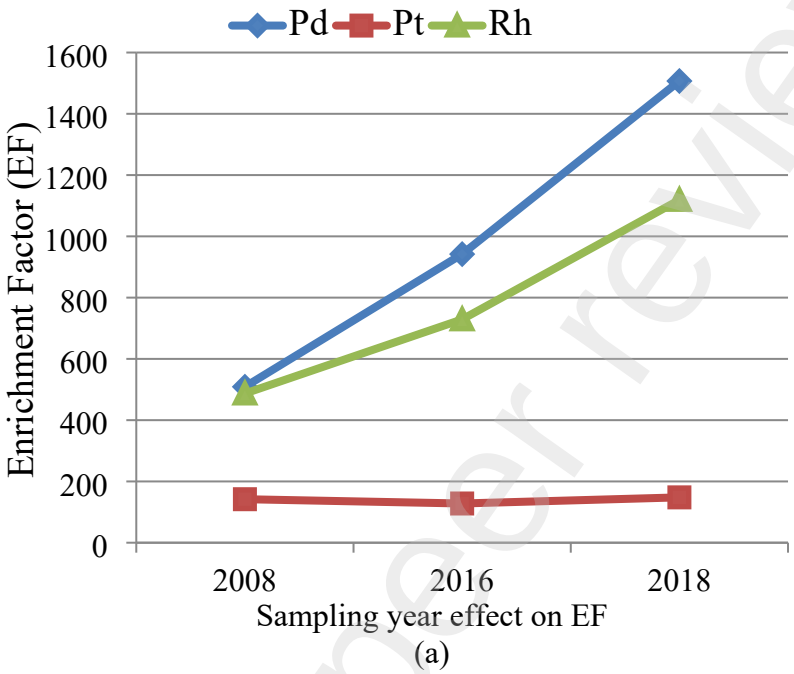
448 In general terms, the most critical areas concerning PGEs accumulation (EF>40) are sites P-12, P-13,
449 P-14 and P-10. These locations are also situated near heavily congested avenues with stop-and-go traffic,
450 traffic lights, and a speed limit of 50 km h^{-1}.

451 Fig. 2b shows an increase of Cu, Zn and Mo EF in road dusts sampling 2008, 2016 and 2018, likely
452 attributed to the increasing number of vehicles, suggesting their vehicular origins.

453 On the other hand, Pb and Ni do not seem to be associated with contamination due to vehicular
454 origins. Since the average EFs did not increase with the increase in the vehicle fleet between 2008 to 2018.
455 Ni showed EF< 2 (mean) with deficiency to minimal enrichment for the three sampling campaigns 2008,
456 2016 and 2018. Only 4 of 54 samples showed EF 2–5 indicative of a moderate enrichment.

457 Pb concentration in 20% of total of 54 samples presented EF < 2 (Deficiency to minimal
458 enrichment), 60% presented EF 2 - 5 (moderate enrichment) and 20% presented EF 5- 20 (Significant
459 enrichment). Part of Pb contamination in tunnel dust analyzed by Nory et al. (2021) was attributed to the

burning of fossil fuels. The addition of Pb to gasoline in Brazil was only done until 1989. However, the Pb emitted by leaded gasoline can still be found in the urban environment due to resuspension from the superficial layer of soil (Lima et al., 2023). The average residence time of Pb ranges from 170 to 250 years (Klaminder et al., 2006). EF results for 54 samples and all metals are present in Supplementary Information Section.



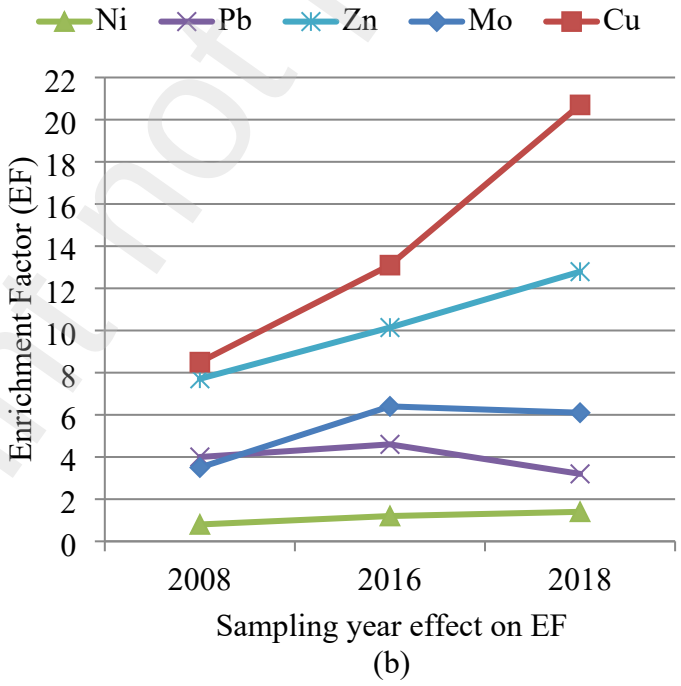


Fig. 2. Enrichment factors in road dust samples for PGEs (Fig.2a) and Cu, Mo, Ni, Pb and Zn (Fig.2b) using Sm as the crustal source reference.

Fig. 3d shows a box plot with the Pt, Pd, and Rh EF from all 54 samples in three sampling campaigns, where an increase in Pd and Rh contamination, but stabilization in Pt contamination, was observed.

3.7.3. Statistical analyses

Variations in the PGEs ratio among three samples campaigns, 2008, 2016, 2018, were determined with ANOVA and considered statistically significant ($p < 0.05$), suggesting that annual variations may contribute to change the ratio of PGEs. However, changes of PGEs ratios for all site in the same year, also were compared using ANOVA and considered statistically insignificant ($p > 0.05$), suggesting that PGEs ratio in these road dust samples did not change significantly in the same year.

3.7.3.1. Box plot from PGEs ratio at the three sampling campaigns.

The box plot method was used to better illustrate changes in the PGEs ratio in road dust samples at three sampling campaigns (Figure 3). The box plot uses the median, the approximate quartiles, and the lowest and highest data points to convey the level, spread, symmetry of a distribution of data values and a normal distribution curve. The changes of PGEs concentration ratios (Pt/Pd, Pt/Rh and Pd/Rh) have been evident in the last years.

Fig. 3a illustrates a decline in Pt concentration and a rise in Pd concentration over the years 2008, 2016, and 2018. The median Pt/Pd ratio for the 2008 samples is significantly higher compared to that of 2016 and 2018. A wider normal distribution curve indicates increased data dispersion, leading to a wider range of values and higher variability. Additionally, outlier values were observed for Pt/Pd in samples P-03, P-05, P-10, P-11, and P-15 during the 2008 sampling campaign, and in samples P-01 and P-11 during the 2016 sampling campaign. However, the data from 2018 reveal a smaller amplitude, and the normal distribution curve remains relatively narrow, concentrated around the median in the observed values. This signifies a reduced range of values and consistent data distribution. In such cases, without outlier values, it indicates a stabilization of the Pt/Pd ratios. These findings validate the ongoing shift in automotive catalysts over the past 20 years, which involves an increase in Pd concentrations and a decrease in Pt levels.

Fig. 3b shows a decrease in the Pt/Rh ratio from 2008 to 2016 and 2018. This can be attributed to the limited effectiveness of Pt/Rh in reducing aldehyde emissions from Brazilian ethanol-fueled vehicles (Miguel and de Andrade, 1990). Additionally, a wider normal distribution curve and a presence of outlier's values and a narrow normal distribution curve were detected in 2008 and 2016. However, no outlier's values and a relative narrow normal distribution curve were detected in 2018, indicating that the ratios have reached a state of stability.

Fig. 3c shows an increase in the Pd/Rh ratio, indicating a rise in both Pd and Rh concentrations from 2008 to 2016. However, from 2016 to 2018, the ratio remained relatively constant, accompanied by a relatively narrow normal distribution curve.

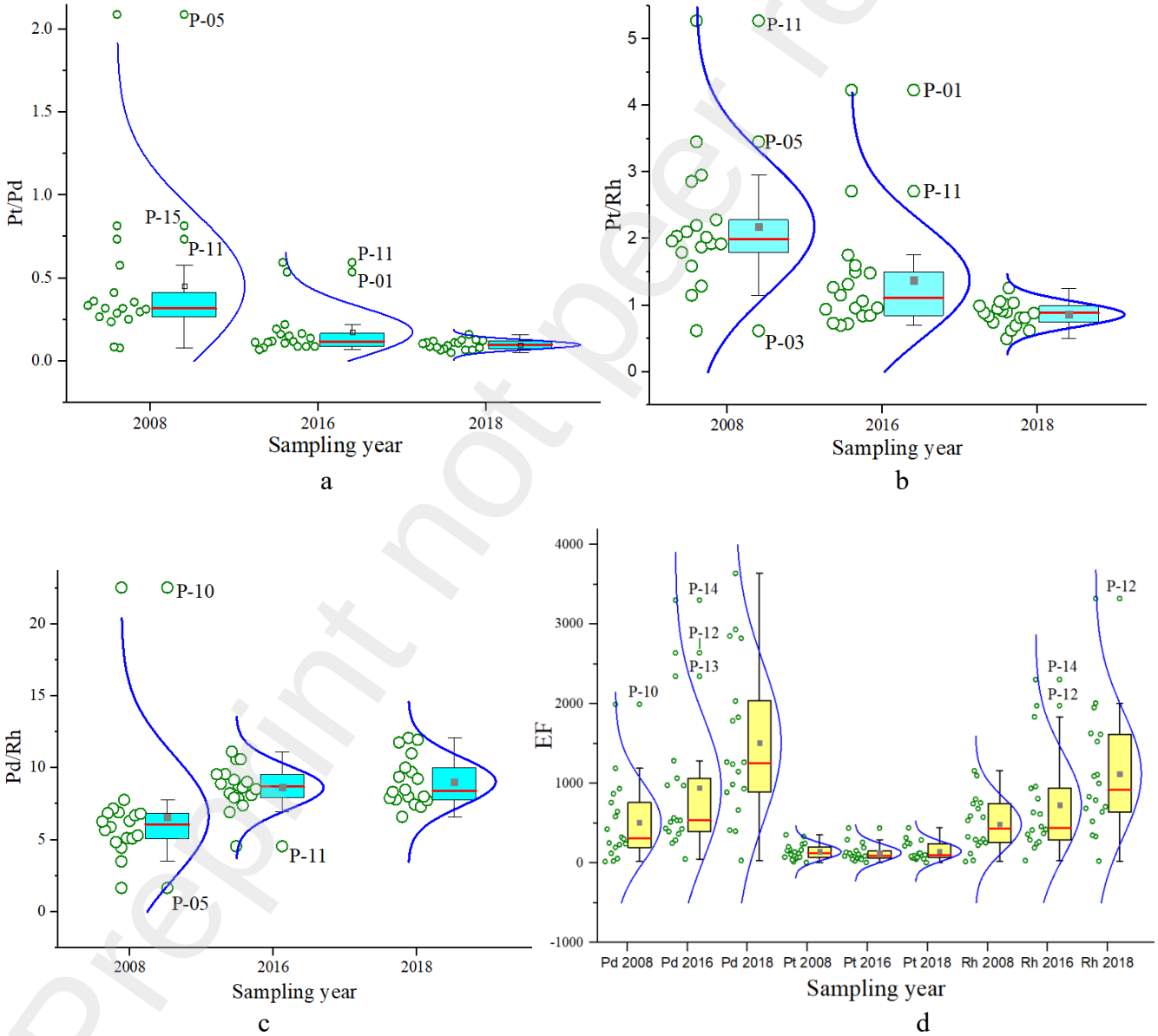


Fig. 3. Box plot of PGEs ratios Pt/Pd (a), Pt/Rh (b), Pd/Rh (c) and EF (d) for 54 road dust samples collected in three sampling campaigns. A solid red line within the box indicates a median value. Horizontal lines

in the boxes represents 25, 50(median) and 75% of values; error bars indicate 5 and 105% of these values. Green open circle on the left side of the box represents the 18 samples of each collection. Green open circle above or below the box represents outlying points and a normal distribution curve is indicated with blue vertical lines.

3.7.3.2. Application of ternary diagram in the PGEs results

Ternary diagrams, Fig. 4, display PGEs proportions (Pd, Pt, and Rh) in the three sampling campaigns (this study), compared with 2 São Paulo soil samples, three certified materials and road dust samples from another country.

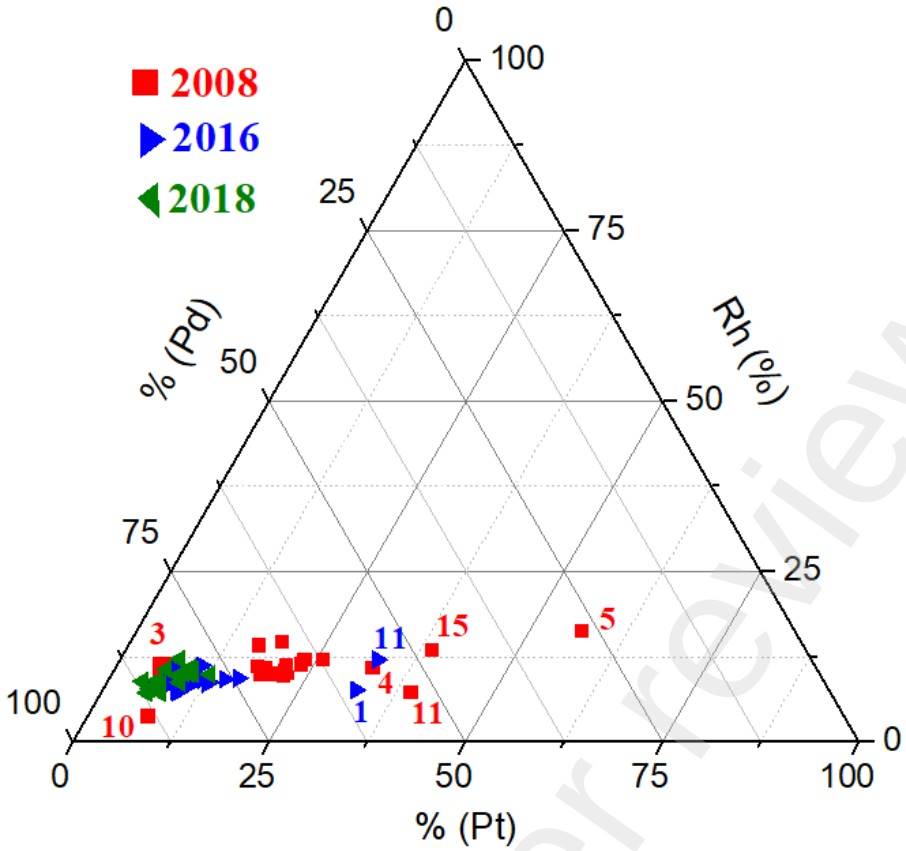
The total sum of PGEs concentrations is represented as 100% in the ternary representation. Fig. 4a indicates a higher point dispersion in the 2008 sampling collection (red color), suggesting a transition in PGEs concentrations in catalysts. Considering the average age of São Paulo vehicles is 9.7 years, potential scenarios encompass older cars with higher Pt content and newer ones with reduced Pt.

Samples from 2016 also in Fig. 4(a), (blue color) had only 2 points (11 and 1) close to 2008 samples. Furthermore, it's evident that the 2018 samples (green color) are closely grouped, suggesting stabilization in the reduction of Pt and an increase in Pd concentration. Points have little dispersion, close to most 2016 samples. These data align with automotive catalyst composition changes, reducing Pt content from 2000 (Birke et al., 2018).

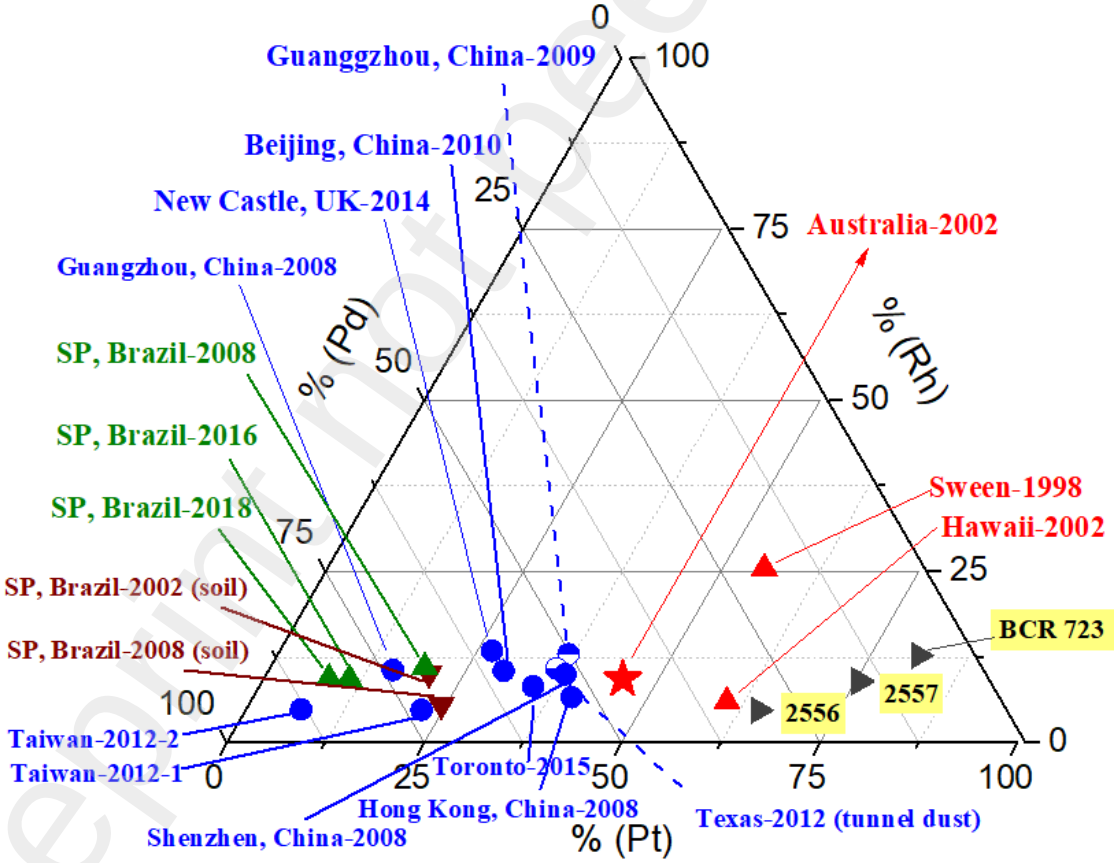
Fig. 4b shows the mean proportions of Pt, Pd, and Rh in road dust samples from 2008, 2016, and 2018, along with three certified reference materials and soil samples from São Paulo (Morcelli et al., 2005; Ribeiro et al., 2012). The 2008 road dust samples showed a 7-fold increase in PGEs concentrations compared to 2002 soil samples. However, in 2008, there was a 3-fold increase in Pt and Pd, and a 6-fold increase in Rh compared to 2008 soil samples. PGEs proportions in road dusts and soils align with known catalytic converter composition, indicating that the PGEs remain associated during mobilization and transport (Whiteley, 2005).

Figure 4b also compares the mean proportions of Pt, Pd, and Rh in road dust samples from various countries. Cities with the highest Pt/Pd ratio, such as Sweden 1998 (Motelica-Heino et al., 2001) and Hawaii 2002 (Sutherland et al., 2008), are positioned to the right of Perth, Australia 2002 (Whiteley & Murray, 2003) on the Pt and Pd axis (with a Pt/Pd ratio of 1), represented by a red star. Conversely, all other cities

positioned to the left exhibited a higher concentration of Pd compared to Pt. São Paulo's 2018 samples resemble Taiwan's 2012 sample (HSU et al., 2013). Various fuel types (diesel, gasoline, and alcohol) influence the PGEs compositions of automotive catalytic converters. In Europe, the predominance of diesel vehicles results in relative Pt enrichment and Pd depletion (Spada et al., 2012). Conversely, in Brazil, alcohol use leads to Pt depletion due to less effective Pt/Rh utilization, while Pd increases when used as Pd/Mo, demonstrating better efficiency (Miguel and de Andrade, 1990; Baldanza et al., 2000).



(a)



(b)

Fig. 4: Ternary diagram comparing the relative proportion of Pd, Pt and Rh in the 54 road dust samples collected in three sampling campaigns (this study) Fig. 4a. and mean of Pd, Pt, and Rh relative proportion for 2008, 2016 and 2018 samples campaing compared to mean of soil samples collected in 2002 from other studies by (Morcelli et al., 2005) and in 2008 by (Ribeiro et al., 2012) in São Paulo city, three certified reference materials (SRM 2556, SRM 2557, and BCR723), and to other studies in Fig. 4b.

3.7.3.3. Correlation matrix

A Pearson correlation analysis was performed to assess the strength of relationships between the analyzed metals. The metals Pd, Rh, Pt, and Mo showed a strong correlation ($p < 0.01$), indicating a common origin, likely from vehicle emissions. Cu and Zn also had a significant correlation ($p < 0.01$) with Pt, Pd, Rh, and Mo, suggesting a similar source from vehicles. The rare earth elements (Ce, La, Nd, Pr, Eu, and Sm) exhibited a significant correlation ($p < 0.01$) among themselves, implying erosion of crustal materials as their source. However, neither Ni nor Pb showed a significant correlation with any other elements. This analysis did not identify distinct groups of metals with similar behavior.

3.7.3.4. Cluster and PCA Analysis

Cluster analysis groups similar elements and samples using a dendrogram, examining distances between datasets to summarize similarity of variables (PGEs, Mo, Cu, Zn, Ni, Pb, and rare earth elements). Figure 5 shows the dendrogram with horizontal links for elements/sites and numbers indicating similarity levels (0 to 25). Sites clustered into two groups (G1 and G2) based on maximum dissimilarity among PGEs, Mo, Cu, Zn, Ni, Pb, and rare earth elements (Fig. 5a) and PGEs' content in road dust samples (Fig. 5c).

Fig. 5a shows a group G1 whit the PGEs Pd, Rh, Mo and Pt grouping by their similarity, Pd, Rh and Mo have been a significant increase in their concentration over this ten-year period, and Pt had a little dissimilarity with a small decrease in its concentration in that same period, group G1-A-1. These small dissimilarities between the PGEs were caused by a decrease in the concentration of Pt (platinum) due to Pt/Rh (platinum/rhodium) exhibiting low efficiency when used with alcohol fuel, and an increase in the concentration of Pd (palladium) used as Pd/Mo (palladium/molybdenum) with better efficiency (Miguel and de Andrade, 1990). Cu and Zn contamination, (Group G1-A-2) seemed to have been caused by tires and brakes from the same vehicular sources (non-exhaust emissions).

The Group 1B with the Pb and Ni was isolated from the group of PGEs because Ni presented moderate enrichment in 7% of the 54 samples and Pb presented 60% of the samples with a moderate contamination and spread by São Paulo and 20% with a significant enrichment. These observations suggested that the Pb has a moderate contamination and spread by São Paulo, although Pb and Ni that presented some sites with significant enrichment, but not in the same sites most impacted with very high

enrichment and extremely high enrichment as for the PGEs. While, the group G2 (Ce, La, Nd, Pr and Sm) was separated from the group G1 by the maximum dissimilarity. This G2 presented concentration seemed to be associated with erosion of crustal material or natural weathering processes.

Fig. 5b displays the results of the principal component analysis (PCA), where the 14 variables are represented by three new variables called Main Components (PC). These PCs account for 74.9% of the total variance in the original data set.

The first principal component (PC1) contains information primarily about rare earth elements. The correlation of each element with PC1 is as follows: Ce(0.982), La(0.979), Pr(0.992), Nd (0.994), Sm(0.995), and Eu (0.789).

The second principal component (PC2) encompasses information mainly about PGEs - Mo, Cu, and Zn. Below, are the correlations of these elements with PC2: Pd(0.896), Pt(0.765), Rh(0.930), Mo(0.833), Cu(0.673), Zn(0.609), and Ni(0.306).

The third principal component (PC3) solely contains information about Pb(0.787) and Ni(0.612), isolating them from the other two groups.

Positioning the variables in a three-dimensional space, as shown in Fig. 5b, reveals that Pd, Pt, Rh, Mo, Zn, and Cu are separated by PC2 from another group composed of rare earth elements (Ce, La, Nd, Pr, and Eu) with similar behavior. Additionally, Pb and Ni are separated by PC3 from the groups formed by elements showing contamination due to the growth of the vehicle fleet and from the other group of rare earth elements originated from natural weathering processes.

Figure 5c illustrates the groups characterized by the average values and standard deviations of each analyzed PGE. Group G1, comprising 11 samples, displayed significantly higher average concentrations of Pd, Pt, and Rh compared to Group G2, which consisted of 32 samples. Specifically, the concentrations of Pd, Pt, and Rh in G1 were found to be 4.2, 2.2, and 3.3 times higher, respectively, than those observed in G2. These findings indicate that G1 corresponds to sites with a critical level of PGE contamination, while G2 represents road dust samples with lower levels of PGEs.

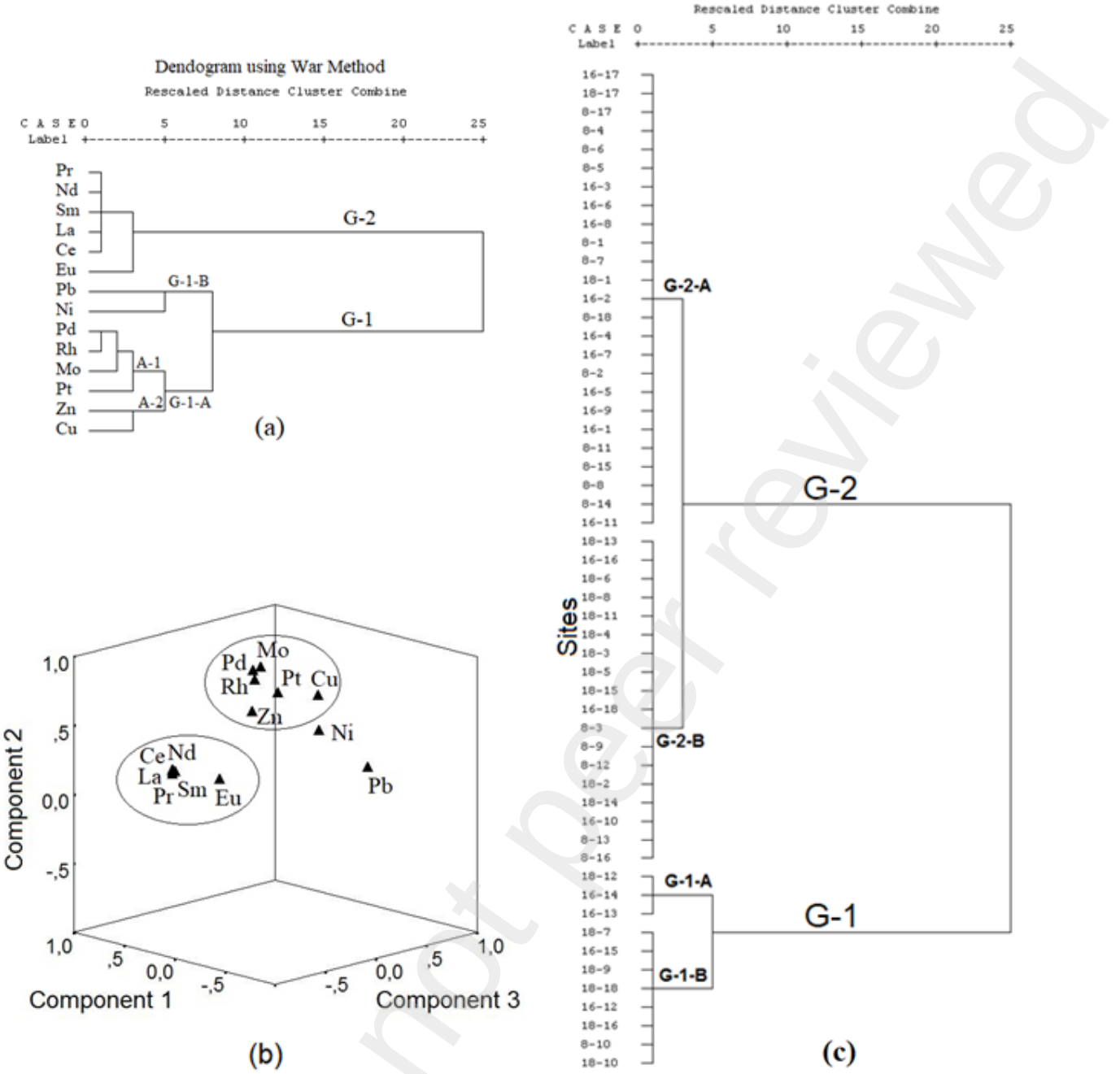


Figure 5. Dendrogram from the cluster analysis for PGEs, Mo, Pb, Ni, Cu, Zn and rare earths (a), PCA for the elements (b) and PGEs concentrations in road dust samples collected from São Paulo (c).

The group G-1 was divided into two other closely similar groups. G1-A comprised three samples from Rebouças Avenue (P12-2018), Paulista Avenue (P14-2016), and Consolação Avenue (P13-2016), which showed the highest concentrations of PGEs. The average concentrations of Pd, Pt, and Rh in G1-A were respectively 1.7, 1.6, and 1.9 times higher than those elements in Group-1-B. Group 2 was also divided into two highly similar subgroups based on the concentration of PGEs in the samples. Group-2-B, consisting of 18 samples, exhibited mean concentrations of Pd, Pt, and Rh that were 2.8, 1.1, and 2.2 times higher, respectively, than those elements in Group-2-A, which included 25 samples. At the top of Fig. 5c are

displayed the samples with the lowest concentrations of PGEs, namely P17-2008, P17-2016, and P17-2018, collected from road dust samples in low traffic volume local pavements (Ipen-Parking).

4. Conclusions

PGEs levels in road dust samples collected from the city of São Paulo in 2008, 2016, and 2018 showed a significant increase over the ten-year period. The median concentration of Palladium (Pd) increased by 139%, Rhodium (Rh) increased by 87%, while Platinum (Pt) decreased by 19%.

The PGEs increase was supported by the metal pollution index (MPI) mean, which varied from 90 in 2008 to 123 in 2016 and 143 in 2018. Locations with the highest MPI values during all collections were streets or avenues with speed limits of 40 or 50 km/hour, traffic lights, and frequent stop-and-go traffic, leading to increased fuel burning.

Enrichment factors (EF) also supported the rise in PGEs levels over this 10-year period, with EF values compared to Samarium's (Sm) crustal abundance exceeding 40, indicating extremely high enrichment. Specifically, EF values for Pd and Rh increased between 2008, 2016, and 2018: Pd EF values of 509, 942, and 1507, and Rh EF values of 487, 729, and 1119, respectively. In contrast, Pt EF values were lower, measuring 142, 128, and 148 for the corresponding years. These increases align with the growing number of vehicles equipped with catalytic converters in São Paulo city, suggesting vehicular sources contribute to the presence of PGEs in the collected road dust samples.

PGEs, Mo, Zn, and Cu EF exhibited an increase in road dust samples from 2008 to 2018, showing strong correlations among themselves. This supports the hypothesis that PGEs, Mo, Cu, and Zn in the São Paulo environment likely originate from the same source, namely automotive emissions. On the other hand, the other elements did not show an increase in EF during this 10-year period. Although Pb and Ni presented some sites with significant enrichment, these sites were not the same as those most impacted by very high enrichment and extremely high enrichment observed for the PGEs. Therefore, Pb and Ni enrichment seem to be of non-vehicular origins. The rare earth elements in road dust samples predominantly originated from the natural erosion of crustal material.

The presence of PGEs in road dust samples, with potential health risks, is little known. Long-term vehicle catalyst use may lead to PGEs bioaccumulation in urban areas. While converters reduce toxic

emissions, they add to pollution. São Paulo's high vehicle numbers impact human health and the urban environment, necessitating mobility and pollution reduction policies. Limited mobility and traffic hinder engine efficiency and emission reduction progress. Electric and hydrogen cars control pollution without PGE-containing converters, but the environmental impact of electric car batteries, as well as the origin of the energy that supplies the batteries, must be considered. Policies promoting zero-emission electric public transport can enhance urban mobility. This study provides PGEs concentration data from São Paulo, enabling pollution monitoring in future research.

Acknowledgments

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Appendix A. Supplementary data

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

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