Brazilian PGE Research Data Survey on Urban and Roadside Soils

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Abstract Since the 1990s, investigations on the increase of platinum (Pt), palladium (Pd), and rhodium (Rh) levels in urban environments of big cities all over the world due to catalytic converters emissions have increased enormously, mainly in developed countries. Nevertheless, relatively few studies were performed in developing countries, such as Brazil. The state of São Paulo is the most populous and richest Brazilian state, and the city of São Paulo is the largest city in South America, and the 7th largest metropolitan region of the world. In this article, a discussion about the results obtained for the platinum group elements (PGE) Pt, Pd and Rh concentrations in soils adjacent to a major road in São Paulo state and in soils adjacent to seven main high density traffic avenues in the metropolitan region of São Paulo City are presented. Pt, Pd and Rh were found in much higher concentrations than PGE geogenic background, showing a catalytic converter origin. The platinum group elements levels obtained in São Paulo urban soils were much higher than those obtained for the roadside soils. Pd levels about seven times higher than the results obtained for the roadside soils were observed. The highest concentrations obtained for Pt (208 ng g^{-1}) and Rh (45 ng g^{-1}) were of about 12 and 5 times higher than the results obtained for the roadside soils. The results indicate that the PGE concentrations in São Paulo soils are directly influenced by traffic conditions. The concentrations of traffic-related elements such as Pb, Zn and Cu were also determined in the studied soils. Factorial analysis and cluster analysis discriminated the traffic related metals from PGE in the urban soils. However, in the roadside soils PGE were well correlated with Pb, Cu and Zn. The results obtained at present for PGE levels in São Paulo soils demonstrate the importance of continuous monitoring, since the rapid increase of the vehicular fleet in Brazil should also increase PGE emissions.

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1 Introduction

There is little information on platinum group elements (PGE) contamination in countries with growing economies, such as China, India or Brazil, in spite of the expending automobile industry in these countries. The automobile industry in China and India have grown at an average of more than 15 % over the past few years, and last year alone 30 % of world passenger car sales were from China and India (Sen 2013). Brazil has ended 2012 with a total vehicular fleet of about 80 million vehicles. According to the National Traffic Department, between September/2003 and September/2013, there was an increase of 123 % in the Brazilian vehicular fleet. On the other hand, the population growth between 2000 and 2010 was of 11.8 %. The number of passenger cars jumped from about 24.5 millions in 2001 to 50.2 millions in 2012, showing a growth of 104.9 %, being 44.4 % in the 15 main metropolitan regions and 10.8 % in the metropolitan region of São Paulo (Rodrigues 2013).

São Paulo state, Brazil, is the most populous and richest Brazilian state, with an estimate population of 43.6 million inhabitants (IBGE 2013). The city of São Paulo is the largest city in South America, and the 7th largest metropolitan region of the world. This metropolitan region has a population of about 20 million people and a vehicular fleet of about 8.5 million circulating motor vehicles in the city. These vehicles are, according to the Environmental Protection Agency of the State of São Paulo (CETESB 2013), the governmental agency of air quality control, the main source of air pollution. An estimate of 4.46 thousand ton/year of particulate matter (PM) is released into the atmosphere, and 50 % of this PM is the result of automotive vehicle emissions.

In the last decade there has been a growing interest in determining PGE in different environmental compartments after the introduction of automobile catalytic converters (Rauch et al. 2000; Jarvis et al. 2001; Gómez et al. 2001; Morton et al. 2001; Ely et al. 2001; Whiteley and Murray 2003; Riga-Karandinos et al. 2006; Sutherland et al. 2007; Pan et al. 2009; Mathur et al. 2011; Jackson et al. 2007; Prichard and Fischer 2012). Most studies had demonstrated increased concentrations of PGE at roadside environments providing evidence that automobile catalysts are the predominant source of PGE (Whiteley and Murray 2003).

Thus, due to the increase in the number of vehicles in the last decade in Brazil, a similar increase in the number of catalytic converters and accompanying PGE pollution is to be expected. Automobile catalytic converters appeared in Brazil in 1996, and contain about 1.5 g of PGE. Brazilian vehicles use gasohol, a mixture of gas and alcohol in a proportion of 8:2, and the catalytic converters have mainly Pd and Rh. This differs from Europe, where the three-way catalysts based on Pt and Rh with a ratio of 5:1, and the high temperature threeway catalyst, with variable combinations of Pt, Pd and Rh, are used (Fritsche and Meisel 2004). Since 1993, Pd has been increasingly used to substitute the Pt/Rh catalysts in automobile catalytic converters (Zereini et al. 2007). Therefore, possible environmental and human health consequences can be expected. Pd is the most mobile of all platinum metals as a result of its chemical properties and can be taken up by plants in considerably greater amounts than Pt and Rh (Zereini et al. 2001). Ek et al. (2004) reported that evidence indicates that the PGE, especially Pd, are transported to biological materials, in this case, plants, through deposition in roots by binding to sulphur-rich low molecular weight species. PGE uptake to exposed animals showed that liver and kidney accumulate the highest levels of PGE, especially Pd. The PGE concentration in human urine and blood has been investigated in several studies. In road construction workers, the urinary Pt level was 0.9 ng l^{-1} and the Pd level was 52.2 ng L^{-1}. The urinary Pd level was below 10 ng L^{-1} in unexposed individuals. Urinary Pd and Rh, but not Pt, levels were correlated with traffic intensity. Adults from a large city (Rome) with dense traffic had greater urinary Pt and Rh concentrations than adults from a smaller town (Foligno) with relatively low traffic density, but no clear trend was found for Pd. In contrast, a significant correlation between urinary Pd and Rh concentrations and traffic density was found in children, but no correlation was observed for Pt (Yajun et al. 2012).

Risk assessments to human health of exposures to PGE, especially through inhalation of PGE-associated airborne particulate matter (PM), have been recently investigated. Colombo et al. (2008) studied the potential pathways of PGEs from vehicle exhaust catalysts into humans, by using a physiologically based extraction test (PBET) to verify the uptake of PGEs by the human digestive tract. These authors reported that solubilization of PGEs in the human digestive tract could involve the formation of PGE-chloride complexes, which are known to have toxic and allergenic effects.

Zereini et al. (2012) simulated human lung fluids; [artificial lysosomal fluid (ALF) and Gamble's solution] were used to assess the mobility of Pt, Pd and Rh in airborne PM of human health concern. Airborne PM samples (PM_{10}, $PM_{2.5}$, and PM_1) were collected in Frankfurt and Main, Germany. The mobility of PGE in airborne PM_1 samples was notable, with a mean of 51 Rh, 22 Pt, and 29 Pd present in PM_1 being mobilized by ALF after 24 h.

There has been little research on PGE levels in Brazil. da Silva et al. (2008) determined Pd and Rh, as well as other elements, such as Cd, Ce, Cu, La, Mo, Ni and Pb, in 24-h PM_{10} samples collected in five locations with different traffic densities and anthropogenic activities in Rio de Janeiro, Brazil. The results suggest that vehicular traffic is the most important source of environmental pollution at the studied sites.

There is little information about PGE levels in São Paulo soils, and almost none concerning Brazilian soils. With an expected continuous growth of the Brazilian vehicular fleet, and the implementation of the PGE based catalytic converters, there is a growing interest in studies of assessment of PGE in the environment. This chapter presents a survey of the studies performed in São Paulo roadside and urban soils (Morcelli et al. 2005; Ribeiro et al. 2012a), to assess PGE and the relationship between the results obtained and the catalytic converter abrasion. The elements Ba, Ce, Cu, La, Mo, Ni, Pb and Zn were also determined and their correlation with PGE is discussed.

2 Materials and Methods

Roadside soils from a major road (SP348), with high traffic flow (ca. 30,000 vehicles/day), running between São Paulo city and another important industrial regions of São Paulo State, and soils adjacent to the most important traffic arteries of São Paulo city were studied. For the roadside soils, the sampling strategy was based on a rectangular grid, in which composite samples were prepared by taking five samples that were collected at 1 m, along the 4-m stretch of the road. The sampling took place on a 40-cm grass strip beside the asphalt and up to 540 cm from the roadway. High-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) with NiS fire assay collection and Te coprecipitation was used as analytical procedure. Sampling was undertaken in October 2002 (Morcelli et al. 2005). For the street soils of São Paulo city, sampling was performed between October/2007 and February/2008. Seven important avenues were chosen based on varying traffic volumes and driving styles (stop and go and high constant speed). Areas of 1 m^2, forming a rectangular grid, were sampled. Composite samples were prepared, from three samples, collected at each point of the rectangle. Sampling took place from the grass strip 15 cm beside the asphalt up to 115 cm from the roadway. The sampling depth was 5 cm. Soils were digested with aqua regia in an ultrasonic bath at 65 °C for 35 min. Samples were centrifuged (t = 10 min and rpm = 3,000). The solutions obtained were transferred to Teflon beakers and the procedure was repeated with the solid residue. Samples were evaporated to dryness and diluted in HNO3 2 %. PGE levels were determined by ICP MS technique (Ribeiro et al. 2012a), while the other metals (Cu, Mo, Ni, Pb and Zn) concentrations were quantified by ICP OES technique (VARIAN, Model 710 ES). For the non-PGE elements, the quality control of the data was performed by analyzing the reference material SOIL 7 (IAEA). The results obtained for three replicates showed relative errors below 10 % and coefficients of variation better than 5 %. The elements Ba and Zn, and the lanthanides La and Ce were determined by instrumental neutron activation analysis (INAA). The analytical procedure is described in Ribeiro et al. (2012b).

3 Results

3.1 PGE Levels and Behavior

A summary of the results obtained for Pd, Pt and Rh in the studied soils, compared to other studies all over the world, is shown in Table 1. The obtained values showed a significant enrichment in relation to the continental crust levels ((Pd: 0.4 ng g-1; Rh: 0.06 ng g-1; Pt: 0.4 ng g-1, Wedepohl 1995). These values have been used as background values for PGE in several environmental studies (Zereini et al. 2005; Orecchio and Amorello 2011).

Table 1 Pt, Pd, and Rh levels in soils in different countries (literature data)

City/sampling year	Location	Pd (ng g^{-1})	Pt (ng g^{-1})	Rh (ng g^{-1})	References
Mexico City, Mexico	Roadside High density stop and go traffic High constant speed traffic densities	46.8–74 15.2–101.1	307.5–332.7 91.2–207.7	26–39.1 7.8–22.7	Morton et al. (2001)
Rome, Italy, 2001	Urban area		7.0–19.4		Cinti et al. (2002)
Napoli, Italy, 2000	Urban and suburban areas	8–110	1.6–52		Cicchella et al. (2003)
Perth, Australia, 2002–2003	Roadside	13.79–108.45	30.96–153.20	3.47–26.55	Whiteley and Murray (2003)
Athens, Greece, 2003	Highway roads Urban roads	25.4–236 20.3–185	73.3–254 34–216	–	Riga-Karandinos et al. (2006)
Braunschweig, Germany, 2005	Roadside High constant speed traffic densities High density stop and go traffic[a]	14.4–43.3 124	29.5–50.4 261	5.98–10.7 38.9	Wichmann et al. (2007)
Oxfordshire and London, England, 2000	Roadside	84.2–120.8	2.04–15.9	3.5–22.4	Hooda et al. (2007)
Hong Kong, China, 2007	Urban environments	6.93–107	15.4–160	1.61–34.5	Pan et al. (2009)
Palermo, Italy, 2010	Urban area		0.6–2240		Orecchio and Amorello (2011)
Seoul, Korea, 2008	Roadside		0.7–221		Lee et al. (2012)
São Paulo, Brazil, 2002	Roadside	1–58	0.3–17	0.1–8.2	Morcelli et al. (2005)
São Paulo, Brazil, 2007 and 2008	Highly dense traffic urban avenues	3–378	1–208	0.2–45	Ribeiro et al. (2012a)

[a] Highest concentration

As can be seen in Table 1, the highest results obtained for Pd and Rh concentrations in São Paulo urban soils were higher than those obtained in the other cities. Pt levels were at the same level as obtained for cities as Seoul, Mexico city and Athens.

On the other hand, the results obtained for the São Paulo urban soils were much higher than the results obtained for the São Paulo roadside soils. Pd levels about seven times higher than the results obtained for the roadside soils were observed. The highest concentrations obtained for Pt (208 ng g^{-1}) and Rh (45 ng g^{-1}) were of about 12 and 5 times higher than the results obtained for the roadside soils. These results can be explained by the traffic characteristics of the studied avenues. The highest levels were obtained in one avenue which presents stop & go traffic all day long, which can explain the high PGE concentrations obtained in the soil next to this avenue in relation to the other avenues, which alternates between constant speed and stop & go traffic flow.

Whiteley (2004) and Ward and Dudding (2004) reported the influence of traffic density and flow conditions in the PGE particle release and accumulation in the adjacent motorway environment. Wichman et al. (2007) observed a significant difference between the concentration levels of Pt, Pd and Rh in soils collected at one road outside the city of Braunschweig, Germany, where traffic moved with a constant speed, and a crowded street in the centre of Braunschweig with stop and go traffic (Table 1). Mathur et al. (2011) studied road dusts from Hyderabad city, India, along city roads with heavy, medium and low traffic and under different driving conditions. The highest PGE levels were observed at high traffic density, busy roads. The more pronounced PGE concentrations was attributed to the very high frequency of traffic jams, with many vehicles undergoing stop/start and variable speed conditions. Speed variation can damage the catalyst material due to large temperature gradients resulting in abrasion of the catalyst and release of PGE to the roadway environment. It is well established that maximum emission of PGE from the catalyst's surface occurs at frequent speed changes of the vehicle or with repeated stop and go conditions rather than from vehicles moving at constant average speed (Ward and Dudding 2004; Mathur et al. 2011). Lee et al. (2012) observed a remarkable difference in average Pt level between heavy traffic roads (av. 132.2 ng/g) and light traffic roads (av. 22.8 ng/g) in road dusts from Seoul.

The high PGE concentrations observed in the present study may be associated to the São Paulo traffic style and to the rapid increase of the vehicular fleet over the last years. Thus, as there has been a continuous growing in the number of circulating vehicles in São Paulo, an increase in PGE levels in São Paulo should be expected.

Zereini et al. (2007) in comparing PGE concentrations in soil samples collected along a major highway in Germany in 1994 and 2004, observed concentrations of Pd about 15 times higher on average than those measured in 1994. Pt and Rh concentrations increased 2 and 1.6 times, respectively, during this time period. Zereini et al. (2012), observed a significant increase in PGE concentrations in fractionated airborne dust (PM) collected in 2002 and in 2008–2010, in Frankfurt, Germany (increases of 12, 6 and 3 times for Pd, Pt and Rh, respectively). This reflects an increased use of Pd as an active catalyst in automobiles.

Wichmann et al. (2007) compared PGE analytical data, all generated in 1999 and in 2005 in the same sampling sites located mainly close to heavily used roads in the region of Braunschweig, an urban area in Germany. The comparison revealed a distinct increase of PGE concentrations in soils along heavy traffic roads by a factor of 2.1–8.9; once even a factor of 15 was determined.

Similarly to the results obtained in other studies (Schafer and Puchelt 1998; Morton et al. 2001), higher PGE concentrations were observed in the vicinity of roadways in São Paulo. The highest concentrations were found at 40 cm from the roadway. At about 140 cm of the roadway the concentrations are ca. 90 % lower compared to the samples collected at 40 cm from the road. This indicates the anthropogenic origin of the PGE.

For the adjacent soils of main avenues in São Paulo city, Pt, Pd and Rh presented higher concentrations in the samples collected at 15 cm from the asphalt, in 4 of the 7 studied avenues. Brown (2002) investigated the spatial distribution of the PGE in UK soils, comparing the levels of PGE in superficial soil samples (0–2 cm to 2–10 cm). Besides this, the author also considered the distance from the road. Samples were collected from the asphalt to a distance of 10 m. A decrease of about 12 times for Pt concentration and of about 9 times for Rh concentration with depth was observed. In the case of Pd, the concentration at 20 cm was about half of its level at the top samples. In relation to the distance, no change in concentration was observed up to a distance of 1.20 m. Nevertheless, from a distance of 2 m, there was a decrease of 60, 70 and 65 % in the concentration levels of Pd, Pt and Rh, respectively (Brown 2002). Wichmann et al. (2007) also reported the highest PGE concentrations in soils close to a road in Germany, declining exponentially with growing distance.

3.2 PGE Ratio

The PGE ratio (Pt/Pd; Pt/Rh; Pd/Rh) is an important indicator of the catalytic converter source (Jarvis et al. 2001; Whiteley 2005). The three-way catalysts based on Pt and Rh with a ratio of 5:1 and the high temperature three-way catalyst with variable combinations of Pt, Pd and Rh (e.g. 5:1 in a Pd/Rh catalyst or 1:14:1 in a Pt/Pd/Rh catalyst) have been widely used (Fritsche and Meisel 2004). Nevertheless, the development of new technologies for catalytic converter production and the replacement of Pt by Pd in the catalytic converter composition have changed the PGE concentrations in the environment. There has been a gradual shift of Pt based catalysts to Pd usage in the late 1990s and an introduction of only Pt, Pd–Rh, and Pd only or Pt–Pd–Rh catalysts. As a result, Pt/Pd and Pd/Rh ratios, derived from environmental samples analyzed, are non-uniform today (Wichmann et al. 2007).

In spite of the great increase of Pt and Pd concentrations in relation to the results obtained in roadside soils of São Paulo, the Pt/Pd ratios obtained in urban soils (0.2–0.4) did not differ much from the ratios obtained for the roadside soils, of 0.3–0.4. The results were lower than those obtained by Mathur et al. (2011), 0.3–7.5, lower than the values reported by Ely et al. (2001), 1.0–2.5, in soils along

U.S roads, and by Jarvis et al. (2001), that found a mean ratio of Pt/Pd of 6.6 and a range from 2.01 to 26.6 in road dust and surface samples adjacent to major UK roads. A lower concentration of Pt in Brazilian soils is expected, since the catalyst converters in Brazil contain mainly Pd and Rh.

The Pt/Rh ratio in the São Paulo roadside soils São Paulo was relatively constant, at 1.7 with a range from 0.54 to 4.7. The Pt/Rh ratios in São Paulo urban soils were more variable, with a range from 3.0 to 7.8, which agrees with the Pt/Rh ratios obtained in other autocatalyst-derived PGE studies. These values are in the range of 4.2–9.1 obtained in soils along a main highway in Germany (Zereini et al. 2007), of 5–16 given by Ely et al. (2001), but are lower than the Pt/Rh obtained by Fritsche and Meisel Meisel (2004), in soils along Austrian motorways (10.2–11.8) (Fritshe e Meisel 2004). Bocca et al. (2006) obtained Pt/Rh ratios ranging from 2.1 to 8.1 in urban aerosols from Buenos Aires, Argentina. The average Pt/Rh ratio of 5.1 ± 0.9 (range 4.0–9.0) is characteristic of autocatalyst emissions.

The relatively large variability of the Pt/Rh ratios compared with the Pt/Pd ratios suggests a significant difference in chemical behavior between Rh and Pd. Parry and Jarvis (2006) have observed that the ratios of Pt/Rh had decreased on UK roads from 1998 to 199, compared to values in 1995/1996, indicating a reduction of about 30 % in Pt compared to Rh and an increase in Pd of about 40 %. This may indicate that there is no apparent solubility difference between Rh and Pt in the environments studied, suggesting that not only are Pt and Rh associated during emission but they remain associated during any subsequent mobilization (Whiteley 2005).

The urban soil ratio Pd/Rh ranged from 10.6 to 25.4 which are much higher than the Pd/Rh ratios found by da Silva et al. (2008), in 24-h PM_{10} collected in five locations in the city of Rio de Janeiro, which ranged from 4.0 to 7.3, with an overall mean of 5.9. The 10.6–25.4 range is also higher than that for roadside soils from São Paulo (Morcelli et al. 2005) (0.4–5.4 m distance from roads), which ranged from 2 to 20, with a mean of 7.2. Zereini et al. (2007) obtained Pd/Rh ranging from 1.6 to to 8.4, Whiteley (2005) obtained ratios ranging from 1.7 to 8.7, and Ely et al. (2001), from 4 to 9, which may indicate the replacement of Pt by Pd in autocatalysts. Different types of catalytic converters are now available in the market, such as Pt only, Rh-Pd, Pd only or Pt-Pd-Rh catalysts. Since Pd appears to be the most mobile of all platinum metals, concerns are now being raised about possible environmental and human health consequences and risks.

3.3 Other Metals Present in the Soil and Their Correlation with Pt, Pd and Rh

Traffic derived trace elements (Ba, Ce, Cu, La, Mo, Ni, Pb, and Zn) were also analyzed in the studied roadside and urban soils (Table 2). These metals are usually associated with high traffic densities, originating from exhaust emissions, tires, braking, vehicle and engine wear, and/or the re-suspension of road dusts (Peachey et al. 2009).

Table 2 Metal range concentration in São Paulo roadside and urban soils

Element	Range (mg kg^{-1})	
	Urban soils of São Paulo City	Roadside soils (40 cm up to 140 cm from the roadway)
Ba	105–713	259–2221
Cu	3–838	27–110
Mo	1–6	<1–4.9
Ni	1–152	16–31
Pb	6–470	46–153
Zn	58–1669	170–592
La	14–90	29–61
Ce	3–186	58–233

For a better comparison of the behavior of the PGE and the other traffic-related elements in the roadside and the urban soils studied, a statistical approach was employed. Figure 1 shows the hierarchical dendrograms obtained by cluster analysis of the data set (PGE and other elements) obtained for the roadside soils (Fig. 1a) and for the urban soils (Fig. 1b). In this approach, the data obtained up to 140 cm for the roadside soils were used, since it was up to this distance that there was more influence of the vehicular emissions (Morcelli et al. 2005).

For the roadside soils (Fig. 1a), two main groups can be identified. The first group is integrated by two sub-groups that are strongly associated: PGE, Cu, Pb and Zn are included in one sub-group and Mo and Ni in another sub-group. The second group includes Ba, La and Ce. The correlation of the PGE and Pb, Cu and Zn can be explained by the fact that Pb, Cu and Zn are metals known to be associated with motor vehicle pollution. Copper is added as an antioxidant and may be present in the coarse fraction of the particles originating from the wearing down of engine bearings or other components. Zn is associated with the use of additives and lubricants (da Silva et al. 2010). The strong association between Mo and Ni may be

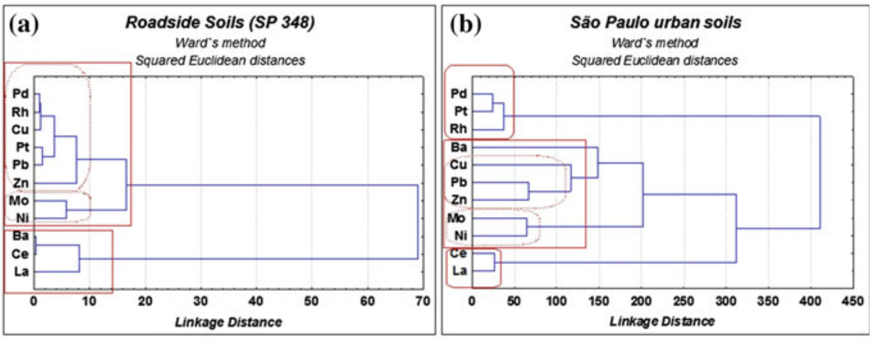

Fig. 1 Hierarchical dendrograms obtained by cluster analysis of the PGE and traffic-related element concentrations in the roadside soils (**a**) and in the urban soils (**b**) of São Paulo

due to the fact that these elements are used to coat cylinders of diesel vehicle motors (Tomanik 2000). Table 2 shows that lead levels were comparable to other studies (9–154 mg/kg, Tsogas et al. 2009) indicating the influence of car traffic on its accumulation in roadside soils. The other metals presented similar levels to other populous cities, such as Athens and Mexico City (Morton et al. 2001; Riga-Karandinos et al. 2006).

The correlation between PGE and Pb has already been reported in other studies. Riga-Karandinos et al. (2006) obtained a positive correlation between Pt and Pb (r = 0.436) but not very high, while no correlation between Pd and Pb was demonstrated.

Ba, La, and Ce are present as additives in catalytic converters. La and Zr oxides are added to the washcoat as stabilizers (Rauch et al. 2000). Ce, employed as a promoter in catalytic converters, is used in a Ce/Pt ratio of about 20–100 (Zereini et al. 2001). Nevertheless, no correlation was observed between PGE and Ba, La and Ce.

A constant La/Ce ratio was obtained for all samples in São Paulo roadside and urban soils indicating a soil origin (Morcelli et al. 2005). As observed by Jarvis et al. (2001), the background concentrations of Ce in soil are typically many tens of $\mu g\ g^{-1}$ and the addition of autocatalyst derived particulate containing Ce to this system can hardly change the background.

The hierarchical cluster obtained for the urban soils data set (PGE and other elements) (Fig. 1b) compared to the dendrogram obtained for the roadside soils (Fig. 1a), shows a slight difference in the distribution of the studied elements. In Fig. 1b, three main groups are identified. The first group is integrated only by the PGE: Pt, Pd and Rh. A second cluster group includes Cu, Pb, Zn, Mo and Ni, with Ba less correlated, while La and Ce are separated in the third group. One possible explanation for the fact that the PGE did not correlated with Pb, Cu and Zn as strongly as observed for the roadside soils (Fig. 1a), is that in street soils of São Paulo, the wear and tear of certain automobile materials and parts during driving are more intense, due to the higher density of traffic in São Paulo city and the stop and go conditions rather than vehicles moving at constant average speeds. This can favor the release of traffic-related elements such as Cu and Zn rather than PGE, which originate from automotive catalysers.

Factorial analysis (FA) with extraction principal components, using the Windows STATISTIC® 8.0 program, was applied to the results obtained for Pt, Pd and Rh and the other elements determined in São Paulo urban soils. Kaiser criterion (Yeomans and Golder 1982) was used to assess the results of initial eigenvalues (Table 3). Applying the varimax-raw rotation, three principal components were considered, which accounted for about 72 % of the total variance. The matrix of the components for data set indicated that Pt, Pd and Rh presented strong correlation and were associated into the first component (F1), with a factor loading of ≥0.96. This result indicates that these elements have the same source, catalytic converter exhausts. As observed in the cluster analysis (Fig. 1b), the elements Ba, Ce and La were grouped, presenting the highest factor loads associated to factor 2. The higher Cu, Mo, Ni, Pb and Zn factor loads were observed in Factor 3, indicating a common

Table 3 Factor loadings, eigenvalues and total variance (%)

Variables	Factor 1	Factor 2	Factor 3
Pd	0.93	−0.01	0.08
Pt	0.96	−0.07	0.05
Rh	0.90	0.03	0.14
Ba	0.05	0.66	0.31
Cu	0.24	0.03	0.61
Mo	0.08	0.03	0.84
Ni	0.04	−0.05	0.79
Pb	0.18	0.33	0.65
Zn	0.47	0.28	0.72
Ce	−0.06	0.93	0.05
La	0.03	0.94	0.03
Eigenvalues	4.07	2.38	1.48
(%) Total variance	36.99	21.59	13.49
(%) Cumulative	36.99	58.58	72.08

origin, apparently associated to general motor wear. These metals are present in the chemical composition of automotive fuels, such as diesel and gasoline, or as impurities in the alcohol used as vehicle fuel in Brazil. Thus, Factorial Analysis showed that, even though the analyzed elements are originated from automotive emissions, it was possible to distinguish the automotive catalyser source (Pd, Pt e Rh) and the fuel oils and other parts of the vehicles origin (Cu, Mo, Ni, Pb, and Zn).

The results indicate that, although the vehicular emissions must be the main source of Pd, Pt, Rh, Ba, Cu, Mo, Ni, Pb and Zn in urban soils adjacent to São Paulo city avenues, no significant correlation was obtained between the PGE elements and other traffic-related elements determined. These results differ from the results obtained for the São Paulo roadside soils and from other studies. Ely et al. (2001) studying the Pd, Pt and Rh behavior in urban environments verified a strong correlation with the metals Ni, Cu, Zn and Pb. Schäfer and Puchelt (1998) observed positive correlations between the PGE and Zn, Cu and Pb. On the other hand Zereini et al. (2001) and Whiteley (2004) have observed no correlations between PGE and Pb.

4 Conclusions

In soils next to roads and avenues in São Paulo, Pt, Pd and Rh were found in much higher concentrations than PGE geogenic background. These high concentrations indicate catalytic converter origin. The PGE levels obtained in São Paulo urban soils were much higher than those obtained for roadside soils adjacent to a major road in São Paulo. This may be attributed to the São Paulo traffic density and style and to the rapid increase of the numbers of cars equipped with catalytic converters circulating in the city in the last years. The results of this study further indicate that the PGE concentrations in São Paulo soils are directly influenced by traffic conditions and distance. Lower levels of Pt/Pd ratios compared to other similar studies were observed due to the different Pt/Pd/Rh ratio in Brazilian automobile catalytic converters.

In São Paulo roadside soils, Pb, Cu and Zn showed positive correlations with Pt, Pd and Rh. In contrast, in São Paulo urban soils, these correlations were not observed. This indicates that in the urban soils studied, it was possible to distinguish the automotive catalyser source (Pd, Pt e Rh) and the fuel oils and other parts of the vehicles origin (Cu, Pb and Zn).

The results obtained at present for PGE levels in São Paulo soils demonstrate that, with the rapid increase of the vehicular fleet in Brazil, and the use of cars equipped with PGE based catalytic converters, PGE emissions are expected to soon increase.

The potential risk to human health due to the presence of PGE in the environment is not at present well established. Therefore, it is extremely important to continue monitoring PGE levels, their mechanisms of migration, accumulation and bio effects, mainly in developing countries such as Brazil.

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