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First study on anthropogenic Pt, Pd, and Rh levels in soils from major avenues of São Paulo City, Brazil

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Abstract Over the last years, investigations on the increase of platinum (Pt), palladium (Pd), and rhodium (Rh) levels in urban environments of big cities all over the world - especially to catalytic converters emissions - have been grown up enormously. São Paulo City is the 6th largest megacity in the world having about 20 million inhabitants and an ever increasing seven million motor vehicle fleet. In spite of this, there has never been an investigation regarding Pt, Pd, and Rh levels in the city. In the present study, Pt, Pd, and Rh concentrations were determined in soils adjacent to seven main high-density traffic avenues in the metropolitan region of São Paulo City. Inductively coupled plasma mass spectrometry was employed - after ultrasound-assisted *aqua regia* leaching - as analytical technique. The results showed concentration levels up to 378 ng g^{-1} for Pd, 208 ng g^{-1} for Pt, and 0.2 to 45 ng g^{-1} for Rh. These levels are much higher than those considered for the geochemical background of soils, indicating a catalytic converter source. Due to the different Pt/Pd/Rh ratio in Brazilian automobile catalytic converters, lower levels of Pt/Pd ratios compared with other similar studies were observed. The obtained results are the first data for monitoring Pt, Pd, and Rh pollution in São Paulo City soils.

Keywords Platinum group elements · Catalytic exhausts · Urban soil · São Paulo

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Introduction

Automobile catalytic converters have been used increasingly over the years to minimize significantly the emission of toxic gases produced during combustion, removing about 90% of the carbon monoxide, hydrocarbons, and nitrogen oxides from exhausts (Barefoot 1999; Zereini et al. 2001; Hooda et al. 2007). The platinum group elements (PGE) platinum (Pt), palladium (Pd), and rhodium (Rh) play a decisive role in the performance of automobile catalytic converters. However, elevated temperatures and vibration of the catalyst material in the converter release small amounts of PGE in the exhaust fumes (Zereini et al. 2007). Emissions of PGE into the urban environment have led to environmental and human health concerns. These PGE emissions have become studies on their final chemical speciation, their transformation in the environment and their possible health repercussions for living organisms (Reinhard 2006; Rauch 2010).

There are several studies suggesting that PGE originating from traffic emissions are relatively inert, since they are mostly emitted in elemental form. Some studies, however, have shown that a minor fraction is emitted as compounds of various solubility, such as palladium nitrate (Fritsche and Meisel 2004). Metallic PGE in the bulk form are inert as far as biological reactions are concerned (Palacios et al. 2000). On the other hand, Speranza et al. (2010) have studied pollen treated with 5–10-nm-sized Pd particles, similar to those released into the environment by catalytic car exhaust converters. Pd-nanoparticles altered the kiwifruit pollen morphology and entered the grains more rapidly to a greater extent than soluble Pd(II) (Speranza et al. 2010).

PGE analyses have been carried out in plant samples to be used as bioindicators and biomonitors of toxic elements in the environment (Markert 1996; Djingova et al. 2003; Fränzle et al. 2012). Mulholand and Turner (2011) examined the accumulation of catalytic PGE by the mollusc *Littorina littorea* observing metal accumulation occurring in the visceral complex and kidney. Osterauer et al. (2011) tested the genotoxicity of Pt on two freshwater organisms, zebrafish (*Danio rerio*) and ramshorn snail (*Marisa cornuarietis*). Their results indicated a significantly DNA damage in *M. cornuarietis* starting from about 1 μg/l $PtCl_2$.

PGE detection in plants and trees along roads indicates that PGE reflect transformations into more environmentally reactive and bioavailable species (Hooda et al. 2007). Schaefer et al. (1998) have studied the distribution of PGE from autoexhaust catalysts in soils and different types of plants grown near a German highway as well in uncontaminated soils. The main result of the experiments was a measurable transfer of PGE from contaminated soil to plants.

Studies on PGE toxicity and environmental bioavailability indicate that environmental exposure to these metals may be a threat to human health. PGE and their complex salts can affect and cause human health problems, such as asthma, conjunctivitis, and allergy (Cicchella et al. 2003). These diseases are a cause of concern of the public health authorities. Very little data are currently available regarding the effects of chronic low-dose exposures. Furthermore, a significant proportion of PGE in airbone PM are in the fine fraction, which has been related to increases in mortality (Pope et al. 2009).

As a result, there has been an increasing interest in determining PGE in environmental compartments along roadsides after the introduction of automobile catalytic converters (Schaefer et al. 1999; Jarvis et al. 2001; Gómez et al. 2004; Morton et al. 2001; Cinti et al. 2002; Cichella et al. 2003; Whiteley and Murray 2003; Djingova et al. 2003; Pan et al. 2009; Mathur et al. 2011). A summary of the reports including measurement of PGE contents in environmental samples in different cities can be found in Jackson et al. (2007). Reviews concerning PGE emissions, environmental concentrations, and related toxicity are available (WHO 1991, 2002; Merget and Rosner 2001; Ravindra et al. 2004; Wiseman and Zereini 2009). Most studies demonstrated increasing concentrations of PGE in roadside environments providing automobile catalysts as predominating source of PGE (Whiteley and Murray 2003).

With the rapid growth of the automobile industry in Brazil (Markert et al. 2011), large numbers of vehicles are being equipped with catalytic converters. Thus, considerable emissions of Pt, Pd, and Rh can be expected. Automobile catalytic converters in Brazil have been in use since 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. The catalytic converters contain mainly Pd and Rh. In contrast, Europe uses a three-way catalyst based on Pt and Rh with a 5:1 ratio and a high-temperature threeway catalyst with variable combinations of Pt, Pd, and Rh (e.g., 5:1 in a Pt/Rh catalyst or 1:14:1 in a Pt/Pd/Rh catalyst; Fritsche and Meisel 2004). Since 1993, Pd has been used to substitute Pt/Rh catalysts in catalytic converters increasing the concentration of this element in the environment (Zereini et al. 2007).

São Paulo, Brazil, is the 6th largest metropolitan region of the world. The city is the capital of the State of São Paulo, the most populous and rich Brazilian state. São Paulo metropolitan area has an estimated population of 21 million in an area of 7,944 km^2 (Instituto Brasileiro de Geografia e Estatística 2008). There are more than seven million circulating motor vehicles in the city (DETRAN 2011), which are, according to the Environmental Protection Agency of the State of São Paulo (CETESB (São Paulo) 2009) and the Governmental Agency of Air Quality Control the main source of air pollution data. On some days this very intensive traffic leads to a complete standstill reaching traffic jams of 290 km.

In a previous study, roadside soils from an important road in the State of São Paulo showed a significant increase in the PGE levels attributed to catalytic converter exhausts (Morcelli et al. 2005). There has been little research on metal levels in São Paulo City soils, and none about the levels and distribution of PGE derived by autocatalysts. This article presents data from a study of PGE levels in urban soils collected next to seven main avenues with high traffic density in the metropolitan region of São Paulo and the relationship between the results obtained and the catalytic converters abrasion. This study is the first to present the distribution of PGE related to the use of catalysts in São Paulo City.

Materials and methods

Study area and sampling strategy

Seven avenues with high density traffic of different regions of São Paulo City were chosen for this study (Fig. 1). Marginal Pinheiros and Marginal Tietê avenues are the two most important avenues in the city. They border the two main rivers crossing the city (the Pinheiros and Tietê Rivers). A historical analysis of vehicle fluxes show that, in 1996, one stretch of Marginal Tietê Avenue was the most congested of South America, having 400,000 vehicles/day. The Marginal Pinheiros Avenue was the second highest congested street in South America, with 300,000 vehicles/day (Braz and Vianna Jr. 1996). Since then, the number of vehicles circulating in the city increased to a fleet of seven million vehicles. The 23 de Maio Avenue is another very important avenue in São Paulo, connecting the North and South regions of the city. These three avenues can be classified as high constant speed traffic driving style due to the lack of traffic lights or roundabouts. The other avenues in this study are among the biggest avenues in the city, with high-density stop-and-go traffic.

The studied avenues and the sampling points are presented in Fig. 1. The distance between the sampling points was from 3 to 5 km, providing 110 samples for 36 points throughout the city's metropolitan region. Areas of 1 m^2, forming a rectangular grid, were sampled (Fig. 2). Four different samples were taken at each of the four corners of the grid, and each of the four samples consisted of three sampling points. The 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. A polyethylene tube with 4 cm diameter was used to collect the samples, which were stored in inert plastic bags.

Physico-chemical characteristics

Once in the laboratory, the samples were dried at 40°C and were sieved through plastic sieves into <2-mm fractions. The parameters pH, organic carbon and granulometry were determined. The granulometry was determined by the pipette and Bouyoucos' densimeter methods (Gee and Bauder 1986). The pH was determined on a 1:5 soil to 0.01 M $CaCl_2$ suspension (Rayment and Higginson 1992). The organic carbon was determined by the Walkley–Black method (Walkley and Black 1934). For the determination of PGE the samples were ground in an agata grinder and then homogenized and quartered.

Analytical procedure

Determination of Pt, Pd, and Rh by HR-ICP-MS

Two grams of the samples were accurately weighted in 50-mL centrifuge tubes adding 10 mL of *aqua regia*. The tubes were warmed 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 HNO_3 2%.

A HR-ICP-MS Instrument, Element, Finnigan MAT, was used. Method detection limits (3σ) obtained for procedural blanks - analyzed by three replicate measurements of two different blanks - resulted in 0.1 ng g^{-1} for Pd and Pt, and 0.2 ng g^{-1} for Rh, respectively. The HR-ICP-MS Instrument was calibrated with solutions containing 0.1, 0.5, 1.0, 2.5, and 5.0 ng mL^{-1} of each PGE prepared from a PGE standard solution (Specpure, ALFA AESAR). A 10-ng mL^{-1} Indium solution was used to optimize the instrumental parameters and to maximize the signal intensity. Potential interferences from MO^+, MOH^+, and MAr^+ species were evaluated and mathematically corrected.

Quality control The precision and accuracy of the analytical method were assessed by the analysis of the reference materials SARM 7 (SABS) and UTM 1 (CANMET) (Table 1). Zischa and Wegscheider (1999) have estimated the uncertainty of about 10-30 % for the determination of Au, Pd, Pt, and Rh when *aqua regia* leaching or fire assay was employed to prepare the samples before ICP-MS-determination.

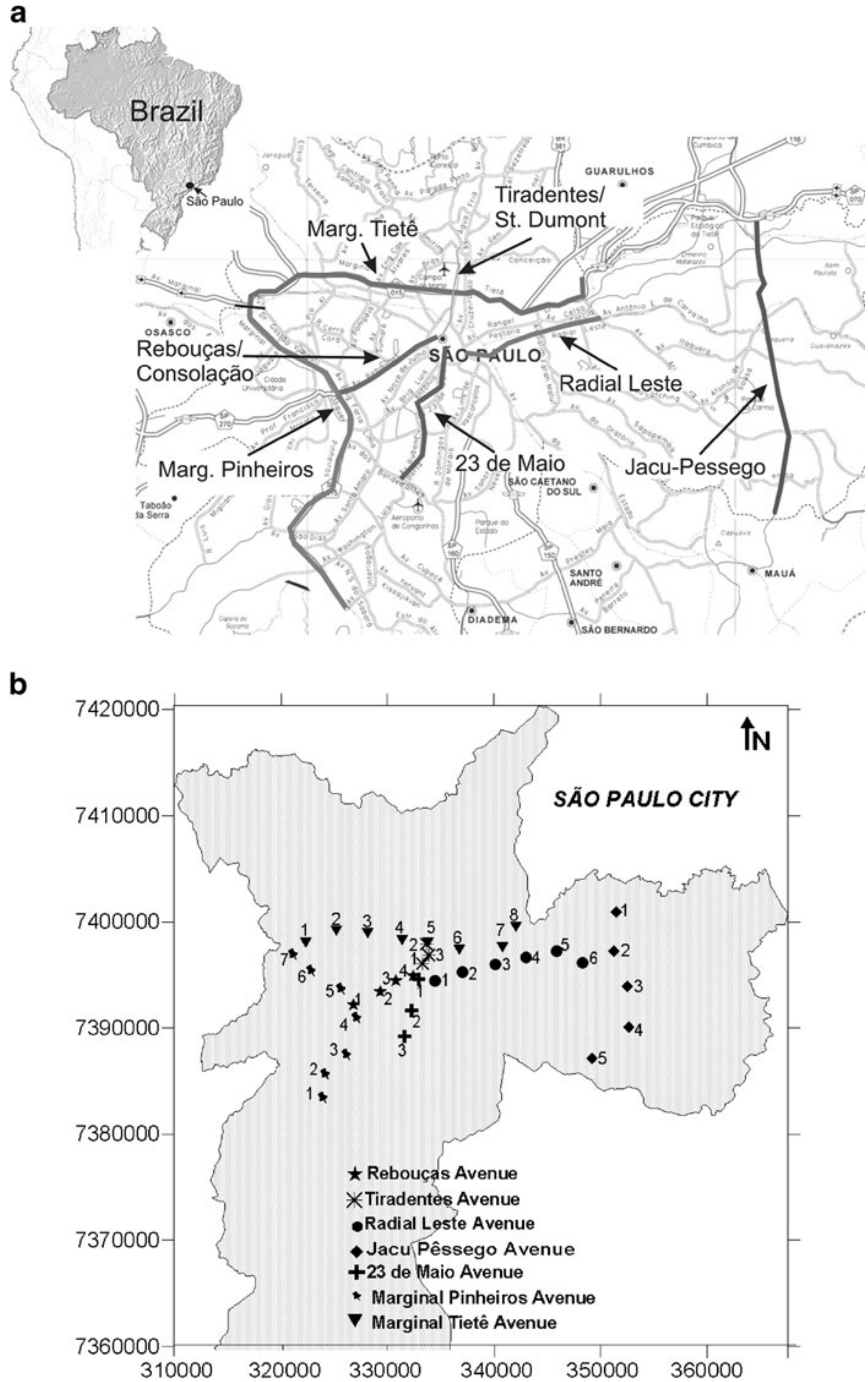

Fig. 1 Areas studies close to given avenues in São Paulo City (**a**) and sampling stations (**b**). Further information of various characteristics (e.g. on stop and go phases) of avenues investigated are given in the text

The analytical procedure used to prepare the reference material was the same as for the samples. The results showed an acceptable accurency for the instrumental measurements (relative errors of 13%, 16%, and 10% for Pt, Pd, and Rh, respectively, in SARM-7, and of 1%, 22%, and 18% for Pt, Pd, and Rh, respectively, in UTM-

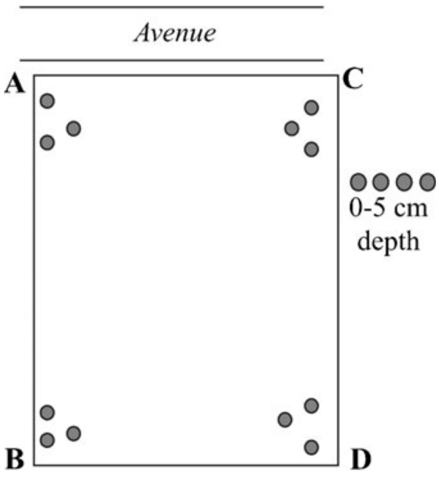

Fig. 2 Sampling strategy. Details are given in the text

1) and an acceptable precision (reproducibility), means a procentual Relative Standard Deviation (RSD) equal or less than 18% for five replicates.

Results and discussion

Soil properties

Soil samples from São Paulo avenues present acid to neutral pH-values in between 6 to 7. The content of organic matter in the soil ranged from 4% to 7%. Only few samples (one sampling point in the Marginal Pinheiros Avenue and one sampling point in Jacu Pêssego and Rebouças/Consolação Avenues, respectively) presented organic matter of about 2%. The content of clay-size particles ranged from 40% to 50% characterizing loam sandy clay soils.

PGE levels and behavior

The average values obtained from the four composed samples collected at each sampling point are presented in Table 2. The results obtained for Pd, Pt, and Rh showed a significant PGE enrichment in relation to the continental crust levels. These values have been used as background values for PGE in several environmental studies (Zereini et al. 2005; Whiteley 2004). As can be seen, there is a significant variability in the PGE levels, with the highest concentrations in soils of Radial Leste Avenue. The lowest values, f.e. 1 ng g^{-1} for Pt, were obtained at the beginning of Marginal Pinheiros Avenue, where the influence of traffic is less significant.

In general, PGE derived from autocatalytic converters may form soluble species by reactions with humic substances and other secondary organic compounds. Organic matter content can affect the PGE solubility and mobility in the environment (Lottermoser and Morteani 1993; Whiteley 2004; De Vos et al. 2006; Parry and Jarvis 2006). This fact can possibly be the reason for lower PGE levels at sampling areas characterized by lower organic matter (2%). On the other hand, samples presenting a higher organic matter content (7%) showed the highest PGE levels. It has to be mentioned - spite of the importance of the granulometry in metal adsorption processes - that there was no correlation observable between the PGE distribution patterns to the granulometric soil characteristics.

Table 1 Results obtained for Pd, Pt, and Rh in the reference materials SARM-7 and UTM-1

Element	Concentration (ng g^{-1})		Relative error (%)	Relative standard deviation (%)
	Certified value	Obtained value[a]		
SARM 7				
Pd	1,530±31	1,278±42	16	3
Pt	3,740±37	3,272±244	13	7
Rh	240±12	215±17	10	8
UMT 1				
Pd	104.2±5.9	127±23	22	18
Pt	128.3±9.8	127±19	1	15
Rh	9.8±2.9	8±1	18	13

[a]Mean of five replicates and standard deviation

Table 2 Mean and concentration ranges (ng g^{-1}) for Pt, Pd, and Rh in soils adjacent to main avenues of São Paulo City

Highways and avenues	Pd (ng g^{-1})		Pt (ng g^{-1})		Rh (ng g^{-1})	
	Mean	Range	Mean	Range	Mean	Range
Marginal Pinheiros Avenue	58.6	3.3–117	11.4	1–41	2.3	0.2–5
Marginal Tietê Avenue	81.7	35–163	23.2	3–107	6.4	1–14
Jacu Pêssego Avenue	41.5	5–133	16.4	2–51	2.1	0.1–8
Radial Leste Avenue	172.3	51–378	78.5	7–208	16.2	3–45
23 de Maio Avenue	76.0	34–123	28.2	8–61	7.1	2–17
Rebouças/Consolação Avenues	70.4	21–233	17.8	4–76	6.1	1–12
Tiradentes/Santos Dumont Avenues	47.1	23–77	15.2	5–27	3.2	2–5

Several studies have demonstrated that the PGE levels show a rapid decrease as a function of distance from the road edge (Brown 2002; Morcelli et al. 2005; Hooda et al. 2007). In our studies Pt, Pd, and Rh presented higher levels in the samples collected 15 cm from the avenue edge (Marginal Pinheiros, Marginal Tietê, Radial Leste and Jacu Pêssego avenues). There was no significant variation in PGE levels in Rebouças/Consolação, Tiradentes/Santos Dumont and 23 de Maio soil samples. In these avenues, the middle divider was not wider than 2 m.

Comparison with other studies

The results obtained were compared with other studies of autocatalyst-derived PGE in roadside soils and road dusts from different countries all over the world (Table 3), showing concentration levels of the same order of magnitude, except for the results obtained in soils adjacent to Radial Leste Avenue. The highest Pt concentration obtained (208 ng g^{-1}), was lower than the concentrations reported in roadside soils of a UK road (up to 500 ng g^{-1} of Pt, Jarvis et al. 2001) and in soils from Mexico City (332.7 ng g^{-1}, Morton et al. 2001).

Compared with the results obtained by Morcelli et al. (2005) in soils adjacent to a major road (SP348) in São Paulo (concentration levels from 58 to 1.1 ng g^{-1} for Pd, from 17 to 0.3 ng g^{-1} for Pt, and from 8.2 to 0.07 ng g^{-1} for Rh), Pt, Pd, and Rh levels were much higher than the highest values obtained by Morcelli et al. (2005). In soils adjacent to the Radial Leste

Table 3 PGE level comparison with other autocatalyst-derived PGE studies (ng g^{-1})

PGE studies	Pd (ng g^{-1})	Pt (ng g^{-1})	Rh (ng g^{-1})
São Paulo topsoils (present study)	3–378	1–208	0.2–45
Roadside soils, São Paulo (Morcelli et al. 2005)	1–58	0.3–17	0.1–8.2
Soils along a major highway in Germany (Zereini et al. 2007)	20–191	41–254	7–36
Road dusts and roadside soils from Australia (Whiteley and Murray 2003)	13.8–440	30–420	3.5–91
Soils adjacent to roads, England (Hooda et al. 2007)	84.2–120.8	2.04–15.9	3.5–22.4
Soils from Mexico City[a] (Morton et al. 2001)	15.2–101.1	91.2–207.7	4.7–22.7
Soils from Mexico City[b] (Morton et al. 2001)	46.8–74	307.5–332.7	26–39.1
Road dust/surface soil samples from UK roads (Jarvis et al. 2001)	2–70	50–500	1–20
Road dust/gullies in Sheffield, England (Prichard et al. 2009)	26–472	37–416	14–113
Soils from Hong Kong, China (Pan et al. 2009)	6.93–107	15.4–160	1.61–34.5
Concentrations of the continental crust (Wedepohl 1995)	0.4	0.4	0.06

[a] High constant speed traffic

[b] High-density stop-and-go traffic

Avenue, Pd levels up to 378 ng g^{-1} were observed. This is about seven times higher than the results obtained by Morcelli et al. (2005). Again, 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 by Morcelli et al. (2005), respectively. These results can be explained by the traffic characteristics of the studied avenues. Besides high dense traffic, there are slow and stop-and-go driving conditions rather than accelerated traffic. According to Morton et al. (2001), soils from Mexico City presented lower PGE levels in urban areas submitted to high speed car flux than slow stop-and-go traffic (Table 3). Whiteley (2004) and Ward and Dudding (2004) also reported the influence of traffic density and flow conditions in the PGE particle release and accumulation in the adjacent motorway environment. Speed variation can damage the catalyst material due to large temperature gradients which contribute to the breakdown of catalytic converters, releasing the PGE via the exhaust emission (Ward and Dudding 2004). Prichard et al (2009), however, observed high Pt, Pd, and Rh concentrations close to roundabouts rather than to traffic lights and topographic lows. The downtown Radial Leste Avenue presents stop-and-go traffic during the whole day explaining the high PGE concentrations of Radial Leste Avenue in relation to avenues, alternating constant speed and stop-and-go flow. Furthermore, soil samples from Rebouças/Consolação and 23 de Maio Avenues were collected along exclusive bus lanes. Buses in Brazil do not have catalytic converters, which may also justify the lower PGE concentrations obtained in relation to the Radial Leste soil levels.

The PGE levels in soils adjacent to Marginal Pinheiros and Marginal Tietê avenues are of the same order of magnitude as the other avenues (except Radial Leste). It should be pointed out that these highways have high-density traffic of trucks not yet equipped with catalytic converters.

The São Paulo City vehicular fleet enlarged from six to seven million in only three years (DETRAN 2011). This may undoubtedly have contributed to the increase of PGE levels in the soil. Zereini et al. (2007) reported a similar increase of PGE levels in the last years in Germany. These authors have evaluated the spatial distribution of PGE in soils next to an important road in Germany from 1994 to 2004, and they have observed that the concentrations of Pd in soils along the highway were found to be about - on average - 15 times higher than those measured in 1994. Pt and Rh concentrations increased 2 and 1.6 times, respectively, during this period. Parry and Jarvis (2006) reported PGE temporal variations in roadside environment in London during a short period of time (1995/1996 to 1998/1999). The authors observed that in about three years Pd, Pt, and Rh concentrations increased 1,230%, 232%, and 372%, respectively. Therefore, the high concentrations observed in the present study may be associated to the São Paulo traffic style and to the increase of the vehicular fleet over the last years.

PGE ratio

The PGE ratio (Pt/Pd, Pt/Rh, and Pd/Rh) can be an important indicator of the catalytic converter source (Jarvis et al. 2001; Whiteley 2005). The most common catalytic converters are the three-way catalysts based on Pt and Rh representing a ratio of 5:1 (Fritsche and Meisel 2004). Nevertheless, the development of new technologies for catalytic converters production and the replacement of Pt by Pd in the catalytic converter composition have changed the PGE concentrations in the environment (Morcelli 2005). Since the 1990s, the use of Pd in automobile industry has increased considerably. Therefore, besides the Pt/Rh or only Pt converters, variable combinations of Pt, Pd, and Rh were introduced (only Pd, Pd/Rh, or Pt/Pd/Rh), significantly changing the PGE ratios in the environment.

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 the present study (0.2–0.4) did not differ much from the ratios (0.3-0.4) obtained by Morcelli et al. (2005). Both results were much lower than the ratios reported in other studies. Jarvis et al (2001) 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. On the other hand, Prichard et al. (2009) observed Pt/Pd ratios less than 1 in road dust and road sweeper samples. A lower concentration of Pt in Brazilian soils is expected, since the catalyst converters in Brazil have mainly Pd and Rh. The Pt/Rh ratio was more variable, with a range from 3.0 to 7.8, which agree with the Pt/Rh ratios obtained in other autocatalyst-derived PGE studies. The average Pt/Rh ratio of 5.1 ± 0.9 (range, 4.0–9.0) is characteristic of autocatalyst emissions. This suggests that not only Pt and Rh are associated during emission, but they remain associated during any subsequent mobilization (Whiteley 2005). Jarvis et al. (2001) obtained Pt/Rh ratio from 4.5 to 15.8 for samples collected adjacent to major UK roads. Barefoot (1999) reported ratios of Pt/Rh of about 5:1 or 6:1. Zereini et al. (2007) obtained Pt/Rh ratios ranging from 4.2 to 9.1 in soils along a main highway in Germany. 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 1998/1999, compared with values in 1995/1996, indicating a reduction of about 30% in Pt compared with Rh and an increase in Pd of about 40%. The Pd/Rh ratio ranged from 10.6 to 25.4 which is much higher than the Pd/Rh ratios obtained by Zereini et al. (2007), from 1.6 to 8.4, and by Whiteley (2005), from 1.7 to 8.7 possibly indicating the replacement of Pt by Pd in the autocatalysts. Since Pd appears to be the most mobile of all platinum metals, concerns are now being raised about possible environmental and human health consequences.

Conclusions

In soils next to avenues in São Paulo City, Pt, Pd, and Rh concentration levels were much higher than the PGE geogenic background. The high concentrations of Pt, Pd, and Rh found in the soils next to major avenues indicate catalytic converter origin.

Lower levels of Pt/Pd ratios compared with other similar studies were observed due to the different Pt/Pd/Rh ratio in Brazilian automobile catalytic converters.

The high PGE levels obtained 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.

Considering that PGE emitted by catalysers may be easily mobilized and solubilized by various compounds commonly present in the environment, increasing their bioavailability and hazard potential, and that these emissions in São Paulo will continue to rise, since more automobiles are equipped with exhaust catalysts, greater exposure levels can be expected. Consequently, the high PGE concentration levels obtained may become a human health concern to the São Paulo City population.

This study is the first of its kind to address the problem of PGE catalyst-derived contamination in urban soils in the city of São Paulo.

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