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Science of the Total Environment
An International Journal for Scientific Research

Science of the Total Environment 345 (2005) 81-91

www.elsevier.com/locate/scitotenv

# PGEs and other traffic-related elements in roadside soils from São Paulo, Brazil

C.P.R. Morcelli<sup>a</sup>, A.M.G. Figueiredo<sup>a,\*</sup>, J.E.S. Sarkis<sup>a</sup>, J. Enzweiler<sup>b</sup>, M. Kakazu<sup>a</sup>, J.B. Sigolo<sup>c</sup>

<sup>a</sup>Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, Av. Prof. Lineu Prestes 2242, Cidade Universitária, São Paulo, SP CEP 05508-000, Brasil <sup>b</sup>Instituto de Geociências, UNICAMP, CP 6152, Campinas, SP 13083-970, Brasil <sup>c</sup>Instituto de Geociências, Universidade de São Paulo, São Paulo, SP, Brasil

> Received 1 June 2004; accepted 26 October 2004 Available online 21 December 2004

#### **Abstract**

The distribution of platinum, palladium, and rhodium in soils adjacent to a major road in São Paulo, Brazil, is presented. Sampling was made at four sites with varying traffic volumes and driving styles (stop/start vs. constant speed). High-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) with NiS fire assay collection and Te coprecipitation was used as analytical procedure. The platinum group element (PGE) pattern distribution in the analyzed roadside soil was similar to that of other traffic-related elements such as Zn and Cu, characterized by a strong decrease of the PGE content with increasing distance from the traffic lane. The results indicate that the PGE concentrations in roadside soil are directly influenced by traffic conditions and distance, which characterize their catalytic converter origin. Pt, Pd, and Rh contents range between 0.3 and 17 ng g<sup>-1</sup>, 1.1 and 58 ng g<sup>-1</sup>, and 0.07 and 8.2 ng g<sup>-1</sup> respectively. Lower levels of Pt and lower Pt/Pd ratios in relation to similar studies in other countries were observed due to the different Pt/Pd ratios in Brazilian automobile catalytic converters. This is the first study to assess traffic-derived Pt, Pd, and Rh deposition in Brazil.

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Keywords: Rhodium; Platinum; Palladium; Catalytic exhausts; Urban pollution; Traffic-related elements

E-mail address: grafigue@curiango.ipen.br (A.M.G. Figueiredo).

### 1. Introduction

Cars fitted with exhaust catalysts containing platinum group elements (PGEs) significantly minimize toxic gas emissions produced during gas combustion. Catalysts remove about 90% of carbon monoxide, unburned hydrocarbons, and nitrogen oxides ( $NO_x$ )

<sup>\*</sup> Corresponding author. Tel.: +55 11 3816 9182; fax: +55 11 3816 9188.

from car exhaust and transform these pollutants into more innocuous carbon dioxide, nitrogen, and water (Palacios et al., 2000, Barefoot, 1999; Zereini et al., 2001). Both platinum and palladium are used to oxidize carbon monoxide and hydrocarbons. Rhodium must be present in order to reduce nitrogen oxides (Morton et al., 2001). However, catalytic converter surface abrasion and deterioration release these elements, adsorbed on small particles, into the environment, causing PGE deposits near roads, in vegetation, and in other environmental compartments such as rivers, as a result of wind and water transport (Zereini et al., 2001). Artelt et al. (2000), in engine bench test experiments, found emission factors ranging from 2 to 120 ng km<sup>-1</sup>, depending on test conditions and catalyst age. The probable emission rate of Pt from vehicles equipped with catalytic converters has been estimated as 0.5-0.8 μg km<sup>-1</sup> Pt (Helmers, 1997). The geogenic PGE concentration background in soils is estimated to be ca. 1 μg kg<sup>-1</sup>, whereas contaminated soils along roadsides show contents up to several hundred micrograms per kilogram (Zereini et al., 2000).

The toxic effects of platinum emitted by automobile exhaust converters are only expected if platinum is bioavailable. Only soluble platinum compounds are of any possible toxicological relevance (Rosner and Merget, 2000). Respiratory sensitization to certain platinum salts is the relevant end-point for assessing the health risk potential of platinum. Platinum in dust emitted from automobile catalytic converters is mostly in metallic form, although small amounts of oxidized Pt(IV) have also been found in exhaust gases (Schlogl et al., 1987). Rhodium is present in the autocalyst in a metallic form and as an oxide. PGE transformations during vehicle operation might change the form in which PGE occurs in the autocatalyst (Rauch et al., 2000). Converter-emitted PGE may undergo rapid transformations in the environment and subsequently behave similarly to soluble PGE salts (Whiteley and Murray, 2003). Little work has been carried out with the bioavailability of Pt. Zereini et al. (1997) demonstrated the low Pt and Rh solubility both in soil and surface waters. Uptake experiments in plants showed that Pt and Rh present transfer coefficients below 0.1 (Schafer et al., 1998). Begerow and Dunemann (2000) reported that, in comparison with control groups, people heavily exposed to traffic do not show increased urinary Pt and Pd excretion and that, apparently, emissions from catalyst-equipped automobiles do not contribute to the internal background exposure of the general population.

Recent studies show that the cheaper price of Pd resulted in the development of catalytic converters with lower levels of Pt and constituted by Pd/Rh (Farrauto and Heck, 1999). This means that the potential effect of Pd to cause allergic reactions will become more important in the future (Jarvis et al., 2001).

There has been an increasing interest in determining PGE concentrations in environmental compartments along roadsides after the introduction of automobile catalytic converters (Jarvis et al., 2001; Gómez et al., 2001; Morton et al., 2001; Cinti et al., 2002; Cichella et al., 2003; Whiteley and Murray, 2003). A summary of the reports including measurement of PGE contents in environmental and biological samples (dust, vegetation, soil, sediments, water, blood, and urine) is found in Barefoot (1997). Most of the studies demonstrated increasing concentrations of PGE in roadside environments, providing evidence that the automobile catalysts are the predominant source of PGE (Whiteley and Murray, 2003).

Most of the studies have focused on Pt levels in a variety of environmental matrices, while Pd and Rh have only been monitored more recently (Helmers, 2000). According to Barefoot (1999), the concentration of Pt near German roads is about 70 times higher than background values. Schafer and Puchelt (1998) evaluated the concentrations and distribution patterns of Pt, Pd, and Rh in soil samples next to highways in Southwest Germany, and found high PGE concentrations in the uppermost soil layer, decreasing farther from the road. This is a result of large particle or whole catalyst piece emissions, which are deposited a very short distance from the roads (Rosner and Merget, 2000). In those catalytic converters produced between 1984 and 1992, there is a characteristic relationship between Pt and Rh, and a relatively constant Pt and Rh ratio (~5:1 or 6:1) can be observed in environmental samples (Zereini et al., 1997; Schafer and Puchelt, 1998). Since then, catalytic converter development has led to a wide range of Pt, Pd, and Rh combinations and concentrations, as well as to the introduction of Pd-Rh, Pt-Rh, Pt-only, or Pt-Pd-Rh catalysts. Therefore, these differences in composition may bring about concentration changes of these metals in environmental samples. Table 1 shows some results found for Pt, Pd,

Matrix	Concentration range (µg kg <sup>-1</sup> )			Local	Reference
	Pt	Pd	Rh		
Soil	2–159	1–7	1–28	Hessen, Germany	Zereini et al., 1998
Road dust and soil	< 0.30 - 40.1	<2.1-57.9	_	SE England	Farago et al., 1998
Road dust	31-2252	_	11-182	Madrid, Spain	Gómez et al., 2001
Soil	3.1-332.7	2.5-101.1	0.7 - 39.1	Mexico City, Mexico	Morton et al., 2001
Soil and road dust	<10-500	1-70	1-70	Major UK roads	Jarvis et al., 2001
Soil	<2-52	<10-110	_	Naples metropolitan area	Cichella et al., 2003
Soil	<1-13.8	_	_	Naples metropolitan area	Angelone et al., 2002
Soil	7.0-19.4	_	_	Urban area—Rome, Italy	Cinti et al., 2002
Road dust and roadside soil	30.96–419.41	58.15-440.46	3.47-91.40	Perth, Western Australia	Whiteley and Murray, 2003

Table 1 Pt, Pd, and Rh levels ( $\mu$ g kg<sup>-1</sup>) in soil and road dust from highway sides in different countries (literature data)

(-) Not determined.

and Rh concentrations in soil and road dust from different urban sites. In all studies, much higher PGE concentrations were found in urban road dust than those in roadside soils collected at the same location. In Mexico, vehicles with catalytic converters were introduced in 1994, and in a 10-year accumulation period, PGE levels up to 200 times higher than background levels were found in soil collected next to roads.

In Brazil, the automobile catalytic converters have been in use since 1996, and in their composition, there is about 1.5 g of PGE. Brazilian vehicles use gasohol, a mixture of gas and alcohol in a 8:2 proportion, and the catalytic converters contain mainly Pd and Rh.

This article presents data from a first study of PGE levels in roadside soil collected from a high-density traffic road in São Paulo, and the relation between the results obtained and the catalytic converter abrasion. The analytical technique employed was NiS fire assay with Te coprecipitation and high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). The soil samples were analyzed for trace metals by instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF). A PGE correlation with other known potentially toxic metals (e.g., Pb, Zn, and Cu) was verified.

# 2. Materials and methods

## 2.1. Sampling

For this study, four sampling locations were chosen adjacent to a major road (SP348), with high-density

traffic flow (ca. 30,000 vehicles per day) running between the city of São Paulo and other important industrial regions of the state of São Paulo. Sampling was undertaken in October 2002.

Sampling points were located between the cities of São Paulo and Jundiaí, where the highest traffic density of the road is found at 31, 39, 45, and 55 km from the city of São Paulo. Areas of 20 m<sup>2</sup>, forming a rectangular grid, were sampled. Composite samples were then prepared by taking five samples, each 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 (Fig. 1). The sampling depth was 5 cm. The covering vegetation was separated. Roadside soil sampling locations were carefully selected to represent a cross-section of traffic volumes and driving styles (stop/start vs. constant speed). The speed limit is 120 km h<sup>-1</sup>. The sampling point at km 39 was just after a tollbooth, where vehicles have to come to a full stop and then accelerate

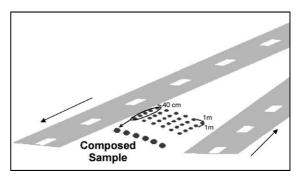


Fig. 1. Sampling scheme.

very quickly. A 4-cm-diameter polyethylene tube was used to take the samples, which were then stored in inert plastic bags. In the laboratory, the samples were dried at 40–50 °C and were sieved through plastic-only sieves into <2 mm fraction. Before and after sieving, the samples were homogenized and quartered.

#### 2.2. Analytical methods

## 2.2.1. NiS fire assay with Te coprecipitation

NiS buttons were prepared by thoroughly mixing 10-15 g of the sample with the fusion mixture, which consisted of 10 g of sodium carbonate (anhydrous extra pure; Merck), 20 g of sodium tetraborate (anhydrous GR; Merck), 1 g of nickel powder (INCO Metals), and 0.75 g of purified sulfur (Merck). The mixture was transferred into a fire clay crucible and fused at 950 °C for 30 min, and then again for another 30 min at 1050 °C. After cooling, the crucible was broken, the NiS button was separated from the slag, crushed into large particles, and weighed to assure that there were no losses during the procedure. Better results were obtained when the NiS button was crushed into large particles instead of pulverizing the button. The NiS button was dissolved in 20 ml of suprapur hydrochloric acid (Merck) in a Teflon closed vessel (Savillex, USA), at 150 °C on a hot plate for about 14 h. The solution was cooled to room temperature and 2 ml of a 2000-ppm Te solution, prepared as described by Stockman (1983), was added. The solution was heated to 95-100 °C and 10 ml of Sn(II) chloride solution (13.5 g of SnCl<sub>2</sub>·2H<sub>2</sub>O dissolved in 9 ml of concentrated HCl and diluted to 60 ml with water), freshly prepared, was added to precipitate the metallic Te. The solution was boiled to coagulate the precipitate. One milliliter of the Te solution was added, and the solution boiled for 5 min. This solution was then filtered onto a 0.45µm membrane filter (Millipore) and the precipitate washed with a 10% HCl solution and dissolved with 2 ml of suprapur HCl and 2 ml of suprapur HNO<sub>3</sub>. The solution was made up to 100 ml by adding pure water (Milli-Q; Millipore) for ICP-MS analyses.

## 2.2.2. HR-ICP-MS

An HR-ICP-MS instrument (Element; Finnigan MAT) was used. The instrumental parameters and the isotopes used are described in Table 2. Method

Table 2 HR-ICP-MS (Element; Finnigan MAT) operating conditions and measurement parameters

d passes)
<sup>05</sup> Pd (22.23),
nd <sup>195</sup> Pt (33.8)

detection limits (3 $\sigma$ ) obtained for procedural blanks, in three replicate measurements of two different blanks, were respectively 0.04, 0.1, 0.03, and 0.7 ng g<sup>-1</sup> for Rh, Pd, Ir, and Pt. The HR-ICP-MS instrument was calibrated with solutions containing 0.2, 0.4, 0.8, 1.0, 2.0, 5.0, 10.0, and 20.0 ng ml<sup>-1</sup> of each PGE prepared from a PGE standard solution (Specpure; ALFA AESAR). A 10-ng ml<sup>-1</sup> indium solution was used to optimize the instrumental parameters and to maximize the signal intensity. Potential interferences from MO<sup>+</sup>, MOH<sup>+</sup>, and MAr<sup>+</sup> species were evaluated in previous studies (Shibuya et al., 1998; Jorge et al., 1998). None, however, was found to be significant for the range of concentrations measured for this study.

## 2.2.3. INAA

INAA was used to analyze the elements Ba, Ce, La, and Zn. Samples were homogenized and ground in agate mortars. One hundred to 150 mg of each sample and of the geological reference materials BE-N (ANRT) and Soil-7 (IAEA) was accurately weighed in polyethylene bags. Samples and reference materials were irradiated for 8 h at a thermal neutron flux of  $10^{13}$  n cm<sup>-2</sup> s<sup>-1</sup> at the IEA-R1 nuclear reactor of IPEN. The measurements of the induced gamma-ray activity were carried out in gamma-ray spectrometer with a GX20190 hyperpure Ge detector (Canberra).

#### 2.2.4. XRF

XRF was employed to determine Cu, Mo, Pb, and Zr. Pellets (40 mm diameter) consisting of a

Table 3 Results for other metallic elements obtained by INAA and XRF for certified reference materials (mg kg $^{-1}$ )  $\pm 1$  s

Element	Analytical	Soil-7 (IAEA)		
	technique	Found value	95% Confidence interval	
Ba Ce La Zn	INAA	$159\pm28$ $61\pm7$ $28\pm1$ $104\pm6$	131–196 50–63 27–29 101–113	
Element	Analytical	GSS-2 (IGGE, China)		
	technique	Found value	Recommended value ±2 s	
Cu Mo Pb Zr	XRF	$13.8\pm0.1$ $1.1\pm0.1$ $19\pm1$ $207\pm2$	$16.3 \pm 2.8$ $0.98 \pm 0.34$ $20 \pm 8$ $209 \pm 46$	

mixture of 9 g of the sample and 1.5 g of powdered wax (Hoechst) were prepared and measured in a sequential XRF spectrometer (PW 2404; Philips), equipped with a rhodium tube. The details of the procedure are described elsewhere (Zambello and Enzweiler, 2002).

#### 2.2.5. Reference material analysis

The precision and accuracy of the analytical method employed to determine Pt, Pd, and Rh were previously verified by the analysis of geological reference materials (Morcelli et al., in press). The analytical procedures of INAA and XRF were validated by analyzing the certified reference materials Soil-7 (IAEA) and GSS-2 (soil; IGGE, China), respectively (Table 3).

#### 3. Results and discussion

The results obtained for Pd, Rh, and Pt are presented in Table 4 and are shown in Figs. 2–4, respectively, where Pd, Rh, and Pt concentrations in the continental crust are also presented (Pd: 0.4 ng g<sup>-1</sup>; Rh: 0.06 ng g<sup>-1</sup>; Pt: 0.4 ng g<sup>-1</sup>; Wedepohl, 1995). These values were used as reference since there is no information available on PGE levels in Brazilian soils.

As can be seen in Figs. 2-4, the distribution patterns for Pd, Rh, and Pt are similar and concen-

tration levels higher than the continental crust levels were observed. The PGE concentrations ranged from 58 to 1.1  $\mu$ g kg<sup>-1</sup> for Pd; from 17 to 0.3  $\mu$ g kg<sup>-1</sup> for Pt; and from 8.2 to 0.07 µg kg<sup>-1</sup> of Rh. Considering the highest concentration obtained for each element. the obtained results are more than two orders of magnitude higher than geogenic background values for Pd and Rh, and 40-fold higher for Pt. The highest PGE concentrations were found 40 cm from the roadway. At about 140 cm from the roadway, the concentrations are ca. 90% lower when compared to the samples collected 40 cm from the road. This indicates the anthropogenic origin of the PGE. These data agree with results obtained in other studies, where higher concentrations of the PGE were also observed in the vicinity of roadways (Schafer and Puchelt, 1998; Morton et al., 2001).

No previous data for PGE values in Brazilian soils are available to compare with the obtained results. Data

Table 4
Pd, Rh, and Pt concentration<sup>a</sup> in SP348 roadside soils

Sampling	Distance	Pd	Rh	Pt
site	from roadway	$(\mu g kg^{-1})$	$(\mu g k g^{-1})$	$(\mu g kg^{-1})$
	(cm)			
km 31	40	$58\pm2$	$7.2 \pm 0.1$	$13.0 \pm 0.1$
	140	$12.6 \pm 0.2$	$3.9 \pm 0.2$	$5.2 \pm 0.4$
	240	$7\pm2$	$3.5 \pm 0.2$	$3.4 \pm 0.4$
	340	$8.5 \pm 0.1$	$3.8 \pm 0.2$	$3.8 \pm 0.1$
	440	$8.2 \pm 0.8$	$1.27 \pm 0.04$	$3.3 \pm 0.2$
	540	$4.2 \pm 0.9$	$0.83 \pm 0.15$	$1.48 \pm 0.35$
km 39	40	$45.0 \pm 0.5$	$8.2 \pm 0.1$	$17.4 \pm 0.7$
	140	$35 \pm 1$	$6.03 \pm 0.01$	$10.8 \pm 0.6$
	240	$22\pm4$	$3.5 \pm 1.4$	$6\pm2$
	340	$17 \pm 1$	$2.4 \pm 0.2$	$4.0 \pm 0.2$
	440	$19.8 \pm 0.8$	$2.5 \pm 0.2$	$2.4 \pm 0.2$
	540	$8.5 \pm 0.3$	$1.40\pm0.10$	$3.1 \pm 0.8$
km 45	40	$40 \pm 1$	$6.0 \pm 0.2$	$6.3 \pm 0.1$
	140	$7.5 \pm 1.7$	$1.1 \pm 0.3$	$1.9 \pm 0.6$
	240	$5.1 \pm 0.5$	$0.54 \pm 0.11$	$1.6 \pm 0.8$
	340	$3.6 \pm 0.1$	$0.42 \pm 0.06$	$0.84 \pm 0.01$
	440	$2.2 \pm 0.1$	$0.25 \pm 0.03$	$0.50 \pm 0.05$
	540	$1.4 \pm 0.1$	$0.07 \pm 0.10$	$0.31 \pm 0.01$
km 53	40	$18 \pm 3$	$2.3 \pm 0.1$	$7\pm1$
	140	$6.8 \pm 0.1$	$0.88 \pm 0.01$	$1.2 \pm 0.1$
	240	$3.3 \pm 0.1$	$0.46 \pm 0.01$	$1.30 \pm 0.01$
	340	$2.8 \pm 0.1$	$0.37 \pm 0.01$	$1.5 \pm 0.8$
	440	$1.2 \pm 0.1$	$0.15 \pm 0.01$	_
	540	$1.1 \pm 0.1$	$0.13 \pm 0.02$	$0.61 \pm 0.11$

<sup>&</sup>lt;sup>a</sup> The results are the mean and standard deviation of two replicates.

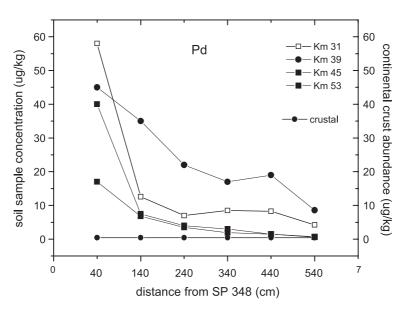


Fig. 2. Pd distribution patterns in roadside soil samples collected at SP348.

on natural soils from different geographic areas (Cinti et al., 2002) suggest that Pt concentrations between 2 and 5 ng g<sup>-1</sup> could be considered as the geochemical background for soils developed on different parent materials. Considering this Pt level in soils, the Pt concentration found is one order of magnitude higher.

In other studies concerning autocatalyst-derived Pt in roadside soil, higher Pt concentrations were observed (up to 500 ng g<sup>-1</sup> of Pt in a UK road; Jarvis et al., 2001). A lower concentration of Pt in Brazilian soil is expected, since the catalyst converters in Brazil contains mainly Pd and Rh. The concentration of Pt

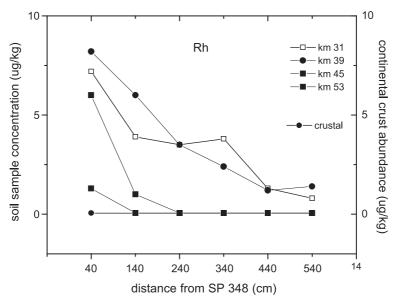


Fig. 3. Rh distribution patterns in roadside soil samples collected at SP348.

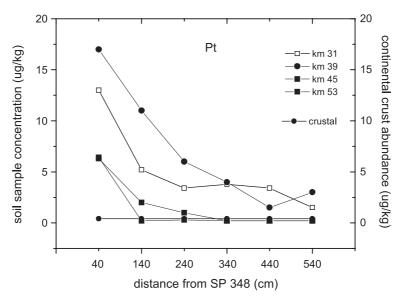


Fig. 4. Pt distribution patterns in roadside soil samples collected at SP348.

found can be attributed to the great quantity of foreign cars Brazil has imported over the last years.

A particular behavior was observed in the results corresponding to km 39, next to the tollbooth. The highest levels of Pt and Rh were obtained at this site, 40 cm from the road. For Pd, the same order of concentration was obtained at the other studied sites. What is remarkable is the difference observed in PGE distribution pattern at km 39. The curve is smoother, showing that PGE reached farther distances from the roadway, in relation to the other studied sites, in what may be attributed to the severe driving conditions at that site, which produces an increase in exhaust gases. Zereini et al. (1998) related a higher emission of PGE from the catalytic converters to the velocity and driving conditions of the vehicle. Changes of velocity such as rapid acceleration cause stress to the catalyst and the exhaust gas system (e.g., variations of temperature and redox conditions). According to Zereini et al. (2001), higher acceleration and higher speed appear to increase PGE emission. In soils from a German Autobahn rest stop, 50% higher Pt concentrations were found at the exit, where drivers speed up to merge into traffic, than in samples collected at the entrance where the drivers slow down.

The concentrations of PGE decreased from km 39 to km 53. At this part of the road, traffic density decreases because there is an exit to other important

cities of the state of São Paulo, and the concentration of PGE also decreased.

In order to verify the PGE distribution pattern that is not present in the catalytic converter, Ir was also analyzed in some of the studied sites. Concentrations in the range of  $0.01-0.03~\mu g~kg^{-1}$  Ir were obtained, which is the same concentration of Ir in the continental crust ( $0.04~\mu g~kg^{-1}$ ; Wedepohl, 1995). This indicates that Pt, Pd, and Rh are derived from catalytic converters.

The Pt/Rh ratio is relatively constant at 1.7 with a range from 0.54 to 4.4, except for km 53 (Pt/Rh ratio range from 1.36 to 4.7) and differs significantly from the results reported by Jarvis et al. (2001) for samples collected adjacent to major UK roads (ratio of Pt/Rh of 7.10 with a range from 4.5 to 15.8). Barefoot (1999) reported Pt/Rh ratios of about 5:1 or 6:1. On the other hand, the Pt/Pd ratio was very consistent at 0.3-0.4 in all sampling sites. Jarvis et al. (2001) found a mean Pt/Pd ratio of 6.6 and a range from 2.01 to 26.6. As mentioned before, with the changes introduced in catalytic converters, the Pt/Pd or Pd/Rh ratios are less well defined (Morton et al., 2001; Whiteley and Murray, 2003). Brazilian autocatalysts have a lower concentration of Pt in relation to their European counterparts. The Pd/Rh ratio varied more in a range from 2 to 20. The relatively large variability of the Pt/Pd ratios compared with the Pt/Rh ratios

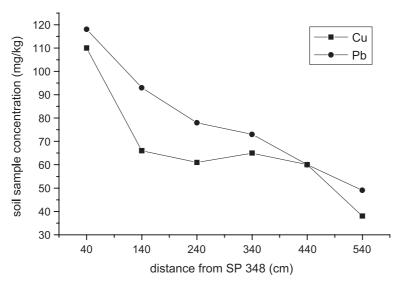


Fig. 5. Pb and Cu distribution patterns in roadside soil samples collected at SP348 (km 31).

suggests a significant difference in chemical behavior between Rh and Pd.

As Pd is increasingly being used in new catalytic converters, possible environmental and human health consequences can be expected. Pd is the most mobile of all platinum metals due to its chemical properties and it can be taken up by plants in considerably greater amounts than Pt and Rh (Zereini et al., 2001).

Traffic-derived trace elements (Pb, Cu, and Zn) were also analyzed. The distribution patterns of Pb and Cu and of Zn for samples collected at km 31 are presented in Figs. 5 and 6, respectively. Cu and Zn accumulation in particulate matter is due to the wear and tear of certain automobile materials and parts during driving (Hildemann et al., 1991). Pearson's correlation coefficients between Pt, Pd, Rh, and Cu,

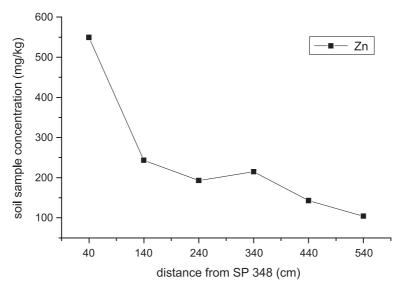


Fig. 6. Zn distribution patterns in roadside soil samples collected at SP348 (km 31).

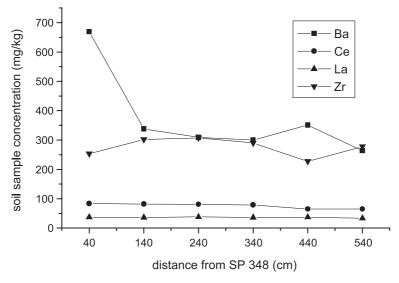


Fig. 7. Ba, Ce, La, and Zr distribution patterns in roadside soil samples collected at SP348 (km 31).

Zn were equal or higher than 0.94 in all analyzed samples, which points to a common source. Pb showed positive correlations with Pt, Pd, and Rh. Zereini et al. (2001) report an average Pb concentration of about 5000 times that of Pt. A much lower Pb/Pt average was obtained in this work, of about 30, due to the use of unleaded gas in Brazil since 1983.

Ba, Zr, 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). However, a constant La/Ce ratio was obtained for all samples indicating a soil origin. As observed by Jarvis et al. (2001), the background concentrations of Ce in soil are typically many tens of micrograms per gram, and the addition of autocatalyst-derived particulate containing Ce in this system can hardly change the background. Pearson's correlation coefficients between Pt, Pd, Rh, and Ba were equal or higher than 0.82 in all analyzed samples, which suggests the catalytic converter as a common source. In Fig. 7, it is evident that, except for Ba, different distribution patterns from the PGE ones were observed in the analyzed soil samples. Negative correlation coefficients were obtained for Zr, showing that here, Pt, Pd, and Rh are not associated to Zr.

## 4. Conclusions

The main conclusions arising from this study can be summarized as follows:

- In SP348 roadside soils, in São Paulo, Pt, Pd, and Rh were found in much higher concentrations than PGE geogenic background.
- The high concentrations of Pt, Pd, and Rh found in the roadside soils suggest an anthropogenic source.
   All three are employed in catalytic converters.
- Traffic-related elements such as Zn and Cu were positively correlated to the PGE, which points to a common source, in this case, automobile exhausts.
- The results obtained indicate that the PGE concentrations in the roadside soils are directly influenced by traffic conditions and distance.
- The emitted PGE-containing particles from catalytic converters are restricted to the immediate vicinity of the roadside.
- Lower levels of Pt and lower Pt/Pd ratios compared to other similar studies were observed due to the different ratio Pt/Pd in Brazilian automobile catalytic converters.
- The average ratio Pb/Pt was much lower than those observed in studies made in Europe due to the wide use of unleaded gas in Brazil.

 This study can be used as a preliminary reference for further studies aiming to monitor PGE pollution in urban areas of Brazil.

## Acknowledgements

The authors thank FAPESP and FINEP/PADCT for financial support.

#### References

- Angelone M, Armiento G, Cinti D, Somma R, Trocciola A. Platinum and heavy metal concentration levels in urban soils of Naples (Italy). Fresenius Environ Bull 2002;11(8):1-5.
- Artelt S, Levsen K, Konig P, Rosner G. Engine tests bench experiments to determine platinum emissions from three-way catalytic converters. In: Zereini F, Alt F, editors. Anthropogenic platinum group element emissions Their impact on man and environment. Berlin Heidelberg: Springer-Verlag; 2000. p. 33-44.
- Barefoot RR. Determination of platinum at trace levels in environmental and biological materials. Environ Sci Technol 1997;31(2):309-14.
- Barefoot RR. Distribution and speciation of platinum group elements in environmental matrices. Trends Anal Chem 1999;18(11):702-7.
- Begerow J, Dunemann L. Internal platinum and palladium exposure of the general population with emphasis on the exposure from automobile exhaust and dental restorative alloys. In: Zereini F, Alt F, editors. Anthropogenic platinum group element emissions. Their impact on man and environment. Springer; 2000. p. 227–36.
- Cichella D, De Vivo B, Lima A. Palladium and platinum concentration in soils from the Napoli metropolitan area, Italy: possible effects of catalytic exhausts. Sci Total Environ 2003;308:121-31.
- Cinti D, Angelone M, Masi U, Cremisini C. Platinum levels in natural and urban soils from Rome and Latium (Italy): significance for pollution by automobile catalytic converter. Sci Total Environ 2002;293:47–57.
- Farago ME, Kavanagh P, Blanks R, Kelly J, Kazantzis G, Thorton I, et al. Platinum concentrations in urban road dust and soil, and in blood and urine in the United Kingdom. Analyst 1998;123:451-4.
- Farrauto RJ, Heck RM. Catalytic converters: state of the art and perspectives. Catal Today 1999;51:351-60.
- Gómez B, Gómez M, Sanchez JL, Fernández R, Palacios MA. Platinum and rhodium distribution in airborne particulate matter and road dust. Sci Total Environ 2001;269:131–44.
- Helmers E. Platinum emission rate of automobiles with catalytic converters. Comparison and assessment of results from various approaches. Environ Sci Pollut Res Int 1997;4(2):100–3.

- Helmers E. PGE emissions of automobile catalysts-identifying their track in the environment. A challenge to analytical strategy and assessment. In: Zereini F, Alt F, editors. Anthropogenic platinum group element emissions. Their impact on man and environment. Springer; 2000. p. 133-44.
- Hildemann LM, Markoxski GR, Cass GR. Chemical composition of emissions from urban sources of fine organic aerosol. Environ Sci Technol 1991;25:744–59.
- Jarvis KE, Parry SJ, Piper JM. Temporal and spatial studies of autocatalyst-derived platinum, rhodium and palladium and selected vehicle-derived trace elements in the environment. Environ Sci Technol 2001;35:1031-6.
- Jorge APS, Enzweiler J, Shibuya EK, Sarkis JES, Figueiredo AMG. Platinum group elements and gold determination in NiS fire assay buttons by UV laser ablation ICP-MS. Geostand Newsl 1998;22(1):47-55.
- Morcelli CPR, Figueiredo AMG, Enzweiler J, Sarkis JES, Jorge APS, Kakazu APS. Determination of platinum group elements in geological reference materials by HR-ICP-MS after nickel sulfide fire-assay collection and Te co-precipitation. Geostand Geoanal Res 2004;28(2): [in press].
- Morton O, Puchelt H, Hernández E, Lounejeva E. Traffic-related platinum group elements (PGE) in soils from Mexico City. J Geochem Explor 2001;72:223-7.
- Palacios MA, Gómez MM, Maldovan M, Morrison G, Rauch S, McLeod C, et al. Platinum-group elements: quantification in collected exhaust fumes and studies of catalyst surfaces. Sci Total Environ 2000;257:1–15.
- Rauch S, Morrison GM, Motelica-Heino M, Donard OFX, Muris M. Elemental association and fingerprint of traffic-related metals in road sediments. Environ Sci Technol 2000;33:3119–23.
- Rosner G, Merget R. Evaluation of the health risk of platinum emissions from automotive emission control catalysts. In: Zereini F, Alt F, editors. Anthropogenic platinum group element emissions. Their impact on man and environment. Springer; 2000. p. 267–81.
- Schafer J, Puchelt H. Platinum group metals (PGM) emitted from automobile catalytic converters and their distribution in roadside soils. J Geochem Explor 1998;64:301–14.
- Schafer J, Hannker D, Echardt J, Stben D. Uptake of traffic-related heavy metals and platinum group elements (PGE) by plants. Sci Total Environ 1998;215:59-67.
- Schlogl R, Indlekofer G, Oelhafen P. Mikropartikelemissionen von Verbrennungsmotoren mit Abgasreinigung—Rontgen-Photoelektronenspektroskopie in der Umweltanalytik. Angew Chem 1987;99:312–22.
- Shibuya EK, Sarkis JE, Enzweiler J, Jorge APS, Figueiredo AMG. Determination of platinum group elements and gold in geological materials using an ultraviolet laser ablation high-resolution inductively coupled plasma mass spectrometric technique. J Anal At Spectrom 1998;13:941–4.
- Stockman HW. Neutron determination of noble metals in rocks a rapid radiochemical separation based on tellurium coprecipitation. J Radioanal Chem 1983;78(2):307-17.
- Wedepohl KH. The composition of the continental crust. Geochim Cosmochim Acta 1995;59:1217-32.

- Whiteley JD, Murray F. Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dust and roadside soils from Perth, Western Australia. Sci Total Environ 2003;317:121–35.
- Zambello FR, Enzweiler J. Multi-element analysis of soils and sediments by wavelength-dispersive X-ray fluorescence spectrometry. J Soils Sediments 2002;2(1):29–36.
- Zereini F, Skerstupp B, Alt F, Helmers E, Urban H. Geochemical behaviour of platinum-group elements (PGE) in particulate emissions by automobile exhaust catalysts: experimental results and environmental investigations. Sci Total Environ 1997;206:137–46.
- Zereini F, Dirksen F, Skerstupp B, Urban H. Sources of anthropogenic platinum-group elements (PGE): automotive catalysts

- versus PGE-processing industries. Environ Sci Pollut Res 1998;5(4):223-30.
- Zereini F, Skerstupp B, Rankenburg F, Dirksen F, Beyer JM, Claus T, et al. Anthropogenic emission of platinum-group elements (Pt, Pd and Rh) into the environment: concentration, distribution and geochemical behaviour in soils. In: Zereini F, Alt F, editors. Anthropogenic platinum group element emissions. Their impact on man and environment. Springer; 2000. p. 73–83.
- Zereini F, Wiseman C, Beyer JM, Artelt S, Urban H. Platinum, lead and cerium concentrations of street particulate matter (Frankfurt am Main, Germany). J Soils Sediments 2001;3:188–95.