Water Air Soil Pollut (2022) 233: 91
https://doi.org/10.1007/s11270-022-05549-1

Metrological Aspects of Platinum Group Elements Atmospheric Deposition in Roadside Tree Leaves: Uncertainties and Environmental Data Interpretation

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Received: 4 November 2021 / Accepted: 10 February 2022 / Published online: 6 March 2022

Abstract Atmospheric pollution is one of the main concerns in modern society and it poses a direct impact on the environment and public health. Therefore, an enormous number of environmental samples are collected and analyzed around the world on a daily basis. In order to obtain reliable and comparable results, it is paramount to establish a well-defined protocol for environmental sampling and analysis considering the more relevant variations associated with these activities and the processes that affect the distribution of the analytes in the environment. The present case study proposes a protocol to determine the amounts of the platinum group elements (PGEs: palladium, platinum, rhodium) due to atmospheric deposition in *Tibouchina granulosa* leaves that takes into account the estimation of measurement uncertainties including the sampling component. The samples were collected at a standardized height, in the second node of the branches, with approximately 2 months of environmental exposure. The particulate matter was extracted from the leaf surface by acid leaching using an ultrasonic bath followed by aqua regia digestion. Platinum (Pt), palladium (Pd), and rhodium (Rh) were separated from impurities by cation chromatography and analyzed by ICP-MS. The measurement uncertainties found were in the range of 24 to 33% while the analytical uncertainty lied between 4.5 and 7.3%. The results were expressed regarding metrological aspects, with the expanded uncertainty, within a 95% confidence level, to allow for a more robust interpretation of their relevance in the environmental and regulatory context.

Keywords Uncertainty from measurement · Sampling · Platinum group elements · Atmospheric deposition · Biomonitor

1 Introduction

Environmental monitoring plays a crucial role in the quality of life and the future of our planet. For this reason, an enormous number of field campaigns and chemical analyses are daily performed to diagnose the present-day environmental situation and predict future threats for the human being (Kłos et al., 2018; Stubbington et al., 2018). During the last decades, biomonitoring has been one of the most used procedures for identifying potentially toxic elements, or even substances, released by natural and anthropogenic sources to the environment (Bargagli, 2016;

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Dolegowska et al., 2017; Kłos et al., 2018). Its proper use depends, mainly, on four main factors: the selection of a biomonitor, the sampling procedures, the analytical methodology, and the correct data interpretation (Bargagli, 2016; Castanheiro et al., 2016; Dolegowska et al., 2017; Kłos et al., 2018; Zampieri et al., 2013). The biomonitor selection depends on the fauna and flora of the region where the work is being developed (Markert et al., 2003). It is always recommendable to use indigenous species considering the objectives of the work. The sampling procedure requires detailed planning bearing in mind the environmental characteristics of the study area such as topography; climatic conditions; and, when known, the contamination source. In addition, it is essential to note that anthropogenic substances' concentrations in environmental matrices are heterogeneous even in samples collected at the same site.

For this reason, the sampling strategy has to be as comprehensive as possible, allowing the acquisition of robust results with a representative estimate of uncertainty. The analytical methodology has to be strictly fit-for-purpose. It means it is not a matter of employing the most expensive technique or most complex methodology. On the contrary, in environmental studies, where it is common to analyze a significant number of samples, it is crucial to consider all procedures' costs and time consumption. It means that an environmental study is not simply the collection and analyses of environmental samples. It involves detailed planning and a series of decisions that can play a vital role in the quality of the obtained data and the adequacy of its purpose (Busso et al., 2018).

In addition, environmental pollutants do not recognize walls, barriers, or even political borders; therefore, it is necessary to adopt, by the international community, common, accepted, and standardized procedures to identify the presence and origin of pollutants and for the environmental data interpretation. In this scenario, environmental metrology emerges as a key tool allowing the consistency, traceability, and comparability of the obtained data and its interpretation (Barbieri and Sarkis, 2018; Petersen et al., 2005; Ramsey and Ellison, 2007; Thompson, 1998).

Among several pollution sources, vehicle exhaust causes significant impact on the atmosphere's quality, mainly in mega-cities like São Paulo, the most populous metropolis in Brazil, with circa 12 million inhabitants and 8 million vehicles (IBGE, 2020). In order to ensure the reduction of exhaust gas emissions from the internal combustion engine vehicles since the decade of 1990, platinum group elements (PGEs) have been used in exhausts as catalytic converters. During the last decades, the relative amounts of PGEs in catalytic converters have been changed to suit environmental quality standards, as well as to achieve the best performance for different types of vehicles and models. However, due to surface abrasion of the catalyst during the car operation, small amounts of PGEs are continuously released into the environment. Consequently, since the 1990s, these elements have been found in several environmental compartments (Bencs et al., 2003; Morcelli et al., 2005; Prichard & Fisher, 2012; Ribeiro et al., 2012), being reported that more than 80% of the PGE particles come from automotive converter catalytic and, due to their potential risks for human health and the environment, they are a matter of concern (Ottelé et al., 2010).

This work will describe how metrology can be an essential tool in the interpretation of environmental data regarding the impact of the sampling uncertainty in the analysis results. For this purpose, a case study of Pt, Pd, and Rh atmospheric deposition in leaves of *Tibouchina granulosa* (Desr.) Cong. (Melastomataceae) in one of the main streets of São Paulo City, Brazil, was conducted.

2 Material and Methods

In this study, a proposed standardization of data collection is presented. When data collection is performed randomly, it faces problems such as lack of information about the environment in which the species is located, the position in which the samples are collected in relation to the source of pollution, and the height at which the collections are performed. The standardization of data is a crucial factor for research in all sectors, with the reliability of the information generated as a differential factor, since it allows the actual comparison of data gathered in different sites and or studies.

There are in the literature (Thompson, 1998; Petersen et al., 2005; Ramsey & Ellison, 2007; Cotman & Paint, 2013; Vossler et al., 2015) several guides, protocols, and scientific papers about

environmental sampling. They bring us important and general rules to be followed while planning an environmental study. However, a universal procedure does not exist. Each case must be designed considering the purpose of the study. This work focused on the identification of anthropogenic PGEs in tree leaves situated at a height where particles can be subject to human inhalation. For this purpose, the experimental design was divided into four main activities: the sampling area selection, the choice of a biomonitor, the strategy for sample collection, and the sample analysis.

2.1 Sampling Site

The selected sampling site was situated in Jabaquara Avenue (23° 37′ 8.57″ S, 46° 38′ 22″ O), in São Paulo City. This area is considered a mixed zone, with commerce and residences; road traffic is intense with different vehicles categories (Zampieri, 2017).

2.2 The Chosen Biomonitor

Tibouchina granulosa (Desr.) Cong. (Melastomataceae) is a semideciduous perennial tree indigenous to the Brazilian Atlantic Forest and commonly cultivated as an ornamental tree along streets in many cities in the state of São Paulo (Brazil). A previous study of its anatomical characteristics (Zampieri et al., 2013) identified various types of trichomes located on adaxial and abaxial surfaces of its leaves, resulting in high capacity to retain particulate matter (PM) within the size range of 2.5 to 100 µm, making this species a valuable alternative for passive air monitoring.

2.3 Sample collection

At the selected sampling site, eight branches of a *Tibouchina granulosa* (Desr.) Cong. (Melastomataceae) individual located at 1.30 m of the avenue curb were collected at a height of 2 m from the sidewalk level. These branches (R1, R2, R3, R4, R5, R6, R7, and R8) were collected in eight different positions within an angle of 90°, in the northeast quadrant of the cross section of the tree crown, facing the roadway as shown in Fig. 1.

Branch R1 was parallel to the vehicle's flow; consequently, its leaves were disposed transversally to the flow. On the other hand, the R8 branch was transversal to the flow of vehicles and, consequently, its leaves were parallel to the Avenue.

In each branch, two opposite leaves of the second node, located circa 25 cm from the tree trunk, were collected using a pruning shears. In this position, leaves were exposed to the environment for at least 2 months and had, on average, an area of 70 cm^2. Leaf area was obtained using scanned images and the

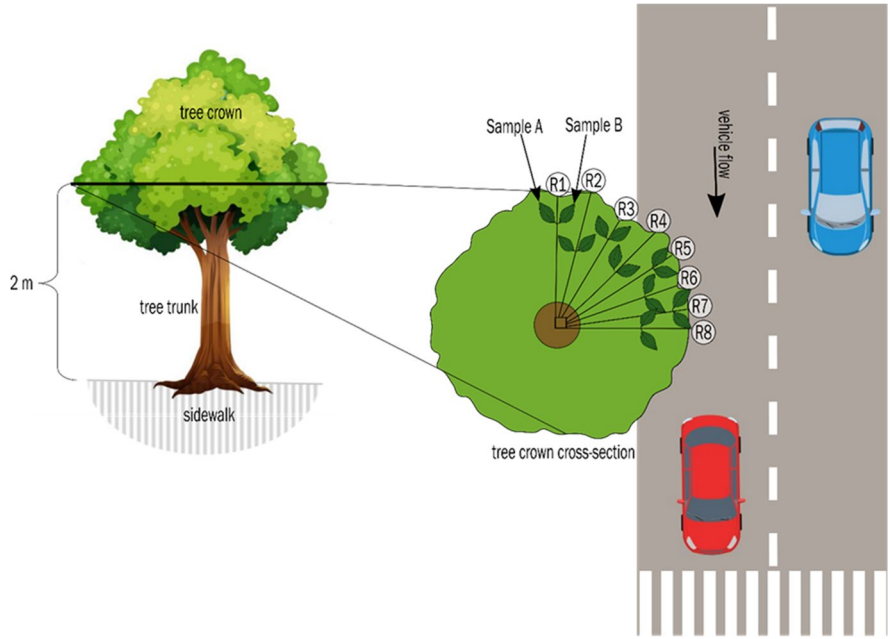


Fig. 1 Diagram of the sampling scheme at the selected sampling site where R1 to R8 are tree branches and sample A and sample B the leaves

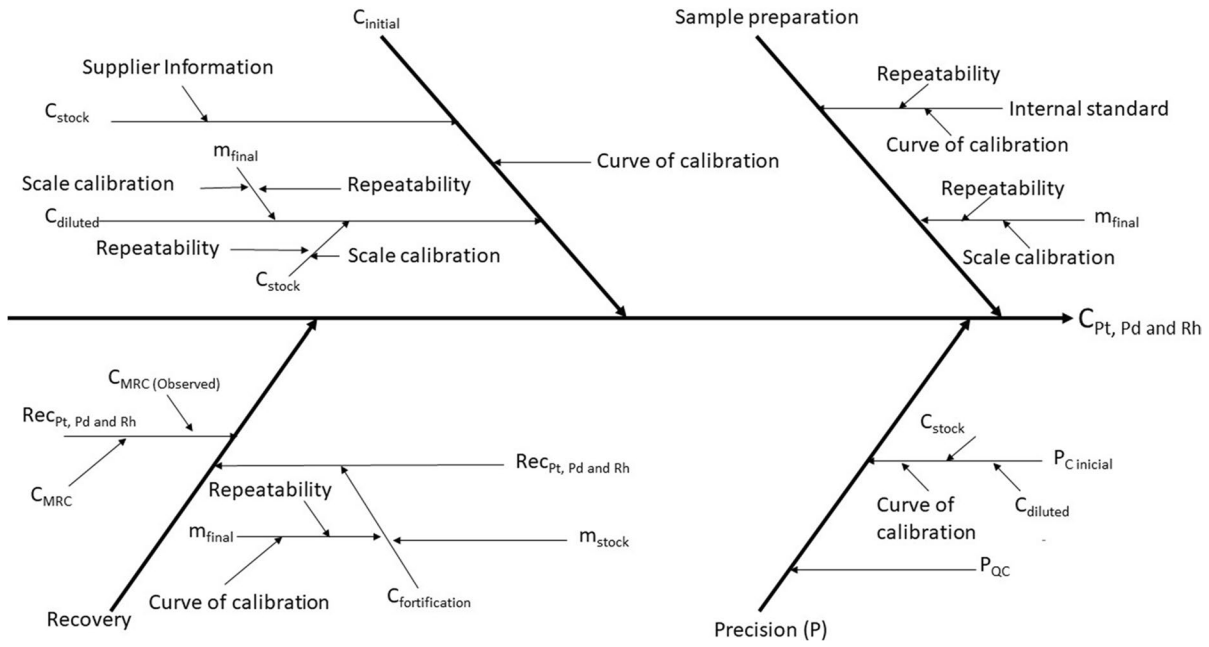


Fig. 2 Cause-and-effect diagram for PGEs analysis

ImageJ 1.44p software with Java 1.6.0., according to the E1382-97 Standard Method (ASTM 2010). After collection, the leaves were individually packed in paper bags for transportation.

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDS) was applied in the present study to determine the distribution of particulate matter adsorbed onto leaves because this technique provides qualitative and quantitative information concerning the elements present on the surface of a sample. These analyses were performed in leaf samples sectioned from the apical part of each leaf blade using a scalpel. For each of the portions, two areas (1 cm × 1 cm) of the adaxial and abaxial surfaces were mounted individually onto specimen stubs and held by double-sided conductive carbon tape (Zampieri et al., 2013). Digital images (× 600 magnification) were acquired using a Hitachi Tabletop microscope model TM-3000 (High Technologies America, Schaumburg, IL, USA) equipped with a Bulker Quantax 70 X-ray (Billerica, MA, USA) microanalysis system.

2.4 Analytical Methodology

Initially, the leaves were placed inside the drying and sterilization oven (mod. 315SE-FANEM) at a controlled temperature of 40 °C for 120 h, and then, their moisture content was calculated using Eq. (1).

$$\%\text{humidity loss} = 100 - \frac{\text{Dry mass} \times 100}{\text{Fresh mass}} \quad (1)$$

The extraction of particulates deposited in each leaf was obtained by leaching procedure with freshly prepared "aqua regia" (HCl to HNO_3; 3:1), assisted by an ultrasonic bath system (Ultrasonic Cleaner-THORTON), for 60 min. The leached mixture was transferred to a conical tube and centrifuged for 10 min at 10,000 rpm in centrifuge (EXCELSA® II-mod. 206bl-FANEM). Supernatant was transferred to polyethylene beakers previously washed in EXTRAN® (5%) solutions for at least 2 h, ultra-pure water (SYNERGY®UV-Millipore-Millisul) three times, and nitric acid (35%) for 24 h. The supernatant solution was dried in a controlled temperature, up to 80 °C, in a heating plate (mod. Q313M21I-QUIMIS®), almost completely drying

it. After the first drying, 2 mL of HCl (10 M) was added and drying was completed; this procedure was performed twice. In the beakers with the dried residue, at room temperature, 15 mL of HCl (0.5 M) was added. In order to eliminate potential isobaric interferences, chemical separation of PGEs was accomplished prior to analysis by cation exchange chromatography based on Spada et al (2012). The analysis was performed with an inductively coupled mass spectrometer (ICP-MS), NEXION 300 D (Perkin Elmer) using ^{115}In as internal standard. The methodology's validation was accomplished following the recommendations of the National Institute of Metrology, Standardization, and Industrial Quality (INMETRO 2016) and using a standard reference material (SRM 2557—Auto Used Catalyst). The SRM was prepared according to the methodology described for the extraction of particulates deposited in leaves, but with more dilutions, reaching about 150,000-fold.

2.4.1 Analytical Uncertainty

The modeling, or bottom-up, approach (Ramsey and Ellison, 2007) was used to estimate the analytical uncertainty in this work. The sources of uncertainty in PGE determination were identified and quantified and combined as follows to obtain the combined standard uncertainty (Ellison et al., 2002). The relevant uncertainty sources for the leachable PGE determination were defined and a cause-and-effect diagram was built (Fig. 2) as recommended by Ellison and Williams (2012).

The sources of uncertainty of the PGE concentration determination were quantitatively expressed as uncertainty components in Eq. (2) that was used to calculate the combined standard uncertainty (u_C):

$$u_{c_{PGEs}} = C_{PGEs} \times \sqrt{\left(\frac{uC_0}{C_0}\right)^2 + \left(\frac{u\left(Cdil_{10}\frac{ug}{g}\right)}{Cdil_{10}\frac{ug}{g}}\right)^2 + \left(\frac{u\left(Cdil_{100}\frac{ug}{kg}\right)}{Cdil_{100}\frac{ug}{kg}}\right)^2 + \left(\frac{u(m_f)}{m_f}\right)^2 + \left(\frac{u(Rec)}{Rec}\right)^2 + \left(\frac{u(intstd)}{m_{intstd}}\right)^2 + \left(\frac{u(P)}{P}\right)^2} \quad (2)$$

where:

$\frac{u(C_0)}{C_0}$ is the uncertainty derived from the analyzed aliquot; where uC_0 is uncertainty from analyzed aliquot, and C_0 is analyte concentration determined in the analysis solution.

$\frac{u(Cdil_{10})}{Cdill_{10}}$ and $\frac{u(Cdil_{100})}{Cdil_{100}}$ are uncertainty relative from stock standard dilution to prepare analytical curve; where $u(Cdil_{10})$ and $u(Cdil_{100})$ are uncertainty of the solutions 10 ug g^{-1} and 100 ug kg^{-1}; $Cdil_{10}$ and $Cdil_{100}$ are calculated concentrations for solutions of 10 µg g^{-1} and 100 µg kg^{-1}.

$\frac{u(_{m_f})}{m_f}$ is uncertainty from prepared solution final mass; where $u(m_f)$ is uncertainty from solution prepared mass, and m_f is the solution final mass.

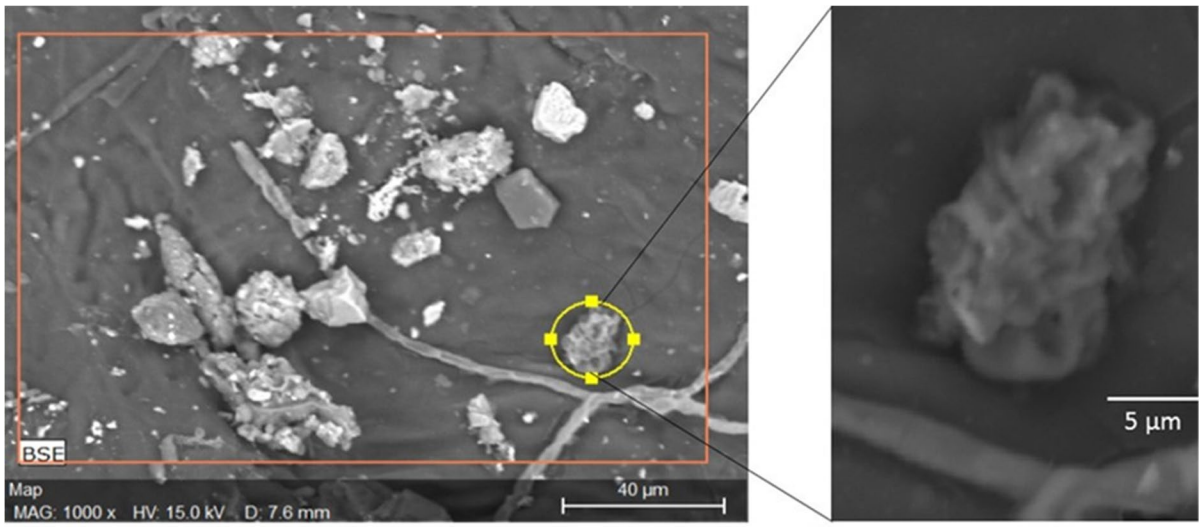
$\frac{u(\mathrm{Rec})}{\mathrm{Rec}}$ is the uncertainty of the recovery rate; where u(Rec) is the uncertainty of the prepared CRM solution (experimental), and Rec is the calculated value (expected) obtained from the certification letter.

$\frac{u(\mathrm{intstd})}{m_{\mathrm{intstd}}}$ is uncertainty from internal standard; where u (int std) is the uncertainty from internal standard solution prepared, and $m_{\mathrm{int\ std}}$ is the internal standard mass.

$\frac{u(P)}{P}$ is uncertainty from measurement accuracy, where $u(P)$ is average relative standard deviation, and P is average concentration obtained in the analyte determination.

2.4.2 Measurement Uncertainty

The uncertainty of measurement estimates, including the sampling component, was performed with a top-down approach, using range statistics with a single split design as proposed by Magnusson et al. (2020). The developed protocol considers the uncertainties caused by heterogeneity in the distribution of atmospheric deposition on the leaves. To apply the single split design, each one of the eight branches (R1 to R8) was considered a sampling target and the opposite leaves of a node of each branch the duplicates (sample A and sample B). The leaves were individually subjected to the analytical methodology procedures previously described.



Spectrum: Point

Element	AN	Series	Net	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Calcium	20	K-series	118	4.47	34.08	34.13	0.2
Silicon	14	K-series	102	2.07	15.74	22.49	0.1
Sulfur	16	K-series	99	2.16	16.43	20.57	0.1
Aluminium	13	K-series	65	1.32	10.09	15.01	0.1
Rhodium	45	L-series	40	1.63	12.39	4.83	0.1
Cerium	58	L-series	7	0.62	4.70	1.35	0.0
Platinum	78	M-series	15	0.62	4.73	0.97	0.0
Palladium	46	L-series	4	0.17	1.33	0.50	0.0
Praseodymium	59	L-series	1	0.07	0.52	0.15	0.0
			Total:	13.12	100.00	100.00	

Fig. 3 Micrograph with emphasis on the catalytic converter particle on *Tibouchina granulosa* leaf surface

The estimation of the measurement uncertainty sampling was performed using the sequence of equations listed (Eq. (3) to Eq. (8)).

The absolute value of the difference D_i was calculated for each set of duplicates according to the equation:

$$D_i = \left| x_{iA} + x_{iB} \right| \tag{3}$$

The average $\overline{X}$ of two measurements in each duplicate is calculated according to the equation:

$$\overline{X_i} = \frac{x_{iA} + x_{iB}}{2} \tag{4}$$

The relative difference, d_i, is calculated from the difference, D_i, and the mean for each set of duplicates, according to the equation:

$$d_i = \frac{D_i}{\overline{x_i}} \tag{5}$$

The mean relative difference $\overline{d}$ was calculated by the difference the sum of the relative difference of n duplicate numbers, according to the equation:

$$\overline{d} = \frac{\sum d_i}{n} \tag{6}$$

The relative standard deviation (RSD) was calculated using statistical factor 1.128 (Montgomery, 2009) for duplicate analysis, according to the equation:

$$u_{\text{measurement}} = \frac{\overline{d} \times 100}{1.128}\% \tag{7}$$

The expanded uncertainty (U) was obtained by multiplying the measurement uncertainty obtained (Eq. (8)) by 2, for a 95% confidence level. The expanded uncertainty was calculated according to the equation**:**

$$U = u \times 2 \tag{8}$$

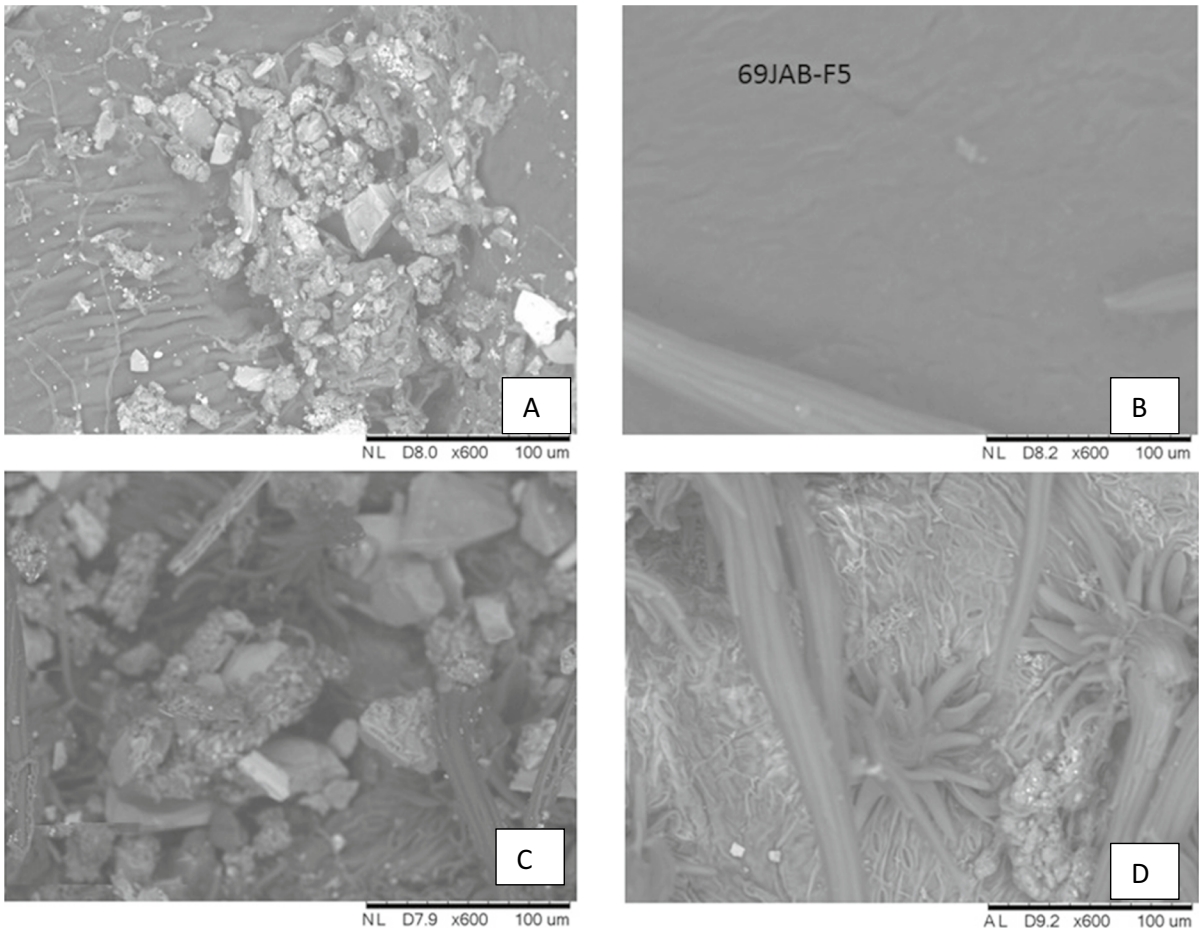


Fig. 4 Micrograph of leaves before and after PM removal. **A** (before) Adaxial face and **B** (after) adaxial face. **C** (before) Abaxial face and **D** (after) abaxial face

The sampling uncertainty was obtained using the expression:

$$u_{\text{sampling}} = \sqrt{\left(u_{\text{measurement}}\right)^2 - \left(u_{\text{analysis}}\right)^2} \tag{9}$$

3 Results and Discussion

Characterization of atmospheric deposition aims at determining the concentration or load of pollutants in the air, generally during an extended period. It is a helpful strategy for a preliminary evaluation of the presence of air pollutants providing important data for a more extensive environmental sampling planning.

In this work, tree leaves of *Tibouchina granulosa* were chosen to identify atmospheric deposition of platinum group elements and demonstrated a high capacity to retain particulate matter (PM) size of 2.5 to 100 µm. Among numerous particles of a wide array of constituents deposited on the biomonitor leaf's surface, the particles from the automotive catalytic converter are found. Most catalytic converters consist basically of a monolithic support, made of either alumina, and a mixture of base metal additives, mainly oxides of Ce, Zr, La, Ni, Fe, Ti, Y, and W in addition to the noble metals, PGE (Pt, Pd, and Rh) (Ravindra et al., 2004). Figure 3 shows the micrograph of a particle from catalytic converter, deposited on the *Tibouchina granulosa* leaf. In this particle, the elements Ca, Si, S, Al, Rh, Ce, Pt, Pd, and Pr were detected; this particle can be attributed to the catalytic converter degradation due to its morphology, presence of S from fuels, lubricants, and engine wear

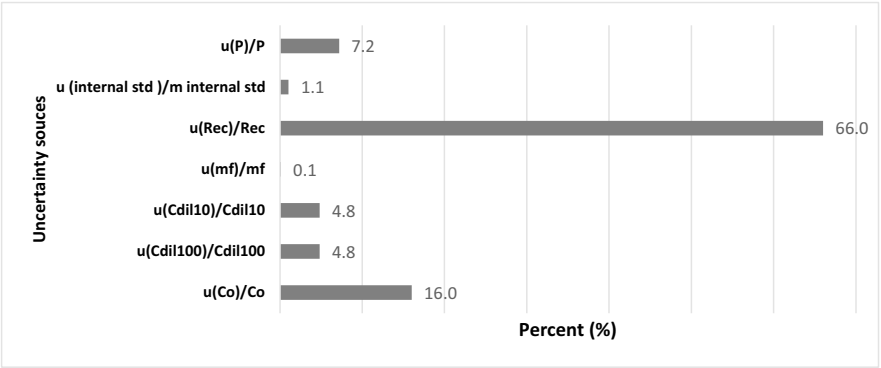


Fig. 5 Uncertainty sources' contributions in Pd analysis

and, mainly, of the PGEs. PGEs have been found in relatively high concentrations: Pt (2000 ng g^{-1}), Pd (1000 ng g^{-1}), and Rh (100 ng g^{-1}) (Bencs et al., 2003), in regions near highways and avenues in urban centers (Prichard & Fisher, 2012; Ribeiro et al, 2012), while the natural background of PGEs in the environment can range from 1 to 3 ng g^{-1}, except in some cases of geological occurrences (Prichard & Fisher, 2012).

The aqua regia procedure allowed for the complete removal of PM deposited on leaves without any damage to their surfaces as observed in Fig. 4 and the leaching of metals, including PGEs.

The recovery of the PGEs in the CRM-NIST 2557 for all analyzed elements reached circa 100%. The mass was measured in femtograms in solution, and conversion factors with relative recovery uncertainties $\frac{u(\mathrm{Rec})}{\mathrm{Rec}}$ were 4 to 7%. This result may be due to the 150,000-fold dilution factor of the CRM. In spite of that, all results obtained (11 mg kg^{-1} for Pt, 1.9 mg kg^{-1} for Pd, and 1.9 mg kg^{-1} for Rh) are within the certified concentration range.

The relative contribution of the analytical uncertainty sources defined as relevant (Fig. 2) for each PGE is shown in Figs. 5, 6, and 7. The combined standard uncertainty calculated with the source's contribution, using Eq. (2), is 7.3% for Pd, 4.5% for Pt, and 4.6% for Rh.

Sampling protocols play a critical role in environmental studies. The distribution of particles in the environment is heterogeneous presenting variations even on a restricted area of sampling. Depending on the magnitude of these variations, the final interpretation of results can be strongly impacted. Therefore, to obtain reproducible and comparable results, it is important to establish a well-defined procedure for sampling. This is especially important when tree leaves are used as a biomonitor. In this case, that procedure must be considered the main objective of the study and then defined as the most suitable branch height; the more representative branch position concerning the particulate emission direction; and, considering that the leaves exposure time is directly related to its position in the branch, the node position.

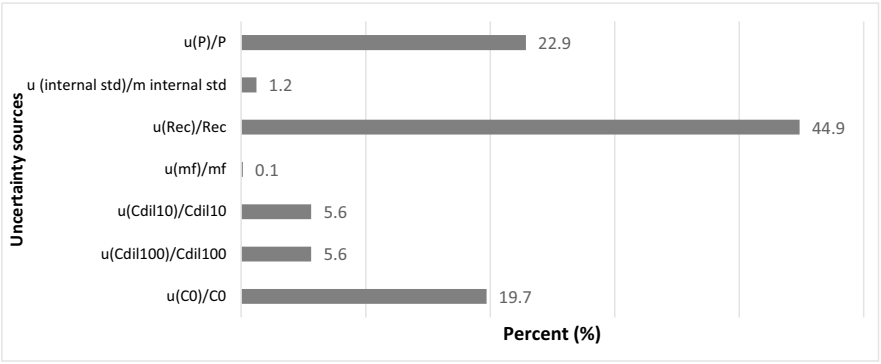


Fig. 6 Uncertainty sources' contributions in Pt analysis

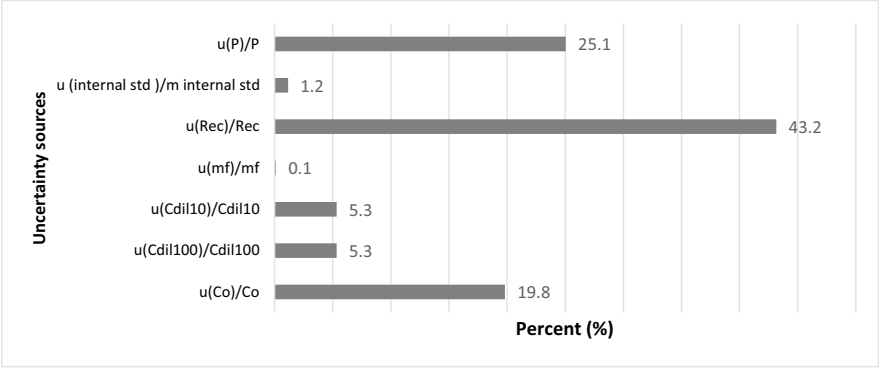


Fig. 7 Uncertainty sources' contributions in Rh analysis

The results presented in Tables 1, 2, and 3 demonstrate noteworthy PGE concentration variations among the branches. The branches disposed at 90° and 77° in relation to the roadway consistently displayed higher concentrations of the PGEs when compared to the other branches. This is, probably, because the leaves positioned transversally to the vehicle flow are somehow more exposed to exhaust particles from vehicles circulating on the roadway at those positions. These results reveal the importance of a detailed sampling protocol that takes into account the specific position of the samples in order to provide comparable results.

The contribution of the measurement uncertainty including the sampling uncertainty, expressed as RSD, varied from 24% for Pt to 33% for Pd concentrations, and was 27% for Rh. These results are in accordance with the findings of Dołęgowska (2016) for Fe concentrations in moss samples estimated by range statistics that were 22%. It has to be remarked that the cited author has determined the concentrations in the whole sample unlike this work where only the fraction deposited on leaves was analyzed.

The results from the duplicate analysis presented a relatively low variation between samples A and B (leaves) and a higher variation among branches R1 to R8. This variation of the branches position appears to contribute more to the deposition of PM on leaves than the position of the leaves in the node and the whole analytical procedures including sample

Table 1 Relative standard deviation estimation of Pd determinations in leaves of *Tibouchina granulosa* (samples A and B) of branches (R1 to R8) collected in eight positions within a 90° angle of the northwestern quadrant of the tree crown

Branches ($n=8$)	Sample A concentration (μg m^{-2})	Sample B concentration (μg m^{-2})	Absolute value of the difference (μg m^{-2})	Mean (μg m^{-2})	Relative difference
	x_{iA}	x_{iB}	$D_i = \lvert x_{A1} - x_{A2} \rvert$	$\overline{x_i} = \frac{x_A + x_B}{2}$	$d_i = \frac{D_i}{\overline{x_i}}$
R1 (90°)	2.1303	2.2511	0.1208	2.1907	0.0551
R2 (≈ 77°)	1.5392	1.5592	0.0200	1.5492	0.0129
R3 (≈ 64°)	0.5806	0.5781	0.0000	0.5806	0.0000
R4 (≈ 51°)	0.0667	0.0752	0.0086	0.0710	0.1206
R5 (≈ 39°)	0.1247	0.1886	0.0640	0.1566	0.4084
R6 (≈ 26°)	0.0149	0.0238	0.0090	0.0194	0.4636
R7 (≈ 13°)	0.0386	0.1106	0.0721	0.0746	0.9663
R8 (0°)	0.0821	0.0277	0.0544	0.0549	0.9898
Mean relative difference			$\overline{d} = \sum \frac{d_i}{n} = \frac{3.02}{8} = 0.38$		
Relative standard deviation (RSD %)			$\mathrm{RSD} = \frac{\overline{d} \times 100}{1.128*} = \frac{0.38 \times 100}{1.128} = 33\%$		

*Statistical factor for analysis in duplicates (Montgomery, 2009).

Table 2 Relative standard deviation estimation of Pt determinations in leaves of *Tibouchina granulosa* (samples A and B) of branches (R1 to R8) collected in eight positions within a 90° angle of the northwestern quadrant of the tree crown

Branches ($n=8$)	Sample A concentration ($\mu g\ m^{-2}$)	Sample B concentration ($\mu g\ m^{-2}$)	Absolute value the of difference ($\mu g\ m^{-2}$)	Mean ($\mu g\ m^{-2}$)	Relative difference
	x_{iA}	x_{iB}	$D_i = \lvert x_{A1} - x_{A2} \rvert$	$\overline{x_i} = \frac{x_A + x_B}{2}$	$d_i = \frac{D_i}{\overline{x}_i}$
R1 (90°)	0.5818	0.5564	0.0254	0.5691	0.0446
R2 (≈ 77°)	1.3070	1.9021	0.5951	1.6046	0.3709
R3 (≈ 64°)	0.1742	0.2403	0.0661	0.2073	0.3189
R4 (≈ 51°)	0.0038	0.0029	0.0009	0.0034	0.2687
R5 (≈ 39°)	0.2264	0.5835	0.3571	0.4050	0.8818
R6 (≈ 26°)	0.0108	0.0102	0.0006	0.0105	0.0571
R7 (≈ 13°)	0.4003	0.4253	0.0250	0.4128	0.0606
R8 (0°)	0.0135	0.0156	0.0021	0.0146	0.1443
Mean relative difference			$\overline{d} = \sum \frac{d_i}{n} = \frac{2.1}{8} = 0.27$		
Relative standard deviation			$\mathrm{RSD} = \frac{\overline{d} \times 100}{1.128*} = \frac{0.27 \times 100}{1.128} = 24\%$		

*Statistical factor for analysis in duplicates (Montgomery, 2009).

Table 3 Relative standard deviation estimation of Rh determinations in leaves of *Tibouchina granulosa* (samples A and B) of branches (R1 to R8) collected in eight positions within a 90° angle of the northwestern quadrant of the tree crown

Branches ($n=8$)	Sample A concentration ($\mu g\ m^{-2}$)	Sample B concentration ($\mu g\ m^{-2}$)	Absolute value the difference ($\mu g\ m^{-2}$)	Mean ($\mu g\ m^{-2}$)	Relative difference
	x_{iA}	x_{iB}	$D_i = \lvert x_{A1} - x_{A2} \rvert$	$\overline{x_i} = \frac{x_A + x_B}{2}$	$d_i = \frac{D_i}{\overline{x}_i}$
R1 (90°)	0.0920	0.0921	0.0001	0.0921	0.0011
R2 (≈ 77°)	0.1272	0.1912	0.0640	0.1592	0.4020
R3 (≈ 64°)	0.0180	0.0290	0.0110	0.0235	0.4681
R4 (≈ 51°)	0.0005	0.0004	0.0001	0.0005	0.2222
R5 (≈ 39°)	0.0023	0.0052	0.0029	0.0038	0.7733
R6 (≈ 26°)	0.0009	0.0008	0.0001	0.0009	0.1176
R7 (≈ 13°)	0.0396	0.0385	0.0011	0.0391	0.0282
R8 (0°)	0.0009	0.0013	0.0004	0.0011	0.3636
Mean relative difference			$\overline{d} = \sum \frac{d_i}{n} = \frac{2.4}{8} = 0.30$		
Relative standard deviation			$RSD = \frac{\overline{d} \times 100}{1.128*} = \frac{0.30 \times 100}{1.128} = 27\%$		

*Statistical factor for analysis in duplicates (Montgomery, 2009).

Table 4 Uncertainties associated with the PGEs determinations in this study

PGE	$u_{measurement}$ RSD%	$u_{analysis}$ Combined standard u %	$u_{sampling}$	U
Pd	33	7.3	32.2	66
Pt	24	4.5	23.6	48
Rh	27	4.6	26.6	54

preparation, which supports the consistency of the methodology adopted.

The top-down approach based on a single split design used for the estimation of the measurement uncertainty can be considered a bulk measurement of the overall uncertainty including the contribution from the sampling process. This method does not allow for the computation of the analytical and sampling uncertainties separately, but the analytical combined

Table 5 Results of the PGE determination in *Tibouchina granulosa* leaves with the corresponding expanded uncertainty of the measurement for a confidence interval of 95%

Branches	Pd (μg m^{-2}) Mean value ± U	Pt (μg m^{-2}) Mean value ± U	Rh (μg m^{-2}) Mean value ± U
R1	2.1907 ± 1.4458	0.5691 ± 0.0119	0.0921 ± 0.0017
R2	1.5492 ± 1.0225	1.6046 ± 0.0334	0.1592 ± 0.0029
R3	0.5793 ± 0.3823	0.2072 ± 0.0043	0.0235 ± 0.0004
R4	0.0710 ± 0.0468	0.0034 ± 0.0001	0.0004 ± 0.0000
R5	0.1566 ± 0.1034	0.4050 ± 0.0084	0.0038 ± 0.0001
R6	0.0194 ± 0.0128	0.0105 ± 0.0002	0.0009 ± 0.0000
R7	0.0746 ± 0.0492	0.4128 ± 0.0086	0.0391 ± 0.0007
R8	0.0549 ± 0.0363	0.0145 ± 0.0003	0.0011 ± 0.0000

uncertainty was estimated with a bottom-up approach, so it was possible to infer the sampling uncertainty. The resulting estimated uncertainties are displayed in Table 4.

The highest uncertainties were found in Pd determinations with a relatively higher combined standard uncertainty in this element determination compared to Pt and Rh. The relatively similar sampling uncertainty for the PGEs studied could be explained by the fact that those elements are usually clustered together in the converter particles as demonstrated in the energy-dispersive X-ray spectroscopy analysis of the catalytic analysis (Fig. 3). The higher analytical uncertainty in Pd analysis is associated with the recovery step (Fig. 5). Rinkovec et al. (2017) also describe a lower recovery for Pd in relation to Pt and Rh in spiked CRM samples (NIST 1648a and ERM CZ120). The major contribution to the measurement uncertainty is the sampling component, with the uncertainty from the analytical steps being considerably lower. In this study, the combined standard uncertainty of the analyses calculated with the bottom-up approach was lower than 5% for Pt and Rh determinations and 7.3% for Pd; therefore, the confidence limit ranges considering only the analytical uncertainty are relatively narrow. The sampling and handling/preparation steps of the measurement process add a much higher level of uncertainty in the results as shown in Table 4; hence, its estimation cannot be disregarded in environmental quantitative analyses.

To properly express the results of the PGE measurements in leaves of the differently positioned branches, the expanded uncertainty of the mean values obtained from sample A and sample B was calculated and the resulting values are in Table 5. The results are thus expressed with metrological consistency within the range of certainty that the described environmental conditions and analysis, including the sampling steps, define.

4 Conclusion

Uncertainty of sampling is a topic that has to date received scant attention by metrologists or analytical chemists. In this study, the overall uncertainties of the concentrations of the PGEs in the atmospheric deposition, including those derived from sampling, were estimated for the first time. The atmospheric deposition of particles of vehicular catalyst mechanical degradation containing PGEs on the leaves of the trees occurs continuously in the urban regions. In Brazil and worldwide, there are no standards that regulate PGE levels in the air. Therefore, monitoring is necessary to assess their presence in the environment and possible ecological and public health risks derived from them. Environmental metrology has a critical role to play in environmental biomonitoring and its use to implement measures and policies that are based on solid science with accurate data. Robust data on atmospheric deposition are essential to assess air pollution and formulate uncertainty modeling. The expression of the results within their "range of certainty" regarding the metrological aspects, as proposed in this study, allows for a more robust interpretation of the results and their relevance in the environmental and regulatory context. Ignoring the impact of sampling uncertainty leads to underrated general uncertainty and may adversely affect the conformity assessment of pollutant levels in regulatory criteria. We encourage researchers to conduct similar studies investigating aspects of the sampling protocols that have not been standardized and quantify the sampling uncertainty generated by each analyte in biomonitoring studies. This

would increase the confidence of decision-makers and promote their use beyond scientific research.

Funding The Nuclear Energy and Research Institute and the National Nuclear Energy Commission awarded scholarships to Maria Cristina Tessari-Zampieri.

Data Availability All data used and analyzed in this study are available from the corresponding author on reasonable request.

Declarations

Competing Interests The authors declare no competing interests.

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This work was performed at the Center for Lasers and Applications at IPEN-CNEN/SP.