

Platinum, palladium, and rhodium deposition to the *Prunus laurus cerasus* leaf surface as an indicator of the vehicular traffic pollution in the city of Varese area

An easy and reliable method to detect PGEs released from automobile catalytic converters

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Abstract

Background, aim, and scope The widespread use of some platinum group elements as catalysts to minimize emission of pollutants from combustion engines produced a constantly growing increase of the concentration of these elements in the environment; their potential toxicological properties explain the increasing interest in routine easy monitoring. We have found that leaves of *Prunus laurus cerasus* are efficient collectors of particulate with a dimension <60–80 μm, and a simple and reliable procedure was developed to reveal traces of platinum, palladium, and rhodium released from automotive catalysts. The analysis of the dust deposited on the foliage is a direct indicator of traffic pollution.

Materials and methods Leaves of *P. laurus cerasus* were washed by sonication in a mixture of water and 2-propanol and the washings, to be discarded, were separated by centrifugation to yield typically 0.05–1.2 g of dust that, after mineralization, was directly submitted for atomic absorption analysis.

Results Comparison of the 2007 and 2004–2005 results showed a dramatic reduction of the platinum levels and revealed that palladium is now the main component of this traffic-related pollution.

Discussion The results are consistent with the increasing diffusion of cars with a diesel engine whose catalysts are

made up of Pt and/or Pd alone, and gives a significant insight into the recent evolution in catalyst design that replaces platinum for palladium.

Conclusions The proposed analytical procedure is simple, with short preparation times, and greatly reduces matrix effects so that atomic absorption spectroscopy can easily detect the three noble metals at the ng/g level in the dust.

Recommendation and perspectives The results clearly show that Pd concentrations have increased over time, and must be cause for concern.

Keywords Atomic absorption · Automobile catalysts · Foliage uptake · GFAA · Metal pollution · Palladium · PGE · Platinum group elements · Platinum · *Prunus laurus cerasus* · Rhodium · Road dust · Traffic pollution · Varese

1 Background, aim, and scope

Since the beginning of the 1980s, the widespread use of some platinum group elements (PGE) as catalysts to minimize emission of pollutants from combustion engines produced a slow but constantly growing increase in the concentration of these elements in the environment (Zereini and Alt 1999). During this time period, the auto catalysts have progressed through many development phases and have been tailored upon different engines. Thus, different devices have been developed, from those based on platinum alone to combinations of Pt–Rh, Pd–Rh, Pt–Pd–Rh, and Pd alone (Heck and Farrauto 2001). The three metals platinum,

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palladium, and rhodium are released with catalyst aging, essentially as metal particles bonded to fragments of the ceramic support (Moldovan et al. 2002), as a consequence of surface abrasion during car operation. Sometimes they have been detected as oxides and even as soluble chloro-complexes (Palacios et al. 2000; Gomez et al. 2002). Toxicological data available so far are relative to soluble compounds of Pt(II), Pt(IV), Pd(II), Pd(IV), Rh(III), and Rh(II) essentially as chloro-complexes (Bikhazi et al. 1995; Gebel et al. 1997; Merget and Rosner 2001). Bioaccumulation of PGEs has been shown to possibly be influenced by the presence of complexing agents (Zimmerman et al. 2003); in organisms such as *Asellus aquaticus* (Moldovan et al. 2001), it depends upon the exposition time. Remarkably, a recent paper stressed the possible role of PGEs in the formation of free radicals (Botrè et al. 2007). The potential toxicological properties of PGE explain the increasing interest in routine easy monitoring.

Our studies started in 2002 with a preliminary survey directed toward analysis of road dust; typically, the samples were collected over a 1-m² surface by means of a pure bristle brush, and then sifted through a <0.05-mm sieve. To evaluate a possible retention of PGEs by the plants, we also examined a few plant samples and we soon decided to restrict our investigation to the leaves of *Prunus laurus cerasus* because of its almost ubiquitous presence in the northern Italian urban environment and its evergreen nature that allows round-the-year samplings. An additional remarkable feature is that these leaves act as passive collectors of particulate matter (PM), like a sheet of fly paper. In fact, the waxed surface collects, mostly on the upper side, dust from a maximum of ca. 60–80 µm down to the very minute PM (Giovannardi 2008, personal communication—an observation made with a confocal microscope; 60–80 µm is the maximum size of the granules stuck on the upper page of a leaf of *P. laurus cerasus*; the lower side holds a minor fraction of particulate made of even smaller granules), an efficient size selection comparable to that performed by means of a sieve. The dust recovery was then easily performed with sonication in water (with some 2-propanol added as a wetting agent) that suitably cleans the leaf surface.

For each sampling location, we therefore compared the results from four types of samples: (1) the sifted road dust, (2) the dirty leaves, (3) the cleaned ones, and (4) the foliar dust recovered from the washings. In cases (2) and (3), the leaves, prior to the mineralization process, were dried and then incinerated at 800°C for 3–4 h. Mineralization was applied, with some variation, to all the samples (as described below) to obtain the solutions that, analyzed by atomic absorption, allowed the detection of the three PGEs at a level of µg/l translating, with reference to the original samples, in a few ng/g. In this first phase of the investigation, many analyses were made with the standard

addition methods to overcome possible matrix effects. Actually, all the plant samples gave a large matrix effect, which often severely hindered reliable results. In a few cases, filtration of the solutions (through a C18 packed reversed-phase column) was experimented; these samples showed a better instrumental signal with some reduction of the matrix effects though, particularly the samples with the lowest content of metals, they also exhibited a systematic retention of analyte. In any case, the results obtained with the washed leaves revealed amounts of the three platinoids under the instrumental detection limits (IDL). Thus, we retained this as a proof that the three metals are essentially present in the particulate deposited on the surface, with no significant absorption by the leaves. Tests to evaluate the efficiency of the recovery were also tried by addition of standard solution of the three metals or of a certified NIST standard obtained from milled auto catalyst (see experimental); the plant samples were doped in this way prior to the incineration step. The recovery was generally better than 80%.

At the end of these sets of experiments, we could deduce that only the dust samples, particularly those retained by the leaf surface, could be the realistic object of a study on the PGE pollution in urban environment.

2 Materials and methods

2.1 Analysis of the foliar dust

2.1.1 Sampling sites

On the basis of our preliminary results, we decided to focus only on the particulate matter (PM) collected by the leaf surface of the species *P. laurus cerasus*. With reference to the map in Fig. 1, monthly samples were collected during two periods, October 2004–May 2005 and January–September 2007 (hereafter indicated briefly as 2004–2005 and 2007), at four sites characterized by major vehicular traffic; two of these locations were chosen along viale Borri, the urban section of SS233 (Strada Statale, a state road), nearby Istituto Molina (Borri-Molina, Bm), and at the intersection with Via Valmorea (Borri-Valmorea, Bv). In this second site, leaves were collected also at ca. 20 m from the main traffic flux of viale Borri, inside via Valmorea (Bvi). A third location was chosen at the intersection of Via Virgilio with Via Molini Grassi (Mg) and the fourth one at the Rotonda di Gazzada (Gz), a great intersection of SP57 (Strada Provinciale, a county road) out of the city limits of Varese and connected to the highway. The traffic fluxes in the three town sites can be somewhat estimated from an official report (Comune di Varese, Ufficio Tecnico Traffico e Trasporti 2003): in the peak hours (7:30–8:30 and 17:30–

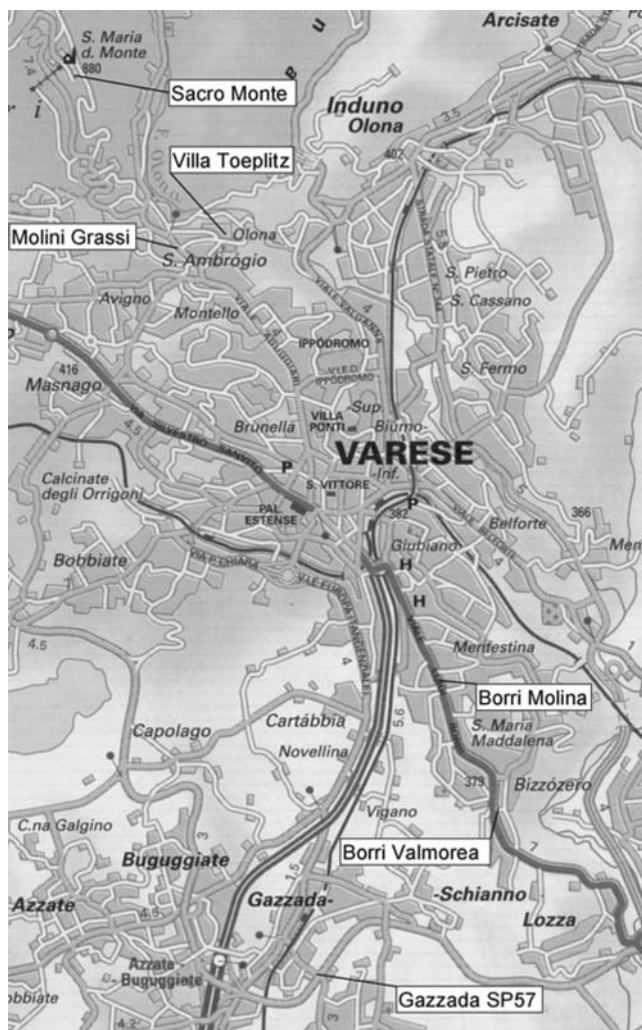


Fig. 1 A map of the city of Varese and a part of its surrounding area, showing the location of the six sampling sites

18:30), approximately 4,500 motor vehicles pass Viale Borri, while in via Virgilio-Aguggiari, close to the Mg site, they may be approximately 2,500. The site Gz is substantially different from the previous ones because of the transit of many heavy vehicles; according to recent data (Provincia di Varese, <http://www.provincia.va.it/viabilita.htm>), in an average day of January 2008, more than 4,000 trucks (ca. 15%) were counted from a total of 28,000 vehicles.

As a reference for minimal exposure to the traffic pollution, we chose the site of Villa Toeplitz (To, within a city park and approximately 500 m from the heavy traffic of Mg) and in 2007, regular samplings began also at Sacro Monte (Sm), a small traffic-restricted neighborhood of Varese, on the top of a hill. In the following, we will discuss in detail the more recent data very indicative to define the levels of traffic pollution. The previously obtained data (2004–2005) will then be taken into account to evidence temporal trends.

2.1.2 Sample treatment

Samples of leaves, typically 40–50 g (fresh weight, FW), were collected at each site once a month, picking up the old and the new leaves randomly between 0.5 and 1.5 m above the ground (see Section 3.2) and, when possible, at least 10–15 days after any heavy raining event.

All the chemicals used for the sample pre-treatments and mineralization were for metal trace analysis (or equivalent) grade: water was purified using a Milli-Q water system (Millipore); 2-propanol (Fluka 59300); hydrochloric acid (Baker 9530 for metal trace analysis, 36.5–38%); nitric acid (Baker 9598 for metal trace analysis, 69–70%); hydrogen peroxide (Fluka 95313, not stabilized, 30%). Calibration standard solutions were prepared daily from 1,000 mg/l standard solutions of Pt, Pd, or Rh purchased from J. T. Baker Instra-Analyzed. A reference standard, made from milled auto catalyst (NIST, standard reference material 2556, used auto catalyst pellets), with a certified content of Pt, Pd, and Rh (697.4, 326, and 51.2 mg/kg, respectively) was used to evaluate trueness; results generally showed a recovery within the limits of SD.

The sample treatments can be summarized as follows:

- (a) *Recovery of the dust stuck on the leaves*—the leaves (ca. 40 g, FW), contained in an Erlenmeyer flask, were submersed with a mixture of water and 2-propanol (3:1, ca. 200–250 ml) and sonicated for 1 h. The ‘cleaned’ leaves were taken off with Teflon-covered tweezers and discarded or, if the case, treated as below at point (b). It must be pointed out that the washing must be as short as possible, since the solvent mixture may extract some unwanted stuff from the leaves. At the beginning of our study, the precipitated-suspended dust was simply recovered by evaporation of the solution on a hot plate; in those conditions, the samples retained all the material possibly solubilized in the washing procedure (typical in this regard is the winter de-icing salt). Based on the assumption that the particulate matter we were looking for is insoluble in the solvent mixture (this was proved with the standard from used auto catalyst as mentioned above), we devised an alternative method. Thus, in the second period of our survey (2007), we experimented with the centrifugation (in 250-ml bottles at 5,000 rpm, 20’, in a Sorvall GSA rotor) as a method for easy separation of most of the washing solvent that was discarded as a clear supernatant. Only a minor residual fraction of the solvent was then evaporated on a hot plate to typically yield 0.05–1.2 g of dust. It must be noted that this procedure not only considerably saves time but greatly reduces interferences from matrix effects on the subsequent AA analysis.

- (b) *Leaves*—the leaves, typically 40 g (as collected, or with the dust removed as described above), were dried in an oven at 110°C overnight and then incinerated in a large porcelain crucible at 800°C for 3 h.
- (c) *Mineralization*—dust or ashes, obtained as above, were at first digested with hydrochloric acid and hydrogen peroxide (6 and 8 ml, respectively, added in several small portions), till evidence of complete decomposition of the organic matter (the thick foam subsides); the samples were evaporated to incipient dryness on a hotplate and then treated with aqua regia (a mixture of concentrated nitric acid and hydrochloric acid of 1:3, 2 and 6 ml, respectively). The sample was again cautiously almost reduced to dryness and, after addition of some HCl (0.25–1 ml, to reach a final content of approximately 1%), transferred in a suitable volumetric flask (25–100 ml) making up the volume with Milli-Q water. It must be said, after this procedure, that a precipitate was generally present on the bottom of the volumetric flask. In any case, atomic absorption analyses were performed on the clear decanted aqueous solutions. Blanks were made with the same solvents and chemicals employed in the treatment and digestion of the samples, or with just 1% hydrochloric acid in Milli-Q water. The certified standard from used auto catalyst was used to check the reliability of our procedure. Thus, in a few tests, 1–2 mg of this standard (exactly weighted, with 0.01 mg accuracy), suspended in the washing mixture, underwent the above-described procedure; recovery was generally better than 80%.

2.1.3 Atomic absorption spectrophotometry

Measurements were performed on a Thermo-Electron atomic absorption spectrometer: Pt, Pd, and Rh, at ng/ml (ppb) levels, were determined by graphite furnace (GFAA) coupled with Zeeman background correction. Thermal ramps with double drying and ashing steps were specifically developed, according to Table 1.

Table 1 Thermal ramps for GFAA

	Pt			Pd			Rh		
	Temp (°C)	Time (s)	Ramp (°C/s)	Temp (°C)	Time (s)	Ramp (°C/s)	Temp (°C)	Time (s)	Ramp (°C/s)
Drying	90	5	5	95	5	5	95	5	10
	115	20	2	115	30	3	115	20	2
Ashing	800	5	50	800	1	25	800	5	25
	1,200	30	100	1,100	45	100	1,300	20	50
Atomization	2,500	3	0	2,200	3	0	2,800	3	0
Cleaning	2,600	6	0	2,500	3	0	2,900	6	0

Note the double drying and ashing steps

Wavelength, bandpass, and all other instrumental parameters were set according to the usual recommendations of the instrument Cookbook.

2.2 Data treatment

The reported analytical results (actual concentration, in ng/ml) are the mean of three measurements with their inherent σ . Conventional instrumental detection limits (IDL, based on three standard deviations of the blank signal), were calculated at each monthly run for each analyzed element. On this basis, three categories of data values were considered: (1) fully significant ones, above the IDL, (2) values <IDL, ranging within 3σ blank (IDL) and 1σ blank (marked in Table 2 in *italics*), and (3) values < 1σ of the blank that were marked ‘nd’ (not detected, virtually ‘zero’ concentration). A few values <IDL, but having an inherent σ >IDL, were discarded.

Evaluating and discussing the data, along with *mean* values, we also considered the *median* as a representative index. In these latter cases, with uneven data amounts, the median value was extracted as usual. If a data amount was even with the two central data belonging to the same category (see above), the mean was calculated as usual (in the event of two “nd”, the result was only “nd”). If the mean had to be calculated with data values of two different categories, we selected the most reliable one. For example, with a value >IDL and the other <IDL, we simply chose the first one.

The results of the 2007 survey are reported in Table 2 with the Pt, Pd, and Rh showing amounts in 1 g of fresh weighed leaves collected at a specific site (ng/g FW leaf) and the concentrations of the three metals in the particulate matter (ng/g PM).

3 Results and discussion

3.1 Influence of the atmospheric precipitations

The average fresh weight (FW) of one *P. laurus cerasus* leaf is around 1 g and the surface (of one page) has been

Table 2 Results of the January–September 2007 period

Site	Date	Leaf (FW g)	PM (g)	Actual concentrations (ng/ml)			Leaf collected PGE (ng/g FW leaf)			PM composition (ng/g PM)		
				Pt	Pd	Rh	Pt	Pd	Rh	Pt	Pd	Rh
Bm	jan-07	48.641	1.072	1.36±0.38	5.30±0.33	1.16±0.18	1.40	5.45	1.19	63.6	247	53.9
Bv	jan-07	56.279	0.400	0.25±0.19	3.49±0.57	0.50±0.23	0.22	3.10	0.45	31.1	437	63.0
Bvi	jan-07	49.068	0.906	nd	-	nd	nd	-	nd	nd	-	nd
Gz	jan-07	57.339	0.691	0.40±0.27	3.59±1.03	0.59±0.22	0.35	3.13	0.51	29.1	260	42.4
Mg	jan-07	53.018	1.190	0.12±0.08	6.14±0.98	0.92±0.02	0.12	5.79	0.87	5.1	258	38.6
Sm	jan-07	52.293	0.165	0.11±0.04	nd	nd	0.11	nd	nd	34.2	nd	nd
To	jan-07	50.849	0.924	nd	2.19±0.83	nd	nd	2.15	nd	nd	119	nd
IDL	jan-07			0.36	2.66	0.68						
Bm	feb-07	48.641	1.130	1.85±0.28	4.09±2.39	2.93±0.90	0.95	2.10	1.51	40.9	90.6	64.8
Bv	feb-07	56.279	1.146	2.69±0.79	2.08±0.60	1.61±0.81	1.19	0.92	0.71	58.7	45.4	35.1
Bvi	feb-07	49.068	0.417	3.88±0.93	10.05±0.62	0.57±0.34	1.98	5.12	0.29	233	603	34.3
Gz	feb-07	57.339	1.292	3.98±0.88	2.36±0.36	3.23±0.70	1.74	1.03	1.41	77.1	45.7	62.5
Mg	feb-07	49.345	0.867	4.04±1.03	2.53±0.62	3.05±0.71	2.05	1.28	1.55	117	72.9	88.0
Sm	feb-07	53.119	0.068	0.99±0.31	nd	0.34±0.09	0.47	nd	0.16	364	nd	127
To	feb-07	47.394	0.168	nd	1.34±1.05	0.26±0.10	nd	0.71	0.14	nd	200	39.1
IDL	feb-07			2.34	0.87	0.72						
Bm	mar-07	48.811	0.858	2.37±0.68	4.57±0.12	4.19±0.20	1.22	2.34	2.15	69.1	133	122
Bv	mar-07	52.242	1.183	nd	2.01±0.60	2.91±0.51	nd	0.96	1.39	nd	42.4	61.5
Bvi	mar-07	40.500	0.396	-	nd	nd	-	nd	nd	-	nd	nd
Gz	mar-07	56.741	1.201	0.95±0.37	2.83±0.98	2.70±0.63	0.42	1.25	1.19	19.7	59.0	56.1
Mg	mar-07	48.684	0.656	nd	3.88±0.98	2.16±0.88	nd	1.99	1.11	nd	148	82.3
Sm	mar-07	52.521	0.098	nd	-	nd	nd	-	nd	nd	-	nd
To	mar-07	53.389	0.049	nd	1.08±1.59	0.53±0.71	nd	0.50	0.25	nd	547	267
IDL	mar-07			1.39	3.14	0.84						
Bm	apr-07	50.686	0.988	2.27±0.38	11.87±1.44	3.61±0.54	1.12	5.85	1.78	57.6	300	91.3
Bv	apr-07	52.300	0.585	nd	2.63±0.53	1.65±0.61	nd	1.26	0.79	nd	113	70.5
Bvi	apr-07	45.586	0.411	-	nd	nd	-	nd	nd	-	nd	nd
Gz	apr-07	56.644	1.200	1.13±0.59	5.82±1.56	4.66±0.46	0.50	2.57	2.06	23.6	121	97.1
Mg	apr-07	48.693	0.984	1.78±0.04	7.10±0.18	4.64±0.42	0.91	3.65	2.38	45.2	180	118
Sm	apr-07	51.957	0.744	nd	1.72±1.06	0.56±0.20	nd	0.83	0.27	nd	57.9	19.0
To	apr-07	56.122	0.315	nd	0.96±0.34	1.39±0.60	nd	0.43	0.62	nd	76.6	111
IDL	apr-07			1.55	0.56	0.66						
Bm	may-07	42.987	0.152	1.36±0.26	3.52±1.05	2.68±0.09	0.79	2.04	1.56	225	580	442
Bv	may-07	48.378	0.558	nd	1.84±0.40	1.17±0.76	nd	0.95	0.61	nd	82.3	52.4
Bvi	may-07	50.463	0.576	nd	nd	0.79±1.29	nd	nd	0.39	nd	nd	34.3
Gz	may-07	51.773	0.478	1.38±0.32	6.34±0.53	3.85±0.23	0.67	3.06	1.86	72.3	331	201
Mg	may-07	45.358	0.434	nd	4.52±1.12	1.67±0.37	nd	2.49	0.92	nd	261	96.3
Sm	may-07	57.727	0.174	nd	nd	0.52±0.23	nd	nd	0.22	nd	nd	74.3
To	may-07	55.064	0.215	nd	nd	1.63±0.73	nd	nd	0.74	nd	nd	190
IDL	may-07			2.51	1.94	0.34						
Bm	jun-07	48.559	0.356	0.21±0.06	3.35±1.19	4.44±0.42	0.11	1.73	2.28	14.5	236	312
Bv	jun-07	52.478	0.985	0.72±0.10	5.25±0.54	5.00±0.57	0.34	2.50	2.38	18.2	133	127
Bvi	jun-07	43.596	0.475	-	1.37±0.49	1.39±2.60	-	0.78	0.80	-	71.9	73.0
Gz	jun-07	56.725	1.248	2.55±0.23	3.49±0.30	6.38±0.71	1.13	1.54	2.81	51.2	69.8	128
Mg	jun-07	48.861	1.086	1.63±0.41	4.08±1.28	9.01±0.49	0.83	2.09	4.61	37.5	93.9	207
Sm	jun-07	52.379	0.102	-	1.29±0.56	1.44±2.98	-	0.62	0.69	-	318	353

Table 2 (continued)

Site	Date	Leaf (FW g)	PM (g)	Actual concentrations (ng/ml)			Leaf collected PGE (ng/g FW leaf)			PM composition (ng/g PM)		
				Pt	Pd	Rh	Pt	Pd	Rh	Pt	Pd	Rh
To	jun-07	55.130	0.192	nd	1.30±0.22	1.69±2.18	nd	0.59	0.77	nd	169	220
IDL	jun-07			0.20	2.70	3.50						
Bm	jul-07	48.487	0.508	0.64±0.06	8.38±1.28	0.72±0.13	0.33	4.32	0.37	31.5	413	35.6
Bv	jul-07	51.735	0.550	0.76±0.11	2.31±0.49	0.53±0.08	0.37	1.12	0.26	34.4	105	24.2
Bvi	jul-07	39.186	1.626	nd	nd	nd	nd	nd	nd	nd	nd	nd
Gz	jul-07	47.224	0.570	2.16±0.96	3.17±0.61	1.36±0.08	1.15	1.68	0.72	94.9	139	59.8
Mg	jul-07	44.602	0.582	1.65±0.25	4.48±0.23	1.26±0.12	0.92	2.51	0.70	70.8	192	54.0
Sm	jul-07	52.369	0.361	nd	nd	0.33±0.04	nd	nd	0.16	nd	nd	23.1
To	jul-07	53.660	0.274	nd	3.66±0.35	1.50±0.10	nd	1.70	0.70	nd	334	137
IDL	jul-07			1.13	2.27	0.88						
Bm	aug-07	46.113	0.225	nd	2.19±0.42	nd	nd	1.19	nd	nd	243	nd
Bv	aug-07	52.136	0.415	nd	0.71±0.27	nd	nd	0.34	nd	nd	42.5	nd
Bvi	aug-07	35.622	0.123	–	nd	0.41±0.06	–	nd	0.28	–	nd	82.4
Gz	aug-07	56.102	0.405	nd	1.57±0.26	0.24±0.13	nd	0.70	0.11	nd	97.3	15.1
Mg	aug-07	48.116	0.425	0.58±0.06	2.40±0.39	0.37±0.01	0.30	1.24	0.19	34.4	141	21.6
Sm	aug-07	51.522	0.025	–	nd	0.33±0.24	–	nd	0.16	–	nd	325
To	aug-07	55.018	0.212	nd	–	0.21±0.12	nd	–	0.09	nd	–	24.4
IDL	aug-07			0.73	0.85	0.50						
Bm	sep-07	45.766	0.281	–	3.40±0.89	nd	–	1.86	nd	–	303	nd
Bv	sep-07	47.878	0.399	nd	2.49±1.19	nd	nd	1.30	nd	nd	156	nd
Bvi	sep-07	49.872	0.307	–	1.50±0.07	nd	–	0.75	nd	–	122	nd
Gz	sep-07	50.247	0.648	2.61±0.08	1.79±0.99	nd	1.30	0.89	nd	101	69.0	nd
Mg	sep-07	51.740	0.415	nd	3.29±0.52	nd	nd	1.59	nd	nd	198	nd
Sm	sep-07	46.344	0.126	–	nd	nd	–	nd	nd	–	nd	nd
To	sep-07	46.557	0.083	nd	0.73±1.09	nd	nd	0.39	nd	nd	220	nd
IDL	sep-07			0.62	1.47	0.78						

estimated at approximately 32 cm². Leaf collecting is not expected to be selective with respect to the traffic-borne PGE pollution, and in fact, ordinary soil can stick on the leaves as well, particularly in extra-urban and/or open locations. Thus, in those cases, the PGE result is somewhat more diluted than elsewhere and, in this respect, the sites of Gz and Bvi are found to be remarkable. The total collected particulate matter reached particularly high levels in dry periods, up to 40 mg per 1 g of leaves or approximately 1.25 mg/cm² (see jul-07, Bvi). In Fig. 2, the monthly PM depositions (in mg of PM per g of leaf), averaged over the four traffic exposed locations (with Bvi too), are compared with the rain records in Varese (Centro Geofisico Prealpino, <http://www.astrogeo.va.it/statisti/statmet.htm>). In fact, the highest PM loadings were observed in the unusually dry period of January–April 2007 (with only 155 mm of rain, as compared with the expected 418 mm averaged on 30 years of records) and in July (44 mm as compared with the expected 102).

Heavy atmospheric precipitations can scale down the amounts of collected PM 2–3-fold, as observed in the sampling made on May 31, 2007, just 3 days after a period of unusually heavy rain (68 mm in 24 h, approximately 200 mm in the month), and in August–September, where a total of 439 mm of rain (300 expected) led to poor dust collection and levels of Pt and Rh mostly under the IDL. Of course, these results are not unexpected and similar relationships have already been reported. For example, a connection between the road-dust PGE levels and rainfall was evidenced in a survey made in Perth, West Australia (Whiteley 2005).

3.2 Influence of the location

It can be seen in Table 2 that over the period January–September 2007, in the two ‘clean’ locations at Sacro Monte (Sm) and Villa Toeplitz (To), we got values essentially under the detection limits. Particularly, minimal

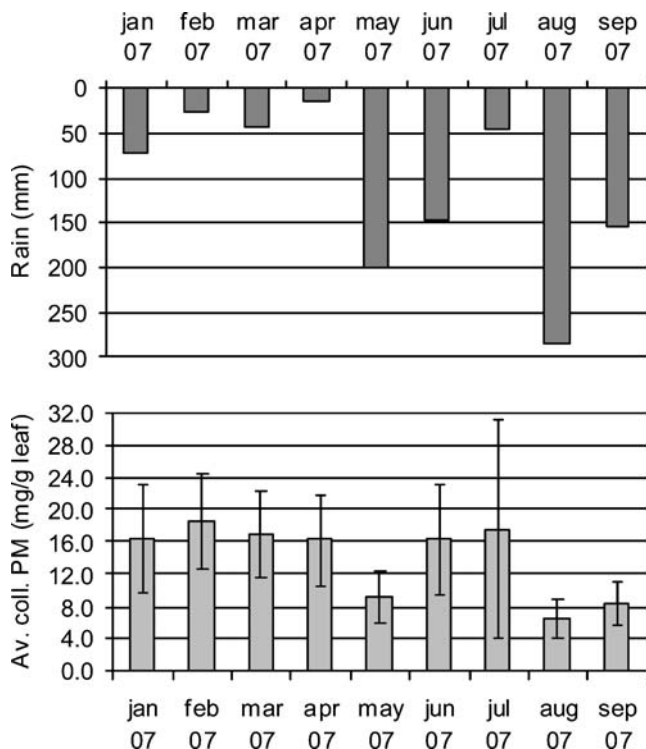


Fig. 2 Monthly PM depositions (in mg per 1 g of leaf) averaged on the four traffic exposed sites, compared with the Varese raining records

and yet significant (i.e., >IDL) amounts of palladium and rhodium were observed in Sm just once (in April and May, respectively), while the two metals are just slightly more recurrent in To; in both sites, platinum went mostly undetected. The chart in Fig. 3 reports the median values calculated for each site; these values appear to us to be more realistic indicators of the local pollution than the means. One thing is quite remarkable: platinum never

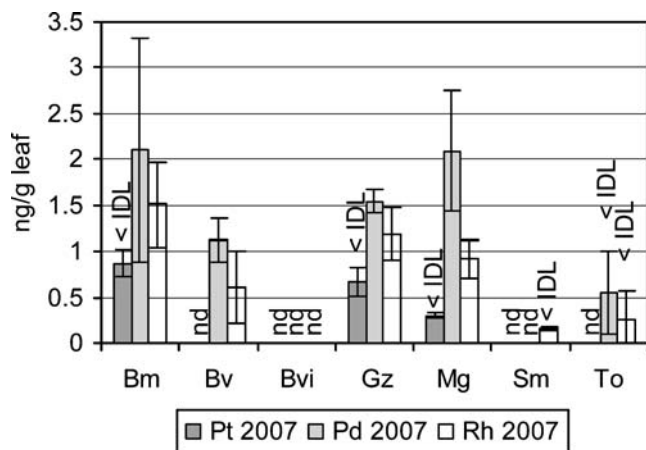


Fig. 3 The Pt, Pd, and Rh depositions (ng per 1 g of leaf) representative of the local pollution in the sampling sites. The reported values are the median calculated over the period January–September 2007

reaches significant (>IDL) values. The three PGEs reach the highest levels at Bm, Bv, Gz, and Mg, five to ten times that which can be found in the other locations, a clear indication that the pollution strictly depends on the distance from the traffic fluxes and their intensity. This correlation was particularly evident in sampling site Bvi (inside via Valmorea, approximately 20 m from the main traffic flux close to Bv), with the three PGEs essentially being undetected. Similarly, in the 2004–2005 period, the PM deposition in Bvi was found, on average, to have 20–25% of that found in the Bv exposed location.

It must also be said that, in the Bv site, for a few months in 2004–2005, we could find evidence that the samplings made close to the ground (less than 0.5 m) showed an average metal content 35–45% higher with respect to the samplings made approximately 2 m high. These results are consistent with a dry deposition, with relatively low mobility from the pollution source.

3.2.1 Composition of the PM: a comparison with the 2004–2005 results

As seen above, the amount of PGEs collected by the leaves in a location can be taken as an index of its specific pollution. However, since the collected PM can also greatly change in dependence of the atmospheric precipitations, it is convenient considering the results with reference to the composition of the PM itself. Thus, the PGE’s contents of the particulate, in ng (10^{-9} g) per 1 g of PM, are reported in Table 2 and illustrated in Fig. 4.

Palladium is clearly the most abundant of the three PGEs and it can presently be up to 3–3.5 times as high (w/w) as that of the platinum (approximately 6–7 mol/mol). This is quite remarkable because only a few years ago the

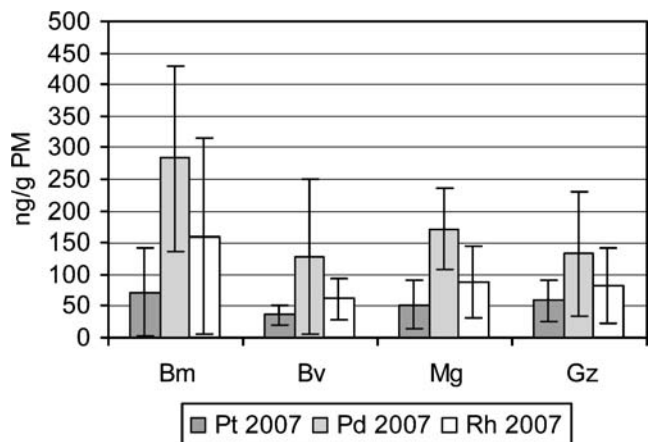


Fig. 4 Pt, Pd, and Rh content of the particulate (ng per 1 g PM) in the four traffic exposed locations, averaged on the period January–September 2007

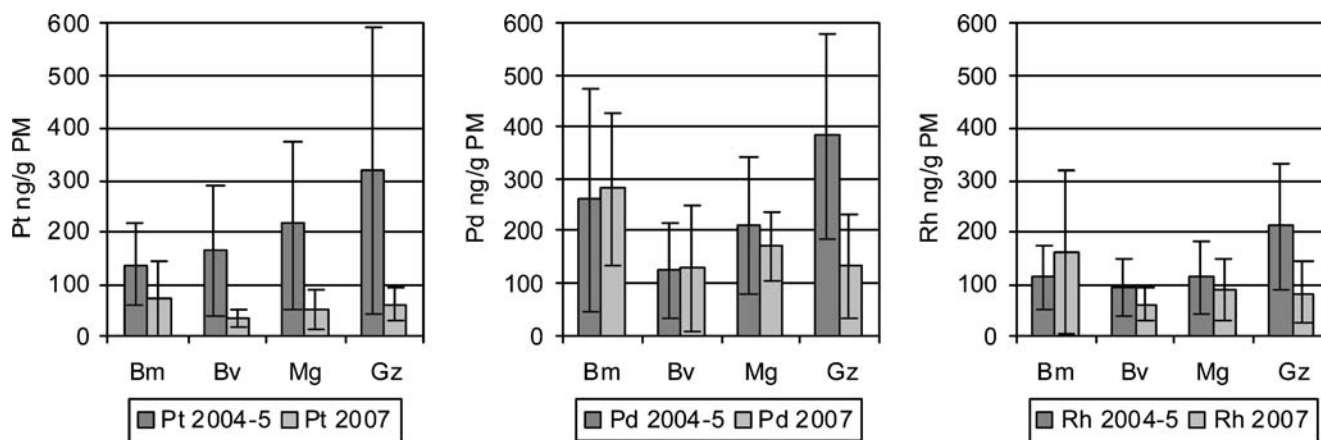


Fig. 5 The changing PGEs content of the particulate in the four selected locations (ng per 1 g PM) from 2004–2005 to 2007, averaged over the two periods

relationship between Pt and Pd concentrations was reversed; in fact, Pt/Pd *w/w* ratios ranging between 10 and 5 were found in various polluted matrices such as grass, soil, and road dust (Helmert et al. 1998), consistently with catalytic converters operating at that time, based essentially on Pt–Rh or Pt only. However, it has to be pointed out that in the USA (San Diego, CA) a somewhat different situation has been emerging since 1986, with Pt/Pd ratios as low as 2.5, reflecting the use of new catalytic converters (Hodge and Stallard 1986). In this respect, the Pt/Pd *w/w* ratio of 2.14 characterizing the abovementioned NIST standard from used auto catalysts (see Section 2.1.2) is also indicative.

With reference to Figs. 5 and 6, we may say that the relative composition of the particulate appeared to be comparable in all the four sites in 2004–2005, within approximately 20% of variance. In fact, the Pt/Rh and Pd/Rh *w/w* ratios, averaged on the four sites, resulted in 1.59 ± 0.30 and 1.84 ± 0.41 , respectively. The most relevant result of the 2007 survey, with respect to the 2004–2005 one, is the dramatic, generalized reduction of the relative (with respect to Rh) PM platinum content. The drop was more important in the three urban sites of Bm, Bv, and Mg, with

an average Pt/Rh ratio of 0.54 ± 0.08 , approximately 1/3 of the previous ones, while the relative Pt content was reduced to about half in Gz (Pt/Rh ratio of 0.71). The peculiar traffic of Gz, with a high number of heavy trucks, may explain this difference: these diesel-fueled vehicles still have catalysts mostly based only on platinum and, very likely, this somewhat counterbalances a general tendency towards a reduction of the Pt levels. In 2007, the relative palladium content showed the same average value ($\text{Pd/Rh} = 1.85 \pm 0.21$) as found in 2004–2005. However, in all cases, the results are quite far from the ‘classical’ Pt/Rh *w/w* ratio of 5:1 that was a common marker of the traffic pollution just a few years ago (Petrucci et al. 2000; Schramel et al. 2000; Gomez et al. 2002; Lesniewska et al. 2004; Whiteley 2005).

4 Conclusions

Comparison of the 2004–2005 and 2007 data gives a significant insight into 2 years of evolution in catalyst design and automotive trends. The changes can be explained with two recent occurrences: (1) the increasing

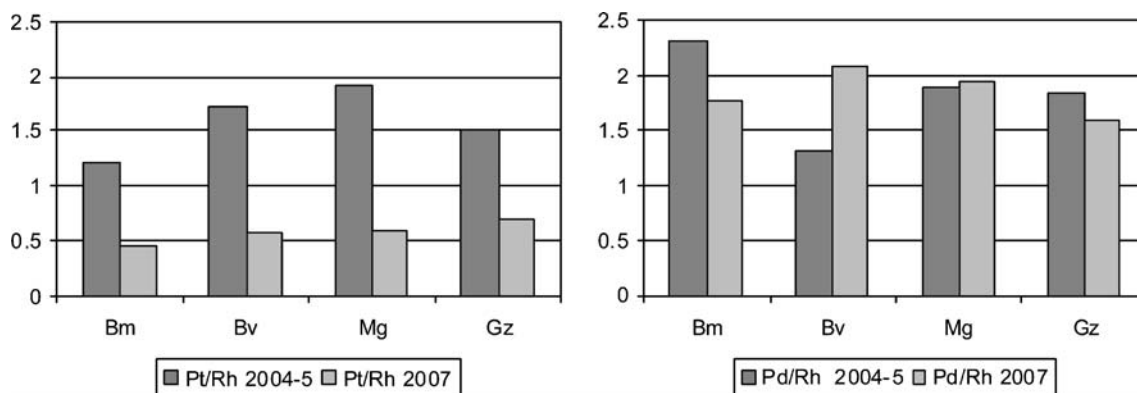


Fig. 6 The Pt/Rh and Pd/Rh *w/w* ratios, averaged over the two periods 2004–2005 and 2007

diffusion of cars with a diesel engine (Automobile Club d'Italia, ACI 2008), whose catalysts are made up without any rhodium, and (2) the latest changes in catalyst technology that, based also on the vicar role played by the two metals, tend to replace the high-priced platinum with the cheaper palladium. Our results can somehow be compared with those reported in a recent report about changes in PGE concentrations, along a major highway in Germany, from 1994 to 2004 (Zereini et al. 2007); in this important study, a dramatic surge of the Pd levels has been demonstrated, a 15-fold increase over the 10-year period, while the levels of Pt and Rh were only 2 and 1.6 times higher.

About our survey and the supporting procedure, we may say that the leaves of *P. laurus cerasus* are efficient PM collectors and the analysis of the road-side dust stuck on foliage is a good indicator of traffic-borne pollution; the collected PGE amounts strictly depend on the distance from the traffic fluxes and their intensity. The proposed analytical procedure, restricted to the leaf dust recovered with an efficient washing procedure, greatly reduces the matrix effect and does not require a prior preconcentration and/or matrix separation. Therefore, it is simple and reliable and can be easily performed with a graphite furnace-equipped atomic absorption spectrophotometer (GFAA), overcoming the problems occurring in Pd quantification with ICP-MS (Moldovan 2007). We suggest that this dust recovery procedure can be extended to other broad-leaved plants exposed to vehicular traffic (Hodge and Stallard 1986).

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