Scientific Annals, School of Geology, Aristotle University of Thessaloniki Proceedings of the XIX CBGA Congress, Thessaloniki, Greece	Special volume 100	47-54	Thessaloniki 2010

ENVIRONMENTAL IMPACT OF Pt, Pd, Rh AND Au FROM CATALYTIC CONVERTERS ALONG ROADSIDES: THE CASE OF ATTICA, GREECE

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Abstract: Platinum (Pt), palladium (Pd), rhodium (Rh) and gold (Au) were investigated along highways of Attica, Greece, with varying traffic, like Katehaki, Messoghion, the intersection between Katehaki, Messoghion and Acharnon avenues, and residential roads, like Pindos and Navarinou roads. Platinum ranges between 110 and 960 ppb in dust samples and from 44 to 820 ppb in soils, Pd ranges between 90 and 1300 ppb in dust samples and from 36 to 1100 ppb in soils. The analysis of dust collected from parts of the roadsides closed to water sewerages reached as high as 2070 ppb Pt and 1980 ppb Pd contents. Gold ranges from 14 to 990 ppb Au (average 230) in dust samples and from 27 to 160 ppb Au (average 95) in soil ones. Any relationship between Au and Pt or Pd is not obvious. The significant fraction of the traffic-related emissions, reaching values over 4 ppm (Pt+Pd), suggest that they may be concentrated into local water systems resulting an environmental risk. Palladium was the most abundant PGE in the grasses ranging from 0.6 to 23 ppb (average 6.8 ppb), Pt ranges between 2.3 and 6.6 ppb (average 4.2 ppb) while Rh is < 0.1 ppb. Average values of the Pd/(Pd+Pt+Rh), Pt/(Pd+Pt+Rh) and Rh/Pd/(Pd+Pt+Rh) ratios decrease from 0.62 to 0.33 and 0.05 respectively, suggesting the Pd>Pt>Rh bioavailability order.

Key words: catalytic converter, recycle, environment, automobile emission, bioavailability, Greece

1. Introduction

The increased use of platinum (Pt), palladium (Pd), and/or rhodium (Rh) in automobile catalyst converters, has led to their release into the environment and biological accumulation on roadsides, since 1974 in USA and 1993 in European countries (Hoffman, 1989; Zereini et al., 1998; Palacios et al., 2000; Ely et al., 2001; Jarvis et al., 2001; Kendal, 2004; Croy et al. 2008). Catalytic converters are used to treat automobile emissions by catalysing the oxidation of carbon monoxide and hydrocarbons, and the reduction of NOx. They are constructed by applying a film of 1-3g Pt- Pd-Rh alloy, in proportion typically 0.08% Pt, 0.04% Pd and 0.005-007% Rh, on a ceramic "monolith" (Hoffman, 1988, 1989). The amount and rate of the Pt, Pd and Rh release from catalytic converters is affected by the speed of the automobile, type of engine, type and age of catalyst, and type of fuel additives (Ely et al., 2001; Whiteley and Murray, 2003).

The investigation of samples from road dust, soil and grass indicated that greater proportion of PGE emissions is from automobile catalysts, in the form of nanometer-sized catalyst particles, which deposit on roadside surfaces. In soil, PGE can be transformed into more mobile species through complexation with organic matter and can be solubilised in low pH rainwater. There are indications that environmentally formed Pd species are more soluble and hence more mobile in the environment than Rh and Pt (Dahlheimer et al., 2007).

Average Pt and Pd concentrations in rural and suburban roadside top soils (2.0 and 1.4 ppb, respectively), and high-way roadside top-soil (140 ppb Pt, and 130 ppb Pd) have been determined in Athens, Greece, recently (Riga-Karandikos et al., 2006). In the present study platinum, palladiun, rhodium and gold along with other traffic related elements were determined (a) in road dust and roadside soils and (b) in grasses and tree-leaves close to highway roads of Attica, Greece, in an attempt to present an assessment of the autocatalyst derived PGE in Greece. They are compiled with published data and the possibility for their bioavailability is discussed.

2. Material and methods

The sampling areas selected for this pilot study include sites with varying traffic and driving style

(stop/start vs. constant speed): (a) parts of the Katehaki high-way road, to the east peripheral of Athens, from the intersection between Katehaki and Messoghion road to the turn to the Panepistimiopolis of Zografou, where there is a change in its geomorphological feature from almost flat to a relatively higher positive slope (b) the urban Messohgion road, from the intersection between Katehaki to Aghia Paraskevi, (c) the Pindos and Navarinou residential roads (d) a few only samples from the National high-way road Athens - Thessaloniki, from about 50 km, (e) the Iera odos and the (f) Acharnon high-way road (Fig.1).

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All samples were analysed at ACME Laboratories, for Pt, Pd, Rh and Au, using the litharge (PbO) - collection fire-assay fusion for total sample decomposition, digestion of the Ag bead and ICP-MS analysis technique. Detection limits are 0.5 ppb for Pd, 0.1 ppb for Pt and Rh, and 1 ppb for Au. Trace element concentrations (Fe, Mn, Pb, Zn, Cu, Ni, Zr etc) in whole dust samples were determined by ICP/MS analysis at Activation Laboratories, Ltd, Canada, after an alkaline peroxide.

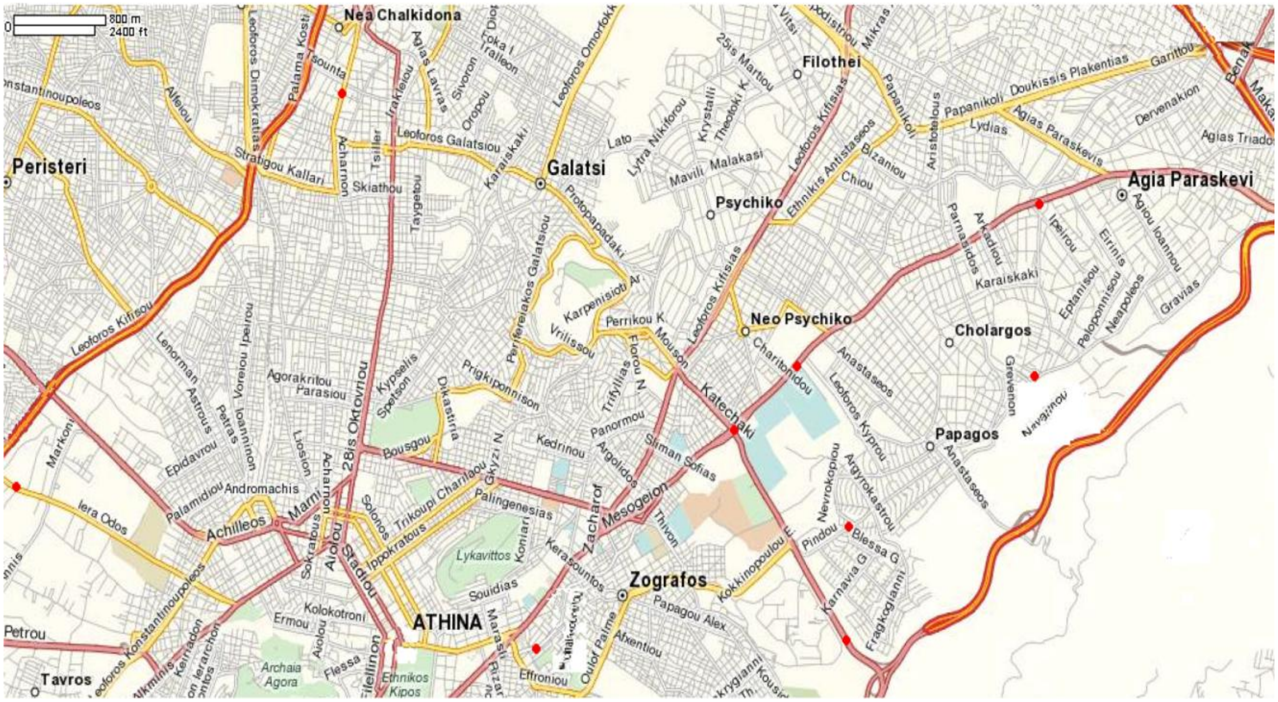

Fig. 1. Location map of Attica, showing the sites (●) of sampling.

Roadside dust samples (n = 29) were collected from the surface along roadways from the above major highways, major intersections and residential roads. Topsoil samples (n = 9) were taken from areas directly exposed to traffic emissions along the highways roadside and also from residential side streets, where traffic flows were low. They were collected from the surface soil (0-4 cm depth) with a plastic spatula in an area approximately 10 cm^2 and stored in plastic sample bags. They were air dried and then sieved using a nylon sieve to produce a 2 mm fraction. Grass samples (n = 22) and leaves from olive and *Laurus nobilis* trees (n = 7) were dried in an oven at 70 ^oC, and then powdered in an agate mortar. Sample preparation was undertaken at the Laboratories of the Department

Polished sections prepared from the most PGE-rich road dust samples (Katehaki road) were examined by reflected light microscopy and scanning electron (SEM). Quantitative analyses were carried out at the University of Athens, Department of Geology, using a JEOL JSM 5600 scanning electron microscope, equipped with automated OXFORD ISIS 300 energy dispersive analysis system. Analytical conditions were 20 kV accelerating voltage, 0.5 nA beam current, b2 μm beam diameter and 50 s count times.

3. Results

The presented analytical platinum-group element data demonstrate significant abundances of Pt, Pd and Au above background in each of the dust and

Table 1. Precious metal content in dust and soils along roadside.

Date (year, month)	**(ppb)**				
Sample location	Pt	Pd	Rh	Au	Pd/Pt
2006-10-KAT1.dust	710	1000	4	14	1,41
2006-10-KAT2.dust	960	1300	5	51	1,35
2007-3-KAT3.dust	440	630	130	60	1,43
2007-04-KAT6.dust	900	670	3	360	0,74
average	*750*	*800*	*35*	*121*	*1,23*
2007-04-KAT.S4.dust	1720	1570	6	71	0,91
2007-04-KAT.S5.dust	2420	2400	4	180	0,99
average	*2070*	*1980*	*5*	*125*	*0,95*
2007-03-KAT2-3.soil	200	196	bdl	93	0,98
2007-04-KAT-MES1.soil	440	510	bdl	160	1,16
2007-04-KAT-MES2.soil	820	1100	3	120	1,34
average	*610*	*800*		*140*	*1,25*
2007-04-Pi.soil	60	70	1,5	56	1,17
2006-10-MES1.dust	290	500	3	220	1,72
2007-03-MES2.dust	210	300	26	460	1,43
2007-04.P.MES3.dust	210	300	3	240	1,43
average	*255*	*365*	*17*	*307*	*1,53*
2006-10-MES1.soil	44	90	8	150	2,04
2006-10-MES2.soil	36	74	10	6	2,06
average	*40*	*82*			*2,05*
2007-03-P.MES.soil	230	360	2	143	1,58
2007-03.NAV.soil	150	230	34	26	1,5
2007-04-MIXAL.dust	400	550	bdl	990	1,38
2006-10-Iera Odos1.dust	500	750	22	90	1,5
2006-10-Iera Odos2.dust	230	350	24	25	1,52
average	*665*	*550*	*23*	*58*	*1,51*
2006-10-N.h.Ath-Th1.dust	190	220	20	27	1,16
2006-10-N.h.Ath-Th2.dust	120	180	16	70	1,5
average	*155*	*200*	*18*	*47*	*1,33*
07-03-N.h.Ath-Th1.soil	92	100	35	27	1,11
2007-05-ACHAR1.dust	380	650	24	120	1,7
2007-05-ACHAR2.dust	240	280	7	530	1,2
2007-05-ACHAR3.dust	140	180	2	120	1,3
2007-05-ACHAR4.dust	200	300	2	660	1,5
2007-05-ACHAR5.dust	320	660	47	1340	2,1
2007-05-ACHAR6.dust	170	260	bdl	160	1,5
2007-05-ACHAR7.dust	350	490	2	1000	1,4
2007-05-ACHAR8.dust	320	460	44	210	1,4
2007-05-ACHAR9.dust	300	450	49	300	1,6
2007-05-ACHAR10.dust	220	320	9	1040	1,4
2007-05-ACHAR11.dust	160	190	bdl	570	1,2
2007-05-ACHAR12.dust	110	90	bdl	210	0,8
2007-05-ACHAR13.dust	160	260	15	900	1,6
2007-05-ACHAR14.dust	170	220	13	550	1,3
2007-05-ACHAR15.dust	170	210	5	260	1,2
average	227	335	15	530	1,4
STANDARD FA-100S	48,1	48,6		49	

Symbols: KAT = Katehaki; MES = Messoghion; P.MES. = Aghia Paraskevi; NAV = Navarinou; MIXAL. = Michalakopoulou; N.h.Ath-Th = National high-way Athens-Thessaloniki; ACHAR = Acharrnon; bdl = below detection limit

soil samples, especially those closest to the road, whilst Rh is decreased to within error of background level (Table 1). Although present data are limited, they suggest an increasing trend between platinum and palladium contents in plants and the associated soils (Fig. 2, Tables 1 & 2) confirming previous aspect that the catalytic converter attrition is responsible for the elevated abundances along highways (Ely et al., 2001; Dahlheimer et al., 2007). Platinum ranges between 110 and 960 ppb (average 550 ppb) in dust samples and from 44 to 440 ppb (average 200 ppb) in soils (Table 1). Palladium ranges between 90 and 1300 ppb (average 680 ppb) in dust samples and from 36 to 820 ppb (300 ppb) in soils. Dust samples showed extremely high concentrations in those collected from small cavities on the road substrate, at the contact with water sewerage (Table 1, samples labelled as KAT.S4 and KAT.S5) exhibit as high as 2070 ppb Pt and 1980 ppb Pd. Gold ranges between 14 and 990 ppb Au (average 230) in dust samples and from 27 to 160 ppb Au (average 95) in soil samples. The lack of any relationship between Au and Pt or Pd is obvious (Table 1).

Representative dust samples from Katehaki, Messoghion, Iera odos roads and the National high-way road Athens - Thessaloniki, were analysed for several trace elements indicated Pb, Cr, Zn, Cu, Ni and Zr contents (Table 3). They range from 130 to 830 ppm Pb, 320 to 530 ppm Zn, 290 to 480 ppm Mn, 100 to 370 ppm Cu, 70 to 135 Cr, 60 to 160 ppm Ni, 11 to 18 ppm Ce, 3.1 to 4.6 ppm Y and 0.5 to 1.3 ppm Zr. Although the roadside dust is derived by various sources, such a composition fell within the typical range of traffic related metals in highways (Ely et al., 2001; Jarvis et al., 2001; Moldovan et al., 2002; Riga-Karandinos et al., 2006). Road dust (polished sections) and atmospheric particle emissions (collected on multiple filters, one day) from the Katehaki high-way peripheral road and were investigated by scanning electron microscope with energy-dispersive X-ray analysis. They showed abundant PM10 (smaller than 10 μm) and PM2.5 (smaller than 2.5 μm) particles which are dominantly crystalline materials such as quartz, calcite, barite, Al, Mg, K, Na-silicates, Fe, Ti, Mn-oxides, metal iron showing a varying degree of oxidation, Cr- , Pb- , and Ce-phases, and zirconium (Fig. 3). Elevated contents and and such Zr, Ce, Cr, Cu, Zn, Mn-phases may be related to brake wear emissions (Schaller, 1991).

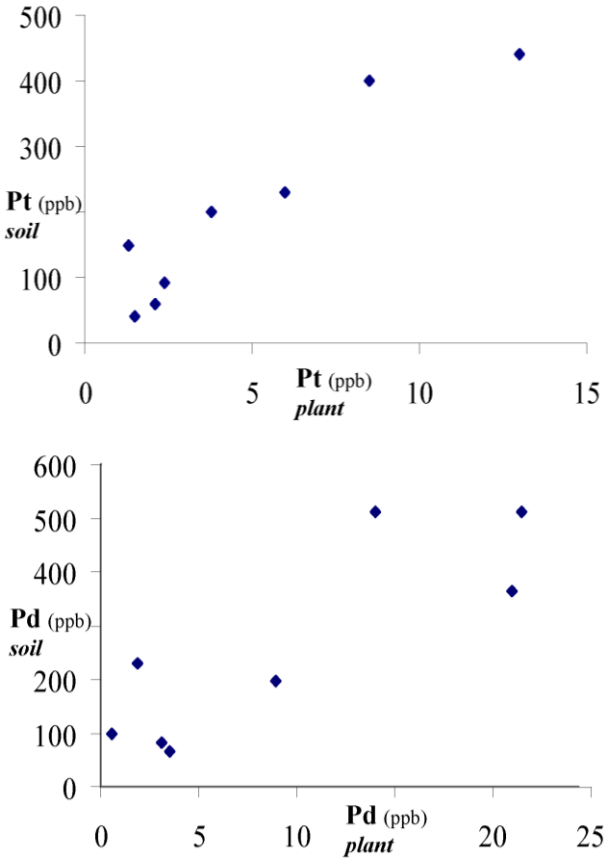

Fig. 2(a,b). There is an increasing trend between platinum and palladium contents in plants and the associated soils, along roadsides of Greece. Data from Tab. 1 & 2.

Palladium was the most abundant PGE in the grasses ranging from 0.6 to 23 ppb (average 6.8 ppb), while Pt ranges between 2.3 and 6.6 ppb (average 4.2 ppb), but compared to the analysed soils, the grasses contained the lowest PGE abundances. There is a good relationship between both Pd and Pt contents in plants with their corresponding contents in soils (Tables 1 & 2; Fig 2a,b). Concentrations below of 0.5 ppb Pd and 0.1 ppb Pt were found in two grass samples in about 100 m distance from the roadside confirming previous studies, e.g. PGE abundances in soils decreased away from road surfaces (Ek et al., 2004; Dahlheimer et al., 2007).

4. Discussion

The presented PGE data from highways of Greece (Table 1) demonstrate that catalytic converter attrition is responsible for the elevated abundances and that concentrations of PGEs increased with traffic density, reaching values up to 2070 ppb Pt and 1980 ppb Pd in dust. Gold, ranging between 14 and 990 ppb (average 310) in dust samples and from 27 and 160 ppb Au (average 95) in soils, is much lower than PGE and does not show any relationship with Pt and Pd, confirming previous study in U.K. (Farago et al., 1996).

Table 2. Precious metal content in grasses and tree-leaves along roadside.

Date (year, month),	(ppb)				
sample location	Pt	Pd	Rh	Au	Pd/Pt
Grassy					
2006-10-KAT.G1	2	3,8	bdl	21	1,9
2007-03-KAT.G2	7	20	bdl	25	2,9
2007-03-KAT.G3	10	23	5	22	2,3
2007-04-KAT.G4	3,2	5,3	0,1	13	2,3
2007-04-KAT.G5	1,2	2,1	bdl	5	1,75
2007-04-KAT.G6	1,5	1,7	bdl	38	1,13
2007-04-KAT.G7.	1,8	4,8	0,2	10	2,67
average	*3,8*	*8,9*			*2,2*
2007-03-MES-KAT.G8	16	20	1,4	22	1,2
2007-03-MES-KAT.G9	10	8	bdl	120	0,8
average	*13*	*14*			*1,07*
2006-10-MES.G10	2	4,4	bdl	250	2,2
2006-10-MES.G11	1	1,8	bdl	16	1,8
average	*1,5*	*3,1*			*2,07*
2007-03-P.MES.G12	6	21	bdl	16	3,5
2006-10-Pi-G13	0,2	4	bdl	7	
2006-10-Pi-G14	1,1	6,5	bdl	2	5,9
2007-03-Pi.G15	2,5	2,4	bdl	1350	1
2007-03-Pi.G.16	4,6	1	bdl	35	0,22
average	*2,7*	*3,3*			*2,37*
2006-10-NAV.G.17	1,3	2	bdl	16	1,5
2006-10-NAV.G.18	0,8	4,7	bdl	170	1,5
2007-03-NAV.G19	1	0,6	bdl	8	0,6
2007-03-NAV.G20	3,6	4,2	bdl	48	1,2
2007-03-NAV.G21	0,8	1,6	bdl	28	2
average	*1,5*	*2,2*			*1,36*
2007-03-N.h.Ath-Th3.G	2,4	0,6	bdl	21	0,25
2007-03-KAT-T1	3,5	4	0,7	110	1,1
2007-03-KAT-T2	5,2	4,4	0,7	30	0,9
2007-04-KAT-T3	4	6,1	bdl	7	1,52
average	*4,2*	*4,6*			*1,17*
2007-03-P.MES.T4.	2,8	2,5	bdl	44	0,9
2007-03-MES.T5	4	6	bdl	55	1,5
2007-03-P.MES.T6	1,2	3,8	bdl	67	3,2
2007-03-P.MES.T7	2,2	2,3	bdl	36	1,05
average	*2,5*	*3,6*			*2,22*
background-G1	<0.1	<0.5	bdl		
background-G2	<0.1	<0.5	bdl		
STANDARD FA-100S	41	40,6	38,2		

Symbols: G = grass; T = tree; KAT = Katehaki; MES = Messoghion; P.MES. = Aghia Paraskevi; NAV = Navarinou; MIXAL. = Michalakopoulou; N.h.Ath-Th = National high-way Athens-Thessaloniki, bdl = below detection limit.

Traffic emissions and their impact on urban air quality, health, and atmospheric processes have been the subject of increasing interest in recent years (Ely et al., 2001; Dahlheimer et al., 2007). The amount and rate of PGE emissions are affected by the speed of the automobile, and the type and age of the catalyst (Artelt et al., 1999). Several studies have focused on the comparison between the gasoline engine type (Pt-Pd-Rh and Pd-Rh) and diesel engine catalysts (Pt), and the three-way catalytic converter: Reduction of nitrogen oxides to nitrogen and oxygen ($2NO_x \rightarrow xO_2 + N_2$), oxidation of (toxic) carbon monoxide to harmless carbon dioxide ($2CO + O_2 \rightarrow 2CO_2$) and oxidation of unburnt carcinogenic hydrocarbons (HC) to carbon dioxide and water ($2C_xH_y + (2x+y/2)O_2 \rightarrow 2xCO_2 + yH_2O$). Platinum and rhodium are used as a reduction catalysts, while platinum and palladium are used as an oxidization catalyst (Fly et al., 2001; Moldovan et al., 2002; Dahleimer et al., 2007).

The PGE level along the highways of Greece (Table 1) that may be washed by rain and concentrated into local water systems, is comparable to that given for many other countries (Hodge and Stallard, 1986; Ely et al., 2001; Dahlheimer et al., 2007). Although some authors have suggested that such Pt-Pd concentrations are high enough to recover PGE from roadside soils and/or dust (Hilliard and Henry, 1998 Hoffman, 1988; Hilliard, 1998, 2001) available data for Greece are very limited for such an assessment. However the recovery of PGE from scrapped catalysts could contribute to the recycled PGE, in particular Pt, depending on the materials composition of the catalyst (Hilliard and Henry, 19989) in every country.

5. Bioavailability of PGE

Platinum concentrations in urban air have increased by more than two orders of magnitude in the last 20 years. It is present mainly in the small particle size fraction (0.5-8 μm), and pose a poten-

Table 3. Trace element contents in dust along roadside

Samples	KAT1	MES1	MES2	Iera Odos	N.h.Ath-The1	STANDARD
	dust	dust	dust	dust	dust	DS7
Date	2006-10	2006-10	2007-03	2006-10	2006-10	
				(wt %)		
Fe	2,0	1,7	1,8	2,6	2,4	2,41
Al	0,4	0,4	0,6	0,3	0,7	1,03
Ti	0,01	0,014	0,01	0,01	0,01	0,12
Mg	0,7	0,81	0,68	1,24	1,01	1,02
Ca	18,1	21,5	17,2	24,9	20,3	0,93
Na	0,01	0,03	0,02	0,06	0,02	0,12
K	0,08	0,07	0,15	0,1	0,2	0,48
P	0,06	0,04	0,06	0,05	0,11	0,08
S	0,01	0,01	0,03	0,01	0,01	0,17
				(ppm)		
Cr	120	103	71	135	113	252
Cu	370	520	200	650	160	103
Pb	830	130	860	306	230	68
Zn	320	320	370	530	490	410
Ni	66	63	57	68	158	55
Co	7	7	8	6	13	10
Mn	290	400	350	480	400	620
As	12	13	15	9	11	52
Sr	79	100	75	114	331	75
Ba	120	114	123	125	120	390
Cd	0,5	0,4	0,9	1	0,8	6
Sb	17	16	12	14	5	5
La	7	5	6	12	7	13
Ce	18	11	13	14	15	39
Sc	1,1	1,4	1,5	1	2,2	2,8
Zr	0,8	0,5	1	0,2	1	6
Y	3,5	3,1	4,4	2,4	4,6	5,5

Symbols: KAT = Katehaki; MES = Messoghion; NAV = Navarinou; Pi = Pindos; N.h.Ath-Th = National high-way Athens-Thessaloniki

tial health risk (Zereini et al., 2001). The results of the speciation studies indicated that various naturally occurring ligands have the potential to increase the mobilities of Pt, Pd and Rh through the formation of soluble complexes that can easily be transported in environmental and biological systems, (Colombo, 2008). The determination of the PGE content of different plants grown on contaminated soil close to highways shows a transfer of the PGE from the contaminated soil to the plants (Table 2). The enrichment of the Pd and Pt contents in grasses and tree-leaves (average 5.6 ppb and 3.8 ppb, respectively) along roadsides (Table 2) confirm the aspect that under appropriate pH and redox potential conditions (humic or fulvic acids) they are more mobile (Lustig et al., 1997; Lustig and Schramel., 2000; Kraemer, 2004; Dahleimer et al., 2007). The good positive relationship between both Pd and Pt contents in plants with their corresponding contents in soils (Fig 1a,b) is consistent with their solubility in soils. It has been demonstrated that the PGEs can be mobilized by natural organic matter and that humic acids and some organic ligands have been shown to enhance the solubility of various forms of Pt and Pd (Wood, 1990, 2005; Wood et al., 1994; Artelt et al., 1999; Rauch and Morrison, 2000). Experimental data on the bioaccumulation of Pt, Pd and Rh by grass grown with nutrient solutions containing these metals showed that most of the metals were accumulated in the roots, and only a small fraction was metabolized and transported to the leaves (Lesniewska et al., 2004). Klueppel et al. (1998) showed that Pt was bound to sulphur in a mechanism involving a phytochelatine (low molecular mass peptide).

In addition, the presented data on the Pt, Pt and Rh contents in grasses indicated the following bioavailability order Pd>Pt>Rh, as is exemplified by the higher Pd than Pt content (Table 2), and the decreasing average values of the ratios Pd/(Pd+Pt+Rh), Pt/(Pd+Pt+Rh) and Rh/Pd/(Pd+Pt+Rh) from 0.62 to 0.33 and 0.05, respectively. This bioavailability order is consistent with the experimental data on synthetic siderophore desferrioxamine- DFO-B enhances the solubility of Pt and Pd due to the formation of Pt- and Pd-DFO-B aqueous complexes at pH 7 (Danhleimer et al., 2007).

6. Conclusions

Although further detailed investigation of Pt, Pd, Rh and Au contents in dust, soil and plant samples along roadsides is required to define their distribution in space and time, present data lead to the following conclusions:

1) Significant abundances of Pt, Pd and Au were recorded in each of the dust and soil samples, whilst Rh content was very low.
2) Palladium in the grasses was more abundant (average 6.8 ppb) than Pt (average 4.2 ppb) and Rh (< 0.1 ppb), suggesting that it is more bioavailable to plants.
3) An increasing trend between platinum and pal-

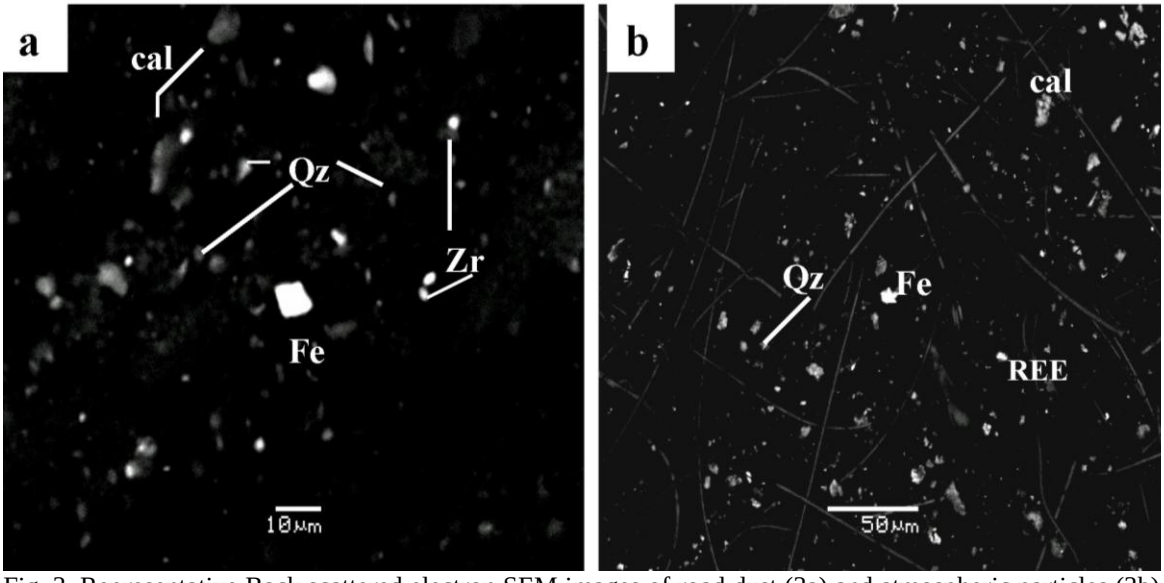

Fig. 3. Representative Back scattered electron SEM images of road dust (3a) and atmospheric particles (3b) collected from the Katehaki high-way peripheral road. There are abundant PM10 and PM2.5 particles, dominated by quartz (Qz), calcite (cal), barite, Al, Mg, K, Na-silicates, metal-Fe (Fe), Fe, Ti, Mn-oxides, Cr-bearing alloy, Ce-minerals (REE) and zirconium (Zr).

ladium contents in plants and the associated soils, along roadsides of Greece is consistent with their solubility in soils and confirm their bioavailability.

4) The highest values up to 2070 ppb Pt and 1980 ppb Pd were determined in dust samples collected from roadsides near water sewerages, although Pd content was higher than Pt in the majority of the analysed dust, soil and plant samples.

Acknowledgements

The University of Athens is greatly acknowledged for the financial support of this work. We thank two anonymous reviewers for their constructive comments and suggestions.

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