

Article

Cycling of Pt, Pd, and Rh Derived from Catalytic Converters: Potential Pathways and Biogeochemical Processes

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Abstract: The present study is an integrated approach to the Pt, Pd, and Rh cycling derived from catalytic converters along highway roadsides of the Athens Basin, including their contents, the dispersed Pt- and Pd-bearing nano- and microparticles in dust and bioaccumulation in plants, aiming to assess the auto-catalyst-derived environmental impact to the large city of Athens and the potential human health risk. The determined mean values of 314 Pt, 510 Pd, and 23 Rh (all in $\mu\text{g/kg}$) in dust samples are much lower than the 2070 $\mu\text{g/kg}$ Pt and 1985 $\mu\text{g/kg}$ Pd contents in gully pots in the Katechaki peripheral highway and higher than the mean values of 230 Pt, 300 Pd, and 13 Rh (all in $\mu\text{g/kg}$) in the soil samples. With the exception of two samples from gully pots, from 51% to 70% of the samples (for the Pd and Pt, respectively) fall in the range from 100 to 400 $\mu\text{g/kg}$. The calculated accumulation factors showed means of 3.88 $\mu\text{g/kg}$ Pd and 2.95 $\mu\text{g/kg}$ Pt for plants and tree leaves, but any significant difference (*t*-test) is lacking, and they are much lower than those reported for roots of plants (literature data). Although the Pt, Pd, and Rh bioaccumulation factors for shoots of plants/crops are relatively low, the increasing number of cars with catalytic converters in Greece and the relatively high bioaccumulation in the food chain may highlight a potential risk for human health and ecosystems, and the need for special attention on their bioaccumulation and bioaccessibility on a global scale.

Keywords: catalytic converter; metal recycling; environment; automobile emission; bioaccumulation



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1. Introduction

The critical platinum-group elements (Os, Ir, Ru, Rh, Pt, and Pd), or PGE, are the most valuable elements in nature, with strategic importance, due to their high melting points, high heat resistance, high corrosion resistance, excellent electrical conductivity, ability to form alloys, and unique catalytic properties [1]. They are used widely in advanced technologies in many industrial fields and automobile catalytic converters [1,2]. The PGE can be classified into two subgroups: the Os, Ir, and Ru-rich group (IPGE or Ir-group, compatible) characterized by the partition or distribution coefficient between solids and magma, with $D \geq 1$ during large-degree mantle melting, and the Au, Rh, Pt, and Pd-rich group (PPGE, incompatible), with $D \geq 1$, showing enrichment as a function of the differentiation degree [3]. Traditionally, they are associated with mafic-ultramafic complexes, and the majority of the PGE supply worldwide is produced from large layered intrusions, such as the Bushveld Complex (South Africa). Furthermore, elevated Pd, Pt, and Au contents in certain porphyry deposits are encouraging economic factors that contribute to global (Pd + Pt) production [4–6].

Catalytic converters have been used since 1970 in the USA and later in Europe since 1980 [7]. They are commonly constructed by applying a very fine active layer of a 1–3 g (Pt-Pd-Rh) alloy. At the same time, the relative PGE contents in catalytic converters vary,

depending on the type and age of the vehicle, in a decreasing proportion of Pt > Pd > Rh, on a ceramic monolith [7]. Platinum catalyzes the oxidation of carbon monoxide and hydrocarbons (CO and C_xH_y); Rh is essential for NO_x reduction, and Pd is very active for CO and C_xH_y oxidation and NO_x reduction, although it is less active than Rh [8]. Heavy metal contamination of roadside dust due to high traffic in urban areas is responsible for increased particulate contents within the breathing zone in the near-surface atmosphere and suspension of particles from the road surface, depending mostly on the traffic densities and topography [9]. Moreover, the amount and rate of the Pt, Pd, and Rh release from catalytic converters depend on the speed of the automobile, engine type, age of the catalyst, and type of fuel additives [10–17]. The long-distance transport of Pt, Pd, and Rh has been documented for roads, rivers, and lakes [18]. The PGE are emitted in inert form as nanoparticles attached to *fine* fragments of the original substrate, but their contact with various soil compounds may result from their incorporation into bioavailable molecules and transformation into more mobile species through complexation with organic matter in low pH rainwater [19–21]. Microorganisms (primarily bacteria and fungi), which are abundant in natural environments, facilitate biogeochemical processes, such as breaking down organic and inorganic materials and biomineralization (carbonates, oxides, sulfides, silicates, phosphates, phosphates, and silicates) in order to gain energy [22]. The thermodynamic computer model, HSC, has been used to predict the interactions of Pt, Pd, and Rh with different inorganic ligands and to estimate their thermodynamic stability in the environment [23]. These authors have shown that Pt, Pd, and Rh can form complexes with all of the inorganic ions studied, suggesting that they are capable of mobilizing the PGEs as aqueous complexes and of being transported easily in biological systems entering into the food chain. Thus, since traffic impacts urban air quality and human health, atmospheric processes have been the subject of increasing interest in recent years. In the present study, Pt, Pd, Rh, and Au, along with other traffic-related elements, were determined (a) in road dust and gully pots and (b) in roadside top soils and their corresponding grasses and tree leaves close to the highway roads of Attica (Athens Basin, Greece). The calculated accumulation factors for Pt, Pd, and Rh are combined with the literature data on their bioaccessibility in an attempt to assess the auto-catalyst-derived environmental impact on human health risk.

2. Materials and Methods

The sampling areas selected for this study include representative sites with varying traffic in Attica: (a) highway roads; (a₁) parts of the Katechaki to the east peripheral of Athens city, which cover the part from the intersection between Katechaki and Messoghion road to the turn toward Panepistimiopolis of Zografou, where there is a change in its geomorphological feature from almost flat to a relatively higher positive slope (a₂); the urban Messoghion road; (a₃) the Iera Odos; (a₄) the Acharnon/National highway road from Athens to Thessaloniki; and (b) a low-way road, the Papagos municipality (Pindos and Navarinou residential roads) (Figure 1). Roadside dust samples (n = 30) were collected from the surface and gully pots or draining roads (road dust is transferred from the roads by natural runoff) along roadways from the above major highways. The soil samples (n = 10) were collected from the surface soil (0–4 cm depth) with a plastic spatula in an area of approximately 10 cm² and stored in plastic sample bags. They were air dried and then sieved using a nylon sieve to produce a 2 mm fraction. The collected grass samples (n = 22) and leaves from olive and *Laurus nobilis* trees (n = 7) corresponded to certain soil samples in their rhizosphere or were from the same soil sample (Tables 1 and 2). All grass and leaf samples were washed with deionized water and dried in an oven at 70 °C and then powdered in an agate mortar. Sample preparation was undertaken at the Laboratories of the Department of Geology and Geoenvironment, University of Athens.

Table 1. Precious metal contents ($\mu\text{g}/\text{kg}$) in dust and soil samples along roadsides (Figure 1). Background values (*) [18].

Location	Pt	Pd	Rh	Au	Pd/Pt
Highway Dust					
KAT1	710	1000	4.0	14	1.41
KAT2	960	1300	5.0	51	1.35
KAT3	440	630	130	60	1.41
KAT4	900	670	3.0	360	0.74
MES12	290	500	3.0	220	1.72
MES13	210	300	26	460	1.43
MES14	210	300	3.0	240	1.43
MES15	400	550	<0.1	990	1.38
I. Odos1	500	750	22	90	1.50
I.Odos2	230	350	24	25	1.52
N.Ath-Th1	230	340	15	530	1.40
N. Ath-Th2	190	220	20	27	1.16
N. Ath-Th3	120	180	16	70	1.50
ACHAR1.	380	650	24	120	1.70
ACHAR2.	240	280	7.0	530	1.20
ACHAR3.	140	180	2.0	120	1.30
ACHAR4.	200	300	2.0	660	1.50
ACHAR5.	320	660	47	1340	2.10
ACHAR6.	170	260	<0.1	160	1.50
ACHAR7.	350	490	2.0	1000	1.40
ACHAR8.	320	460	44	210	1.40
ACHAR9.	300	450	49	300	1.60
ACHAR10.	220	320	9.0	1040	1.40
ACHAR11.	160	190	4.0	570	1.20
ACHAR12.	110	90	<0.1	210	0.80
ACHAR13.	160	260	15	900	1.60
ACHAR14.	170	220	13	550	1.30
ACHAR15.	170	210	5.0	260	1.20
mean	314	509	23	411	1.40
Gully pot					
KAT5	1720	1570	6.0	70	0.91
KAT6	2420	2400	4.0	180	0.99
mean	2070	1985	5.0	125	0.95
Soil					
KAT7	200	196	<0.1	93	0.98
KAT-MES8	440	510	<0.1	160	1.16
KAT-MES9	820	1100	3.0	120	1.34
MES10	44	90	8.0	150	2.04
MES11	36	74	10	6	2.06
N.Ath-Th	92	100	35	27	1.11
Lowway Soil					
Pi-MES	230	360	2.0	143	1.58
Pi	60	70	1.5	56	1.17
NAV	150	230	34	26	1.50
mean	230	303	13	87	1.50
Background (*)	1.15	<2.1			

Symbols: KAT = Katechaki; MES = Messoghion; Pi = Pindos (Papagos); NAV = Navarinou; N.Ath-Th = highway Athens-Thessaloniki.

Table 2. Precious metal contents ($\mu\text{g}/\text{kg}$) in grassy and tree leaf samples along roadsides (Figure 1). Background values [18].

	$\mu\text{g}/\text{kg}$				
	Pt	Pd	Rh	Au	Pd/Pt
Highway					
Grassy					
KAT1	2.0	3.8	<0.1	21	1.9
KAT2	7.0	20	<0.1	25	2.9
KAT3	10	23	5.0	22	2.3
KAT4	3.2	5.3	0.1	13	2.3
KAT5	1.2	2.1	<0.1	5	1.8
KAT6	1.5	1.7	<0.1	38	1.1
KAT7	1.8	4.8	0.2	10	2.7
Tree-leaves					
KAT-8	3.5	4.0	0.7	110	1.1
KAT9	5.2	4.4	0.7	30	0.9
KAT10	4.0	6.1	<0.1	7.0	1.5
KAT-MES1	16	20	1.4	22	1.2
KAT-MES2	10	8.0	<0.1	120	0.8
Grassy					
MES3	6.0	21	<0.1	16	3.5
MES4	2.0	4.4	<0.1	250	2.2
MES5	1.0	1.8	<0.1	16	1.8
Tree-leaves					
MES6	2.8	2.5	<0.1	44	0.9
MES7	4.0	6.0	<0.1	55	1.5
MES8	1.2	3.8	<0.1	67	3.2
MES9	2.2	2.3	<0.1	36	1.1
MES10	2.0	4.4	<0.1	250	2.2
MES11	1.0	1.8	<0.1	16	1.8
N.Ath-Th	2.4	0.6	<0.1	21	0.3
Lowway					
Grassy					
Pi-MES.	1.2	4.0	<0.1	7.0	3.3
Pi.1	1.1	6.5	<0.1	2.0	5.9
Pi.2	4.6	1.0	<0.1	35	0.2
NAV.1	1.3	2.0	<0.1	16	1.5
NAV.2	0.8	4.7	<0.1	170	1.5
NAV.3	1.0	0.6	<0.1	8.0	0.6
NAV.4	3.6	4.2	<0.1	48	1.2
NAV.5	0.8	1.6	<0.1	28	2.0
background-G	<1.1	<1.7			
STANDARD FA-100S	41	41	38		

Symbols: As in the Table 1.

The Pt, Pd, and Rh analyses were obtained using the litharge (PbO)-collection fire-assay fusion as a total sample decomposition technique for large (25 g) samples at Genalysis Laboratory Services, Perth, Australia. This method allows for the complete dissolution of samples and the ICP-MS analysis technique. The detection limits were $0.5 \mu\text{g}/\text{kg}$ for Pd and $0.1 \mu\text{g}/\text{kg}$ for Pt and Rh. Major and trace element concentrations in whole dust samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis after multi-acid digestion ($\text{HNO}_3\text{--HClO}_4\text{--HF--HCl}$) at the ACME Laboratories Ltd., Vancouver, BC, Canada. The detection limits, quality control samples, and the precision of the analyses are in agreement with international standards ($\sim 10\%$).

The polished sections prepared from the most PGE-rich road dust samples (Katechaki road) were examined by reflected light microscopy and scanning electron microscopy (SEM). Quantitative analyses were carried out at the University of Athens, Department of Geology, using a JEOL JSM 5600 scanning electron microscope equipped with an automated

OXFORD ISIS 300 energy dispersive analysis system. The analytical conditions were 20 kV accelerating voltage, 0.5 nA beam current, $b2\ \mu\text{m}$ beam diameter, and 50 s count times.



Figure 1. Map of Attica, showing the sites (★) of sampling).

3. Mineralogical Characteristics

The investigation of polished sections from the Katechaki road dust and atmospheric particle samples by scanning electron microscopy (SEM) show abundant PM_{10} and $\text{PM}_{2.5}$ particles, with dominant quartz, calcite, zircon, rare earth minerals (monazite), barite, galena, goethite, apatite, pyrite, chalcopryrite, and alloys such as Fe-Cr and occasionally Fe-Pt and Fe-Pd (Figure 2).

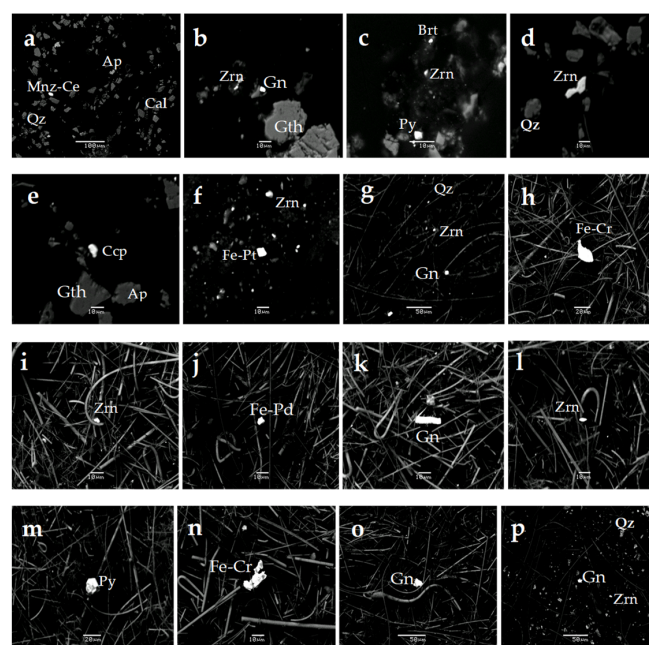


Figure 2. Representative backscattered electron images (BSE) images of road dust (a–f) and atmospheric particles (g–p) collected from the Katechaki highway peripheral road. There are abundant PM_{10} and $\text{PM}_{2.5}$ particles, with dominant quartz (Qz), calcite (Cal), zircon (Zrn), monazite (Mnz), barite (Brt), galena (Gn), goethite (Gth), metal-Fe (Fe), alloys (Fe-Cr and occasionally Fe-Pt and Fe-Pd), apatite (Ap), pyrite (Py), and chalcopryrite (Ccp).

4. Geochemical Characteristics

Platinum ranges between 210 and 960 $\mu\text{g/kg}$ (mean 314 $\mu\text{g/kg}$) in dust samples and from 44 to 820 $\mu\text{g/kg}$ (mean 509 $\mu\text{g/kg}$) in soils. Palladium ranges between 180 and 1300 $\mu\text{g/kg}$ (mean 536 $\mu\text{g/kg}$) in dust samples and from 36 to 1100 $\mu\text{g/kg}$ (mean 300 $\mu\text{g/kg}$) in soils. Dust collected from parts of the roadsides near water sewerages reached as high as 2070 $\mu\text{g/kg}$ Pt and 1980 $\mu\text{g/kg}$ Pd in content (Table 1). With the exception of two samples from gully pots showing much higher Pd and Pt contents (Table 1), the calculated total frequency showed that from 51% to 70% of the samples fall in the range from 100 to 300 $\mu\text{g/kg}$ for Pd and Pt, respectively (Figure 3). The calculated mean accumulation factor is 3.88 for Pd, 2.95 for Pt, and 2.76 for Rh, while any significant difference is lacking (*t*-test). The Pt and Pd contents in the samples of dust and soil from Attica are consistent with those from previous studies and other countries [11–17]. The Pd/Pt ratio shows an increasing trend of the mean values from the dust (1.4) and soils (1.5) to plants (2.03) (Tables 1 and 2).

Despite the different Pt and Pd contents in the dust and soil samples from Athens (a large city with dense traffic) and the smaller Ioannina town [16], with relatively low traffic, their plots show similar positive trends and similar changes in their curve directions (Figure 4).

Various plant species grown on potentially contaminated roadside soil were collected, corresponding to soil samples from their rhizosphere (Table 2), in order to assess the bioaccumulation of Pt, Pd, and Rh. The background values used for soils and plants from Attica were those reported by the GEMAS (Geochemical Mapping of Agricultural and grazing land Soil) [18].

Palladium was the most abundant PGE in the grasses, ranging from 0.6 to 23 $\mu\text{g/kg}$ (mean 6.8 $\mu\text{g/kg}$), while Pt ranged between 2.3 and 6.6 $\mu\text{g/kg}$ (mean 4.2 $\mu\text{g/kg}$), suggesting that they are more bioavailable to plants than Rh (<0.1 $\mu\text{g/kg}$). The gold content ranged from 14 to 990 $\mu\text{g/kg}$ (mean 226 $\mu\text{g/kg}$ Au) in the dust and gully pot samples and from 6 to 160 $\mu\text{g/kg}$ (mean 87 $\mu\text{g/kg}$ Au) in the soil samples (Table 1). Any relationship between Au and the other precious metals is not obvious.

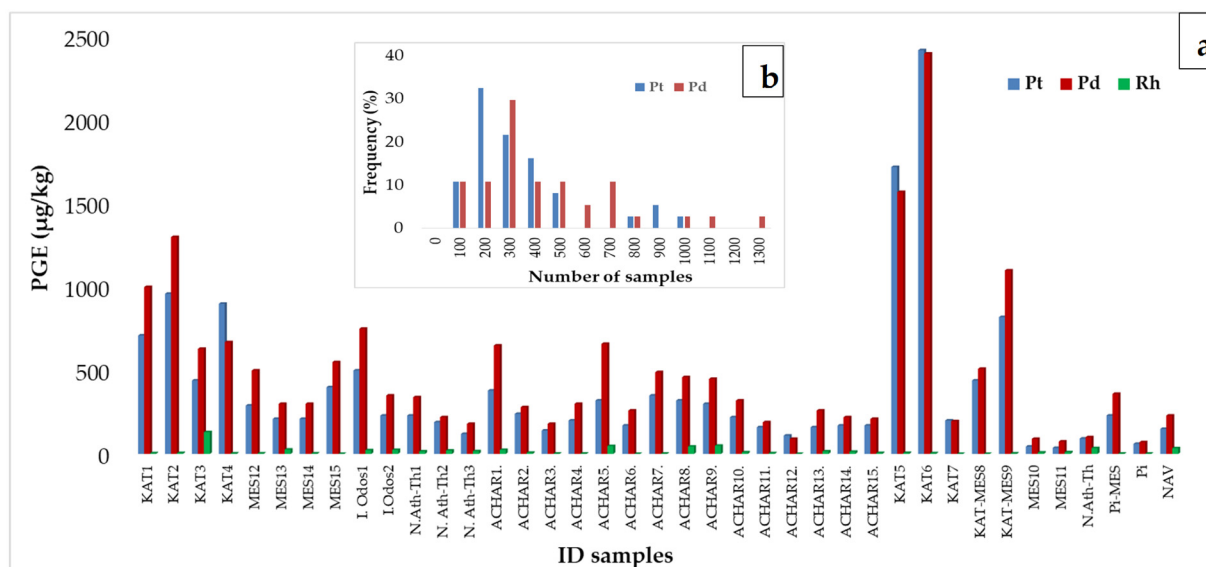


Figure 3. Variation in the Pt, Pd, and Rh contents (in $\mu\text{g/kg}$), in dust and soil samples along the roadsides of highways of Attica (a); total frequency (%) versus number (b), without the two samples from gully pots. Data from Table 1.

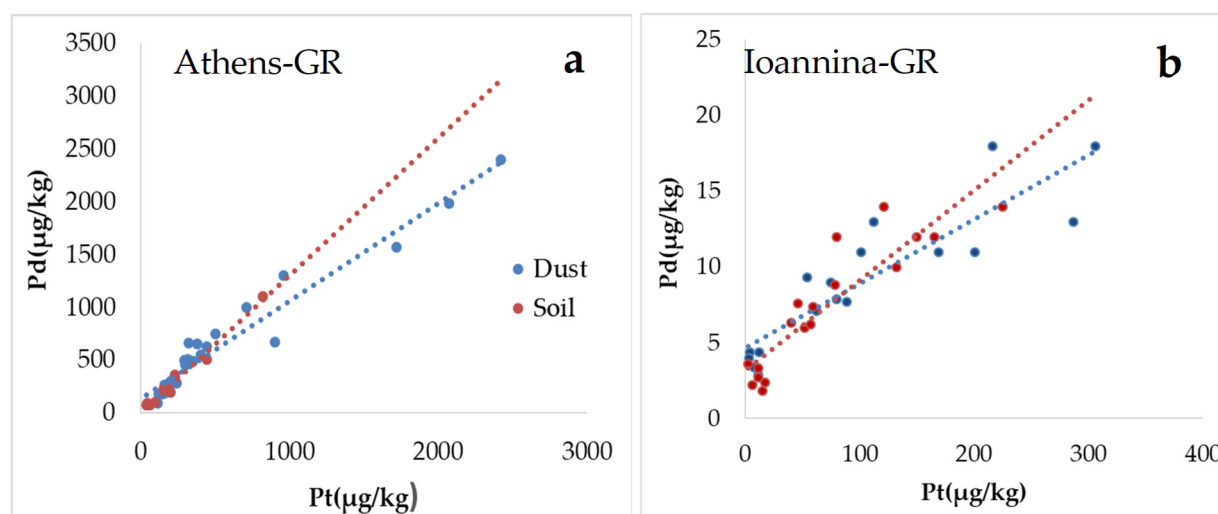


Figure 4. Plots of Pd versus Pt content in dust and soil samples along roadsides of the Athens Basin (a) and the Ioannina city (b). Data from Table 1 and [16].

Since in soil, PGE may be transformed into mobile species as organometallic compounds, special attention has been paid to the accumulation or transfer factor, which is the ratio of elemental content in plants relative to the total element content in the relative soil (accumulation factor = $\text{metal}_{\text{plant}}/\text{metal}_{\text{soil}} \times 100$) (Table 3). The accumulation factor for Pd, ranging from 0.61 to 12 (mean 3.88), is higher than that for Pt, ranging from 1.00 to 5.00 (mean 2.95) (Table 3). However, the *t*-test used to determine if there is a significant difference between the means of the Pt group and Pd group showed that there is no significant difference. Nevertheless, the Pt and Pd mean values are clearly higher than the background values provided by the GEMAS for the land soil and plants for Attica [18]. The Rh is commonly lower than the detection limit (Table 3). The percentage for Au shows a wide variation while the mean value (92) is much higher than those for PGE.

Table 3. Percentage of soil Pt, Pd, Rh, and Au in plants from the Athens Basin, Greece. Data from Tables 1 and 2.

Greece	$(m_p/m_s) \times 100$			
	Pt	Pd	Rh	Au
Highway				
Grassy				
KAT3	5.00	12.00	3.84	24
KAT4	1.61	2.70	1.67	27
MES10	4.54	4.89	n.d.	167
MES11	2.77	2.43	n.d.	267
Tree-leaves				
KAT-MES8	3.64	3.92	n.d.	14
KAT-MES9	1.22	0.72	n.d.	100
N.Ath-Th	2.61	0.61	n.d.	78
Lowway				
Grassy				
Pi-K	2.61	5.83	n.d.	4.9
Pi-s	4.51	4.71	n.d.	30
Pi-N	1.00	0.96	n.d.	207
Mean	2.95	3.88	2.76	92
Australia [11]				
Shoots	1.91	5.56	2.97	
Roots	9.58	21.00	31.25	
Mean (n = 4)	4.40	12.43	6.96	

Symbols: $(m_p/m_s) \times 100 = (\text{metal}_{\text{plant}}/\text{metal}_{\text{soil}}) \times 100$; n.d.=No data; ID of samples as in Table 1.

Representative dust samples from the Katehaki, Messoghion, Iera Odos, and the National Thessaloniki highway roads, analyzed for traffic- and soil-derived trace elements showed significant Pb, Cr, Zn, Cu, Ni, and Zr contents (Table 4), but any significant correlation with precious metals is not obvious. Calcium is a major element in all the samples, ranging from 17.2 to 24.9 wt.% Ca, while trace elements range from 130 to 830 mg/kg Pb, 320 to 530 mg/kg Zn, 290 to 480 mg/kg Mn, 160 to 650 mg/kg Cu, 114 to 125 mg/kg Ba, 71 to 135 mg/kg Cr, 57 to 160 mg/kg Ni, 11 to 18 mg/kg Ce, 5 to 12 mg/kg La, 3.1 to 4.6 mg/kg Y, and 0.5 to 0.9 mg/kg Zr.

Table 4. Trace element contents in dust samples along roadsides of the Athens Basin.

mg/kg	KAT1	MES1	MES2	Iera Odos	N. Ath-Th	STD, DS7
Cr	120	103	71	135	113	252
Ni	66	63	57	68	160	55
Co	7.0	7.0	8.0	6.0	13	10
Mn	290	400	350	480	400	620
Cu	370	520	200	650	160	103
Pb	830	130	860	310	230	68
Zn	320	320	370	530	490	410
As	12	13	15	9.0	11	52
La	7.0	5.0	6.0	12	7.0	13
Ce	18	11	13	14	15	39
Ba	120	114	123	125	120	390
Sr	79	100	75	114	330	75
Cd	0.5	0.4	0.9	1.0	0.8	6.0
Sb	17	16	12	14	5.0	5.0
Zr	0.8	0.5	0.9	0.2	0.9	6.0
Y	3.5	3.1	4.4	2.4	4.6	5.5
wt. %						
Al	0.4	0.4	0.6	0.3	0.7	1.03
Fe	2.0	1.7	1.8	2.6	2.4	2.41
Ti	0.01	0.01	0.01	0.01	0.01	0.12
Mg	0.7	0.8	0.7	1.2	1.0	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

5. Discussion

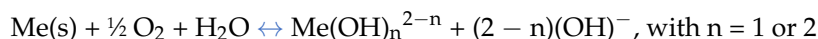
5.1. Dissolution and Bioaccumulation of Pt, Pd, and Rh

The deposition of nanoparticles of precious metal-iron oxide compounds in dust samples (Figure 2) and elevated Pt and Pd contents in plants up to 6 µg/kg Pt (mean 3.9) and up to 21 µg/kg Pd (mean 6.2) along highways in the Athens Basin (Tables 1 and 2) are comparable to those in Perth (W. Australia), London and Sheffield (UK), the Bialystok area of Poland, Frankfurt (Germany) [13,14,17,19,24,25], and elsewhere [12]. The mean accumulation factor for Pd (mean 3.88) and that for Pt (mean 2.95) and Rh (2.76) (Table 3) do not show any significant difference. These values for the accumulation factor in plants and tree leaves are much lower than those deposited in the roots of plants [26,27]. For example, 8 µg/kg Pt, 25 µg/kg Pd, and 5.5 µg/kg Rh in shoots, and 762 µg/kg Pt, 663 µg/kg Pd, and 437 µg/kg Rh in tree leaves have been noted [21]. In addition, cultivated plants, using Rh salt, have shown as high as 650–1300 accumulation factors for roots and much lower (7) for stems leaves (4) [21].

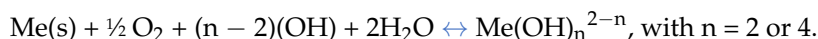
The potential environments in which the emitted precious metals are dispersed [10], the soil pH, redox, salinity, and the presence of inorganic (mostly chlorides) and organic ligands (humic acids) may be major controlling factors for the dissolution of Pt, Pd, and Rh, and the oxidation and formation of Pt(II), Pd(II), and Rh(III) complexes [10,12,20,21,25,28].

The most common oxidation state of Rh is +3, whereas Pt and Pd can occur in either the +2 or the +4 valence states in nature, and the main processes leading to uncharged and charged species are as follows [12]:

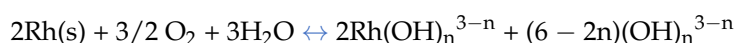
If Me represents Pt and Pd:



or



If Me = Rh:



In addition, these authors, based on the analysis of TEM (transmission electron microscopy) images, have shown that the leaves and roots of mustard grown plants in the presence of Rh nanoparticles contain Rh nanoparticles (2–3 nm in size). The uptake mechanism of PGE from the soil may be linked to siderophores used by plants as a source of metals [29,30]. In addition, the importance of sulfur species in the transport of precious metals in plants is exemplified by the examples of Pd(II) binding to metallothionein [31] and Pt(II) binding to a low molecular mass peptide [27]. The PGE–ammonium compounds and PGE–chloride complexes may be important in mobilizing PGEs in roadside environments as well [32]. The higher bioavailability of the Pd compared to that of Pt and Rh has been attributed to its high mobility and high tendency to form coordination complexes in environmental conditions [33].

Based on a thermodynamic approach [23], bisulfide complexes could transport Pt and Pd leading to the formation of Pt and Pd solid phases such as sulfides. In addition, the Gibbs free energy of formation (ΔG) values for PtS, PdS, and Rh₂S₃, at standard state conditions, as they are given from the experimental data [34,35] and calculations [36], are –66 kJ/mol for PdS, –76 kJ/mol for PtS, and –252 kJ/mol for Rh₂S₃. The more negative Gibbs free energy values for the Rh₂S₃ compared to those for the PdS and PtS seem to be in good agreement with the lower availability and the lower Rh content in plants (Table 2) and in shoots than in the roots [21]. Thermodynamic properties have also been applied to explain the difference in mobility between Au and Pt [37]. However, these authors, based on thermodynamic calculations and the presence of active biofilms developing on the surface of Au grains, concluded that differences between Au and Pt mobility may be derived from differences in chemical solubility and biogeochemical processes facilitated by the action of microorganisms [37].

5.2. Health Risk

The effects of Pt and Pd, depending on the metal speciation, the toxicity of soluble compounds and the role of microorganisms catalyzing redox reactions due to produced enzymes, have been considered as major factors controlling metal cycling [22,38]. Platinum complexes, such as cis-diaminedi-chloro-platinum(II), strongly inhibit binary fission in the bacterium *Escherichia coli* by cross-linking DNA [39]. Certain Pt compounds are known to be cytotoxic and have mutagenic and carcinogenic effects, having effects on microorganisms even at very low concentrations. The potential Pt-protein complexes may cause a reduction in enzymatic activity, with the toxicity of Pt decreasing in the following order: PtCl₄ > Pt(SO₄)₂·4H₂O > PtCl₂ > PtO₂, while methionine may be a primary binding compound for Pt [31,40]. Moreover, Pt based on the cis-diaminedi-chloro-platinum(II) has been applied widely as anticancer drugs [41,42]. Recently, the potential applications in the biomedical field of Pd nanoparticles have been highlighted as well [43–45]. The direct deposition of Pt, Pd, and Rh complexes and particles in freshwater, estuarine, and marine environments and the accumulation in aquatic organisms have been emphasized by many authors [9,14,19–21,24,36,46–49]. The low pH of the human stomach (approximately 2.5),

due to the presence of HCl, could cause a transformation into PGE–chloride complexes, and the mobile Pt-chloro-compounds and Pd-complexes with organic acids may be of potential health risks, in particular for those living in an urban area, near major highways [8,23]. Thus, the introduction of the Euro Stage III legislation (January 2000), considering that the Pd-rich catalysts can meet stricter emission limits for petrol-fueled vehicles [50], may point to the need to protect human health and ecosystems. Although the bioaccumulation factor for these precious metals in shoots is relatively low, their unexpected high bioaccumulation in roots [21] may highlight the need for special attention on the bioaccumulation of Pt, Pd, and Rh in certain crops, such as carrots, potatoes, and onions growing in a subsurface environment.

5.3. Bioaccessibility of Pt and Pd

The bioaccessibilities of the Pt, Pd, and Rh associated with automotive catalytic converters have been expressed in terms of the amount of an ingested nutrient that is available for absorption in the gut after digestion, relative to the corresponding total certified NIST-SRM (National Institute of Standards and Technology-SRM 2556). This can be determined using an *in vivo* physiologically based extraction test (PBET) that simulates the chemical conditions encountered in the human stomach and intestine [51]. Specifically, the accessibility of these precious metals, relative to the total metal content, is relatively low, but it increases from the acidic stomach (pH approximately 2.5) to the neutral environment of the intestine, with increasing chloride concentration and decreasing particle concentration [51]. These authors provide valuable insight into the PGE evolution via oxidation of ultrafine particles emitted from the catalytic converter and their stabilization by chloride and carbonate ions during the application of the PBET methodology, although there is considerable variation in the human gastrointestinal environment. The calculated bioaccessible Pd and Pt fractions in PM₁₀ airborne particulate samples (downtown Vienna) have shown wide distributions [52], with mean gastrointestinal tract extractable fractions for Pd and Pt exceeding previously determined values for similar extractions [23,51].

Nevertheless, it was shown that overall digestive bioaccessibilities of the PGE in autocatalytic particles were decreased in the order Pd > Rh > Pt and solubilization in the near-neutral conditions of the intestine was greater than that in the acidic conditions (pH 2.5) of the stomach [51]. Furthermore, it has been reported that the highest PGE concentrations were found to be in the range of 1–2.15 µm [53]. These small sizes of particles fall in the size range that can easily penetrate and deposit into the lungs of humans and mediate serious health effects [33,53]. These authors highlight the need to conduct bioaccessibility experiments using samples collected in the field to enable an adequate assessment of risk.

5.4. Implications to the Green Economy

The recycling of PGE from all kinds of waste that contains Pt, Pd, and Rh, such as catalytic converters, is very important due to the high cost of precious-metal recovery from primary raw materials and the supply–demand imbalance [54]. Furthermore, the increasing number of cars and spent catalytic converters, containing from 1 to 15 g of Pt, Pd, and Rh may be an important secondary source for these precious metals on a worldwide scale [55]. Assuming that the amount and rate of PGE emissions are a function of the speed of the automobile and the type and age of the catalyst [56], attention has been paid to the recycling of catalytic converters, in an attempt to reduce the soil and in turn the ecosystem contamination. Thus, the application of these methodologies (pyrometallurgical or hydrometallurgical) for precious-metal recovery from scrapped catalytic converters [57,58] is an important economic resource for PGE and the circular economy. In addition, the significant Pt and Pd values (>4 µg/kg (Pt + Pd) in road dust near water sewerages of the Katechaki road (Table 1) may suggest a possible concentration of traffic-related emissions within reservoirs connected to the local water sewerage systems, and an additional resource for Pt and Pd recycling.

In summary, Pt, Pd, and Rh-bearing minerals hosted in primary raw materials can be recovered as main and/or by-products. Among the major applications of these precious metals are automobile converters. The cycling of Pt, Pd, and Rh derived from catalytic converters in Earth surface environments may be achieved by integrating their contents with the dispersed Pt- and Pd-containing nano- and microparticles along highway roadsides, and the potential transformation by biogeochemical processes. Hence, dust, soil, and plant data on Pt, Pd, and Rh contents along highway roads of Attica, Greece, are combined with the literature data aiming to evaluate the potential accumulation processes of Pt, Pd, and Rh and pathways from their emission to their bioavailability, plant accumulation, the chain food, and human health. Their bioaccessibility is relatively low, following the order $\text{Pd} > \text{Pt} \geq \text{Rh}$, while solubilization under near-neutral conditions in the intestine was greater than that in the acidic conditions (pH 2.5) of the stomach [51] (Figure 5).

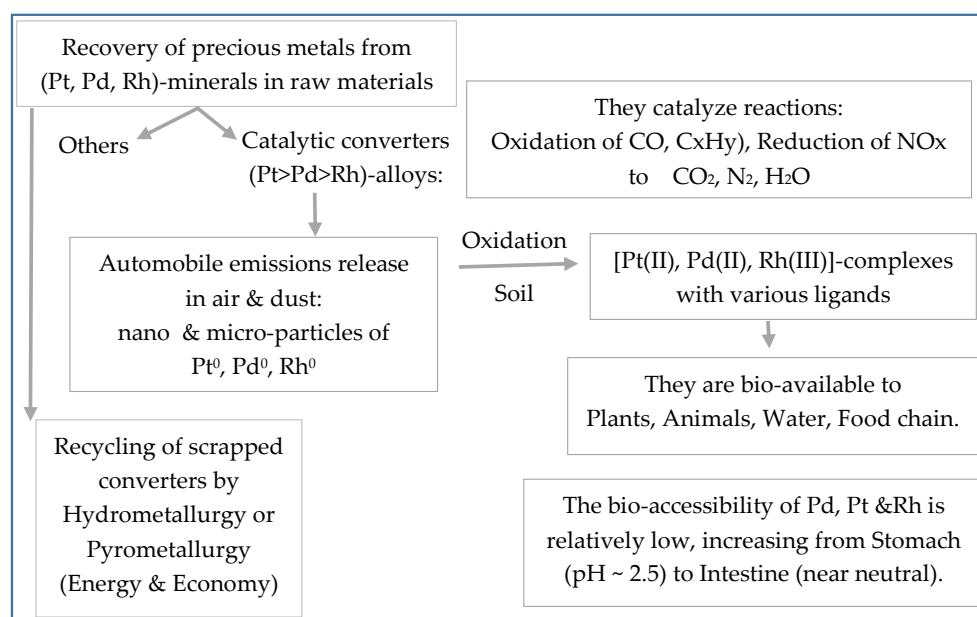


Figure 5. Potential pathways and biogeochemical processes of Pt, Pd, and Rh derived from catalytic converters.

6. Conclusions

An integrated approach to the Pt, Pd, and Rh cycling derived from catalytic converters along roadsides of the Athens Basin, combined with the literature data from the health sciences on precious metal accessibility, may allow us to make the following conclusions:

- The mean contents of 314 Pt, 509 Pd, and 23 Rh (all in $\mu\text{g}/\text{kg}$) in dust samples along highways in Athens are comparable to those in other countries, while in gully pots, on the Katechaki peripheral highway, Pt (2070 $\mu\text{g}/\text{kg}$) and Pd (1985 $\mu\text{g}/\text{kg}$) show the highest contents.
- With the exception of the samples from gully pots showing relatively high Pd and Pt contents, the calculated total frequency showed that from 51% to 70% of the samples fall in the range from 100 to 300 $\mu\text{g}/\text{kg}$ for Pd and Pt, respectively.
- The calculation of the translocation factors showing that Pt, Rh, and Pd can migrate from soil to shoots suggests that plant/crop uptake is a possible pathway toward the food chain and human risk.
- Although the bioaccumulation factors for Pt, Pd, and Rh in the shoots of plants/crops are relatively low, their high bioaccumulation in roots, coupled with the use of Pd-rich catalysts since 2000, may highlight the need for special attention on their bioaccumulation in crops, growing in a subsurface environment.

- The cycling of precious metals includes (a) the release of emissions from catalytic converters into the air and dust as nano- and micro-particles, their oxidation in the soil environment, and their bioaccumulation.

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