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Vehicular and industrial sources of PGEs, Au and Ce in surface soil and roadside soils and dusts from two cities of Turkey

Murat ÖZEN[1], Songül AKBULUT ÖZEN[2*], Ugur CEVIK[3]

Abstract

In this study, rhodium, palladium, platinum, gold and cerium were determined by ICP-MS after trace-matrix separation in roadside dusts and soil samples along different motorways in Ankara and Bursa, and in soil samples taken from industrial locations in Nilüfer, Bursa. The clear presence of Pd and Rh was determined at different traffic locations. Platinum remained below the method's quantification limit for most of the samples. Results showed that both cities showed relatively high concentrations of; Rh and Pt in tunnels and downtowns, Pd in tunnels, bus stations and crossroads, and Au in downtowns. Consistent with the daily road traffic, relatively high concentrations of Rh, Pd and Pt were determined for Ankara. Based on the limited data available for Pt, Pt:Pd ratios varied between 0.04 and 0.25, and Pt:Rh ratios varied between 0.59 and 2.1. Measurements at the industrial location showed an average Rh and Pd concentration of 11 and 359 µg/kg, respectively. On the other hand, Au concentrations remained below the method's quantification limit except for one sampling location. The average Ce concentration was determined as 23 mg/kg. Platinum remained below the method's quantification limit for all industrial sampling locations. Overall, high average Rh and Pt concentrations were determined at the traffic sites, while higher average Pd concentration was determined at the industrial locations. Cerium remained consistently below the earth's crustal levels, which infers that no anthropogenic source can be attributed to Ce.

Keywords: platinum group elements, vehicular traffic, industrial region, surface soil, roadside dusts.

1. INTRODUCTION

Platinum group elements (PGEs) consist of six elements, namely iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh), and ruthenium (Ru). They are naturally present in the earth's crust in a few parts per billion. PGEs are categorized under precious metals together with gold (Au) due to their economic value and their rare occurrences. These precious elements are the

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least abundant elements in the earth's crust and are present in the environment in ultra-trace quantities. The bulk of the continental crust includes 0.38, 1.50 and 2.00 μg/kg of, respectively, Rh, Pd and Pt, while the lithosphere contains 0.10, 1 – 10.0 and 15.0 μg/kg of Rh, Pd and Pt, respectively [1]. The upper continental crust, on the other hand, contains 0.018, 0.599, 0.526 μg/kg Rh, Pd and Pt respectively [2].

Platinum group elements are applied in, e.g., fuel cells, electronics, cancer therapies, catalysts and are thus strategic elements. The automotive sector is leading on demand for PGEs (especially Pt, Pd and Rh) [3].

Emission of PGEs into the environment has been traced back to exhaust catalysts in automotive catalytic converters. Due to traffic density and industrial organizations large cities are obvious locations where the potential hazardous effects of PGEs might be observed [4]. A number of articles has been published concerning PGEs and their increasing concentrations in different environmental media such as: air and airborne particulate matter [5-6], soil [7], road dust [8–10], vegetation [11], organisms [12-13], and sewage sludge [14].

Some PGE elements and their complex salts such as Pd-, Rh- and Pt-chlorides, have been reported as potential risks, not only to the environment [15-16], but also to the human health, causing tumor, asthma, rhinoconjuctivitis and other serious health problems [16-17]. While particulate PGEs are said to be biologically inert, soluble PGEs can pose an environmental hazard due to their biological availability, which leads to accumulation in the environment [18-19]. In addition, PGEs are resistant to poisoning of sulfur oxide residues in the exhaust [17]. PGEs have the required potential for the chemical reduction of pollutants such as hydrocarbons, nitrogen oxides, and carbon monoxide.

Due to its use in automotive electronics (electronic fuel injection, anti-lock brake and ignition control) in recent years, gold (Au) was additionally measured in this study [20].

PGEs are coated onto the surface of the catalytic converter together with cerium dioxide, usually in combination with zirconium dioxide, to promote oxygen storage and thermal stability [21]. Because of this, cerium is emitted with PGE exhaust catalysts. In many countries, CeO_2 nanoparticles are added to diesel fuels to improve fuel combustion efficiency and to reduce soot emissions [22]. Several studies have reported Ce accumulation in the environment [23-25]. Potential human health implications of Ce emissions have received limited attention. In this study, PGEs, Au and Ce were investigated in the summer of 2010 at different traffic locations with varying daily traffic and driving styles in Ankara and Bursa, and at an industrial area in Nilufer, Bursa. The available publications on PGEs in Turkey are confined to ore mines, such as ophiolitic chromitite deposits [27-28]. Anthropogenic input of PGEs, Au and Ce in the environment received much less attention, and to the best of the authors' knowledge no publication has been made on the subject in Turkey. The aim of this study is to examine PGEs, Au, Ce and their enrichment in the environment especially in roadside dust and roadside soil. The concentrations of these elements will be examined as a function of proximity to roadways with high to medium traffic densities in two major Turkish cities (Bursa and Ankara). Soil samples collected at nine locations from a heavily industrialized region in Bursa was also examined.

2. MATERIAL AND METHODS

2.1. Study area

In this study, traffic-sampling locations in Ankara and Bursa with different characteristics were selected, such as parking lots, highways, bus stations, tunnels, downtown, and crossroads. Road characteristics that are believed to be of importance in this study are: start-stop frequency of vehicles, speed limits, closed environments such as tunnels, and the average daily road occupancy. All sampling locations geographical coordinates are given in Table 1. The average road occupancy for the year 2010 as given by the Road, Traffic and Safety Association can be summarized as follows: State roads were occupied by 526.541 vehicle per day (annual average) in Bursa and 478.134 vehicle per day (annual average) in Ankara. The yearly average number of vehicles per day on motorways in Bursa was 67.727, of which 60.67% were automobiles, and 91.168 vehicle per day in Ankara, of which 71.00% were automobiles [29]. The average number of vehicles at the selected roads, their average speed and sample designations are summarized in Table 1.

Table 1
Traffic sampling locations, vehicle speed, and densities [26]

Sampling Points	Speed (km/h)		Location Bursa	Av. vehicle per day		Location Ankara	Av. vehicle per day
Parking Lot	-	B1	Uluyol (40°11'37.7"N, 29°04'12.9"E)	1500	A1	Mesrutiyet St. (39°55'07.1"N, 32°51'39.7"E)	3000
Highway	> 120	B2	Istanbul-Ankara road (40°15'59.9"N, 28°57'15.8"E)	28000	A2	Konya road (39°53'18.8"N, 32°48'44.4"E)	45000
Bus Station	-	B3	Bursa bus terminal (40°15'55.6", 29°03'12.9"E)	850	A3	Ankara bus terminal (39°55'05.9"N, 32°48'44.4'E)	1250
Tunnel	< 90	B4	Izmir road (40°12'41.9"N, 28°56'25.3"E)	13000	A4	M. Kemal St. (39°54'49.4"N, 32°51'09.4"E)	30000
Downtown	< 50 – 60	B5	Heykel St. (40°11'0.03"N, 29°03'41.5"E)	45000	A5	Akay St. (39°54'48.1"N, 32°51'19.0"E)	58000
Cross Road	< 80	B6	Sirameseler St. (40°12'49.6"N, 29°01'32.3"E)	35000			

Furthermore, soil samples were collected from nine different locations in Nilufer (Bursa), a heavily industrialized area. There are several types of industry in the vicinity such as; agro-based industry, iron-steel factories, petro chemistry, automotive, electronics, generator production factories, arms factories, textile, and tannery. At the same time, the area is known for agricultural activities. Bursa's soil profile has a typical aluminum enriched weathering profile and is developed on a variety of rocks such as granite, sand-shale, limestone, and basalt [30]. All sampling coordinates are shown in Figure 1.

2.2. Sampling

Samples were collected in August 2010, approximately 2 weeks after the last rainy period during dry and warm weather. Roadside soil samples from the surface layer (0-3 cm) were collected at a distance of 4 m from the sidewalk close to traffic lights from downtown areas, crossroads and highways. Soil samples from bus stations were collected at a distance of 4 m from the bus platforms.

Parking lot dust samples were collected around the edge of the parking lot at a distance of 2 m from an area of 4×0.5 m. The roadside dusts were hand-brushed along kerb stones from an area of 4×0.5 m. Wall dust from tunnels was also hand brushed from an area of 0.5×0.9 m above the ground up to 1 m. Soil samples (from nine sampling point) from the industrial area were collected from the surface of the soil (0 – 3 cm). Samples were transferred to the laboratory in plastic bags.

2.3. Sample preparation

The collected samples were dried at room temperature for a week. Afterwards, the samples were sieved through a 2 mm stainless steel sieve. A portion of the sieved samples was homogenized by grounding in a porcelain mortar and sieving again with a 63 μm sieve and stored in polypropylene bottles at room temperature.

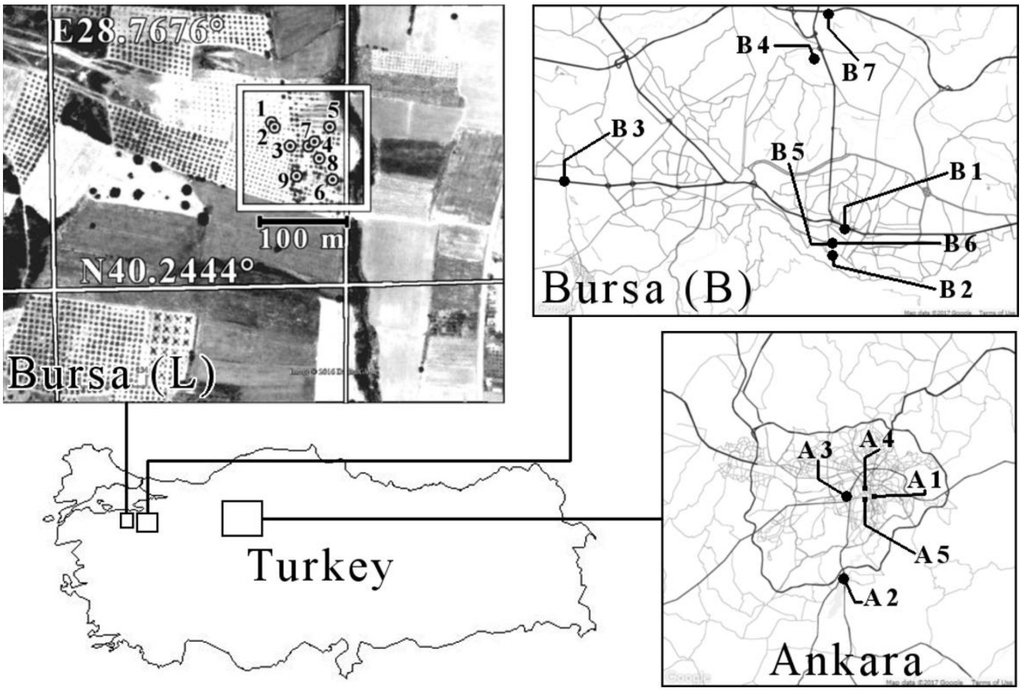

Figure 1 Sampling locations in Bursa (L: industrial area, B: traffic locations) and Ankara (A: traffic locations)

A digestion procedure was applied before analysis. Digestion of samples was conducted in a professional microwave oven (ETHOS 900, Milestone/Shelton). 0.3 g of the pre-prepared sample was transferred into a teflon digestion vessel. A mixture of 4.5 mL HNO_3 (69%) and 1.5 mL HCl (37%) was added and the vessel was closed. Each set of vessels included at least one standard reference sample (BCR-141R) with about 0.17 g and one blank that went in the microwave with a capacity of 10 samples. Five standard reference samples and five acid blank samples were prepared. The microwave digestion program was carried out in the following sequence: 5 min at 90 W, 3 min at 200 W, 5 min at 350 W, and 5 min at 500 W. All vessels were transferred to an ice-water bath when the microwave procedure was completed and kept in the water bath for a minimum of 30 min. Afterwards, the samples (solutions and any solid residues) were quantitatively transferred into 50 mL polypropylene vials with milli-Q water.

The polypropylene tubes were centrifuged at 300 rpm for 5 min. Afterwards, 50 mL of aqua regia (70%) was added. Finally, 4 mL aliquots were pipetted into polypropylene tubes and 8 mL of H_2O_2 was added before ICP-MS analysis.

2.4. Measurement of PGEs (Rh, Pd, Pt), Au and Ce

Samples were analyzed with high resolution inductively coupled plasma-mass spectroscopy equipment (HR-ICP-MS, Thermo Scientific ELEMENT XR) after a chemical digestion process. The ICP-MS ELEMENT XR equipment had a wide crossover range (> 2 orders of magnitude) between different detector modes that allowed accurate and automated cross-calibration, with a dynamic range of 5×10^7 to 1×10^{12} cps (1 ms sample time). Any limitation on the upper level of quantification was removed due this increase in the dynamic range as the maximum measurable concentration achievable with the equipment was over 1000 µg/g. The flow rates of the instrument were as follows: 15.09 L/min for the coolant argon flow rate, 0.8 L/min for the sample argon flow rate, and 1.078 L/min for plasma argon flow rate. The plasma power was 1350 W. An external calibration was used with solutions prepared from a PGEs standard solution ın order to calibrate the HR-ICP-MS instrument [11]. The instrument's detection limit and the method's quantification limit were calculated using blank analyses and dilution factors. Detection limits and measurement results for Rh, Pd, Pt, Au and Ce were summarized in Table 2.

Table 2
Results for Rh, Pd, Pt, Au and Ce of the standard reference material, Instrument Detection Limit (IDL) and Method Quantification Limit (MQL). [BMQL: Below Method Quantification Limit)]

	Rh	**Pd**	**Pt**	**Au**	**Ce**
Average	15	336	BMQL	22	13
St. dev.	1	17	BMQL	4	1
IDL ($\times 10^{-9}$ g/kg)	< 10	< 100	< 10	< 100	< 10
MQL ($\times 10^{-6}$ g/kg)	1	1	1	1	1

3. RESULTS AND DISCUSSION

PGEs, Au and Ce concentrations of roadside soil and dust samples from Ankara and Bursa are summarized in Figure 2. The highest Rh concentration in Ankara was measured in a tunnel as 60 µg/kg, while the Rh concentration in a tunnel in Bursa was determined as 10 µg/kg. The Pd concentration was the highest in a tunnel in Ankara with 648 µg/kg, which was 307 µg/kg in a tunnel in Bursa. Tunnels are closed environments where accumulation of heavy metals was to be expected (Table 3). Hence, these relatively high values might be attributed to the daily vehicle traffic (see Table 1), but also the fact that tunnels are closed environments as opposed to open air locations. High Pd values in roadside dust are known to occur in areas of high traffic flow [9]. In urban areas where vehicle engines that are not warmed up enough to be operating at peak efficiency, precious metal concentrations are higher at roundabouts or traffic lights [31-32]. The relatively high Rh and Pd concentration found in a tunnel in Ankara can be related to the high vehicle traffic (see Figure 2 and Table 1). The Pt concentration found in dust sample in a tunnel in Ankara was 124 µg/kg, 62 µg/kg in soil sample in downtown Ankara and 10 µg/kg in soil sample from a bus station in Bursa. The Pt concentration for the remaining samples was below the method's quantification limit (see Figure 2). The relatively high Pt abundance found in tunnel dust was due to the isolated environment from ambient meteorology and from dispersion. The ratios of Pt, Pd and Rh vary depending on parameters such as engine capacity, fuel used, and vehicle mass. A logical assumption would be that the number of vehicles crossing a particular location per day and the speed of the vehicle will have an effect on the deposited PGEs in the area.

It is interesting to note that differences were observed between roadside dust samples and roadside soil samples with regard to PGEs concentrations. In this study roadside soil samples had, relatively speaking, lower PGEs contents in comparison to dust samples, except for downtown areas (higher rates of stop-start actions and stationary traffic and daily vehicle flow).

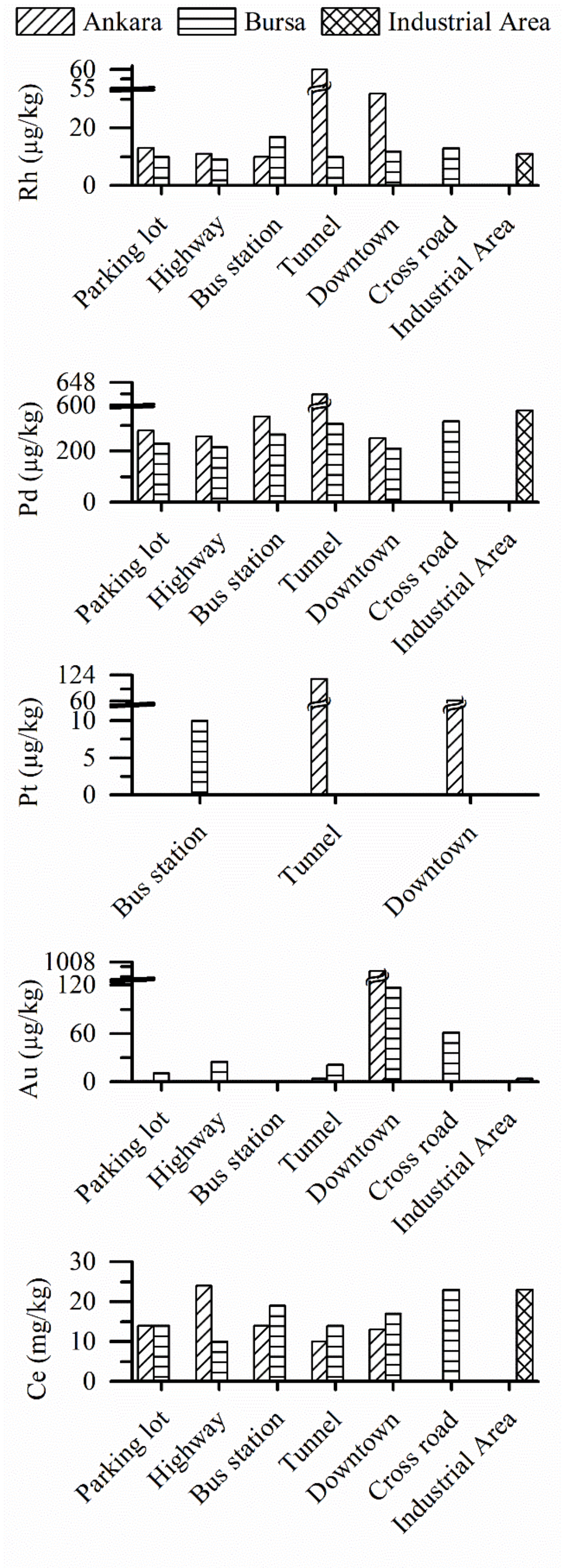

Figure 2 The concentrations of PGEs, Au and Ce measured from samples at different traffic locations and industrial area

Table 3
The concentrations for Rh, Pd, Pt and Pt:Pd, Pt:Rh, Pd:Rh ratios of samples taken at different traffic locations in Ankara (A) and Bursa (B), and *average concentrations of samples taken from the industrial area in Nilüfer, Bursa. (BMQL: Below Method Quantification Limit)

	Rh	**Pd**	**Pt**	**Pt:Pd**	**Pt:Rh**	**Pd:Rh**
A-1	13	279	BMQL			21.46
A-2	11	258	BMQL			23.45
A-3	10	334	BMQL			33.40
A-4	60	648	124	0.19	2.07	10.80
A-5	32	249	62	0.25	1.94	7.78
B-1	10	229	BMQL			22.90
B-2	9	216	BMQL			24.00
B-3	17	265	10	0.04	0.59	15.59
B-4	10	307	BMQL			30.70
B-5	12	210	BMQL			17.50
B-6	13	316	BMQL			24.31
Ind.*	11	359	BMQL			32.64

Compositional differences in the reported ratios for PGEs are mainly due to the differences in auto-catalyst compositions used in different countries; differences in sample matrices etc. Various sources have reported different ratios for PGEs, such as Pt:Pd between 1 and 2.5 [33-34], Pt:Rh ratios between 5 and 16 [33], [35], 5.8 [19], and 2.40 – 19.6 [19]; Pd:Rh ratios of 5 [35], 4 – 9 [33], 3.7 [19], and 1.83 – 31.3 [19]. The Pt:Pd ratios in this work were rather on the low side (see Table 3). Likewise, the Pt:Rh ratios were relatively lower than those mentioned in literature. Pt-Rh catalysts dominated the market for many years. Technological developments have stimulated the (partial) substitution of Pt and Rh by Pd. In the 1980s, Pt:Pd-catalysts were used and in the beginning of 1990 Pt was replaced by Pd giving combinations of Pt:Pd:Rh with varying ratios from 1:14:1 to 1:28:1 [35]. Finally, Pd:Rh and Pd-only catalysts were used [17]. As can be seen from Table 3, Pd:Rh ratios lie in the range given in literature, however, they vary considerably. In all cases, Pd concentrations were determined to be relatively higher than Pt and Rh. With the advent of new technologies, palladium costs were reduced. Hence, additional Pd emissions were to be expected.

Gold concentrations were also measured. A concentration of 1008 µg/kg was determined in downtown Ankara, the highest Au concentration of all samples, while a concentration of 117 µg/kg was found in a sample in downtown Bursa. A sample taken from a crossroad in Bursa had a gold concentration of 61 µg/kg and varied between 5-25 µg/kg at other locations, except for a bus station location that remained below the method's quantification limit. Gold's catalytic reaction temperature is too high, hence, it is not used in catalysts [43].

Table 4
Comparison of PGEs concentrations (µg/kg) from different countries and locations obtained from roadside dust and soil samples (***Bursa industrial area soil samples, BMQL: Below Method Quantification Limits)

Country	Location	Year	Dust	Soil	Rh	Pd	Pt	Vehicle/day	Reference
China	Hong Kong	2008	+		11	83	64	/	[36]
	Hong Kong	2007		+	11	39	62	59	[37]
	Guangzhou	2008	+		7	87	22	/	[36]
	Guangzhou	2008		+	1	13	7	/	[37]
	Beijing	2010	+		98	58	28	/	[38]
	Beijing	2007		+	10	21	40	300	[37]
Germany	Braunschweig(city)	2005	+		110	410	2	16.000	[39]
	Braunschweig(city)	2005		+	39	124	261	16.000	[39]
Greece	Athens	2003		+	/	1 - 126	2 - 141	36.510 - 48.756	[34]
Hungary	Budapest	2010	+		/	50	36	/	[40]
India	Hyderabad	2007	+		2	18	15	/	[41]
	Mumbai	2007		+	1	16	6	/	[37]
USA	Houston, Texas (tunnel)	2012	+		152	770	208	25.000	[42]
	Houston, Texas	2012	+		6 - 8	10 - 88	35 - 131	220.000	[42]
Turkey	Ankara	2010	+		36	464	62	16.500	This study
	Ankara	2010		+	18	280	21	34.750	This study
	Bursa	2010	+		10	268	BMQL	7.250	This study
	Bursa	2010		+	10	275	2	21.786	This study
	***Bursa	2010		+	11	359	BMQL	-	This study

Au behaved in a different way to PGEs, which is not surprising since it is primarily used in automotive electronics. Gold does not vary in the same way as the other precious metals. Hence, gold does not increase with higher traffic flow in any of the sample types. Heavier Au particles move by gravity to the bottom of the drain. The lack of correlation of Au with the other precious metals (Figure 3) also confirms that gold's origin are different from the platinum group elements' (jewelry, for example).

PGEs have been said to be emitted in the form of monocrystals. As a result of chemical reactions, mechanical abrasion and high temperatures wash coated particles and other components such as Ce, Al and related lanthanides are emitted from vehicles [44]. As can be seen from Figure 2, Ce concentrations varied between 10 – 23 mg/kg. Cerium is more abundant, with an estimated concentration of 60 mg/kg in the earth's crust [10]. Hence, Ce could not be traced back to a anthropogenic source.

Figure 3 revealed a linear relation between Pd-Rh and Ce-Pd. When disregarding extremes in Figure 3, the remaining plots did not show such correlations. Also, it is interesting to note that Ce was correlated with Pd, but not Rh. This might very well be the result of technological improvements whereby catalytic converters were mainly Pd-based[17] and Ce was added to the Vehicle Exhaust Catalysts (VEC) for stability and for particulate matter control in diesel fuels (in the form of cerium oxide) [45]. Although Pt data was only analyzed for a small number of samples, higher Rh values tend to occur with high Pd and Pt values. The roadside samples suggest that Pt, Rh and Pd were derived from, predominantly, vehicle catalytic converters. This is in agreement with previous studies [8], [11], [46], [47].

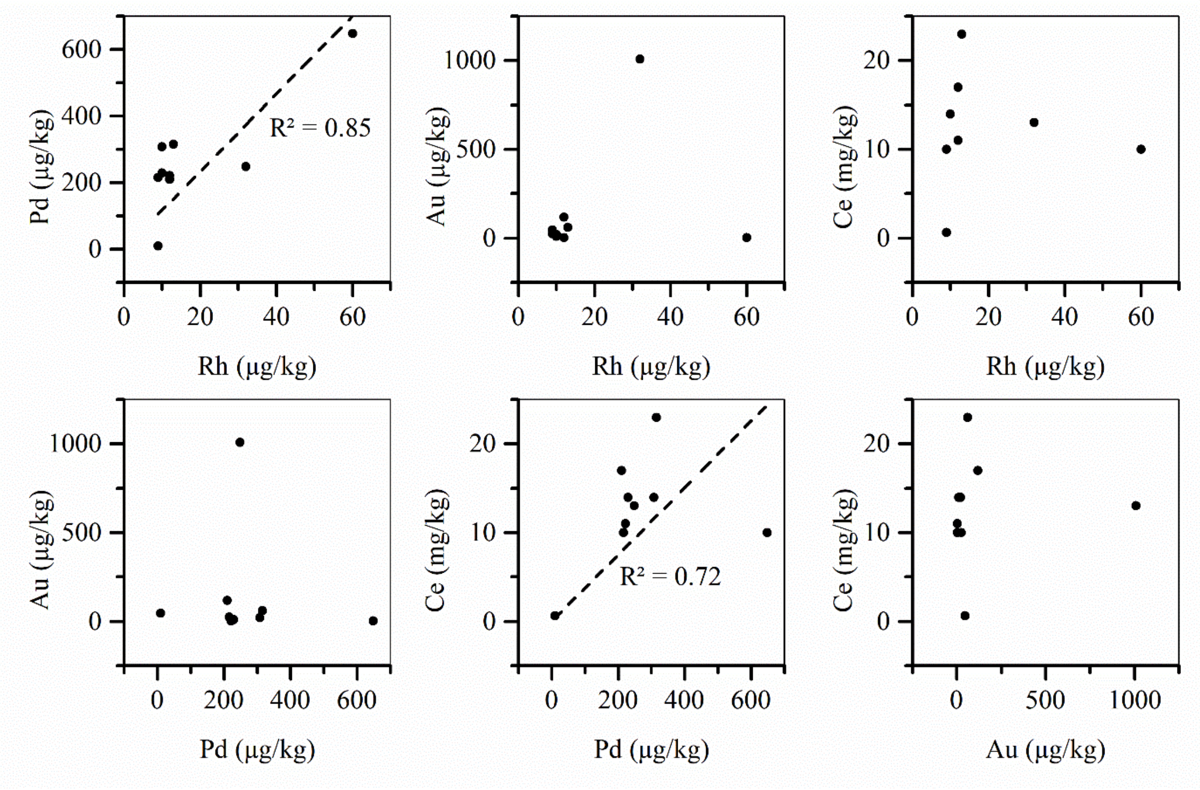

Figure 3 Correlation graphs for elements studied in this work.

Results obtained from samples taken from the industrial area in Nilufer showed that Pt concentrations were below the method’s quantification limit. Average Rh and Pd concentrations were 11 µg/kg and 359 µg/kg, respectively. Rhodium and Pd were attributed to the industrial area in the vicinity, but the Pt was surprisingly below the method’s quantification limit. Rhodium is used in electrical connections, glass production, and optical instruments. Palladium’s uses are numerous and include areas such as dental alloys, chemicals (e.g., ethanol fuel production, oil refining, polyester), and the electronics sector. Only one sample of the nine sampling locations had detectable Au concentration of 38 µg/kg (i.e., above the method’s quantification limit).

The average Ce concentration was 23 mg/kg. Higher Rh and Pt concentrations were found for samples taken from the traffic locations compared to the industrialized areas. Since agricultural lands are extensively abraded by heavy vehicles such as tractors, the Pd discharge by exhaust catalysts of these heavy vehicles might have been larger than expected. Similar to the case where PGEs concentrations were more pronounced at stationary traffic locations (bus station, parking lots, tunnels), heavy vehicles on agricultural lands can also be regarded as partially stationary due to the frequency they are used in the same limited piece of land. A different explanation for the relatively high Pd concentration at the industrial and agricultural area might be related to palladium's higher solubility (relatively to Rh and Pt) when in contact with inorganic anions, such as Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} [48].

While Rh and Pt total average concentrations were relatively higher for traffic-related locations, the total average Pd concentration was higher for the industrial locations (see Figure 4). Although Pd can be found naturally in soils and water, the relatively high Pd level, a typical traffic-related element, was surprising to observe at the industrial area. However, Pd is known to be mainly used in the manufacture of steel, steel alloys and stainless steel, which are important products fabricated in the industrial area in Nilüfer, Bursa.

Table 4 summarizes some literature values for Rh, Pd and Pt from different countries and different locations. Palladium concentrations found in literature were considerably lower compared to Pd concentrations in this study. Rhodium concentrations were comparable to results from this study. Platinum concentrations consistently remained below the method's quantification limit. Literature data and to a certain extent this study showed that accumulation of elements was higher in dust samples. Soil samples are affected by weathering conditions that speeds up the diffusion process, leading to lower concentrations detected at the upper parts of the soil.

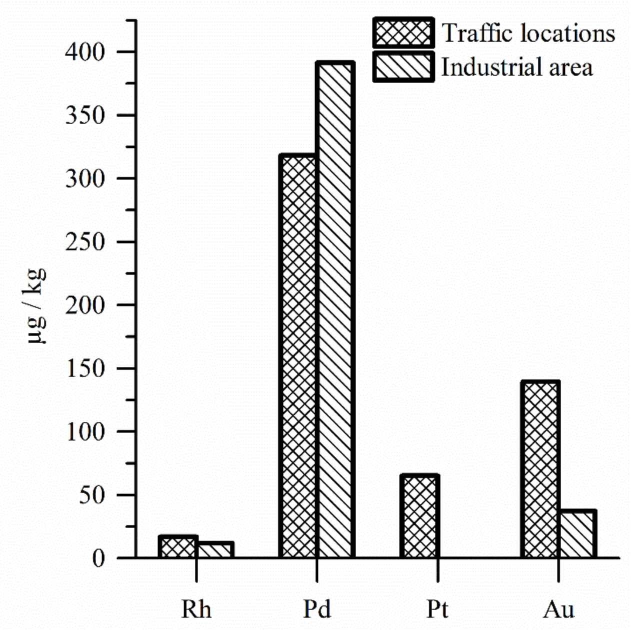

Figure 4 The overal average concentrations for PGE and heavy metals for the different traffic locations in Ankara and Bursa, and the soil surface (0 – 3 cm) at the industrial area of Nilufer, Bursa

4. CONCLUSIONS

This pilot study presents the results of Pt, Pd, Rh, Au and Ce determination in environmental samples. The concentration of the measured elements was largely concentrated at traffic locations (mainly dust samples) as opposed to industrial locations (mainly soil samples). Higher concentrations of PGEs were determined at traffic locations where vehicles remained stationary for a relatively long time, such as bus stations, downtown and tunnels. Although the number of vehicles per day that had used the highway in Ankara and Bursa was much greater than the other traffic locations, the relatively high speeds of vehicles on highways did not allow the accumulation of PGEs. Any preventive and remedial measures should begin at locations where vehicles remain stationary for a relatively long time. These are locations where people face real-time environmental and health implications of accumulated heavy metals including PGEs.

The clear presence of Pd and Rh was determined at different traffic locations. Platinum remained below the method's quantification limit for most of the samples. The relatively high Pd and Rh levels confirmed the shift from Pt to Pd and Rh seen in modern Vehicle Exhaust Catalysts (VEC) technologies.

Cerium concentrations found in this study remained well below the earth's crustal Ce-levels. Hence, Ce could not be traced back to a anthropogenic source.

These precious elements occur in ultra-trace quantities in the environment. The fact that Rh, Pd, Pt, and Au concentrations were well above the earth's crustal concentrations, shows the necessity to further investigate the anthropogenic nature of these elements. This pilot study serves as a reference for future studies on PGEs and other precious metals in the region.

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The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

Authors' Contribution

The idea of the studies belongs to Songül AKBULUT ÖZEN. Murat ÖZEN had a great contribution in providing support for the experiments and writing & editing of the manuscript. Ugur CEVIK had a contribution in investigation and analysis of the data.

The Declaration of Ethics Committee Approval

The authors declare that this document does not require an ethics committee approval or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the article and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

REFERENCES

[1] G. Schmidt and H. Palme, "Abundances of Os, Ir, Ru, Rh, Pt and Pd in the Earth's crust," in *The origin and fractionation of highly siderophile elements in the Earth's mantle*, 1997.

[2] F. R. Hartley, Ed., *Chemistry of the platinum group metals: recent developments*. Amsterdam ; New York: Elsevier, 1991.

[3] A. Fornalczyk, "Industrial catalysts as a source of valuable metals," *Journal of Achievements in Materials and Manufacturing Engineering*, vol. 55, no. 2, pp. 864–869, Dec. 2012.

[4] B. Gómez *et al.*, "Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities," *Sci Total Environ*, vol. 299, no. 1–3, pp. 1–19, Nov. 2002, doi: 10.1016/S0048-9697(02)00038-4.

[5] C. L. S. Wiseman and F. Zereini, "Airborne particulate matter, platinum group elements and human health: A review of recent evidence," *Science of The Total Environment*, vol. 407, no. 8, pp. 2493–2500, Apr. 2009, doi: 10.1016/j.scitotenv.2008.12.057.

[6] O. Morton-Bermea, O. Amador-Muñoz, L. Martínez-Trejo, E. Hernández-Álvarez, L. Beramendi-Orosco, and M. E. García-Arreola, "Platinum in PM2.5 of the metropolitan area of Mexico City," *Environ Geochem Health*, vol. 36, no. 5, pp. 987–994, Oct. 2014, doi: 10.1007/s10653-014-9613-8.

[7] M. Ďuriš, "Geochemical and Ecological Survey of the Prague City Area, Czech Republic," in *Mapping the Chemical Environment of Urban Areas*, C. C. Johnson, A. Demetriades, J. Locutura, and R. T. Ottesen, Eds. Chichester, UK: John Wiley & Sons, Ltd, 2011, pp. 364–374.

[8] K. Boch and M. Schuster, "Determination of palladium in road dust and sewage sludge ashes," in *Palladium Emissions in the Environment*, F. Zereini and F. Alt, Eds. Berlin/Heidelberg: Springer-Verlag, 2006, pp. 191–201.

[9] S. J. Parry and K. E. Jarvis, "Temporal and Spatial Variation of Palladium in the Roadside Environment," in *Palladium Emissions in the Environment*, F. Zereini and F. Alt, Eds. Berlin/Heidelberg: Springer-Verlag, 2006, pp. 419–432.

[10] C. L. S. Wiseman, Z. Hassan Pour, and F. Zereini, "Platinum group element and cerium concentrations in roadside environments in Toronto, Canada," *Chemosphere*, vol. 145, pp. 61–67, Feb. 2016, doi: 10.1016/j.chemosphere.2015.11.056.

[11] B. Leniewska, B. Godlewskaykiewicz, B. Bocca, S. Caimi, S. Caroli, and A. Hulanicki, "Platinum, palladium and rhodium content in road dust, tunnel dust and common grass in Biaystok area (Poland): a pilot study," *Science of The Total Environment*, vol. 321, no. 1–3, pp. 93–104, Apr. 2004, doi: 10.1016/j.scitotenv.2003.07.004.

[12] K. H. Ek, G. M. Morrison, and S. Rauch, "Environmental routes for platinum group elements to biological materials—a review," *Science of The Total Environment*, vol. 334–335, pp. 21–38, Dec. 2004, doi: 10.1016/j.scitotenv.2004.04.027.

[13] K. H. Ek, S. Rauch, G. M. Morrison, and P. Lindberg, "Platinum group elements in raptor eggs, faeces, blood, liver and kidney," *Sci Total Environ*, vol. 334–335, pp. 149–159, Dec. 2004, doi: 10.1016/j.scitotenv.2004.04.067.

[14] M. T. Jackson, H. M. Prichard, and J. Sampson, "Platinum-group elements in sewage sludge and incinerator ash in the United Kingdom: Assessment of PGE sources and mobility in cities," *Science of The Total Environment*, vol. 408, no. 6, pp. 1276–1285, Feb. 2010, doi: 10.1016/j.scitotenv.2009.09.014.

[15] I. Bednarova *et al.*, "Study of the influence of platinum, palladium and rhodium on duckweed (Lemna minor)," *Neuroendocrinol Lett*, vol. 35, no. 2, pp. 35–42, 2014.

[16] J. Pawlak, E. Łodyga-Chruścińska, and J. Chrustowicz, "Fate of platinum metals in the environment," *J Trace Elem Med Bio*, vol. 28, no. 3, pp. 247–254, Jul. 2014, doi: 10.1016/j.jtemb.2014.03.005.

[17] F. Zereini and F. Alt, Eds., *Palladium emissions in the environment: analytical methods, environmental assessment and health effects*. Berlin ; New York: Springer, 2006.

[18] K. E. Jarvis, S. J. Parry, and J. M. Piper, "Temporal and Spatial Studies of Autocatalyst-Derived Platinum, Rhodium, and Palladium and Selected Vehicle-Derived Trace Elements in the Environment," *Environ Sci Technol*, vol. 35, no. 6, pp. 1031–1036, Mar. 2001, doi: 10.1021/es0001512.

[19] G. Nordberg, Ed., *Handbook on the toxicology of metals*, 3rd ed. Amsterdam ; Boston: Academic Press, 2007.

[20] G. Hutchings, “A golden future,” *Nature Chem*, vol. 1, no. 7, pp. 584–584, Oct. 2009, doi: 10.1038/nchem.388.

[21] J. Kašpar, P. Fornasiero, and N. Hickey, “Automotive catalytic converters: current status and some perspectives,” *Catalysis Today*, vol. 77, no. 4, pp. 419–449, Jan. 2003, doi: 10.1016/S0920-5861(02)00384-X.

[22] F. R. Cassee *et al.*, “Exposure, Health and Ecological Effects Review of Engineered Nanoscale Cerium and Cerium Oxide Associated with its Use as a Fuel Additive,” *Critical Reviews in Toxicology*, vol. 41, no. 3, pp. 213–229, Mar. 2011, doi: 10.3109/10408444.2010.529105.

[23] J. D. Whiteley and F. Murray, “Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia,” *Science of The Total Environment*, vol. 317, no. 1–3, pp. 121–135, Dec. 2003, doi: 10.1016/S0048-9697(03)00359-0.

[24] F. Zereini *et al.*, “Concentration and Distribution of Heavy Metals in Urban Airborne Particulate Matter in Frankfurt am Main, Germany,” *Environ. Sci. Technol.*, vol. 39, no. 9, pp. 2983–2989, May 2005, doi: 10.1021/es040040t.

[25] V. Lyubomirova, R. Djingova, and J. T. van Elteren, “Fractionation of traffic-emitted Ce, La and Zr in road dusts,” *J. Environ. Monit.*, vol. 13, no. 6, p. 1823, 2011, doi: 10.1039/c1em10187k.

[26] S. Akbulut and U. Cevik, “Accumulation of Metals in Roadside Soil, Dust and Pine Needles in Different Characteristic Traffic Areas,” *Fresen Environ Bull*, vol. 23, no. 2A, pp. 516–522, 2014.

[27] A. Ucurum, P. J. Lechler, G. B. Arehart, and F. Molnar, “Platinum-Group Element, Stable Isotope, and Fluid Inclusion Investigation of the Ultramafic Rock-Hosted Gunes-Sogucak Ni-Cu-Sulfide Mineralization in the Gunes Ophiolite, East-Central Turkey,” *Int Geol Rev*, vol. 49, no. 2, pp. 169–192, Feb. 2007, doi: 10.2747/0020-6814.49.2.169.

[28] H. Kozlu, H. Prichard, F. Melcher, P. Fisher, C. Brough, and D. Stueben, “Platinum group element (PGE) mineralisation and chromite geochemistry in the Berit ophiolite (Elbistan/Kahramanmaraş), SE Turkey,” *Ore Geol Rev*, vol. 60, pp. 97–111, Jul. 2014, doi: 10.1016/j.oregeorev.2013.12.011.

[29] M. C. Turhan, “Traffic and Transportation Survey of Highway (KGM), General Directorate of Highways, Turkey,” 2010. [Online]. Available: http://www.kgm.gov.tr/SiteCollectionDocuments/KGMdocuments/Istatistikler/TrafikveUlasimBilgileri/10TrafikUlasimBilgileri%20.pdf.

[30] MTA, “General Directorate of Mineral Research and Exploration, Turkey,” 2017. http://yerbilimleri.mta.gov.tr/anasayfa.aspx.

[31] N. I. Ward and L. M. Dudding, “Platinum emissions and levels in motorway dust samples: influence of traffic characteristics,” *Science of The Total Environment*, vol. 334–335, pp. 457–463, Dec. 2004, doi: 10.1016/j.scitotenv.2004.04.049.

[32] D. Fliegel, Z. Berner, D. Eckhardt, and D. Stüben, “New data on the mobility of Pt emitted from catalytic converters,” *Analytical and Bioanalytical Chemistry*, vol. 379, no. 1, pp. 131–136, May 2004, doi: 10.1007/s00216-004-2556-7.

[33] J. C. Ely, C. R. Neal, C. F. Kulpa, M. A. Schneegurt, J. A. Seidler, and J. C. Jain, “Implications of Platinum-Group Element Accumulation along U.S. Roads from Catalytic-Converter Attrition,” *Environ Sci Technol*, vol. 35, no. 19, pp. 3816–3822, Oct. 2001, doi: 10.1021/es001989s.

[34] A. N. Riga-Karandinos, C. J. Saitanis, and G. Arapis, “First Study of Anthropogenic Platinum Group Elements in Roadside Top-Soils in Athens, Greece,” *Water Air Soil Poll*, vol. 172, no. 1–4, pp. 3–20, May 2006, doi: 10.1007/s11270-005-9016-7.

[35] J. Fritsche and T. Meisel, “Determination of anthropogenic input of Ru, Rh, Pd, Re, Os, Ir and Pt in soils along Austrian motorways by isotope dilution ICP-MS,” *Sci Total Environ*, vol. 325, no. 1–3, pp. 145–154, Jun. 2004, doi: 10.1016/j.scitotenv.2003.11.019.

[36] L. Qi, M.-F. Zhou, Z. Zhao, J. Hu, and Y. Huang, “The characteristics of automobile catalyst-derived platinum group elements in road dusts and roadside soils: a case study in the Pearl River Delta region, South China,” *Environ Earth Sci*, vol. 64, no. 6, pp. 1683–1692, Nov. 2011, doi: 10.1007/s12665-010-0635-y.

[37] S. Pan, G. Zhang, Y. Sun, and P. Chakraborty, “Accumulating characteristics of platinum group elements (PGE) in urban environments, China,” *Sci Total Environ*, vol. 407, no. 14, pp. 4248–4252, Jul. 2009, doi: 10.1016/j.scitotenv.2009.03.030.

[38] B. Gao, Y. Yu, H. Zhou, and J. Lu, “Accumulation and distribution characteristics of platinum group elements in roadside dusts in Beijing, China,” *Environ Toxicol Chem*, vol. 31, no. 6, pp. 1231–1238, Jun. 2012, doi: 10.1002/etc.1833.

[39] H. Wichmann, G. A. K. Anquandah, C. Schmidt, D. Zachmann, and M. A. Bahadir, “Increase of platinum group element concentrations in soils and airborne dust in an urban area in Germany,” *Sci Total Environ*, vol. 388, no. 1–3, pp. 121–127, Dec. 2007, doi: 10.1016/j.scitotenv.2007.07.064.

[40] M. Sager, H.-T. Chon, and L. Marton, “Spatial variation of contaminant elements of roadside dust samples from Budapest (Hungary) and Seoul (Republic of Korea), including Pt, Pd and Ir,” *Environ Geochem Hlth*, vol. 37, no. 1, pp. 181–193, Feb. 2015, doi: 10.1007/s10653-014-9639-y.

[41] R. Mathur, V. Balaram, M. Satyanarayanan, S. S. Sawant, and S. L. Ramesh, “Anthropogenic platinum, palladium and rhodium concentrations in road dusts from Hyderabad city, India,” *Environ Earth Sci*, vol. 62, no. 5, pp. 1085–1098, Mar. 2011, doi: 10.1007/s12665-010-0597-0.

[42] N. Spada, A. Bozlaker, and S. Chellam, “Multi-elemental characterization of tunnel and road dusts in Houston, Texas using dynamic reaction cell-quadrupole-inductively coupled plasma–mass spectrometry: Evidence for the release of platinum group and anthropogenic metals from motor vehicles,” *Anal Chim Acta*, vol. 735, pp. 1–8, Jul. 2012, doi: 10.1016/j.aca.2012.05.026.

[43] F. Zereini, C. Wiseman, F. Alt, J. Messerschmidt, J. Müller, and H. Urban, “Platinum and Rhodium Concentrations in Airborne Particulate Matter in Germany from 1988 to 1998,” *Environ. Sci. Technol.*, vol. 35, no. 10, pp. 1996–2000, May 2001, doi: 10.1021/es001126z.

[44] S. Artelt, H. Kock, H. P. König, K. Levsen, and G. Rosner, “Engine dynamometer experiments: platinum emissions from differently aged three-way catalytic converters,” *Atmospheric Environment*, vol. 33, no. 21, pp. 3559–3567, Sep. 1999, doi: 10.1016/S1352-2310(99)00109-0.

[45] J. G. Dale, S. S. Cox, M. E. Vance, L. C. Marr, and M. F. Hochella, “Transformation of Cerium Oxide Nanoparticles from a Diesel Fuel Additive during Combustion in a Diesel Engine,” *Environ. Sci. Technol.*, vol. 51, no. 4, pp. 1973–1980, Feb. 2017, doi: 10.1021/acs.est.6b03173.

[46] R. A. Sutherland, “A First Look at Platinum in Road-Deposited Sediments and Roadside Soils, Honolulu, Oahu, Hawaii,” *Archives of Environmental Contamination and*

Toxicology, vol. 44, no. 4, pp. 430–436, May 2003, doi: 10.1007/s00244-002-2096-0.

[47] M. E. Kylander, S. Rauch, G. M. Morrison, and K. Andam, “Impact of automobile emissions on the levels of platinum and lead in Accra, Ghana,” *J. Environ. Monitor.*, vol. 5, no. 1, pp. 91–95, Jan. 2003, doi: 10.1039/b211736c.

[48] F. Zereini, C. L. S. Wiseman, J. Poprizki, P. Albers, W. Schneider, and K. Leopold, “Assessing the potential of inorganic anions (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) to increase the bioaccessibility of emitted palladium in the environment: Experimental studies with soils and a Pd model substance,” *Environmental Pollution*, vol. 220, pp. 1050–1058, Jan. 2017, doi: 10.1016/j.envpol.2016.11.039.