Accumulation and Distribution of Pt and Pd in Roadside Dust, Soil and Vegetation in Bulgaria

Valentina Lyubomirova and Rumyana Djingova

Abstract The concentration of Pt and Pd in Bulgaria resulting from traffic pollution has never been investigated. Samples of roadside dust, soils and *Taraxacum officinale*, collected along highways, some major and secondary roads and a smelter region during the summer of 2012 are analyzed by ICP-MS. The comparison to literature values shows that the average concentrations in road dusts along Bulgarian roads are lower than the average for Pt and around the average for Pd. Hotspots with concentrations of Pd up to 800 ng/g and Pt up to 220 ng/g were established. The transfer factors (plant/soil) determined in the present study and the results form the analysis of washed and unwashed plant samples give a serious indication that a substantial part of Pt and Pd, released into the environment enters the plants.

1 Introduction

The three-way catalytic converters, mainly using platinum, palladium and rhodium as active metals to control the vehicle pollutant emission have caused significant environmental increase of platinum metals. (Niemelä et al. 2005; Pan et al. 2013). A problem created by the use of these car catalysts is that a portion of the Platinum group elements (PGE) is released from the catalyst surface and they are spread and bioaccumulated into the environment. PGE emission rate and the proportions between Pt/Pd/Rh were found to be strongly correlated to several parameters like car speed, driving style (erratic stop-start flows), age and type of the catalytic converter (Zechmeister et al. 2006; Ward and Dudding 2004; Whiteley and Murray 2003).

PGE are released in small amounts, together with particles from the wash coat of the catalytic converter, due to fast-changing oxidative and reductive conditions, high temperatures and mechanical abrasion of the catalytic material. This has led to

---

V. Lyubomirova · R. Djingova (✉)
Trace Analysis Laboratory, Faculty of Chemistry and Pharmacy, University of Sofia,
1, J.Bourchier Blvd, 1164 Sofia, Bulgaria
e-mail: RDjingova@chem.uni-sofia.bg

F. Zereini and C.L.S. Wiseman (eds.), *Platinum Metals in the Environment*,
Environmental Science and Engineering, DOI 10.1007/978-3-662-44559-4_15

increasing concentrations of these metals in the environment, as has been documented in a number of studies (e.g. Gómez et al. 2000; Kanitsar et al. 2003; Leopold et al. 2008; Pan et al. 2009; Rauch et al. 2001; Wichmann et al. 2007; Zereini et al. 2001a, b; Zereini et al. 2007).

Previous studies have found elevated PGE levels in urban airborne dusts (e.g. Alsenz et al. 2009; Rauch et al. 2005; Wichmann et al. 2007; Zereini et al. 2012), road dusts and roadside soils (e.g. Boch et al. 2002; Cicchella et al. 2003, 2008; Djingova et al. 2003a, b; Ely et al. 2001; Hooda et al. 2007; Jarvis et al. 2001; Lee et al. 2012, Lesniewska et al. 2004; Ljubomirova et al. 2008; Morcelli et al. 2005; Qi et al. 2011; Schäfer et al. 1999; Wang et al. 2007), sediments (e.g. Rauch et al. 2004; Sutherland et al. 2007; Whiteley and Murray 2005), in plants grown on soil collected from road verges (Djingova et al. 2003a, b; Hooda et al. 2008; Schäfer et al. 1998; Zechmeister et al. 2005, 2006), and in sediments in local water bodies receiving runoff from road networks (Rauch and Hemond 2003).

However, the catalyst technology is continuously changing. According to previous reports, there is a rapid growth in the amounts of Pd used in catalytic converters since 1990s, for example from 22t in 1993 to 126t in 2009 (Zereini et al. 2012), and more than 90 % of the worldwide Rh supply were related to production of catalytic converters (Tuit et al. 2000). The catalyst industry is shifting from a Pt-Rh- to a Pd-Rh-version as the active layer of the monolithic catalyst body (Helmers et al. 1998). Cytotoxicity, mutagenic effects, bioaccumulation capability and other undesirable effects in living organisms have already been reported for environmental Pd (Gómez et al. 2003). Demand for palladium is intensifying worldwide as a result of (1) price-driven substitution of palladium for platinum in gasoline and diesel catalytic converter applications, (2) expanding automotive production and 3) ever more stringent governmental emission regulations. Observed environmental increases of Pd concentrations, reflect the increased its use in place of Pt in catalytic converters since the 1990s (Zereini et al. 2007). The chemical and noble metal extraction and processing industries are also important sources of PGE to the atmosphere (Barbante et al. 2001; Rauch et al. 2006; Reimann et al. 2006; Zereini et al. 1998). Automobile catalytic converters have, however, received the most attention as a primary contributor of PGE to the environment. Changes in proportions of PGE in catalyst products could also reflect certain development and improvement of catalyst technology in developing countries (Pan et al. 2013).

The highways in Bulgaria have a total length of 620 km (see Fig. 1). The longest one -A-1, Trakia (360 km) was finished July 2013 although parts of it are in exploitation since 1978 (the first 10 km from Sofia) and 1984 (the next 140 km from Sofia). The Hemus highway A-2 is still unfinished. 80 km from Sofia were built in the period 1984–1999, and 83 km from Varna to Sofia are in exploitation since 2005. The rest of the 418 route are still in the planning stage. The smallest highway is A-6, Lyulin (19 km) finished May 2011 and connects Sofia with Pernik. Soon the construction activities of highway Struma (A-3), planned to connect Sofia with Thessaloniki are expected to start. At present the heavy traffic there is running along a major road E-79.

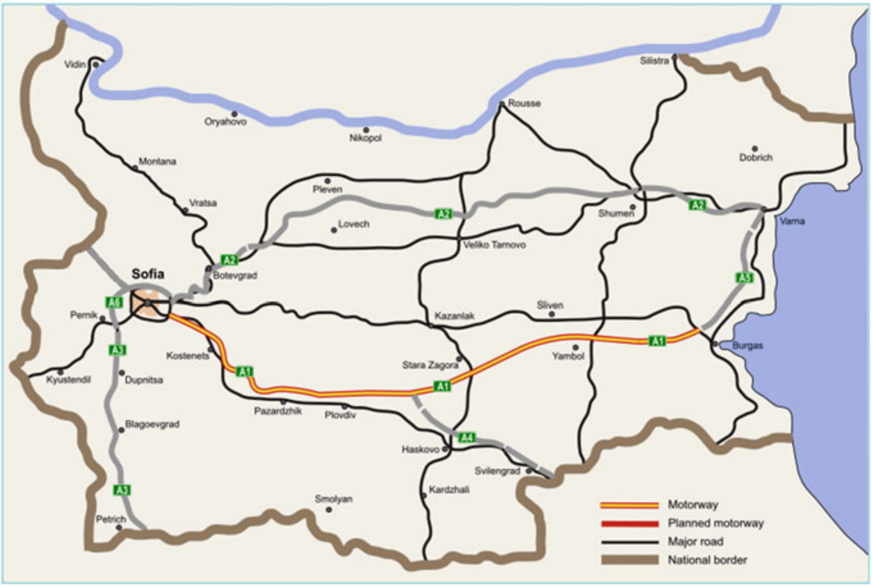

Fig. 1 Road map of Bulgaria

In the autumn of 2011 large scale screening of the distribution of PGE on the territory of Bulgaria has been performed. Samples of soils, road dust and vegetation were collected from 68 locations, situated in background regions (5 sampling sites), along the existing highways (10 locations) along major and secondary roads (30 sites), in towns (10 sites) and around two smelters. The analysis indicated that measurable concentrations of PGE were detected only along the highways, a limited number of secondary roads and around one of the smelters. Therefore in the autumn of 2012 sampling from these locations was performed.

The aim of the present study was: (i) monitoring and assessment of the environmental Pt and Pd concentration changes in Bulgaria as a consequence of human activities (ii) assessment of the bioaccumulation of PGEs in exposed plants under the new environmental concentrations.

2 Experimental

2.1 Samples and Sample Preparation

Samples of road dust, soil and vegetation (*Taraxacum officinale*) were collected along the oldest sections of highway A-1 (the first 150 km) and highway A-2 (the first 60 km). Samples were also collected along the 19 km long highway A-6;

a 10 km distributed along E-79, along the secondary roads 871 near Kazanlak and 55 near Veliko Tarnovo—Central Bulgaria (See Fig. 1) as well as around the Pb-Zn smelter in Kardzhali—South Bulgaria (see Fig. 1).

For comparison of the results samples of road dust, soil and *Taraxcum officinale* were collected from 10 sampling sites in the city of Ljubljana, Slovenia and a limited number of samples of soil and *Taraxacum officinale* from two parking places in Italy and Switzerland (E-35).

Everywhere the road dusts were sampled between the kerb and 50 cm into the road using plastic pan and brush. The soils were collected at a distance not more than 50 cm from the road edge and plants were samples from above the collected soil wherever *Taraxacum officinale* was available. The single sampling sites (within one location) were usually about 25 m long and depending on the specific conditions between 10 individual samples of each kind (for 871 and 55) and 25 (A-1, A-2 and A-6) were collected (soils at 0–5 cm depth).

Plants were sampled at the end of the flowering period by cutting with plastic scissors at 1 cm from the ground, as described in (Djingova and Kuleff 1994). All samples were collected in the autumn of 2012 after at least 20 days dry period. The plant samples were mechanically cleaned from dust and soil particles by blowing with air stream. Immediately after sampling, part of the foliage was washed thoroughly with tap water and rinsed with distilled water and another part was left unwashed. The plant samples were air dried in a clean room for 4–5 days, afterwards put in an oven for 4 h at 85 °C, ground in a polytetrafluoroethylene (PTFE) ball mill to fine powder and subjected to digestion. Approximately 0.3 g of the sample was placed in PTFE pressure vessels with 5 ml 65 % HNO_3 (Merck, suprapure) and 3 ml 30 % H_2O_2 (Merk, suprapure) The mixture was left to stay for 10 min and afterwards the closed vessels were introduced in the Multiwave digestion system using 5 steps of 5 min with the following power: 250, 400, 900, 300 and 0 W (vent, Tmax = 180 °C). The digested samples were quantitatively transferred in 50 mL polypropylene tubes by washing with double deionised water and diluted to 30 mL.

The soil and dust samples were hand cleaned from small stones, roots etc., sieved through 2-mm PTFE sieve and homogenized in a PTFE ball mill. About 0.3 g of the sample was placed in a Teflon pressure vessel and 6 mL aqua regia was added. The closed vessels were introduced in a microwave oven assisted sample digestion system and subjected to microwave digestion using six steps with the following power and time: 250 (2 min), 0 (2 min), 250 (5 min), 400 (4 min), 600 W (3 min) and 0 W (vent, Tmax = 180 °C). After cooling the content of the vessels was quantitatively transferred in 50 mL polypropylene tubes by washing with double deionised water. After centrifugation the supernatants were transferred to 100 mL polypropelene tubes and diluted to 50 ml with double deionized water.

2.2 Reagents

Suprapur chemicals and double deionised water (MilliQ) were used for preparing all solutions. Working standard solutions were prepared from single element calibration solutions (Merck) by appropriate dilution in the respective matrix. Blank determinations were run by using the same reagents in equal quantities as for the plants and the soil/dust samples.

2.3 Instrumentation

Analysis of the samples was carried out using a Perkin Elmer SCIEX DRC-e ICP-MS system with cross-flow nebulizer. The spectrometer was optimized to provide minimal values of the ratios CeO^+/Ce^+ and Ba^{2+}/Ba^+ and optimal intensity of the analytes. External calibration was performed. The calibration coefficients for all calibration curves were at least 0.99.

The optimum ICP-MS measurement conditions and isotopes used in the analysis of the elements of interest are given in Table 1. The spectrometer is equipped with a dynamic reaction cell (DRC) for removal of multi-element interferences using methane as a reaction gas.

The microwave digestion of the samples was performed with Microwave Reaction System (Anton Paar, Multiwave 3000).

Table 1 Measurement conditions for ICP-MS (Perkin-Elmer SCIEX DRC-e)

Argon plasma gas flow		15 L min^{-1}
Auxiliary gas flow		1.20 L min^{-1}
Nebulizer gas flow		0.90 L min^{-1}
Lens voltage		6.00 V
ICP RF power		1,100 W
Pulse stage voltage		950 V
Dwell time		50 ms
Acquisition mode		Peak hop
Peak pattern		One pint per mass at maximum peak
Sweeps/readings		8
Reading/replicate		1
Sample uptake rate		2 mL min^{-1}
Number of runs		6
Rinse time		180 s
Rinse solution		3 % HNO_3
Measured masses		Pd-105, Pd-108, Pt-194, Pt-195
DRC parameters	Pd-105	Cell gas flow-0.2 L min^{-1}; RPq-0.6 V
	Pd-108	Cell gas flow-0.2 L min^{-1}; RPq-0.65 V

2.4 Spectral Interferences

The spectral interferences in the ICP-MS determination of Pt and Pd are well known and much discussed. The spectral overlap of HfO^+ with all Pt isotopes and of ZrO^+, YO^+, SrO^+ Mo^+ and Cd isotopes with Pd were extensively investigated and evaluated in different matrices (see e.g. Djingova et al. 2003a).

Depending on the analyte two different strategies for interferences removal were adopted, including reaction gas and/or correction equations.

The following equation was used for correction of the interference of HfO^+ on Pt (Djingova et al. 2003a):

$$S_{corr} = S_{meas} - (S_{inter}\,A)$$

where S_{corr} is the corrected signal of the analyte, S_{meas} is the measured signal, S_{inter} is the signal of the interfering element and A is the % formation of the respective interfering species (e.g. oxide). The values of A are determined in model solutions with appropriate concentration of the interfering element and measured at the working conditions in Table 1. Pd was determined using the DRC mode with methane as reaction gas.

2.5 Quality Control

Quality control was performed using JSd-2 (Stream sediment, Geological Survey of Japan), BCR 723 and two in- house laboratory standards (dust and plant). The accuracy was better than 5 % for Pt and 8 % for Pd. All samples were analyzed in triplicate and at the start and end of each batch (10 samples) blank and standard samples were assayed. The detection limit was 0.01 ng/g for Pt and 0.05 ng/g for Pd.

3 Results and Discussion

3.1 Road Dust Samples

Table 2 presents the average, minimum and maximum concentrations obtained from the analysis of the road dust samples. For comparison results from the analysis of the samples collected in the city of Ljubljana (Slovenia) in 2012; A-2, the suburbs of Berlin (Germany) and suburbs of Warsaw (Poland), collected 2009 and literature values for the period 1998–2006 (Jackson et al. 2007) are given.

The results show that in all investigated locations in Bulgaria (but the smelter region) as well as in the samples from Ljubljana, Berlin and Warsaw the concentrations of Pd are higher than of Pt following the latest tendencies to substitute Pt

Table 2 Concentration of Pt and Pd [ng/g] in road dust samples

	Pt			Pd		
	min	average	max	min	average	max
Highway A-1	32	30.6	59	60	201.9	380.8
Highway A-2	24	73	204	138	209	247
Highway A-6	1.2	7	32	7.2	59	88
E-79	14	72.7	216	24	370	808
871	18	28	62	30	62	148
55	0.42	55	90	51	131	402
Smelter	16	50.5	85	8	28	50
A-2 (2009)[a]		21.5			53	
Ljubljana 2012	12.8	33	56.9	36.6	52.6	75.6
Berlin 2009[a]		55.6			97.6	
Warsaw 2009[a]		12.3			72.6	
Literature values[b]	0.4	128.3	2252	0	106.4	556.3

[a] Samples from a single location

[b] Jackson et al. (2007)

with Pd in the catalytic convertors. The trend in the concentrations of both elements for the investigated locations in Bulgaria is similar, the correlation coefficient is 0.89. The highest concentrations for Pt and Pd were established along E-79 where not only the traffic is very intensive, being the major road connecting Bulgaria and Greece, but very often intensive traffic jams with erratic stop-and-start mode take place. This explanation is confirmed by the fact that the highest concentrations of Pd (up to 800 ng/g) and Pt along E-79 are established nearest to the border and before tunnels where speed limits exist. Expectedly the two highways A-1 and A-2 have second highest concentrations while amazingly the lowest values were found along A-6. Unexpected hotspot was established along the local secondary road 55 (Pd: 413 ng/g) connecting Veliko Tarnovo and a small resort village (see Fig. 1). The traffic density is highest along the three highways and E-79 and lowest along 55. The traffic conditions permit highest speed along A-6 (where lowest concentrations of Pt and Pd were established) about 140 km/h and lowest along 55. The location where extremely high values for Pt and especially Pd (see Table 2) along 55 were determined is a steep curve where the maximum permitted speed is 30 km/h. These results are an indication that more important factors for the release of PGE to the environment than the traffic density might be slow speed and stop-and-go traffic (Hooda et al. 2007; Wichmann et al. 2007).

The smelter region is characterized by higher Pt concentration than Pd which is an indication for a different type of anthropogenic influence presumably the smelter.

The comparison to earlier results from a single site along A-2 (same sampling location) in 2009, shows about 3.5 times increase in the concentrations of both elements. Obviously for 3 years the increase in PGE concentration along the highway is significant. The comparison to literature values (Jackson et al. 2007) and results from the analysis of samples from Ljubljana, Berlin and Warsaw show that the average concentrations along Bulgarian roads are lower than the average summarized by Jackson et al. (2007) for Pt and around the average for Pd. The slightly higher concentrations in comparison to Berlin and Warsaw are due to the different type of sampling locations-highways or major roads and city suburbs and probably to the difference in time of sampling.

Although the production and use of leaded gasoline is forbidden in Bulgaria since 2004, the majority of cars (more than 70 %) are older than 15 years and if they have catalytic converters at all, these converters are too old to emit PGE. Nevertheless the concentrations obtained in this study are around the values measured in different European countries.

3.2 Soil Samples

The concentrations of Pt and Pd in the soil samples are lower than in the road dust but the difference is not substantial. The concentration of Pt is between 1.4 and 2.8 times lower than in the respective road dust and only for 55 the ratio is 4.4. For Pd the ratio Pd_{dust}/Pd_{soil} varies between 1.1 and 4.9. The trend in the concentrations of both elements in the soil along the highways is similar as presented in Fig. 2. The soils in the smelter region have higher concentrations of Pt than Pd which corresponds to the results from the dust analysis.

Comparison to the results from the analysis of soil samples from Ljubljana, Italy and Switzerland is presented also in Fig. 2. The concentrations of Pt and especially of Pd in Ljubljana soils are higher and similar to those along E-79. This similarity might be mostly due to the fact that sampling was performed in the city center

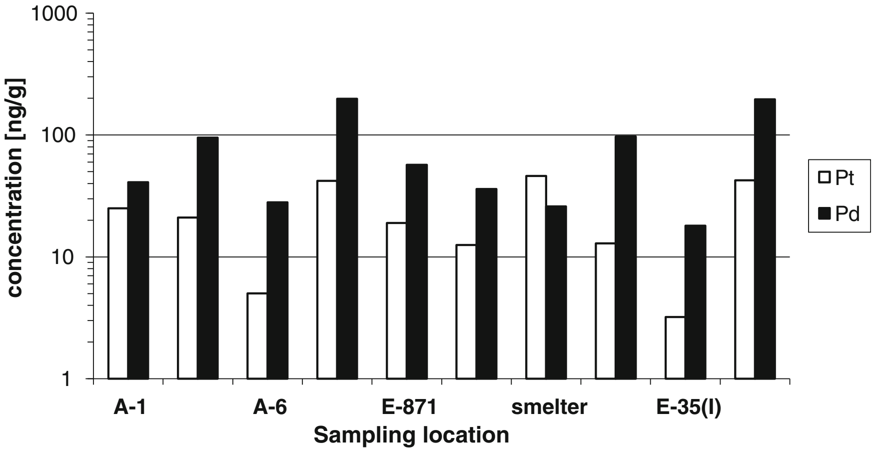

Fig. 2 Concentrations of Pt and Pd [ng/g] in soils from the investigated locations

where not only traffic is intensive but slow speed and stop and go conditions are typical. This was not established in the case of road dusts (see Table 2). However it must be kept in mind that the Bulgarian samples were collected after a prolonged dry period while in Ljubljana often street washing is done leading to removal of road dust but the soil continues to accumulate. This is why the soils in Ljubljana have higher concentrations of PGE than the dusts while along the Bulgarian roads this is not the case after a long lasting dry whether. The concentrations in the samples from Switzerland are similar while those from Italy are considerably lower than in the Bulgarian soils. The parking place in Italy (E-35 near the Swiss border) was situated aside from the road and soil and plants were available rather far from the traffic. This explains the difference to the results from Swiss samples, the site in Switzerland being situated 10 km away on the other side of the border.

3.3 Plant Samples

Figures 3 and 4 present a comparison of the concentrations of Pt and Pd in the investigated dust, soil and *Taraxacum officinale* (washed leaves) samples. Except for the samples from road 55 in the other locations the trend in the concentrations is the same for the three types of samples, the smelter region inclusive. This result is in a very good agreement to earlier investigations using *Taraxacum officinale* to assess PGE pollution along German highways (Djingova et al. 2003b). Correlation between soil and plant concentrations of Pt (though resulting from mining activities) was established also in (Rauch and Fatoki 2013) for several grass species while Hooda et al. 2007 and Pan et al. 2009 do not establish soil/plant correlation. Obviously the reason might be the plant species chosen for the investigation. It is

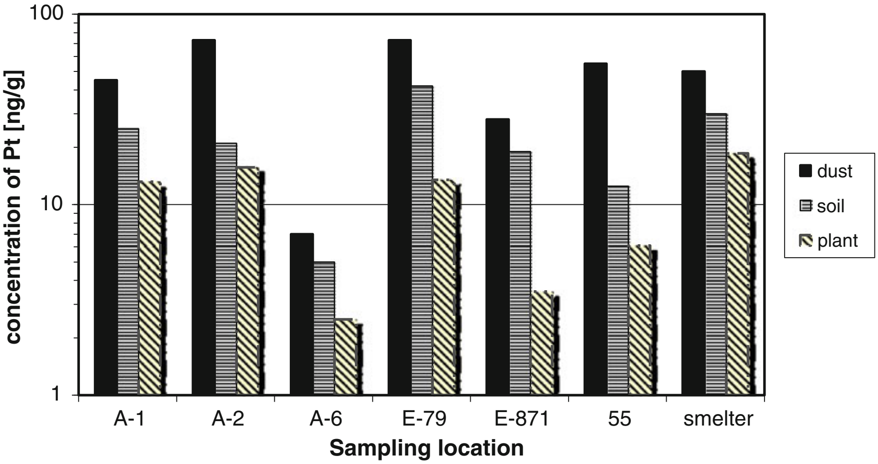

Fig. 3 Concentration of Pt [ng/g] in the investigated dust, soil and plant samples

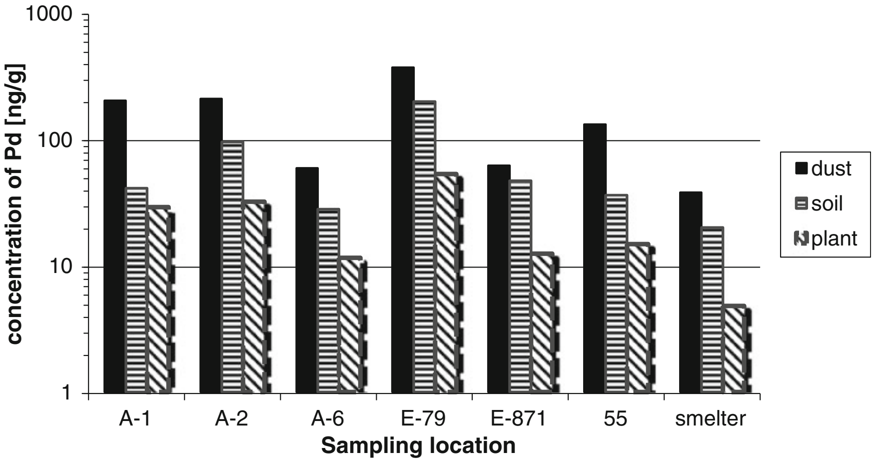

Fig. 4 Concentration of Pd [ng/g] in the investigated dust, soil and plant samples

well known that not all plant species reflect properly environmental conditions (Markert 1993). While *Taraxcum officilale* has been standardized as biomonitor of environmental pollution (Djingova and Kuleff 1993) and the correspondence in its concentration and PGE pollution has been demonstrated (Djingova et al. 2003b) this may not be the case with *Dactylis glomerata* (Hooda et al. 2007) and the undefined plant species, analyzed in (Pan et al. 2009). The difference established for the sampling location along road 55 is between the dust and soil concentrations which are defined by the relief of the sampling site. Soil and plant samples were not taken parallel to the road dust but several meters aside.

Although there are certain indications that the behavior of Pt and Pd differ in respect to plant uptake we did not establish such difference. The transfer factors (ratio between the concentration of the element in the plant to its concentration in the soil) indicate a rather high degree of uptake. The average value for the transfer factor for Pt in Bulgarian samples is (0.26 ± 0.12), and for Pd is (0.43 ± 0.18) and the results are very consistent. These values correspond to the assumption that Pd is transferred more easily to the plant in comparison to Pt. The transfer factors established for the samples from Italy and Switzerland are very similar to the Bulgarian samples: 0.11–0.37 for Pt and 0.22–0.48 for Pd which confirms the results obtained for the Bulgarian samples. The ratio for Ljubljana samples are slightly lower for Pt (0.02–0.2) and very similar for Pd (0.11–0.42). This result is a strong indication about the mobility of PGE in the environment and the respective transfer along the food chain. To investigate further the incorporation of PGE into the plant, unwashed leaves were analyzed as well (as described in the Experimental part). The results are presented in Fig. 5. The concentrations in the washed samples for Pt are between 30 and 88 % and for Pd - between 45 and 90 % from the concentration of the unwashed leaves. Similar results were obtained earlier with *Taraxacum officinale* (Djingova et al. 2003b) and by (Hooda et al. 2007; Pan et al. 2009; Rauch and Fatoki 2013)

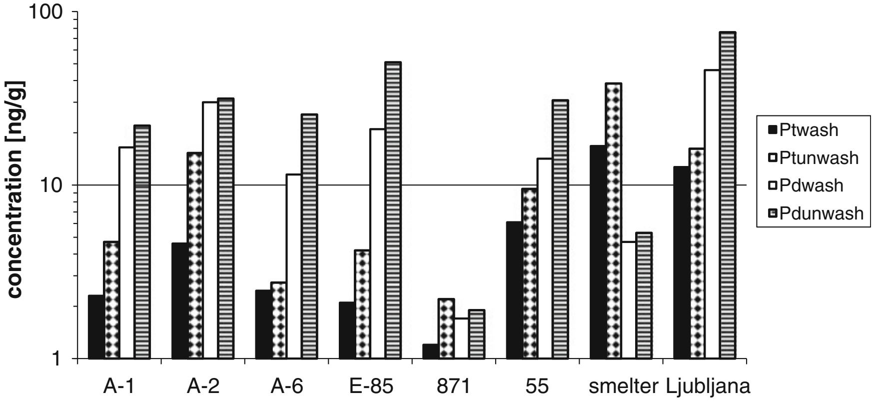

Fig. 5 Concentrations of Pt and Pd [ng/g] in washed and unwashed leaves of *Taraxacum officinale*

with different species. Since all *Taraxacum* samples have been collected after of at least 20 days dry period it might be assumed that a substantial part of the PGE enters the plant which again is a strong confirmation of the obtained rather high results for the transfer factors.

4 Conclusion

The results from the present investigation show uneven distribution of PGE on the territory of Bulgaria. While in background regions, towns and along the majority of secondary roads the concentrations of PGE are still below the detection limit, along highways some major and secondary roads values up to 800 ng/g Pd and 200 ng/g Pt were established in road dust. The results indicate that more important than traffic density and velocity seem to be traffic jams, slow speed and stop-and-go traffic. The concentrations of Pt and Pd in dust, soil and *Taraxacum officinale* have the same trend along the investigated locations. The plant/soil transfer factors and the small difference in the concentrations of washed and unwashed leaves of *Taraxacum officinale* indicate significant transfer of Pt and Pd to the plants. A comparison to samples from other European countries prove medium PGE pollution in Bulgaria and confirm the results obtained for the transfer in the system plant/soil.

Acknowledgments The present investigation was performed with the financial support of the National science fund, Ministry of education, youth and science, contract No DMU 03-54.

References

Alsenz H, Zereini F, Wiseman CLS, Püttmann W (2009) Anal Bioanal Chem 395:1919–1927

Barbante C, Veysseyre A, Ferrari C, van de Velde K, Morel C, Capodoglio G, Cescon P, Scarponi G, Boutron CF (2001) Environ Sci Technol 35:835–839

Boch K, Shuster M, Risse G, Schwarzer M (2002) Anal Chim Acta 459:257–265

Cicchella D, Fedele L, De Vivo B, Albanese S, Lima A (2008) Geochem Explor Environ Anal 8:31–40

Cicchella D, De Vivo B, Lima A (2003) Sci Total Environ 308:121–131

Djingova R, Kuleff I (1994) In: Markert B (ed) Environmental sampling for trace analysis. VCH, Weinheim, pp 395–414

Djingova R, Kuleff I (1993) In: Markert B (ed) Plants as biomonitors. VCH, Weinheim, pp 435–457

Djingova R, Heidenreich H, Kovacheva P, Markert B (2003a) Anal Chim Acta 489:245–251

Djingova, R. Kovacheva P., Wagner G., Markert B., Sci. Total Environ., 2003b, 308, 235–246

Ely JC, Neal CR, Kulpa CR, Schneegurt MA, Seidler JA, Jain JC (2001) Environ Sci Technol 35:3816–3822

Gómez MB, Gómez MM, Palacios MA (2003) J Anal At Spectrom 18:80–83

Gómez MB, Gomez MM, Palacios MA (2000) Anal Chim Acta 404:285–294

Helmers E, Schwarzer M, Schuster M (1998) Environ Sci Pollut Res 5:44–50

Hooda PS, Miller A, Edwards AC (2007) Sci Total Environ 384:384–392

Hooda PS, Miller A, Edwards AC (2008) Environ Geochem Health 30:135–139

Jackson MT, Sampson J, Prichard HM (2007) Sci Total Environ 385:117–131

Jarvis KE, Parry SJ, Piper JM (2001) Environ Sci Technol 35:1031–1036

Kanitsar K, Koellensperger G, Hann S, Limbeck A, Puxbaum H, Stingeder G (2003) J Anal At Spectrom 18:239–246

Lee HY, Chon HT, Sager M, Marton L (2012) Environ Geochem Health 34:5–12

Leopold K, Maier M, Weber S, Schuster M (2008) Environ Pollut 156:341–347

Lesniewska BA, Godlewska-Zylkiewicz B, Bocca B, Caimi S, Caroli S, Hulanicki A (2004) Sci Total Environ 321:93–104

Ljubomirova V, Djingova R, van Elteren JT, Veber M, Kowalkowski T, Buszewski B (2008) Intern J Environ Anal Chem 88:499–512

Markert B (1993) Plants as biomonitors. VCH, Weinheim

Morcelli CPR, Figueiredo AMG, Sarkis JES, Enzweiler J, Kakazu M, Sigolo JB (2005) Sci Total Environ 345:81–91

Niemelä M, Kola H, Perämäki P, Piispanen J, Poikolainen J (2005) Microchim Acta 150:211–217

Pan SH, Sun YL, Zhang G, Chakraborty P (2013) J Geochem Explor 128:153–157

Pan SH, Zhang G, Sun YL, Chakraborty P (2009) Sci Total Environ 407:4248–4252

Qi L, Zhou MF, Zhao Z, Hu J, Huang Y (2011) Environ Earth Sci 64:1683–1692

Rauch S, Ehrenbrink BP, Molina LT, Molina MJ, Ramos R, Hemond HF (2006) Environ Sci Technol 40:7554–7560

Rauch S, Fatoki OS (2013) Water Air Soil Pollut 224:1395–1402

Rauch S, Hemond HF (2003) Environ Sci Technol 37:3283–3288

Rauch S, Hemond HF, Peucker-Ehrenbrink B (2004) Environ Sci Technol 38:396–402

Rauch S, Hemond HF, Peucker-Ehrenbrink B, Ek KH, Morrison GM (2005) Environ Sci Technol 39:9464–9470

Rauch S, Lu M, Morrison GM (2001) Environ Sci Technol 35:595–599

Reimann C, Niskavaara H (2006) In: Zereini F., Alt F. (eds) Palladium emissions in the environment: analytical methods, environmental assessment and health effects. Springer, Heidelberg, p 53–70

Schäfer J, Eckhardt JD, Berner ZA, Stüben D (1999) Environ Sci Technol 33:3166–3170

Schäfer J, Hannker D, Eckhardt JD, Stüben D (1998) Sci Total Environ 215:59–67

Sutherland RA, Pearson DG, Ottley CJ (2007) Appl Geochem 22:1485–1501

Tuit CB, Ravizza GE, Bothner MH (2000) Environ Sci Technol 34:927–932

Wang J, Zhu RH, Shi YZ (2007) J Environ Sci 19:29–34

Ward NI, Dudding LM (2004) Sci Total Environ 335:457–463

Whiteley JD, Murray F (2003) Sci Total Environ 317:121–135

Whiteley JD, Murray F (2005) Sci Total Environ 341:199–209

Wichmann H, Anquandah GAK, Schmidt C, Zachmann D, Bahadir M (2007) Sci Total Environ 388:121–127

Zechmeister HG, Hagendorfer H, Hohenwallner D, Hanus-Illnar A, Riss A (2006) Atmos Environ 40:7720–7732

Zechmeister HG, Hohenwallner D, Riss A, Hanus-Illnar A (2005) Environ Pollut 138:238–249

Zereini F, Alsenz H, Wiseman CLS, Püttmann W, Reimer E, Schleyer R, Bieber E, Wallasch M (2012) Sci Total Environ 416:261–268

Zereini F, Dirksen F, Skerstupp B, Urban H (1998) Environ Sci Pollut Res 5:223–230

Zereini F, Skerstupp B, Rankenburg K, Dirksen F, Beyer JM, Claus T, Urnan H (2001a) J Soils Sed 1:44–49

Zereini F, Wiseman C, Alt F, Messerschmidt J, Müller J, Urban H (2001b) Environ Sci Technol 35:1996–2000

Zereini F, Wiseman C, Püttmann W (2007) Environ Sci Technol 41:451–456