

Platinum Group Elements in Road Dust and Vegetation from Some European and National Roads with Intensive Car Traffic in Romania

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The paper presents a monitoring study of the platinum group metals concentrations in 17 samples of road dust and vegetation from areas with heavy car traffic on several European and national roads in eastern Romania. The Ir, Pd, Pt, Rh, Ru concentrations were determined by the ICP-MS technique, the reported values being below the method's limit of determination for Ir, Pt and Ru both in soil and vegetation. As regards the Pd content, it showed a maximum of 794 µg / kg dry matter in Focsani area (DN2), an area where, according to national data published by National Road Infrastructure Management Company, the traffic average is 16,000 vehicles / 24 h. Approximately 50% of the collected vegetation samples showed a Pd transfer factor from the solid part to the vegetation higher than 0.5, thus indicating the existence of Pd toxic compounds bioavailable for vegetation. The highest concentrations of Rh in soil were recorded on a high traffic section on the E85, in Ramnicu Sarat area, where the traffic interval ranges from 8,001 to 16,000 vehicles / 24 h.

Keywords: PGEs, road dust, vegetation, Pd, Rh, pollution

Over the last decade, the concentration of Platinum Group Elements (PGEs) in environmental samples such as soil, surface water, sediment and vegetation have increased significantly, the main source of contamination with these platinum metals being catalytic converters.

Increased concentrations of platinum group metals have been found in various water samples (rainwater, groundwater, surface water, marine sediments), these concentrations being caused by exhaust emissions. Large platinum concentrations have been also found near mines, especially those extracting nickel ores.

Catalysts containing platinum group metals are used especially in motor vehicles but also in industry as stationary catalysts used for the oxidation of ammonia. The main sources of platinum group metal emissions in Europe can be listed as follows: 50.4% from catalysts, 24.7% from jewelry, 6% from the electrical industry, 4.8% from the chemical industry, 4.6% from the glass industry, 2.6% from the oil industry and 6.8% from other sources [1-3].

Platinum group metals such as platinum, palladium and rhodium are used as catalysts in catalytic converters of thermal motors in order to reduce hydrocarbons, nitrogen oxides and carbon monoxide emissions. Direct measurements of PGE emissions from vehicle catalysts provide estimates of emissions expressed in ng / km traveled. Emissions of platinum-based particles depend on factors such as engine operating conditions, age and type of catalyst, platinum metals content, vehicle speed, and type of additive present in fuel [4]. Platinum metal emissions may increase due to operating conditions, such as excessive heating, which can destroy the converter. It is assumed that the mechanical erosion of the catalyst surface is the main cause of platinum metal emissions, besides the contribution of thermal and chemical processes. The platinum metal particles resulting from the cars evacuation systems have dimensions between 1-63

µm, being absorbed on the surface of particulate matter (PM) and depositions in air [5-6].

Platinum metal content in unpolluted soils is very low, according to data published by various groups of researchers [7-9]. Controlling these elements in environmental factors is difficult because of the performance equipment required to quantify concentrations. Published data on PGEs content in the surface layer of different soil types are discrepant and in some cases are not in accordance with natural abundance in the earth's crust [10]. The differences between the concentration range of PGEs in soil from the published data can be attributed to some aspects such as: the chemical analyzes of these metals are insufficiently elaborated; experimental data is insufficiently systematized in terms of origin (geochemical structure) and soil type, so it is difficult to estimate the representativeness of reported data.

Anthropogenic activity has led to an increase in PGE concentration in soil, especially in areas with high traffic, as evidenced by a series of studies conducted internationally [11]. The results of PGE determination in samples taken from areas located near roadways / highways indicate a decrease in the platinum metal concentration as the distance to roadways / highways increases.

Due to the fact that PGEs are mainly emitted in the metallic form, they show low toxicity. Some of them are transformed into soluble form, becoming bio-available and dangerous for both flora and fauna [1].

Soluble platinum represents less than 10% of total Pt emissions, while soluble Pd and Rh representing more than 50%. Soluble compounds of Pt as well as Pd and Rh chlorides are mutagenic, carcinogenic, and some compounds of platinum metals are strong allergens [4, 12]. Literature data show that PGEs (especially Pd) are

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absorbed from the soil through roots and subsequently incorporated into the vegetative biomass of biologically active substances [13]. The ability of plants to absorb PGE from soil can pose a significant threat to human health.

In order to monitor the emission of platinum metals into the environment, advanced analytical methods for determining these elements are required.

Methods for the determination of platinum metals include: simultaneous determination of Pt, Pd, Ir by SPE-ICP-OES [14]; simultaneous determination of Rh and Ru in river waters and municipal sewage through HR-CS-GFAAS [15]; simultaneous determination of Rh, Ru, Pt, Pd, Ir by ICP-OES and ICP-MS [13, 16]; determination of Pt, Pd and Rh from dust and soil samples by GFAAS [17].

Given that over the last 10 years Romania has become a country in which a large number of second-hand cars with advanced wear degree (mostly diesel) purchased from the West European countries (mainly Germany) and the UK, the purpose of this study was to estimate the impact of PGE emissions from exhaust gases on environmental factors. In this respect, the research consists in the determination of platinum metals group content (Ir, Pd, Pt, Rh and Ru) in road dust and vegetation from 17 locations situated in the eastern part of Romania (European and national roads with intense car traffic) through different analytical techniques (USN-ICP-EOS and ICP-MS).

Experimental part

Studied area

Soil and vegetation samples have been collected according to the international standards in force at several intersections with heavy road traffic on several European roads, including the E85 road linking Turkey, Bulgaria and Ukraine to the Republic of Moldova, highly circulated, with

sampling points in Buzau, Bacau, Roman, Vama Siret; European road E58 (Iasi area); European road E574 (Onesti), as well as from several national roads (eg DN2).

The geographic coordinates and description of the sampling points as well as the types of samples taken are shown in table 1.

The location of the 17 sampling points for road dust and vegetation on the road map of Romania is presented in Figure 1, whereas figures 2-5 detail several areas of interest from where samples were taken.

Materials and methods

Road dust samples were air-dried, ground, sieved, retaining the fraction with a particle size of less than 63µm. Platinum metal extraction was performed with a mixture of royal water in a closed system, the samples being filtered afterwards and brought with ultra-pure water to a 50 mL flask. As far as the preparation of the vegetation samples is concerned, drying was done in a very good ventilation room for a period of 2 weeks. Subsequently, the vegetation samples were milled and processed (about 1 g) with a mixture of hydrogen peroxide (2 mL) and suprapur nitric acid (10 mL).

The calibration curve for the determination of Ir, Pd, Pt, Rh, Ru was performed on a range from 10 to 50 µg / L using a MRC multi-element for ICP-MS standard 3 of 10 mg/L (Sb, Au, Hf, Ir, Pt, Rh, Ru, Te) in 10% HCl and 1% HNO₃ from VWR Chemicals.

According to the data published by the National Road Infrastructure Management Company, the Technical Studies and Informatics Center [18], E85 sections (fig. 2), from which road dust and vegetation samples were collected, shows on average a traffic higher than 16,000 vehicles / 24 hours in Buzau and between Focsani and

Crt. No.	Sampling location	Sample type	GPS coordinates
1	Buzau roundabout (near Petrom gas station, Dedeman, exit to Ramnicu Sarat), E85	S1 – road dust V1 - vegetation	45.170867, 26.816423
2	Ramnicu Sarat roundabout (Maracineni bridge), E 85	S2 – road dust V2 - vegetation	45.382008, 27.037951
3	Focsani roundabout , Vrancea county, DN2	S3 – road dust V3 - vegetation	45.687543, 27.198295
4	Adjud roundabout, Republicii Boulevard	S4 – road dust V4 - vegetation	46.100912, 27.179948
5	Onesti roundabout (Calea Marasesti, Redului stree, exit to Adjud)	S5 – road dust V5 - vegetation	46.252254, 26.795575
6	Onesti roundabout (exit to Tg. Secuiesc), E574	S6 – road dust V6 - vegetation	46.244557, 26.755675
7	Vulturi village roundabout, exit to Iasi E58	S7 – road dust V7 - vegetation	47.239629, 27.532343
8	Vama Siret crossroad, E85	S8 – road dust V8 - vegetation	47.961830, 26.071220
9	Gura Humorului roundabout, Paltinoasa village	S9 – road dust V9 - vegetation	47.544905, 25.946498
10	Roman roundabout (near Petrom gas station, Nicolae Balcescu street, exit to the ring road)	S10 – road dust V10 - vegetation	46.926710, 26.908728
11	Roman roundabout , ring road (Roman Musat Bld, near Mol gas staion), E85	S11 – road dust V11 - vegetation	46.917591, 26.922914
12	Bacau roundabout (Unirii Bld., entry from Roman), E 85	S12 – road dust V12 - vegetation	46.571693, 26.921485
13	Buzau roundabout, Industriilor Bld.	S13 – road dust l V13 - vegetation	45.133551, 26.816032
14	Orbeni village crossroads, Bacau county (near Capul Dacului Motel), E85	S14 – road dust V14 - vegetation	46.280108, 27.053537
15	Varsatura village roundabout, Promenada Mall, Braila county	S15 – road dust V15 - vegetation	45.207500, 27.915151
16	Lacul Sarat roundabout , Chiscani, Braila	S16 – road dust V16 - vegetation	45.216504, 27.922864
17	Slobozia roundabout (Kaufland), Bucuresti-Constanta highroad, Amara highroad, Matei Basarab Bld.	S17 – road dust V17 - vegetation	44.562656, 27.349481

Table 1
GEOGRAPHIC
COORDINATES OF
SAMPLING POINTS FOR
SOIL AND VEGETATION

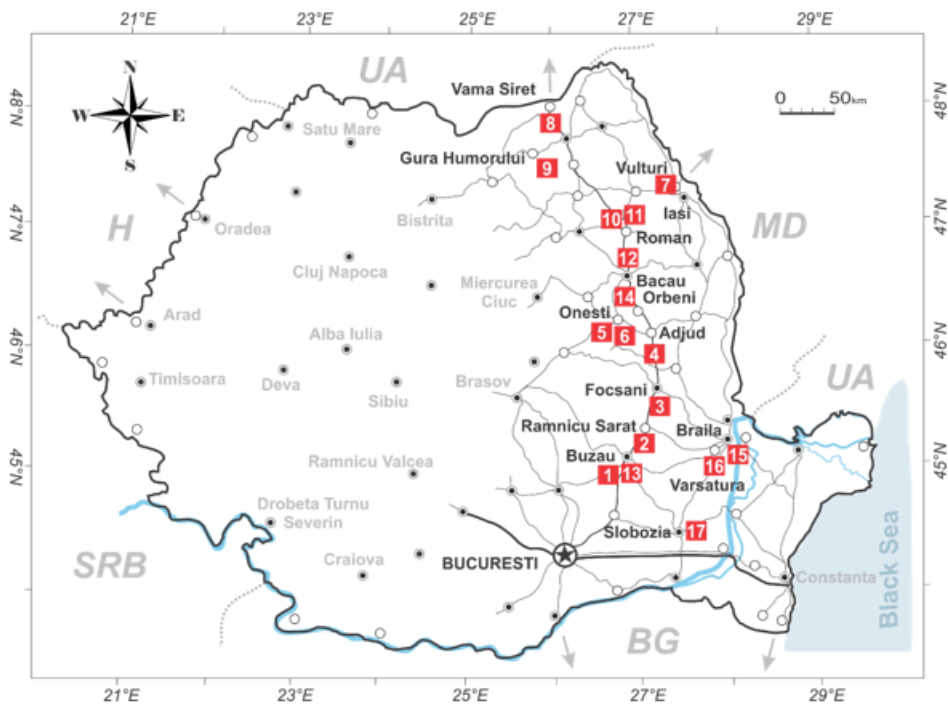


Fig. 1. Location of soil and vegetation sampling points



Fig. 2. Detail of sampling points E85, DN2

Adjud, while in Ramnicu Sarat the car traffic ranges from 8,001 to 16,000 vehicles / 24 h.

In the area of Onesti (E574), the car traffic ranges from 3,501 to 8,000 vehicles / 24 h (fig. 3).

Sampling points 15, 16 in Braila County are located in areas with high car traffic, with the number of vehicles ranging from 8,001 to 16,000 vehicles / 24 h (fig. 4). Slobozia,

with sampling point 17, according to the above mentioned source, falls within the same traffic interval (fig. 5).

Equipment

For the determinations, the following equipment was used:

-ICP-EOS Spectrometer Avio 500 Perkin Elmer coupled with Ultrasonic Nebulizer USN U600AT+ Cetac Tedelyne



Fig. 3. Detail of sampling points Onesti

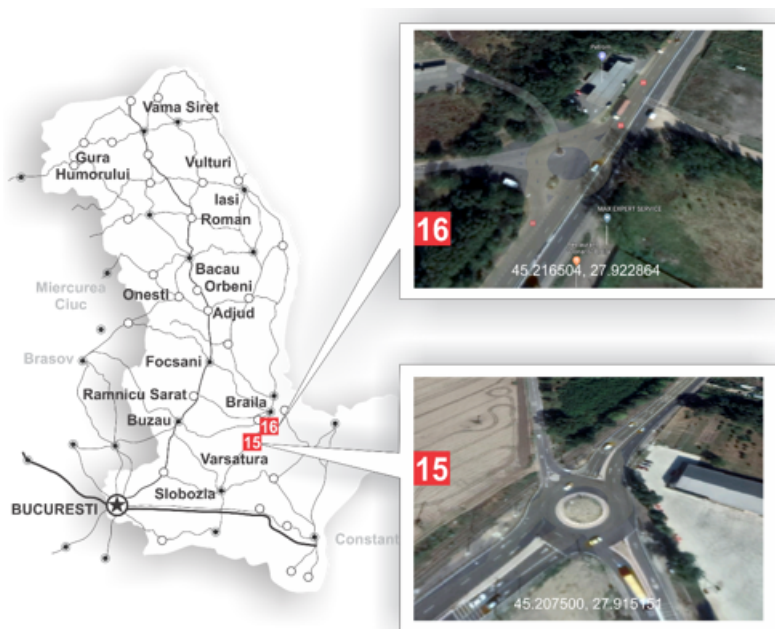


Fig. 4. Detail of sampling points, Braila county



Fig. 5. Detail of sampling points Slobozia

-ICP-MS Aurora M90 Bruker

The performance parameters of the applied methods are presented in tables 2 and 3.

Table 2
PERFORMANCE PARAMETERS OF PGE USING USN-ICP-EOS TECHNIQUE

Metal λ , nm	LOD $\mu\text{g/L}$	LOQ $\mu\text{g/L}$	Accuracy $\mu\text{g/L}$	RSD _r * %	RSD _{Ri} ** %	U _{ex} *** %	Recovery %
Ir 224.268	1.36	4.50	0.6 ± 6.8/30 1.8 ± 4.2/50	2.89	4.91	7.21	83.3 ÷ 95.5
Pd 248.892	1.20	4.00	2.2 ± 3.9/30 1.9 ± 5.9/50	2.56	3.35	13.3	81.2 ÷ 105
Pt 193.700	1.94	6.5	3.7 ± 16/120 14.5 ± 28/200	1.75	2.79	7.38	86.0 ÷ 96.9
Rh 343.489	0.60	2.00	0.6 ± 0.9/30 0.3 ± 3.6/50	3.48	5.84	7.44	98.8 ÷ 105
Ru 349.894	0.72	2.40	1.3 ± 6.4/30 1.7 ± 12/50	2.26	3.26	11.2	75.7 ÷ 96.6

*Repeatability; **Intermediate precision; ***Measurement uncertainty

Table 3
PERFORMANCE PARAMETERS OF PGE USING ICP-MS TECHNIQUE

Metal isotope	LOD $\mu\text{g/L}$	LOQ $\mu\text{g/L}$	RSD _r * %	U _{ex} ** %
Ir 193	0.60	2.00	5.40	10.9
Pd 105	0.07	0.25	1.15	6.85
Pt 195	1.05	3.50	10.7	15.9
Rh 103	0.05	0.17	0.55	5.60
Ru 102	0.09	0.29	1.24	7.54

*Repeatability; **Measurement uncertainty

Results and discussions

Determinations of platinum metals from the road dust and vegetation samples presented in tables 4 and 5 were made by ICP-MS. It is noted that both the iridium, ruthenium and platinum content in road dust and vegetation samples are below the limit of quantification of the applied method (50 µg/kg to Ir, 10 µg/kg to Ru and 90 µg/kg to Pt), while rhodium concentrations are small, below 20 µg/kg for both matrix types (tables 2 and 3). Palladium concentrations are situated in the range of hundreds of µg/kg in soil and in the range of tens of hundreds of µg/kg in vegetation. The highest Pd content was recorded in sections S1 - S4 (fig. 2), S5-S6 (fig. 3), the highest concentration being reported in S3 (Focsani, DN2, 794 µg / kg dm = dry matter), (fig. 4).

As mentioned above, the Focsani area has a very intense car traffic (more than 16,000 vehicles / 24 h), which is reflected also in the recorded PGEs concentrations.

PGEs values for soil samples are compared with both terrestrial crust reference values and other data for different European countries (table 6). Comparing the values obtained for the dust samples for Pd with the values obtained in other geographic areas, it can be observed that the maximum value is below that reported by Gomez et al., the average value being very close to that recorded in Madrid in 2001 [19]. Concerning the Rh content, the concentrations recorded in the studied sections are close to the values recorded in Moscow and reported in the study published by Ladonin in 2018 [12]. The maximum value obtained in the analysed samples (0.014 mg / kg dm) is situated around the mean value (0.0179 mg/kg dm) reported in Moscow. The statistical processing of the obtained results is presented in table 6 for road dust samples, respectively in table 7 for vegetation samples.

Metal	UM	S1	S2	S3	S4	S5	S6	S7	S8	S9
Ir (193)	µg/kg dm	<50	<50	<50	<50	<50	<50	<50	<50	<50
Pd(105)	µg/kg dm	668	780	794	613	556	632	352	319	434
Pt(195)	µg/kg dm	<90	<90	<90	<90	<90	<90	<90	<90	<90
Rh(103)	µg/kg dm	13.7	13.6	11.4	9.38	8.83	8.73	7.15	<5	7.53
Ru(102)	µg/kg dm	<10	<10	<10	<10	<10	<10	<10	<10	<10

Table 4
CONTENT OF PGE IN ROAD DUST SAMPLES

Metal	UM	S10	S11	S12	S13	S14	S15	S16	S17
Ir (193)	µg/kg dm	<50	<50	<50	<50	<50	<50	<50	<50
Pd(105)	µg/kg dm	371	509	430	361	505	309	448	357
Pt(195)	µg/kg dm	<90	<90	<90	<90	<90	<90	<90	<90
Rh(103)	µg/kg dm	5.38	6.65	7.53	6.85	8.06	<5	<5	5.89
Ru(100)	µg/kg dm	<10	<10	<10	<10	<10	<10	<10	<10

Metal	UM	V1	V2	V3	V4	V5	V6	V7	V8	V9
Ir	µg/kg dm	<50	<50	<50	<50	<50	<50	<50	<50	<50
Pd	µg/kg dm	363	13	326	304	85	<6	232	191	134
Pt	µg/kg dm	<90	<90	<90	<90	<90	<90	<90	<90	<90
Rh	µg/kg dm	19.1	<5	10.2	15.6	<5	<5	8.58	<5	5.66
Ru	µg/kg dm	<10	<10	<10	<10	<10	<10	<10	<10	<10

Table 5
CONTENT OF PGE IN VEGETATION SAMPLES

Metal	UM	V10	V11	V12	V13	V14	V15	V16	V17
Ir	µg/kg dm	<50	<50	<50	<50	<50	<50	<50	<50
Pd	µg/kg dm	93	128	205	283	125	172	131	172
Pt	µg/kg dm	<90	<90	<90	<90	<90	<90	<90	<90
Rh	µg/kg dm	<5	5.27	10.2	11.9	5.42	5.74	5.77	9.56
Ru	µg/kg dm	<10	<10	<10	<10	<10	<10	<10	<10

Table 6
RESULTS OF PGE IN SOIL SAMPLES COMPARED TO LITERATURE DATA (mg/kg dm)

Element	Ir	Pd	Pt	Rh	Ru
Average value	<0.05	0.496	<0.09	0.008	<0.01
Minimum value	<0.05	0.309	<0.09	0.003 (<0.005)	<0.01
Maximum value	<0.05	0.794	<0.09	0.014	<0.01
Standard deviation	-	0.127	-	0.002 (<0.005)	-
Crust - reference values					
Fersman [7]	0.01	0.05	0.2	0.01	0.05
Vinogradov [8]	0.001	0.01	0.005	0.001	0.005
Greenwood [9]	0.001	0.015	0.001 - 0.005	0.0001	0.0001
Lide [10]	0.001	0.015	0.005	0.001	0.001
Concentrations in dust - other areas studied					
Moscova [12]					
Average value	0.0039	0.0708	0.158	0.0179	0.0016
Minimum value	0.0016	0.0077	0.0124	0.0027	0.0007
Maximum value	0.0062	0.2253	0.3566	0.0545	0.0022
UK [20]	-	0.0093	0.070	-	-
Israel [21]	-	-	1.230	0.381	-
Madrid [19]	-	0.317 (mean) 2.25 (max)	-	0.074 (mean) 0.182 (max)	-
Viena [22]	-	0.20 - 1.23	0.21 - 1.45	-	-

Element	Ir	Pd	Pt	Rh	Ru
Average value	<0.05	0.174	<0.09	0.007	<0.01
Minimum value	<0.05	0.001 (<0.006)	<0.09	0.001 (<0.005)	<0.01
Maximum value	<0.05	0.363	<0.09	0.019	<0.01
Standard deviation	-	0.048	-	0.002 (<0.005)	-

Table 7
STATISTICAL RESULTS OF
PGE FROM VEGETATION
SAMPLES (mg/kg dm)

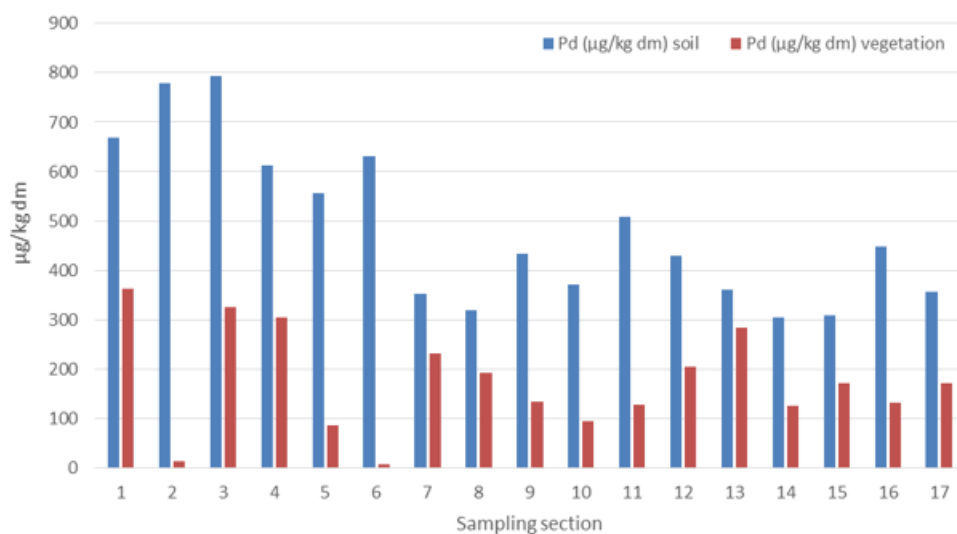


Fig. 6. Distribution of Pd content in samples of dust and vegetation collected from areas with intense traffic

Table 8
Pd TRANSFER FACTOR FROM SOIL TO VEGETATION

FT	1	2	3	4	5	6	7	8	9
Pd	0.54	0.02	0.41	0.50	0.15	0.01	0.66	0.60	0.31
FT	10	11	12	13	14	15	16	17	
Pd	0.25	0.25	0.48	0.78	0.41	0.56	0.29	0.48	

Figure 6 shows graphically the Pd concentrations both in soil and vegetation samples, observing in some areas a high transfer factor. The transfer factor, representing the concentration of metal in vegetation relative to the metal concentration in the soil, ranges from 0.01 to 0.78, with an average value of 0.39, the highest value being recorded at point 13 (Roundabout Buzau, Industriilor Bld.). Another sample of vegetation harvested from another crossroad in Buzau, sample 1, also shows a high transfer factor (0.54).

Approximately 50% of the vegetation samples have a transfer factor higher than 0.5, indicating the presence of bioavailable palladium compounds in the road dust that passes through the root to the aerial parts of the nearby vegetation.

Determinations performed using the USN-ICP-EOS technique both in soil and vegetation indicated concentrations below the determination limit for Pt (<0.20 mg / kg dm), Rh (0.10 mg / kg dm) and Ru (0.12 mg / kg dm), while the Ir and Pd concentrations are altered by interference from other metals (Fe, Ni, W) that cannot be removed by applying interference removal methods from the Syngistics software of the ICP-EOS Avio 500 Perkin Elmer equipment. The peaks of samples and samples overlap, but the interferences are recorded in tens and hundreds of wavelengths, so that these concentrations (in the order of tens-hundred mg / kg dm in the case of soils, respectively units of mg / kg dm in the case of vegetation) did not reflect real situation compared to similar data obtained by other researchers as well as concentrations determined by ICP-MS.

Conclusions

The content of Ir, Pd, Pt, Rh and Ru was determined in 17 samples of road dust and vegetation, samples taken from several European and national roads located in the eastern part of Romania in areas with intense traffic. The concentrations of Ir, Pt, Ru were below the limit of determination of the applied method in both soil and

vegetation samples. Approximately 50% of the vegetation samples have a transfer factor more than 0.5 for Pd, indicating a translocation of bioavailable Pd compounds from the soil through the root to the aerial vegetation part. The reported values for Pd and Rh in road dust are in the range of concentrations similar to other polluted traffic areas in Europe.

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