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SCREENING OF PLATINUM GROUP METALS FROM AUTOMOBILE CATALYSTS IN SOILS OF OSTRAVA CITY

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Research article

Abstract: Automobile catalysts are sources of platinum group metals (PGM) emissions into the environment. Since their introduction, the increase of PGM concentrations in different environmental matrices has been observed. This, together with the information about toxicity of Pt, Pd and Rh, raises concerns about possible health risks. To obtain input data on potential exposure to PGM, soil sampling methodology was developed and screening of PGM in soils was provided in the city of Ostrava at locations with different traffic load, including sites with potential exposure of children. The screening indicates that in immediate proximity to high traffic, increased Pt, Pd and Rh concentrations are observed.

Keywords: Soil contamination, Platinum group metals, Automobile catalysts, Ostrava.

Introduction

In the Czech Republic, automobile catalysts with platinum group metals (PGM) were introduced as a compulsory component of every new passenger car due to stricter emission limits EURO in 1993. In 2009, the number of vehicles equipped with catalysts comprised around 4 million of the total 6 million cars, with passenger cars and vans representing 90 % of all vehicles equipped with catalysts (CDV, 2010).

An automobile catalyst is a unit installed into the exhaust system of a car to reduce the production of gaseous pollutants, such as carbon monoxide, hydrocarbons and nitrogen oxides, by their transformation into harmless components - carbon dioxide, water vapor, and nitrogen gas. The exhaust gases purification takes place as a consequence of oxidation-reduction reactions, which are facilitated by the combination of heat with the platinum metals - platinum (Pt), palladium (Pd) and rhodium (Rh) - contained in this device. (Bliefert, 1994; AECC, 2011).

Currently, three way catalysts (TWCs) are mostly used (see Fig. 1). TWCs consist of a steel or ceramic carrier with a honeycomb structure, which is coated with a highly porous layer, the so called washcoat, made of aluminium oxide, which is resistant to high temperatures and to repeated temperature changes as well. A catalytic layer, consisting of finely dispersed platinum metals, is fixed on the washcoat surface. (Bliefert, 1994; AECC, 2011).

Fig. 1 Automobile catalyst (BOSAL CR, 2009)

There is no dispute that the application of automobile catalysts has an enormous contribution to environmental protection. However, the catalysts present the main source of environmental pollution by platinum metals. During the car operation, the catalyst surface is chemically and physically stressed by fast changing oxidative-reductive conditions, high temperature and mechanical abrasion, thus, producing the emission of PGM primarily to the air with consequent contamination of other environmental matrices (Ravindra et al., 2004).

Apart from automobile catalysts, additional major uses of PGM are in the glass, chemical, electrical, electronics and petroleum industries, the manufacture of jewelry, in medicine as cancer treatment drugs, and in dentistry as alloys. However, automobile catalysts are considered the most important source of environmental burden by PGM. (Ravindra et al., 2004; Wiseman and Zereini, 2009).

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Platinum group elements are released by catalysts together with exhaust gases mostly in the form of finely dispersed metal nanoparticles adsorbed on larger aluminium dioxide particles from the "washcoat" with emission rates of ng.km^{-1} (König et al., 1992; Moldovan et al. 1999; Artelt et al., 1999; Palacios et al., 2000; Moldovan et al., 2002). The amount and rate of PGM emission depend on many factors, such as driving conditions (i.e. the speed of a car, and the exhaust gases temperature), the type of the engine, the type and age of the catalyst (Artelt et al., 1999; Moldovan et al., 2002).

Great attention has been paid to the research of accumulation and distribution of PGM in the environment during the last 10 years. Many studies (e.g. Zereini et al., 2001; Cinti et al., 2002; Gómez et al., 2002; Leśniewska et al., 2004; Pan et al., 2009) have pointed out the significant increase of these precious metals in various environmental compartments. Cinti et al. (2002), for example, recorded 6-fold enhancement in the Pt levels of soil in 2001 in comparison with 1992. Zereini et al. (2001) observed an enhancement in the Pt and Pd levels in air over a 10-year period - Pt concentrations have increased 46-times and concentrations of Pd were 27-fold higher in 1998 than in 1988. With respect to the monitoring of PGM accumulation during the automobile catalyst usage, soil is the most commonly monitored matrice. A review of selected studies focused on PGM determination in soils is presented in Tab. 1. A comparison of results obtained in presented studies is not possible due to different locations, sampling conditions and analytical methods. However, following conclusions can be deduced:

- At sites exposed to traffic, PGM concentrations exceed the natural background levels,
- PGM concentrations decrease with the increasing distance from the road and with the increasing depth of sampling,
- PGM concentrations are in a strong correlation with traffic intensities.

The increase of PGM concentrations in the environment raises concerns over possible health risks. Platinum metals, especially soluble Pt compounds, are well known from working environment as substances with the ability to cause sensitization (Marhold, 1980; Nordberg et al., 2007). Certain Pt compounds exhibit toxic, carcinogenic and mutagenic effects (Nordberg et al., 2007). Metallic Pd is a dermal sensitizer causing contact dermatitis (Kielhorn et al., 2002). Since there is a little knowledge in the area of transformation, behavior, speciation and bioavailability of PGM in the environment and living organisms, it is difficult to make any conclusions with regard to health risks from environmental exposure to these metals. Thus, substances with uncertain hazards are released into the environment.

A review of recent knowledge with regard to the issue of environmental burden by the platinum group metals from transportation and related health risks was discussed in detail in Chemické listy journal (Sikorová et al., 2011).

A screening of PGM concentrations in soils is currently provided in the area of Ostrava city. The attention is focused on urban sites with traffic load and on urban sites with traffic load and the presence of child population. The reason why sites with children are considered is that child population is at high risk of exposure to harmful substances from contaminated soils (SZÚ, 2000 - 2007).

The aims of this contribution are to present a soil sampling methodology to determine platinum metals from automobile catalysts in the area of Ostrava city including the partial results, and to discuss some problematic aspects of environmental monitoring of these ultratrace elements.

Materials and methods

Sampling sites

Sampling sites were divided into three groups - sites with traffic load and the presence of children, locations with traffic load and without the presence of children, and finally sampling sites without traffic load and with the presence of children, so called background sites.

Kindergarten playgrounds, sports grounds and other playgrounds in residential areas and parks (their lists are not maintained) were considered sites with traffic load and the presence of child population. Lists of kindergartens and sports grounds and cartograms of traffic load from 2009 were obtained from the Ostrava City Authority. Traffic intensities gained from the cartograms were supplemented with nation-wide traffic census data from 2011. Kindergartens and sports grounds were reflected to an Ostrava city map with a road and motorway network in the program ArcGIS. For a field reconnaissance, kindergartens and sports grounds up to 200 m away from roads with traffic intensities ≥ 5 001 vehicles per day (vpd) were chosen - see Fig. 2. In total, 30 kindergartens and 18 sports grounds were selected. During field reconnaissance, other playgrounds in residential areas and parks were seeked out.

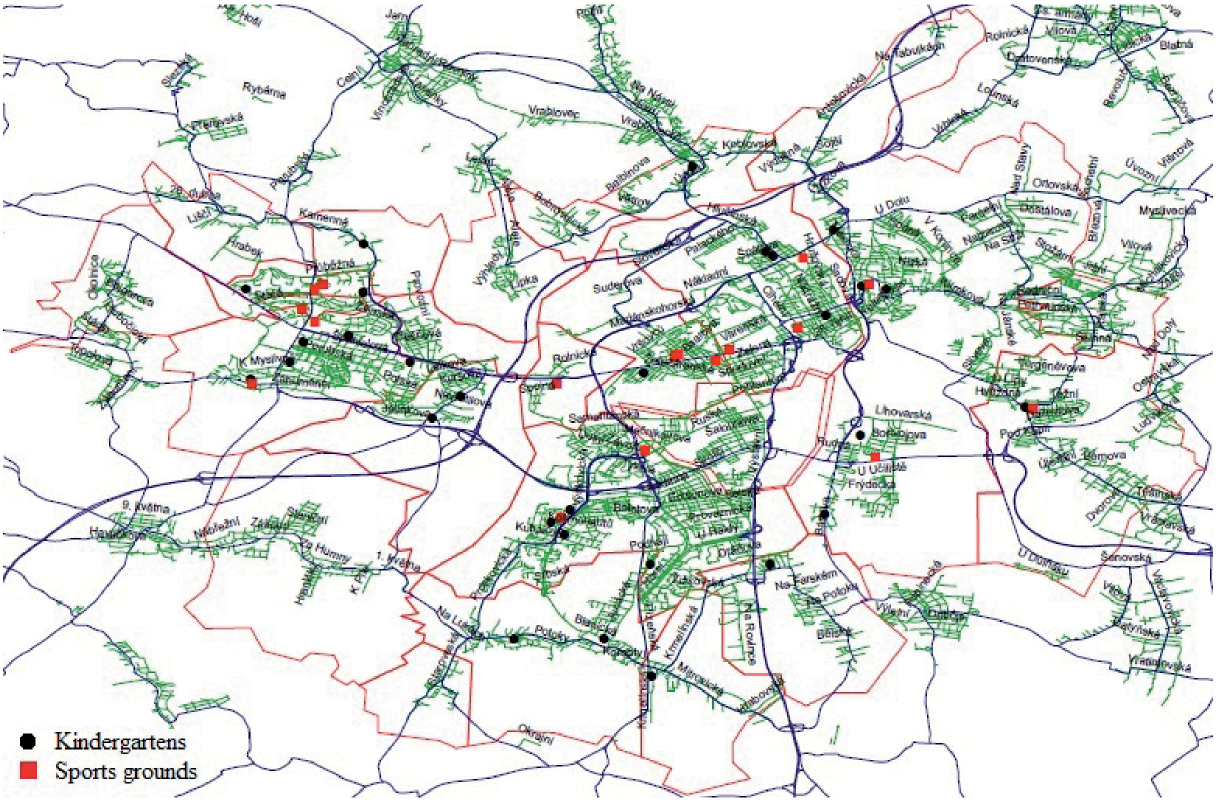

Fig. 2 Kindergartens and sports grounds in the area of Ostrava city chosen for the field reconnaissance

Tab. 1 Review of studies focused on monitoring of PGM in soils - methods and results

City - country (year of sampling)	**Sampling site**	**Samplingů**	**Analytical methods**	**PGM concentrations [ng.g^{-1}]**	**Ref.**
Beijing, Guangzhou, Hong Kong - China (2007)	Sites close to main roads in cities	50-100 g of soil scraped with a plastic trowel close to main roads (more information not available)	Nickel sulphide fire assay; ICP-MS	Beijing: Pt: 39.8 (7.6 - 126) Pd: 20.8 (3.38 - 57.5) Rh: 10.1 (0.97 - 31.4) Guangzhou: Pt: 35.1 (6.56 - 90.9) Pd: 39.9 (6.68 - 120) Rh: 12.1 (1.99 - 31.7) Hong Kong: Pt: 62.2 (15.4 - 160) Pd: 38.7 (6.93 - 107) Rh: 10.8 (1.61 - 34.5)	Pan et al., 2009
Mumbai, Kolkata - India (2007)	Sites close to main roads in cities	50 - 100 g of soil scraped with a plastic trowel close to main roads (more information not available)	Nickel sulphide fire assay; ICP-MS	Mumbai: Pt: 6.24 (3.20 - 9.40) Pd: 15.5 (1.32 - 42.4) Rh: 0.64 (0.24 - 1.36) Kolkata: Pt: 5.59 (2.59 - 9.43) Pd: 2.83 (1.31 - 4.07) Rh: 1.03 (0.40 - 2.27)	Pan et al., 2009
Sheffield - United Kingdom (2000-2006)	Sites close to roundabout and nearby woodland	1 sample down the slope of the roundabout (1 m away from the road), 1 sample in woodland 10 m away from the roundabout; depth of 5 cm	Lead fire assay collection; ICP-MS	Roundabout: Pt: 606 Pd: 1050 Rh: 210 Woodland: Pt: 8 Pd: 9 Rh: 2	Prichard et al., 2007

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Braunschweig - Germany (2005)	Motorway B 248: two-lane motorway, speed limit of 80 km.h^{-1}, 16 000 vpd; Gifhorner street: four-lane road, constant speed of about 50 km.h^{-1}, 230 000 vpd; Hagenring: four-lane road, average speed 40 - 60 km.h^{-1}, 35 000 vpd, traffic lights nearby (stop&go traffic); City park: local background	Motorway B 248: distances from the road: 0.1 m, 2.5 m, 5 m, 7.5 m, 10 m, 20 m, 50 m, depths: 0 - 2 cm, 2 - 5 cm, 5 - 10 cm; Gifhorner street: 0.1 m from the roadside and from the middle of the narrow center strip, depth 0 - 2 cm; Hagenring: 0.1 m from the roadside and from the middle of the center strip, depth 0 - 2 cm; City park: central part of the area, > 70 m away from a road	Nickel sulphide fire assay; ICP-MS	Motorway B 248: Pt_{max}: 50.4 Pd_{max}: 43.3 Rh_{max}: 10.7 Gifhorner street: Pt_{max}:88.9 Pd_{max}: 77.8 Rh_{max}: 17.6 Hagenring: Pt_{max}:261 Pd_{max}: 124 Rh_{max}: 38.9 City park: Pt: 1.10 Pd: 1.02 Rh: 0.10	Wichmann et al., 2007
Oxfordshire, London - United Kingdom (2000)	4 locations in Oxforshire: a main road to a busy roundabout; an intersection of a slip road with a main trunk road with heavy traffic (80 km.h^{-1}); a road from a busy roundabout; a dual carriageway 400 m away from an intersection; 1 location in London: a junction of the slip road with a busy dual carriageway with heavy and fast moving traffic	Distances: 0, 1, 2 a 5 m away from the road edge, from a single side (left) of the road; 10 cm wide and 5 m long strip of top soil - depth: 2 cm; Sampling equipment: stainless steel trowel	Microwave digestion with HNO_3 and H_2O_2; ICP-MS	All locations: 0 m: Pt: 15.9 ± 7.5 Pd: 120.8 ± 12.0 Rh: 22.4 ± 4.7 (1.7) 5 m: Pt: 2.04 ± 7.5 Pd: 84.2 ± 10.9 Rh: 3.5 ± 1.9	Hooda et al., 2007
Brno - Czech Republic (-)	20 locations in urban areas - factors considered: potencial risk of anthropogenic burden, morphology, microclimatic conditions and character of vegetation	Depths: 0 - 2, 0 - 5 a 0 - 20 cm; Composite samples from 5 subsamples, area of 10 m^2; Sampling equipment: soil probe	Nickel sulphide fire assay; ICP-MS	All locations: Pt: 0.4-39.6 Pd: 0.5-18.2 Rh: 0.05-4.89	Adamec et al., 2007
Athens - Greece (2003)	The Athens-Thessaloniki highway: very high traffic flow (48 756 vpd); The Iera Odos street: urban street with high-density traffic flow (36 510 vpd); A suburban street in Filothei suburb: very low traffic flow; A rural road in Marathonas rural area: low traffic flow	Central green-belts/ green-belts at the sides of the roads; 4 samples from each sampling site - 2 kg each; Depth: 0 - 5 cm; Sampling equipment: an acid washed plastic trowel	Lead fire assay; GF-AAS	Rural areas and suburbs: Pt: 2.0 (<0.1 - 8.4) Pd: 1.4 (<0.1 - 11.4) Highway: Pt: 141.1 (73.3 - 254) Pd: 125.9 (25.4 - 236) City: Pt: 93.5 (34 - 216) Pd: 80.7 (20.3 - 185)	Riga-Karandinos et al., 2006
São Paulo - Brazil (2002)	4 locations (31 km, 39 km, 45 km, 53 km) adjacent to a major road (SP348) with high-density traffic flow (ca. 30 000 vpd); Different driving conditions (constant speed vs. stop&go)	Depth: 0-5 cm; Distances: 0.4 m, 1.4 m, 2.4 m, 3.4 m, 4.4 m a 5.4 m; Composite samples from 5 subsamples - area of 20 m^2	NiS fire assay with Te coprecipitation; HR-ICP-MS	All locations: Pt: 0.3 - 17 Pd: 1.1 - 58 Rh: 0.07 - 8.2	Morcelli et al., 2005
Perth - Australia (2002 - 2003)	4 locations near roads (more information not available)	Depth: 0 - 1 cm; Area of 1 m^2; Sampling equipment: an acid washed plastic trowel	Microwave digestion with aqua regia; Separation of PGE from the matrix using ion exchange; ICP-MS	All locations: Pt: 13.9-153.2 Pd: 9.4-100.1 Rh: 1.2-22.6	Whiteley, 2005

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Perth - Australia (-)	5 locations with different traffic intensities (30 500 - 100 000 vpd) and driving conditions (stop&go, constant speed, mixed style) around Perth; Kings Park in the citry center (approx. 750 m away from any major road and 500 m away from the nearest park road) - a local background	Depth: 0 - 1 cm; Area of 1 m^2; Sampling equipment: an acid washed plastic trowel	Microwave digestion with aqua regia; Separation of PGE from the matrix using ion exchange; ICP-MS	5 locations: Pt: 30.96 - 153.20 Pd: 13.79 - 108.45 Rh: 3.47 - 26.55 Background: Pt: 1.21 ± 0.71 Pd: 1.62 ± 0.96 Rh: 0.31 ± 0.08	Whiteley and Murray, 2003
Napoli - Italy (2000)	Urban (city center - flower beds) and suburban locations	195 samples over an area of 120 km^2, grid of 0,5 x 0,5 km in the city and a grid of 1 x 1 km in the suburban areas; 3 sub-sites at distance of 10 m from each other at each site; Depth: 0 - 15 cm; 3 kg of soil	Digestion with aqua regia; ICP-MS	All locations: Pt: <2 - 52 (mean 4.2) Pd: <10 - 110 (mean 12.7)	Cicchella et al., 2003
Rome, Latium - Italy (1992 and 2001)	Urban area of Rome within the “Grande Raccordo Anulare”, the surrounding highway belt of the city - factors considered: traffic intensity, distance from the source, morphology, green area distribution and extension; Natural sites of Latium - local background	1 kg of soil at each site; Depth: 0 - 5 cm; Sampling equipment: plastic trowel	Microwave digestion with aqua regia; ICP-MS	Latium: Pt: 0.1 - 8.4 (3.1 ± 2.1) Rome - 1992: Pt: 0.8 - 6.3 (3.8 ± 1.0) Rome - 2001: Pt: 11.5 ± 4.7	Cinti et al., 2002
Mexico City - Mexico (-)	Areas close to heavily traveled roads and from side streets with lower traffic density; Different traffic conditions (low, high, constant speed, high stop&go speed) and different traffic intensities (60 - 200 vpd)	Different depths and distances from the roads (not specified)	Digestion with $HCl + HNO_3 + HF$; Seperation of PGE by Te precipitation with $SnCl_2$; ICP-MS	All locations: Pt: 1.1 - 332.7 Pd: 1.1 - 101.1 Rh: 0.2 - 39.1	Morton et al., 2001
Stuttgart, Heidelberg - Germany (-)	Sites next to highways, roads and urban areas - factors considered: traffic density, morphology, vegetation barriers and prevailing wind direction; The site near Stuttgart: 120 000 vpd, the site near Heidelberg: 100 000 vpd	Sampling along transects perpendicular to the traffic-lane in 3 depth ranges: 0 - 2 cm, 2 - 5 cm, 5 - 10 cm (more information not available)	Nickel sulphide fire assay; ICP-MS	All locations: Pt_{max}: several hundred $ng.g^{-1}$ Pd_{max}: 10 Rh_{max}: 35	Schäfer and Puchelt, 1998

The intersections, where roads with traffic intensities ≥ 10 001 vpd are crossed, were chosen as locations with traffic load without children. Twenty one intersections were selected in total. When seeking for background locations, the attention was paid to kindergarten playgrounds at least 1 km away from the communications with traffic intensities ≥ 5001 vpd. Eight background kindergartens were picked out for further reconnaissance.

In pursuance of reconnaissance, terrain openness to a communication and the presence of natural and anthropogenic barriers were observed.

A combination of three basic criteria was considered for the determination of locations with traffic load: high traffic intensity, short distance from a communication and high openness of a terrain, i.e. minimal presence of natural and anthropogenic barriers. A terrain disruption due to construction work, trees planting etc. was also taken into account. Based on the above mentioned criteria and the terrain survey, 11 kindergartens, 2 sports grounds, 2 playgrounds and 19 intersections were chosen for sampling. As background sites, locations without significant traffic load, far away from communications and maximally closed were selected. One background location is without industrial load, second one is with partial industrial load and the last one is without industrial load. Sampling locations overview is displayed in Tab. 2.

Sampling was carried out in two time stages. According to results from the first stage, further sampling strategy was specified. Locations, which were chosen in the first sampling stage, are highlighted in bold italic in Tab. 2. Their brief characteristics are presented in Tab. 3.

Tab. 2 Overview of sampling sites

Kindergartens		
Špálova	Petřkovice	Bílovecká
Polanecká	Kokešova	Keramická
Frýdecká	P. Lumumby	Výškovická
Poděbradova	Volgogradská	
Background kindergartens		
Družební	***Kalinová***	***Sládečkova***
Sports grounds		
Swimming pool Sareza - Poruba	Waterland Sareza - Mor. Ostrava	
Other playgrounds		
Jan Hus Park	***Playground Dubina***	
Intersections		
Opavská/ 17. listopadu	Rudná/Frýdecká	Českobratrská/ Bohumínská
Opavská/ Mariánskohorská	Rudná/Fryštácká	Bohumínská/ Těšínská
28. října/Místecká	Plzeňská/Výškovická	Horní/Dr. Martínka
Rudná/D1	Mariánskohorská/ Grmelova	Místecká/ Dr. Martínka
Rudná/Výškovická	Mariánskohorská/ Sokolská třída	Plzeňská/Horní
Rudná/Plzeňská	Muglinovská/ Bohumínská	
Rudná/Místecká	Hlučínská/Slovenská	

Sampling and sample preparation

First 10 soil samples were taken in June 2011 and analysed in July and August. The second round of sampling, when the rest of locations from Tab. 2 were sampled, was carried out in September 2011.

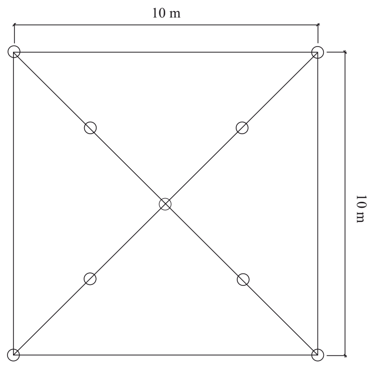

Fig. 3 Sampling scheme

Samples were taken as composite samples from 9 subsamples from the area of about 100 m^2 - usually square area of 10 x 10 m (see Fig. 3). The sampling depth was 5 cm.

Sampling was performed using a soil probe Eijkelkamp. The probe was hammered to the depth of ca. 10 cm, a monolith of sample was obtained after pulling out the probe with rotary motion and finally, a subsample of 5 cm length was cut off from the monolith on a clean plastic tray. Nine subsamples taken from each sampling site were put into polyethylene bags and transported to a laboratory at the Faculty of Safety Engineering.

In the laboratory, obtained composed samples were air-dried on filter papers at laboratory temperature, broken up using a mortar and a pestle and then sieved through a mesh screen of 2 mm and 1 mm. Homogenization and reduction to a sample weight of 100 g was carried out and finally, adjusted samples were handed over to laboratories of the Czech Geological Survey (CGS).

Analytical methods

At CGS, nickel sulphide fire assay technique was applied to preconcentration of PGM. With respect to ultratrace concentrations of PGM in the environment, this preconcentration step is very important. The principle of the technique is as follows: Samples are melted in a schamotte fire clay crucible with a mixture of sodium carbonate and anhydrous borax with addition of nickel and sulphur at 1100 °C. Present platinoids and gold are extracted into nickel sulphide, which is accumulated at the bottom of the crucible in a form of button. Afterwards, the crucible is cooled down and the NiS button is mechanically separated from the silica slag. Finally, the button is crushed and dissolved in HCl. Solid phase containing insoluble PGM sulphides is filtered off and dissolved in a mixture of HCl and H_2O_2. The resulting solutions are analysed.

The analyses were performed by ICP-MS in laboratories of the Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague. The instrumental detection limits were as follows: 2 $ng.g^{-1}$, 2 $ng.g^{-1}$, and 0.5 $ng.g^{-1}$ for Pt, Pd, and Rh, respectively. These isotopes were measured: ^{103}Rh, ^{105}Pd, ^{195}Pt.

Quality of analytical data was verified with the use of internal standards, since the certified reference material BCR 723 - Road dust was not available at the time of the analysis of the first samples.

Results and Discussion

Concentrations of platinum metals (Pt, Pd and Rh) measured in soil samples taken at locations with and without traffic load in Ostrava in June 2011 are listed in Tab. 3. Due to higher detection limits (following detection limits were considered:

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0.5 ng.g^{-1} for Pt and Pd, 0.05 ng.g^{-1} for Rh), the PGM concentrations were not determined in most samples. Detection limits of the whole analytical process are highly influenced by limits of blank from the preconcentration step. If optimal low values of analysed elements in blanks are not achieved (due to insufficient purity of chemicals, contamination of the environment and the apparatus from previous series with high PGM concentrations, etc.), low analyte contents can be covered and these is no possibility to determine particular concentrations in a real sample.

Since determined concentrations in most samples were not significantly higher that blank values and any reference material with certified PGM content was not analysed as well, only a few values of analysed elements were obtained. Platinum and palladium were determined in 3 samples (data are highlighted in bold - see Tab. 3), rhodium was not found in any of the samples. The measured values are in the range of 1.71 - 4.89 ng.g^{-1} and 1.61 - 2.99 ng.g^{-1} for Pt and Pd, respectively.

Local background levels of PGM are not known for Ostrava. Initially suggested background location "Kindergarten Sládečkova" probably does not represent the natural background, since values measured at this site are higher than concentrations measured near the busy intersection Rudná/Místecká. From the air quality maps of PM10 and PM 2.5, it was found out that this location is influenced by industry and it belongs to contaminated areas. Catalysts based on platinum with Pd content are commonly used in chemical industry, which is widespread in the Ostrava region. This can be the explanation of high PGM values at location without traffic load. It can be assumed that the second background location - Kindergarten Kalinová - could better represent the natural background. However, because of the high detection limits, there is not obvious difference between this location and sites with traffic load.

Tab. 3 Concentrations of platinum group metals in soil samples (Ostrava, June 2011)

Sampling site	Site characterization	PGM concentrations [ng.g^{-1}]		
		Pt	Pd	Rh
K[1] Výškovická	A central sampling point 230 m away from the communication "Výškovická" with traffic intensity 17 363 vph; playground partly opened - barriers: church building, deciduous trees	<2	<2	<0,5
K Špálova	A central sampling point 40 m away from the communication "Sokolská třída" with traffic intensity 15 212 vph; close to the intersection "Mariánskohorská/Sokolská třída" (stop&go); playground almost fully opened - barriers: low growing shrub	<2	<2	<0,5
K Polanecká	A central sampling point 23 m away from the communication "Polanecká" with traffic intensity 8 628 vph; playground almost fully opened - single barrier: lime tree	<2	<2	<0,5
K Kalinová	Background location with partial industry load; kindergarten in residential neighbourhood, forest park	<2	<2	<0,5
K Sládečkova	Background location with industry load; kindergarten in residential neighbourhood, forest park	**2,34**	**1,61**	<0,5
Swimming pool Sareza	A central sampling point 157 m away from the communication "Opavská" with traffic intensity 14 267 vph; playground opened, situated in a valley	<2	<2	<0,5
Jan Hus Park	A central sampling point 44 m away from the communication "Českobratrská" with traffic intensity 13 987 vph; close to the intersection "Českobratrská / Sokolská třída" (stop&go); playground almost fully opened - barriers: low growing shrub, deciduous trees	**4,89**	**2,99**	<0,5
Playground Dubina	A central sampling point 54 m away from the communication "Horní" with traffic intensity 19 365 vph; playground in housing estates, fully opened from "Horní"	<2	<2	<0,5
D1/Rudná	A central sampling point 22 m away from the communication "D1" with traffic intensity 11 382 vph and 33 m away from the communication "Rudná" with traffic intensity 23 864; new section of a highway, opened in 2007 - 2008	<2	<2	<0,5
Rudná/Místecká	A central sampling point 165 m away from the communication "Rudná" with traffic intensity 25 040 vph and 13 m away from the communication "Místecká" with traffic intensity 26 605 vph	**1,71**	**2,19**	<0,5

1 K - kindergarten

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The comparison of measured results with global average PGM abundances in the continental crust, which are generally less than 1 $ng.g^{-1}$ (Wadepohl, 1995), can point out the increase of PGM concentrations in Ostrava environment. However, the increase is not as high as it had been expected, especially at the intersection “Rudná/Místecká”. This intersection shows the highest traffic intensities in Ostrava and so the levels higher than 10 $ng.g^{-1}$ could be anticipated. Landscaping, which was probably performed at the location due to the reconstruction of tram tracks, could be the possible explanation for low measured concentrations. For now, information about particular terrain disruption was not definitely confirmed. It is considered a general problem to find out information about construction works and other changes at intersections and near communications, which could disrupt a terrain in the past. Concentrations of PGM measured at location “Jan Hus Park” are, with respect to the distance from the road and the traffic intensity, in good correlation with the values obtained in other countries (see Tab. 2).

Considering kindergarten playgrounds and their distances from communications (usually >50 m), PGM concentrations around 2 $ng.g^{-1}$ can be expected, which is in agreement with measured results. Nonetheless, particular values are not available due to high blank levels again, thus any clear conclusions cannot be drawn.

The most of foreign studies were focused on the determination of PGM in immediate proximity of communications with high traffic volumes. These studies showed that in a distance of >10 m, the PGE concentrations rapidly decrease. It was demonstrated, however, that PGM are released by catalysts also in the ultrafine fraction (Artelt et al., 1999) and so the air transport over longer distances from the source can not be excluded. The attempt of presented screening of PGM in Ostrava at locations with traffic load and the presence of children was, among other things, to point out the possible transport of fine PGM particles further away from the source. Unfortunately, results obtained so far do not enable to neither prove nor disprove this hypothesis.

The above results should have served to make a decision on further sampling strategy (2^{nd} phase of the study). Owing to small amount of obtained results and unclear conclusions, a strategy of the worst-case scenario was finally adopted, i.e. only intersections with the highest traffic intensities and kindergartens close to communications with higher traffic intensities (>10 000 vpd), opened as much as possible against roads were chosen. Sports grounds and other playgrounds were left out due to impossibility of exposure characteristics, such as number of exposed subjects and the time of exposure, determination.

Conclusion

Up to now, there in not unanimous opinion on whether or not platinum metals released by automobile catalysts can cause health risks, since information about their emissions, transport, deposition and transformations in the environment and human body is still at the beginning. Considering the precautionary principle, PGM should be regularly monitored in the environment in order to accept effective precautions if some adverse health effects arise. Special attention should be paid to children, as they are most vulnerable to environmental exposures to toxic substances.

The aim of the conducted screening of PGM in soils of Ostrava city, methods and partial results of which are presented in this contribution, is to provide the first overview of PGM concentrations in soils of the third largest city of the Czech Republic, which is highly influenced not only by traffic but also by industry. The study is concentrated on children as potentially exposed subjects of high sensitivity, since they are the part of the population, which can be highly influenced by contaminated soil. The foreign studies and previous Czech studies (see Tab. 2) were focused especially on immediate proximity of communications and only very rarely dealt with a potential exposure of the population to these metals. The screening conducted in Ostrava is the first of its kind solving the contamination of kindergarten playgrounds soils by PGM with respect to the potential exposure of children to these metals.

Only the first partial results of the conducted screening are presented in this contribution. A complete overview of results from the whole screening study will be published in professional literature as soon as data from the second sampling round will be available.

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References

Introduction to the technology for emissions control [online]. AECC Association for Emissions Control by Catalyst [cit. 2011-10-1]. Available at: http://www.aecc.eu/en/Technology/Introduction.html.

ADAMEC, V., SÁŇKA, M., ŠUCMANOVÁ, M., SCHWARZOVÁ, M., HUZLÍK, J., LIČBINSKÝ, R., EFFENBERGER, K. (2007). Obsahy kovů ze skupiny platiny v půdách intravilánu města Brna. In: *Sborník z konference Mikroelementy 2007*. Kouty, 3.-5.9.2007, pp. 67.

ARTELT, S., KOCK, H., KÖNIG, H. P., LEVSEN, K., ROSNER, G. (1999). Engine dynamometer experiments: platinum emissions from differently aged three-way catalytic converters. *Atmospheric Environment*. 1999, Vol. 33, pp. 3559-3567. ISSN 1352-2310.

BAREFOOT, R. R. (1997). Determination of platinum at trace levels in environmental and biological materials. *Environmental Science & Technology*. 1997, Vol. 31, pp. 309-314. ISSN 0013-936X.

BLIEFERT, C. (1994). *Umweltchemie*. VCH, Weinheim, New York, Basel, Cambridge, Tokio, 1994. ISBN 3-527-28692-6.

CICCHELLA, D., DE VIVO, B., LIMA, A. (2003). Palladium and platinum concentration in soils from the Napoli metropolitan area, Italy: possible effects of catalytic exhaust. *Science of the Total Environment*. 2003, Vol. 308, pp. 121-131. ISSN 0048-9697.

CINTI, D., ANGELONE, M., MASI, U., CREMISINI, C. (2002). Platinum levels in natural and urban soils from Rome and Latium (Italy): significance for pollution by automobile catalytic converter. *Science of the Total Environment*. 2002, Vol. 293, pp. 47-57. ISSN 0048-9697.

GÓMEZ, B., PALACIOS, M.A., GÓMEZ, M., SANCHEZ, J.L., MORRISON, G., RAUCH, S., MCLEOD, C., MA, R., CAROLI, S., ALIMONTI, A., PETRUCCI, F., BOCCA, B., SCHRAMEL, P., ZISCHKA, M., PETTERSON, C., WASS, U. (2002). Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities. *Science of the Total Environment*. 2002, Vol. 299, pp. 1-19. ISSN 0048-9697.

HOODA, P. S., MILLER, A., EDWARDS, A. C. (2007). The distribution of automobile catalysts-cast platinum, palladium and rhodium in soils adjacent to roads and their uptake by grass. *Science of the Total Environment*. 2007, Vol. 384, pp. 384-392. ISSN 0048-9697.

Internal Documents of the Company BOSAL CR, 2009.

KIELHORN, J., MELBER, C., KELLER, D., MANGELSDORF, I. (2002). Palladium - A review of exposure and effects to human health. *International Journal of Hygiene and Environmental Health*. October 2002, Vol. 205, pp. 417-432. ISSN 1438-4639.

KÖNIG, H. P., HERTEL, R. F., KOCH, W., ROSNER, G. (1992). Determination of platinum emissions from a three-way catalyst-equipped gasoline engine. *Atmospheric Environment. Part A. General Topics*. 1992, Vol. 26, pp. 741-745. ISSN 0960-1686.

LEŚNIEWSKA, B. A., GODLEWSKA-ŻYŁKIEWICZ, B., BOCCA, B., CAIMI, S., CAROLI, S., HULANICKI, A. (2004). Platinum, palladium and rhodium content in road dust, tunnel dust and common grass in Białistok area (Poland): a pilot study. *Science of the Total Environment*. 2004, Vol. 321, pp. 93-104. ISSN 0048-9697.

MARHOLD, J. (1980). *Přehled průmyslové toxikologie: anorganické látky*. 2. vyd. Praha: Avicenum, 1980.

MOLDOVAN, M., GÓMEZ, M. M., PALACIOS, M. A. (1999). Determination of platinum, rhodium and palladium in car exhaust fumes. *Journal of Analytical Atomic Spectrometry*. 1999, Vol. 14, pp. 1163-1169. ISSN (printed) 0267-9477. ISSN (electronic) 1364-5544.

MOLDOVAN, M., PALACIOS, M. A., GÓMEZ, M. M., MORISSON, G., RAUCH, S., MCLEOD, C., MA, R., CAROLI, S., ALIMONTI, A., PETRUCCI, F., BOCCA, B., SCHRAMEL, P., ZISCHKA, M., PETTERSSON, C., WASS, U., LUNA, M., SAENZ, J.C., SANTAMARÍA, J. (2002). Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. *Science of the Total Environment*. 2002, Vol. 296, pp. 199-208. ISSN 0048-9697.

MORCELLI, C. P. R., FIGUEIREDO, A. M. G., SARKIS, J. E. S., ENZWEILER, J., KAKAZU, M., SIGOLO, J.B. (2005). PGEs and other traffic-related elements in roadside soils from São Paulo, Brazil. *Science of the Total Environment*. 2005, Vol. 345, pp. 81-91. ISSN 0048-9697.

MORTON, O., PUCHELT, H., HERNÁNDEZ, E., LOUNEJEVA, E. (2001). Traffic-related platinum group elements (PGE) in soils from Mexico City. *Journal of Geochemical Exploration*. 2001, Vol. 72, pp. 223-227. ISSN 0375-6742.

NORDBERG, G. F., FOWLER, B. A., NORDBERG, M. et al. (2007). *Handbook on the Toxicology of Metals*. 3rd ed. Elsevier, 2007. ISBN 978-0-12-369413-3.

PALACIOS, M., GÓMEZ, M., MOLDOVAN, M., MORRISON, G., RAUCH, S., McLEOD, C., MA, R., LASERNA, J., LUCENA, P., CAROLI, S., ALIMONTI, A., PETRUCCI, F., BOCCA, B., SCHRAMEL, P., LUSTIG, S., ZISCHKA, M., WASS, U., STENBOM, B., LUNA, M., SAENZ, J. C., SANTAMARÍA, J., TORRENS, J. M. (2000). Platinum group elements: quantification in collected exhaust fumes and studies of catalyst surfaces. *Science of the Total Environment*. 2000, Vol. 257, pp. 1-15. ISSN 0048-9697.

PAN, S., ZHANG, G., SUN, Y, CHAKRABORTY, P. (2009). Accumulating characteristics of platinum group elements (PGE) in urban environments, China. *Science of the Total Environment*. 2009, Vol. 407, pp. 4248–4252. ISSN 0048-9697.

PRICHARD, H. M., JACKSON, M. T., SAMPSON, J. (2008). Dispersal and accumulation of Pt, Pd and Rh derived from a roundabout in Sheffield (UK): From stream to tidal estuary. *Science of the Total Environment*. 2008, Vol. 401, pp. 90-99. ISSN 0048-9697.

RAVINDRA, K., BENCS, L., VAN GRIEKEN, R. (2004). Platinum group elements in the environment and their health risk. *Science of the Total Environment*. 2004, Vol. 318, pp. 1-43. ISSN 0048-9697.

RIGA-KARANDINOS, A. N., SAITANIS, C. J., ARAPIS, G. (2006). First study of anthropogenic platinum group elements in roadside top-soils in Athens, Greece. *Water, Air and Soil Pollution*. 2006, Vol. 172, pp. 3-20. ISSN (printed) 0049-6979. ISSN (electronic) 1573-2932.

SCHÄFER, J., PUCHELT, H. (1998). Platinum-Group-Metals (PGM) emitted from automobile catalytic converters and their distribution in roadside soils. *Journal of Geochemical Exploration*. 1998, Vol. 64, pp. 307-314. ISSN 0375-6742.

SIKOROVÁ, L., LIČBINSKÝ, R., ADAMEC, V. (2011). Platinové kovy z automobilových katalyzátorů v životním prostředí. *Chemické Listy*. 2011, Vol. 105, pp. 361 - 366. ISSN 1213-7103, 0009-2770 (printed), 1803-2389 (CD-ROM).

Studie o vývoji dopravy z hlediska životního prostředí v České republice za rok 2009. Brno: CDV, 2010.

Systém monitorování zdravotního stavu obyvatelstva České republiky ve vztahu k životnímu prostředí. Souhrnné zprávy za roky 2000 - 2007 [online]. Praha: Státní zdravotní ústav, 2000-2007 [cit. 2011-10-1]. Available at: http://www.szu.cz/publikace/monitoring-zdravi-a-zivotniho-prostredi.

WEDEPOHL, K. H. (1995). The composition of the continental crust. *Geochimica et Cosmochimica Acta*. 1995, Vol. 59, pp. 1217-32. ISSN 0016-7037.

WHITELEY, J. D., MURRAY, F. (2003). Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia. *Science of the Total Environment*. 2003, Vol. 317, pp. 121–135. ISSN 0048-9697.

WHITELEY, J.D. (2005). Seasonal variability of platinum, palladium and rhodium (PGE) levels in road dusts and roadside soils, Perth, Western Australia. *Water, Air and Soil Pollution*. 2005, Vol. 160, pp. 77-93. ISSN (printed) 0049-6979. ISSN (electronic) 1573-2932.

WICHMANN, H., ANQUANDAH, G. A. K., SCHMIDT, C., ZACHMANN, D., BAHADIR, M. A. (2007). Increase of platinum group element concentrations in soils and airborne dust in an urban area in Germany. *Science of the Total Environment*. 2007, Vol. 388, pp. 121-127. ISSN 0048-9697.

WISEMAN, C. L. S., ZEREINI, F. (2009). Airborne particulate matter, platinum group elements and human health: A review of recent evidence. *Science of the Total Environment*. 2009, Vol. 407, pp. 2493-2500. ISSN 0048-9697.

ZEREINI, F., WISEMAN, C., ALT, F., MESSERSCHMIDT, J., MÜLLER, J., URBAN, H. (2001). Platinum and Rhodium Concentrations in Airborne Particulate Matter in Germany from 1988 to 1998. *Environmental Science & Technology*. 2001, Vol. 35, pp. 1996-2000. ISSN 0013-936X.