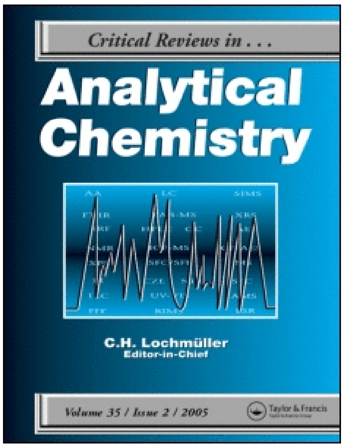

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Environmental Fate of Traffic-Derived Platinum Group Metals

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Environmental Fate of Traffic-Derived Platinum Group Metals

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Subsequently introduced standards on exhaust gas emissions determine the development of motorization industry as well as stimulate the search for new environmentally friendly solutions for road transport. One of such pro-environmental solutions, directed toward reducing emissions of toxic exhaust components, has been a project concerning application of catalytic exhaust gas converters in mechanical vehicles which contained platinum group metals (PGM). Despite undeniable benefits, application of PGM in gas converters is not a perfect solution because of the possible emission of these metals to the environment with exhausts. Presently the problem of increasing PGM content in the environment is the subject of interest of numerous research institute workers all over the world. Results of PGM determinations can form an exit point to run environmental impact assessment of road transport because most of PGM present in the environment comes from vehicle exhaust gas converters. Taking under consideration all of the above, there is a necessity of running wide studies to monitor concentration levels of this polluting group in biological and environmental samples.

Keywords Anthropogenic emission, catalysts, platinum group elements, environment

INTRODUCTION

One of the human basic areas of activity is road transportation, which on one hand is indispensable to meet many social needs and on the other hand is considered to belong to one of the greatest noxiousness of civilization. The greatest and most directly environmentally noticeable threat of motorization development is the emission of toxic substances such as oxides of carbon, nitrogen, and sulphur next to aromatic hydrocarbons, aldehydes, oil-derived hydrocarbons and heavy metals (cadmium, zinc, chromium, iron, lead, copper, nickel, vanadium, manganese).

The harmful substances emission levels connected with the road transport sector has considerably declined (by 24–35%) in parallel to introduction of catalytic exhaust gases converters in mid 1970s in USA and Japan and in 1980s in Europe (1). Presently there are two main types of catalysts distinguished:

- Catalysts of oxidizing character (joined with diesel engines), and
- Trifunctional (used in gasoline engines).

The process of transformation of toxic compounds in gas converters is catalyzed by a specific group of elements, namely Platinum Group Metals (PGM) (Pt, Pd, Rh and more rarely Ru and Ir). Unfavorable conditions of catalysts' work (too high temperature of exhaust gases, mechanical and chemical actions on their surfaces) cause emission of PGM to the environment.

Noble metals reaching the environment as a result of road traffic undergo deposition in particulate matter, road dust, soil, water, sediments and biota. One of the major transport pathways of this polluting group are rain waters and runoff waters resulting from them. Determined content levels of PGM in this type of samples can be the source of unusually important information concerning the bioavailable fraction of these analytes in the environment.

Results of realized studies can be the basis for stating that these metals show the ability to accumulate in living organisms' tissues and can result in numerous health defects (1–4). Taking into account both the increase of concentration levels of PGM in particular environmental compartments as well as the diversity of their toxic influence on living organisms, more and more often there appear statements about the necessity of introducing

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systematic monitoring of concentration levels of this pollutant group in environmental samples (1, 5, 6).

In recent years the amount of literature data concerning concentration levels of these metals in samples of particulate matter, road dust, soil and biota has noticeably increased. Until now, the state of the art on deposition values of these PGM in samples of atmospheric depositions, runoff and surface waters is very limited. Learning the content levels of PGM in these types of samples consists significant problem in studies directed to:

- Assess their spread pathways in the environment, and
- Assess effects of these metals on particular elements of both living and non-living parts of the environment.

SOURCES OF PGM EMISSION TO THE ENVIRONMENT

In the last decade there has been noted the significant increment of PGM concentration in particular types of environmental samples, such as (7–12):

- Particular matter,
- Soil,
- Road dust,
- Surface water,
- Plants, and
- Bottom sediments.

This situation results first of all from widespread use of platinum group elements (PGE) in different industrial branches. The main emission sources of PGE to the environment are automotive catalysts, industrial ones and hospital wastes (Fig. 1).

More detailed information on PGE emission sources' characteristics can be found in the following original and review papers (1, 5, 13–17).

MOBILITY OF PGM IN THE ENVIRONMENT

Until recently, there existed an opinion that the dominating majority of platinum released from catalysts is present in non-metallic form, thus inert one, and only to small extent in oxidized form, probably as Pt^{4+} (1, 18). It was stated that the presence of platinum at this oxidation level results from reaction of its metallic form, being present in active phase, with oxygen or air in 500°C. Nowadays it is thought that mobile fraction of PGE in exhaust gases constitutes a significant part, even a few tens of percent, of the total PGE emission (1, 19, 20).

PGE are present in catalysts in the form of very fine particles. Very small dimensions of these metals are more susceptible to action of factors that can increase their solubility, what makes the dissolved PGE content in exhaust gases increase in correlation to decrement of emitted particles size (20–22).

Furthermore, the percentage content of mobile forms of these metals in exhaust gases increases with the wear out level of the catalyst (16, 20, 22, 23). In some scientific circles there exists opinion that PGE emitted from catalysts in dissolved form constitute a group of the most toxic compounds of these metals—in a form of complexes with halogenated ligands (derived from fuel additives). The presence of carbonyl complexes is also suspected to occur (20).

For a long time it was believed that PGE emitted to the environment in metallic form, due to their chemical inertia, belong there unchanged. However, results of conducted studies devoted to solubility of selected chemical forms of PGE (including platinum black) prove that numerous factors can influence the increment of their bioavailability. Based on data contained in Table 1, it can be concluded that small part of metallic platinum present in the environment can undergo transformation into mobile form as a result of the solubilization process. A significant increase of PGE bioavailability in environmental samples can be observed in the presence of the following organic compounds:

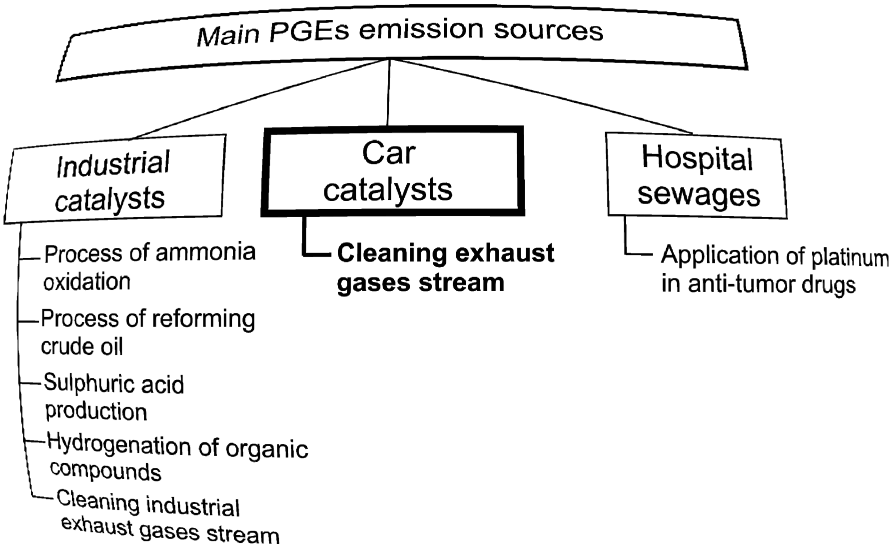

FIG. 1. Main emission sources of PGE to the environment.

TABLE 1
Solubility of selected chemical forms of PGE in model solutions and in environmental samples (22)

Type of samples tested	Solvent*	pH	Time of reaction	Soluble form (%) Pt	Pd	Rh	Litera-ture
Platinum black	H_2O*	~ 7	30 days	0.05	—	—	(27)
PtO_2	H_2O*	~ 7	30 days	0.25	—	—	
Tunnel dust	H_2O*	~ 7	30 days	3.90	—	—	
Disintegrated material of used catalyst	H_2O*	1	3 months	0.35–0.50	—	1.00	(28)
	H_2O*	3–9	3 months	0.01–0.025	—	0.05	
Platinum black	0.2 mol/L methionine	9	30 days	0.79	—	—	(29)
Road dust	0.2 mol/L $Na_5P_3O_{10}$	6–7	30 days	0.02	—	—	
	H_2O*	~ 7	30 days	1.5	—	—	
	0.2 mol/L methionine	9	30 days	2.7	—	—	
	0.2 mol/L $Na_5P_3O_{10}$	6–7	30 days	13.0	—	—	
Road dust	H_2O*	~ 7	15 hours	0.14	5.90	0.57	(30)
	Synthetic rain**	3	15 hours	0.48	35.4	1.21	
Road dust	1 mol/L NH_4NO_3	Unbuffered	24 hours	~ 30	—	—	(31)
Tunnel dust	1 mol/L NH_4NO_3/1 mol/L NH_4Ac	~ 6	24 hours	~ 42	—	—	
Soil samples spiked with catalytic converter	0.11 mol/L	Unbuffered	16 hours	<0.5	27–65	~ 2	(32)
	CH_3COOH/0.5 mol/L	1.5	16 hours				
		Unbuffered	1 hours				
Street dust	ClH_4NO/8.8 mol/L H_2O_2, 1 mol/L NH_4Ac	2.0		<10	61–70	10–22	(32)

*H_2O describes distilled or demineralized water

**Artificial (synthetic) rain contained the same ions that are present in natural rain water

humic acids, fulvic acids, acetates or siderofors (products of metabolism of fungi bacteria and higher plants, resulting in increasing iron bioavailability) (24, 25).

The second (in importance gradation) source of PGE in the environment are hospital and urban sewages. It was stated that most of the dose of a platinum-containing drug is excreted with urea not sooner than in patients house (app. 70%) (25) and there enters communal sewages. Cis-platinum applied to patients is excreted in a very active and cytotoxic form of monoaquacisplatinum and thus is present in this form in sewages (26). In water treatment plants most of platinum resulting from cytostatics (96% cis-platinum, 70% carboplatinum, and 74% oxaliplatinum) undergoes adsorption on active sludge. Thanks to this, the metal does not reach receiving waters (14, 25).

MIGRATION OF PGE IN DIFFERENT ENVIRONMENTAL COMPARTMENTS

Until now there is only limited number of works directed to assess:

- Bioavailability,
- Access routes by living organisms, and
- Environmental fate

of PGE coming from anthropogenic emission sources. This situation results mainly from ultra-low content levels of these metals in environmental samples and analytical problems occurring at the stage of sample preparation and analytes determination.

It seems that there are common opinions among experts on environmental mobility of PGE coming from exhaust gases converters—one that is limited although noticeable (25). PGE released from catalysts in metallic or oxidized form show slight toxic potential. However, the mobile fraction of the emitted metals, as well as the part that undergoes transformation into soluble forms already in the environment, constitute a serious threat both for the floral and faunal worlds (1). In Fig. 2 the schematic transport pathways of PGE coming from vehicles' exhaust systems are presented (5).

Air and Atmospheric Aerosols

Air is the first environmental compartment to which PGE migrate from sources related to vehicle traffic. PGE released from catalysts with exhaust gases reach the atmospheric air and are stopped in it and deposited on solid particles. After some time of being in the atmosphere, dust and suspended matter are removed as a result of wet or dry deposition. The process of wet deposition occurs by flushing pollutants out by

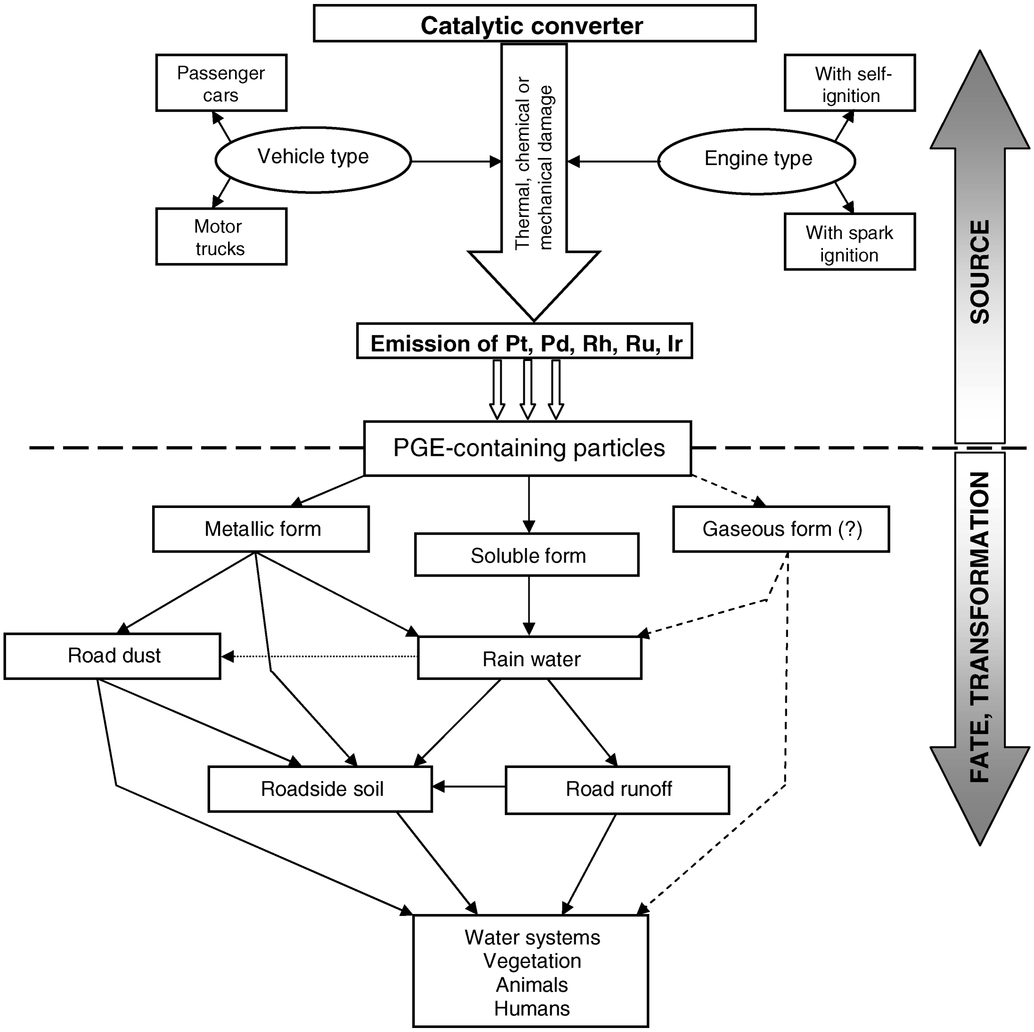

FIG. 2. PGE circulation coming from vehicle catalysts in the environment.

atmospheric precipitation, while dry deposition mainly results from gravitational falling. Wet and dry deposition of PGE can cover the areas within a few hundred kilometers of the source (33).

The first scientific reports on platinum and palladium concentrations in air come from the 1970s (from a period prior to the introduction of vehicle catalysts) and are related to air samples collected in the proximity of arteries with a high traffic intensity (concentrations determined were <0.05 and <0.06 pg/m^3, respectively, for Pt and Pd) (1, 34, 35). In Europe, prior to introducing car catalysts, the concentration level of platinum was below limits of determination of known analytical techniques (0.05–1.0 pg/m^3) (1). Presently, the platinum concentration in samples of particulate matter in air is much higher reaching values of a few ten to a few hundred pg/m^3 (Table 2).

Worrisome high platinum concentrations (33 pg/m^3) in urban areas are proved by the results of analysis of air samples collected in the interior of city buses (in Munich, Germany) coursing at the most jammed routes (1, 46). In Germany, a significant increment (27 folds) of rhodium concentration in air during the 10-year period of 1988–1998 was also observed (1, 21). In Table 2, literature data on PGE concentration in samples of suspended matter are presented. The relatively high spread of results is connected with:

- Differentiated sampling points localization,
- Different traffic conditions,
- Differences in fraction characteristics (molecule size) of collected aerosol samples.

Information contained in recently published works constitute a good basis for proving the thesis that fine particles containing noble metals can be transported for long distances. High PGE concentrations were determined among others in pitbogs in a 250–500 m distance from the nearest communication

TABLE 2
Literature data on PGE content in atmospheric aerosols collected in different city agglomerations (1)

Sampling place	Sampling date	Characteristics of sampling points surroundings	Concentration [pg·m^{-3}] Pt	Pd	Rh	Literature
Dortmund (Germany)	1991–1992	Urban area fastway	0.02–5.1	—	—	(36)
			30			
Berlin (Germany)	1997	Urban area	—	0.2–14.6	—	(37)
Göteborg (Sweden)	1999	Urban area, PM$_{10}$	0.9-19	0.1–10	0.3–4	(38)
Rome (Italy)	1999–2000	Urban area	7.8–38.8	21.2–85.7	2.2–5.8	(39)
Stuttgart (Germany)	1997	Urban area	68$^{1)}$	—	8^{1}	(40)
Madrid (Spain)	2002	Highway M-30, PM$_{10}$	15	5.1	27	(41)
		Suburban area, PM$_{10}$	19	32	9.1	
Vienna	2002	Area with high PM$_{10}$	4.3	2.6	0.4	(42)
		traffic intensity <30 μm	38.1	14.4	6.6	
Kopenhagen	1993	Area with high traffic	13	—	—	(43)
(Denmark)	1995–1997	intensity	250–2740			
Czechy	—	Meteorological stations	9–62	23–283	—	(44)
China	2004	Suburban area	5.9–38.2	—	—	(45)
Muenchen (Germany)	1993–1994	Interiors of buses and	7.3^{2}			
	1995–1996	trams	<LOD-43.1	—	—	(46)
			21.5^{2}	—	—	

[1] Concentration in ng/g
[2] Average concentration

routes (47). Increasing concentrations of PGE in the environment for the period of time of hundreds of years are also proved by results of analysis of ice core samples collected from the Alps, Antarctic and Greenland (Fig. 3) (25). Representatives of several scientific circles state that in a roads' proximity less than 5% of total deposition of these metals occur, while a major role in transferring this pollutant group to the environment is played by transborder transport (48).

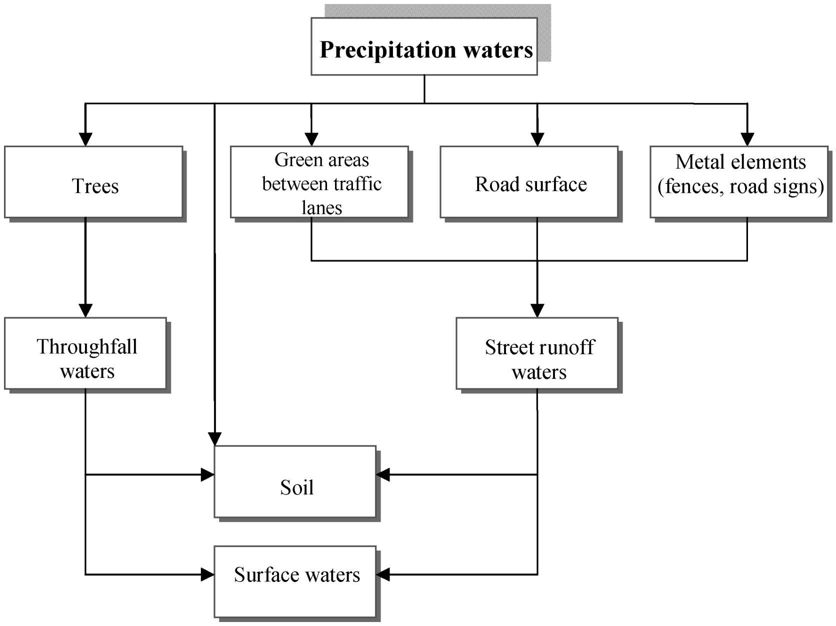

FIG. 3. PGE transport routes with precipitation waters.

TABLE 3
Literature data on PGE concentration levels in samples of road dust and soil (1)

Sampling place	Sampling date	Characteristics of sampling place surroundings	Concentration (ng/g) Pt	Pd	Rh	Literature
Road dust						
San Diego (USA)	1985	Highway	100–680	38–280	—	(65)
Göteborg (Sweden)	1991	Parking lot fastway <63 μm	26[1]			(66)
	1998		196 ± 22	80 ± 13	93 ± 15	(67)
England	—	Fastway (London suburbs)	0.35–32.7	—	—	(68)
Germany	—	highway fastway	1000	1–146	110	(69)
Karlsruhe (Germany)	1997	—	112–169			(70)
Scotland (England)	1999	Roads with high and medium traffic intensity	1.8–335.1	—	—	(71)
Frankfurt (Germany)	1994	—		6–117		(28)
	1995		170			
Madrid (Spain)	—	city ring road <65 μm		39–191		(72)
Rome (Italy)	—	urban area	14.4–62.2	102–504		(39)
Germany	1999	A-1 highway	303 ± 40	95 ± 2	—	(73)
		A-61 highway	280 ± 20	82 ± 7		
		cB-262 road	269 ± 20	60 ± 4		
Białystok (Poland)	2000–2001	Road with traffic intensity app. 30 k vehicles/day	34.2–110.9	32.8–42.2	6.0–19.7	(74)
Perth (Australia)	2000	Road with diversified traffic (12–100 k vehicles/day)	53.84–419	58.2–440.5	8.8–91.4	(75)
Göteborg (Sweden)	1999–2000	Roads with high and medium traffic intensity	325.5	70.8	101.8	(76)
Madrid (Spain)			317	202.7	74	
Rome (Italy)			34.0		4.8	
Muenchen (Germany)			178.8		31.2	
Londyn (Anglia)			73.7			
Tunnel dust						
Białystok (Poland)	2000–2001	City tunnel (28 k vehicles/day)	4.17–23.3	3.1–23.9	6.76 ± 1.28	(74)
Austria	—	Tunnel's ceiling	68.2	—	—	(77)
Styria (Austria)	1994	Ventilation shaft	55	4.0	10.3	(78)
	1998		81	5.5	12.8	
Japan	1987	—	170	297	—	(40)
Soil						
Germany	—	Area in highway's vicinity	27	—	—	(79)
Road A3 Frankfurt-Köln	—	16 k vehicles/day	330 ± 223 —	—	— —	(80)

(Continued on next page)

TABLE 3
Literature data on PGE concentration levels in samples of road dust and soil (1) *(Continued)*

Sampling place	Sampling date	Characteristics of sampling place surroundings	Concentration (ng/g)			Literature
			Pt	Pd	Rh	
Road Wiesbadener-Kreuz (Germany)				6.6 ± 0.19		
Germany	—	Barren lands	0.03–0.26	—	—	(81)
		Cultivated lands	0.15–3.9			
		Land in road proximity	15.6–31.7			
Hanau (Germany)	1995	Area in highway's vicinity	23–112	—	—	(82)
Frankfurt (Germany)	—	Area in highway's vicinity	72	6	18	(83)
Rome (Italy)	1992	Area with high traffic intenisty	0.8–6.3	—	—	(84)
	2001		7.0–23.7			
Mainz (Germany)		BAB66 highway				(85)
		0.6 m from the road	87 ± 17	7.2 ± 1.5		
		1.8 m from the road	8.7 ± 1.5	1.2 ± 0.3		
		3.0 m from the road	2.5 ± 1.4	1.1 ± 0.5		
Road Braunschweig –Wolfsburg (Germany)	2005	16 k vehicles/day	50.40	43.30	10.7	(86)
		Pojazdów/doba				
		layer 0–2 cm	19.30	17.60	4.45	
		0.1 m from the road	4.90	3.18	1.10	
		2.5 m from the road	2.10	0.89	0.29	
		5 m from the road	4.00	0.90	0.18	
		10 m from the road				
		50 m from the road				
Perth (Australia)	2000	Road with diversified traffic (12–100 k vehicles/day)	31–153	13.79–108.4	3.5–26.5	(75)

[1] ng/m

Road Dust and Soil

Road dust is second after the air environmental component that receives PGM coming from vehicle catalysts. The chemical composition of road dust samples has significantly changed (as far as trace components are concerned) during the last decade (1998–2005); it reflects decreasing lead content (by 50%) and detectable and continuously increasing platinum concentrations (49). Results of the studies represent a comprehensive source of information on fact that the platinum content in environmental compartments localized in roads' proximity has increased 90 times when compared to the biogeochemical background concentration already 5 years after introducing vehicle catalysts. Results of monitoring studies conducted on areas localized in highways' proximity in Austria, Belgium, Sweden, Germany and Great Britain show that within 10 years the platinum concentration in samples of road dust, sediments and plants has increased 3–6 fold (50). What is more, analytical information gained due to road dust analysis show that PGE content level in this type of sample is characterized by an increasing trend with time and in the easily observed way correlates to (1):

- Road traffic intensity,
- Atmospheric conditions, and
- Type of pavement sampled.

In Table 3 the literature data are presented with respect to concentration levels of PGE in samples of road dust and soil.

Soil is one of the most important environmental compartments to which PGE reach. Anthropogenic emission of PGE leads to a significant increase of their concentration in soils located in roads' proximity. This process can be observed by comparing mean platinum concentration in samples of different types of soil (28, 51):

- Barren lands—0.14 μg/kg,
- Cultivated lands—1.1 μg/kg, and
- Soil coming from area localized in road proximity—20.9 μg/kg.

Distribution of PGE in soils adjacent to communication arteries is similar to one of other heavy metals emitted from sources connected to road traffic and shows direct correlation to traffic intensity and road conditions (49, 52–54). Results of PGE determinations in soil samples prove that Pt, Pd and Rh concentrations decrease with distance from communication routes, while the soil strip characterized by the highest concentrations of these metals is placed in close distance from the road curb (0–2 m) (55). PGE content in soils decreases also with sampling depth (8, 56), which can prove a small migration of PGE in this environmental compartment (28).

Physicochemical characteristics of soil is of key significance for bioavailability, because processes of chemical transformations into easily or poorly available forms taking place in it decide about further PGE migration routes in the environment (57). Mobility of PGE mobility in soil depends on numerous factors, like pH, redox potential, soil salinity. Mechanisms of transformation of metallic forms of PGM and their relationship with bioavailable forms relies usually on:

- Chemical oxidation and complexation reactions by organic ligands present in soil, and
- Biochemical transformations (with microbial assistance).

It was shown that several naturally occurring organic ligands influence the bioavailability of platinum and palladium, namely L-methionine, fulvic acids, humic acids, siderofors (25, 29, 58, 59). The presence of humic acids in the soil leads to platinum salts immobilization in the forms of poorly soluble organic complexes. Furthermore, organic compounds like EDTA or thiourea present in the soil influence the Pt and Pd bioavailability increment by even 50% (27). Besides, as already mentioned, one of routes of emerging bioavailable forms of PGE is the process of biomethylation of these elements by bacteria present in the soil (60–64).

Aqueous Environment

An increased concentration of PGE, related mainly to emission of these metals from vehicle catalysts, was determined in collected samples of numerous aqueous ecosystems like atmospheric, surface, sea, ground, drinking waters, sewages and river, ocean and sewage sediments (1, 87–89) (Table 4). Runoff waters resulting from atmospheric precipitation are characterized by relatively high PGE concentration and constitute a second (after atmospheric deposition) medium enabling transport of these metals in the environment (62) (Fig. 3).

Knowledge of concentration levels of PGM in atmospheric water samples, particularly in runoff waters from communication arteries, is of key significance for assessing the bioavailable fraction amount of these analytes coming from exhaust gases converters. PGE content in this type of sample depends on many factors, just to mention a few:

- Distance from emission source,
- Daily traffic intensity,
- Type of sampled road pavement,
- Terrain type in vicinity of communication artery,
- Load of pollutants present in the precipitate, and
- Climatic conditions.

In urban areas PGE transported with runoff waters are drained into sink basins, dewatering gutters and impounding reservoirs of storm waters. Sewage sediments present in these types of reservoirs are most often characterized with much higher platinum concentrations when compared to supernatant waters (even by a factor of 4000) (57, 90). In Table 4, there are presented literature data related to concentration levels of PGE in analyzed samples of waters and bottom sediments.

Migration of PGE in the aqueous ecosystem depends on chemical forms of their occurrence as well as on environmental conditions. The essential parameter reflecting mobility of these metals compounds is their solubility. Results of studies on the solubility of PGE present in the grinded catalyst material and exposed to action of precipitate water of different pH can be the basis for the statement that platinum and rhodium show the greatest mobility in a strongly acidic environment (pH = 1) (28, 57, 91). However, results on solubility of palladium present in road dust prove that in the presence of precipitate water of low pH (pH = 3) 30% of this metal becomes mobile form. Under natural conditions, when pH of precipitate water is within the range 5–8, platinum does not dissolve. Thr presence of salt (NaCl) in samples of rain water has only slightly influenced the mobility of platinum (57). These results show that seasonal variations of atmospheric waters content (e.g., due to application of deicing salts) don't influence platinum and rhodium solubility.

PGM can also form complex bonds with organic matter present in waters (e.g., palladium shows affinity to fulvic acids similar to one of mercury and copper). Results of studies conducted prove the thesis that dissolved organic compounds present in water stabilize both palladium (92) and platinum (63) by binding them in the form of complexes. Due to a lack of complexing substances, the dominating form of palladium in a wide pH range is $Pd(OH)_2$, while in the presence of chloride ions, the dominating form is a mixture of chlorides and chloride and hydroxychloride complexes (e.g., $PdCl_2$, $[PdCl_4]^{2-}$, $[PdCl_3(OH)]^{2-}$). Relatively strong complexes are also formed by rhodium ($[RhCl_{6-x}(H_2O)_x]^{x-3}$, where $0 \leq x \leq 6$) and platinum ($[PtCl_5(OH)]^{2-}$) (92–94).

Results of studies conducted under laboratory conditions showed that in water reservoirs PGE undergo partitioning

TABLE 4
Literature data on determined PGE concentration levels in samples of water and sediments [2].

Sampling place/date	Characteristics of sampling place surroundings	Concentration			Literature
		Pt	Pd	Rh	
		Sea water			
Pacific Ocean	—	—	40 pg/L	—	(95)
Pacific Ocean	—	150 pg/L	—	—	(96)
Menai Straits (Indian Ocean) (1986)	depth 6 m	37 pg/L	—	—	(97)
	Depth 2000 m	154 pmol/L			
Indian Ocean	Depth <500 m	74 pg/kg	—	—	(98)
Indian Ocean	Depth <500 m	55 pg/kg	—	—	(99)
Baltic Sea	—	2.2 ng/L	—	—	(100)
California Coast	Surface layer depth 4500 m	100 pg/L 250 pg/L	—	—	(101)
		River water			
Rhine, Schwarzach (Germany)	—	—	0.4 ng/L	—	(102)
Germany	—	0.22–0.64 ng/L	—	—	(103)
Göteborg (Sweden)	Close to parking lot	—	10.2 ng/L	—	(10)
		Drinking/ground water*			
Liverpool (England)	—	58.5 pmol/L	—	—	(97)
Germany	—	0.1 ng/L	—	—	(103)
Germany*		3–38 ng/L	—	—	(103)
Anglia		0.2 μg/L	—	—	(104)
Germany	Place distant from road traffic	1.0×10^{-4} ng/g^{-1}	—	—	(81)
Germany	Precipitation water	1.4–74.5 ng/L	—	—	(103)
Germany	Precipitation water	<5 ng/L	<5 ng/L		(105)
Germany	Precipitation water, place distinct from road	$8–17 \times 10^{-5}$ ng/g	—	—	(81)
Germany	Street runoff waters	15–1600 ng/L $x_{śr}$–117 ng/L	—	—	(106)
Germany	Street runoff waters (at the end of rainy period)	2 ng/L	—	—	(106)
		Atmospheric waters			
Grenlandia, Alps	Snow	0.0008–2.7 pg/g	—	—	(12) (107)
Mont Blanc	Snow, ice	0.08–0.62 pg/g	0.01–16.9 pg/g	0.0005–0.39 pg/g	(108)
		Sewage waters			
Germany (1994–1995)	Raw sewage		—	—	(109)
	Arid period	8.1–41.8 ng/L			
	Rain period	10.3–91.7 ng/L			

(Continued on next page)

TABLE 4

Literature data on determined PGE concentration levels in samples of water and sediments [2]. *(Continued)*

Sampling place/date	Characteristics of sampling place surroundings	Concentration			Literature
		Pt	Pd	Rh	
Germany	Secondary sewages		—	—	(110)
	Arid period	4.4–9.2 ng/L			
	Rain period	8.2–12.4 ng/L			
	Hospital sewages				
	Day time	110–176 ng/L			
	Night time	38 ng/L			
		Sediments			
Sweden	River sediment (city area)	4.8–15 ng/g	—	2.5 ng/g	(111)
Mölnda River, Göteborg (Sweden) (1998)	—	—	13.9 ng/g	0.67 ng/g	(112)
Mölnda River, (Sweden) (1999)	—	53.9 ng/g	38.7 ng/g	9.4 ng/g	(113)
Boston Harbour (USA)	1987	4.2 ng/g	19.93 ng/g	—	(114)
	1993	4.62 ng/g	3.24 ng/g		
	1996	3.75 ng/g	4.22 ng/g		
Stour River, (England) (1999)	River sediments from road runoffs	<0.29–4.42 ng/g	0.08–5.71 ng/g	<0.11–0.26 ng/g	(115)
Australia	River sediments from road runoffs	9.03–103.80 ng/g	5.41–61.2 ng/g	1.59–17.2 ng/g	(116)

between aqueous phase (fraction of diameter less than 0.45 μm) and solid phase (fraction coagulated and fraction with diameter greater than 0.45 μm, adsorbed onto solid particles of the sediment). With increasing salinity level and chloride ions concentration, the process of palladium and rhodium adsorption on surfaces of sediment samples also increased in opposition to platinum, whose content in the solid phase was decreasing (25, 92). Studies on the adsorption/desorption process were also conducted by introducing bottom sediment into a river water sample spiked with a known amount of platinum, palladium and rhodium. It was stated that after reaching an equilibrium state PGE mobility increased in the following order: Pt $<$ Rh $<$ Pd. Furthermore, adsorption level of metals on sediment material differed depending on analyte chemical form; inorganic complexes were more easily sorbed when compared to complexing with organic matter (25, 92).

Plant Organisms

Plants constitute the first link of the human food chain and for this reason learning about the possibility of plants assimilating PGE from soil and the level of their accumulation in particular plant parts is important in terms of human health.

The assimilation of heavy metals immobilized by organic matter contained in the soil takes place mainly due to the presence of complexing agents present in plants' root systems. Available literature data prove that PGE (most particularly Pd) are transported from soil to plants by roots due to binding with large mass molecules containing sulphur (64, 117). The process of PGE accumulation takes place first of all in vegetative parts of plants and decreases in the following order: roots > stalks > leaves. Furthermore, greater amounts of PGE accumulate in the surface layer of underground parts of plants (25, 50, 118). The type of plant species is also not meaningless—bifoliate plants, due to better developed vascular transport systems, are capable of assimilating and accumulating greater amounts of metals when compared to monofoliate plants (119).

Results of studies of samples of plants (cress, spinach, nettle) cultivated on soil collected from highways shoulders show that palladium is characterized with the highest bioavailability, followed by rhodium and platinum (25, 64, 118). Determined coefficients of bioaccumulation (defined as the ratio of element concentration in plant material to its concentration in soil at the habitat of a given plant) place PGE between metals poorly available and medium available for plants (with mobility close to Cu and Ni) (118, 120). Also, the chemical form influences availability of PGE by plants. In the case of platinum the most poorly assimilable form is metallic platinum; PtCl4 is more easy assimilable while complex $Pt(NH_3)_4(NO_3)_2$ is most easily assimilable (57).

Not only land plants but also aquatic plants show the ability to accumulate PGM. The concentration of PGE in water hyacinth (*Eichhornia crassipes*) was increasing with increments of these metals' concentration in broth. Just like for land plants, toxicity of PGE depends on their chemical form and increases in the following order Rh (III)≪Os (IV)∼Pt (IV)<Ir (III)∼Ru (II)∼Ru (III)<Pd (II), Pt (II) (121).

The presence of PGE is being observed mainly in plants growing in areas in the vicinity of busy streets and highways. Results of studies conducted on moss samples (122) and grass collected a few tens of centimeters from the road shoulder (81) prove that one of the main sources of platinum emissions to the environment are catalysts, as the correlation between amounts of cars equipped with gas converters and platinum concentration increments in plant material samples was observed.

High PGE concentration levels in studied plant samples are not only the result of assimilating metals from the soil or water but also result from sedimentation of these pollutants on plants' surfaces. Results of studies relying on verification of high PGE concentration levels in plants do not lead to equivocal conclusions: in several works there were observed 2–3 times lower PGE content after washing sampled plant material while in other works the results were presented where concentration of these metals in cleaned plant samples has not changed (55, 120, 123).

Summing up presented literature information it can be stated that the toxicity of PGM coming from road transport, related to plants, depends on the following conditions:

- Metal concentration in soil,
- Exposure time,
- Chemical form of the metal,
- Soil chemical composition, and
- Plant species.

In Table 5 there are presented selected literature data on PGE concentration levels in plant material samples.

Animal Organisms

Data dealing with the toxic effects of PGE on animal organisms under natural conditions are very fragmentary. Most of the literature information on toxicity of PGE toward animals comes from experiments conducted in the laboratory. Basic knowledge on concentration levels of PGE in animal tissues and toxic

TABLE 5
Literature data on PGE content in samples of plant material collected in areas characterized with high traffic intensity

Type of plant material	Sampling place/date	Concentration (ng/g) Pt	Pd	Rh	Literature
Grass	Poland (2000–2001)	8.98 ± 0.39 8.27 ± 0.83	3.20 ± 0.23	0.68 ± 0.18 0.63 ± 0.07	(74)
Grass	Germany	2.9	—	—	(124)
Grass	Belgium	1.4–1.7	—	—	(117)
Grass	Germany	0.14–0.29	—	—	(81)
Bark	England	0.1–5.4 Średnia 1.5	1.6–3.2 Średnia 2.1	<0.05–1.8	(125)
Pine, birch, grass	Germany (1995–1996)	12	2	2	(126)
Pine's needles	Italy (2000)	1–102	1–45	—	(127)
Tomato (peeled)	Germany	0.10	—	—	(81)
Carrot	Germany	0.31	—	—	(81)
Cabbage	Germany	1.1	—	—	(81)
Lettuce	Germany	2.1	—	—	(81)
Celery	Germany	1.3	—	—	(81)
Onion (peeled)	Germany	0.03	—	—	(81)
Dandelion	Germany (1999)	5.4–30	0.83–1.5	2.0–7.0	(128)
Greater plantain	Germany (1999)	3.6–10.1	0.45–2.1	1.1–3.4	(128)
Mushrooms	Germany (1999)	5.9 ± 0.6	0.2 ± 0.1	0.5 ± 0.1	(128)
Moss	Germany (1999)	30 ± 2	2.4 ± 0.3	5.4 ± 0.5	(128)
Ryegrass	Germany (1999)	4.6–5.8	0.10 ± 0.3	2.1–2.2	(128)
Ryegrass	Germany	1.5	—	—	(129)

effects of exposure to these metals is insufficient in order to assess toxic potential of PGE in relation to human organism.

Platinum was stated to be present in organisms of molluscs (*Lumbricus terrestris* and *Lumbricus rubellus*) habituating the shoulder of fastways (120, 130). Furthermore, it was stated that PGE adsorbed on sediment particles can be assimilated by organisms feeding at the bottom of water reservoirs, such as bivalves (*Dreissena polymorpha*) or crustaceans (*Asellus aquaticus*), while Pd is the most easily available element, followed by Pt and Rh (25, 160).

It was also proved that aquatic organisms are capable of assimilating PGE from environmental samples (tunnel dust, road dust, bottom sediments). It was observed that the accumulation degree of metals increases with analyte and exposure time increments as well as being dependent on water chemical composition (113, 120, 131). Furthermore, bioavailability of platinum coming from bottom sediments was stated to be greater than one of platinum from road dust (25, 113). Results of studies of the palladium bioaccumulation coefficient (defined as the ratio of palladium concentration in tissue to the concentration of road dust) in relation to bivalves (*Dreissena polymorpha*) showed that it is only 3 to 10 times lower than for other metals like Pb, Sb, Cd or Fe (176). Results of similar studies conducted with the use of crustaceans (*G. pulex*) showed that the platinum bioaccumulation factor is of the same level as for zinc (33). The ability to assimilate PGE [salts (Pt (IV) and Rh (III)] by fish was assessed with the application of European eel (*Anguilla anguilla*). Elevated platinum and rhodium concentration in tissues where normally heavy metals accumulate was observed; these tissues are liver, intestines, kidneys, and gills (120, 133, 134). Furthermore, it was stated that European eels are able to accumulate palladium present in road dust. This metal was found in the liver, while it was not detected in the kidneys of organisms exposed.

The ability to bioaccumulate platinum and rhodium in organisms of parasites (*Paratenuisentis ambiguus*) of European eels exposed to catalysts feed was also assessed. 50– and 1600-fold increases of these metal concentrations were stated in parasite tissues when compared to water samples. In host organisms PGE accumulation was not observed which can prove that parasitic organisms are a good bioindicator of accumulation processes of these elements.

A significant influence on assimilability of noble metals present in waters is also due to the presence of humic substances. Results of studies conducted on bivalves (*Dreissena polymorpha*) show that the presence of humic substances results in increased solubility of Pd and Rh in water while solubility of Pt decreases in such conditions. Despite the fact that Pd is the most easily assimilable element in this group, in the presence of humic acids it forms more heavily available complex compounds with fulvic acids, which results in reducing its assimilation by water organisms. Platinum, however, binds to a biologically available fraction of humic substances, thus its compounds are very easily absorbed by animals and undergo accumulation in their tissues (29, 120, 132).

PGE accumulation in organisms of higher trophic level can lead to an increase of these metal concentrations in higher organisms (birds, mammals). Analysis of blood, liver, kidneys, droppings, eggs and feather samples of peregrine falcons (*Falco peregrinus*) can prove the thesis about PGE' environmental concentrations increments and their ability to bioaccumulate in animal tissues (120, 135). PGE were also assessed in feathers of gyrfalcons (*Falco rusticolus*), eurasian sparrow hawks (*Accipiter nisus*), willow ptarmigans (*Logopus logopus*) and house sparrows (*Passer domesticus*). Results obtained were of the same magnitude in all samples, which results mainly from the common presence of vehicles and birds travelling for long distances in search of food. Furthermore, it was observed that only palladium was penetrating the feathers, while platinum and rhodium were adsorbed on their surfaces (25, 136).

In studies dealing with platinum and palladium bioavailability to rats type CD-1 (Charles River), model solutions of these metals were applied orally, intravenously, tracheally and by inhalation. After several months of exposure, platinum and palladium were detected in many organs, mainly kidneys, livers, spleen, suprarenal glands, lungs and bones. After oral application of $PtCl_4$ and $PdCl_2$, the bioavailable fraction of these metals constituted approximately 1% of the total applied dose (120, 133, 134). The accumulation of car catalysts' derived platinum was also studied in tissues of female rats of Lewis-type by applying model solutions with molecules similar to those emitted by car catalysts. Application of metal was by inhaling or by intratracheal instillation . Platinum content assimilated by inhaling appeared to be greater then by intratracheal instillation and after 90 days constituted over 30% of the total dose (137). In Table 6 available literature data on PGE concentration levels in animal tissues samples are presented.

INFLUENCE OF PGE ON HUMAN HEALTH

Currently there are only a limited number of works devoted to studying environmental exposure to PGE by assessing their content in tissue and biological fluid samples of human origin. The majority of the articles deal with toxicity of pharmacological products containing PGE, as well as professional exposure (25).

It is believed that PGE emissions from car catalysts at current levels do not threaten human health and life. However, due to PGE ability to undergo accumulation in living organisms' tissues the negative impact of these metals as a result of direct contact with road dust, inhaling solid particles (that constitute approximately 30% of all particles emitted from vehicle catalysts (10)) as well as by food and drinking water can not be totally excluded (141, 142).

PGE concentration increments were observed both in biological fluids of people professionally exposed and in people endemically exposed (exposure related to contact with particular environmental compartments). For this reason it is very important to assess the threat posed to human health resulting from the presence of these elements in the workplace and monitor PGE

TABLE 6
Literature data on PGE concentration levels in animal tissue samples (1, 138)

Sample type	Sampling place/data	Concentration (ng/g) Pt	Pd	Rh	Literature
Crustaceans tissue (*Asellus aquaticus*)	Sweden (urban area) (1999)	38.0 ± 34.6	155.4 ± 73.4	17.9 ± 12.2	(113)
Crustaceans tissue (*Asellus aquaticus*)	Sweden (urban area)	0.04–12.4			(131)
Bivalves tissue (*Dreissena polymorpha*)	Austria (area in highway's proximity)	0.1–0.5	1.0		(132)
Peregrine falcon (*Falco peregrinus*)	Sweden				(135)
Feather	1986–2000	0.5	1.4	0.3	
Blood	1995–2001	2.7	0.8	0.6	
Eggs	1992–2000	0.4	0.5	0.3	
Faeces	1997–2001	0.2	—	—	
Liver	1985–1995	0.2	0.7	0.5	
Kidneys	1985–1995	0.2	0.3	0.3	
Eel's liver (*Anguilla anguilla*)	Germany (individual living in water polluted by road dust) (0.1 g/L of dust)		0.18 ± 0.05		(139)
Fish tissue (*Barbus barbus*)	Hungary	0.1–0.4	0.3–7.0	0.1–2.0	(140)

levels in areas where their introduction to the environment takes place. PGE released to the environment initially concentrate in the suspended matter, road dust, soil, water and sediments, and then can undergo accumulation in tissues of living organisms. Metallic forms of these elements generally do not participate in reactions occurring in organisms, contrary to soluble PGE compounds which are responsible for the occurrence of numerous diseases. The presence of PGE in organisms can cause disease symptoms like (141, 143):

- Asthma,
- Miscarriages,
- Allergic reactions,
- Nausea,
- Loosing hair,
- Skin diseases,
- Mucous membranes irritation, and
- Other serious health disorders.

Among PGE, platinum exhibits the strongest toxic action toward living organisms (its excess in organism is bound by proteins) (57, 143). Toxicity of this element is related to its oxidation state and electron structure (57). Particularly toxic is small group of platinum compounds containing active substitutes with chlorides being the most toxic ones. The frequency of allergic reactions appearing due to the presence of platinum salts increases with the number of substitutes containing Cl^- ions, while the strongest allergens in this group are:

- hexachloroplatinic acid (IV),
- ammonium and sodium hexachloroplatinate (IV), and
- sodium and potassium tetrachloroplatinate (II).

Furthermore, long term exposure to platinum can cause anemia and kidney failure (119, 143).

It was stated that palladium and rhodium content in children's urea samples is strongly related to traffic intensity, while this dependence was not observed in the case of platinum (3). Higher PGE concentration levels were assessed in adults' urea samples (46, 144) when compared to this metal content in children's urea samples. Not statistically relevant differences were observed between platinum concentration in biological fluid samples of the policemen control group (office workers) and the group potentially exposed to vehicle exhausts (road policemen) (144). No differences were noted for iridium and platinum concentrations in biological fluid samples of people living in urban and suburban areas (145, 146). There was a significant difference in platinum and rhodium concentrations in urea samples of people living in urban areas exposed to intense road traffic when compared to Pt and Rh content in urea samples of people living in suburban areas (147). Furthermore, results of studies indicate that in biological fluids there can be observed a higher palladium and rhodium content than of platinum which can be basis for the statement that these metals are characterized by higher bioavailability. The increment of platinum concentration in tissue with age increment shows that its accumulation in internal organs is a natural consequence of an organisms' exposure to

TABLE 7
Literature data on PGE concentration in human urea samples

Group examined	Concentration (ng/L)				Literature
	Pt	Pd	Rh	Ir	
Tram drivers (n = 64)	$1.23^{1,4}$	$11.47^{1,4}$	$19.16^{1,4}$	—	(2)
Control group (n = 58)	$1.03^{1,4}$	$8.75^{1,4}$	$11.18^{1,4}$		
Children in age 6–10 years (urban and suburban areas) (n = 310)	$0.9 \pm 1.1^{1,4}$ <0.03–9.5 0.9^{2} 1.1 ± 1.1^{1}	$7.5 \pm 5.4\ ^{1,4}$ 0.1–28.9 8.8^{2} 9.6 ± 5.1^{1}	$8.5 \pm 8.0^{1,4}$ 1.4–38.6 8.9^{2} 10.5 ± 6.9^{1}	—	(3)
Policemen:	0.2–15.29	—	—	—	(144)
- Office (n = 49)	4.56 ± 2.84^{1}				
- Road service (n = 94)	0.28–13.67 4.45 ± 2.42^{1}				
Hospital's drugstores personnel (n = 86), scientific workers (n = 12), mechanics (n = 13), bus drivers (n = 29), taxi drivers (n = 10)	$6.5 \pm 6.4^{1,4}$ $4.3^{2,4}$ $45^{3,4}$ $<20^{4}$ (in case of 96% of donors)	—	—	—	(46)
Road workers (n = 15)	0.1–4.4	9.5–133.7	—	—	(147)
Control group (n = 17)	0.3–2.2	13.1–48.3			
People of age range: 23–88 lat,	0.24–3.11	1.99–17.2	0.53–14.8	—	(145)
Low traffic intensity (n = 100)	1.09^{1} 0.52^{2}	7.45^{1} 6.02^{2}	5.32^{1}		
High traffic intensity (n = 157)	0.49–8.13 2.43^{1} 1.70^{2}	0.71–17.0 7.67^{1} 7.79^{2}	3.50^{2} 4.10–38.6 15.31^{1} 12.85^{2}		
Tram drivers (n = 64)	—	—	—	1.14–53.2 13.8 ± 15.7^{1} 6.60^{2} $0.56–49.7^{4}$ $9.2 \pm 10.3^{1,4}$ $4.44^{2,4}$	(146)
Office workers (n = 58)				2.00–38.6 13.4 ± 10.8^{1} 9.83^{2} $1.06–35.2^{4}$ $11.2 \pm 8.72^{1,4}$ $7.32^{2,4}$	

*n- donors number, ^{1} mean value, ^{2} median, ^{3} maximal value, ^{4} ng/g^{-1} of creatinine

this metal. In Table 7 there are presented available literature data on PGE concentration levels of anthropogenic origin in human urea samples (25).

Issues connected with PGE action on human organisms, both of professional and environmental exposure, are more widely described in the review literature (20, 138, 148).

ANALYTICAL PROBLEMS OF PGE DETERMINATION IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES

Due to the differentiated application of PGE there is an increasing necessity to assess the content of noble metals in a wide spectrum of samples (environmental, biological, industrial, and pharmaceutical). A reliable determination of these analytes in environmental samples is a difficult and complex task from an

TABLE 8
Problems and challenges of PGEs analytics in environmental samples

Problem	Description	Advised solution
• Seasonality of atmospheric precipitation occurrence	• Average number of rain days with >1,0mm along Gdañsk Gulf equals app. 100 days annually • Average number of days with snowfalls equals over 50 days annually (north-eastern part of the country)	• Longer monitoring period • Collecting samples in many locations in amount indispensable for basic statistical evaluation
• Influence of sampling devices construction material and ware applied in PGEs analytics as well as sampling and preservation methods on their chemical composition	• Possibility of occurring processes like: wall memory effect, wall adsorption/desorption, cross-contamination effect, secondary contamination effect, permeation via sampler/ware walls	• Applying samplers and ware build of proper materials (borosilicate glass (152, 153), polystyrene (154)) • Proper sampling technique (representivity of sample) • Proper technique of sample preservation (applying reagents of high purity grade) (56)
• Ultra-low analytes concentration levels • Complex chemical properties of PGEs • Specific content of samples matrices • Possibility of interferences occurrence with other constituents of samples, that show similar physicochemical properties and/or are present at higher concentration levels	• Significant time dependant variability of analytes concentrations, what is related to their tendency of undergoing hydrolysis, interactions with other constituents and walls of ware, transformations during storing and preparing samples of high dilution factor • Low reactivity of PGEs toward many reagents (necessity of applying drastic conditions and/or long reaction time)	• Derivatization of analytes (e.g., into chlorocomplex forms) • Using proper techniques of analytes separation from other constituents of sample and effective preconcentration techniques (64, 158) • Running reliable optimization of conditions of running process
• Difficulty of assuring proper reliability level of result of measurements as a source of analytical information	• Lack of proper reference materials indispensable to validate applied analytical methods • Inconvenience of calibrating analytical devices with application of solutions with low analytes concentrations (possibility of over and underestimating of analytes concentrations) • Insufficient sensitivity of measuring devices (too high LOD) • Possibility of high inaccuracy of final results	• Applying sensitive and specific determination techniques • Obeying specific restrictions connected with trace analytics

analytical point of view. In Table 8 there basic problems and challenges connected with analytics of this group of analytes in environmental samples and suggested ways to make it possible are presented. Issues dealing with problems of sample preparation and analysis of environmental and biological samples for PGE content are described in more detail in reviews and original literature (6, 149–154).

Techniques of Collecting, Storing and Preservation of Environmental Samples for PGE Content Determination

Results of analysis of environmental samples are a valuable source of information on the content of bioavailable forms of PGE (from anthropogenic sources) in the environment. An incredibly important issue is the reliability of results obtained, depending mainly on preserving good laboratory practice conditions and first of all on representativeness of the sample collected. It is essential to control important sampling parameters of this group of samples such as:

- Localization of sampling points,
- Weather conditions,
- Choosing a proper sampling device,
- Proper way of preparing the sampling device, and
- Proper mass and preservation of collected samples.

Environmental samples, devoted to conducting analytical studies aiming at determining PGE concentration level, are collected mainly in areas directly exposed to their action (fastways, highways, and urban areas) and from adjacent areas (roads with lower traffic intensity and areas with low urbanization level). The following factors should be considered when planning the sampling campaign:

- Road conditions (different vehicles velocities),
- Terrain shape,
- Weather conditions (wind direction and frequency of atmospheric precipitation),
- Sampling data (considering high PGE concentration in runoff water samples in initial state of atmospheric precipitate—"first flush"), and
- Depth of sampling (in case of soil, surface waters and snow).

Due to the specification of PGE determination procedures (a necessity of preconcentration of analytes in samples considered) and the possibility of uneven distribution of analytes in a given object (samples of soil, road dust, snow), it is necessary to properly sample large volumes/masses. The most common way of sample preservation is acidification with high purity chemicals.

Devices applied for sampling should be carefully chosen with special attention paid to the specificity of sampled medium. Review of construction solutions of samplers applied to collect atmospheric, runoff and surface water samples are described in literature (155–157). It is extremely important to apply proper surface preparation both for devices applied for sampling and during the next stages of analysis. Cleaning procedures most often cover:

- Washing with detergent containing water,
- Multiple flushing with deionized water,
- Flushing with acid solutions (HCl, HNO_3), and
- Multiple flushing with deionized water.

After delivering to the laboratory, samples should undergo analysis as soon as possible, preferably the same day because longer storage leads to analytes losses (e.g., due to adsorption on ware walls).

REFERENCES

1. K. Ravindra, L. Bencs, and R. Van Grieken, Platinum group elements in the environment and their health risk. *Science of the Total Environment* 318 (2004):1–43.
2. I. Iavicoli, B. Bocca, G. Carelli, S. Caroli, S. Caimi, A. Alimonti, and L. Fontana, Biomonitoring of tram drivers exposed to airborne platinum, rhodium and palladium. *International Archives of Occupational and Environmental Health* 81 (2007):109–114.
3. S. Caroli, A. Alimonti, F. Petrucci, B. Bocca, M. Krachler, F. Forastiere, M. T. Sacerdote, and S. Mallone, Assessment of exposure to platinum-group metals in urban children. *Spectrochimica Acta B* 56 (2001):1241–1248.
4. S. Artelt, H. Kock, D. Nachtigall, and U. Heinrich, Bioavailability of platinum emitted from automobile exhaust. *Toxicological Letters* 96–97 (1998):163–167.
5. M. Moldovan, Origin and fate of platinum group elements in the environment. *Analytical and Bioanalytical Chemistry* 388 (2007):537–540.
6. L. Bencs, K. Ravindra, and R. Van Grieken, Methods for the determination of platinum group elements originating from the abrasion of automotive catalytic converters. *Spectrochimica Acta B* 58 (2003):1723–1755.
7. B. Bocca, F. Petrucci, A. Alimonti, and S. Caroli, Traffic-related platinum and rhodium concentrations in the atmosphere of Rome. *Journal of Environmental Monitoring* 5 (2003):563–568.
8. J. Schäfer and H. Puchelt, Platinum-Group-Metals (PGM) emitted from automobile catalytic converters and their distribution in roadside soils. *Journal of Geochemical Exploration* 64 (1998):307–314.
9. B. Gómez, M. A. Palacios, M. Gómez, J. L. Sanchez, G. Morrison, S. Rauch, C. McLeod, R. Ma, S. Caroli, A. Alimonti, E. Petrucci, B. Bocca, P. Schramel, M. Zischka, C. Petterson, and U. Wass, 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* 299 (2002):1–19.
10. M. Moldovan, M. M. Gómez, and M. A. Palacios, On-line preconcentration of palladium on alumina microcolumns and determination in urban waters by inductively coupled plasma mass spectrometry. *Anaytica Chimica Acta* 478 (2003):209–217.
11. O. Morton, H. Puchelt, E. Hernández, and E. Lounejeva, Traffic-related platinum group elements (PGE) in soils from Mexico City. *Journal of Geochemical Exploration* 72 (2001):223–227.
12. C. Barbante, A. Veysseyre, Ch. Feerrari, K. Van de Velde, Ch. Morel, G. Capodaglio, P. Cescon, G. Scarponi, and C. Boutron, Greenland snow evidence of large scale atmospheric contamination for platinum, palladium, and rhodium. *Environmental Science and Technology* 35 (2001):835–839.
13. A. Dubiella-Jackowska, Ż. Polkowska, and J. Namieśnik, Platinum group elements: A challenge for environmental analytics. *Polish Journal of Environmental Studies* 16 (2007):329–345.
14. K. Lenz, S. Hann, G. Koellensperger, Z. Stefanka, G. Stingeder, N. Weissenbacher, S. N. Mahnik, and M. Fuerhacker, Presence of cancerostatic platinum compounds in hospital wastewater and possible elimination by adsorption to activated sludge. *Science of the Total Environment* 345 (2005):141–152.
15. K. Kümmerer, E. Helmers, P. Hubner, G. Mascart, M. Milandri, F. Reinthaler, and M. Zwakenberg, European hospitals as a source

for platinum in the environment in comparison with other sources. *Science of the Total Environment* 225 (1999):155–165.

16. 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* 33 (1999):3559–3567.
17. M. Moldovan, M. M. Gomez, and M. A. Palacios, Determination of platinum, rhodium and palladium in car exhaust fumes. *Journal of Analytical Atomic Spectrometry* 14 (1999):1163–1169.
18. S. Artelt, K. Levsen, H. P. König, and G. Rosner, Engine test bench experiments to determine platinum emission from three-way catalytic converters, in *Anthropogenic Platinum-Group Element Emissions. Their Impact on Man and Environment* eds. F. Zereni and F. Alt (Springer-Verlag, Berlin, 2000).
19. M. A. Palacios, M. Gomez, M. Moldovan, and B. Gomez, Assessment of environmental contamination risk by Pt, Rh and Pd from automobile catalyst. *Microchemical Journal* 67 (2000):105–113.
20. M. Moldovan, M. A. Palacios, M. M. Gomez, G. Morrison, S. Rauch, C. McLeod, R. Ma, S. Caroli, A. Alimonti, F. Petrucci, B. Bocca, P. Schramel, M. Zischka, C. Pettersson, U. Wass, M. Luna, J. C. Saenz, and J. Santamarıa, Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. *Science of the Total Environment* 296 (2002):199–208.
21. 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. *Environmental Science and Technology* 35 (2001):1996–2000.
22. J. D. Whitely, "Autocatalyst-derived platinum group elements in the roadside environment—occurrence, mobility and fate," Ph.D. thesis, Murdoch University, 2004), http://wwwlib.murdoch.edu.au/adt/pubfiles/adt-MU20051012.143138/01Front.pdf.
23. H. P. König, R. F. Hertel, W. Koch, and G. Rosner, Determination of platinum emissions from a three-way catalyst-equipped gasoline engine. *Atmospheric Environment* 26 (1992):741–745.
24. W. Barabasz, M. J. Chmiel, D. Albińska, and K. Vorisek, Role and meaning of siderofors as iron ions carriers in microorganisms and plants (in Polish). *Ecological Chemistry and Engineering* 6 (1999):575–585.
25. J. Malejko, B. Leśniewska, and B. Godlewska-Żyłkiewicz, Are noble metals noble that is on platinum and palladium bioavailability (in Polish). *Wiadomości Chemiczne* 61 (2007):387–416.
26. S. Hann, G. Koellensperger, Zs. Stefánka, G. Stingeder, M. Fürhacker, W. Buchberger, and R. M. Mader, Application of HPLC-ICP-MS to speciation of cisplatin and its degradation products in water containing different chloride concentrations and in human urine. *Journal of Analytical Atomic Spectrometry* 18 (2003):1391–1395.
27. S. Lustig, S. Zang, B. Michalke, P. Schramel, and W. Beck, Transformation behaviour of different platinum compounds in a clay-like humic soil: Speciation investigations. *Science of the Total Environment* 188 (1996):195–204.
28. F. Zereini, B. Skerstupp, F. Alt, E. Helmers, and H. Urban, Geochemical behaviour of platinum-group elements (PGE) in particulate emissions by automobile exhaust catalysts: Experimental results and environmental investigations. *Science of the Total Environment* 206 (1997):137–146.
29. S. Lustig, S. Zang, W. Beck, and P. Schramel, Dissolution of metallic platinum as water soluble species by naturally occurring complexing agents. *Mikrochimica Acta* 129 (1998):189–194.
30. 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. *Environmental Science and Technology* 35 (2001):1031–1036.
31. D. Fliegel, Z. Berner, D. Eckhardt, and D. Stubien, New data on the mobility of Pt emitted from catalytic converters. *Analytical and Bioanalytical Chemistry* 379 (2004):131–136.
32. V. Ljubomirova, R. Djingova, J. T. van Elteren, M. Veber, T. Kowalkowski, and B. Buszewski, Investigation of the solubilization of car-emitted Pt, Pd and Rh in the street dust and spiked soil samples. *International Journal of Environmental Analytical Chemistry* 88 (2008):499–512.
33. N. Haus, S. Zimmermann, J. Wiegand, and B. Sures, Occurrence of platinum and additional traffic related heavy metals in sediments and biota. *Chemosphere* 66 (2007):619–629.
34. D. E. Johnson, J. B. Tillery, and R. J. Prevost, Levels of palladium, platinum and lead in populations of Southern California. *Environmental Health Perspectives* 12 (1975):27–33.
35. D. E. Johnson, R. J. Prevost, J. B. Tillery, D. E. Caman, and J. M. Hosenfeld, "Baseline levels of platinum and palladium in human tissue," Southwest Research Institute, San Antonio, Texas, USA, 1976, Report: EPA-600/1-76-019.
36. F. Alt, A. Bambauer, K. Hoppstock, B. Mergler, and G. Tolg, Platinum traces in airborne particulate matter. Determination of whole content, particle size distribution and soluble platinum. *Fresenius Journal of Analytical Chemistry* 346 (1993):693–696.
37. J. Tilch, M. Schuster, and M. Schwarzer, Determination of palladium in airborne particulate matter in a German city. *Fresenius Journal of Analytical Chemistry* 367 (2000):450–453.
38. S. Rauch, M. Lu, and G. M. Morrison, Heterogeneity of platinum group metals in airborne particles. *Environmental Science and Technology* 35 (2001):595–599.
39. F. Petrucci, B. Bocca, A. Alimonti, and S. Caroli, Determination of Pd, Pt and Rh in airborne particulate and road dust by high resolution ICP-MS: A preliminary investigation of the emission from automotive catalysts in the urban area of Rome. *Journal of Analytical Atomic Spectrometry*15 (2000):525–528.
40. E. Helmers and N. Mergel, Platinum and rhodium in the polluted environment: Studying the emissions of automobile catalysts with emphasis on the application of CSV rhodium analysis. *Fresenius Journal of Analytical Chemistry* 362 (1998):522–528.
41. M. B. Gomez, M. M. Gomez, and M. A. Palacios, ICP-MS determination of Pt, Pd and Rh in airborne and road dust after tellurium coprecipitation. *Journal of Analytical Atomic Spectrometry* 18 (2003):80–83.
42. K. Kanitsar, G. Kollensperger, S. Hann, A. Limbeck, H. Puxbaum, and G. Stingeder, Determination of Pt, Pd and Rh by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) in size-classified urban aerosol samples. *Journal of Analytical Atomic Spectrometry* 18 (2003):239–246.
43. T. U. Probst, B. Rietz, and Z. B. Alfassi, Platinum concentrations in Danish air samples determined by instrumental neutron activation analysis. *Journal of Environmental Monitoring* 3 (2001):217–219.

44. R. Vlasankova, V. Otruba, J. Bendl, M. Fisera, and V. Kanicky, Preconcentration of platinum group metals on modified silicagel and their determination by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry in airborne particulates. *Talanta* 48 (1999):839–846.
45. S. F. Kan and P. A. Tanner, Platinum concentrations in ambient aerosol at a coastal site in South China. *Atmospheric Environment* 39 (2005):2625–2630.
46. R. Schierl, Environmental monitoring of platinum in air and urine. *Microchemical Journal* 67 (2000):245–248.
47. S. Rauch, H. F. Hemond, and B. Peucker-Ehrenbrink, Source characterisation of platinum group element deposition in an ombrotrophic peat bog. *Journal of Environmental Monitoring* 6 (2004):335–343.
48. S. Rauch, H. F. Hemond, C. Barbante, M. Owari, G. M. Morrison, B. Peucker-Ehrenbrink, and U. Wass, Importance of automobile emissions for platinum, palladium and rhodium deposition in the northern hemisphere. *Environmental Science and Technology* 39 (2005):8156–8162.
49. M. Bojanowska, Wpływ antropogenicznej platyny na elementy środowiska. *Acta Agrophysica* 5 (2005):535–541.
50. S. Lustig, Platinum in the environment. Car-catalyst emitted platinum, transformation behaviour in soil and platinum accumulation in plants (Speciation Investigations), UTZ, München 1997. http://www.utzverlag.de/shop.php?bn=31235
51. M. Kolodziej, I. Baranowska, and A. Matyja, Determination of platinum in plant samples by voltammetric analysis. *Electroanalysis* 19 (2007):1585–1589.
52. D. Cicchella, B. De Vivo, and A. Lima, Palladium and platinum concentration in soils from the Napoli metropolitan area, Italy: Possible effects of catalytic exhausts. *The Science of the Total Environment* 308 (2003):121–131.
53. M. Hallberg, G. Renman, and T. Lundbom, Seasonal variations of ten metals in highway runoff and their partition between dissolved and particulate matter. *Water Air and Soil Pollution* 181 (2007):183–191.
54. R. J. Hares and N. I. Ward, Comparison of the heavy metal content of motorway stormwater following discharge into wet biofiltration and dry detention ponds along the London Orbital (M25) Motorway. *Science of the Total Environment* 235 (1999):169–178.
55. P. S. Hooda, A. Miller, and A. C. Edwards, The plant availability of auto-cast platinum group elements. *Environmental Geochemistry and Health* 30 (2008):135–139.
56. R. R. Barefoot, Distribution and speciation of platinum group elements in environmental matrices. *Trends in Analytical Chemistry* 18 (1999):702–707.
57. B. Leśniewska and K. Pyrzyńska, Platinum and its compounds in the human natural environment—do they pose a threat? (in Polish) *Wiadomoci Chemiczne* 55 (2001):33–351.
58. J. F. W. Bowles and A. P. Gize, A preliminary study of the release of platinum and palladium from metallic particles in the surface environment by organic acids: relevance to weathering of particles from vehicle exhaust catalysts. *Mineralogical Magazine* 69 (2005):687–693.
59. S. R. Dahlheimer, C. R. Neal, and J. B. Fein, Potential mobilization of platinum-group elements by siderophores in surface environments. *Environmental Science and Technology* 41 (2007):870–875.
60. E. Helmers, Platinum emission rate of automobiles with catalytic converters. *Environmental Science and Pollution Resources* 4 (1997):100–103.
61. C. Wei and G. M. Morrison, Platinum analyses and speciation in urban gulleypots. *Anaytica Chimica Acta* 284 (1994):587–592.
62. B. Godlewska-Żyłkiewicz, Preconcentration and separation procedures for the spectrochemical determination of platinum and palladium. *Mikrochimica Acta* 147 (2004):189–210.
63. WHO, Environmental Health Criteria for Palladium, International Programme on Chemical Safety. World Health Organization, Geneva (2000).
64. F. S. Rojas, C. B. Ojeda, and J. M. C. Pavón, Automated on-line separation preconcentration system for palladium determination by graphite furnace atomic absorption spectrometry and its application to palladium determination in environmental and food samples. *Talanta* 70 (2006):979–983.
65. V. F. Hodge and M. O. Stallard, Platinum and palladium in roadside dust. *Environmental Science and Technology* 20 (1986):1058–1060.
66. C. Wei and G. M. Morrison, Platinum in road dusts and urban river sediments. *Science of the Total Environment* 146–147 (1994):169–174.
67. M. Motelica-Heino, S. Rauch, G. M. Morrison, and O. F. X. Donard, Determination of palladium and rhodium concentrations in urban road sediments by laser ablation-ICP-MS. *Anaytica Chimica Acta* 436 (2001):233–244.
68. M. E. Farago, P. Kavanagh, R. Blanks, J. Kelly, G. Kazantzis, I. Thornton, P. R. Simpson, J. M. Cook, S. Parry, and G. M. Hall, Platinum metal concentrations in urban road dust and soil in the United Kingdom. *Fresenius Journal of Analytical Chemistry* 354 (1996):660–663.
69. J. Schafer, J. D. Eckhardt, and H. Puchelt, Traffic-related nobel metal, emissions in Southwest Germany, VM Goldschmidt Conf. *Journal of Conference Abstracts* 1 (1996):536.
70. J. Schafer, J. D. Eckhardt, Z. A. Berner, and D. Stuben, Time-dependent, increase of traffic-emitted platinum group elements (PGE) in different environmental compartments. *Environmental Science and Technology* 33 (1999):3166–3170.
71. E. Higney, V. Olive, A. B. MacKenzie, and I. D. Pulford, Isotope dilution ICP–MS analysis of platinum in road dusts from west central Scotland. *Applied Geochemistry* 17 (2002):1123–1129.
72. R. Garcıa, M. Gomez, M. A. Palacios, J. Bettmer, and C. Camara, On-line removal of mass interferences in palladium determination by ICP-MS using modified capillaries coupled to microflow nebulizers. *Journal of Analytical Atomic Spectrometry* 16 (2001):481–486.
73. P. Kovacheva and R. Djingova, Ion-exchange method for separation and concentration of platinum and palladium for analysis of environmental samples by inductively coupled plasma atomic emission spectrometry. *Anaytica Chimica Acta* 464 (2002):7–13.
74. B. A. Leśniewska, B. Godlewska-Żyłkiewicz, B. Bocca, S. Caimi, S. Caroli, and A. Hulanicki, Platinum, palladium and rhodium content in road dust, tunnel dust and common grass in Bialystok area (Poland): A pilot study. *Science of the Total Environment* 321 (2004):93–104.
75. 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* 317 (2003):121–135.

76. B. Gomez, M. A. Palacios, M. Gomez, J. L. Sanchez, G. Morrison, S. Rauch, C. McLeod, R. Ma, S. Caroli, A. Alimonti, F. Petrucci, B. Bocca, P. Schramel, M. Zischka, C. Petterson, and U. Wass, 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* 299 (2002):1–19.
77. P. Schramel, I. Wendler, and S. Lustig, Capability of ICP-MS (pneumatic nebulization and ETV) for Pt-analysis in different matrices at ecologically relevant concentrations. *Fresenius Journal of Analytical Chemistry* 353 (1995):115–118.
78. P. Schramel, M. Zischka, H. Muntanu, B. Stojanik, R. Dams, M.G. Gomez, and P. Quevauviller, Collaborative evaluation of the analytical state-of-the-art of platinum, palladium and rhodium determinations in road dust. *Journal of Environmental Monitoring* 5 (2000):443–446.
79. F. Zereini, C. Zientek, and H. Urban, Concentration and distribution of platinum group elements (PGE) in soil–platinum metal emission by abrasion of catalytic converter materials (in German). *UWSF–Z Umweltchemie und Okotoxicologie* 5 (1993):130–134.
80. E. Heinrich, G. Schmidt, and K. L. Kratz, Determination of platinum group elements (PGE) from catalytic converters in soils by means of docimasy and INAA. *Fresenius Journal of Analytical Chemistry* 354 (1996):883–885.
81. F. Alt, H. R. Eschnauer, B. Mergler, J. Messerschmidt, and G. Tölg, A contribution to the ecology and enology of platinum. *Fresenius Journal of Analytical Chemistry* 357 (1997):1013–1019.
82. F. Zereini, F. Dirksen, B. Skerstupp, and H. Urban, Sources of anthropogenic platinum-group elements (PGE): Automotive catalysts vs. PGE-processing industries. *Environmental Science and Pollution Resources* 5 (1998):223–230.
83. F. Zereini and F. Alt, (eds.) *Anthropogenic platinum-group element emissions. Their impact on man and environment* (Springer-Verlag, Berlin, 2000).
84. D. Cinti, M. Angelone, U. Masi, and C. Cremisini, Platinum levels in natural and urban soils from Rome and Latinum (Italy): Significance for pollution by automobile catalytic converter. *Science of the Total Environment* 293 (2002):47–57.
85. M. Muller and K. G. Heumann, Isotope dilution inductively coupled plasma quadrupole mass spectrometry in connection with a chromatographic separation for ultra trace determinations of platinum group elements (Pt, Pd, Ru, Ir) in environmental samples. *Fresenius Journal of Analytical Chemistry* 368 (2000):109–115.
86. 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. *Science of the Total Environment* 388 (2007):121–127.
87. B. Godlewska-Zylkiewicz, J. Malejko, P. Hataburda, B. Leśniewska, and A. Kojto, Separation of matrix by means of biosorption for flow-injection chemiluminescent determination of trace amounts of Pt(IV) in natural waters. *Microchemical Journal* 85 (2007):314–320.
88. S. Rauch, H. F. Hemond, and B. Peucker-Ehrenbrink, Recent changes in platinum group element concentrations and osmium isotopic composition in sediments from an urban lake. *Environmental Science and Technology* 38 (2004):396–402.
89. R. A. Sutherland, D. Graham Pearson, and C. J. Ottley, Platinum-group elements (Ir, Pd, Pt and Rh) in road-deposited sediments in two urban watersheds, Hawaii. *Applied Geochemistry* 22 (2007):1485–1501.
90. F. Zereini, Zur Analytik der Platingruppenelemente (PGE) und ihren geochemischen Verteilungsprozessen in ausgewählten Sedimentgesteinen und anthropogen beeinflußten Umweltkompartimenten Westdeutschlands, Shaker Verlag, Aachen (1997).
91. WHO, "Platinum. Air Quality Guidelines," WHO Regional Office for Europe, Kopenhagen, Denmark, 2000.
92. A. Turner, Particle-water interactions of platinum group elements under estuarine conditions. *Marine Chemistry* 103 (2007):103–111.
93. W. Hummel, U. Berner, E. Curti, F. J. Pearson, and T. Thoenen, Nagra/PSI Chemical Thermodynamic Data Base 01/01, (Universal publishing, Parkland, 2001). http://cat.inist.fr/?aModele=afficheN&cpsidt=14400699
94. G. H. Gammons, Experimental investigations of the hydrothermal geochemistry of platinum and palladium: V. Equilibria between platinum metal, Pt (II), and Pt (IV) chloride complexes at 25 to 300°C. *Geochimica Cosmochimica Acta* 60 (1996):1683–1694.
95. D. S. Lee, Palladium and nickel in northeast Pacific waters. *Nature* 305 (1983):47–48.
96. E. D. Goldberg, V. Hodge, P. Kay, S. Stallard, and M. Koide, Some comparative marine chemistries of platinum and iridium. *Applied. Geochemistry* 1 (1986):227–232.
97. C. M. G. Van den Berg, and G. S. Jacinto, The determination of platinum, in sea water by adsorptive cathodic stripping voltammetry. *Anaytica Chimica Acta* 211 (1988):129–139.
98. G. S. Jacinto and C. M. G. Van den Berg, Different behavior of platinum in the Indian and Pacific Oceans. *Nature* 338 (1989):332–334.
99. D. C. Colodner, E. A. Boyle, and J. M. Edmond, Determination of rhenium and platinum in natural waters and sediments, and iridium in sediments by flow injection isotope dilution inductively coupled plasma mass spectrometry. *Analytical Chemistry* 65 (1993):1419–1425.
100. J. Messerschmidt, F. Alt, and G. Tolg, Beitrag zur extremen Spuren-analyse der Platinmetalle in biotischen und umweltrelevanten, Materialen. 4. Statusseminar, Forschungsverband 'Edelmetalemissionen' (1992).
101. V. Hodge, M. Stallard, M. Koide, and E. D. Goldberg, Determination of platinum and iridium in marine waters, sediments and organisms. *Analytical Chemistry* 58 (1986):616–620.
102. R. Eller, F. Alt, G. Tolg, and H. J. Tobschall, An efficient combined procedure for the extreme trace analysis of gold, platinum, palladium and rhodium with the aid of graphite furnace atomic-absorption spectrometry and total-reflection X-ray fluorescence analysis. *Fresenius Journal of Analytical Chemistry* 334 (1989):723–739.
103. D. Laschka, M. Nachtwey, Untersuchungen zum Eintrag von Platin aus Kfz-Katalysatoren in die Umwelt. Report Bayerisches Landesamt fur Wasserwirtschaft, Institute fur Wasserforschung, Munich (1993).
104. H. Wildner, Kalibration, Probenzufuhr und Detektion fur die Platinbestimmung im sub pg/g-Bereich. Proceedings 3, Platin–Anwendertreffen, Herausgeber: Lustig S., Schramel P. (eds.), PGSP-Forschungszentrum, 14–15 October 1996, Institute fur Ecologische Chemie, Munich (1996).

105. E. Helmers, M. Schwarzer, and M. Schuster, Comparison of palladium and platinum in environmental matrices: Palladium pollution by automobile emissions? *Environmental Science and Pollution Resources* 5 (1998):44–50.
106. D. Laschka, T. Striebel, J. Daub, and M. Nachtwey, Platinum in rainwater discharges from roads. *UWSF – Z Umweltchemie und Okotoxikologie* 8 (1996):124–129.
107. C. Barbante, G. Cozzi, G. Capodaglio, K. Van de Velde, C. Ferrari, A. Veysseyre, C. F. Boutron, G. Scarponi, and P. Cescon, Determination of Rh, Pd and Pt in polar and Alpine snow and ice by double focusing ICP-MS with microconcentric nebulization. *Analytical Chemistry* 71 (1999):4125–4133.
108. K. Van de Velde, C. Barbante, G. Cozzi, I. Moret, T. Bellomi, C. Ferrari, and C. Boutron, Changes in the occurrence of silver, gold, platinum, palladium and rhodium in Mont Blanc ice and snow since the 18th century. *Atmospheric Environment* 34 (2000):3117–3127.
109. D. Laschka and M. Nachtwey, Platinum in municipal sewage treatment plants. *Chemosphere* 34 (1997):1803–1812.
110. K. Kümmerer and E. Helmers, Hospital effluents as a source for platinum in the environment. *The Science of the Total Environment* 193 (1997):179–184.
111. S. Rauch, G. M. Morrison, M. Motelica-Heino, and O. F. X. Donard, Evaluation of Speciation, Transport and Ecological Risks of Palladium, Platinum and Rhodium in Urban Stormwater Systems. 8th International Conference on Urban Storm Drainage Proceedings, The Institution of Engineers, Sydney, Australia, 1 (1999):202–209.
112. S. Rauch, M. Motelica-Heino, G. M. Morrison, and O. F. X. Donard, Critical assessment of platinum group element determination in road and urban river sediments using ultrasonic nebulization and high resolution ICP-MS. *Journal of Analytical Atomic Spectrometry* 15 (2000):329–334.
113. M. Moldovan, S. Rauch, M. Gomez, M. A. Palacios, and G. M. Morrison, Bioaccumulation of palladium, platinum and rhodium, from urban particulates and sediments by the freshwater isopod *Asellus aquaticus*. *Water Resources* 35 (2001):4175–4183.
114. C. B. Tuit, G. E. Ravizza, and M. H. Bothner, Anthropogenic platinum, and palladium in the sediments of Boston Harbor. *Environmental Science and Technology* 34 (2000):927–932.
115. E. De Vos, S. J. Edwards, I. McDonald, D. S. Wray, and P. J. Carey, A baseline survey of the distribution and origin of platinum, group elements in contemporary fluvial sediments of the, Kentish Stour, England. *Applied Geochemistry* 17 (2002):1115–1121.
116. J. D. Whiteley and F. Murray, Autocatalyst-derived platinum, palladium and rhodium (PGE) in infiltration basin and wetland sediments receiving urban runoff. *Science of the Total Environment* 341 (2005):199–209.
117. T. Hees, B. Wenclawiak, S. Lustig, P. Scramel, M. Schwarzer, M. Schuster, D. Verstraete, R. Dams, and E. Helmers, Distribution of platinum group elements (Pt, Pd, Rh) in environmental and clinical matrices: Composition, analytical techniques and scientific outlook—Status report. *Environmental Science and Pollution Research International* 5 (1998):105.
118. J. Schäfer, D. Hannker, J. D. Eckhardt, and D. Stüben, Uptake of traffic-related heavy metals and platinum group elements (PGE) by plants. *Science of the Total Environment* 215 (1998):59–67.
119. J. Kowalska, M. Asztemborska, and J. Golimowski, Why do we watch nanogram platinum content in the environment (in Polish). *Analityka* 2 (2008):47–51.
120. S. Zimmermann and B. Sures, Significance of platinum group metals emitted from automobile exhaust gas converters for the biosphere. *Environmental Science and Pollution Research International* 11 (2004):194–199.
121. M. E. Farago and P. J. Parsons, The effects of various platinum metal species on the water plant *Eichhornia Crassipes (Mart.) Solms. Chem. Spec. Bioavail*. 6 (1994):1–12.
122. M. Niemela, J. Piispanen, J. Poikolainen, and P. Peramaki, Preliminary study of the use of terrestial moss (*Pleurozium Schreberi*) for biomonitoring traffic-related Pt and Rh deposition. *Archives of Environmental Contamination and Toxicology* 52 (2007):347–354.
123. 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. *Environmental Science and Technology* 35 (2001):3816–3822.
124. E. Helmers, N. Mergel, and R. Barchet, Platinum in ash from sewage sludge incinerators and in grass (in German). *UWSF – Z Umweltchemie und Okotoxikologie* 6 (1994):130–134.
125. J. S. Becker, D. Bellis, I. Staton, C. W. McLeod, J. Dombovari, and J. S. Becker, Determination of trace elements including platinum in tree bark by ICP mass spectrometry. *Fresenius Journal of Analytical Chemistry* 368 (2000):490–495.
126. E. Helmers, Platinum emission rate of automobiles equipped with catalytic converters: Comparison and assessment of result from various approaches. *Environmental Science and Pollution Research* 4 (1997):100–103.
127. G. Dongarra, D. Varrica, and G. Sabatino, Occurrence of platinum, palladium and gold in pine needles of *Pinus pinea* L. from the city of Palermo (Italy). *Applied Geochemistry* 18 (2003):109–116.
128. R. Djingova, P. Kovacheva, G. Wagner, and B. Markert, Distribution of platinum group elements and other traffic related elements among different plants along some highways in Germany. *Science of the Total Environment* 308 (2003):235–246.
129. K. Hoppstock, F. Alt, K. Cammann, and G. Weber, Determination of platinum in biotic and environmental materials. Part II: A sensitive voltammetric method. *Fresenius Journal of Analytical Chemistry* 335 (1989):813–816.
130. J. Schäfer, "Einträge und Kontaminationspfade Kfz-emittierter Platin-Gruppen-Elemente (PGE) in verschiedenen Umweltkompartimenten," Ph.D. thesis, University of Karlsruhe, Karlsruhe, Germany, 1998.
131. S. Rauch and G. M. Morrison, Platinum uptake by the freshwater isopod *Asellus aquaticus* in urban rivers. *Science of the Total Environment* 235 (1999):261–268.
132. S. Zimmermann, F. Alt, J. Messerschmidt, A. von Bohlen, H. Taraschewski, and B. Sures, Biological availability of traffic-related platinum-group elements (palladium, platinum, and rhodium) and other metals to the zebra mussel (*Dreissena polymorpha*) in water containing road dust. *Environmental Toxicology and Chemistry* 21 (2002):2713–2718.
133. W. Moore, Jr., D. Hysell, L. Hall, K. Campbell, and J. F. Stara, Preliminary studies on the toxicity and metabolism of palladium and platinum. *Environmental Health Perspectives* 10 (1975):63–71.

134. W. Moore, Jr., M. Malanchuk, W. Crocker, D. Hysell, A. Cohen, and J. Stara, Whole body retention in rats of different 191 Pt compounds following inhalation exposure. *Environmental Health Perspectives* 12 (1975):35–39.
135. K. H. Ek, S. Rauch, G. M. Morrison, and P. Lindberg, Platinum group elements in raptor eggs, faeces, blood, liver and kidney. *Science of the Total Environment* 334–335 (2004):149–159.
136. K. H. Jensen, S. Rauch, G. M. Morrison, and P. Lindberg, Platinum group elements in the feathers of raptors and their prey. *Archives of Environmental Contamination and Toxicology* 42 (2002):338–347.
137. S. Artelt, O. Creutzenberg, H. Kock, K. Levsen, D. Nachtigall, U. Heinrich, T. Rühle, and R. Schlögl, Bioavailability of fine dispersed platinum as emitted from automotive catalytic converters: A model study. *Science of the Total Environment* 228 (1999):219–242.
138. 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* 334–335 (2004):21–38.
139. B. Sures, S. Zimmermann, J. Messerschmidt, A. von Bohlen, and F. Alt, First report on the uptake of automobile catalyst emitted palladium by European eels (*Anguilla anguilla*) following experimental exposure to road dust. *Environmental Pollution* 113 (2001):341–345.
140. B. Sures, F. Thielen, F. Baska, J. Messerschmidt, and A. von Bohlen, The intestinal parasite Pomphorhynchus laevis as a sensitive accumulation indicator for the platinum group metals Pt, Pd, and Rh. *Environmental Resources* 98 (2005):83–88.
141. R. Merget and G. Rosner, Evaluation of the health risk of platinum group metals emitted from automotive catalytic converters. *Science of the Total Environment* 270 (2001):165–173.
142. A. Dubiella-Jackowska, Ż. Polkowska, and J. Namieśnik, Platinum group elements and the road transport (in Polish). *Analityka* 4 (2007):11–16.
143. M. Kaczmarczyk and E. Bulska, Platinum and human health. Element dangerous or helpful? *Analityka* 2 (2007):34–39.
144. I. Iavicoli, B. Bocca, F. Petrucci, O. Senofonte, G. Carelli, A. Alimonti, and S. Caroli, Biomonitoring of traffic police officers exposed to airborne platinum. *Occupational and Environmental Medicine* 61 (2004):636–639.
145. B. Bocca, A. Alimonti, A. Cristaudo, E. Cristallini, F. Petrucci, and S. Caroli, Monitoring of the exposure to platinum-group elements for two Italian population groups through urine analysis. *Analytica Chimica Acta* 512 (2004):19–25.
146. I. Iavicoli, G. Carelli, B. Bocca, S. Caimi, L. Fontana, and A. Alimonti, Environmental and biological monitoring of iridium in the city of Rome. *Chemosphere* 71 (2008):568–573.
147. J. Begerow and L. Dunemann, in Antropogenic platinum group element emissions. Their impact on man and environment. F. Zereini and F. Alt (eds.) (Springer-Verlag 2000).
148. A. Dubiella-Jackowska, Ż. Polkowska, and J. Namieśnik, Platinum group elements in the environment: Emissions and exposure. *Reviews on Environmental Contamination and Toxicology*, ed. D. M. Whitacre. (Springer US) 199 (2008): 1–25.
149. C. R. M. Rao and G. S. Reddi, Platinum group metals (PGM): occurrence, use and recent trends in their determination. *Trends in Analytical Chemistry* 19 (2000):565–586.
150. M. Balcerzak, Analytical methods for the determination of platinum in biological and environmental materials. *Analyst* 122 (1997):67R-74R.
151. M. Balcerzak, Sample digestion methods for the determination of traces of precious metals by spectrometric techniques. *Analytical Science* 18 (2002):737–750.
152. A. Cobelo-Garcia, A. Turner, G. E. Millward, and F. Couceiro, Behaviour of palladium(II), platinum(IV), and rhodium(III) in artificial and natural waters: Influence of reactor surface and geochemistry on metal recovery. *Anaytica Chimica Acta* 585 (2007):202–210.
153. B. Godlewska-Żyłkiewicz, Hazards of errors in the palladium storage in determination by GFAAS. *Analytical and Bioanalytical Chemistry* 372 (2002):593–596.
154. J. Kowalska, M. Asztemborska, B. Godlewska-Żyłkiewicz, and J. Golimowski, Systematic errors in the determination of trace metals, Part II. Memory effects of quartz vessels used for sample preparation in the determination of ultra-trace levels of platinum. *Microchimica Acta* 150 (2005):55–58.
155. S. V. Krupa, Sampling and physico-chemical analysis of precipitation: A review. *Environmental Pollution* 120 (2002):565–594.
156. M. Grynkiewicz, Ż. Polkowska, and J. Namieśnik, Sampling of atmospheric precipitation for analysis. Description of samplers used (in Polish). *Ecological Chemistry and Engineering* 9 (2002):853–867.
157. K. Skarżyńska, Ż. Polkowska, and J. Namieśnik, Sampling of atmospheric precipitation and deposits for the analysis (in Polish). *Ecological Chemistry and Engineering* 11 (2004):343–397.
158. A. Limbeck, Microwave-assisted UV-digestion procedure for the accurate determination of Pd in natural waters. *Anaytica Chimica Acta* 575 (2006):114–119.