Environ. Sci. Technol. **2005**, *39,* 8156−8162

Importance of Automobile Exhaust Catalyst Emissions for the Deposition of Platinum, Palladium, and Rhodium in the Northern Hemisphere

SEBASTIEN RAUCH,*,†,‡ HAROLD F. HEMOND,‡ CARLO BARBANTE,§,# MASANORI OWARI,¶ GREGORY M. MORRISON,† BERNHARD PEUCKER-EHRENBRINK,£ AND URBAN WASS⊥

Water Environment Technology, Chalmers University of Technology, 412 96 Göteborg, Sweden, School of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, Department of Environmental Science, University of Venice, Ca' Foscari, 30123 Venice, Italy, Institute for the Dynamics of Environmental Processes-CNR, University of Venice, Ca' Foscari, 30123 Venice, Italy, Environmental Science Center, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, and Volvo Technology Corporation, Department 6700, M1.4, 405-08 Göteborg, Sweden

An estimated 500 million vehicles worldwide are equipped with an exhaust catalyst that uses platinum group elements (PGE) as the main active components and thus contribute to global PGE emissions. Although PGE emitted from automobile exhaust catalysts were first believed to remain in the roadside environment, we propose here that fine PGE-containing particles in automobile exhaust have resulted in a widespread distribution of emitted PGE. Regional and long-range transport of PGE from automobile exhaust catalysts is supported by elevated PGE deposition in both a peat bog located 250 m from traffic and in central Greenland, respectively. Russian smelters were also found to contribute to PGE contamination in central Greenland. Deposition rates estimated for the roadside environment, the peat bog, and central Greenland were used to provide a first estimate of PGE deposition in the northern hemisphere. The results show that deposition of regionally or long-range transported PGE accounts for a large fraction of total PGE deposition, and PGE deposition in the roadside environment represents less than 5% of the total deposition. Transport at the regional and global scales represents an important component in the environmental cycle of emitted PGE and needs to be further studied to fully assess the environmental fate of PGE from automobile exhaust catalysts.

* Corresponding author phone: +46-31-772-2123; fax: +46-31-772-5695; e-mail: sebastien.rauch@wet.chalmers.se.
† Chalmers University of Technology.
‡ Massachusetts Institute of Technology.
§ Department of Environmental Science, University of Venice.
# Institute for the Dynamics of Environmental Processes-CNR, University of Venice.
¶ University of Tokyo.
£ Woods Hole Oceanographic Institution.
⊥ Volvo Technology Corporation.

Introduction

Elevated PGE concentrations, which have been measured in the urban and roadside environment (*1*−*3*), are believed to be the result of automobile exhaust catalyst emissions (*4*−*6*). Automobile exhaust catalysts are devices fitted into the exhaust systems of vehicles to reduce the emission of carbon monoxide, hydrocarbons, and nitrogen oxides from the engine. Palladium, platinum, and rhodium are the principal active components in automobile exhaust catalysts, and it has been demonstrated that PGE are released into the environment during vehicle operation (*4*−*6*). Reported PGE emission rates are believed to lie in the ng km^{-1} range (*6*). Platinum emission may be as high as 0.8 $\mu g\ km^{-1}$ depending on speed and vehicle condition, with engine malfunction causing higher emission as a result of higher exhaust temperatures (*7*). Although PGE emission rates are relatively low, an estimated 500 million vehicles worldwide are equipped with catalyst technology (*8*). It comes as no surprise that PGE are found in urban air (*9*−*14*), road dust (*10*, *12*, *15*, *16*), roadside soil (*15*−*17*), and roadside vegetation (*18*, *19*).

While PGE from automobile exhaust catalysts were first believed to remain in the roadside environment due to rapidly decreasing concentrations with increasing distance from roads (*18*, *20*, *21*), the recent finding of elevated PGE concentrations in central Greenland (*8*) has raised concern over the lack of knowledge of atmospheric dispersion of emitted PGE. It is shown here that PGE are widely dispersed in the environment as a result of their emission as fine particles, and deposition on regional and long-range scales represents a large fraction of the global PGE deposition.

Materials and Methods

This paper synthesizes results obtained within the framework of a project on platinum group element dispersion at the regional and global scales. The project aims to (1) characterize PGE-containing airborne particles in urban areas, (2) assess regional atmospheric and stormwater transport, and (3) provide an explanation for the elevated PGE concentrations reported in Greenland ice and snow. A detailed presentation of the procedures for sample collection and analysis is not provided here but can be found in the cited literature.

Airborne particles were collected at two sites in Boston (U.S.A.) on Whatman 41 filters using a high volume PM-10 impactor (Thermo Andersen, U.S.A.; PM10, particle matter with a size below 10 μm) operated for 24 h at an approximate flow rate of 67 $m^3\ h^{-1}$. The impactor was equipped with optional size-fractionation impaction plates for the collection of particles with diameters of <0.48 (backup filter), 0.48−0.96, 0.96−1.48, 1.48−3.0, 3.0−7.2, and 7.2−10.0 μm. The obtained samples were analyzed by quadrupole ICP-MS (Elan6000, PE Sciex, Canada) after closed vessel microwave-assisted digestion. Potential interferences were corrected mathematically (*11*).

Airborne particles were collected in Tokyo, Japan and Göteborg, Sweden for characterization by microanalytical techniques. In Tokyo, airborne particles (PM-7, particle matter with a size below 7 μm) were collected on polycarbonate filters using a low flow sampler (SL-30, Sibata, Japan) for 1−100 hours at an approximate flow rate of 1.8 $m^3\ h^{-1}$. In addition, one sample was collected using a cellulose acetate

10.1021/es050784m CCC: $30.25

Published on Web 09/30/2005

filter at a flow rate of 1 m^3 h^{-1} for 7 days to determine PGE concentrations in Tokyo air. In Göteborg, airborne particles (PM-10 and PM-2.5, particle matter with a size below 10 and 2.5 μm, respectively) were collected on PTFE filters using a virtual impactor (Thermo Andersen, U.S.A.) operated for 24 h at an approximate flow rate of 1 m^3 h^{-1}. Particles on PTFE filters were transferred to a carbon adhesive tape for analysis. PGE-containing particles in Tokyo and Göteborg samples were identified by electron probe microanalysis (EPMA, JXA-8900R, JEOL Ltd, Tokyo, Japan) with both wavelength-dispersive spectroscopy and energy-dispersive X-ray spectroscopic detection. PGE-containing particles were then observed by field emission scanning electron microscopy (FE-SEM, JSM-6500F, JEOL Ltd, Tokyo, Japan), and major component concentrations in individual particles were determined by energy-dispersive X-ray spectroscopy (*22*, *23*).

Sediment cores were collected in Upper Mystic Lake (UML, 42°,26′ N; 71°,09′ W) in MA. The lake receives the entire runoff from a 67 km^2 watershed with urban and industrial areas, as well as high traffic roadways. Sediment cores were collected by freeze coring and dated using ^{210}Pb dating and the concentration profiles of elements with known historical trends (*24*). Samples were analyzed by quadrupole ICP-MS (Elan6000, PE Sciex, Canada) after closed vessel microwave-assisted digestion and mathematical correction of potential interferences (*24*), as well as by sector field ICP-MS (Element2, ThermoFinnigan, Germany) after NiS fire assay and with isotope dilution-based quantification (*25*).

Peat cores were collected from Thoreau's Bog, in MA (42°,-38′ N; 71°,21′ W). The bog is located approximately 250 m from the closest road. Samples were dated using ^{210}Pb dating and a physical marker (*26*). Characterization of peat samples was performed by X-ray fluorescence (XRF, X-Lab 2000, Spectro, Canada). As the peat bog is ombrotrophic, the source of metals to the bog is purely atmospheric (*26*, *27*). Samples were analyzed by sector field ICP-MS (Element2, ThermoFinnigan, Germany) after NiS fire assay and with isotope dilution-based quantification (*26*). Osmium concentrations and isotopic composition were used to determine the natural input into the bog (*26*).

Additional results for regional scale dispersion were obtained from an ice core project in the Monte Rosa Massif (45°,55′ N; 7°,53′ E; elevation 4633 m) in the Swiss−Italian Alps (*28*). The ice cores were drilled using an electromagnetic corer and were dated using a combination of techniques including counting of seasonally varying ionic species and ^{210}Pb dating (*28*). PGE concentrations were determined in melted samples by sector field ICP-MS (Element2, ThermoFinnigan, Germany) with mathematical correction of potential interferences (*29*).

Ice and snow cores were obtained from the Summit area (72°,34′ N; 37°,38′ W; elevation 3240 m) in central Greenland. Samples include snow samples collected from a snow pit and dated using seasonal variations of ionic species (*8*), snow samples from a 10.7 m core collected by Auger drilling and dated using seasonal variations of ionic species (*8*), and ancient ice samples collected within the 3028.8 m Greenland Ice Core Project (GRIP) (*8*). PGE concentrations were determined in melted samples by sector field ICP-MS (Element2, ThermoFinnigan, Germany) with mathematical correction of potential interferences (*29*).

The origin of the air mass over an area can be determined using atmospheric models, and therefore these models have been used for the identification of the source of air pollutants from long-range transport (*30*). Daily 10 day atmospheric air mass trajectories to Summit were obtained for 1992 using METEX (Meteorological Data Explorer, Center for Global Environmental Research, Tsukuba, Japan) and HYSPLIT (Air Resources Laboratory, National Oceanic and Atmospheric Administration, U.S.A.) with the National Center for Environmental Prediction (NCEP, U.S.A.) Reanalysis weather data. Back-calculations were based on the 3-D Wind model (METEX) and vertical velocity (HYSPLIT).

Results and Discussion

Platinum Group Elements in Urban Aerosols. Although it is now generally accepted that PGE are released from automobile exhaust catalysts into the environment, the emission mechanisms and the physicochemical forms of emitted PGE are still unclear. Mechanical erosion of the catalyst surface has been suggested as the main mechanism for PGE emission (*4*, *5*). Particles emitted by mechanical processes are expected to have diameters of several micrometers. However, 11−36% of PGE-containing particles in the exhaust of catalyst-equipped gasoline engines were found to have diameters smaller than 3.14 μm (*31*). The emission of fine PGE-containing particles is supported by atmospheric measurements (*11*−*13*) and suggests that chemical reactions and/or thermal processes are also involved in the release of PGE from catalysts.

As a result of automobile emissions, PGE occur in urban air with concentrations typically in the lower pg m^{-3} range (*9*−*14*). Reported PM-10 concentrations in Göteborg are 14.1 ± 3.7 pg of Pt m^{-3}, 4.9 ± 3.1 pg of Pd m^{-3}, and 2.9 ± 1.0 pg of Rh m^{-3} (average ± 1σ, n = 7) (*11*). Atmospheric PGE concentrations in Boston and Tokyo, for which concentrations had not been previously reported, were in the same order of magnitude with 6.7 ± 4.8 pg of Pt m^{-3}, 7.5 ± 5.0 pg of Pd m^{-3}, and 1.1 ± 0.9 pg of Rh m^{-3} (average ± 1σ, n = 12), and 2.1 pg of Pt m^{-3}, 0.79 pg of Pd m^{-3}, and 0.47 pg of Rh m^{-3} (n = 1) for Boston and Tokyo, respectively. PGE in urban areas including Boston, MA (this study), Frankfurt am Main, Germany (*14*), Göteborg, Sweden (*11*), Madrid, Spain (*12*), and Vienna, Austria (*13*) are present in both fine (<2.5 μm) and coarse (>2.5 μm) particles, although the size distribution was found to vary between cities. Further evidence of the occurrence of PGE in particles with diameters ranging from approximately 1.5 to 10 μm in automobile exhaust and urban air has also been obtained from direct observation of individual air particles by scanning electron microscopy (Figure 1); the lower size limit is the result of instrumental detection limits, while the upper size limit is the result of size selective sample collection. Observed particles had different sizes, shapes, and compositions (Figure 1) with PGE being present either as major components (Figure 1B) or as a minor component on an Al/Si oxide matrix (Figure 1A).

Long-range transport of particles with diameters smaller than 6 μm has been reported (*32*). Therefore, the emission of fine PGE-containing particles and their occurrence in urban air suggest the possibility that PGE from automobile exhaust catalysts can be transported over long distances and become widely dispersed in the environment.

Regional Transport of Platinum Group Elements. PGE concentrations are highest in the roadside environment as a result of automobile exhaust catalyst emissions. Platinum, palladium, and rhodium deposition rates in the road and roadside environment were in the following estimated ranges: 0.4−6.2, 0.4−8.8, and 0.1−1.8 μg m^{-2} $year^{-1}$, respectively (Table 1). A sharp concentration decrease has been observed within a few meters from roads (*15*, *17*, *18*, *20*, *21*), although elevated PGE concentrations compared with expected natural levels have been reported in soil and grass up to 100 m from roads (*15*, *17*, *18*).

Elevated PGE concentrations have also been found in Thoreau's Bog, a peat bog located approximately 250 m from automobile traffic, and their source was established to be almost exclusively anthropogenic (*26*). Catalysts are the only known anthropogenic source of PGE in the vicinity of the bog, which receives mineral inputs through purely atmo-

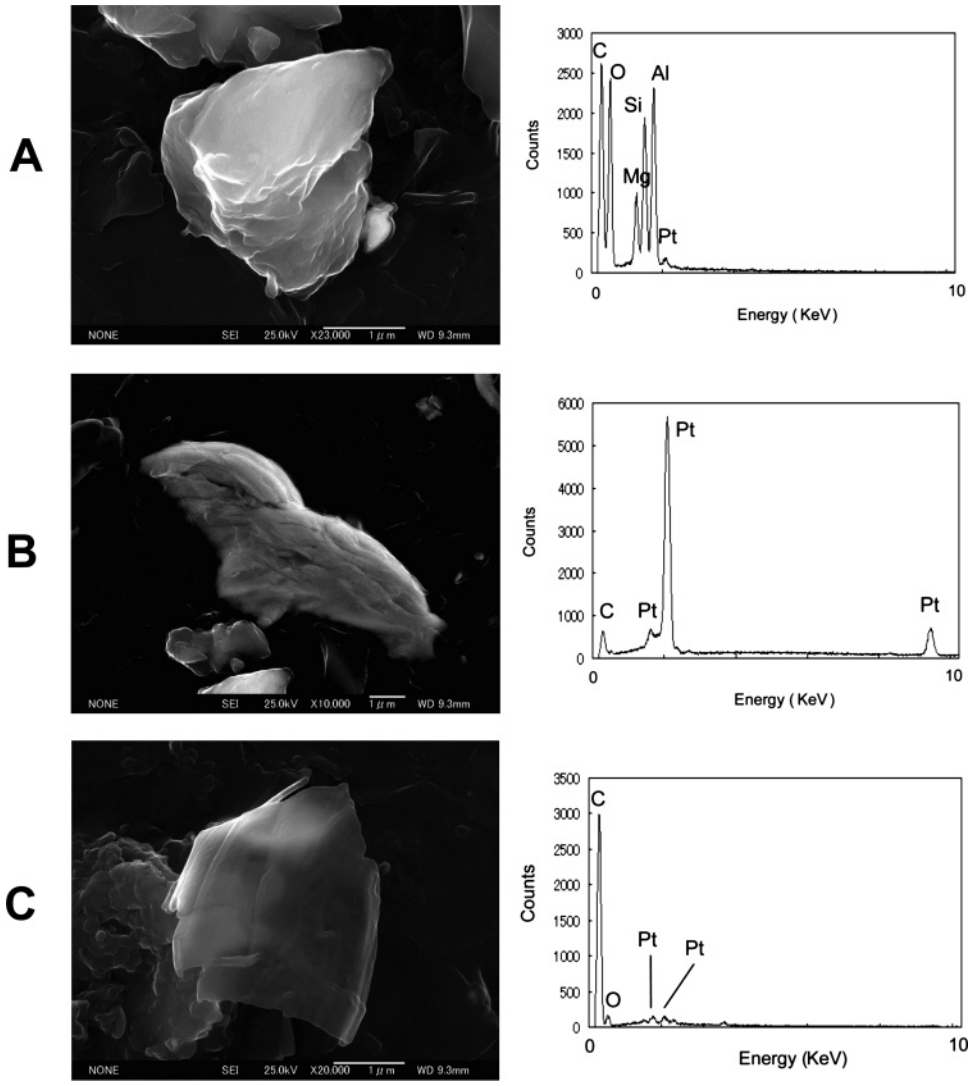

FIGURE 1. Field emission scanning electron microscope images of PGE-containing airborne particles collected in Göteborg, Sweden. Scale bars are displayed on the pictures. Respective EDS spectra are shown on the right. Observed C peaks may be due to the use of a C-containing substrate.

TABLE 1. PGE Deposition Rates in Environmental Compartments

	deposition rate (μg m^{-2} year^{-1})			
location[a]	Pt	Pd	Rh	ref
road surface, Germany (0 m)	5			34
road surface (0 m)[b]	0.4−5.6	0.4−8.8	0.1−1.8	
roadside, Germany (2 m)	2.2−6.2			48
Thoreau's Bog, U.S.A. (250 m)				
total deposition[c]	0.55−0.77	0.68	0.21	26
natural deposition	0.05	0.05	0.01	26
lake sediments, U.S.A.				
1992−2002	9 ± 5	10 ± 4	1.3 ± 0.4	25
prior to catalyst introduction	0.6 ± 0.3	1.2 ± 0.6	0.22 ± 0.06	25
Massachusetts Bay sediments, U.S.A.	44	78		39
Germany, average atmospheric deposition	0.73			49
central Greenland				
total deposition[d]	0.08 ± 0.04	0.22 ± 0.14	0.011 ± 0.00 5	
natural deposition during the Holocene	0.00015			47

[a] Distance to traffic in brackets when available. [b] Estimated using a Pt settling velocity of 350 m year^{-1} (*50*) and PGE concentrations in the range of 1−16 pg of Pt m^{-3}, 1−25 pg of Pd m^{-3}, and 0.3−5.0 pg of Rh m^{-3} (*9*, *11*−*14*), and assuming identical settling velocities for Pt, Pd, and Rh. [c] Estimated from Pd and Rh deposition (*26*) assuming deposition has the same relative Pt, Pd, and Rh composition Boston air. [d] Estimated for 1990−1995 using data in refs 8, 40.

spheric deposition. The results therefore provide evidence for regional transport of PGE from catalysts. At 250 m from traffic, Pd and Rh deposition rates are in the lower range of estimated on-road deposition (Table 1), indicating a relatively efficient transport of emitted PGE takes place at a regional scale.

Further indication for regional atmospheric PGE transport has been obtained from alpine ice cores (*28*), although additional source characterization is needed to fully establish all the major sources of PGE in the alpine cores. Platinum concentrations increased in the 1980s when automobile exhaust catalysts were first introduced in Europe, but elevated Pd and Rh concentrations prior to the introduction of catalysts indicate that additional sources contribute to the occurrence of these metals in Alpine glaciers (*28*).

Transport of deposited PGE-containing particles in stormwater is also expected to result in dispersion of PGE and in contamination of the aquatic environment, especially where roadway drainage systems are in place (*33*). Consequently, PGE are found in stormwater (*34*), roadside catch basins (*35*), road drainage basins (*33*, *36*), urban rivers (*37*, *38*), urban lakes (*24*, *25*), and coastal zones (*39*). In the aquatic environment PGE accumulate in sediments, and therefore, sediment cores have provided chronological records of PGE contamination. In Upper Mystic Lake, PGE concentrations increased exponentially following the introduction of automobile exhaust catalysts in 1975 as a result of anthropogenic PGE deposition. The flux of PGE reached a plateau during the 1990s, possibly owing to the stabilization of the percentage of catalyst-equipped vehicles in the watershed (*25*). Catalysts are mandatory on new cars, and it can therefore be hypothesized that PGE contamination reach a steady state when most vehicles have been produced after the introduction of legislation requiring catalysts. Further transport of PGE in the aquatic environment is also expected to result in the contamination of coastal areas. Elevated Pt and Pd concentrations have been reported in Massachusetts Bay, downstream from Upper Mystic Lake (*39*). The higher deposition rates in Massachusetts Bay may be the result of additional input from high traffic areas in Boston, as well as from hospitals that use cis-platin and carboplatin for cancer treatment.

Platinum Group Elements in Greenland. To investigate the possibility of long-range transport of PGE-containing particles, ice and snow cores were collected at Summit in central Greenland, far from anthropogenic sources. PGE concentrations in 1969−1995 were higher than background levels in ancient ice with a sharp concentration increase after 1990 (Figure 2) (*8*, *40*). While the results indicate long-range PGE transport, the source of PGE in Greenland is unknown. The timing of the concentration increase suggests an anthropogenic source. Automobile exhaust catalysts and Russian smelters, in the vicinity of which elevated PGE concentrations have been reported (*41*−*43*), have been suggested as potential sources of PGE in Greenland (*8*, *40*). Atmospheric PGE emission by industrial activities has not been documented but is expected to be limited in importance compared with emissions from automobile exhaust catalysts and smelters. There is, however, no direct relationship between either Russian production or the PGE demand for catalysts (Figure 3), and the concentration trend in Greenland (Figure 2). A multiple source origin of PGE in Greenland is supported by the following points: (a) Particles with diameters <6 μm can reach polar regions (*31*), and fine anthropogenic particles, including fly ash, soot, and metal oxides have been found at Summit (*44*). Therefore, the occurrence of PGE in fine particles in urban air suggests that automobile exhaust catalysts may be a potent source of PGE in Greenland. (b) Air mass trajectories determined using METEX and HYSPLIT indicate that both automobile exhaust catalysts and

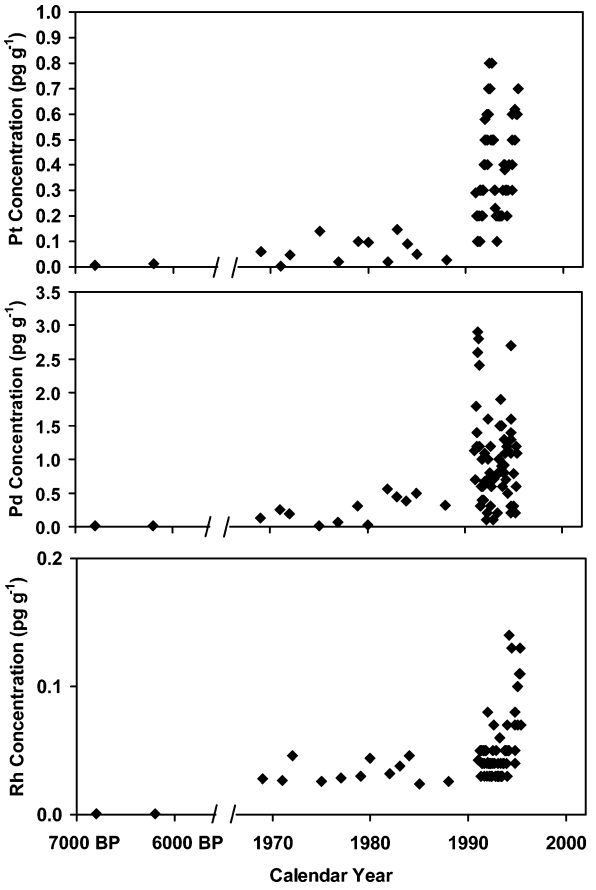

FIGURE 2. Platinum group element concentrations in ice and snow from Summit in central Greenland (adapted from refs 8, 39).

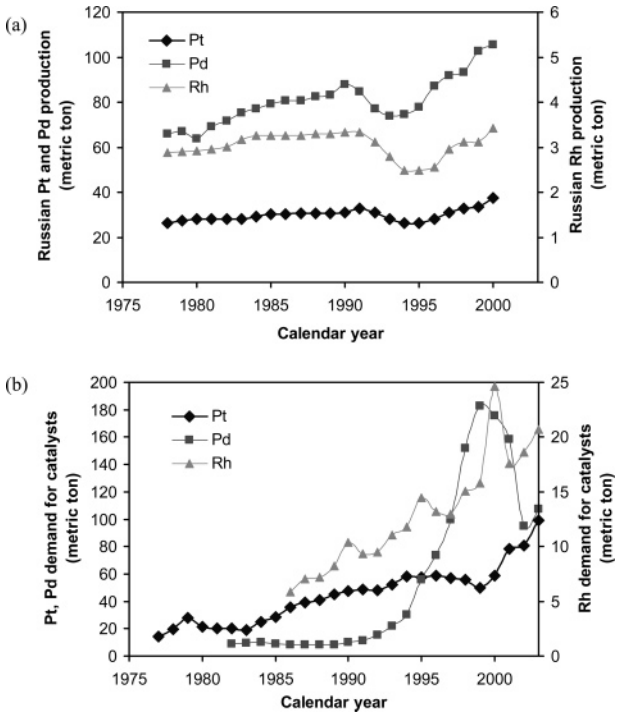

FIGURE 3. Changes in (a) Russian PGE production in 1975−2000 (*52*) and (b) PGE demand for catalyst production from 1977 to 2003, estimated from ref 53.

Russian smelters are potential sources of PGE in central Greenland. Ten day trajectories pass over both urban areas in North America and Europe, as well as smelting centers in

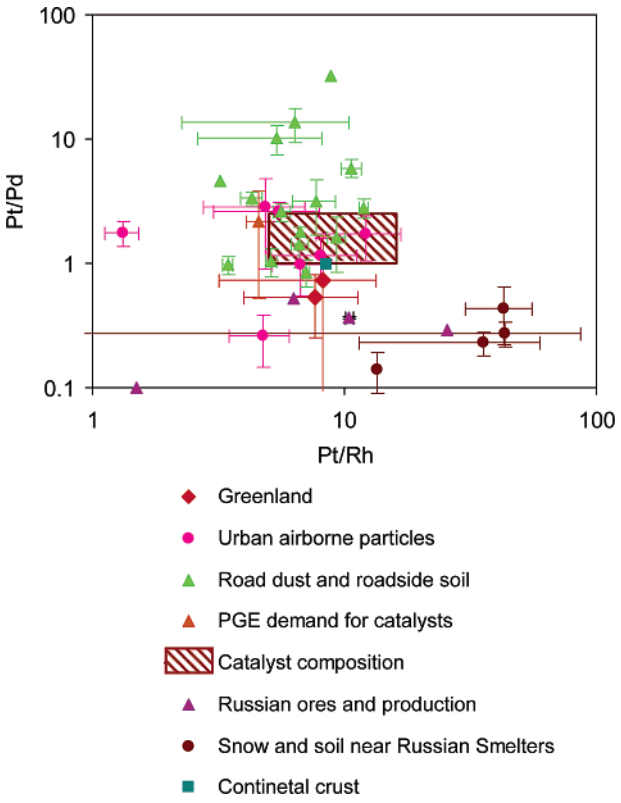

FIGURE 4. Comparison of Pt/Pd vs Pt/Rh in Greenland ice and snow (*8*, *39*), and the Continental crust (*46*, *47*), Russian ores (*41*, *42*), snow (*41*), and soil (*42*) near Russian smelters, Russian PGE production (*52*), catalyst production (*54*), catalyst composition range (*17*), urban airborne particles (Austria (*13*), Germany (*14*), Italy (*10*), Sweden (*11*), U.S.A. (this study)), tunnel dust (Austria (*55*), Poland (*56*)), road dust (Australia (*16*), Poland (*56*), Sweden (*12*), U.K. (*15*)), roadside soil (Australia (*16*, *17*), Austria (*57*), Germany (*36*), U.S.A. (*17*)), sediments (Australia (*33*), U.S.A. (*25*)).

Russia. Potential contribution from a wide range of geographical locations is supported by a study of isobaric trajectories to Summit over a 44 year period (*45*), with potential source areas including North America, Asia, and to a smaller extent, Europe. There was, however, no direct correlation between a particular source and concentration in Greenland (Figure 2), and the late PGE concentration increase in Greenland compared to the 1975 catalyst introduction could not be explained by the predominance of Europe as a source area. (c) PGE ratios have been used to identify the source of PGE in the urban environment, with environmental ratios similar to those in catalysts indicating an automobile exhaust catalyst source (*16*, *17*, *25*). PGE ratios in Greenland were compared with ratios estimated for catalysts and urban samples, and for dispersed Russian ores, Russian PGE production, and contaminated samples in the vicinity of Russian smelters (Figure 4). The comparison of PGE ratios supports a combination of sources with long-range transport of PGE emitted from automobile exhaust catalysts and Russian smelters.

It is therefore likely that elevated PGE concentrations in central Greenland are the result of long-range transport from both urban areas where automobile exhaust catalysts are in use and Russian smelters. Although PGE emitted by smelters have been reported to mostly deposit in the vicinity of the smelters (*43*), a small fraction may be transported further and may represent a significant input in remote areas including Greenland. Platinum, palladium, and rhodium deposition rates in Greenland in the mid-1990s were estimated to be approximately 0.08 ± 0.04, 0.2 ± 0.1, and 0.011 ± 0.005 μg m^{-2} year^{-1}, respectively, based on PGE concentrations and snow accumulation rates (Table 1). Comparison between deposition rates in urban areas and Greenland indicate a relatively high deposition rate for Greenland, considering that Pt input in Greenland is from long-distance atmospheric transport. The high deposition rates in Greenland could, however, be related to additional input from Russian smelters. PGE ratios (Figure 4) and the absence of correlation with air mass trajectory, PGE production (Figure 3a), and PGE demand for catalysts (Figure 3b) suggest that both automobile exhaust catalysts and Russian smelters represent a significant fraction of total PGE deposition.

TABLE 2. Catalyst-Derived Pt Deposition Rate and Total Deposition in the Northern Hemisphere

location[a]	deposition rate (g km^{-2} year^{-1})	area (10^3 km^2)[b]	deposition (metric ton year^{-1})
roadside environments	0.4−6.2	51	0.03−0.4
regional environments	0.5−0.7[c]	7583	4−6
remote environments	0.02−0.06[d]	247402	5−15
northern hemisphere		255036	9−20

[a] Roadside environments represent roads and highways of countries with large numbers of catalysts, i.e., the U.S.A., western Europe, and Japan; regional environments represent countries with large numbers of catalysts (because a large portion of the U.S., Sweden, and Norway can be considered remote, only half the area was taken into account for these countries; Canada was considered to be essentially remote and therefore not taken into account); remote environments represent areas, including oceans, not included in road and regional environments. [b] Road lengths and surface areas were obtained from ref 51; widths of 8 and 14 m were assumed for roads and highways, respectively. [c] The deposition rate at Thoreau's Bog was used as a proxy for regional deposition. [d] The deposition rate at Summit was used as a proxy for deposition in remote environments; as both catalysts and smelter are considered to be major sources of PGE in central Greenland, the catalyst-derived Pt deposition rate in Greenland was estimated to be 25−75% of the total deposition.

Importance of Automobile Exhaust Catalyst Emission for Global PGE Deposition. PGE are concentrated in the Earth's core and mantle with only trace concentrations in the Earth's crust (*46*, *47*). Therefore, the natural cycling of PGE at the Earth's surface and in the atmosphere is expected to be limited in importance, and even a small anthropogenic input may significantly affect PGE fluxes. There is now increasing evidence that PGE fluxes have been altered by automobile exhaust catalyst emission into the atmosphere. Platinum, palladium, and rhodium deposition rates in Thoreau's Bog increased up to 15-, 14-, and 21-fold, respectively, over natural deposition rates owing to anthropogenic input from automobile exhaust catalysts (Table 1) (*26*). Platinum, palladium, and rhodium deposition rates on road surfaces are 10−100, 10−200, and 10−200 times higher than natural deposition in Thoreau's Bog. A more dramatic increase in deposition was found for Pt in Greenland, with 1992−2002 deposition corresponding to 600 times the estimated natural deposition (*48*). Although the source of Pt in Greenland may include both automobile exhaust catalysts and smelters, catalysts are expected to represent a significant fraction of Pt deposition in Greenland.

A global catalyst emission of 0.8−6.0 metric tons of Pt year^{-1} can be estimated assuming that 500 million vehicles are equipped with catalysts with an average yearly mileage of 15 000 km vehicle^{-1} (*8*) and an average emission rate of 0.1−0.8 μg km^{-1} (*7*). A first estimate of Pt deposition in the northern hemisphere can also be obtained from deposition rates in Table 1 and using Pt deposition rates at Thoreau's Bog and Summit as proxies for the deposition of Pt in regional and remote environments. The total Pt deposition was found to be 9−20 metric tons year^{-1} (Table 2). The observed difference between emission and deposition may be the result of an underestimation of emission rates, an overestimation

of deposition rates, or the occurrence of additional sources. Underestimation of emission rates may result from differences between emission tests and actual on-road emission (*7*). Error in the global estimates may arise from spatial variations of deposition rates, especially for deposition in regional and remote environments for which results from two sites are used to represent large areas. Despite potential errors in the estimation of Pt deposition, it is clear that deposition at regional and global scales represent a large fraction of total Pt deposition (Table 2). In contrast, roadside deposition represents only a small fraction (≤4.5%) of total Pt deposition. A similar distribution can be inferred for Pd and Rh using the same assumptions as for Pt deposition. Total Pd and Rh depositions in the northern hemisphere are 20−50 metric tons year^{-1} and 2−4 metric tons year^{-1}, respectively, although Pd deposition may be affected by higher input from Russian smelter owing to the relatively high Pd concentration in Pd ores. Roadside deposition represents less than 3.1% and 5.1% of total Pd and Rh deposition, respectively.

The number of cars equipped with catalysts is expected to increase in coming years, with their introduction in developing countries and rapidly growing markets including China and India. Thus, there is a need for improved understanding of the still relatively unclear fate of PGE emitted from automobile exhaust catalysts. The first assessment of PGE deposition in the northern hemisphere provided here indicates that a relatively large fraction of PGE emitted from catalysts is transported at both regional and global scales, resulting in a widespread contamination. It is therefore clear that further assessment of the fate of emitted PGE should include regional and long-range transport. This study also indicates that fine metal-containing particles emitted from automobiles are ubiquitous in the environment.

Acknowledgments

This research was funded by the Alliance for Global Sustainability, Project 2227. Ice and snow core samples were obtained and analyzed within the framework of ongoing collaborative projects at the University of Venice, including the Greenland Ice Core Project (GRIP) and projects funded by ENEA and the Italian National Program for Antarctic Research. The Laboratoire de Glaciologie et Geophysique de l'Environnement in Grenoble, France is acknowledged for collaboration on the ice core studies and the Paul Scherrer Institute and the University of Berne, Switzerland for collaboration on the Alpine ice core study. Sediment and peat core analysis was also supported by the Knut and Alice Wallenberg Foundation, Stockholm (Sweden). The authors gratefully acknowledge the Centre for Global Environmental Research in Tsukuba, Japan for enabling trajectory calculations using METEX and the NOAA Air Resources Laboratory (ARL), U.S.A., for the provision of the HYSPLIT transport and dispersion model used in this publication. The authors would also like to acknowledge the participation of Anita Varga, Kristine Ek, Nozomi Tsuzaki, Mayuko Osaki, and Tracy Abbruzzese, as well as Lary Ball and David Schneider of the WHOI ICP facility.

Literature Cited

(1) Zereini, F.; Alt, F. *Anthropogenic Platinum-Group Element Element Emissions—Their Impact on Man and Environment*; Springer-Verlag: Berlin, 2000.

(2) Ravindra, K.; Bencs, L.; Van Grieken, R. Platinum group elements in the environment and their health risk. *Sci. Total Environ.* **2004**, *318*, 1−43.

(3) Hoppstock, K.; Sures, B. Platinum Group Elements. In *Elements and Their Compounds in the Environment*; Merian, E., Anke, M., Ihnat, M., Stoeppler, M., Eds.; Wiley-VCH Verlag: Weinheim, Germany, 2004; pp 1047−1086.

(4) König, H. P.; Hertel, R. F.; Koch, W.; Rosner, G. Determination of Platinum Emissions from a 3-Way Catalyst-Equipped Gasoline-Engine. *Atmos. Environ., Part A:* **1992**, *26*, 741−745.

(5) Palacios, M. A.; Gomez, M. 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.; Santamaria, J. Platinum-group elements: quantification in collected exhaust fumes and studies of catalyst surfaces. *Sci. Total Environ.* **2000**, *257*, 1−15.

(6) Moldovan, M.; Palacios, M. A.; Gomez, M. M.; Morrison, 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.; Santamaria, J. Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. *Sci. Total Environ.* **2002**, *296*, 199−208.

(7) Helmers, E. Platinum emission rate of automobiles with catalytic converters—Comparison and assessment of results from various approaches. *Environ. Sci. Pollut. Res.* **1997**, *4*, 100−103.

(8) Barbante, C.; Veysseyre, A.; Ferrari, C.; Van de Velde, K.; Morel, C.; Capodaglio, G.; Cescon, P.; Scarponi, G.; Boutron, C. Greenland snow evidence of large scale atmospheric contamination for platinum, palladium, and rhodium. *Environ. Sci. Technol.* **2001**, *35*, 835−839.

(9) Alt, F.; Bambauer, A.; Hoppstock, K.; Mergler, B.; Tölg, G. Platinum Traces in Airborne Particulate Matter—Determination of Whole Content, Particle-Size Distribution and Soluble Platinum. *Fresenius' J. Anal. Chem.* **1993**, *346*, 693−696.

(10) Petrucci, F.; Bocca, B.; Alimonti, A.; Caroli, S. 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. *J. Anal. At. Spectrom.* **2000**, *15*, 525−528.

(11) Rauch, S.; Lu, M.; Morrison, G. M. Heterogeneity of platinum group metals in airborne particles. *Environ. Sci. Technol.* **2001**, *35*, 595−599.

(12) Gomez, B.; Palacios, M. A.; Gomez, M.; Morrison, G. M.; Rauch, S.; McLeod, C.; Ma, R.; Caroli, S.; Alimonti, A.; Schramel, P.; Zischka, M.; Pettersson, C.; Wass, U. Platinum, palladium and rhodium contamination in airborne particulate matter and road dust of European cities. Risk assessment evaluation. *Sci. Total Environ.* **2002**, *299*, 1−19.

(13) Kanitsar, K.; Koellensperger, G.; Hann, S.; Limbeck, A.; Puxbaum, H.; Stingeder, G. Determination of Pt, Pd and Rh by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) in size-classified urban aerosol samples. *J. Anal. At. Spectrom.* **2003**, *18*, 239−246.

(14) Zereini, F.; Alt, F.; Messerschmidt, J.; Von Bohlen, A.; Liebl, K.; Puttmann, W. Concentration and distribution of platinum group elements (Pt, Pd, Rh) in airborne particulate matter in Frankfurt am Main, Germany. *Environ. Sci. Technol.* **2004**, *38*, 1686−1692.

(15) Jarvis, K. E.; Parry, S. J.; Piper, J. M. Temporal and spatial studies of autocatalyst-derived platinum, rhodium, and palladium and selected vehicle derived trace elements in the environment. *Environ. Sci. Technol.* **2001**, *35*, 1031−1036.

(16) Witheley, J. D.; Murray, F. Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia. *Sci. Total Environ.* **2003**, *317*, 121−135.

(17) Ely, J. C.; Neal, C. R.; Kulpa, C. F.; Schneegurt, M. A.; Seidler, J. A.; Jain, J. C. Implications of platinum-group element accumulation along US roads from catalytic-converter attrition. *Environ. Sci. Technol.* **2001**, *35*, 3816−3822.

(18) Helmers, E. Elements accompanying platinum emitted from automobile exhaust catalysts. *Chemosphere* **1996**, *33*, 405−419.

(19) Dongarra, G.; Varrica, D.; Sabatino, G. Occurrence of platinum, palladium and gold in pine needles of Pinus pinea L. from the city of Palermo (Italy). *Appl. Geochem.* **2003**, *18*, 109−116.

(20) Zereini, F.; Skerstupp, B.; Rankenburg, K.; Dirksen, F.; Beyer, J.-M.; Claus, T.; Urban, H. Anthropogenic emission of platinum-group elements (Pt, Pd and Rh) into the environment: concentration, distribution and geochemical behaviour in soils. In *Anthropogenic Platinum-Group Element Emissions—Their Impact on Man and the Environment*; Zereini, F., Alt, F., Eds.; Springer-Verlag: Berlin, 2000; pp 73−83.

(21) Eckhardt, J. D.; Schäfer, H.; Puchelt, H.; Stuben, D. Environmental PGE contamination in Southwest Germany. In *Anthropogenic Platinum-Group Element Emissions—Their Impact on Man and the Environment*; Zereini, F., Alt, F., Eds.; Springer-Verlag: Berlin, 2000; pp 47−55.

(22) Tsuzaki, N.; Osaki, M.; Owari, M.; Nihei, Y. Characterization of environmental particles originating from automobile catalyst. In *Third Seoul National University-University of Tokyo Joint Workshop on Environmental Science and Engineering*, Seoul, South Korea, October 31, 2003; pp 49−52.
(23) Tsuzaki, N.; Osaki, M.; Tomiyasu, B.; Owari, M.; Nihei, Y. Development of analytical method to detect individual airborne particle emitted from automobile catalysts. *Bunseki Kagaku*, in press.
(24) Rauch, S.; Hemond, H. F. Sediment-based evidence of platinum concentration change in an urban lake near Boston, MA. *Environ. Sci. Technol.* **2003**, *37*, 3283−3288.
(25) Rauch, S.; Hemond, H. F.; Peucker-Ehrenbrink, B. Recent changes in platinum group element concentrations and osmium isotopic composition in sediments from an urban lake. *Environ. Sci. Technol.* **2004**, *38*, 396−402.
(26) Rauch, S.; Hemond, H. F.; Peucker-Ehrenbrink, B. Source characterisation of atmospheric platinum group element deposition into an ombrotrophic peat bog. *J. Environ. Monit.* **2004**, *6*, 335−343.
(27) Hemond, H. F. Biogeochemistry of Thoreaus Bog, Concord, Massachusetts. *Ecol. Monogr.* **1980**, *50*, 507−526.
(28) Barbante, C.; Schwikowski, M.; Doring, T.; Gaggeler, H. W.; Schotterer, U.; Tobler, L.; Van De Velde, K.; Ferrari, C.; Cozzi, G.; Turetta, A.; Rosman, K.; Bolshov, M.; Capodaglio, G.; Cescon, P.; Boutron, C. Historical record of European emissions of heavy metals to the atmosphere since the 1650s from Alpine snow/ice cores drilled near Monte Rosa. *Environ. Sci. Technol.* **2004**, *38*, 4085−4090.
(29) Barbante, C.; Bellomi, T.; Mezzadri, G.; Cescon, P.; Scarponi, G.; Morel, C.; Jay, S.; VanDeVelde, K.; Ferrari, C.; Boutron, C. F. Direct determination of heavy metals at picogram per gram levels in Greenland and Antarctic snow by double focusing inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* **1997**, *12*, 925−931.
(30) Blanchard, C. F. Methods for attributing ambient air pollutants to emission sources. *Annu. Rev. Energy Environ.* **1999**, *24*, 329−365.
(31) Artelt, S.; Kock, H.; König, H. P.; Levsen, K.; Rosner, G. Engine dynamometer experiments: platinum emissions from differently aged three-way catalytic converters. *Atmos. Environ.* **1999**, *33*, 3559−3567.
(32) Steffensen, J. P. The size distribution of microparticles from selected segments of the Greenland Ice Core Project ice core representing different climatic periods. *J. Geophys. Res., C: Oceans* **1997**, *102*, 26755−26763.
(33) Whiteley, J. D. Seasonal variability of platinum, palladium and rhodium (PGE) levels in road dusts and roadside soils, Perth, Western Australia. *Water, Air, Soil Pollut.* **2005**, *160*, 77−93.
(34) Lashka, D.; Striebel, T.; Daub, J.; Nachtwey, M. Platin im Regenfluss einer Strasse (Platinum in street runoff). *Umweltwiss. Schadst.—Forsch.* **1996**, *8*, 124.
(35) Wei, C.; Morrison, G. M. Platinum Analysis and Speciation in Urban Gullypots. *Anal. Chim. Acta* **1994**, *284*, 587−592.
(36) Zereini, F.; Skerstupp, B.; Alt, F.; Helmers, E.; Urban, H. Geochemical behaviour of platinum-group elements (PGE) in particulate emissions by automobile exhaust catalysts: experimental results and environmental investigations. *Sci. Total Environ.* **1997**, *206*, 137−146.
(37) Moldovan, M.; Rauch, S.; Gomez, M.; Palacios, M. A.; Morrison, G. M. Bioaccumulation of palladium, platinum and rhodium from urban particulates and sediments by the freshwater isopod *Asellus aquaticus*. *Water Res.* **2001**, *35*, 4175−4183.
(38) Rauch, S.; Morrison, G. M. Platinum uptake by the freshwater isopod *Asellus aquaticus* in urban rivers. *Sci. Total Environ.* **1999**, *235*, 261−268.
(39) Tuit, C. B.; Ravizza, G. E.; Bothner, M. H. Anthropogenic platinum and palladium in the sediments of Boston harbor. *Environ. Sci. Technol.* **2000**, *34*, 927−932.
(40) Barbante, C.; Boutron, C.; Morel, C.; Ferrari, C.; Jaffrezo, J. L.; Cozzi, G.; Gaspari, V.; Cescon, P. Seasonal variations of heavy metals in central Greenland snow deposited from 1991 to 1995. *J. Environ. Monit.* **2003**, *5*, 328−335.
(41) Gregurek, D.; Melcher, F.; Niskavaara, H.; Pavlov, V. A.; Reimann, C.; Stumpfl, E. F. Platinum-group elements (Rh, Pt, Pd) and Au distribution in snow samples from the Kola Peninsula, NW Russia. *Atmos. Environ.* **1999**, *33*, 3281−3290.
(42) Boyd, R.; Niskavaara, H.; Kontas, E.; Chekushin, V.; Pavlov, V.; Often, M.; Reimann, C. Anthropogenic noble-metal enrichment of topsoil in the Monchegorsk area, Kola peninsula, northwest Russia. *J. Geochem. Explor.* **1997**, *58*, 283−289.
(43) Niskavaara, H.; Kontas, E.; Reinmann C. Regional distribution and sources of Au, Pd and Pt in moss and O-, B- and C-horizon podzol samples in the European Arctic. *Geochem.: Explor., Environ., Anal.* **2004**, *4*, 143−159.
(44) Drab, E.; Gaudichet, A.; Jaffrezo, J. L.; Colin, J. L. Mineral particles content in recent snow at Summit (Greenland). *Atmos. Environ.* **2002**, *36*, 5365−5376.
(45) Kahl, J. D. W.; Martinez, D. A.; Kuhns, H.; Davidson, C. I.; Jaffrezo, J. L.; Harris, J. M. Air mass trajectories to Summit, Greenland: A 44-year climatology and some episodic events. *J. Geophys. Res., C: Oceans* **1997**, *102*, 26861−26875.
(46) Peucker-Ehrenbrink, B.; Jahn, B. M. Rhenium−osmium isotope systematics and platinum group element concentrations: Loess and the upper continental crust. *Geochem. Geophys. Geosyst.* **2001**, *2*.
(47) Wedepohl, K. H. The Composition of the Continental-Crust. *Geochim. Cosmochim. Acta* **1995**, *59*, 1217−1232.
(48) Gabrielli, P.; Barbante, C.; Plane, J. M. C.; Varga, A.; Hong, S.; Cozzi, G.; Gaspari, V.; Planchon, F. A. M.; Cairns, W.; Ferrari, C.; Crutzen, P.; Cescon, P.; Boutron, C. F. Meteoric smoke fallout over the Holocene epoch revealed by iridium and platinum in Greenland ice. *Nature* **2004**, *432*, 1011−1014.
(49) Schäfer, J.; Eckhardt, J. D.; Berner, Z. A.; Stuben, D. Time-dependent increase of traffic-emitted platinum-group elements (PGE) in different environmental compartments. *Environ. Sci. Technol.* **1999**, *33*, 3166−3170.
(50) Helmers, E.; Kummerer, K. Anthropogenic platinum fluxes: Quantification of sources and sinks, and outlook. *Environ. Sci. Pollut. Res.* **1999**, *6*, 150−150.
(51) Central Intelligence Agency. *World Factbook 2004*; Washington, DC, 2004.
(52) CPM Group. *Platinum Group Metals Survey*; CPM Group: New York, 2001.
(53) Johnson-Matthey. *Platinum, various issues*, London, 1987−2004.
(54) Johnson-Matthey *Platinum*, London, 2003.
(55) Zischka, M.; Schramel, P.; Muntau, H.; Rehnert, A.; Gomez Gomez, M.; Stojanik, B.; Wannemaker, G.; Dams, R.; Quevauviller, P.; Maier, E. A. A new certified reference material for the quality control of palladium, platinum and rhodium in road dust, BCR-723. *Trends Anal. Chem.* **2002**, *21*, 851−868.
(56) Lesniewska, B. A.; Godewska-Zylkiewicz, B.; Bocca, B.; Caimi, S.; Caroli, S.; Hulanicki, A. Platinum, palladium and rhodium content in road dust, tunnel dust and common grass in Bialystok area (Poland): a pilot study. *Sci. Total Environ.* **2004**, *321*, 93−104.
(57) Fritsche, J.; Meisel, T. Determination of anthropogenic input of Ru, Rh, Pd, Re, Os, Ir and Pt in soils along Austrian motorways by isotope dilution ICP-MS. *Sci. Total Environ.* **2004**, *325*, 145−154.

Received for review April 25, 2005. Revised manuscript received August 26, 2005. Accepted August 29, 2005.

ES050784M