

Implications of Platinum-Group Element Accumulation along U.S. Roads from Catalytic-Converter Attrition

JAMES C. ELY,*† CLIVE R. NEAL,†
CHARLES F. KULPA,‡
MARK A. SCHNEEGURT,‡,§
JAMES A. SEIDLER,† AND
JINESH C. JAIN†

*Department of Civil Engineering and Geological Sciences,
156 Fitzpatrick Hall, University of Notre Dame,
Notre Dame, Indiana 46556, Center for Environmental
Science and Technology, 152A Fitzpatrick Hall,
University of Notre Dame, Notre Dame, Indiana 46556, and
Department of Biological Sciences, 403 Hubbard Hall, Box 26,
Wichita State University, Wichita, Kansas 67260*

Automobile catalytic converters are dispersing platinum-group elements (PGEs) Rh, Pt, and Pd into the environment (1–3). This paper represents the first detailed study to assess the PGE content of soils and grasses from U.S. roadsides. These soils were analyzed using cation exchange pretreatment and ultrasonic nebulizer-ICP-MS (4). Highway and several urban sites showed Pt abundances of 64–73 ng/g immediately adjacent to the roadside, with corresponding Pd and Rh abundances of 18–31 ng/g and 3–7 ng/g, respectively. All Pt and most Pd and Rh abundances are statistically above local background soil values. Platinum, Pd, and Rh show positive correlations with traffic-related elements (Ni, Cu, Zn, and Pb) but no correlations with nontraffic-related elements (Y, Ga). Iridium and Ru show no correlations with any of these trace elements. These PGE abundances are comparable to European studies (5–7) and are approaching concentrations that would be economically viable to recover. This study also demonstrates transport of Pt statistically above background more than 50 m from the roadside. Further study is necessary to see how mobile the PGEs are in roadside environments, but these initial data indicate only Pt is taken up by plants.

Introduction

Catalytic converters have been in use on U.S. automobiles since 1975 removing gaseous pollutants, such as CO, hydrocarbons, and NO_x, from exhaust by promoting chemical reactions that change these pollutants into less toxic substances (i.e., CO₂, N₂, and H₂O). Catalytic converters use an alumina or cordierite monolith treated with an Al₂O₃ washcoat containing rare earth oxides and 0.10–0.15% (w/w) Pt, Pd,

and/or Rh to catalyze the removal of pollutants (8). The Clean Air Act of 1990 required catalytic converters to be attached to small gasoline engines such as those on lawn mowers, chain saws, etc. However, it has become evident that attrition of platinum group elements (PGEs) from the catalyst and its subsequent release into the environment and deposition on roadsides (e.g., ref 1) could be creating an unintended problem (9).

The amount and rate of PGE release from catalytic converters is affected by the speed of the automobile, type of engine, type and age of catalyst, and type of fuel additives. A 1977 study (10) found that under highway driving conditions, Pt is lost at a rate of 0.19 μg/km, whereas a 1992 study (11) measured levels that were 10–100 times lower. Both studies concluded that higher speeds and catalyst temperatures enhanced attrition and emissions of PGEs. Most PGE emissions from catalytic converters are in particulate form (Pt > 95%, Pd > 85%, and Rh > 90%) and are dispersed into the environment at rates of ng of PGE per kilometer per car (11, 12). Examination of the particulates released from catalytic converter materials has shown that ~99% of Pt is in the metallic state, with ~1% present as oxidized Pt, presumably Pt⁴⁺ (13, 14). The particulate Pt exists as a surface oxidized metal nanoparticle that is attached to a larger alumina (substrate) particle. However, the assumption that PGEs are mostly released in metallic form has been challenged by a recent study based on solubility experiments with roadside PGEs (7), which concluded that the PGEs may not be in a metallic form or that they have been rapidly altered once they are deposited in the environment. Studies in Germany demonstrated that Pt is accumulating in the upper (0–4 cm) layers of the soil and is being immobilized, presumably by humic acids or other organics, because natural waters in the study area have low Pt concentrations (15). This is consistent with laboratory studies of interactions of Pt with natural organic matter analogues (16) as well as environmental studies of Pt and Pd concentrations near ore deposits (17) and roadsides (7), confirming that Pd is more easily solubilized and transported than Pt.

Several studies have documented Pt uptake in plants, but these were conducted using high and environmentally unrealistic doses of Pt (18–22). Other studies have documented Pt contamination of roadside vegetation (23, 24), and Pt has been shown to accumulate in Douglas fir twigs (25). The roadside vegetation studies have suggested some uptake of Pt into roots, leaves, and stems but not into the fruit (24), although at least 50% of the Pt concentration on roadside grass was adhering to the surface (23). Another study (26) looked at transformations of Pt compounds in a humic soil using tunnel dust and artificial Pt compounds at high concentrations. They concluded that Pt binds to humic acid and some of the tunnel dust Pt may be oxidized but reported no Pt abundance data or associated error analysis for comparison. A different study (27) looked at plant uptake grown on soils contaminated with PGEs from catalytic converters. However, detection limits range from 0.21 to 2.5 ng/g for Rh, Pd, and Pt and all Rh and Pd abundances shown in the paper are all less than 2 ng/g. The proximity of the PGE abundances (except Pt) in roadside soils to the detection limits (usually low ng/g) in these studies (18–26) illustrates the difficulties in using traditional techniques such as fire assay or Te coprecipitation to analyze for PGEs, which is an inherent problem in most of these published works (e.g., ref 7). The near detection limit PGE abundances, in combination with the lack of tabulated PGE concentration data with 2 sigma errors, makes comparisons difficult and makes in-

* Corresponding author phone: (219)631-4308; fax: (219)631-9236; e-mail: ely.1@nd.edu.

† Department of Civil Engineering and Geological Sciences, University of Notre Dame.

‡ Center for Environmental Science and Technology, University of Notre Dame.

§ Wichita State University.

terpretation of such data containing inherently large errors (even if those errors are not explicitly quantified in the paper) circumspect. The cation exchange-ultrasonic nebulization (USN)-ICP-MS method developed at the University of Notre Dame allows simultaneous determination of PGEs (Ir, Ru, Rh, Pt, and Pd) in a sample with measured detection limits in the fg/g (10^{-15} g/g or part per quadrillion) range (4, 28). In particular, it makes possible the accurate analysis of a local background sample, which is necessary to demonstrate the amount of enrichment of roadside PGEs.

There have been several studies of environmental PGE accumulation in the U.K., Sweden, and Germany (1, 5), and these studies often have governmental cooperation. Since 1988, a German Cooperative Project has been sponsored by the Ministry of Research and Technology to assess the impact of "Emissions of Precious Metals" (18). A 1997 study in the U.K. (29) highlighted that further work on the transport of the platinum group metals was critical. This project resulted in a database for the concentrations of Pt, Pd, and Rh in road dust and soil adjacent to a major highway in the U.K. While there have been recent studies of PGEs in harbor and coastal sediments (30–32), only cursory roadside studies have been conducted in the U.S. (2, 3). These were performed before the complete conversion of automobiles to unleaded gasoline and modern monolith catalytic converters (as opposed to older pelletized catalysts) and were severely limited by the high PGE detection limits of the analytical techniques used. In recent years, more sensitive instrumentation with lower detection limits has renewed interest in anthropogenic PGE contamination of the environment.

This paper represents the first stage of an in-depth study of PGE (Ir, Ru, Rh, Pt, and Pd) pollution in soils along U.S. highways in relation to their potential adverse health effects and possible economic exploitation. The study includes local roads, interstates, and urban highways and has quantified the PGE contents of roadside soils and grasses.

Experimental Section

Soil samples were collected from interstate highways, urban roads, and side streets in and around South Bend, IN (33). All soils collected were of the Tyner-Oshmeto soil association (34) and were sandy loams or loamy sands collected from flat slopes (0–2%). Three soils immediately adjacent to highways were also collected from Perth, Western Australia and are included here only for comparative purposes (33) but were mostly unconsolidated bedrock. Soils were collected by scraping up the surficial soil (0–1 cm depth) with a plastic (HDPE) spatula in an area approximately 10 cm² and stored in plastic sample bags. Soils from the Indiana Toll Road (I-80/90, mile-marker 68) were separated using HDPE sieves with polyester-mesh screen sizes of 10 (2 mm), 18 (1 mm), 35 (0.5 mm), and 60 (0.25 mm) and a receiver pan. On the basis of catalytic converter attrition studies (13), the majority of PGE particles should be in the finest fraction (i.e., <0.25 mm). Consequently, all "pan" samples were analyzed, along with two coarser fractions from the soil immediately adjacent to the road. Soils from Australia and around the University of Notre Dame campus were processed as bulk samples. A South Bend, IN, background soil sample of the same type and general composition as the other South Bend area soil samples was collected approximately 1000 m from the nearest road. No background soil for the Australian samples was collected. All soil samples were powdered in an alumina mill and dissolved following the method of Ely et al. (4). Only grass leaves and shoots were collected (no roots), with half of the sample being rinsed with ethanol to wash off surface materials. All grass samples were weighed, dried in an oven at 100 °C, reweighed, and then powdered in an agate mortar and pestle for dissolution.

The cleaning of the agate mortar and pestle followed the protocol described in ref 4.

Results and Discussion

Identification of elevated PGE contents of soils through anthropogenic contributions requires that a natural background level be established as a reference point. PGE abundances in soils are dependent on such factors as soil composition, mineralogy, grain size, and underlying bedrock, and these factors can be locally highly variable. Therefore, a local background sample of the same soil type and general composition as the roadside soils was used as a normalization reference (Table 1). This background sample has PGE abundances generally similar to literature values for upper crust (35–37), which are provided in Table 1 for comparison. However, each upper crust sample has slight differences in different PGEs, highlighting the variability of, and therefore the importance of, establishing a local background reference soil composition. The PGE data demonstrate significant abundances of Rh, Pt, and Pd above background in each of the soil samples, especially those closest to the road (Table 1). On the basis of Pt/Rh, Pt/Pd, and Pd/Rh ratios, we can demonstrate that catalytic converter attrition was responsible for the elevated abundances (Figure 1A–C). The majority of data fell within the field defined by catalytic converter compositions (38), although the pan samples from the Indiana Toll Road persistently plotted toward lower Rh and Pd values for a given Pt concentration (Figure 1A,B). When starting at the PGE abundances of the local background soil (black cross in Figure 1A–C), these samples form a trend of increasing PGE abundances that is parallel or subparallel to the field formed by the PGE ratios of three way catalytic converters. As PGE ratios in catalytic converters are variable (38), it is likely that studies that draw conclusions from ratio data alone to determine differential PGE mobility are potentially flawed (e.g., ref 7).

The soils from less traveled roads (Douglas Road and University Drive) near the University of Notre Dame campus also exhibited higher abundances of Rh, Pt, and Pd relative to Ir and Ru (Table 1). However, these Rh, Pt, and Pd abundances were lower than those from the soil at 0–1 m from IN-933 or the 0 m soil from the IN Toll Road, demonstrating the positive correlation of Rh, Pt, and Pd abundances with the traffic volume data (see ref 33). The three Australian highway soils do not exhibit the same degree of enrichment in Rh, Pt, and Pd as seen in the U.S. roadside soils (Table 1; Figure 1A–C).

Both the washed and unwashed grass samples contained PGE abundances within error of each other (Figure 1A–C; Table 1). Platinum was the most abundant PGE in the grasses ranging from 1.2 to 1.7 ng/g, but, compared to the analyzed soils, the grasses contained the lowest PGE abundances.

PGE abundances in soils decreased away from road surfaces (Figure 2). Two sampling traverses were conducted, one perpendicular to the Indiana Toll Road (I-80/90; Figure 2A) and one perpendicular to IN-933 (US-31; Figure 2B) (33). There was little change in Rh, Pt, and Pd abundance between 0 and 2 m from I-80/90 (Figure 2A). Both traverses demonstrated that 4–5 m from the road, Rh, Pt, and Pd abundances decreased dramatically, by a factor of 2 along I-80/90 (Figure 2A) and by a factor of 5 along IN-933 (Figure 2B). At a distance of 10 m from I-80/90 the abundances were further reduced, but by a factor of 3–5 along I-80/90. However, beyond 10 m, there was no further decrease in the PGE content of the soil, but the abundances still are above local background (Figure 2A; Table 1). Iridium and Ru, which supposedly are not present in catalytic converters (but may possibly be present as impurities; Ir may also be present in some new diesel catalysts), were detectable in the soils at

TABLE 1: PGE Abundances for 16 Roadside Soils, 4 Roadside Grasses, Local Background, Reference Material UMT-1, and Literature Upper Crust Estimates with Errors Given As 2 Sigma Values^a

sample name	Ir (ng/g)	2 sigma	Ru (ng/g)	2 sigma	Rh (ng/g)	2 sigma	Pt (ng/g)	2 sigma	Pd (ng/g)	2 sigma
IN Toll Road 0 m soil (pan)	0.43	0.07	0.59	0.11	3.35	0.25	64.44	7.55	18.52	0.88
IN Toll Road 2 m soil (pan)	0.34	0.11	0.57	0.11	3.85	0.33	66.13	6.31	18.24	1.46
IN Toll Road 4 m soil (pan)	0.14	0.04	0.38	0.13	1.54	0.21	35.46	1.99	9.76	2.03
IN Toll Road 10 m soil (pan)	0.20	0.11	0.64	0.44	0.24	0.11	12.27	1.42	2.08	0.90
IN Toll Road 18 m soil (pan)	0.41	0.11	0.93	0.27	0.32	0.14	17.65	0.92	4.62	1.03
IN Toll Road 24 m soil (pan)	0.17	0.13	0.41	0.16	0.16	0.08	11.15	1.86	3.72	0.81
IN Toll Road 0 m soil mesh 35 (18–35)	0.21	0.06	0.44	0.09	1.11	0.06	17.54	0.74	6.34	0.35
IN Toll Road 0 m soil mesh 60 (35–60)	0.21	0.07	0.24	0.05	1.38	0.09	11.26	1.00	4.62	0.46
IN-933 0–1 m	0.30	0.10	0.71	0.13	6.68	0.81	73.25	4.85	31.48	3.10
IN-933 3–4 m	0.39	0.08	0.28	0.08	1.75	0.21	16.95	1.11	6.61	0.34
IN-933 50 m	0.27	0.05	0.18	0.05	0.34	0.06	5.17	0.59	2.51	0.32
Douglas Road 0–1 m	0.21	0.15	0.44	0.08	6.20	0.60	37.35	9.87	13.16	1.32
University Drive 0–1 m	0.09	0.06	0.27	0.02	0.84	0.07	10.61	0.84	6.51	0.81
Australian (Tonkin Highway)	0.73	0.30	0.55	0.12	3.54	0.57	22.79	3.02	14.39	1.12
Australian (Leach Highway #1)	0.69	0.21	0.63	0.12	2.73	0.22	16.24	1.06	8.40	0.36
Australian (Leach Highway #2)	0.59	0.17	0.75	0.21	2.63	0.44	13.26	1.14	10.32	1.23
IN Toll Road 0 m washed grass	0.07	0.04	0.22	0.05	0.10	0.02	1.23	0.27	1.03	0.23
IN Toll Road 18 m washed grass	0.09	0.04	0.20	0.05	0.10	0.03	1.69	0.19	0.97	0.37
IN Toll Road 0 m unwashed grass	0.07	0.05	0.16	0.02	0.11	0.04	1.73	0.44	1.29	0.25
IN Toll Road 18 m unwashed grass	0.06	0.04	0.23	0.04	0.12	0.05	1.41	0.68	1.44	0.30
UMT-1 average (n = 7)	7.50	1.10	10.03	0.98	9.18	0.96	119.4	12.8	97.8	10.7
UMT-1 certified values	8.8	0.6	10.9	1.5	9.5	1.5	129	5	106	3
upper crust (37)	0.025		0.407				0.39		0.653	
upper crust (38)	0.03		1.06		0.38				2.0	
upper crust (39)	0.05		0.10		0.06				0.40	
South Bend, IN background soil	0.06	0.04	0.43	0.13	0.09	0.03	3.63	0.82	1.54	0.41
average upper crust (refs 37–39 + S.B. bkgd)	0.04		0.50		0.18		2.01		1.15	

^a 10–200 g samples were rehomogenized to minimize the “nugget effect”. Aliquots of ~250 mg were dissolved and analyzed. Determination limits (10 sigma) for this technique are given in ref 32 and are in the 0.07–3 pg/g range. A VG Elemental PQII STE quadrupole ICP-MS was used for analysis. Two sigma errors were based on standard addition regression error with details of error calculations in ref 44.

levels less than 1 ng/g and at relatively constant abundances (within error) across the length of each traverse (Figure 2).

Normalization of the roadside soil PGE abundances to the background soil produces profiles that are instructive for examining relative enrichment above background as well as differences between the samples (Figure 3A–D). All soil samples generally contain Pd (except the Toll Road 10 m pan soil) and Pt abundances statistically different from (i.e., higher) those of South Bend background soil abundances (Table 1) at the 95% confidence level. Rhodium abundances for all soils except the Toll Road 10 and 24 m pan soils were also statistically higher than background soil concentrations at the 95% confidence level. Somewhat surprisingly, Ir abundances for all soil samples except the Toll Road 10 and 24 m, Douglas Road and University Drive soils were statistically higher than background soil abundances at the 95% confidence level. Enrichments of Ir were 5–7 times above background within 4 m of both the Toll Road and IN-933. For Ru, only the Toll Road 0 m, 18 m, and the IN-933 0–1 m soils were statistically higher than background soil abundances at the 95% confidence level. These enrichments are also seen in the normalization plots.

In the Indiana Toll Road (I-80/90) soils, the finest fraction contained the greatest PGE concentrations. Enrichments were approximately 18 times above background for Pt, 12 times above background for Pd, and 40 times above background for Rh. The coarser fractions of the I-80/90 soils contained almost an order of magnitude lower abundances of Pt, Pd, and Rh (enrichments of Pt, Pd, and Rh were 3–5 times, 3–4 times, and 12–15 times, respectively, see Figure 3A). Platinum and Pd appeared to be more widely dispersed compared to Rh, consistent with experimental observations and laboratory studies (15–17). All soils analyzed in this study contained Pt and Pd abundances above the natural background, whereas Rh decreased to within error of background levels at distances approximately 10 m from the road (Table

1; Figures 1, 2A, and 3A). This may reflect lower amounts of Rh relative to Pt and Pd in catalytic converters and the fact that Rh has only been used in catalytic converters since the mid-1980s, while Pt and Pd have been used since 1975. This is particularly relevant for understanding any potentially adverse impact such dispersion could have.

The situation is similar with the traverse perpendicular to IN-933 (US-31) (Figure 3B), although here bulk soils were analyzed. In comparing the data from I-80/90, IN-933 (US-31), Douglas Road, and University Drive there was a direct correlation between Rh, Pt, and Pd contents of the roadside (0 m) soils and the amount of traffic on these roads (33), even though the PGEs in the I-80/90 soils have been concentrated through sieving. This clearly demonstrates the anthropogenic input of PGEs through the attrition of automobile catalytic converters. Enrichments were even higher than the Toll Road 0 m soil, with Pt, Pd, and Rh being 20 times, 20 times, and 74 times above background, respectively. The Australian roadside soils also exhibit enrichment of Rh, Pt, and Pd but to a lesser degree than the South Bend soils (Pt, Pd, and Rh enrichments were on average 9 times, 9 times, and 17 times, respectively, compared to average upper crust—see Figure 3D). However, interpretations are limited because a local background soil was not collected, so the average upper crust-normalized profiles only show the general degree of enrichment. These profiles do illustrate that Pt in the Australian soils is less enriched relative to Pd and Rh than the South Bend soils, as the upper crust average Pt value is lower than the South Bend background Pt abundance.

Caution should be exercised in trying to compare PGE roadside abundances from different regions because of the generally poor quality of data in the literature as well as the large number of variables affecting the production, accumulation, and subsequent transformations of PGEs in the roadside environment. The quality of PGE data in the

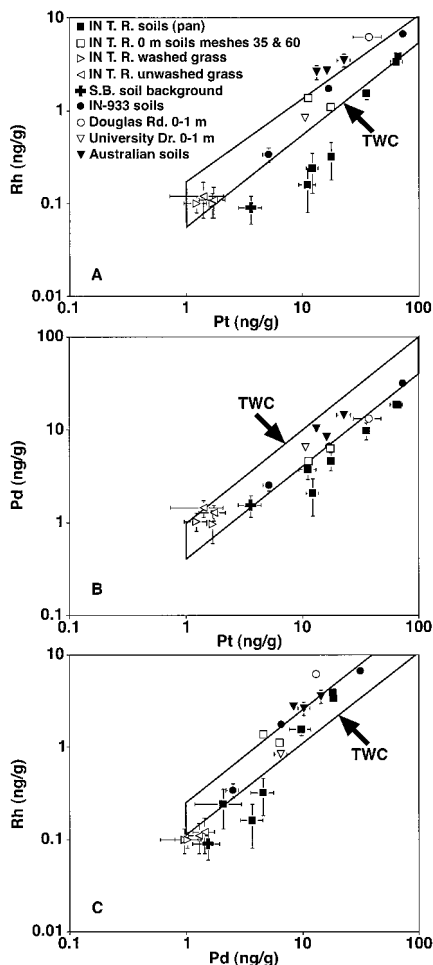


FIGURE 1. Element–element plots of Rh, Pd, and Pt abundances in soil and grass samples. Errors shown are 2 sigma and if not visible are within the size of the symbol. A: log–log plot of Rh vs Pt abundances. Abbreviations in the legend are as follows: T.R.-Toll Road; S.B.-South Bend, IN. IN Toll Road soils (pan) were sampled at 0, 2, 4, 10, 18, and 24 m and IN Toll Road 0 m soils mesh sizes shown are 35 (0.5–1 mm diameter) and 60 (0.25–0.5 mm diameter). IN-933 soils were sampled at 0–1, 3–4, and 50 m. The gray field represents three-way (Pt–Pd–Rh) catalytic converter (TWC) ratios (36). B: log–log plot of Pd vs Pt abundances. Symbols and field are as in A. C: log–log plot of Rh vs Pd abundances. Symbols and field are the same as in A.

literature has been commented upon (39, 40) and discussed above and is most often affected by factors such as compositional sample heterogeneities (“nugget effect”), the lack of errors provided with the data, and the insufficient use of direct methods of reproducibility to assess the precision of the data (39).

While the same general group of auto manufacturers supply Australia as well as Europe, Japan, and the U.S., there are marked differences in roadside Pt, Pd, and Rh enrichments, as demonstrated by the European studies (1). These differences may be due to the different timing of mandatory catalytic converter use by individual countries in conjunction with other factors (e.g., variable composition of each country’s car population by automaker and car model, age of catalytic converter, speed of car, volume of traffic, climate and rainfall, soil type, etc.). Furthermore, necessary information about how the PGEs transform in the roadside environment, how mobile they are, or even the bioavailability and toxicity of PGEs from catalytic converters are only now beginning to be investigated. Note that the apparent Ir enrichment in the Australian soils (Figure 3D) is a function of the different

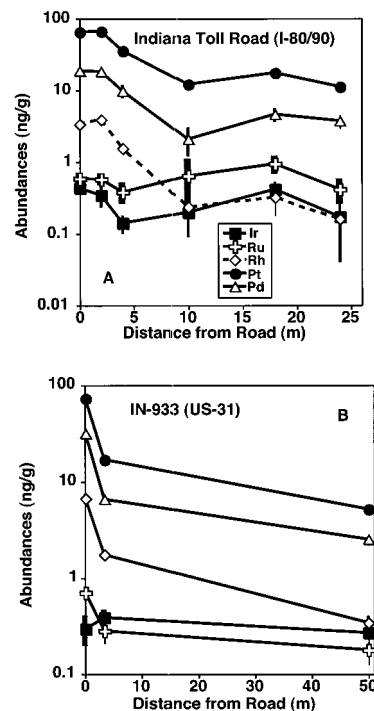


FIGURE 2. Perpendicular PGE profiles away from the roads. A. Indiana Toll Road, with PGE abundances given in ng/g (vertical log scale) and pan soil samples at 0, 2, 4, 10, 18, and 24 m. Errors on the points are 2 sigma and are within the size of the symbol if not visible. Note that Pt, Pd, and Rh are significantly elevated near the Toll Road, while Ir and Ru are always below 1 ng/g. When compared with the background soil sample, Ir abundances in all Toll Road samples are elevated above the background, while Ru abundances in all samples are similar to the background abundance. B. IN-933 with PGE abundances given in ng/g (vertical log scale) and bulk soil samples at 0–1, 3–4, and 50 m. Symbols are the same as in A. Errors on the points are 2 sigma and are within the size of the symbol if not visible.

normalization used in this diagram (see Table 1). Further study is necessary to determine the precise causes for the lower Pt, Pd, and Rh abundances in Australia compared to published studies in Europe and this U.S. study.

Certain trace metals (e.g., Ni, Cu, Zn, and Pb) have been used to evaluate the contribution of traffic to the surrounding urban environment (41–43). As an illustration, Pt, Pd, and Rh and Ir abundances from IN-933 were plotted against Ni, Cu, Zn, and Pb to see if any correlation was present (Figure 4A–D). The PGEs were also plotted against the lithophile elements Y and Ga, for which there should be no correlation, as these elements should be constant in all the soils as there is no documented anthropogenic input of Y and Ga. As can be seen in Figure 4A–C, Pt, Pd, and Rh all show positive correlations with Ni, Cu, Zn, and Pb. Note that the PGE abundances are plotted increasing from right to left, as the distance from the road is shown from left to right (actual distance data is in Table 1 and Figure 2B). Also note that the two sigma errors for the PGEs are for clarity only shown on the Ni data points, but are the same for all trace element data shown for each given PGE. These positive correlations of Pt, Pd, and Rh with Ni, Cu, Zn, and Pb further demonstrate that all of these metals are anthropogenic inputs to the roadside from automotive traffic. Also note that the Ni, Cu, Zn, and Pb background soil abundances are much lower than even the IN-933 50 m soil abundances, indicating substantial transport of these elements as well as the PGEs. There are no correlations of Pt, Pd, and Rh with Y and Ga (i.e., they are flat), and all Y and Ga abundances in the IN-933 soils are within error of those in the South Bend background soil.

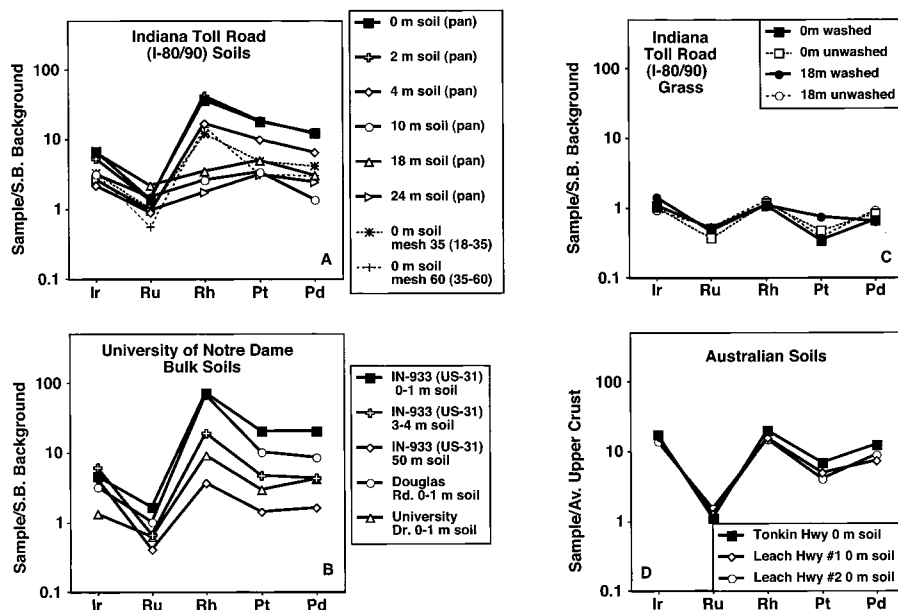


FIGURE 3. Soil and grass PGE data normalized to local background soil sample for South Bend, IN samples and average upper crust for Australian samples. Two sigma errors for all the samples were omitted for the sake of clarity (see Table 1 for all errors). A: Indiana Toll Road (I-80/90) soils. The dashed lines represent soil fractions other than those of the sieve pan. B: Soils taken from roads around the Notre Dame campus. All analyses were conducted on the bulk soil. C: Indiana Toll Road (I-80/90) grass samples. "Washed" indicates that the grass was washed with ethanol to remove the outer cuticle and any PGEs adhering to the surface. D: Soils from Australian highways around Perth, Western Australia. Note that the Australian soils are normalized to average upper crust as a local background (i.e., uncontaminated) soil was not collected in this area.

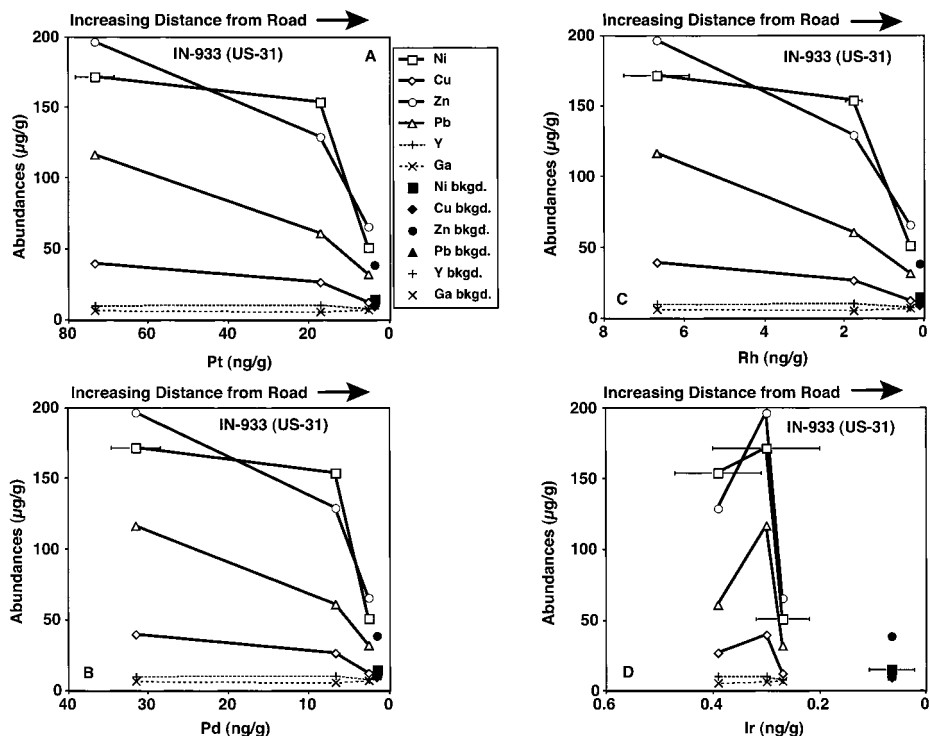


FIGURE 4. Soil PGE data plotted against traffic-related (Ni, Cu, Zn, and Pb) and lithophile (Y, Ga) trace element data for samples from IN-933. Local background soil PGE and trace element abundances are also plotted as points for comparison. A: Pt. Two sigma errors are shown for Pt on the Ni data points and are the same for all other series but were omitted for clarity. Trace element errors and errors not visible are within the size of the symbol. B: Pd. Symbols and errors are the same as in A. C: Rh. Symbols and errors are the same as in A. D: Ir. Symbols and errors are the same as in A. Note the lack of a positive correlation for any of the automotive-related trace elements (Ni, Cu, Zn, and Pb) and that all Ir abundances are within error of each other.

Iridium was also plotted against Ni, Cu, Zn, and Pb but showed no consistent positive correlations (Figure 4D). Note the much smaller Ir abundance scale compared to Figures 4A–C and the fact that all of the Ir abundances shown are within error of each other (note again that the two sigma

errors are shown only on the Ni data points for clarity, but are the same on Ir for all trace elements shown). While it was noted earlier that Ir abundances are elevated above local background (Figure 3B, Table 1), the geochemical data do not confirm traffic as the source. However, the elevated Ir

abundances in the soil are most likely being deposited along with Pt, Pd, and Rh as Ir is probably present as an impurity in automotive Pt–Pd–Rh catalysts and also is being used in some new diesel catalysts with Pt (8). Ruthenium (not shown) also demonstrated no correlations with any of the trace elements, and abundances were within error of that in the local background soil.

The results of the I-80/90 grass analyses demonstrate that Pt was taken up by the grass (Table 1, Figures 3C). However, the Pt abundances in all grass samples were not statistically different from those of the local background soil (Table 1) at the 95% confidence level. There was also no difference between the Pt abundances of the washed and unwashed grasses, demonstrating that Pt adhering to the surface of the grass leaves and stems was insignificant and that the Pt was incorporated into the grass tissue. Previous work (23, 24) had shown that Pt was taken up by roadside vegetation and that a positive correlation of Pt abundances and volume of traffic was documented. Other studies contradicted these conclusions (44, 45), stating “the bioavailability of catalyst emitted Pt is remarkably low”. Based on our preliminary data, there is uptake of Pt by grass. It also appears there is no correlation between the Pt abundances in the grass and the amount of Pt deposited in the roadside soils. This may be a function of the amount of Pt the grass can incorporate into its structure. Further study is required to conclude whether there is a correlation with traffic volume on U.S. roads, especially as the previous studies that showed such a correlation (23, 24) may have had another source of Pt present (i.e., industrial). Clearly future work is needed and will clarify whether the correlation with volume of traffic can be reproduced, what local background grass PGE abundance is (i.e., grass grown on uncontaminated soil), and whether this Pt uptake poses any health risks.

A positive impact of increased usage of catalytic converters in automobiles is that roadside soils may become an economic resource for the PGEs. For example, 100 ng/g translates to 0.1 g per metric ton. The only operating Pt mine in the U.S., the Stillwater Mining Company of Montana, processed 1.6 million metric tons of ore in the year 2000, producing 12 190 kg of Pt+Pd at a cash cost of \$9300 per kg and resulting in an economically viable ore grade of 7.47 g per metric ton (46). If the roadside soil 0–1 m from the roadway and 1 cm deep were collected from all the urban and interstate roadways in Indiana (34 000 km, which is 23% of the total road mileage in Indiana), and assuming an average Pt concentration in the soil of 100 ng/g and Pd concentration of 50 ng/g, then 510 000 metric tons of soil would be processed, producing 76 kg of Pt+Pd for an ore grade of 0.15 g per metric ton. While this ore grade is lower, the cash cost of collecting and processing the soil would be considerably reduced. The roadside soil is easily accessible and simpler and more environmentally friendly to process, compared to mining PGE ore from 1.6 km depth and smelting and processing that ore. As PGE roadside abundances will continue to accumulate (e.g., a German study (5) found Pt values of 1100 ng/g in roadside dust from Stuttgart and a recent British study (7) found Pt abundances of greater than 500 ng/g in road dust and surface samples), this recycling of PGEs from roadside soils could become economically viable and merits further research. Finally, if the PGEs were recycled, any potentially adverse effect to human health would be negated.

In summary, it is evident that attrition of automobile catalytic converters is introducing an anthropogenic contribution of Rh, Pt, and Pd into roadside soils. The data presented here shows that Pt and Pd were being transported relatively large distances (up to 50 m) from the road. Because of vegetation between the IN-933 50 m soil site and IN-933 as well as the level terrain, it appears that the transport

mechanism for the PGEs to this site is airborne. This is consistent with a recent study from Germany (47) where increased Pt and Rh abundances were detected in airborne samples collected at distances of 150 m from the road. Furthermore, the data also show that at least Pt was being incorporated into plants. With agricultural crops bordering much of the Indiana Toll Road, it remains to be seen how Pt is being incorporated into these foodstuffs; our study demonstrated the potential is there, and we caution that the toxic effects of Pt (+ Rh and Pd) should not be underestimated.

While catalytic converters are essential in reducing smog-causing automobile emissions, it is essential that we do not replace one pollutant with another. A solution to what is a potential problem also has an economic advantage. The roadside soils, especially in urban areas, would be nearly enriched enough to make them economically viable as sources of Pt and possibly Rh and Pd. If such exploitation were conducted, the PGEs would be removed from the environment before they could enter the food chain.

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