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Platinum Group Element Concentrations and Osmium Isotopic Composition in Urban Airborne Particles from Boston, Massachusetts

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Platinum, Pd, Rh, and Os were found to occur at elevated concentrations in airborne particles (PM10) collected at urban sites in Boston, MA. Average Pt, Pd, Rh, and Os concentrations were 6.9 ± 1.9, 8.1 ± 1.8, 1.50 ± 0.50, and 0.068 (−0.068 + 0.070) pg m^{-3}, respectively. Elevated Pt, Pd, and Rh concentrations are attributed to automobile catalysts, which use Pt, Pd, and Rh for the removal of pollutants from engine exhaust gas. An automobile catalyst source is supported by significant correlations between these elements and by a Pt/Rh similar to that in catalysts. Elevated Os concentrations are also believed to be the result of emission from automobile catalysts in which Os occurs as an impurity. The isotopic composition of Os (^{187}Os/^{188}Os) ranged from 0.30 to 2.90, indicating large variations in Os sources. Osmium has a predominantly anthropogenic origin at concentrations >0.1pg m^{-3}, whereas natural sources are more important at lower Os concentrations. Osmium isotopic composition also indicates that Pt, Pd, and Rh in Boston air are of almost exclusive anthropogenic origin, with a relatively small natural contribution. Our results indicate that scavenging by rain plays a major role in the atmospheric residence time and environmental fate of PGE.

Introduction

Platinum group elements (PGE) are among the least abundant elements in the Earth's crust (*1*, *2*), and natural PGE concentrations at the Earth's surface and in the atmosphere are therefore expected to be low. However, emissions of Pt, Pd, and Rh from automobile catalysts (*3*−*5*) have resulted in elevated concentrations of these elements in the urban and roadside environment (*6*−*8*). Emission of Os from automobile catalysts has recently been reported (*9*), and elevated Os concentrations in the environment been attributed, at least partly, to automobile catalyst emissions (*10*−*12*). Osmium has no intended function in automobile catalysts but may be present as an impurity (*10*).

While a number of studies have provided Pt, Pd, and Rh concentrations in airborne particles (*6*, *13*−*19*), road dust (*6*, *14*, *20*, *21*), and roadside soil (*20*−*22*) in urban areas of Europe, few studies have been performed elsewhere, including the United States where automobile catalysts were first introduced. Sediment records from an urban lake in Massachusetts indicate that urban PGE concentrations in the United States rapidly increased following the introduction of catalysts in 1975, and PGE input into the environment reached a plateau in the 1990s, possibly reflecting improved catalyst technology and the stabilization of the number of cars equipped with catalysts (*10*, *23*). Other studies in Massachusetts have demonstrated elevated Pt and Pd concentrations in Boston Harbor sediments (*24*) and Pt, Pd, and Rh concentrations in an ombrotrophic peat bog (*11*). Elevated PGE concentrations in urban road dust compared with background sites have been reported in California (*25*) and in Indiana (*26*).

Airborne particles represent a major environmental compartment for Pt, Pd, and Rh, which are primarily emitted as particles from automobile catalysts (*5*). They are also a primary form of human exposure and may therefore result in potential health effects (*27*). Platinum, Pd, and Rh concentrations in the pg m^{-3} range have been reported in urban air in Europe, with lower concentrations being reported at background sites (Table 1). Here, we report the first extensive study of Pt, Pd, Rh, and Os in urban aerosols in the United States where automobile catalysts were first introduced and provide evidence for an anthropogenic source of these elements.

Experimental Section

Sampling. Airborne particles were collected at two urban sites in Boston (42°22′ N; 71°02′ W), MA. Boston has a population of approximately 600 000 with a total of 3.5 million living in the metropolitan area. Over 375 000 vehicles are registered in the City of Boston and another estimated 600 000 are driven in daily (*30*).

Both sampling sites are located in the urban area and have similar PM10 concentrations with an annual arithmetic mean between 20 and 30 μg m^{-3} for 1989−2001. The first sampling site is located at Kenmore Square at the intersection of three high-volume roadways; Beacon Street (19 000 vehicles day^{-1}), Commonwealth Avenue (20 000 vehicles day^{-1}), and Brookline Street (23 000 vehicles day^{-1}). The sampler was positioned on the roof of a trailer with the inlet at a height of approximately 5 m. The second site is located on Columbus Avenue (10 000 vehicles day^{-1}), near the intersection with Berkeley Street (20 000 vehicles day^{-1}), and the sampler was placed on a roof top at a height of approximately 15 m.

Twelve samples were collected at Kenmore Square from November 2002 to March 2003, and 42 samples were collected at Columbus Avenue from March 2003 to October 2003 (Table 2). Sampling was performed for approximately 24 h starting at 09:00 using a high-volume PM10 impactor (Thermo Andersen, U.S.A.) at a flow of approximately 67 m^3 h^{-1}, resulting in sample volumes of approximately 1500 m^3. The flow rate was continuously monitored, and sampling time was recorded. Particles were collected on 20 × 25 cm^2 cellulose filters (Whatman 41, Whatman, U.S.A.). High trace element content in filter materials is a commonly reported limitation in the determination of trace element concentra-

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TABLE 1. Reported Average PGE Concentrations in Airborne Particles at Background and Urban Sites

			concn (pg m^{-3})				
sample	location	year	Pt	Pd	Rh	note	ref
background	Germany	1998–1999	<1		0.47	background site	(*6*)
	Germany	2001–2002	5	3	1	background site	(*19*)
	Italy	1998–1999	<1	3.6	<1	background site	(*6*)
	Spain	1998–1999	<1		0.5	background site	(*6*)
	Sweden	1999	2.7	5.2	0.9	background site, low traffic	(*6*)
	U.S. (California)	1975	<0.05			year of catalyst introduction	(*28*)
urban sites	Austria (Vienna)	2002	4.3	2.6	0.4	PM10, heavy traffic, stop and go	(*17*)
	Austria (Klagenfurt)	2001		3.9		PM10, urban	(*18*)
	Austria (Salzburg)	2001		16. 5		PM10, urban	(*18*)
	Germany (Dortmund)	1991–1992	1.3			PM10, urban	(*13*)
	Germany (Munich)	1998–2000	4.1		0.3	PM10, urban	(*6*)
	Germany (Frankfurt)	2001–2002	23	15	4	PM10, urban, high traffic	(*19*)
	Italy (Rome)	1998–1999	10.5	51. 4	2.6	PM10, urban	(*6*)
	Japan (Tokyo)	2003	2.1	0.8	0.5	PM7, urban	(*29*)
	Spain (Madrid)	1998–1999	15.6		4.2	PM10, urban	(*6*)
	Sweden (Göteborg)	1999	14.1	4.9	2.9	PM10, urban	(*15*)
	Sweden (Göteborg)	1999	5.4	1.5	1.6	PM2.5, urban	(*15*)
this study	Columbus Ave	2003	6.2	7.1	1.3	PM10, average	
	Kenmore Square	2002–2003	9.4	11	2.2	PM10, average	

tions in aerosol samples. Whatman 41 filters were selected because of low blank concentrations (*31*), although the filters have a slightly, but not significantly, lower retention efficiency under high-volume conditions (*32–34*), and their hygroscopic nature does not allow precise weight measurements (*31*). All samples were stored at ambient temperature in sealed polyethylene sheet protectors until analysis.

Weather data, including average daily temperature, rainfall, wind speed, and wind direction, were obtained from the U.S. National Oceanographic and Atmospheric Administration (*35*). Notes were taken during sampling to provide complementary weather information.

Fire Assay and ICP-SFMS Procedure. Forty-four PM10 filters were prepared by NiS fire assay, which uses the high affinity of PGE for sulfide, resulting in the preconcentration of PGE and the removal of interfering elements, as described by Ravizza and Pyle (*36*) and Hassler et al. (*37*). An extensive assessment of analytical uncertainties is provided in ref *38*. Analysis was performed by inductively coupled plasma-sector field mass spectrometry (ICP-SFMS, ELEMENT2, ThermoFinnigan, Bremen, Germany) with a desolvating nebulizer (Aridius, Cetac, Omaha, NE).

Filter samples were cut into small pieces with ceramic scissors, weighed, and spiked with a mixed PGE spike enriched in ^{99}Ru, ^{105}Pd, ^{190}Os, ^{191}Ir, and ^{198}Pt. A flux mixture of sodium tetraborate (Fisher Scientific, Houston, TX), nickel (99.99%, Aldrich, Milwaukee, WI), and sublimed elemental sulfur (Fisher Scientific, Houston, TX) was mixed with the sample in glazed ceramic crucibles. The crucibles were then covered with a glazed ceramic lid and the mixture fused at 1000 °C for 1.5 to 2 h. After cooling, the sulfide bead was separated from the glass and dissolved under reducing conditions in 6.2 N HCl at ~150 °C. The solution containing insoluble PGE-rich particles was filtered through a 0.45 μm cellulose filter. The filter paper was then transferred to a Teflon vial and digested in 1 mL of concentrated HNO_3. To fully dissolve the PGE-rich particles and oxidize Os to volatile OsO_4 the closed Teflon vial was heated to ~100 °C for about 90 min. After chilling the vial in ice water and diluting the solution 5-fold with Millipore water, the Teflon lid was replaced with a two-port cap, one end of which was connected to the Ar supply and the other to the ICP-MS torch. When Ar was bubbled through the solution, volatile OsO_4 was carried with the Ar stream into the plasma, allowing the determination of Os and its isotopic composition. Complementary PGE concentrations were determined by ICP-SFMS in the liquid residue after it was taken to dryness and redissolved in 5% HNO_3.

Three isotope ratios were used to determine Os and Ru concentrations, two ratios were used for Pt and Pd, and the 191/193 ratio was used to determine Ir concentrations. Concentrations generally agreed within a few percent of each other, except for Ru and Ir which are present at concentrations that are too low for their accurate determination using the described procedure, and therefore, Ru and Ir concentrations are not reported here. Rhodium is monoisotopic, and therefore rhodium concentrations were calculated from Pt and Pd concentrations by ratioing Rh count rates to normalized Pt and Pd count rates. A total of four concentration values, two for each element, were calculated. Rhodium concentrations were removed when the standard deviation of the four measurements was larger than 30%. Blank values were obtained from an unexposed filter.

Microwave Digestion and ICP-QMS Procedure. Ten PM10 filters were analyzed by inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS, Elan 6000, PE Sciex, Canada) after microwave digestion (*15*) for comparison with ICP-SFMS analysis. Comparison of the methods is especially important for Rh because Pt and Pd isotopes were used to determine its concentrations. In addition, microwave digestion enabled the analysis of Cd, Cu, Pb, and Zn.

Approximately one-quarter of the PM10 filters was ashed at 550 °C for 2 h in porcelain crucibles and placed in sealed Teflon vessels together with 8 mL of aqua regia (HCl/HNO_3, 3:1, v/v, Suprapure grade, Promochem AB, Ulricehamn, Sweden). The filters were mineralized in a CEM Mars5 microwave digestion system (CEM, Mattheus, U.S.A.) using a controlled program with stepwise increase of power, temperature, and maximum pressure to 1200 W, 200 °C, and 300 psi, respectively. Samples were then heated to dryness on a hot plate, and residues were dissolved in 2% hydrochloric acid (5 mL) (*15*).

Platinum, Pd, Rh, Cd, Cu, Pb, and Zn were determined by ICP-QMS. The formation of oxides, argides, and doubly charged ions in the plasma produce interference during the

TABLE 2. PGE Concentrations and Os Isotopic Composition in All Analyzed PM10 Samples

sample	location[a]	start date	[Os] (pg m^{-3})	^{187}Os/^{188}Os	[Pt] (pg m^{-3})	[Pd] (pg m^{-3})	[Rh] (pg m^{-3})
1	CA	04-03-03	0.006	1.35	5.7	9.9	
2	CA	05-03-03	0.003	1.02	3.6	4.3	1.2
3	CA	06-03-03	0.003	1.89	36	5.1	
4	CA	07-03-03	0.004	1.13	5.3	8.3	1.8
5[b]	CA	08-03-03			3.2	1.9	0.34
6	CA	10-03-03			0.6	2.7	
7[b]	CA	11-03-03			4.5	7.9	0.87
8	CA	12-03-03	0.003	1.65	4.5	7.3	1.3
9	CA	08-03-03	0.008	0.67	4.0	7.1	0.58
10	CA	09-03-03	0.007	1.13	4.1	6.9	1.9
11	CA	11-03-03	0.020	0.62	8.5	14	1.5
12	CA	13-03-03	0.002	2.83	2.1	4.0	0.85
13[b]	CA	14-04-03			4.9	4.2	0.37
14[b]	CA	15-04-03			5.6	4.2	0.48
15	CA	14-04-03	0.003	1.37	4.4	7.6	1.4
16	CA	16-04-03	0.004	1.42	35	9.6	
17	CA	17-04-03	0.12	0.50	2.9	3.8	0.39
18	CA	22-04-03			3.4	3.7	0.86
19	CA	23-04-03			4.2	6.5	
20	CA	25-04-03	0.023	0.37	3.0	3.7	
21	CA	26-04-03	0.002	1.12	2.5	3.0	0.74
22	CA	29-04-03	0.011	1.74	12	16	
23	CA	12-07-03			5.0	5.7	
24	CA	13-07-03			4.1	9.8	
25	CA	15-07-03	0.005	1.26	1.4	2.0	0.33
26	CA	16-07-03	0.82	0.43	7.0	12	2.7
27	CA	17-07-03			4.9	5.6	1.6
28	CA	18-07-03			6.5	5.6	
29	CA	22-07-03			3.1	3.0	
30	CA	23-07-03	0.012	0.43	2.1	0.8	
31	CA	24-07-03			3.4	5.1	0.99
32	CA	28-07-03	0.41	0.68	5.7	18	2.0
33	CA	14-10-03	0.002	1.34	4.6	6.2	1.3
34	CA	15-10-03			3.9	4.5	
35	CA	16-10-03			5.0	5.6	
36	CA	17-10-03			3.1	5.3	0.9
37	CA	18-10-03	0.38	0.58	16	39	5.9
38	CA	19-10-03			4.8	5.4	
39	CA	20-10-03	0.001	2.35	6.9	7.8	
40	CA	21-10-03	0.008	0.46	4.5	4.6	
41	CA	28-10-03	0.003	0.98	3.6	6.5	1.1
42	CA	29-10-03	0.018	0.30	5.9	4.1	
43[b]	KS	26-11-02			4.9	2.8	0.50
44[b]	KS	27-11-02[c]			4.2	5.5	0.89
45	KS	02-12-02			8.2	6.6	
46[b]	KS	03-12-02			15	16	3.2
47	KS	05-12-02			0.62	1.0	
48	KS	09-12-02[c]	0.026	0.30	17	26	5.9
49	KS	06-02-03	0.001	2.66	8.5	18	
50[b]	KS	09-02-03			12	7.1	1.4
51	KS	10-02-03[c]	0.003	1.65	7.4	11	
52[b]	KS	12-02-03			6.0	8.8	1.2
53[b]	KS	21-02-03			17	16	2.1
54	KS	24-02-03			12	18	

[a] Columbus Avenue (CA) and Kenmore Square (KS). [b] Samples analyzed using the ICP-QMS procedure. [c] Sampled for 24 h over a 48-h period.

determination of ^{105}Pd ($ArCu^+$, YO^+, SrO^+, and RbO^+), ^{195}Pt (HfO^+), and ^{103}Rh ($ArCu^+$, Pb^{2+}, SrO^+, and RbO^+) (*39*). Blank values were obtained from an unexposed filter. Interferences were corrected mathematically by estimating the contribution of interfering species to PGE signals in standard solutions (eqs 1–3).

$$I_{\mathrm{Pt}} = I_{\mathrm{Pt,s}} - (I_{\mathrm{Hf,s}} R_{\mathrm{HfO,Hf}}) \quad (1)$$

$$I_{\mathrm{Pd}} = I_{\mathrm{Pd,s}} - (I_{\mathrm{Cu,s}} R_{\mathrm{ArCu,Cu}} + I_{\mathrm{Y,s}} R_{\mathrm{YO,Y}} + I_{\mathrm{Sr,s}} R_{\mathrm{SrO,Sr}} + I_{\mathrm{Rb,s}} R_{\mathrm{RbO,Rb}}) \quad (2)$$

$$I_{\mathrm{Rh}} = I_{\mathrm{Rh,s}} - (I_{\mathrm{Cu,s}} R_{\mathrm{ArCu,Cu}} + I_{\mathrm{Pb,s}} R_{\mathrm{Pb}}{}^{2+}{}_{,\mathrm{Pb}} + I_{\mathrm{Sr,s}R\mathrm{SrO,Sr}} + I_{\mathrm{Rb,s}R\mathrm{RbO,Rb}}) \quad (3)$$

where in eq 1: I_{Pt} stands for the corrected Pt intensity; $I_{\mathrm{Pt,s}}$ is the apparent Pt intensity in the sample; $I_{\mathrm{Hf,s}}$ is the Hf intensity in the samples; $R_{\mathrm{HfO,Hf}}$ is the ratio HfO^+/Hf^+ determined previously in Hf-containing standard solutions. $I_{\mathrm{Pt,s}} - I_{\mathrm{Pt}}$ represents the interference. The same nomenclature applies to eqs 2 and 3 (*15*).

Quality Control and Statistical Analysis. The quality of analytical procedures was assessed by the determination of PGE concentrations and osmium isotopic composition in tunnel dust reference material BCR-723 (Institute for Reference Materials and Measurements, IRMM) and in rock reference materials, including TDB-1 and WGB-1 (Canadian Certified Reference Materials Project, CCRMP). Results and certified values generally were in good agreement (Table 3).

TABLE 3. Measured and Certified Os, Pt, Pd, and Rh Concentrations and ^{187}Os/^{188}Os in Rock Reference Materials TDB-1 and WGB-1 (Canadian Certified Reference Materials Project, CCRMP) and in Tunnel Dust Reference Material BCR-723 (Institute for Reference Materials and Measurements, IRMM)[a]

material	sample weight (g)	method	measurement	repetitions	obtained results	certified value	unit	ref
TDB-1	4.6−6.9	fire assay + ICP-SFMS	Os	8	122 ± 5		pg g^{-1}	(*38*)
			^{187}Os/^{188}Os	8	0.83 ± 0.04			
			Pt	8	4.4 ± 0.2	5.8 ± 1.1	ng g^{-1}	
			Pd	8	24.8 ± 1.0	22.4 ± 1.3	ng g^{-1}	
WGB-1	4.7−5.9	fire assay + ICP-SFMS	Os	8	693 ± 361		pg g^{-1}	(*38*)
			^{187}Os/^{188}Os	8	0.187 ± 0.012			
			Pt	8	5.8 ± 2.6	6.1 ± 1.6	ng g^{-1}	
			Pd	8	16.2 ± 2.2	13.9 ± 2.1	ng g^{-1}	
BCR-723	0.2	fire assay + ICP-SFMS	Os	1	1.2		ng g^{-1}	(*10*)
			^{187}Os/^{188}Os	1	0.2707			
			Pt	1	97	81.3 ± 3.3	ng g^{-1}	
			Pd	1	6.7	6.0 ± 1.8	ng g^{-1}	
			Rh	1	15	12.8 ± 1.2	ng g^{-1}	
BCR-723	0.10−0.25	microwave digestion + ICP-QMS	Pt	6	79.6 ± 1.7	81.3 ± 3.3	ng g^{-1}	
			Pd	2	3.7	6.0 ± 1.8	ng g^{-1}	
			Rh	6	12.5 ± 1.0	12.8 ± 1.2	ng g^{-1}	

[a] Additional information is provided in the references.

In addition, good agreement between Pt, Pd, and Rh concentrations determined by ICP-SFMS and ICP-QMS in collected samples provides a further, favorable assessment of the quality of PGE measurements (Mann−Whitney U-test with 5% decision level).

Data are presented in the text as mean ± half-width of the 95% confidence interval. Because concentrations cannot be negative, data are presented as mean (− mean + half-width of the 95% confidence interval) when the lower end member is negative. Comparison of data groups was performed using the *t*-test if assumptions of normal distribution and equal variances were satisfied. The Mann−Whitney U-test was used when the assumptions could not be satisfied.

Results and Discussion

Concentration Levels in Boston Air. Concentrations in all analyzed PM10 samples are provided in Table 2. Average Pt, Pd, and Rh concentrations were 6.2 ± 2.2 pg m^{-3} (n = 42), 7.1 ± 1.9 pg m^{-3} (n = 42), 1.3 ± 0.5 pg m^{-3} (n = 24), respectively, at the Columbus Avenue site and 9.4 ± 3.3 pg m^{-3} (n = 12), 11 ± 5 pg m^{-3} (n = 12), 2.2 ± 1.7 pg m^{-3} (n = 7), respectively, at the Kenmore Square site. Platinum, Pd, and Rh concentrations at Kenmore Square were higher than at the Columbus Avenue site, possibly due to higher traffic volume and sampling inlet height at the Kenmore Square site, although the difference was only significant for Pt (Mann−Whitney U-test with a decision level of 5% for Pt and a decision level of 10% for Pd and Rh). Platinum, Pd, and Rh concentrations in Boston are comparable to concentrations in European cities (Table 1). The osmium concentration at the two sites was 68 (−68 + 70) fg m^{-3} (n = 28; results for Os are not presented for individual sites owing to the small amount of data at Kenmore Square).

Cadmium, Cu, Pb, and Zn in Boston air were 0.20 ± 0.06 ng m^{-3}, 55 ± 8 ng m^{-3}, 7.0 ± 1.5 ng m^{-3}, and 25 ± 6 ng m^{-3} (n = 10), respectively, and there was no statistical difference between the two sampling sites. The concentrations of PGE and other metals in Frankfurt, Germany (*19*) were higher than in Boston, although of the same order of magnitude.

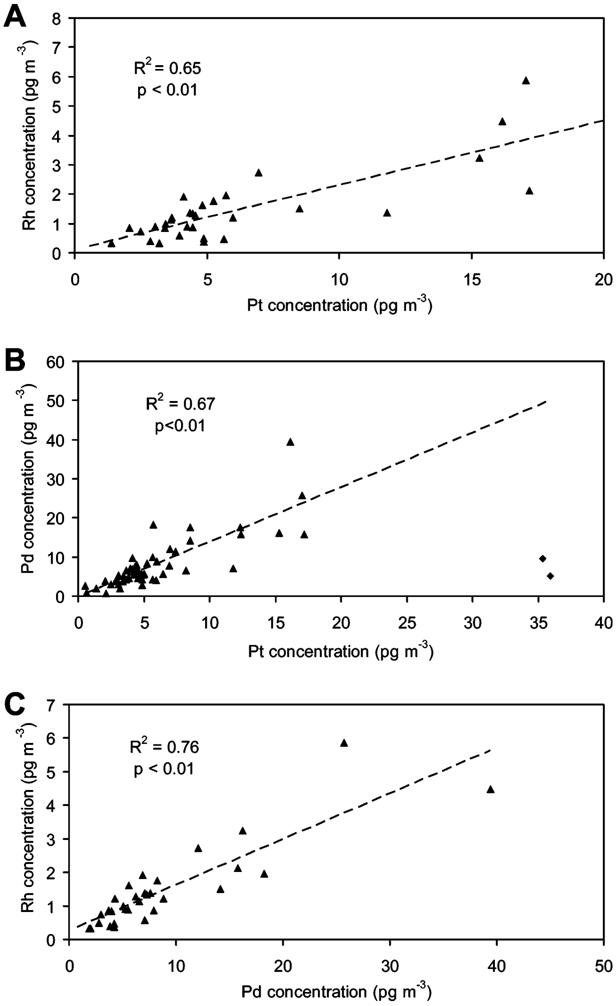

FIGURE 1. Correlation between Pt, Pd, and Rh in Boston air. The dashed line shows the correlation between the elements. For the Pt−Pd plot, two data points with elevated Pt concentrations and relatively low Pd concentrations were considered as outliers.

Source of PGE in Boston Air. Elevated Pt, Pd, and Rh concentrations in Boston air compared with expected background concentrations (Table 1) and significant correlations ($R^2 \geq 0.65$, $p < 0.01$) between Pt, Pd, and Rh concentrations (Figure 1) suggest a common anthropogenic source for these elements. In contrast, there was no correlation between PGE and Cd, Cu, Pb, and Zn concentrations. Automobile catalysts are the only known source of airborne

PGE in the Boston region. Catalysts use a combination of Pt, Pd, and Rh, and ratios of these elements have been used to determine the source of PGE in the environment (*10*, *15*, *26*, *29*, *40*−*41*). Three way catalysts have been estimated to have Pt/Rh and Pt/Pd of 5−16 and 1−2.5, respectively (*26*, *41*), and average Pt/Rh and Pt/Pd in the ranges of 3.7−13.7 and 0.2−2.9, respectively, have been reported for urban air (*6*, *15*, *17*, *19*). Pt/Rh and Pt/Pd in Boston airborne particles were 5.06 ± 1.07 ($n = 54$) and 1.01 ± 0.27 ($n = 31$), respectively, supporting an automobile catalyst source. Both sites had similar Pt/Pd, but the Pt/Rh was higher at the Kenmore Square site (Mann−Whitney U-test with a 10% decision level).

There was no correlation between Os and Pt, Pd, or Rh concentrations. As automobile catalysts are the only known source of Os in Boston air, the absence of significant correlation may be the result of a different emission mechanism or environmental behavior of Os compared with the other PGE. While Pt, Pd, and Rh are primarily emitted in a particulate form (*5*), Os is principally emitted as OsO_4 gas (*9*).

The $^{187}Os/^{188}Os$ in Boston airborne particles ranged from 0.30 to 2.90. The source of Os is reflected in its isotopic composition with crustal Os having a high (i.e., radiogenic) $^{187}Os/^{188}Os$ of ~1.40 (*1*) and commercial Os having a relatively low $^{187}Os/^{188}Os$ of ~0.1 to 0.2 (*9*, *10*, *42*−*45*). Therefore, the isotopic composition of Os in PM10 samples indicates significant anthropogenic and natural contributions, with variations in the Os sources on different days. Samples with Os concentrations <0.1 pg m^{-3} have a statistically more radiogenic (i.e., larger) $^{187}Os/^{188}Os$ than samples with Os concentrations >0.1 pg m^{-3} (Mann−Whitney U-test, decision level 5%), indicating that high Os concentrations result from anthropogenic emissions. The anthropogenic fraction of Os (AF_{Os}) and natural and anthropogenic Os concentrations can be estimated using eqs 4−6, assuming a natural $^{187}Os/^{188}Os$ of 1.4 (average $^{187}Os/^{188}Os$ for samples with concentration <0.01 pg m^{-3}, similar to Earth crust estimate), an anthropogenic $^{187}Os/^{188}Os$ of 0.175 (*9*), and neglecting small variations in the atomic weight between the end members. Samples with $^{187}Os/^{188}Os \geq 1.40$ were considered to have an exclusively natural source of Os.

$$AF_{Os} = \frac{(^{187}Os/^{188}Os)_{natural} - (^{187}Os/^{188}Os)_{sample}}{(^{187}Os/^{188}Os)_{natural} - (^{187}Os/^{188}Os)_{anthropogenic}} \qquad (4)$$

$$[Os]_{anthropogenic} = [Os]_{sample}(AF_{Os}) \qquad (5)$$

$$[Os]_{natural} = [Os]_{sample}(1 - AF_{Os}) \qquad (6)$$

The anthropogenic fraction represents 35 ± 13 % ($n = 28$) of the total Os concentration in airborne particles in Boston. For samples with Os concentrations >0.1 pg m^{-3}, the anthropogenic contribution represents 70 ± 14 % ($n = 4$) of the total Os concentration, while for samples with lower Os concentrations the anthropogenic fraction represents 29 ± 14 % ($n = 24$). The average natural Os concentration in Boston airborne particles was 0.021 ± 0.018 pg m^{-3} ($n = 28$). The relatively large variability results from elevated natural concentrations in samples with Os concentrations >0.1 pg m^{-3}.

Natural and anthropogenic PGE contributions can be estimated from the relative PGE concentrations using Os concentration in the natural sources and assuming that the natural sources have the same relative composition as the upper continental crust. The crustal PGE composition has been reported for Os, Pt, and Pd (*1*) and for Rh (*2*). Average natural Pt, Pd, and Rh concentrations in Boston airborne particles were 0.34, 0.35, and 0.040 pg m^{-3}. Despite potential errors in the estimation of natural concentrations resulting from the fractionation of PGE in the environment, the large difference between natural and total Pt, Pd, and Rh concentrations indicate that Pt, Pd, and Rh in Boston air are almost exclusively of anthropogenic origin.

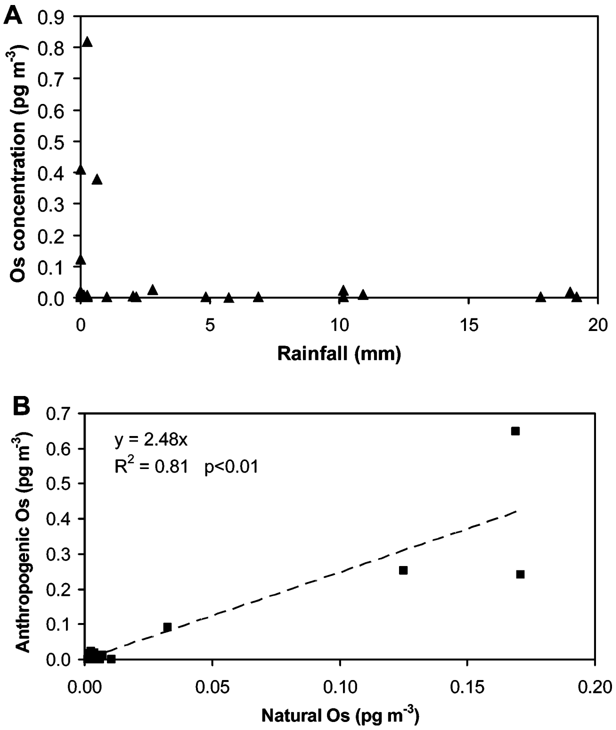

FIGURE 2. (A) Plot of Os concentration vs rainfall. (B) Correlation between natural and anthropogenic Os concentrations. The dashed line shows the correlation between natural and anthropogenic Os.

Factors Affecting PGE Concentrations. Traffic and weather conditions were investigated to determine a possible relationship with PGE concentrations in urban air. The higher concentrations observed at Kenmore Square indicate that traffic density is a key parameter controlling PGE concentrations in urban air. However, no significant difference in PGE concentration was observed between samples collected on weekdays and on the weekend. As a higher traffic is normally encountered on weekdays, the comparison of weekdays and weekends indicates that traffic density is not the only factor influencing PGE concentration in urban air.

Seasonal variations in atmospheric PGE concentration have been reported (*18*, *46*), and therefore, climatic conditions may affect PGE concentrations in urban air. No clear seasonal variation in PGE concentrations was observed in Boston, however, possibly because precipitation in Boston occurs fairly evenly throughout the year. In addition, no significant correlation was established between PGE concentrations and ambient temperature, rainfall, wind speed, or wind direction. Although there is no linear relationship between PGE concentrations and rainfall, there is a tendency for high PGE concentrations to occur at low rainfall, while low concentrations are associated with high rainfall, possibly due to the scavengging of aerosols by rain. The trend is particularly pronounced for Os, possibly due to a higher solubility (Figure 2A). The importance of rain in the cycle of Os is supported by the study of an ombrotrophic peat bog, which suggests that wet deposition is a major scavenging mechanisms for natural Os (*11*). The correlation between natural and anthropogenic Os (Figure 2B) indicates that both natural and anthropogenic PGE are scavenged by rain and that factors affecting the concentration of PGE in airborne particles affected both natural and anthropogenic contributors. The absence of correlation with wind direction is probably due to the urban setting of the sampling sites with traffic sources in all directions.

The research presented here demonstrates that automobile catalysts have resulted in elevated Pt, Pd, and Rh concentrations in airborne particles in Boston. The concentration of these metals is of the same magnitude as in European cities. We also report elevated Os concentrations in urban air as a result of anthropogenic emission, possibly from automobile catalysts. Airborne particles are a primary form of human exposure to PGE (*27*), and atmospheric transport of PGE-containing particles has been reported to result in the widespread dispersion of these elements (*29*). Our results indicate that scavenging by rain plays a major role in the atmospheric residence time and environmental fate of PGE.

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