

# Platinum Group Elements in Airborne Particles in Mexico City

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Automobile exhaust catalysts using platinum group elements (PGE) have been mandatory on new cars in the Mexico City Metropolitan Area (MCMA) since 1991. Platinum, Pd, Rh, Ir, and Os concentrations and the isotopic composition of Os were determined in PM<sub>10</sub> samples from the MCMA. Samples were prepared by isotope dilution NiS fire assay, and analysis was performed by magnetic sector ICP-MS using a single collector instrument for Pt, Pd, Rh, and Ir analysis and a multicollector instrument for Os analysis. Pt, Pd, and Rh concentrations at a downtown location (Merced) increased from  $\leq 1.7$  pg of Pt m<sup>-3</sup>, 2.7 (4.0) pg of Pd m<sup>-3</sup>, and  $1.2 \pm 0.9$  pg of Rh m<sup>-3</sup> in 1991 to  $9.6 \pm 1.8$  pg of Pt m<sup>-3</sup>,  $10.2 \pm 1.8$  pg of Pd m<sup>-3</sup>, and  $2.8 \pm 0.6$  pg of Rh m<sup>-3</sup> in 2003. Concentrations at five sites in MCMA in 2003 averaged  $9.3 \pm 1.9$  pg of Pt m<sup>-3</sup>,  $11 \pm 4$  pg of Pd m<sup>-3</sup>, and  $3.2 \pm 1.0$  pg of Rh m<sup>-3</sup>. In contrast, Ir and Os concentrations and Os isotopic composition remained relatively constant and were  $0.08 \pm 0.04$  pg of Ir m<sup>-3</sup>,  $0.030 \pm 0.007$  pg of Os m<sup>-3</sup>, and  $0.60 \pm 0.04$ , respectively, in the MCMA in 2003. Elevated Pt, Pd, and Rh concentrations in the MCMA are attributed to automobile catalysts. A Pt–Pd–Rh concentration peak in 1993 suggests that early catalysts emitted a larger amount of PGE, possibly due to factors inherent in the technology or the use of inappropriate gasoline. Therefore, this study suggests that the current introduction of automobile catalysts in developing countries may result in elevated PGE concentrations if it is not accompanied by infrastructures and policy measures supporting their efficient use.

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## Introduction

Automobile catalysts use Pt, Pd, and Rh as main active components, and emission of these elements from automobile catalysts (1) has been reported to result in their occurrence at elevated concentrations in the urban and roadside environment (2, 3). Atmospheric dispersion of platinum group elements (PGE) has also been reported to result in widespread environmental contamination (4) with increasing PGE concentrations measured as far from automobile traffic as Central Greenland (5). Airborne particles are a primary form of human exposure, and elevated PGE concentrations in urban air raise concern over potential health effects. Therefore, a number of studies have aimed at determining PGE concentrations in urban air. Most studies have, however, been performed in Europe (e.g., refs 2 and 6–9), with only a few studies elsewhere (10–13).

In developing countries, catalyst requiring legislations or import of cars from catalyst requiring countries have resulted in the introduction of automobile catalysts into the vehicle fleet. Because of the rapid increase in vehicle sales in developing countries, especially India and China (14), a rapid increase in catalyst numbers is expected in these countries. Conditions in developing countries are different than in developed countries, with congested traffic in rapidly growing megacities, older vehicle fleets, and lower fuel quality. It is therefore important to assess PGE levels in developing countries.

The research presented here provides Pt, Pd, Rh, Ir, and Os concentrations in PM<sub>10</sub> particles collected in the Mexico City Metropolitan Area (MCMA) from 1991 to 2003. With nearly 20 million inhabitants, Mexico City is one of the world's most populated urban centers, and rapid population growth in the MCMA has generated greater demand for transportation. As a result, the vehicle population in the MCMA is now estimated to be 3.5 million (15), and the transportation sector is an important source of air pollution (16). In the 1990s, the Mexican government implemented measures on vehicles and fuel to reduce emissions from automobile traffic. Catalysts have been mandatory on new cars in Mexico City since 1991. Three way catalysts (TWC) and computerized engine control (closed loop control using an oxygen sensor to regulate fuel injection) have been mandatory on new cars in Mexico since 1993. In 2001, an estimated 1.3 million vehicles (46%) were equipped with an exhaust catalyst, with 0.6 million catalysts being more than 6 years old (17).

## Experimental Procedures

**Sampling.** PM<sub>10</sub> samples were obtained from stations of the Ambient Air Monitoring Network of Mexico City (Table 1, Figure S1). Six sets of three samples each were obtained at the Merced site during the first halves of 1991, 1993, 1994, 1997, 2000, and 2003 to study PGE concentration changes from 1991 to 2003. In addition, five sets of three samples each were obtained from five sites in the MCMA in the second half of 2003 to assess the spatial variability in PGE concentrations. The samples were randomly selected in the indicated time periods. Samples were collected on 20 cm × 25 cm glass fiber filters using a Sierra Andersen high volume PM<sub>10</sub> sampler operated at constant flow rate (1.13 m<sup>3</sup> min<sup>-1</sup>) and programmed to collect 24 h samples. The PM<sub>10</sub> mass was determined by gravimetric analysis in the gravimetric laboratory of Mexico City's Ambient Air Monitoring Network with filters weighed before and after sampling (40% humidity;  $22 \pm 2$  °C constant temperature). After weighing, filters were stored in Manila envelopes and identified by day and site of sampling, until requested for analysis.

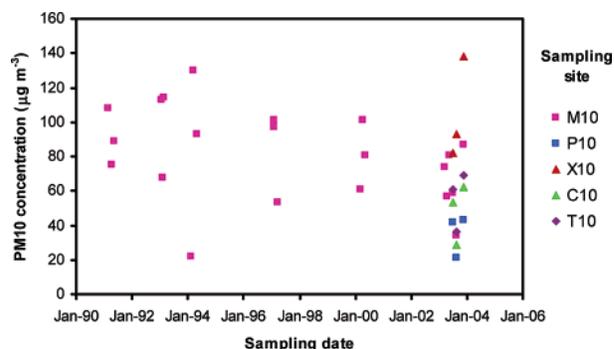
**TABLE 1. Characteristics of Sampling Stations<sup>a</sup>**

station	ID	MCMA zone	height of station (m)	characteristics
Merced	M10	downtown	4	Ave. Congreso de la Union commercial and administrative district with high traffic
Xalostoc	X10	northeast	4	Mexico–Pachuca Motorway/Hierro St. in Ecatepec industrial area with high traffic
Tlalnepantla	T10	northwest	6	Av. Toluca and Atlacomulco in Tlalnepantla residential and industrial area with low traffic
Pedregal	P10	southwest	4	in park on Cañada St. and Crater Ave. in San Angel residential and commercial zone with medium traffic
Cerro de la Estrella	C10	southeast	4	on San Lorenzo Ave. in Iztapalapa residential area with high traffic

<sup>a</sup> Locations are provided in Figure 1A and the Supporting Information.

**Sample Preparation.** Filter sections of 2.5 cm × 20 cm were cut for analysis according to U.S. EPA standard methods (18). Samples were prepared by NiS fire assay for analysis by inductively coupled plasma-mass spectrometry (ICP-MS). Spectral interferences are a major obstacle in the analysis of PGE at environmentally relevant concentrations (19), and the fire assay procedure, which uses the high affinity of PGE for sulfide, offers the advantage of simultaneously preconcentrating PGE and removing most interfering elements, as described by Ravizza and Pyle (20) and Hassler et al. (21). Filter samples were cut into small pieces with ceramic scissors, weighed, and spiked with a mixed PGE spike enriched in <sup>99</sup>Ru, <sup>105</sup>Pd, <sup>190</sup>Os, <sup>191</sup>Ir, and <sup>198</sup>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 was fused at 1000 °C for 1.5–2 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<sub>3</sub>. To fully dissolve the PGE-rich particles and oxidize Os to volatile OsO<sub>4</sub>, the closed Teflon vial was heated to ~100 °C for about 60 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 for the plasma and the other to the torch of a multicollector ICP-MS. When Ar was bubbled through the solution, volatile OsO<sub>4</sub> was carried with the Ar stream into the instrument, allowing the determination of Os and its isotopic composition. Complementary PGE concentrations were determined by magnetic sector ICP-MS in the liquid residue after it was taken to dryness and redissolved in 5% HNO<sub>3</sub>.

**Sample Analysis.** PGE analysis was done on a single collector, magnetic sector ICP-MS (ELEMENT 2, Thermo-Finnigan, Bremen, Germany) equipped with a desolvating nebulizer (ARIDIUS, Cetac, Omaha, NE), except for Os analysis, which was performed by sparging OsO<sub>4</sub> into the torch of a multicollector ICP-MS (NEPTUNE, Thermo-Electron, Waltham, MA) equipped with multiple continuous dynode electron multipliers (channeltrons). Osmium isotopic composition was determined using three channeltrons in a multidynamic acquisition routine (22) that corrects for variable channeltron counting efficiencies and instrumental mass fractionation. Subsequently, complementary PGE concentrations were obtained by conventional solution analysis using the single-collector ICP-MS ELEMENT 2. Os, Pt, and Pd concentrations were calculated using at least two isotope ratios each to check for consistency. Concentrations generally agreed within a few percent of each other; data are not reported when the standard deviation of the two results



**FIGURE 1. PM<sub>10</sub> concentration from 1991 to 2003 at the Merced site (first semester) and at the five sampling sites in Mexico City (2003, second semester).**

exceeds 20%. Rhodium is mono-isotopic, and therefore, isotope dilution analysis is not possible for this element. Rhodium quantification was therefore performed using Pt and Ir isotopes as internal standards (3, 10). The precision, accuracy, and procedural blanks of the analytical method have been documented in detail by Peucker-Ehrenbrink et al. (23).

PGE concentrations in analyzed samples are provided as Supporting Information (Table S1). Results are presented in the text as mean ± the half width of the 95% confidence interval (when the half width is larger than the mean, it is provided in brackets). PGE concentrations in blank filters were 0.5 ± 0.5 ng of Pt g<sup>-1</sup>, 0.5 ± 0.2 ng of Pd g<sup>-1</sup>, 0.13 ± 0.08 pg of Rh g<sup>-1</sup>, 0.014 ± 0.003 pg of Ir g<sup>-1</sup>, and 0.0026 ± 0.0003 pg of Os g<sup>-1</sup> (relative to filter mass). Samples with PGE concentrations lower than the concentration in the blank filter + the half width of the 95% confidence interval were removed from the dataset.

## Results and Discussion

**PM<sub>10</sub> Concentrations.** PM<sub>10</sub> concentrations in analyzed samples ranged from 21 to 138 μg m<sup>-3</sup> with an average concentration of 74 ± 11 μg m<sup>-3</sup> (Figure 1). All PM<sub>10</sub> concentrations were below the 150 μg m<sup>-3</sup> Mexican standard. In 2003, the average PM<sub>10</sub> concentration was 62 ± 14 μg m<sup>-3</sup> with the Xalostoc site and the Pedregal site having the highest concentration (104 ± 74 μg m<sup>-3</sup>) and lowest concentration (35 ± 5 μg m<sup>-3</sup>), respectively. The only sample with a PM<sub>10</sub> concentration larger than 100 μg m<sup>-3</sup> in 2003 was collected at the Xalostoc site. No significant temporal trend in PM<sub>10</sub> concentration was observed at the Merced site, but the relatively large concentration variations and the small number of samples may have masked a trend. However, the results do suggest a decrease in PM<sub>10</sub> concentration between 1991 and 2003 with all PM<sub>10</sub> concentrations at the Merced site being below 100 μg m<sup>-3</sup> in 2003 (Figure 1).

**Temporal Trends at Merced.** PGE concentrations relative to sampled air volume at the Merced site are presented in

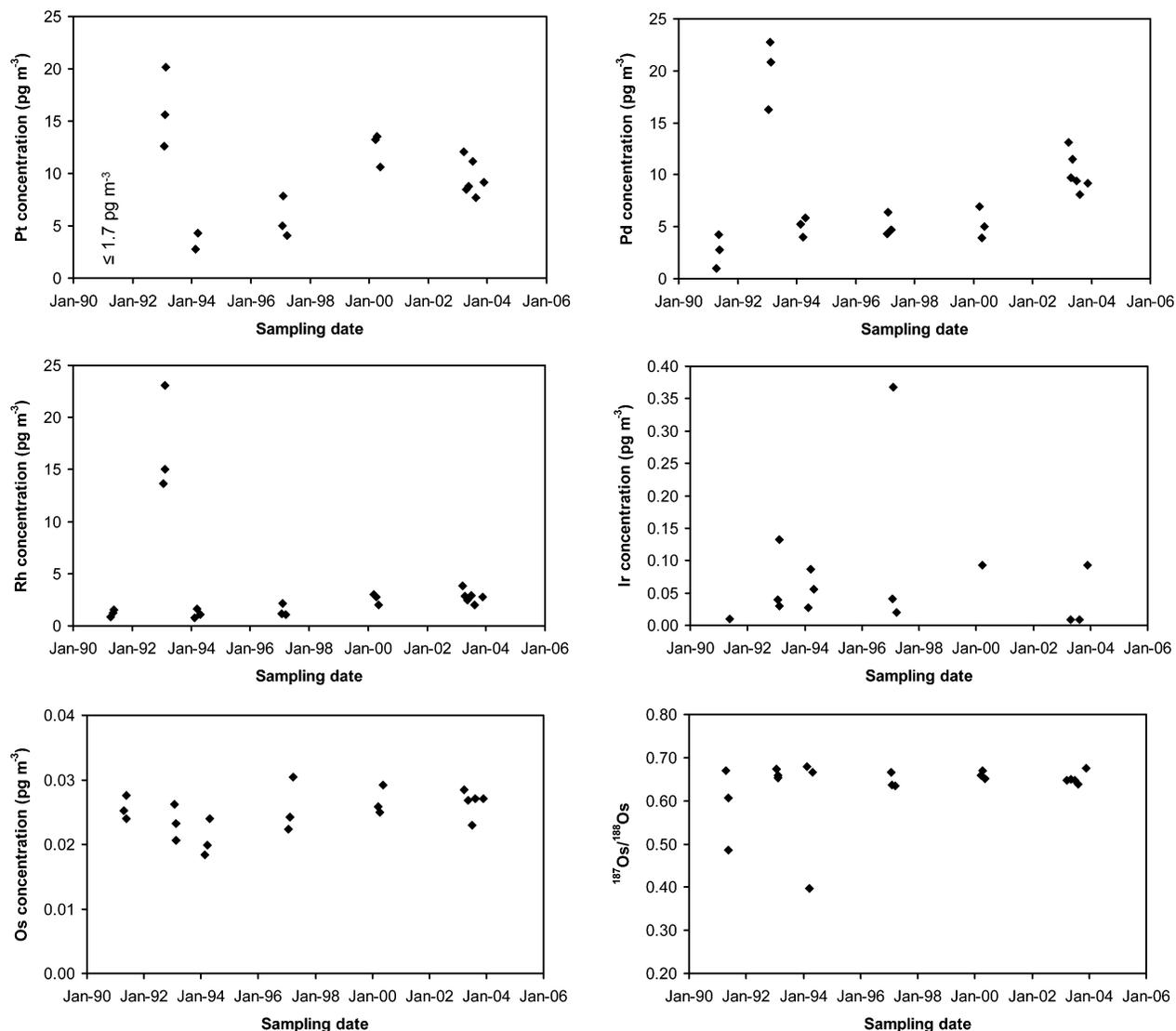


FIGURE 2. PGE concentrations relative to air volume and  $^{187}\text{Os}/^{188}\text{Os}$  at the Merced site.

Figure 2. Pt, Pd, and Rh trends from 1991 to 2003 are characterized by concentration peaks in 1993, followed by lower but upward-trending concentrations (Figure 2). Concentrations of Pt, Pd, and Rh at the Merced site in 1991 were  $<1.7$  pg of Pt  $\text{m}^{-3}$ , 2.7 (4.0) pg of Pd  $\text{m}^{-3}$ , and  $1.2 \pm 0.9$  pg of Rh  $\text{m}^{-3}$ . Concentrations in 1991 do not represent a strict natural background because of the likely import of catalyst equipped vehicles from the U.S., as well as regional or global atmospheric dispersion of PGE emitted elsewhere, but they do represent concentrations prior to the widespread introduction of automobile catalysts in Mexico. Except for the 1993 concentration peak, Pt, Pd, and Rh concentrations follow an increasing trend from 1991 to 2003. Concentrations at the Merced site in 2003 were  $9.6 \pm 1.8$  pg of Pt  $\text{m}^{-3}$ ,  $10.2 \pm 1.8$  pg of Pd  $\text{m}^{-3}$ , and  $2.8 \pm 0.6$  pg of Rh  $\text{m}^{-3}$  and were significantly higher than in 1991 (Mann-Whitney U-test,  $p < 0.05$ ). In 1993, Pt, Pd, and Rh concentrations were  $18 \pm 9$  pg of Pt  $\text{m}^{-3}$ ,  $22 \pm 8$  pg of Pd  $\text{m}^{-3}$ , and  $18 \pm 13$  pg of Rh  $\text{m}^{-3}$ .

Similar trends were obtained when concentrations were expressed relative to sampled PM<sub>10</sub> mass (Figure S2). Pt, Pd, and Rh concentrations at the Merced site increased from  $<23$  ng of Pt  $\text{g}^{-1}$ , 32 (59) ng of Pd  $\text{g}^{-1}$ , and  $14 \pm 14$  ng of Rh  $\text{g}^{-1}$  in 1991 to  $157 \pm 49$  ng of Pt  $\text{g}^{-1}$ ,  $165 \pm 46$  ng of Pd  $\text{g}^{-1}$ , and  $45 \pm 12$  ng of Rh  $\text{g}^{-1}$  in 2003, with a concentration peak in 1993. The increase of Pt, Pd, and Rh concentrations relative to both sampled volume and PM<sub>10</sub> mass demonstrate that

the amount of these metals has increased in the air of Mexico City.

In contrast, results for Os and Ir do not show increasing trends for these elements from 1991 to 2003. Concentrations were 0.010 pg of Ir  $\text{m}^{-3}$  and  $0.025 \pm 0.007$  pg of Os  $\text{m}^{-3}$  in 1991 and 0.07 (0.13) pg of Ir  $\text{m}^{-3}$  and  $0.026 \pm 0.003$  pg of Os  $\text{m}^{-3}$  in 2003. The  $^{187}\text{Os}/^{188}\text{Os}$  also remained relatively constant with  $0.60 \pm 0.25$  in 1991 and  $0.65 \pm 0.02$  in 2003. Concentrations relative to sampled PM<sub>10</sub> mass also remained relatively constant with concentrations of 0.13 ng of Ir  $\text{g}^{-1}$  and 0.28  $\pm 0.12$  ng of Os  $\text{g}^{-1}$  in 1991 and 0.5 (1.0) ng of Ir  $\text{g}^{-1}$  and  $0.44 \pm 0.25$  ng of Os  $\text{g}^{-1}$  in 2003.

**PGE Concentrations in the MCMA in 2003.** PGE concentrations were determined in samples collected at five sites in the MCMA in 2003. Three samples from each site were analyzed, except for the Merced site for which six samples were analyzed. PGE concentrations in 2003 in the MCA were  $9.3 \pm 1.9$  pg of Pt  $\text{m}^{-3}$ ,  $11 \pm 4$  pg of Pd  $\text{m}^{-3}$ ,  $3.2 \pm 2.2$  pg of Rh  $\text{m}^{-3}$ ,  $0.08 \pm 0.05$  pg of Ir  $\text{m}^{-3}$ , and  $0.029 \pm 0.007$  pg of Os  $\text{m}^{-3}$  with a  $^{187}\text{Os}/^{188}\text{Os}$  of  $0.60 \pm 0.04$ . Concentrations relative to sampled PM<sub>10</sub> mass were  $0.16 \pm 0.03$   $\mu\text{g}$  of Pt  $\text{g}^{-1}$ ,  $0.19 \pm 0.04$   $\mu\text{g}$  of Pd  $\text{g}^{-1}$ ,  $55 \pm 15$  ng of Rh  $\text{g}^{-1}$ ,  $1.3 \pm 0.8$  ng of Ir  $\text{g}^{-1}$ , and  $0.64 \pm 0.14$  ng of Os  $\text{g}^{-1}$ . Although these concentrations are not fully representative of PGE concentrations in the MCMA in 2003 owing to the limited number of samples collected, they provide a first assessment of PGE concentra-

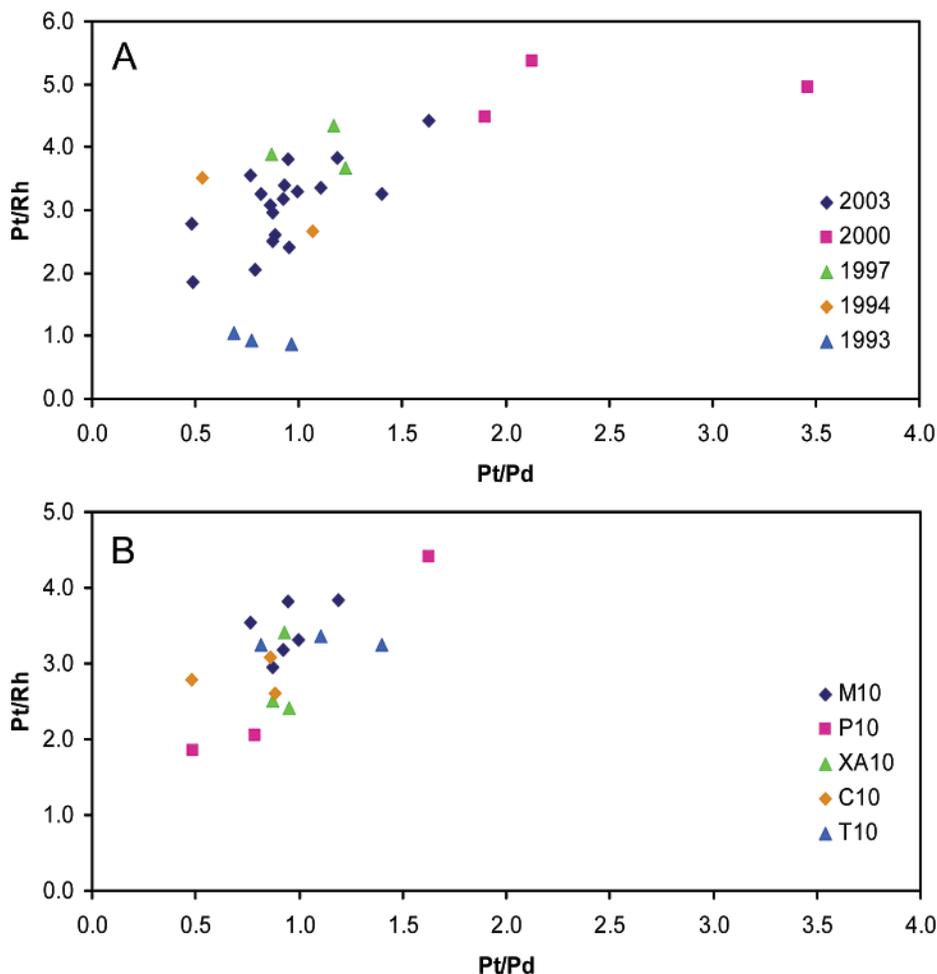


FIGURE 3. Changes in Pt/Pd and Pt/Rh ratios in the MCMA with (A) year (1991–2003) and (B) location (2003).

tion levels and geographical variations in the MCMA. No significant difference was observed between sites, except for Rh between the C10 and P10 sites (paired *T*-test,  $p < 0.05$ ). The absence of significant difference is likely to be the result of small dataset and between-day variations, as well as the dispersion of PM10 particles. X10 was found to be site with the highest average PGE concentration relative to sampled air volume for the second half of 2003, and the sum of Pt, Pd, and Rh concentration averages at each site for the same period was found to be in the order X10 > T10 = M10 > P10 = C10.

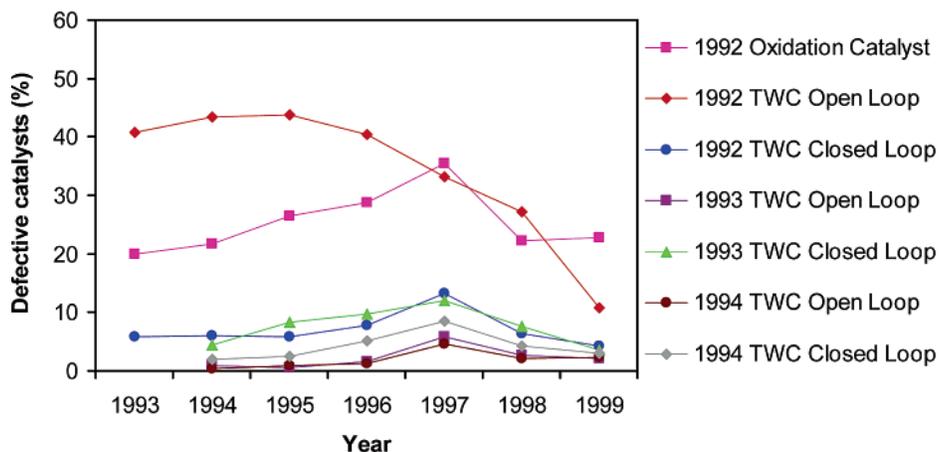
Given that Pt, Pd, and Rh concentrations in the MCMA in 2003 are significantly higher than at the Merced site in 1991 (Mann–Whitney U-Test,  $p < 0.01$ ), we suspect that the concentration increase observed at the Merced site is representative of a temporal trend throughout the MCMA. Pt, Pd, and Rh concentrations in the MCMA are in the same range as in other urban areas in South America (13), Europe (2, 6–8), and the U.S. (10) and higher than at background sites (2).

**Source of PGE in the MCMA.** The observed increase in Pt, Pd, and Rh concentrations at the Merced site, and the relatively high concentrations in the MCMA in 2003, indicate the occurrence of an anthropogenic source of PGE. Automobile catalysts are believed to be the main anthropogenic source of Pt, Pd, and Rh in urban air (2). With over 1.3 million vehicles equipped with a catalyst in the MCMA (24), catalysts represent a likely source of PGE. Attribution to an automobile catalyst source is supported by the relative timing of the trends in Pt, Pd, and Rh concentrations. The observation of Pt increasing first is interpreted as due to the introduction

of Pt-based oxidation catalysts in 1991, while the later increase in Rh concentration is consistent with the introduction of TWC in 1993 (Figure 2). The relatively high PGE concentrations at X10 and the average PGE concentration order at the five sites provide further support for an automobile catalyst with the order matching the expected traffic conditions (Table 1), except for the relatively high concentrations measured at T10 despite moderate traffic conditions. High PGE concentrations at X10 may also be the result of an unidentified industrial source.

PGE concentration ratios have been used for PGE source identification (2–10, 25). Pt/Pd and Pt/Rh in the MCMA in the second half of 2003 were  $0.96 \pm 0.16$  and  $3.1 \pm 0.4$ , respectively. Whereas Pt/Pd is similar to the reported values for Boston (10) and to the expected catalyst composition (25), a lower Pt/Rh was found in the MCMA in 2003. Relative changes in PGE concentrations can be seen in Figure 3. In 1991, samples have a relatively low Pt ( $\leq 1.7 \text{ pg m}^{-3}$ ), resulting in  $\text{Pt/Pd} \leq 0.4$  and  $\text{Pt/Rh} \leq 1.1$ . The observed increase in Pt concentration in the 1990s (Figure 2) results in an increase in Pt/Pd and Pt/Rh, with ratios reaching maxima of  $2.5 \pm 2.1$  and  $4.9 \pm 1.1$  in 2000. The relatively low Pt/Pd and Pt/Rh in 2003 can be attributed to the increasing use of Pd as an alternative Pt in catalysts, which is confirmed by an increase in Pd concentrations in 2003 (Figure 2). There was no significant difference in PGE ratios at the five sites where samples were obtained in 2003 (Figure 3B), consistent with PGE at the different sites having the same source.

A small amount of Ir has been used in automobile catalysts, but catalysts using Ir are not expected to represent a significant fraction of the vehicle fleet. The limited use of Ir



**FIGURE 4. Percentage of defective automobile catalysts for different model years and emission control technologies (adapted from ref 23). Deactivated catalyst refers to emissions higher than CO > 0.3%, CO<sub>2</sub> < 14%, and O<sub>2</sub> ≥ 0.4%.**

in catalysts can explain the absence of a clear trend for this element. Osmium has no intended use in automobile catalysts, but it has been suggested that Os is present as impurity in catalysts (3, 10, 26), and Os emissions from automobile catalysts have been reported (26). Elevated Os concentrations in Boston, MA have been attributed to automobile catalyst emission (10). However, concentrations in Mexico City do not support the existence of a link between catalyst numbers and Os concentrations. Filter type may account for some of the differences between studies in Boston and Mexico City. Cellulose filters (Whatman 41) with a relatively high hygroscopy and the possibility to absorb gases were used in Boston. In contrast, glass fiber filters were used in Mexico City, and therefore, the difference may be due to the occurrence of Os as a gas in urban air, in accordance with the emission of gaseous PGE from automobile catalysts. This is supported by the lower Os concentration in Mexico City that indicates that particulate Os in Mexico City is the result of natural processes (i.e., transport of erosion-derived and soil particles). In that perspective, the use of different filters for the determination of Os concentrations in urban air could provide valuable information.

Although catalysts appear to be a logical source of Pt, Pd, and Rh in MCMA, relatively high concentrations at T10 in 2003, the potential contribution from industrial or volcanic activity and the relatively high Pt, Pd, and Rh concentrations in 1993 when few vehicles were equipped with a catalyst, need to be explained.

(i) The T10 site is located in the northwest portion of the MCMA and is characterized by medium traffic density. The relatively high Pt, Pd, and Rh concentrations measured at T10 can therefore not be explained by traffic intensity at the sampling site. PGE-containing particles emitted from automobile catalysts and present in urban air have been reported to have diameters ranging from submicrometer to 63 μm (2, 7, 27). Whereas the larger particles have short residence times and are expected to deposit within meters from roads, PM10 particles have atmospheric residence times ranging from hours to days depending on particle size and density and can be transported regionally. Therefore, complex wind patterns with buildup and convergence zones in the airshed over the MCMA (28) are likely to affect metal concentrations in PM10 particles at specific sites. Average wind direction for all sampling days in the second half of 2003 is from the south (Table S2), and PGE may therefore be transported to T10 from higher traffic areas in the MCMA.

(ii) PGE emissions from industrial activity may be the cause of the higher PGE concentrations measured at X10. However, there is no documented industrial source of PGE at X10 or in the MCMA. In addition, industries are likely to

use single PGE in specific applications, and the combination of Pt, Pd, and Rh is a characteristic of automobile exhaust catalyst emissions in urban areas. As for T10, wind from the south may transport additional PGE to X10.

(iii) Mexico City is located in an area of volcanic activity. Because the Earth's mantle is rich in PGE, volcanic activity might represent an important source of PGE in the MCMA, and eruptions could therefore result in PGE concentration peaks. The Popocatepetl, a stratovolcano located within 70 km southeast of downtown Mexico City, has been active since 1993 with several eruptions accompanied by the emission of ash since December 1994. However, the absence of correlation between volcanic eruptions at the Popocatepetl and PGE concentrations in the MCMA does not support a volcanic contribution. In addition, volcanic ash and lava have a relatively low <sup>187</sup>Os/<sup>188</sup>Os ratio and an <sup>187</sup>Os/<sup>188</sup>Os ratio of ~0.128–0.207 has been reported for primitive lava and scoriae from the western Mexican volcanic belt, Mexican basin, and Range Province (29). Therefore, an increase in the atmospheric concentrations of volcanic ash should be accompanied by a decrease in <sup>187</sup>Os/<sup>188</sup>Os. The relatively constant <sup>187</sup>Os/<sup>188</sup>Os ratio supports that the observed 1993 Pt–Pd–Rh peak and concentration increase are not the result of volcanic activity.

(iv) Catalysts were first mandated on new cars in Mexico City in 1991, and relatively few cars were equipped with a catalyst in 1993 (24). Therefore, the observed Pt–Pd–Rh peak in 1993 cannot be explained by the number of vehicles equipped with a catalyst. However, the absence of other known PGE sources in the MCMA in 1993 and a similar Pd–Rh peak recorded in lake sediments when catalysts were first introduced in the U.S. (4) indicate that catalysts could have been responsible for the observed 1993 peak with higher emissions at an early stage of catalyst introduction. Higher emission in 1993 might have been the result of catalyst technology and/or the use of inappropriate fuel. In 1993, 25% of the gasoline vehicle fleet in the MCMA was equipped with a catalyst, with 3% using an oxidation catalyst, 4% using a TWC without computerized engine control, and 18% using a TWC with computerized engine control (24). The use of TWC using Rh might explain the occurrence of Rh prior to the legislation requiring TWC. A large fraction of 1992 oxidation catalysts and TWC without computerized engine control was found to be deactivated in 1993 (Figure 4), indicating a rapid deactivation of these catalysts in 1992–1993. The deactivation of catalysts might be associated with higher PGE emissions. The absence of engine control may result in elevated temperatures in the exhaust and higher PGE emissions (30). In addition, catalyst deactivation may have been amplified by the continued use of leaded gasoline,

which was taken off the market in Mexico in 1997 (24). The use of leaded gasoline can result in higher PGE emissions due to engine misfiring and subsequent catalyst overheating, as well as the possible formation of Pb–PGE alloys in the catalyst (31). If this was the case in the vehicle fleet in Mexico City in the early years of catalyst introduction, the occurrence of a Pt–Pd–Rh peak could be the result of automobile catalyst emissions, and the small number of vehicles without computerized engine control suggests that emissions are the result of a few high emitters.

Increasing Pt, Pd, and Rh concentrations measured in the MCMA and reports of increasing or elevated Pt, Pd, and Rh concentrations at urban locations in both developed and developing countries (3–8, 31) indicate that these elements have become widespread in the urban environment as a result of the increasingly widespread use of automobile exhaust catalysts. Rapid economic growth in developing countries, including China and India, is expected to result in a further increase in car numbers and thus Pt, Pd, and Rh emissions in the next 50 years (15).

If in fact the 1993 Pt–Pd–Rh peak is an artifact associated with the early introduction of catalysts, it is suggested that the current introduction of catalysts in developing countries should be performed carefully, a number of conditions being needed for automobile catalysts to perform efficiently. These include the availability of unleaded gasoline and no adulteration of gasoline, as well as a vehicle inspection program and infrastructures for vehicle maintenance that allow the detection and remediation of malfunctioning catalyst systems (32). Because higher PGE concentrations in urban air are expected when automobile catalysts are not properly used, monitoring PGE concentrations in urban air can provide an assessment of catalyst introduction programs.

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## Supporting Information Available

Map of the MCMA with sampling locations (Figure S1), PGE concentration trends relative to PM10 mass at Merced (Figure S2), PGE concentrations relative to sampled air volume (Table S1), and weather conditions on sampling days in 2003 (Table S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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