# In Vitro Investigations of Platinum, Palladium, and Rhodium Mobility in Urban Airborne Particulate Matter (PM$_{10}$, PM$_{2.5}$, and PM$_1$) Using Simulated Lung Fluids

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ABSTRACT: Environmental concentrations of platinum group elements (PGE) have been increasing since the introduction of automotive catalytic converters to control harmful emissions. Assessments of the human health risks of exposures to these elements, especially through the inhalation of PGE-associated airborne particulate matter (PM), have been hampered by a lack of data on their bioaccessibility. The purpose of this study is to apply in vitro methods using simulated human lung fluids [artificial lysosomal fluid (ALF) and Gamble's solution] to assess the mobility of the PGE, platinum (Pt), palladium (Pd), and rhodium (Rh) in airborne PM of human health concern. Airborne PM samples (PM$_{10}$, PM$_{2.5}$, and PM$_1$) were collected in Frankfurt am Main, Germany. For comparison, the same extraction experiments were conducted using the standard reference material, Used Auto Catalyst (monolith) (NIST 2557). Pt and Pd concentrations were measured using isotope dilution ICP-Q-MS, while Rh was measured directly with ICP-Q-MS (in collision mode with He), following established matrix separation and enrichment procedures, for both solid (filtered residues) and extracted sample phases. The mobilized fractions measured for PGE in PM$_{10}$, PM$_{2.5}$, and PM$_1$ were highly variable, which can be attributed to the heterogenic nature of airborne PM and its composition. Overall, the mobility of PGE in airborne PM samples was notable, with a mean of 51% Rh, 22% Pt, and 29% Pd present in PM$_1$ being mobilized by ALF after 24 h. For PM$_1$ exposed to Gamble's solution, a mean of 44% Rh, 18% Pt, and 17% Pd was measured in solution after 24 h. The mobility of PGE associated with airborne PM was also determined to be much higher compared to that measured for the auto catalyst standard reference material. The results suggest that PGE emitted from automotive catalytic converters are likely to undergo chemical transformations during and/or after being emitted in the environment. This study highlights the need to conduct bioaccessibility experiments using samples collected in the field to enable an adequate assessment of risk.
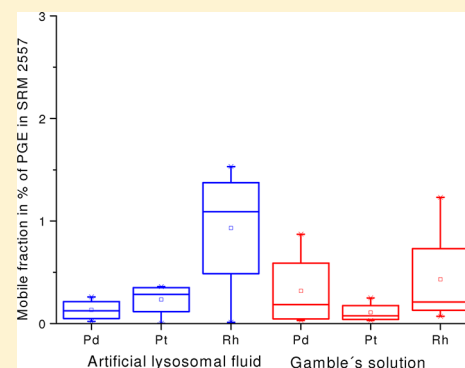
INTRODUCTION

There has been a great deal of debate regarding the health impacts of platinum group element (PGE) emissions from automotive catalytic converters since their introduction in North America in the 1970s and Europe in the early 1980s. Elevated environmental concentrations of PGE, most notably platinum (Pt), palladium (Pd), and rhodium (Rh), and their accumulation in various media over time, have been well-documented.[1−8] PGE are emitted in small amounts from catalytic converters, due to mechanical, thermal, and chemical erosion of the wash coat's surface which contains these catalysts.[9−13] PGE emission rates from three way catalytic converters, which are strongly dependent on driving speed and behavior (e.g., stop-and-go), lie in the ng/km range. Pt has been determined to be released primarily in metallic form, together with small amounts of Pt(II) and Pt(IV), likely in the form of oxides.[11] Standing motor bench tests have also demonstrated that Pt is emitted in automotive exhaust together with wash coat particles in the size range 20−0.1 μm, as well as in the form of nanoparticulate Pt and Pt−O$_2$ clusters of <5 nm.[11] Pt sampled directly from the tailpipe has been determined to have a solubility of ca. 1% in 0.1 N HCl.[13]

Little data exists on the environmental behavior and chemical form or species of PGE under field conditions. The environmental behavior and chemistry of PGE has been shown to be strongly influenced by pH, redox conditions, and the chloride ion concentration in soil solution.[14,15] Most of what we know about the environmental fate of PGE relates to Pt, which has been shown to be chemically transformed in soils using controlled laboratory experiments.[14,16,17] In studies using synthetic Pt-containing aluminum oxide particles (ca. 5% Pt), chloride, present in the form of NaCl, was shown to strongly influence Pt solubility.[18] Pt salts, especially those containing Cl, are known to be the most toxic and can induce allergic responses in sensitive individuals.[19−21]

Table 1. Mobile Fractions of Pd, Pt, and Rh in PM_{10}, $PM_{2.5}$, and PM_1 and the SRM 2557 (in %) in Artificial Lysosomal Fluid (ALF) and Gamble's Solution after 24 h and 30 Days[a]

PGE	ALF 24 h	ALF 30 days	Gamble's solution 24 h	Gamble's solution 30 days
PM_{10} $n = 15$				
Pd	11 (4−30)	9 (2−15)	17 (7−27)	14 (7−19)
Pt	23 (10−48)	14 (4−34)	24 (2−48)	39 (7−68)
Rh	33 (8−75)	17 (8−21)	28 (12−68)	51 (13−84)
$PM_{2.5}$ $n = 14$				
Pd	25 (3−57)	7 (3−12)	8 (4−19)	8 (3−12)
Pt	23 (5−38)	15 (3−19)	17 (2−34)	29 (<1−73)
Rh	34 (15−61)	37 (13−70)	42 (15−58)	31 (<1−66)
PM_1 $n = 14$				
Pd	29 (13−50)	16 (7−33)	17 (8−38)	4 (3−6)
Pt	22 (5−47)	33 (1−87)	18 (10−40)	42 (39−44)
Rh	51 (29−75)	44 (2−92)	44 (6−83)	42 (36−52)
SRM 2557 $n = 14$				
Pd	0.1 (0.02−0.26)	0.38 (0.13−0.77)	0.32 (0.03−0.87)	0.16 (0.1−0.24)
Pt	0.2 (0.002−0.36)	0.32 (0.03−0.52)	0.11 (0.03−0.25)	0.09 (0.05−0.15)
Rh	0.9 (0.1−1.53)	2.47 (1.7−2.6)	0.43 (0.07−1.23)	0.22 (0.12−0. 28)

[a]Average values (min/max values); n = filter no.

To date, very little data on the bioaccessibility of PGE in environmental and biological media has been published. Three studies have investigated PGE solubility in the human gut using simulated gastrointestinal fluids,[22−24] which is highly relevant for assessing the health risks associated with ingesting these elements (i.e., in dust, soils, and foodstuffs). Even less data exists for PGE solubility in the human lung upon inhalation or respiration, perhaps an even more important pathway of environmental exposures to these elements.[25] Puls et al. [24] recently assessed the bioaccessibility of PGE in airborne particulate matter (PM) collected in Vienna, Austria, in the human gut using synthetic gastric juice. This was based on the assumption that coarse particles (PM_{10}) are more likely to be cleared from the lungs following inhalation and transported to the gastrointestinal tract. Only one known study has examined the mobility of PGE using simulated lung fluids to model the human respiratory tract.[26] Using artificial lysosomal fluid (ALF) and Gamble's solution, Colombo et al.[26] demonstrated that significant fractions of the PGE in two certified reference materials, Road Dust [BCR 723, Institute for Reference Materials and Measurements (IRMM)] and Used Auto Catalyst [SRM 2557, National Institute of Standards and Technology (NIST)], are mobile.

There are no published data available on the bioaccessibility of PGE in airborne PM collected under field conditions. This is a crucial gap in knowledge, given the relevance of this exposure route in assessing possible risks, and the potential for airborne PM-associated PGE to be chemically distinct compared to that in synthetic or reference materials. There is an increasing body of evidence which indicates that transition metals associated with airborne PM are capable of inducing the generation of reactive oxygen species, which have been linked to a number of negative cardiopulmonary effects observed in exposed individuals.[27,28] Although not as abundant in relative mass terms, PGE are part of this larger suite of transition metals commonly associated with airborne PM of human health concern. This further highlights the need to investigate the bioaccessibility of PGE-associated airborne PM to assess their potential to impact human health. The purpose of this study is to examine the solubility of PGE in airborne PM samples of biological relevance (i.e., PM_{10}, $PM_{2.5}$, and PM_1) collected in Frankfurt am Main, Germany, using widely accepted in vitro methods to simulate conditions in the human lung.

■ SAMPLE COLLECTION AND PROCESSING

Sampling. Airborne PM (PM_{10}, $PM_{2.5}$, and PM_1) was sampled at the curbside of a busy four lane road in central Frankfurt am Main, Germany, at the monitoring station of the Hessisches Landesamt für Umwelt und Geologie (Office for Environment and Geology in Hessen) between June 2009 and November 2010 (coordinates: 50°07′28.56″ N; 8°41′30.77″ E). There is a speed limit of 50 km/h and traffic volume of ca. 32 500 vehicles/day at this site. Given its location in a major metropolitan area, the airborne PM samples collected at this site were predicted to have elevated PGE concentrations.

PM_{10} was collected on cellulose−nitrate filters with a pore size of 3 μm (diameter: 150 mm), while $PM_{2.5}$ and PM_1 samples were collected on quartz microfiber filters (diameter: 150 mm). All samples were collected on the roof of the monitoring station at a height of ca. 4 m above the ground using a high volume sampler (Digitel DHA-80). The sampling times for PM_{10}, $PM_{2.5}$, and $PM_{1.0}$ per filter were 48, 72, and 96 h, respectively. The average air volume sampled (per filter) was 1350 m³ for PM_{10}, 2150 m³ for $PM_{2.5}$, and 2070 m³ for $PM_{1.0}$. A total of 43 airborne PM samples were collected according to air quality sampling guidelines, as established by the Umweltbundesamt (Federal Environment Agency), for the in vitro experiments with simulated lung fluids.

Experimental Procedures. Artificial lysosomal fluid (ALF) and Gamble's solution were used to conduct in vitro measurements to measure PGE bioaccessibility in the human lung. The use of physiologically based extraction tests employing simulated lung fluids for assessing the bioaccessibility of metals and metallic compounds such as Co,[29] stainless steel,[30] and Cu[31] has been successfully demonstrated elsewhere. Readers are also referred to these studies for further details regarding methods, including the exact chemical composition of the simulated fluids.

The pH and chemical composition of ALF simulate the more acidic cellular conditions (pH 4.5), which occur following

phagocytosis.[32] Gamble's solution represents the neutral conditions of the interstitial fluid found deep in the human lung (pH 7.4). In addition to the 43 PM samples, the solubility of 14 samples of the standard reference material, Used Auto Catalyst (monolith) (SRM 2557 (NIST)), was also examined using the simulated lung fluids. The certified concentrations for Pt, Pd, and Rh for this material are 1131, 233.2, and 135.1 mg/kg, respectively.

The sample filters (whole) were placed in 250 mL amber nontransparent, high density polyethylene bottles containing 50 mL of the respective solutions. The filters contained an average of 43 mg of airborne PM sample material, determined by subtracting postsample from presample filter weights (maximum amount: 100 mg/filter). It should be noted that different samples (i.e., filters) were used for each respective extraction test with ALF and Gamble's solution for different time periods. Each filter is a unique sample, reflective of the highly variable particle size and chemical composition of airborne PM collected within a specific time frame. The number of sample filters used for each experiment varied as a function of test (e.g., $n = 3$ filters per sample extraction test/30 days, $n = 4$ filters per sample extraction test/24 h). Readers are referred to Table 1 for details regarding the number of filters analyzed.

For the SRM 2557, ca. 0.08 g of sample material was used for each extraction. Samples were incubated at a constant temperature of 37 °C for either 24 h or 30 days, to investigate the effects of time on elemental solubility. The bottles were manually shaken several times per day in a consistent manner during the incubation periods to minimize sample settlement. Following the reaction period, samples were then filtered with 0.2 μm membrane filters (hydrophilic polypropylene) to separate the solid from the liquid phase for further analysis. Given the fact that ultrafine particles may also pass through the filter in what is commonly defined as the soluble fraction, the term "mobilized" fractions will be used in the following sections.

Analytical Methods. Different analytical methods were applied for the determination of PGE in airborne PM using ICP-MS, which are internationally recognized for their superior reliability and validity (see refs 1, 7, 33–35). Only Suprapur grade acids (Merck) were used in the digestion and analysis of samples. The residue (solid) samples were spiked with Pt- and Pd-standard solutions (95.71% ^{198}Pt and 97% ^{105}Pd from Cambridge Isotope Laboratories, Woburn, MA) and digested in quartz glass containers with 1.5 mL 69% HNO_3 and 4.5 mL 37% HCl (aqua regia, ratio 1:3). Samples were digested in a high pressure asher (HPA, Anton Paar, Austria) for 60 min at a temperature of 320 °C and pressure of 130 bar. The HPA digest solutions were placed in Teflon evaporating dishes and heated at 120 °C to near dryness with 2 mL of 69% HNO_3. This procedure was completed several times with successive additions of 2 mL of concentrated HNO_3. Samples extracted with ALF and Gamble's solution were also subjected to the same procedure, involving the addition of 2 mL of HNO_3 in successive rounds of heating to near dryness on a hot plate at 120 °C. All samples were then transferred to conical tubes and diluted to the 10 mL mark with 0.5% HNO_3.

Samples were coprecipitated with Te to isolate Pt and Rh and minimize matrix effects. Pt concentrations were determined using isotope dilution ICP-Q-MS (Varian 820-MS, Germany), while Rh was measured directly with ICP-Q-MS (in both instances in collision mode with He). The reliability of this method is also described at length in Alsenz et al.,[33] as well as in

Gomez et al.[34] Pt concentrations were calculated, from the isotope ratios ^{194}Pt/^{198}Pt, ^{195}Pt/^{198}Pt, and ^{196}Pt/^{198}Pt while Rh was determined using the signal for ^{103}Rh. For the reagent blank 0.5% HNO_3, PGE concentrations were 0.003–0.01 pg Pd/m^3, 0.02–0.05 pg Pt/m^3, and 0.002–0.008 pg Rh/m^3. The detection limit, calculated as three times the standard deviation for the measured blank filters in 0.5% HNO_3 and a total filtered air volume of 1500 m^3 for sample collection in Frankfurt, was 0.88 pg Pt/m^3 and 0.3 pg Rh/m^3.

Different steps were taken to eliminate molecular interferences present in sample digest solutions for the analysis of Pd, which is more difficult to measure due to matrix effects. For Pd, samples were preisolated and enriched using a Hg coprecipitation technique prior to elemental determination with isotope dilution ICP-Q-MS (in collision mode with He). Two internal standards were used [^{115}In and ^{169}Tm (4 μg/L; Merck)] to correct for spectral drift. Pd concentrations were calculated from the isotope ratios ^{106}Pd/^{105}Pd, ^{108}Pd/^{105}Pd, and ^{110}Pd/^{105}Pd. Alsenz et al.[33] demonstrated the greater reliability of the use of Hg over Te as a coprecipitation method to isolate Pd, with a detection limit of 0.05 pg Pd/m^3. Only Pd is scavenged by Hg, which helps to effectively eliminate matrix effects and attendant molecular interferences in the application of ICP-MS and is, as such, the preferred method of choice. Readers are referred to Messerschmidt et al.[35] and Alsenz et al.[33] for more details regarding this preferred method for the measurement of Pd. The ICP-MS settings used to measure Pd, Pt, and Rh were as follows: plasma flow at 17.7 L/min, auxiliary flow at 1.68 L/min, sheath gas flow at 0.25 L/min, nebulizer flow at 0.94 L/min, ICP RF power at 1.40 kW, and He gas flow at 120 mL/min.

Total PGE concentrations in airborne PM were calculated from the results for each respective solid (filtered residue) and liquid phase (filtered solution) sample.

Quality Assurance/Quality Control. A number of quality assurance and control steps were undertaken to ensure accuracy and reliability in sample measurement. All labware was submerged in a hot bath of 20% HNO_3 for at least 2 h and then rinsed several times with purified water prior to use. Only high purity acids (Suprapur grade, Merck) were used for sample preparation and analysis. Cellulose nitrate filters and quartz microfiber filters were conditioned in a controlled air-conditioned environment for ca. 48 h prior to weighing at temperature of 22 °C and humidity of 54%. Blank and sample filters were weighed 3–5 times using a microbalance (Sartorius BP 210S), depending on weight stability. The weights were noted, and an average weight was determined for each filter.

The concentrations of PGE in ALF and Gamble's solution were also measured and the results adjusted accordingly. Mean PGE concentrations in ALF were 0.03 μg/L for Pd (range: 0.01–0.04 μg/L), 0.15 μg/L for Pt (range 0.07–0.17 μg/L), and 0.01 μg/L for Rh (range 0.003–0.01 μg/L). In Gamble's solution, the mean concentrations of Pd, Pt, and Rh were 0.06 μg/L (range 0.05–0.07 μg/L), 0.12 μg/L (range 0.06–0.19 μg/L), and 0.02 μg/L (range 0.004–0.06 μg/L), respectively.

Both internal standards (^{115}In and ^{169}Tm) and external standards [Pt and Rh standard solution (1.0 g/L) in 20% HCl (Alfa Aesar), Rh standard solution (1.0 g/L) in 10% HCl (Merck), Pd standard solution (1.0 g/L) in 2–3% HNO_3 (Merck)] were used for validation purposes and to correct for spectral drift. Samples were also spiked with ^{198}Pt and ^{105}Pd to confirm the accuracy of measurements. The road dust reference material, BCR 723 (IRMM), was also measured with each

sample series and found to be in good agreement with certified values [i.e., measured values: Pd 4.2 ± 1.4 μg/kg (certified value: 6.1 ± 1.9 μg/kg), Pt 87.6 ± 10.5 μg/kg (certified value: 81.3 ± 2.5 μg/kg), and Rh 12.6 ± 0.6 μg/kg (certified value: Rh 12.6 ± 1.2 μg/kg)].[1,33]

Data Analysis. The program OriginPro 8.5 was used to conduct statistical analyses, including the application of t tests and ANOVA to determine statistically significant differences in measures of central tendency (i.e., means) between Pt, Pd, and Rh concentrations in the respective airborne PM size fractions.

■ RESULTS AND DISCUSSION

PGE concentrations were measured in both filtered solutions (i.e., the mobilized fraction) and filter residues following extractions. The ALF solutions had an average pH of 4.4, upon sample addition. The pH value of samples remained largely unchanged within a 24 h period. As the pH lay within 0.1 unit of the normal expected value of 4.5 for ALF, this was deemed acceptable for the extraction tests. The use of NaOH to adjust for pH was avoided to ensure that the chemical composition (i.e., salt ratios) of the original solution was not altered.

The Gamble's solution had a measured pH value of 7.8, falling at the upper range of what is deemed acceptable for simulated lung interstitial fluid (i.e., 7.4−7.8).[36]

Total PGE Concentrations in Airborne PM. Total PGE concentrations in airborne PM were calculated additively from the results for each respective solid (filtered residue) and liquid phase (filtered solution) sample. It must be emphasized that the purpose of this study was to assess the mobility of PGE associated with airborne PM, and not to comprehensively characterize the airborne PM concentrations of these elements. For a more thorough examination of PGE concentrations in airborne PM in Frankfurt am Main, readers are referred to Zereini et al.[1,7]

Total PGE concentrations in airborne PM were found to be highly variable. In PM$_{10}$, the average Pd concentration was 58 pg/m^3 and varied between 8 and 132 pg/m^3. The mean Pt concentration in PM$_{10}$ was 67 pg/m^3 and ranged from 6 to 135 pg/m^3. Rh concentrations varied between 2 to 35 pg/m^3, with a mean of 13 pg/m^3. Mean concentrations of all PGE were lower in PM$_{2.5}$, with 35 pg Pd/m^3 (range: 11−86 pg/m^3), 28 pg Pt/m^3 (range: 4−120 pg/m^3), and 9 pg Rh/m^3 (range: 1−90 pg/m^3). Mean concentrations in PM$_1$ were comparable to PM$_{2.5}$, with values of 32.4 pg/m^3 for Pd (range: 6−167 pg/m^3), 26 pg/m^3 for Pt (range: 2−75 pg/m^3), and 9 pg/m^3 for Rh (range: 0.3−44 pg/m^3). With the exclusion of identified outliers (n = 2), the mean Pd concentration in PM$_1$ is 18 pg/m^3. These outliers had unusually high Pd concentrations of 167 and 74 pg/m^3. A mean Pt concentration of 22 pg/m^3 is calculated, upon exclusion of one outlier sample with a Pt level of 75 pg/m^3. Two outliers were identified for Rh (33 and 44 pg/m^3, respectively). Without these, the mean Rh concentration is 4 pg/m^3. These outliers are a reflection of the expected heterogeneity of traffic-related PM emissions, due to the erosion and emission of catalyst-containing particles in exhaust, often referred to as the "nugget effect".

Overall, the concentrations measured for PGE are comparable to those determined for PGE concentrations in total PM$_{10}$, PM$_{2.5}$, and PM$_1$ samples collected in a previous study from 2008 to 2010 in Frankfurt am Main, Germany.[1] The observed variability in PGE concentrations measured for airborne PM is to be expected given the fact that particles emitted in automotive exhaust as a function of various factors

are highly heterogeneous. Variable PGE concentrations have also been documented in other environmental media,[6,7] reflecting the range of emissions from automotive traffic.

In general, the PGE concentrations for airborne PM sampled in Frankfurt am Main appear to be strongly dependent on traffic density.[1,7] PGE concentrations also appear to be heavily influenced by seasonally related meteorological factors, such as the occurrence of weather inversions in winter which result in elevated concentrations of these elements compared to the summer.[1] Levels of PGE in airborne PM have also been demonstrated to be influenced by the long-range transport of these elements within Europe.[1]

Artificial Lysosomal Fluid. Overall, the mobility of PGE was found to be highly variable for all airborne size fractions extracted with ALF (Table 1). In PM$_{10}$, a mean of 33% of the total Rh present in this size fraction was mobile in ALF (24 h period). The mobile fraction measured for this element was the most variable, ranging from 8% to 75%. Columbo et al.[26] also observed that Rh was the most mobile of the PGE in the road dust reference material (BCR 723) in ALF. They, however, determined a total mobile fraction of 88% for this element, which is substantially higher than that measured here.

The mean Pt in PM$_{10}$ exposed to ALF was 23% after 24 h (range: 10−48%). This was also lower compared to the extraction experiments conducted in another study[26] using the road dust reference, BCR 723, in which ca. 36% of Pt was determined to be mobile in ALF. The mean Pd associated with PM$_{10}$ was 11% being solubilized after 24 h in ALF (range: 4−30%). Rh fraction measured in ALF after 24 h was 51% in PM$_1$ and 34% for PM$_{2.5}$. The mobile Rh fraction ranged from a low of 29% to 75% for this size fraction. The mean concentration of Pd was 29% in PM$_1$ and 25% in PM$_{2.5}$. The variability in values measured for Pd mobility in PM$_{2.5}$ ranged from 3% to 57%, while the mobile Pd fraction in PM$_1$ ranged from 13% to 50% (Figure 1).

Similar results were also observed with a reaction time of 30 days (Table 1). The mobilized Rh fraction in PM$_{10}$ averaged 17% and ranged from 8% to 21%. The mean mobile Pt fraction was 14% and varied from 4% to 34%. The mobile Pd fraction ranged from 2% to 15% and had a mean of 9%. The mean mobile Rh fraction in PM$_{2.5}$ was 37% and ranged from 13% to
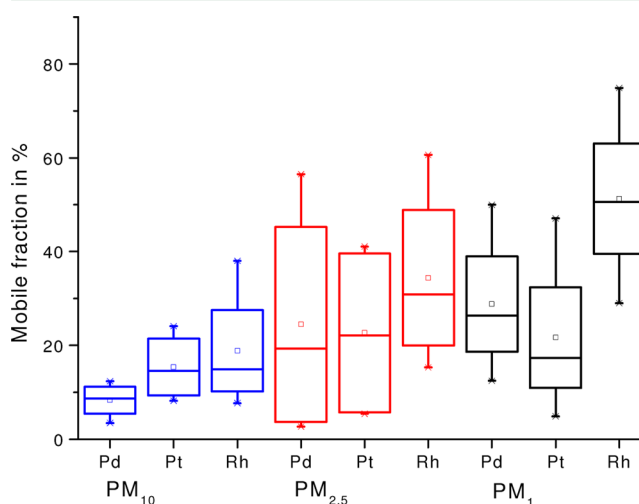

Figure 1. Mobile fraction in % of Pd, Pt, and Rh in PM$_{10}$, PM$_{2.5}$, and PM$_1$ using artificial lysosomal fluid (ALF) (n = 13) after 24 h (min max, 25−75%, average and median).

70%. The mobile fractions in this size fraction were 15% for Pt (varied from 3% to 19%) and 7% for Pd (varied from 3% to 12%). The highest Pd mobility was measured in PM_1, with a mean of 16%. Mean mobile fractions of 33% and 44% were measured for Pt and Rh, respectively. The mobile fraction measured for Rh in PM_{10} exposed to ALF changed from 33% after 24 h to 17% after 30 days.

The results here contrast with the time dependent related increase in PGE bioaccessibility as observed by Colombo et al.,[26] using the certified Road Dust reference material, BCR 723, and Used Auto Catalyst (monolith) reference substance (SRM 2557). For instance, they measured a 2- to 3-fold increase in the mobile fraction of Rh in BCR 723 exposed to ALF over the course of a 700 h reaction period. There are likely several factors which may have contributed to the differences observed over time. In this study, different samples were used for each respective reaction period. As such, expected heterogeneity in the chemical composition of the individual samples may have contributed to the differences observed. It is also possible that the PGE are first mobilized within the initial reaction period only to be reabsorbed to particle surfaces present in the solution, which are later filtered as part of the residue. Sample loss may also occur though the sorption of particles on filters and labware surfaces. It has been argued elsewhere that the optimal reaction period for particles in ALF is 24 h, as this appears to be the time it takes for steady state conditions to be reached.[37] This highlights the need to carefully consider the effects of reaction time on measurements of mobility and their relevance for assessments of human health risk. A 24 h period would represent the upper limit of mobility for airborne PM-associated elements using this model and is, therefore, suggested as the reaction time of choice.

Several statistically significant differences in mean PGE concentrations were observed between the respective airborne PM fractions mobilized by ALF. Mean concentrations of Pt compared to Rh in PM_1 were statistically different at a level of $p \leq 0.05$, which suggests that Rh is more mobile in fine PM. Mean Pd concentrations were also found to be significantly different relative to Pt levels in PM_{10} ($p \leq 0.05$), indicating the presence of a smaller mobile Pd fraction in coarse PM. Mean concentrations of Pd and Rh in PM_{10} were statistically different at a significance of $p \leq 0.10$. Mean levels of Rh compared to Pt and Pd in $PM_{2.5}$ were also statistically different at a significance of $p \leq 0.10$, providing further evidence for the higher mobility of Rh compared to the other PGE. The limited number of statistically significant differences detected for PGE mobility for the various PM fractions, as determined through a comparison of mean concentrations, may be attributed to the relatively small sample size. To increase the statistical power of results, a greater sample size would be recommended to account for the existence of sample heterogeneity in the elemental composition of airborne PM.

The mobile fraction measured for the standard reference material Used Auto Catalyst (monolith) (SRM 2557) in ALF was considerably lower for all PGE compared to that determined for airborne PM. After 24 h, a mean of 0.1% Pd (range: 0.02–0.26%), 0.2% Pt (range: 0.002–0.36%), and 0.9% Rh (range: 0.1–1.53%) of the total PGE present was determined to be mobile. The mobile fractions for these elements were higher after a 30 day extraction period, with 0.38% for Pd (range: 0.13–0.77%), 0.32% Pt (range: 0.03–0.52%), and 2.47% Rh (range: 1.7–2.6%). The mean concentrations of Pd and Pt relative to Rh mobilized by ALF

were statistically different at a significance of $p \leq 0.05$. This also supports observations made regarding the heightened mobility of Rh, most notably in PM_1, compared to the other PGE. The results from this study lie within the range of that determined by Columbo et al.[26] for the same auto catalyst reference material. The higher observed mobility of PGE associated with airborne PM samples compared to the SRM 2557 Used Auto Catalyst (monolith) exposed to ALF strongly suggests that these elements are likely to undergo chemical transformations during and/or following emission (i.e., likely converted to oxides from their original metallic form due to high temperatures and the presence of other chemical constituents found in exhaust).

Gamble's Solution. After a 24 h period, the mobile fraction measured for Rh associated with PM_{10} in Gamble's solution was 28%, compared to 24% for Pt and 17% for Pd (Table 1). The mobile fraction of Rh extracted in Gamble's was the most variable relative to the other PGE, ranging between 12% and 68% for PM_{10}. In $PM_{2.5}$, the mean mobile Rh fraction measured in Gamble's solution after 24 h was 42% (range: 15–58%), compared to 17% for Pt (range: 2–34%) and 8% for Pd (range: 4–19%). This fraction was elevated for Rh in PM_1 after 24 h, with 44% (range: 6 to 83%). PM_1 associated Pd was 17% and ranged from 8% to 38%. The mean Pt fraction in PM_1 exposed to Gamble's solution for 24 h was 18% (range: 10–40%). The mobile fraction of Pt and Rh in PM_{10} exposed to Gamble's solution were measured to be 39% for Pt and 51% for Rh after a 30 day period (Figure 2). The measured fraction of Rh in Gamble's solution over this time period for $PM_{2.5}$ was 31% and PM_1 was 42%.
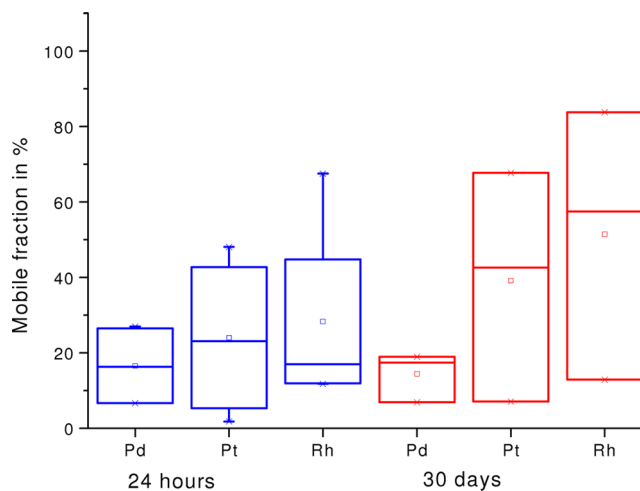

Figure 2. Mobile fraction in % of Pd, Pt, and Rh in PM_{10} using Gamble's solution ($n = 7$) after 24 h and 30 days (min max, 25–75%, average and median).

Similar to that observed for ALF, the variability in results could be due to sample heterogeneity and/or the sorptive dynamics of particles over time. Steady state conditions would likely take longer to be reached with the more neutral Gamble's solution. As such, the observed increases in Pt mobility over time for all airborne PM size fractions suggest that a longer reaction time is indeed required for this element using this in vitro method.

Mean concentrations of Pd compared to Rh in both PM_1 and $PM_{2.5}$ mobilized by Gamble's solution were statistically different at a level of $p \leq 0.05$. In PM_{10}, mean Pd concentrations were

significantly different from mean Rh and Pt concentrations at a level of $p \leq 0.10$. Similarly, mean Pt concentrations were found to be significantly different relative to Rh levels in $PM_{2.5}$ ($p \leq 0.10$), while mean Pd levels were significantly different in PM_1 ($p \leq 0.10$). Similar to ALF, a stronger statistically significant association between Rh and Pd in PM_1 and $PM_{2.5}$ in Gamble's solution provides evidence for the greater relative mobility of this element. In contrast, the weakest relative statistical relationships were calculated for Pd and Pt in solution.

Similarly, the mobility of PGE in the SRM 2557 was lower in Gamble's solution compared to that measured for airborne PM. Mean mobile fractions in Gamble's solution after 24 h were 0.32% for Pd (range: 0.03−0.87%), 0.11% for Pt (range: 0.03−0.25%), and 0.43% for Rh (range: 0.07−1.23). Columbo et al.[26] also determined a low mobility for PGE in the same auto catalyst reference material (<0.5% for all elements). This evidence confirms the stated need to determine the mobility of PGE in environmental media such as airborne PM, as they appear to behave differently under field conditions and are likely present in other chemical forms as in the auto catalyst.

PGE Mobility in Artificial Lysosomal Fluid versus Gamble's Solution. The greater mobility of Rh compared to Pt and Pd, for airborne PM extracted with simulated fluids, could be due in part to this element's stronger association with smaller particle sizes of PM. PGE particles associated with ultrafine fractions may pass through the 0.2 μm membrane filters, contributing to the total amount of that assumed to be soluble in this fraction. Columbo et al.[26] also observed that Rh was the most mobile of the PGE in the road dust reference material (BCR 723) in ALF. The greater solubility of Rh compared to other PGE in environmental media has also been demonstrated for soils.[14]

Interestingly, the pH of ALF versus Gamble's solution had less of a predicted influence on measured proportions of extracted PGE. For instance, a mean of 23% Pt in PM_{10} samples was extracted with ALF after 24 h compared to 24% Pt measured for Gamble's after 24 h. Similarly, Pd concentrations for PM_{10} extracted with Gamble's solution for 24 h were 17% compared to 11% Pd concentrations measured for ALF after 24 h. The concentration of Rh was determined to be 33% for ALF and 28% for Gamble's solution. Rh levels in $PM_{2.5}$ and PM_1 mobilized by the different solutions were either not significantly different or were slightly less in the more neutral pH of Gamble's fluid.

These results do not fully support past studies, which have generally demonstrated that PGE solubility is strongly dependent on pH.[14,22,23] The results for the SRM 2557, in contrast, more clearly demonstrate the effects of pH on solubility. Measured PGE levels in the SRM 2557 mobilized by the simulated lung fluids were relatively consistent. The measured soluble fractions of PGE extracted with ALF (pH 4.3) were higher compared to that determined for samples extracted with Gamble's solution. The mobilized fraction of Rh in the SRM 2557 demonstrated a higher intersample variability compared to Pt and Pd. The particle size of the SRM 2557 spans a relatively broad spectrum of particle diameters, with a maximum particle size of 74 μm. The low sample amounts weighed in for this material (i.e., ca. 0.08 g), combined with the heterogeneous nature of the SRM 2557 in terms of particle size, may have contributed to a nugget effect and, thereby, a greater variability observed in measurements of variability for Rh. The results confirm the need to ensure homogeneity of sample

material to adequately assess the influence of pH on PGE mobility.

Nonetheless, the results strongly suggest that the PGE in airborne PM appear to be more mobile compared to that measured for the Used Auto Catalyst (monolith) (SRM 2557) standard reference material. These differences indicate that Pd, Pt, and Rh are present in a different chemical form or species in airborne PM, which is more soluble. Past studies have demonstrated that PGE in catalytic converters are present primarily in metallic form,[11,12] which is biologically inert and less soluble. Given the results here, we could also assume that the PGE in the SRM 2557 are also predominantly in metallic form. PGE in catalytic converters are often emitted due to mechanical and thermal erosion of the wash coat which contains these catalysts. Chloride and bromine complexes, as well as organometallic complexes, may also be formed with PGE upon being emitted in exhaust and/or their subsequent deposition in the environment.[10] In addition to metallic Pt, Pt(II) and Pt(IV), likely in the form of oxides, have been demonstrated to be present in automotive emissions.[11] The presence of such forms of Pt in airborne PM, which are more mobile and reactive, could in part explain the higher mobility of airborne PM samples observed here. It is has been suggested by Colombo et al.[26] that metallic forms of PGE present in airborne PM are likely to be transformed into more mobile species upon contact with biological fluids due to the presence of Cl ions, among other things. A more likely explanation is that PGE are first emitted primarily in metallic form and are then transformed into more soluble, mobile species upon contact with chemical constituents of exhaust and environmental media such as soils following emission. A variety of organic compounds in soils, for instance, have been shown to readily form complexes with PGE, which can enhance their solubility.[38−42]

Overall, the levels of Pt, Pd, and Rh in airborne PM samples extracted with both simulated lung fluids were found to be highly variable. This relationship was particularly strong for Rh. The mobility of the PGE in airborne PM was found to be highly variable between the individual elements, with Rh demonstrating the greatest mobility for all particle size fractions immersed in simulated lung fluids. The greater mobility of Rh compared to Pt and Pd, for airborne PM extracted with Gamble's solution and ALF, could be due in part to the association of this element with smaller emitted particle size fractions. Other factors apart from particle size such as the elemental species of PGE present in PM fractions may also explain the higher solubility of Rh in simulated lung fluids. The greater concentrations of Rh compared to the other PGE had also been demonstrated in automotive bench test experiments.[12,13] Columbo et al.[26] also observed that Rh present in the certified reference material, Road Dust (BCR 723), had a higher relative solubility in biological fluids. At the same time, Rh is emitted in lower amounts in automotive exhaust and is present at much lower concentrations in the environment relative to the other PGE. Total exposures to this element are, therefore, predicted to be comparatively lower, which serves to reduce the relative hazard potential of Rh.

Pd was found to have a lower mobility compared to Pt and Rh. This finding contrasts with past studies which have shown that Pd has a higher environmental solubility compared to other PGE. The difficulties associated with the measurement of Pd in environmental media due to matrix effects and associated molecular interferences in the application of ICP-MS could

have contributed to elevated estimates of its solubility in previous studies. The need to take extra steps in the isolation and pre-enrichment of Pd prior to analysis to minimize matrix effects in environmental samples has been clearly established.[33,34,43] As such, data which has been generated in the absence of such precautionary analytical measures must be interpreted with caution.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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